Utjecaj adhezijskih parametara na materijalno i organsko recikliranje termokromnih otisaka

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THE INFLUENCE OF ADHESION PARAMETERS ON MATERIAL AND ORGANIC RECYCLING OF THERMOCHROMIC PRINTS

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INFORMATION ABOUT MENTOR

Prof. Mirela Rožić, PhD was born in Zagreb on September 25, 1969.

She graduated from the University of Zagreb, Faculty of Chemical Engineering and Technology in 1994. Since 1994 she has been a teaching assistant at the faculty of Graphic Arts, department of Chemistry in Graphic Technology. She started her postgraduate studies at the University of Zagreb, Faculty of Chemical Engineering and Technology and completed her Master's Degree in natural science discipline, field of chemistry in 1999. She completed her doctoral thesis at the University of Zagreb, Faculty of Chemical Engineering and Technology and was awarded a PhD degree in natural science discipline, field of chemistry in 2002.

She was appointed to the position of research associate in 2005 and to the teaching and research position of an assistant professor in the field of technical sciences, a scientific field of graphic technology for a group of chemistry courses in graphic technology. The appointment of senior research associate she gained in 2009, and to scientific and teaching position as associate professor. In 2015 she gained a position of full professor.

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ABSTRACT

Within this dissertation, material and organic recycling of thermochromic prints was examined. Adhesion parameters between thermochromic printing inks and printing substrates were examined as well, and their impact on studied methods of disposal was elaborated on. The obtained results indicate that thermochromic offset prints are poorly deinkable due to very high adhesion of inks to paper. Since thermochromic printing inks contain some toxic substances, their presence in the recycled pulps was also considered. Results showed that BPA was present in recycled pulps and it was above maximum permitted limits. The concentration of heavy metals cations Zn and Fe in all samples originate from printing substrate, while Mn and Co originate from drying catalysts present in inks. The growth of *Bacillus subtilis* and *Aspergillus niger* was not inhibited in all tested samples indicating that there was no release of toxic substances, despite the presence of BPA and heavy metals. Thermochromic inks also affect the process waters increasing the COD and TOC values. Obtained results of UV curable and offset thermochromic prints biodegradation showed that biodegradation depends upon the adhesion, *i.e.* lower adhesion will result in reduction of biodegradation rate, while the strong adhesion will result in better prints and papers degradation. Reactions between paper and thermochromic ink will form different prints properties due to different affinity of paper for ink while interactions between them will affect the prints and papers biodegradation. Results indicated that better absorption of binder into the absorbent paper structure results in thinner layer of ink binder on the paper surface. In the case of absorbent paper, the higher rate of biodegradation was detected, resulting in a higher number of bacteria, higher weight loss, higher changes in colour (destruction and deformation of microcapsules) and reduction in thermochromic effect of the prints. The thickest layer of ink binder and classic pigment on non-absorbent paper surface causes the slowest rate of biodegradation of print. Results show that microcapsules are promoting the rate of paper biodegradation. Results also indicated that ink vehicle used in thermochromic offset ink is more stable than the polymer resin present in UV curable screen printing thermochromic ink. Thus, organic recycling can be better option for thermochromic prints waste management.

KEY WORDS

Thermochromic inks, deinking flotation, biodegradation, FTIR, SEM, colorimetric properties

PROŠIRENI SAŽETAK

Termokromne boje sve više i više nalaze primjenu u raznim aplikacijama poput pametne ambalaže i sigurnosnog tiska. Iako je njihova uporaba za tisak na papiru i kartonu još uvijek ograničena, bitno je ispitati mogućnosti njihovog zbrinjavanja, ali i njihov utjecaj na recikliranje papira. Proizvodi na bazi papira jedan su od osnovnih komponenti komunalnog čvrstog otpada. Prema EU Direktivi o otpadu, hijerarhija zbrinjavanja otpada za proizvode na bazi papira podrazumijeva da se papirni proizvodi trebaju ponovno koristiti, reciklirati (materijalno ili organski) ili oporabiti u svrhu dobivanja energije. Stoga su u ovom radu ispitane su mogućnosti recikliranja termokromnih otisaka, klasičnom metodom deinking flotacije te organskim recikliranjem. S obzirom da termokromne boje sadrže različite štetne tvari, poput teških metala i bisfenola A, dobiveni reciklirani papir te procesne vode analizirane su na koncentraciju tih onečišćivala. Nadalje, ispitana je mogućnost organskog recikliranja ofsetnih i UV otisaka u anaerobnim uvjetima tla. Dodatna pozornost posvećena je interakcijama između papira i boja te njihovim ulogama u istraživanim metodama. Materijalno recikliranje termokromnih ofsetnih otisaka u svrhu dobivanja recikliranog papira provedeo je klasičnom kemijskom deinking flotacijom. Otisci termokromnih boja pomiješani su u jednakim udjelima i reciklirani u laboratorijskim uvjetima prema INGEDE metodi 11p. Učinkovitost procesa recikliranja procijenjena je izračunavanjem prinosa flotacije, povećanjem stupnja svjetline celulozne papirne pulpe i povećanjem bjeline te kolorimetrijskim svojstvima boje, određivanjem količine zaostale boje, kao i određivanjem sadržaja pepela prema standardnim metodama. Dobiveni rezultati upućuju na to da se termokromni ofsetni otisci loše recikliraju zbog jake adhezije boje na papiru. Slikovna analiza pokazuje da je deinking flotacija uspjela ukloniti samo 12,8% ukupne površine termokromne boje. Također je primjetan samo mali porast svjetline i bjeline (približno 5% i 2%). Rezultati su pokazali da je BPA prisutan u recikliranom papiru što se može objasniti lošim recikliranjem termokromskih otisaka. Uklonjeno je 50 % BPA u uzorcima nakon flotacije. Prema novim strožim graničnim vrijednostima koje je donio Europski lanac za papirnu i kartonsku ambalažu za hranu (CEPI / CITPA / CEFIC / FPE), najveće dopuštene količine BPA u analiziranim uzorcima nisu zadovoljile uvjete čistoće, jer su utvrđene koncentracije bile iznad maksimalno dopuštenih granica. Koncentracijea kationa teških metala određena su iz pepela laboratorijskih listova i fileter kolača načinjenih iz reciklirane papirne pulpe kao i odvojene flotacijske pjene. Veće koncentracije Zn i Fe u svim uzorcima potječu od tiskovne podloge. Koncentracije Mn i Co u recikliranom papiru i flotacijskoj pjeni potječu od katalizatora sušenja prisutnih u bojama. Rast bakterije *Bacillus subtilis* i plijesni *Aspergillus niger* nije bio inhibiran u svim ispitanim uzorcima što ukazuje da nije bilo oslobađanja otrovnih tvari, unatoč prisutnosti BPA i teških metala. Termokromne boje povećavaju organsko onečišćenje procesnih voda što se vidi iz vrijednosti kemijske potrošnje kisika (COD) i ukupnog organskog uljika (TOC). Koncentracije teških metala u procesnim vodama bile su vrlo niske. Također su proučeni aspekti biorazgradivosti termokromnih leuko boja, ofsetne i UV sušeće, na različitim tiskovnim podlogama. Testovi biorazgradnje napravljeni su pod anaerobnim uvjetima tla. Stupanj biorazgradnje određen je vizualnom evaluacijom, određivanjem gubitaka mase, FTIR spektroskopijom, SEM mikroskopijom te određivanjem kolorimetrijskih svojstava. Dobiveni rezultati pokazuju da biorazgradnja otisaka ovisi o adheziji, tj. lošija adhezija će rezultirati smanjenjem brzine biorazgradnje, dok će jača adhezija rezultirati boljom razgradnjom papira. Reakcije između papira i termokromne boje daju različita svojstva otisaka zbog različitog afiniteta papira prema boji, a interakcije između njih će utjecati na biorazgradnju otisaka. Kada se boja nanosi na papir, polarne komponente papira reagirat će s polarnim komponentama boje. Manja količina polarnih komponenata papira dat će otisak s polarnim karakterom. U oba slučaja, za ofsetnu i UV sušeću boju, rezultati pokazuju da bolja apsorpcija veziva u strukturu upojnog papira rezultira tanjim slojem veziva na površini papira. Na neupojnom (sintetskom) papiru, mikrokapsule su prekrivene debljim slojem veziva. U slučaju upojnog papira, uočena je veća brzina biorazgradnje, što je rezultiralo većim brojem bakterija, većim gubitkom mase, većim promjenama u boji (uništavanju i deformiranju mikrokapsula) i smanjenjem termokromnog efekta otisaka. Deblji sloj veziva i klasičnog pigmenta na površini neupojnog papira uzrokuje najsporiju biorazgradnju otisaka. Rezultati pokazuju da mikrokapsule, koje prodiru u strukturu upojnog papira, promiču biorazgradnju papira. Rezultati su također pokazali da je vezivo u termokromnoj ofset boji (vegetabilno ulje + smola) stabilnije od polimerne smole (poliuretan akrilata) prisutne u UV boji. Dakle, organsko recikliranje može biti bolja metoda zbrinjavanja termokromatskih otisaka.

KLJUČNE RIJEČI

Termokromne boje, deinking flotacija, biorazgradnja, FTIR, SEM, kolorimetrijska svojstva

LIST OF PUBLICATIONS

This thesis is a summary of the following papers, which are referred to in the text by their roman numerals. The papers are appended at the end of the thesis

I. **Vukoje, Marina**; Rožić, Mirela. Printing inks and recovery of paper for recycling - A Review. *Subbmited to Cellulose Chemistry and Technology (under revision)*

II. **Vukoje, Marina**; Jamnicki, Sonja; Rožić, Mirela. Deinkability of thermochromic offset inks. Nordic pulp & paper research journal, 31 (2016), 4; 692-699. doi:10.3183/NPPRJ-2016-31-04-p692-699

III. Jamnicki Hanzer, Sonja; Rožić, Mirela; **Vukoje, Marina**; Jukić, Mirela; Galić, Antonija. Safety Evaluation of Deinked Pulp Containing Offset Thermochromic Inks. BioResources, 13 (2018), 1; 678-690. doi:10.15376/biores.13.1.678-690

IV. **Vukoje, Marina**; Rožić, Mirela; Miljanić, Snežana; Pasanec Preprotić, Suzana. Biodegradation of thermochromic offset prints. Nordic pulp & paper research journal, 32 (2017), 2; 289-298. doi:10.3183/NPPRJ-2017-32-02-p289-298

V. Rožić, Mirela; **Vukoje, Marina**; Kapović, Dominik; Marošević, Livia Solvents interactions with thermochromic print. // Journal of graphic engineering and design, 8 (2017), 2; 19-25. doi:10.24867/JGED-2017-2-019

VI. **Vukoje, Marina**; Rožić, Mirela. Thermochromic offset ink – paper interactions and print biodegradation, Accepted for publication in *Acta Graphica*

VII. **Vukoje, Marina**; Miljanić, Snežana; Hrenović, Jasna; Rožić, Mirela. Thermochromic ink – paper interactions and their role in biodegradation of UV curable prints. *Subbmited to Cellulose. (under revision)*

VIII. **Vukoje, Marina**; Rožić, Mirela; Cigula, Tomislav. The role of adhesion on thermochromic printed cardboard biodegradation. Annals of Faculty Engineering Hunedoara, 15 (2017), 1; 75-82.

Contents

1. INTRODUCTION

Municipal solid waste (MSW) is the most complex solid waste stream, consisted of food residues, paper and board, plastics and other components. Paper-based products, altogether with kitchen waste, are one of the most common materials in municipal solid waste and waste material fraction with the highest recycling rates. In 2016, 72.5% of all paper consumed in Europe was recycled (CEPI, 2017). Recovered paper is today the most important raw material for the production of paper, paperboard and corrugated board. According to EU Waste Framework Directive, the waste management hierarchy for paper-based products implies that paper-based products should be re-used, recycled (material or organic recycling) or at least used for energy recovery (COST Action FP1003 - BioMatPack, 2015). Deinking flotation is the most common method for ink removal in the paper recycling process, where hydrophobic ink particles are removed from pulp suspension by adhesion to air bubbles, forming a froth that can be separated from the pulp suspension (Blanco et al., 2013). Ink removal from pulp suspension and the deinkability of printed products mostly depends upon the printing process used, the formulation of inks and the age of printed products (Dumea et al., 2009; Faul, 2010; Nie et al., 1998; Pan and Nguyen, 2007). Paper and board are easily reusable after their manufacture but their conversion into other products undergoes different applications with non-paper components (coatings, varnishes, laminates, adhesives, etc.) which might affect their deinkability or have environmental impact (Faul, 2010). Paper surface energy and wetting properties of ink can also significantly affect the deinkability properties of inks, due to adhesion of ink to paper (Forsström et al., 2005; Nie et al., 1998). Offset printing is a widely used printing technique and the majority of recovered paper is printed using this technique. Conventional offset inks are highly deinkable under alkaline conditions. The latter often occurs in the case of UV-cured prints, digital printing inks or water-soluble inks (Carré et al., 2000; Dumea et al., 2009; Faul, 2010). Some problems in recycling can be avoided by using enzymes or new methods for ink removal, such as ultrasound and adsorption deinking.

The quality of the recycled fibres depends upon the success of recycling process and decreases as the collection rate of recovered paper increases and as more “marginal” paper fractions are collected (Götze et al., 2016; Pivnenko et al., 2015a). Studies on recycled materials have identified a wide range of substances that may be present in the recycled pulp, which mostly originate from printing and converting processes undertaken in the previous use of the paper. Those substances remain in the solid matrix during paper recycling and thereby end up in new products based on recycled fibres (Pivnenko et al., 2015a). Moreover, certain paper and board types in recovered paper collected from households contain relatively high concentrations of chemicals such as mineral oil hydrocarbons, phthalates, phenols, polychlorinated biphenyls, and toxic metals (Cd, Co, Cr, Cu, Ni, and Pb) (Binderup et al., 2002; Götze et al., 2016). In order to maintain the high paper recycling rates with satisfactory quality of the recycled pulp, the presence of chemicals should be taken into account, and it is crucial that paper-recycling processes are highly effective in ink and toxic component removal. If the recycled paper is used in food packaging, it must comply with many specific requirements proposed by the European legislation.

Most of the collected paper will generally be recycled but some of it will be contaminated with food or be wet (about 40%). In these forms it's not suitable for conventional recycling methods but it is suitable for organic recycling (Ervasti et al., 2016; Murphy and Power, 2006). During organic recycling, waste can be subjected to aerobic (composting), anaerobic or anaerobic–aerobic digestion. These methods are also considered as material recycling (Ervasti et al., 2016). In the past decade, it has become the subject of research as a method of waste disposal. When it comes to unprinted paper samples, few studies showed that paper products are anaerobically biodegradable in laboratory-scale landfill reactors (De la Cruz et al., 2014; Wang et al., 2015) or aerobically by composting (López Alvarez et al., 2009; Venelampi et al., 2003). There is a lack of information about the influence of printing inks on the biodegradation of paper.

Due to the increasing use of thermochromic inks in different graphic products, it is necessary to examine the possibility of their waste disposal. Previous studies about thermochromic inks investigated mainly the chemical composition of leuco dyes in microcapsules and their changes (Hajzeri et al., 2015; Oda, 2008a, 2008b, 2005, Panák et al., 2017, 2016, 2015; Raditoiu et al., 2016). For the commercially available thermochromic printing ink different studies have been conducted for the purpose of their colorimetric properties and UV stability (Friškovec et al., 2013; Kulčar et al., 2011, 2010; Rožić et al., 2015). As ink formulation is an essential factor in deinking, it is crucial to determine the deinkability of thermochromic offset inks, which differ from conventional offset inks formulation. In addition, these inks may contain different harmful substances, so the obtained recycled paper should be analysed with respect to the concentration of potential harmful substances. Organic recycling as one of recycling methods, should also be investigated, especially for prints that are generally difficult to recycle using conventional methods. Up to now, there was no available data about recycling and biodegradation of thermochromic prints or thermochromic materials in general.

1.1. Objective and hypotheses of research

The aim of this research is to investigate the possibility of material and organic recycling of UV curable screen printing and offset thermochromic printing inks and to characterize the investigated recycling processes.

Hypotheses of the research are:

- determination of the thermochromic ink adhesion parameters will give an improved evaluation of the efficiency of the thermochromic prints recycling methods,
- the optimal interaction between paper and ink depends upon the physicochemical properties of paper and ink and has an impact on material and organic recycling of thermochromic prints,
- the environmental impact of thermochromic inks can be predicted based on the characterization of interactions between paper and ink.

2. BACKGROUND

2.1. Composition of paper for recycling

Paper and paper products are made primarily of mechanical and/or chemical wood pulp, recycled fibres, non-fibrous components (minerals and additives) and water (Keränen and Ervasti, 2014). Fibres are made of cellulose, hemicellulose and lignin. According to CEPI, the total consumption of non-fibrous materials in pulp and paper production for 2016 was 14.227 million tonnes (CEPI, 2017). Additives and fillers guarantee the particular use properties of the papers while coatings and varnishes improve the surface properties of papers. As presented in the *Table 1,* different paper products will have different composition. Paper products are comprised of cellulose. Office paper contains lower amounts of lignin, compared to other types. Higher amounts of ash originate from fillers in paper products.

Besides minerals and additives, paper for recycling can also contain different materials such as staples, laminated covers, plastic wrapping, inks, thick adhesive layers, *etc.* (Faul, 2010). In general, the printing inks are the most important non-fibres components that can be found in or be the part of paper for recycling. In addition to printing inks, lacquers or overprint varnishes can be also found as non-paper components. They are uncoloured forms of printing inks and can be used to give added gloss and protective properties to the print and substrate (Leach, 2007). Paper based packaging contaminated with food is not desirable in paper recycling facilities due to cleaning difficulties, which leads to contamination issues (Twede et al., 2015).

Table 1. Composition of paper for recycling

Source	% (w/w) cellulose	% (w/w) hemicellulose	% (w/w) lignin	% (w/w) kaolin / $CaCO_3$	Volatile solids, %	Reference
Copy paper	46	11.9	1	33	-	(Elliston et al., 2013)
Office paper	84.9	12.3	1.4	1.4	-	(Yuan et al., 2012)
Office paper 1	61.3	11.4	1.75	-	77.2	(Wang et al., 2015)
Office paper 2	57.8	12.2	0.17	-	77.3	(Wang et al., 2015)
Coated paper	42.3	9.4	15	-	74.3	(Eleazer et al., 1997)
Magazine paper 1	42.3	7.4	3.3	-	94.9	(Wang et al., 2015)
Magazine paper 2	34.5	11.9	19.3	-	92.3	(Wang et al., 2015)
Newspaper	48.5	9	23.9	-	98.5	(Eleazer et al., 1997)
Newspaper 1	45.2	18.0	23.9	-	69.0	(Wang et al., 2015)
Newspaper 2	43.3	17.9	25.5	-	95.6	(Wang et al., 2015)
Newspaper	41.02	24.85	23.07	5.99	-	(Subhedar and Gogate, 2015)
Newspaper	68.5	13.1	23.4	3.9	-	(Yuan et al., 2012)
Cardboard	56.9	10.7	17.8	12.8	-	(Yuan et al., 2012)

The quality of paper for recycling highly depends upon collection system (which is the first step in the recycling process), society's environmental awareness, sorting activities, the price of recovered paper and the impacts of printing and converting techniques (Bobu et al., 2010; Miranda et al., 2010). The sorting of paper for recycling is mainly manual (rarely semi-automatic and automatic) and diverse. Sorting activities play an important role when lower quality sources are exploited for achieving higher collection rates. According to Rahman et al. (2014) the paper industry may choose a specific sensor-based paper sorting system, such as a stiffness sensor for old corrugated cardboard or containers (OCC), a lignin sensor for old newspaper (ONP), a gloss sensor for glossy paper, a colour sensor for writing paper (WP), *etc*. Given the weaknesses of lignin, stiffness, gloss, colour, NIR, and MIR sensor-based systems in paper for recycling sorting process, a webcam sensor-based recyclable paper for recycling sorting process is found to be one of the best low-cost alternatives (Rahman et al., 2014). Besides these factors, the utilization of paper for recycling in the paper industry is affected by its price, processing costs, availability, the production of poorly recyclable products (influence of printing inks and adhesives) and lack of legislation and regulations (Miranda et al., 2010). The increased recycling rate and the use of commingled collection systems have reduced the quality of the collected paper and produced recycled paper (Miranda et al., 2013, 2011). Increased use of non-fibre components can lead to increased difficulties in the later stages of the recycling processing chain (Keränen and Ervasti, 2014). During its lifecycle, paper is in contact with different materials, which results in numerus impurities, thus solid particles, moisture and dissolved substances can migrate from one waste material to another which can have an enormous effect on material recycling (Götze et al., 2016; Onusseit, 2006). Götze et al. (2016) showed that higher concentrations of metals in paper and cardboard waste (Al, As, Ca, Cd, Cr, Cu, Hg, Pb, Sb, Sn, Nd) are not necessarily a result of cross-contamination from other waste materials but may originate from certain paper and cardboard constituents such as inks and fillers. Paper based products can contain ammonia, sulphides, organics (lignin, chlorphenols, halogenated aliphatics, *etc*.) (Chen et al., 2008) as well as different metals (Rožić et al., 2005). Some of these compound may originate from printing inks and coatings (Mertoglu-Elmas, 2017; Rožić et al., 2005).

2.2. Printing inks

Printing inks are coloured complex mixtures, whose main task is to convey a message, provide protection and to give a decorative effect to the substrate to which they are applied. Mostly they are consisted of colorant (pigment or dyes), binder (resins, oils or solvents), solvent (oil or water-based) and additives (chelating agents, anti-oxidants, surfactants, biocides, etc.). Pigments are dispersed solids, insoluble in the support material and almost exclusively used in printing processes. Compared to pigments, dyes are soluble and have lower lightfastness and lower resistance to water. Resins used in printing inks contribute to the properties of hardness, gloss, adhesion and flexibility in an ink (Leach 2007). Mostly, resins or polymers are used as binders (phenolic resins, alkyd resins or synthetic resins (polyacrylates)). The ink binder is responsible for ink properties such as viscosity, drying properties, and surface energy (Pekarovicova and Husovska 2016). Oils in printing inks may be drying, semi-drying or non-drying. Drying vegetable oils are glycerides or triglycerides of fatty acids, varying from those that are completely saturated (no double bonds) to those that contain three or more double bonds. Mineral oil in various forms is used as a binder in printing inks or as a solvent or diluent in the manufacture of ink binders. They consist of varying percentages of aromatic, naphthenic and paraffinic hydrocarbons, with a small sulphur content ranging up to 4% (Leach 2007). Solvents dissolve the binders and adjust the viscosity of the ink for the different printing processes (Robert 2015). Additives are used to improve the ink properties and they are added in ink formulations in amounts not exceeding 5%. These compounds include surfactants to reduce the surface tension and thereby the wetting problem. Adhesion promoters or wetting agents enhance the binding to the printing substrate and biocides prevent microbiological degradation of the ink (Robert 2015). The main function of a plasticizer (expoxidized compounds, phthalates, polyesters, benzoates) is to make the dried ink flexible and driers help with the oxidative drying process and help to supply elasticity to an ink film. Driers are catalysts used to promote oxidation of the drying oils (inorganic salts and metallic soaps of organic acids).

Printing inks are formulated for individual printing processes, classic (offset, flexographic, screen, gravure) and digital (electrophotography, ink jet, laser). They must have certain rheological properties in order to be transferred to the printing plate and afterword from printing plate to the substrate (*e.g.* paper).

After application of printing ink onto the substrate, the binder dries and binds the colorant to the substrate under the press running conditions (Leach 2007). The drying of printing inks must be achieved as quickly as possible and it can be performed by physical (evaporation) and chemical (oxidation, radiation-induced curing) means or a combination of both (Leach, 2007). Radiation-induced drying includes ultraviolet radiation, infrared, electron beam, microwave and radio frequency. The volatile organic compounds (VOC) evaporation from solvent based inks and their emission into the atmosphere during printing can be overcome by the use of water based and UV-cured inks. Besides better environmental appearance, the UV curable printing inks are especially suited for printing on non-absorbent surfaces due to quick drying (Robert, 2015). Radiation curing inks are formulated as other inks, consisting of pigments, binder, solvent and additives. In UV curable printing inks the binders are generally acrylates (epoxy, polyurethane and polyester acrylates). The solvents in these systems are low-viscosity monomers while the additives can be waxes, surfactants, photoinitiators (*e.g.* benzophenone) and photoactivators (*e.g.* amines), inhibitors and in some cases additives to improve printability. Photoinitiators are required in order to achieve solid state of ink after printing, in the presence of UV light by free radical, cationic or hybrid reaction (Leach, 2007). The UV curable printing inks have some drawbacks such as contamination of packaging by residual reactive diluents and photoinitiators which remain in the ink after printing (Robert, 2015), as well as problems during recycling of paper (Carré et al., 2005).

2.2.1. Thermochromic Printing Inks

Smart polymers or stimuli-responsive polymers undergo large reversible changes, either physical or chemical, in their properties as a consequence of small environmental variations, such as temperature, optical wavelength, absorbed gas molecules or pH values (Larrucea and San Roman, 2014). One of the examples of smart polymers are thermochromic materials. Thermochromic materials have a wide range of applications, and their development is still in progress. Each of these applications requires a specific set of material properties and deeper understanding of the physical and chemical background. In thermochromic materials, light can interact with materials in the form of reflection, absorption or scattering (Seeboth and Lotzsch, 2013).

Reversible thermochromic materials based on leuco dyes usually consist of at least three components: chromogenic compound (leuco dye), developer and solvent. In thermochromic leuco dye–developer–solvent system thermochromic effects are based on changes of absorption caused by molecular interactions of the incorporated functional dye within its microenvironment (Aitken et al., 1996; MacLaren and White, 2003; Seeboth et al., 2007; White and LeBlanc, 1999).

The thermochromic effect is caused by the formation of leuco dye–developer complexes in a reversible equilibrium redox reaction between leuco dye and developer. The reaction between dye and developer occurs at lower temperatures, where the solvent exists in its solid form, thus creating a coloured dye developer complex. At higher temperatures the solvent melts, causing a dominant reaction between the solvent and the developer, resulting in the decomposition of dye - developer complexes. This reaction converts the system into its colourless state (Kulčar et al., 2010; MacLaren and White, 2003; Seeboth et al., 2007; White and LeBlanc, 1999). The most common electron-donating chromogenic compounds are phenylmethane and fluoran derivatives bearing a lactone ring moiety. In the lactone ring-closed state these so-called leuco dyes or colour formers are either colourless or weakly yellow coloured. Leuco dye–developer–solvent systems are coloured in the solid state and transform on heating above the melting temperature of the solvent into a colourless liquid (Seeboth and Lotzsch, 2008). Colour developers are usually weak acids (bisphenol A, octyl phydroxybenzoate, methyl p-hydroxybenzoate, 1,2,3-triazoles, and 4-hydroxycoumarin derivatives) while long – chain alkyl alcohols, esters, and acids are commonly used as solvents (MacLaren and White, 2003; White and LeBlanc, 1999).

The temperature range that the transition of coloured to colourless state occurs at is commonly called the activation temperature (TA) (Kulčar et al., 2010). Some leuco dye thermochromic inks change from one colour to another, rather than changing from a coloured to a colourless state. This is achieved with an ink that combines a leuco dye with a conventional ink colorant formulation (Kulčar et al., 2010). For example, adding microcapsules with a blue leuco dye–developer complex to a conventional yellow ink will result in a green ink formulation. In its cooled state, the printed ink layer will be green, and once warmed above its TA, it will revert to yellow as the leuco dye becomes clear or translucent (Homola, 2008).

Thermochromism can appear in all different classes of polymers: thermoplastics, duroplastics and gels, as well as thermochromic colouring agents for toys, temperature indicators for plastic and printing inks, for paints, etc.

Thermochromic printing inks are chromogenic or colour-changing inks, demonstrating a colour change when exposed to different temperatures. They can take two forms: liquid crystals or leuco dyes (Seeboth and Lotzsch, 2013). Both types of thermochromic inks are usually encapsulated to enable easier handling. Commercially available thermochromic printing inks based on leuco dyes are consisted of microencapsulated leuco dye–developer–solvent systems and a resin binder (Seeboth and Lotzsch, 2013; Tang and Stylios, 2006). The sizes of microencapsulated thermochromic pigments (microcapsules) are in the range of 3 to 5 μm, which makes them at least ten times larger than the average pigment particle (Seeboth and Lotzsch, 2013). The most widely used system for microencapsulation of thermochromic and photochromic inks involves urea or melamine and formaldehyde systems (Aitken et al., 1996), gelatine–gum arabic and epoxy resins (Fujinami, 1996a).

2.3. Paper – ink interactions

One of the main functions of printing inks is to adhere on the printing substrate and remain there for the whole lifespan of a print. Adhesion of inks to paper plays an important role in many industrial applications and it can be characterized indirectly through thermodynamic analysis of the paper substrate, or directly through paper laminate or adhesion tape peel testing (Awaja et al., 2009). The bond strength between the paper surface and polymer depends strongly on the physical and chemical structure of the two surfaces that are in contact. For example, the polymer polarity created by the carboxyl content of adhering polymers, would affect the adhesion strength of the cellulose-polymer bond, where peel strength increases when the carboxyl content increases. Thus, polarity of polymer and cellulose substrate affects the strength. In addition, the influence of critical surface tension of paper and ink can have significant influence. Papers having critical surface tensions below that of inks can show the poor adhesion compared to those having critical surface tensions in excess of inks. Pure cellulose shows relatively high values (44-60 mN/m) of the critical surface tension, while the values for lignin-containing and sized paper are lower (Borch, 1991). Adhesion can be affected by inks formulation, *i.e.* upon colorants, solvents and vehicles. The influent of colorants on ink adhesion mostly depends upon their compatibility with the vehicle system, their type, percentage and degree of dispersion in the final ink. Adhesion is influenced by the degree of vehicle penetration on paper while for non-absorbent substrates, is controlled by the film-forming ability of the resin and the molecular affinity for the substrate. Adhesion of printing ink can be affected by solvents in two different ways, enchaining wettability and increasing penetration. Improvement of wetting is essential for good adhesion and flow-out of ink in order to give a continuous film. Improvement of ink penetration into the substrate can assist physical and chemical bonding. Adhesion can also be affected by adding additives in small amounts during manufacturing process in order to improve chemical bonding between printing substrate and ink (Leach, 2007).

Borch, (1991) and Forsström et al., (2005) explained that mechanisms controlling the adhesion between ink and printing substrate are:

- Thermodynamic characteristic. Surface energy has a central role, as the wetting of cellulose by the ink is important for the final ink–cellulose interaction. Wetting is controlled by dispersion and polar interactions between paper and ink.
- Molecular contact area - surface topography (paper roughness). In electrophotography and thermal printing decrease in toner adhesion occurs for rougher papers and similar behaviour described for polymer coatings at low coating levels. The contact area governs interdiffusion and come between the constituents of the ink with the amorphous part of the cellulose.
- Fusing temperature, time and pressure.

Surface interactions between printing ink and cellulose are of importance during printing, as well as during ink removal in paper recycling as a high adhesion between ink and cellulose might cause problems during ink detachment (Forsström et al., 2005). Surface energy studies can explain deinking effectiveness and fact that different compositions of printing inks may cause different problems due to differences in surface chemistry and mechanical dispersion properties (Thompson, 1998). In the case of adsorption deinking, the surface free energy of inks, paper and polymers used as adsorbents, structure and specific surface area of adsorbents can explain the ink detachment and recycling effectiveness (Petzold and Schwarz, 2015).

2.4. Waste management options for paper based products

In 2016, 72.5% of all paper consumed in Europe was recycled. Recovered paper is today the most important raw material for the production of paper, paperboard and corrugated board. CEPI members produced 90.9 million tonnes of paper and board in 2016, while the utilisation of paper and board was 47.8 million tonnes, and the utilisation rate was 52.6% (CEPI, 2017).

Most of the paper based products mostly have a life span of a few days (*e.g.* newspapers) or a few weeks (*e.g.* packaging).

Reducing the amount of all kinds of produced waste streams has been presented through European laws, either by prevention, reusing or recycling (Bartl, 2014; European Commission, 2008). In order to improve recovery of waste, it should be collected separately if technically, environmentally and economically practicable and it should not be mixed with other waste or materials with different properties. Collecting of paper for recycling is very high in Europe, according to CEPI it was 56.406 million tonnes in 2016 (CEPI, 2017).

Different waste management options for paper for recycling have been studied worldwide, due to different issues occurring. For example, poor deinkability of prints, contamination issues related to food, high moisture content of collected paper, *etc*. Despite large percentage of use paper used for recycling for production of recycled paper and board, different authors give various proposals, from incineration, production of bioethanol to biodegradation in aerobic and anaerobic environment. According to European law, waste management should be followed as presented in *Figure 1*. The most important is to prevent and to reduce the amount of all kinds of waste (Bartl, 2014). But, if the waste is produced, than it should be recycled (by means of material or organic recycling) or used for energy production.

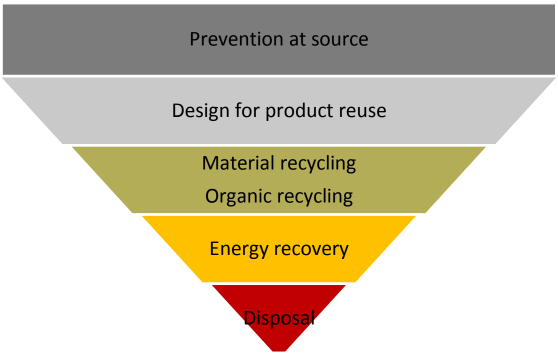

Figure 1. Waste management hierarchy (COST Action FP1003 - BioMatPack, 2015)

Collected paper for recycling that needs to be recycled in some of the proposed ways is usually not clean and very often contains different impurities such as printing inks, coatings, or even residues of food when it comes to food packaging.

Paper I presents a brief review of waste management options for paper for recycling. Different waste management methods can be used, because each of them has a certain advantages and certain drawbacks, depending upon paper types and different prints applied.

Literature review showed that material recycling purposed for production of recycled paper and cellulose derivatives, were mainly studied for graphic papers. Bioethanol production and organic recycling were the subject of research for paper and paper based packaging which is wet and contaminated with different substances (mainly food), or even for wastes obtained during production and recycling of paper (deinking sludge). Printing inks may notably influence the quality of new materials produced, such as recycled paper. If the inks are not removed from pulp, recycled paper will not only have poor optical and mechanical properties, but also it can be problem due to presence of toxic substances. Thus, it is of great importance to provide a toxicological assessment of new materials. In order to avoid different problems related for the printing inks that are generally difficult to remove by classic deinking by flotation method, the use of other methods (enzymatic, adsorption and ultrasound deinking) or their combination with classic method can be conducted. During enzymatic deinking, different enzymes will degrade different prints. There is no unique enzyme, which will be effective for all kinds of prints. When dealing with other waste management methods for paper for recycling (bioethanol production and organic recycling), there is lack of knowledge about the influence of printing inks on their efficiency. Since bioethanol production and organic recycling are dealing with biochemical reactions and living microorganisms, the only available information are the inhibition of enzymes activity by toxic substances present in printing inks (fillers, organics and heavy metals). Therefore, it may be assumed that printing inks can reduce the efficiency of the mentioned processes. In the last decade, the use of paper for recycling for the production of different cellulose derivatives has become a topic of many studies. Most of the studies were only connected to mixed office paper that is printed by non-impact printing. For other types of printing inks, there is no available data. Besides previous mentioned methods, thermal conversion with energy recovery like pyrolysis and gasification can be also useful. The presence of printing inks may disrupt the combustion and influence the quality of produced gases and ash. Paper for recycling is valuable material and thus, landfilling is the only method that is recommended to be avoided. Life cycle assessment (LCA) methods can be a useful tool for the selection of desirable waste management method, but only if the system boundaries are well defined. The main drawback of the LCA studies which were conducted up to now is the lack of information related to printing inks used for calculations of environmental impacts. Comparing all-possible waste management methods for paper for recycling, the most significant influence of printing inks on process efficiency is known to be for classic recycling for the production of recycled paper, but when dealing with other methods there is lack of available data. In these methods (bioethanol production, organic recycling, and energy recovery) the types of paper substrates and their components (*i.e.* presence of lignin, fillers, *etc.*) mostly influence the processes efficiency. Based on the literature presented, in all of these waste management methods, the printing inks play an important role, thus when researchers are dealing with some new recovery method or with new materials, they should always take the presence of printing inks into account.

2.4.1. Material recycling

Products that consume a lot of energy during production from virgin materials have been manufactured from secondary raw materials for a long time, making considerable energy savings (Onusseit, 2006). Recovery of paper for recycling from municipal solid waste is useful since it can be used for production of different valuable products. Paper and cardboard recycling reduces municipal solid wastes and therefore improving sustainability. Production of recycled paper uses less energy (28-70% energy savings), reduces carbon dioxide emission, the volume and loading of effluent, compared to paper produced from virgin fibres (Bobu et al., 2010). Paper for recycling and paper industrial residues containing high cellulose content are also proved to be a promising source of low-cost, raw material for different cellulose derivatives production, as well as for other high value-added bio-conversion processes (Souza et al., 2017), such as ethanol (Brummer et al., 2014; Dubey et al., 2012; Nishimura et al., 2016; Subhedar and Gogate, 2015; Trinh et al., 2013; Wang et al., 2013, 2012) and methane (Baba et al., 2013; Yuan et al., 2012). Pendyala et al. (2013), Argun and Onaran, (2016), Eker and Sarp, (2017) have studied the potential of paper for recycling for hydrogen production, but they didn’t describe the influence of printing inks on hydrogen yield production.

The utilization of paper for recycling for production of valuable added materials increased all over the world in recent years and provided an alternative to classic paper recycling. In addition, it may possibly address this issues arising from classic paper recycling (Joshi et al., 2017, 2015).

Deinking by flotation

Deinking is the most important process in the production of recycled paper and depends on many factors, such as quality of the collected paper for recycling, the type of printing process, properties of the printing inks, age of printed product and climatic conditions during its life cycle (Dumea et al., 2009; Kemppainen et al., 2015, 2013; Nie et al., 1998). In order to achieve desirable properties of recycled pulp (optical and mechanical), improved deinkability of printed paper products has become essential and one of the most important key factors for a potential use of recovered paper in graphic papers production. Moreover, due to the growing tendency to print certain products such as cardboard, deinkability of packaging grades is of an importance (Blanco et al., 2013). When the printing ink colloidal dissolves in the water and colours the entire pulp, a serious problem occurs in the case of graphic paper production, but it is not significant for brown paper production (Grossmann et al., 2014). Packaging paper grades and mixed grades are commonly recycled without deinking. Deinking process is common practice for graphic paper grades, except some high quality grades with little or no ink (Faul, 2010).

Different deinking processes can be used for the production of recycled fibres, based on the quality of paper for recycling and desired quality and requirements of the produced pulp. The most common methods for ink removal use chemical approach and large quantities of chemicals (*Table 2*), which makes the method expensive and resulting in environmental pollution due to release of contaminants and requires costly waste water treatment system. Thus the proper selection of deinking chemicals is often a compromise between costs and performance (Bajpai, 2014; Lee et al., 2013).

However, paper for recycling, which usually comes with different types of applied prints, will not always show positive deinkability tests (*Table 3*). Deinking by flotation is efficient mostly in the case of conventional offset and gravure printing inks where hydrophobic printing inks are present (Dumea et al., 2009; Grossmann et al., 2014). According to Faul (2010), 81% of the offset prints, mostly newspapers and magazines, achieved a positive assessment of their deinkability, while the latter often occurs in the case of UV-cured prints.

Table 2. Deinking chemicals (Bajpai, 2014; Jiang and Ma, 2000)

Chemicals	**Addition point**	**Function**	**Dosage (% of fiber)**	**Furnish type**
Sodium hydroxide	Pulper, bleach tower, disperser	Fibre swelling, breaks down ink vehicle by saponification or hydrolysis, ink dispersion	0-5	All grades
Hydrogen peroxide	Pulper, bleach tower, disperser	Bleaching, ink degradation, anti-yellowing	0.5-2.5	Groundwood grades
Sodium silicate	Pulper, bleach tower	Source of alkalinity and pH buffering agent, wetting, ink dispersion, peroxide stabilisation	0.5-5	Groundwood grades
Chelating agents (EDTA, DTPA)	Pulper, flotation cells	Formation of soluble complexes with heavy metal ions. The complexates prevent these ions from decomposing the hydrogen peroxide	0-0.5	All grades
Soap	Pulper, flotation cells	Ink collector (renders the ink hydrophobic and facilitates its attachment to the air bubble)	0.5-3	All grades
Surfactants	Pulper, flotation	Wetting, ink removal, ink dispersion, emulsification	0.1-2	All grades
Calcium salts	Flotation cells	Reacts with the collector soap to form small insoluble calcium soap particles that adhere to the ink particle; calcium helps agglomerate the ink particles into large hydrophobic clusters	90 – 300 ppm	Groundwood grades
Solvents C_1-C_{14} alphatic saturated hydrocarbons	Pulper	Ink softening, Solvation of wax	0.5-2	Wood free grades

Table 3. Deinkability of prints

Prints	Deinkability	Nature of ink particles	Problems	Reference
Offset	Good	Hydrophobic	After aging, bad ink detachment	(Dumea et al., 2009; Faul, 2010)
Gravure	Good	Hydrophobic	-	(Faul, 2010)
Flexographic	Poor	Hydrophilic	Small and hydrophilic nature of the ink particles which can't attach to the collectors in the flotation process	(Faul, 2010; Grossmann et al., 2014)
Digital	Poor	Hydrophilic	Generating numerous ink particles above 100 μm	(Dumea et al., 2009)
Inkjet	Poor	Hydrophilic	Ink may stain the fibre, formation of small particles	(Carré and Magnin, 2004; Du et al., 2016; Thompson, 1998)
Hot melt based ink jet prints	Poor	Fused during drying – residual toner	Sticky deposits	(Carré et al., 2005)
Toner	Poor	Fused during printing	Formation of larger particles, flat and plate like particles	(Nie et al., 1998; Thompson, 1998)
Liquid toner	Poor	Too soft to pass the screens	Large visible inked film specks	(Carré et al., 2005)
UV curable	Poor	Formation of cross-linked films which are difficult to break down	Visible speck contamination by large flat and plate like particles	(Thompson, 1998)

In addition to conventional printing inks that have been used so far, new ink types are being constantly developed and can be found on the market. Small variations in their chemistry can affect their quality, printing quality as well their deinkability aspects. As the ink formulation is an essential factor in deinking, it is crucial to investigate deinkability aspects of novel printing inks, which may differ from conventional inks in formulation and size of colorants or additives. For example, information about the recycling of functional inks and smart printing inks is very limited. Aliaga et al., (2015) reported about the effects of the printed electronics on the paper recyclability. The analysis was based on a case study focussed on envelopes for postal and courier services provided with these intelligent systems. According to the results of the pilot scale recycling tests, the resistors (silicon-based electronic component) do not disintegrate in the pulping stage and they are retained in the screens and thus do not affect the quality of recycled paper. The results showed that nanosilver inks were dissolved in the pulp suspension and can affect both mechanical and optical properties of the recycled paper. In addition, the authors have emphasized that real impacts on industrial recycling are expected to be even significantly lower since the proportion of paper product with printed circuits in the current paper waste streams are much lower. However, they also point to the fact that further research on the treatment of printed electronics and smart labels is needed in parallel with innovation in these communicative devices (Aliaga et al., 2015).

Pivnenko et al. (2015) showed that paper for recycling might potentially contain a large number of hazardous chemical substances, while many of them can be associated with the printing industry. If the printing inks are not entirely removed during paper recycling, the recycled pulp and the product made of it may contain residues (Laine et al., 2016; Pivnenko et al., 2015a). Paper and cardboard that are partly or fully produced from recycled fibres can be used in contact with dry foodstuff like flour, grain, sugar, salt, rice and pasta and as such must meet certain basic set of criteria concerning safety issues. Different authors have studied the contaminants in recycled fibres, mineral oils hydrocarbons, phenols, phthalates, polychlorinated biphenyls, bisphenol A and toxic metals (Laine et al., 2016; Pérez-Palacios et al., 2012; Pivnenko et al., 2016, 2015a, 2015b; Suciu et al., 2013).

Besides health safety of recycled pulp, paper recycling process may also affect the process water. The type and quality of the raw material (wastepaper) used for recycling as well as pulping and deinking additives, mineral oils and other substances will affect the quality of effluents from paper recycling mills (Dsikowitzky et al., 2015).

Table 4. Organic pollution of effluents from paper recycling effluents generated in laboratory scale due to different deinking processes and samples used

Sample	Deinking process	Parameter		Reference
		COD / (mg/L)	BOD / (mg/L)	
Offset	Chemical - Alkaline	2650	-	(Dumea et al., 2009)
Digital		4950	-	
Flexographic		2150	-	
Flexographic	Chemical - Neutral	1309	-	(Dumea et al., 2009)
School wastepaper with blue ink	Chemical - Alkaline	3750	1136	(Singh et al., 2012)
	Enzymatic - xylano-pectinolytic	1056	368	
Toner	Chemical - Alkaline	270	122	(Pathak et al., 2015)
	Enzymatic - commercial	148	85	
	Enzymatic - isolated	168	99	
Offset	Chemical - Alkaline	779	-	(Marlin et al., 2013)
Newspaper / magazine		921	-	
Mixed - flexographic toner and offset	Chemical - Alkaline	409	240	(Sulbaran-Rangel et al., 2016)
	Chemical - Neutral	479	310	

Table 4 shows that different deinking processes (conducted in laboratory scale) and used raw materials (paper and prints obtained) will have different values of organic components in effluents. Current deinking processes depend upon the use of large amount of chemicals that produce toxic effluents and high chemical oxygen demand (COD) values (Singh et al., 2012).

2.4.2. Organic recycling

Organic recycling is also considered as material recycling due to production of compost or biogas. But the main problem is that, as with incineration and bioethanol production, when paper is composted or digestated it disappears from the paper recycling chain (Ervasti et al., 2016). Biodegradation of paper products is mostly dependent upon the crystalline/amorphous ratio in cellulose and presence of lignin (De la Cruz et al., 2014; Komilis and Ham, 2003; Stinson and Ham, 1995; Venelampi et al., 2003). Amorphous zones of cellulose are more susceptible to biodegradation than the crystalline regions. The relative content of these two components could also vary in the different paper materials making the process of biodegradation different (Pérez et al., 2002; Van Wyk and Mohulatsi, 2003). Different additives in paper are making biodegradation less effective through the inhibition of enzyme action (Van Wyk and Mohulatsi, 2003). Pinzari et al. (2010) showed that clay and aluminium can inhibit fungal development during biodegradation of paper more than $CaCO_3$ (Pinzari et al., 2010). Heavy metals originating from printing inks or fillers in paper are not biodegradable. They can accumulate to potential toxic concentrations and disrupt the enzyme activity. When it comes from pulp and paper industry the most common inhibitors are sulphide, tannins, resin acids, LCFAs, and halogenated compounds (Chen et al., 2008).

Biodegradability aspect of paper and paper based products was the subject of many studies (De la Cruz et al., 2014; López Alvarez et al., 2009; Venelampi et al., 2003; Wang et al., 2015). However, there is lack of knowledge about the biodegradation of printing inks and their influence on paper based products biodegradation. In some studies the printing inks are only referred as the toxic components in biodegradation process (Hermann et al., 2011; López Alvarez et al., 2009). Stinson and Ham (1995) studied a decomposition of printed and unprinted newspaper and based on the generated amount of methane the obtained results indicate that the printing ink did not inhibit the amount or affect the rate of methane production from cellulose in newspaper.

Studies of vegetable based polymers and binders biodegradation, which are commonly used in printing inks, have been investigated by few researches (Erhan et al., 1997; Erhan and Bagby, 1995; Shogren et al., 2004). In addition, there are few available data on biodegradation of printed polymer films in which the reduction of biodegradation rate was noticed for printed samples (Bardi et al., 2014; Hoshino et al., 2003).

3. METODOLOGY

The research was conducted according to the proposed plan including the following:

1. Examination of deinkability aspect of thermochromic offset prints (material recycling)
2. Analysis of recycled pulp quality (in terms of safety evaluation) containing thermochromic offset prints and process water effluents
3. Evaluation of the thermochromic prints (offset and UV curable screen prints) biodegradability (organic recycling).
4. Determination of thermochromic ink – paper interactions.

For the purpose of this study, thermochromic offset and UV curable prints were obtained. Offset prints were produced using the Prüfbau Multipurpose Printability Tester, while the UV curable thermochromic prints were screen-printed using the screen printing machine (Siebdruckgeräte von Holzschuher K.G., Wuppertal) and dried under the UV irradiance using Technigraf Aktiprint L 10-1 device. All samples were printed in full tone. Since UV curable prints cannot be successfully recycled by means of the classic deinking method, UV thermochromic ink were only evaluated for biodegradation.

All the used methods and equipment are described in more detail in the presented Papers II – VIII appended at the end of the thesis.

3.1. Deinkability of thermochromic offset inks

For the evaluation of deinkability aspects, offset paper was printed with three different thermochromic offset inks. Deinkability of thermochromic offset inks on white uncoated paper, in laboratory conditions, was examined by means of chemical deinking flotation according to INGEDE method 11p. Deinkability was evaluated by calculating the flotation yield, the the increase of brightness and whiteness and colour properties of the pulp, by determining residual ink area, as well as ash content elimination. Ash content was determined using the TAPPI method T 211 om – 02. The dirt (residual ink) particle area on handsheets was determined using image analysis and data processing, according to ISO 15755. Undeinked and deinked pulp handsheets were tested for their optical properties. All measurements were carried out in accordance with standard methods, ISO Brightness according to ISO 2470 , while CIE whiteness and colour components CIE L*a*b* were measured according to ISO 11475.

3.2. Analysis of recycled pulp quality containing thermochromic offset prints and process water effluents

The obtained recycled paper was analysed with respect to the concentration of heavy metals and bisphenol A, total organic compound (TOC) and total carbon (TC), and transfer of antimicrobial constituents from the recycled paper. The concentrations of determined chemicals were compared with the limits proposed in the “Industry Guideline for the Compliance of Paper and Board Materials and Articles for Food Contact”, developed by the European paper and board food packaging chain (CEPI/CITPA/CEFIC/FPE, 2012).

Effluents from paper recycling process were examined in the terms of heavy metals concentration, total organic compound (TOC) and chemical oxygen demand (COD).

3.3. Evaluation of the thermochromic prints biodegradability

For the evaluation of biodegradability aspects, offset and UV curable screen printing thermochromic ink were used. The biodegradability aspect of thermochromic leuco dye prints on different paper materials were studied using soil burial test under anaerobic conditions. Laboratory soil burial experiments were conducted at room temperature 25±2 °C by placing the samples horizontally in the forest field soils (containing humus) in glass containers. The water content of the soil was adjusted to 40 % of its maximum water retention capacity. The commercial available reagent Anaerocult A (Merck) was used in order to allow the development of anaerobic conditions.

Printed-paper samples were evaluated for changes by means of: visual examination, microbial growth assay, weight loss measurements, Fourier-transform infrared spectroscopy (FTIR), Scanning electron microscope analysis (SEM), microscopic images, and colorimetric measurements. The morphology of microcapsules and mechanisms of thermochromic inks biodegradation was briefly studied as well. In order to provide better understanding of potential changes in biodegradation and influence of printing substrate, a few different papers were printed and evaluated for biodegradation.

3.4. Determination of paper – ink interactions

In order to gain better understanding of the behaviour of thermochromic inks in previously mentioned studies, paper-ink interactions were studied using thermodynamic work of adhesion. Paper ink interactions and adhesion parameters were studied using contact angle measurements (Bota et al., 2017; Cyras et al., 2007; Moutinho et al., 2011; Tkalčec et al., 2016; Zhao and Kwon, 2010). The Owens-Wendt-Rabel-Kaelble calculation method was applied to the contact angle data of test liquids in order to evaluate the parameters of surface free energy (γ) and its dispersive (γ^{d}) and polar (γ^{p}) components of the paper samples and prints (Cyras et al., 2007; Moutinho et al., 2011; Zhao and Kwon, 2010). From the obtained γ, adhesion parameters were calculated.

4. RESULTS AND DISCUSSION

4.1. Deinkability of thermochromic offset inks (Paper II)

For evaluation of thermochromic offset inks deinkability, three thermochromic inks were printed on white uncoated paper (*Table 5*). These prints were mixed in equal shares and recycled according to INGEDE method 11p.

Table 5. Offset Thermochromic Inks

Thermochromic Ink	Producer	Abbreviation	Activation Temperature
Blue to Colorless	CHAMELEON®	BW	27 °C
Green to Yellow	CTI®	GY	45 °C
Burgundy to Blue	CTI®	BB	63 °C

4.1.1. Determination of thermochromic offset ink – paper interactions

The obtained results show that the interaction between all tested thermochromic inks and printing substrate are strong *Table 6*. The work of adhesion is the highest for paper - BW ink print (49.30 mJ m^{-2}), despite the highest surface free energy of its interphase (2.95 mJ m^{-2}). The obtained works of adhesion are in the range of the work of adhesion for toner formulations, ranging from 41.2 to 62.4 mJ m^{-2} that are known to be very difficult to deink by conventional flotation process (Thompson et al., 2000).

Table 6. Adhesion parameters of components

Sample	Adhesion parameters (mJ m^{-2})	
	Surface free energy of interphase γ_{12}	Work of adhesion W_{12}
Paper –BB	1.25	44.25
Paper –GY	2.11	46.94
Paper –BW	2.95	49.30

4.1.2. Flotation yield

The yield of the deinking process is presented in *Table 7*, as well as the ash content of tested paper and filter pad samples. Obtained flotation yield was 95.8%. From result of ash content determined in froth filter pad (45.9%) it is further possible to calculate the total loss of the fibres during the flotation deinking, which is, in this case, quite small amount of only 2.27%. Ash content elimination, calculated from the ash balance of the undeinked and deinked pulp samples shows that the ash content was reduced for 8.3% by flotation.

Table 7. Yield of deinking process

Sample		**Value**
Flotation yield, %		95.80
Ash content, %	**Froth filter pad**	45.90±0.67
	Original paper	25.38±1.81
	Blank filter pad	25.23±0.87
	UP filter pad	25.50±2.45
	DP filter pad	23.39±1.43

4.1.3. Dirt particle measurements and determination of optical properties

The results of the image analysis are presented in *Table 8*. During the recycling process, ink is disintegrated mainly into very small fragments. The largest number of particles on both, undeinked (UP) and deinked pulp (DP) handsheets can be found in the particles of the size class less than 0.012 mm^2, followed by other, very small particles, ranging from 0.013 to 0.039 mm^2. The results show that deinking flotation reduced the number of disintegrated ink particles smaller than 0.012 mm^2 for 17%, while those in particle size range of 0.04–0.14 mm^2 were reduced for 25%. However, in particle size classes of 0.013-0.039 mm^2 and 0.15-0.39 mm^2 no reduction in number was noticed. No particles larger than 0.4 mm^2 were detected. A reduction of ink area was also noticed. For ink particles that fall within the range of 0.04–0.14 mm^2, a reduction of dirt area was 25%, while for ink particles smaller than 0.012 mm^2, a decrease in the ink area of 9% was determined. The total area of dirt particles has been reduced for only 12.8% (*Table 8*). It is known that the optimal particle size range for flotation deinking is from 10 to 150 μm (Jiang and Ma, 2000). In this case, printed ink film is broken into very small fragments, making flotation more difficult. Very small percentage of removed dirt particles contributes to the poor optical properties of the pulp. Small particles that are not removed from the pulp by flotation reduce the brightness and influence the paper colour properties.

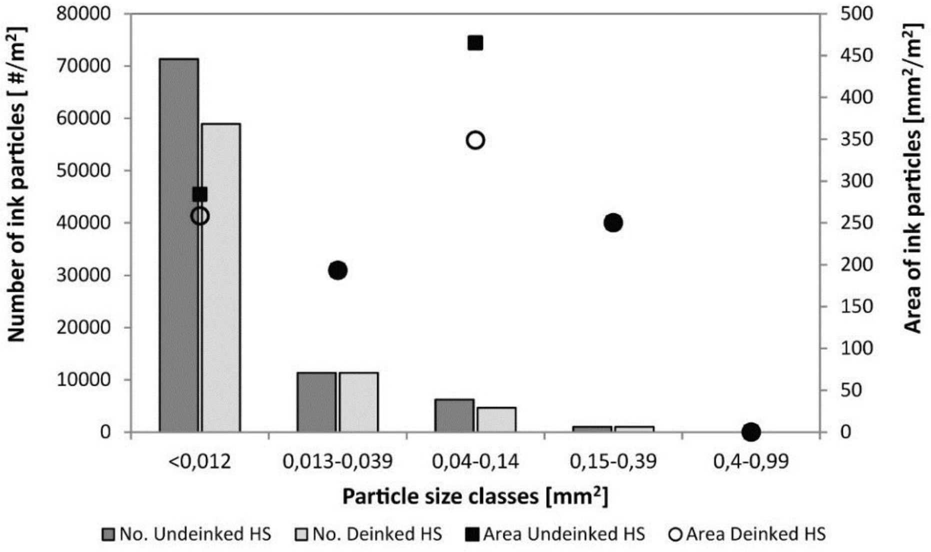

Figure 2. Ink particle size distribution (ISO 15755)

Table 8. Total area of dirt particles (ISO 15755)

Sample	**Total area of dirt particles / [mm^2/m^2]**
Undeinked pulp	908.5
Deinked pulp	792.2

Results of colorimetric values determined on undeinked (UP) and deinked (DP) pulp handsheets are presented in *Table 9.* The obtained results are compared to the target values measured on a blank handsheet. The obtained results show that L^* values are slightly lower than the target value and similar to each other. Only a small increase in the lightness of the pulp was observed after the process of flotation. a^* values are very similar to the target value and b^* values are the same in both, undeinked and deinked handsheets, but are slightly more positive if compared to the target value. The changes of the value b^* could be attributed to unstable BW ink print and its microcapsules which retained in suspension.

Table 9. Colorimetric values of recycled handsheets

Sample	*L**	*a**	*b**
Original paper	95.30±0.03	2.88±0.02	-12.14±0.07
Blank handsheet	95.03±0.04	2.57±0.03	-12.53±0.21
UP handsheet	89.70±0.08	2.64±0.04	-11.41±0.05
DP handsheet	90.34±0.08	2.87±0.09	-11.41±0.24

The efficiency of deinking process is further evaluated through brightness and whiteness increase, which is calculated as follows:

$$\text{Brightness increase (\%)} = \text{DP brightness (\%)} - \text{UP brightness (\%)} \quad (1)$$

$$\text{Whiteness increase (\%)} = \text{DP whiteness (\%)} - \text{UP whiteness (\%)} \quad (2)$$

Figure 3 presents the results of ISO brightness determinations conducted on handsheets and filter pads of undeinked (UP) and deinked (DP) pulps as well as on the blank samples. Results indicate that flotation managed to improve brightness only slightly, as the brightness increase of only 4.2% and 4.8 % was detected on handsheets and filter pads, respectively (*Eq.1*). If the values of deinked pulp’s brightness (measured on handsheets) are compared to the brightness target values (HS blank) it can be seen that the levels of deinked pulp’s brightness deviate from the target brightness values for 9.7%. Comparing the filter pads in the same manner, a deviation of 8.8% is noticed.

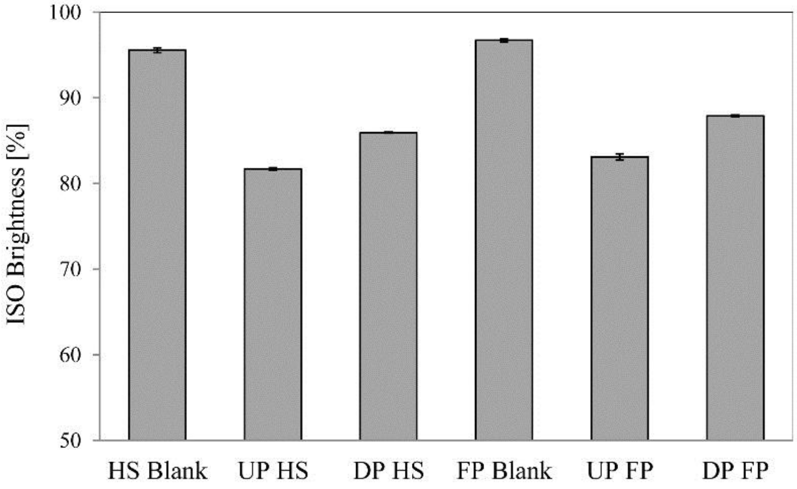

Figure 3. Brightness of blank samples and undeinked (UP) and deinked (DP) pulps

Figure 4 presents the results of CIE whiteness measurements conducted on handsheets and filter pads of undeinked (UP) and deinked (DP) pulps as well as on the blank samples. The results of CIE whiteness determination with and without included UV-content of illumination show an even smaller increase in pulp's whiteness after flotation when compared to brightness increase evaluation. The whiteness increased after flotation for only 1.2% and 1.9%, on handsheets and filter pads, respectively, under UV-content of illumination (*Eq. 2*). Furthermore, the results show large deviations from target whiteness values of 13.4% in case of handsheets and of 11.5% in case of filter pads. The measurements conducted without UV-content of illumination show an increase of only 1% determined on handsheets and of 1.4% measured on filter pads (*Eq. 2*). The obtained results indicate slightly smaller deviations from target whiteness values; deinked pulp whiteness measured on handsheets deviates from target values for 11.1% and for 8.5% when measured on filter pads.

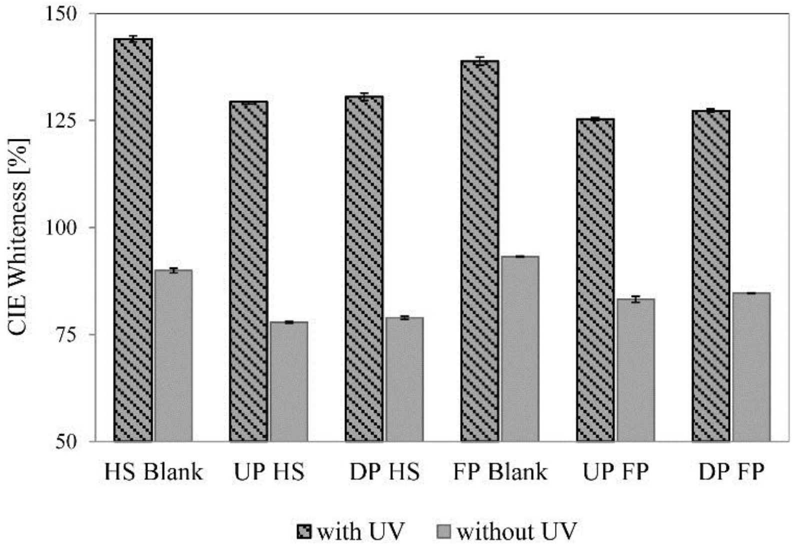

Figure 4. CIE Whiteness with and without UV-content of illumination

4.2. Safety Evaluation of Deinked Pulp Containing Thermochromic Offset Inks (Paper III)

4.2.1. Determination of heavy metals in thermochromic inks and recycled pulp

Table 10 shows the obtained concentrations of heavy metals in the tested thermochromic inks. BW ink contained the highest concentration of Fe (20 mg/kg). In printing inks, iron is used in the form of iron oxide yellows (yellow pigment). Exceptional heat resistance makes them suitable for use in printed furniture surfaces and other high light specifications (Leach, 2007). The GY ink exhibited the highest concentrations of Co (500 mg/kg) and Mn (950 mg/kg). Co and Mn salts are used as catalysts (siccatives) for oxypolymerization drying of vegetable oil. Moreover, in GY ink, notably lower concentrations of Fe (7.90 mg/kg) and Zn (3.80 mg/kg) were observed. In printing inks, Zn is used as white pigment and extender in the form of zinc white (ZnO) and zinc sulphide (ZnS). ZnO is a strong UV absorber and self-fungicidal. It discolours with copper compounds, and it becomes yellow when hot or white when cold. It is used as a white extender in many inks (Leach, 2007). GY ink had the highest concentration of Cr (0.26 mg/kg). Concentrations of other cations were less than 1 mg/kg of ink. In the BB ink, the highest concentrations of Co (700 mg/kg) and Mn (1100 mg/kg) were measured. Zn and Fe were present at concentrations of 1.80 and 10.0 mg/kg, while other cations were present at concentrations lower than 1 mg/kg. Thermochromic offset printing inks contain remarkably lower amounts of heavy metals than digital offset printing inks (Electroink) (Barbaric-Mikocevic et al., 2004).

Table 10. Concentration of Heavy Metals in Used Thermochromic Offset Inks

Heavy Metals (mg/kg)	Thermochromic Printing Inks		
	BW	GY	BB
Pb	0.20	0.20	< 0.10
Cd	< 0.01	< 0.01	< 0.10
Cu	0.53	0.45	0.45
Zn	1.60	3.80	1.80
Fe	20.0	7.90	10.0
Mn	0.35	950	1100
Ni	1.30	0.34	0.44
Cr	0.12	0.26	0.14
Co	0.03	500	700
As	0.01	0.01	< 0.01

According to Rožić et al. (2005), certain cations present in paper can cause problems in paper usage or in paper recycling. Metal (Fe, Cu and Mn) hydroxides/oxides in various additives catalyse paper acidification. During paper recycling, multivalent metal cations reduce swelling of fibre, due to reduction of electrostatic double fibre layer. Reduced swelling inhibits binding of fibres and therefore paper sheets become weak. Taking into account that additives for paper production are not of high chemical purity, it is possible that some elements are introduced as impurities in calcium carbonate, which is used as filler, and in titanium (IV) oxide, which is used as optical brightener (Rožić et al. 2005). Mertoglu-Elmas (2017) showed that presence of heavy metals in recycled corrugated board papers originates from chemical additives used in the process of pulp and paper manufacturing, as well as the finishing operations of paper, such as Pb, Cd, Zn, and Cu deriving from coloured pigments.

Table 11 shows the obtained concentrations of heavy metals in handsheets ashes of blank (B), before (UP) and after (DP) flotation, flotation froth, and process water filtrates that originated from blank (paper + deinking chemicals) and after flotation samples. The B sample contained the highest concentrations of Zn (144 mg/kg) and Fe (78.2 mg/kg), while the concentration was 7.10 mg/kg for Co and 12.2 mg/kg for Mn. Due to very high concentrations of Zn and Fe in B sample, it may be concluded that printing substrate is the main source of these metals. The high concentration of Zn can be explained by the Zn-based compounds used in paper production as fillers for the enchainment of some optical properties of paper such as opacity (Mertoglu-Elmas, 2017). The UP sample contained slightly higher concentrations of Zn (165 mg/kg), Mn (16.2 mg/kg), Ni (0.87 mg/kg), and Co (11.7 mg/kg) than the DP sample. Larger concentrations of these cations are the result of thermochromic inks. The Pb, Cd, Cu, and Fe concentrations were lower in the UP and DP samples than in the B sample. Zn, Fe, Mn, and Co concentrations were reduced in the obtained handsheet after flotation (DP). However, in this sample (DP), the concentrations of Zn, Ni, Mn, and Co were greater than in the B sample due to print particles retention (*i.e.*, poor deinkability). Moreover, the determined quantities of Pb and Cd metals in the B, UP, and DP samples were all below maximum permitted limits in the CEPI/CITPA/CEFIC/FPE Industry Guideline. Even though current EU legislation on paper and board food contact materials, does not provide specific migration limits for other determined heavy metals, it may be assumed that the levels of determined heavy metals (Cu, Zn, Fe, Mn, Ni, Cr, Co, As) could be of potential threat especially if recycled paper is to be brought in direct contact with moist and/or fatty food.

Table 11. Concentration of Heavy Metals in Handsheets (B, UP, DP)

Heavy Metals (mg/kg)	Maximum Permitted Quantity* (mg/kg)	Samples Obtained from Deinking Process			
		Blank (B)	Undeinked pulp (UP)	Deinked pulp (DP)	Filter pad – flotation froth
Pb	3.0 **	2.60	1.70	1.60	4.20
Cd	0.5 **	0.12	0.09	0.09	0.23
Cu	not established	2.60	2.40	2.50	4.90
Zn	not established	144	165	147	458
Fe	not established	78.2	75.9	71.2	142
Mn	not established	12.2	16.2	15.4	32.1
Ni	not established	0.67	0.87	0.79	1.75
Cr	not established	1.85	1.90	1.85	3.80
Co	not established	7.10	11.7	10.7	24.7
As	not established	<0.01	<0.01	0.01	0.01

* Purity requirements set out in the CEPI/CITPA/CEFIC/FPE Industry guideline.
** The concentration of these metals is usually determined in an aqueous extract according to EN 12498. Also, the materials are subjected to tests only if, in normal circumstances, the end use of the paper and board is known to be for contact with moist and/or fatty food.

4.2.2. Determination of BPA, TOC, and TC Content

Table 12 shows the concentrations of BPA, TOC, and TC in filter pad samples. Because no BPA was found in the blank sample, it was concluded that the BPA originated from the thermochromic printing inks. Filter pads obtained after flotation contain 50% less BPA than the undeinked filter pads. Vinković et al., (2017) examined the BPA concentrations in commercially available printing inks where, among others, they also analysed the same inks that were used in this research and their results showed that BPA was present only in BW thermochromic ink, while GY and BB inks did not contain any BPA.

A slight reduction of TOC and TC in filter pads after flotation compared with those obtained before flotation indicated a very slight decrease in the organic content. From the obtained results it can be concluded that TOC in samples originates from paper, *i.e.* cellulose while only small percentage is related to thermochromic printing inks. Small amount of inorganic carbon results from fillers (calcium carbonate) in paper.

Table 12. Concentration of BPA, TOC, and TC in Obtained Filter Pads

Filter Pad Sample	BPA (mg/kg)	TOC (%)	TC (%)
Blank (B)	0	35.8	40.0
Undeinked pulp (UP)	15	37.2	40.8
Deinked pulp (DP)	7.5	36.1	40.2

Purity requirements set out in the CEPI/CITPA/CEFIC/FPE Industry guideline specify the limit value for BPA, which is shown in *Table 13*. The conversion of BPA concentrations to the proposed limits presented in *Table 13* was done by taking into account the actual grammage of analyzed filter pads (225 g/m^2) according to *Eq. 3*

$$Qa = (Qm \times G)/100000 \tag{3}$$

where Qa is the concentration of substance in paper expressed as mg/dm², Qm is the concentration of substance in paper expressed as mg/kg, and G is the grammage of paper as expressed as g/m². Qa is the maximum quantity of the contaminant allowed in the packaging, if it is assumed that 100% of it will migrate into the food. The BPA content of the analyzed filter pads expressed as mg/dm^2 of material is presented in *Table 13.*

Table 13. Purity Requirements for BPA in Food Contact Paper and Board and Concentrations of BPA in Filter Pads Obtained from Deinking Process

Substance	Limit in Food	Tested in Paper and Board	Filter Pad Sample Measured concentrations of BPA (mg/dm^2)		
	SML (mg/kg food)	Limit (mg/dm2)	Blank (B)	Undeinked pulp (UP)	Deinked pulp (DP)
BPA	0.6	0.1	0.0	0.034	0.017
New reduced limit for BPA (from draft regulation)	0.05	0.008			

The converted results indicated that the BPA in the analysed filter pads obtained before and after deinking flotation were below the existing limits as set in Industry Guideline and current Regulation (EC) 10/2011 on plastics FCMs. However, under the stricter and likely new regulation limits, both analysed filter pads failed, as the detected concentrations were above the permitted limits (*Table 13).* The results also showed that deinking flotation did not sufficiently eliminate the BPA content from the pulp to meet the draft regulation's new purity requirements.

4.2.3. Determination of Antimicrobial Properties

Components present in paper as fillers (Zn oxide, titanium oxide, heavy metals) or components of thermochromic inks (bisphenol A, heavy metals) may show antimicrobial activities (Lemire et al., 2013; Muñoz-Bonilla and Fernández-García, 2012). In order to examine release and possible transfer of the antimicrobial constituents from recycled paper pulp, microbiological tests were performed. The total number of sporadic *Aspergillus niger* (*Figure 5a*) was determined by counting in a Thomson Chamber and was 1.3×10^7 cell/mL. The total number of *Bacillus subtilis* cells in 1 mL was 1.4×10^9 cell/mL (*Figure 5b*). The exposure of *Bacillus subtilis* to penicillin resulted in the formation of a 4-cm diameter inhibition zone (*Figure 5c*).

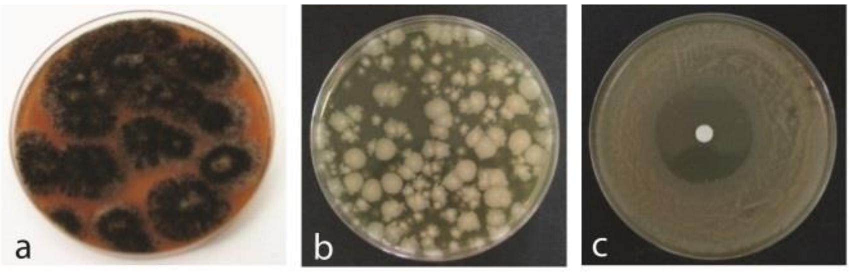

Figure 5. Growth of fungus *Aspergillus niger* (a) and bacteria *Bacillus subtilis* (b); inhibition of *Bacillus subtilis* by penicillin (c)

Samples of B, UP, and DP were tested with *Bacillus subtilis* (*Figure 6*) and *Aspergillus niger* (*Figure 7*). There were no inhibition zones around the paper discs, indicating that the samples did not inhibit microbial growth and that there was no release of any toxic substances from recycled paper pulp. On malt agar, almost no discs were observed because of fungus overgrowth (*Figure 7*).

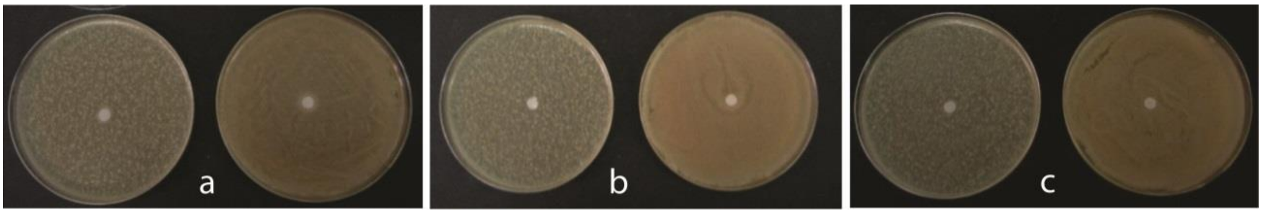

Figure 6. Sensitivity test for bacteria *Bacillus subtilis* in samples B (a), UP (b), and DP (c). In each panel: (left) 1 mL of suspension flushed with s NA; (right): 0.1 mL of suspension homogenized with a Drigalski spatula

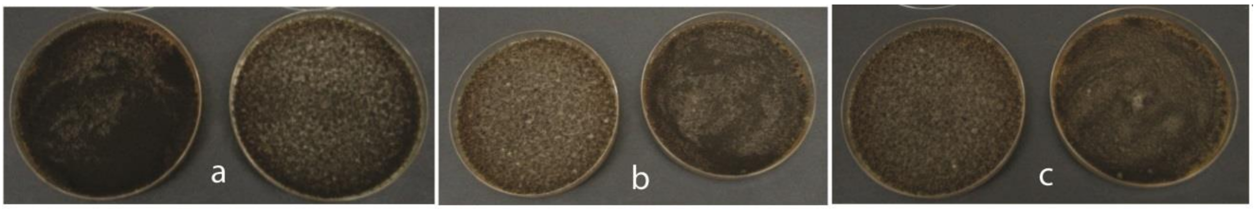

Figure 7. Sensitivity test for the fungus *Aspergillus niger* in samples B (a), UP (b), and DP (c). In each panel: (left) 1 mL of suspension flushed with s NA; (right): 0.1 mL of suspension homogenized with a Drigalski spatula

4.3. Effluent characteristics after deinking of Thermochromic Offset Inks (Paper II and III)

Determined concentration of cations in process waters show that deinking does not affect heavy metals release from thermochromic inks. In process water filtrates, Zn and Fe were present in very low concentrations while concentration of other heavy metals is negligible (*Table 14*). Since thermochromic ink particles are difficult to separate from the pulp suspension, the release of heavy metals in process water is minimal. Results imply that printing substrate is the main source of heavy metals concentrations (Fe, Zn) in the process waters produced by deinking flotation. In addition to this conclusion, it can also be assumed that Fe concentrations in process water may be result of BW thermochromic ink residues present in pulp suspension as described earlier. Concerning the low concentrations of heavy metals in process water, it can be reused and returned into the recycling process.

Table 14. Concentration of Heavy Metals Process Water Filtrates Obtained from Blank and After Flotation

Heavy Metals (mg/kg)	Process Water Filtrate	
	Blank (chemicals and paper)	After flotation
Pb	0.01	<0.01
Cd	<0.01	<0.01
Cu	0.01	0.01
Zn	0.15	0.33
Fe	0.08	0.17
Mn	0.02	0.02
Ni	<0.01	<0.01
Cr	<0.01	<0.01
Co	0.01	0.02
As	<0.01	<0.01

The filtrate of suspension after flotation was analysed in the terms of TOC and COD values that can relate to the biodegradability aspects. The effluents obtained in paper recycling can be strongly influenced by raw materials and chemicals used for the deinking process. Comparing the presented results from effluents generated from blank and after flotation, it is evident that inks contribute to the effluent TOC and COD (*Table 15).*

Table 15. TOC and COD values in effluents after flotation

Parameter / (mg/L)	Value	
	Blank	**After deinking**
TOC	92	176
COD	69	155

Thermochromic inks can affect colouration of wastewater too, due to their interactions with deinking solution and/or because of their mechanical damage during defibration. The filtrate from froth was analysed for absorbance due to visible colour change (*Figure 8*). The absorbance spectra show the yellow coloration of filtrate obtained from the froth derived from the flotation process and it is assumed that this colouration comes from the BW thermochromic ink, as residues of this ink weren't found in UP and DP handsheets, due to its chemical composition and polar component. The solvent in the BW ink is a mineral spirit. A mineral spirit can destroy the capsule wall by increasing the pores and permeability. Hence, a froth filtrate is coloured in yellow. Ketones, diols and aldehydes must be minimized as solvents in thermochromic inks, as well as most mineral spirits (Highberger and Small, 1999). The lower the amounts of these compounds are, the better the performance of the thermochromic ink and the longer the shelf life of the product. Many thermochromic dyes are phenylmethane and fluoran derivates bearing a lactone ring moiety. In the lactone ring-closed state (below activation temperature) these leuco dyes are either colourless or coloured faintly yellow (Seeboth and Lotzsch, 2008).

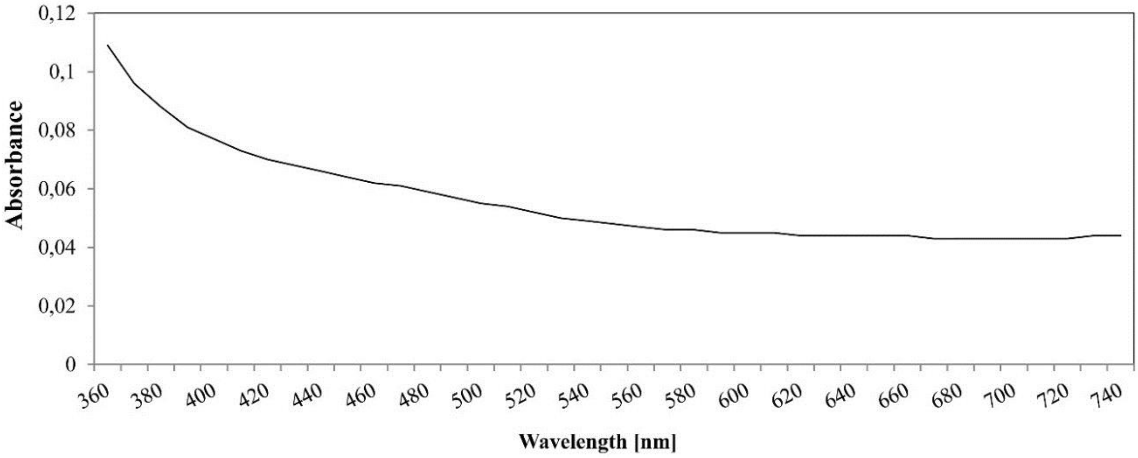

Figure 8. Absorbance spectra of froth filtrate

4.4. Biodegradability of thermochromic offset prints (Paper IV, V and VI)

For the printing of paper samples one leuco dye based thermochromic offset printing ink was used (Chromatic Technologies, Inc.). The activation temperature of thermochromic ink is 45 ºC. Below its activation temperature, the print was coloured in green and above its activation temperature the print was coloured in yellow (GY).

4.4.1. Optical microscopy

Microscopic images showed that the printed thermochromic ink is composed of blue microcapsules dispersed in classic yellow offset ink (*Figure 9*).

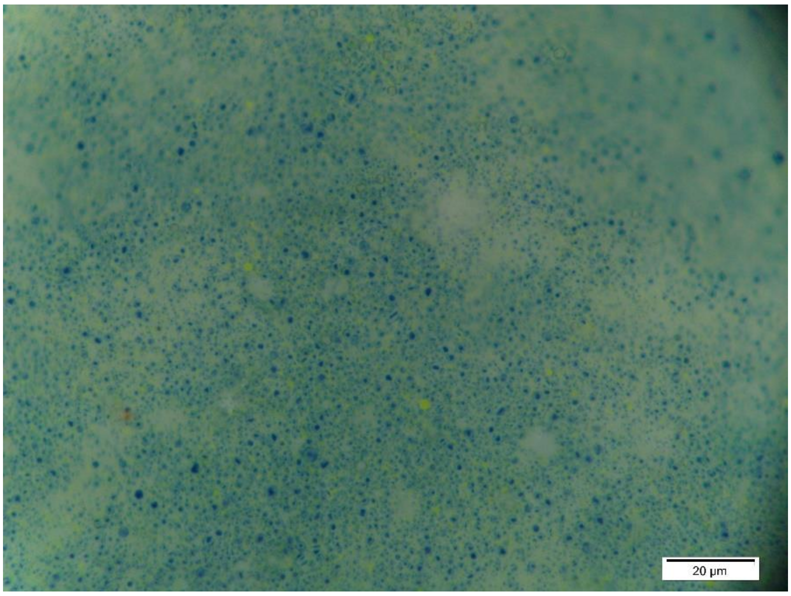

Figure 9. Optical microscopy image of thermochromic offset ink at 23°C

4.4.2. FTIR spectroscopy of thermochromic offset ink

The FTIR spectra of the thermochromic ink were measured at 25 °C and 50 °C (*Figure 10*). Though temperature dependent measurements were followed by the thermally induced change in the sample colour, significant spectral changes in the IR spectrum upon heating were not observed, implying that the obtained vibrational bands did not originate from the thermochromic system. Namely, by heating the thermochromic composites, the IR spectral changes indicate changes in the molecular structure of the components responsible for the colour change (Hajzeri et al., 2015; Panák et al., 2017; Raditoiu et al., 2016). Hence in the IR spectrum of the thermochromic system composed of a leuco dye, bands corresponding the COO⁻ groups (symmetric and asymmetric stretching vibrations) disappear, while the C=O band, characteristic of the colourless lactone form, appears (Hajzeri et al., 2015; Panák et al., 2017; Raditoiu et al., 2016). Given the similarity between the spectra obtained at both temperatures, the observed vibrational bands most likely originated from the thermochromic ink binders, and were not the result of the vibrational modes of the thermochromic composites within the microcapsules.

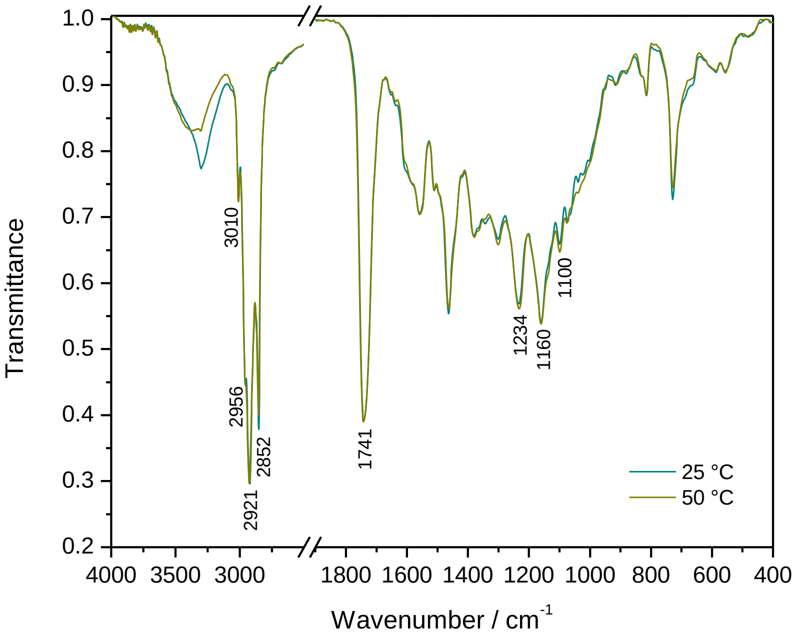

Figure 10. FTIR spectra of the thermochromic offset ink at 25 ºC and 50 ºC

In the IR spectra, bands characteristic of vegetable oils, common components of the ink binders, were observed (Gómez et al., 2016; Vlachos et al., 2006). The bands at 3010, 2956, 2921 and 2852 cm^{-1} were assigned to the stretching modes of CH, CH_2, and CH_3 groups in aliphatic chains of fatty acids, while the carbonyl stretching band at 1741 cm^{-1} accompanied by the bands at 1234, 1160 and 1100 cm^{-1} pointed to the ester group. A broad band in the 3500–3100 cm^{-1} range was attributed to the OH stretching. In addition, this conclusion is supported by the fact that used ink contains Co and Mn salts as catalysts (siccatives) necessary for oxy-polymerization drying of vegetable oil (*Table 10*).

4.4.3. Determination of thermochromic offset ink – paper interactions

For the evaluation of thermochromic offset ink – paper interactions different papers were used (*Table 16*).

Table 16. Papers used for the thermochromic offset ink adhesion evaluation

Paper type	Abbreviation
Synthetic paper	S
33% recycled paper	33R
100% recycled paper	100R
Bulky paper	B
Wood free coated	WFC

Figure 11 shows the calculated values of adhesion parameters. The calculated adhesion parameters can be used to predict the optimal adhesion at the interface. The conditions for the optimal adhesion at the interface between paper and thermochromic printing ink are achieved if the following conditions are met: $\gamma_{12} = 0$, W_{12} = maximal and $S_{12} \geq 0$. The adhesion of ink components to the substrates can be expressed as the sum of works of adhesion for polar and dispersive interaction, giving as a result the overall thermodynamic work of adhesion (Repeta, 2013). *Figure 11* shows that optimum adhesion was achieved in the case of 100R and thermochromic ink interface. The lowest adhesion was achieved in the case of WFC paper and thermochromic ink.

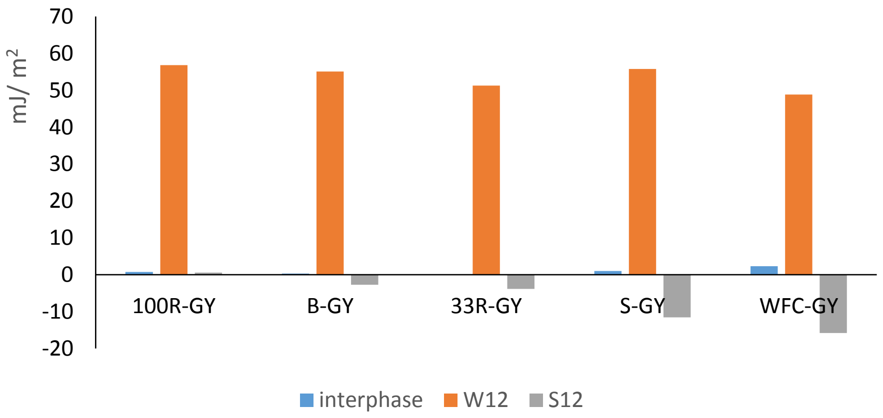

Figure 11. Surface free energies of interphase, work of adhesion (W_{12}) and spreading (S_{12})

4.4.4. Visual evaluation

In *Figures 12 -16* visual appearances after offset prints biodegradation can be seen. All prints show differences in colour, especially after 150 days of biodegradation. From the *Figures 15 and 16* it can be seen that the prints on S and WFC paper are damaged during sampling (stretch marks). Moreover, the print on WFC paper shows the most heterogeneous print degradation, which can be the result of non-crosslinked and non-oxidized ink on the surface of paper. All samples, besides print on S paper, show noticeable degradation not only of the print colour, but the whole sample (paper) as well, especially after 50 and 180 days of biodegradation. Formation of brown spots can be seen which point to significant degradation, and formation of cracks.

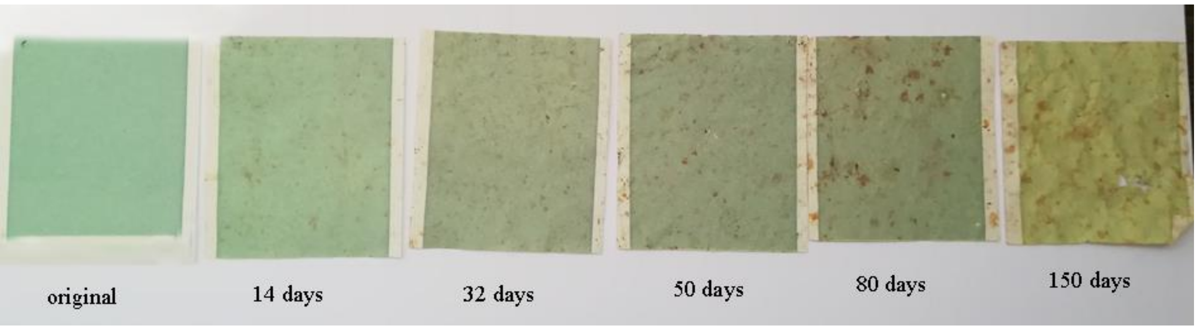

Figure 12. Visual observations; 100% recycled paper - print (100R-GY) before and over 14, 32, 50, 80 and 150 days of biodegradation

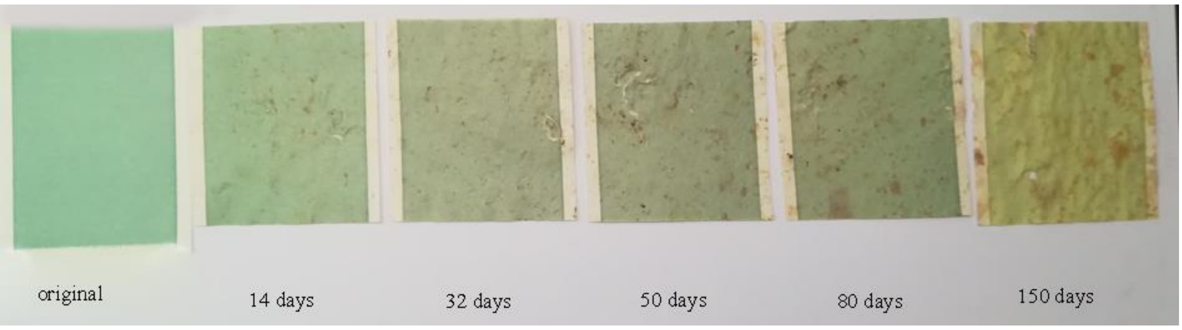

Figure 13. Visual observations; Bulky paper - print (B-GY) before and over 14, 32, 50, 80 and 150 days of biodegradation

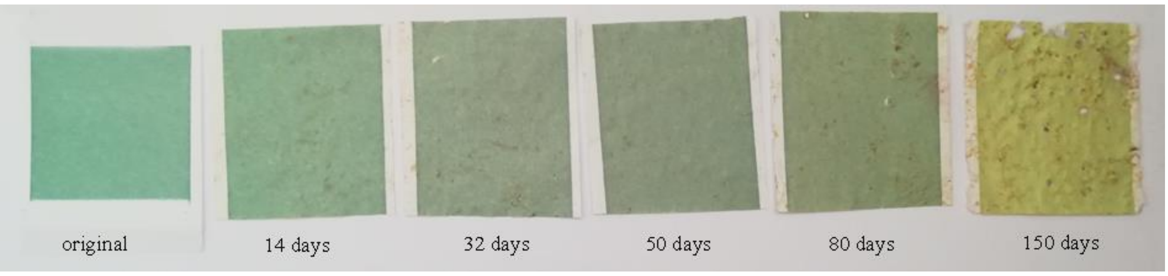

Figure 14. Visual observations; 33 % Recycled paper - print (33R-GY) paper before and over 14, 32, 50, 80 and 150 days of biodegradation

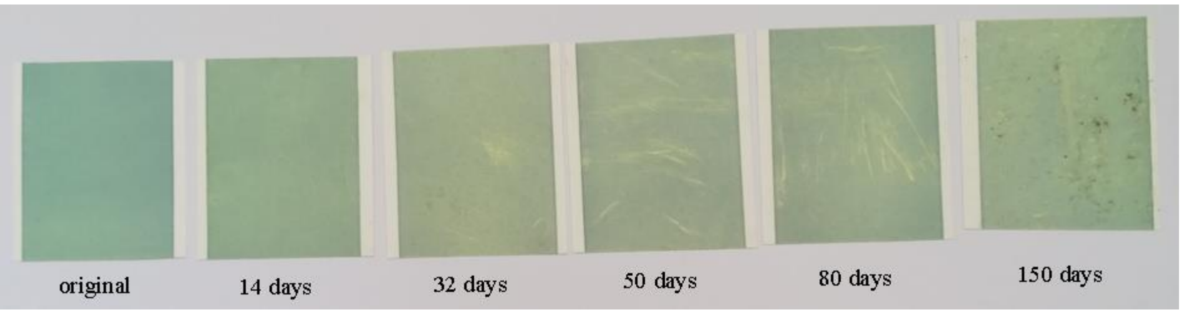

Figure 15. Visual observations; Synthetic paper - print (S-GY) before and over 14, 32, 50, 80 and 150 days of biodegradation

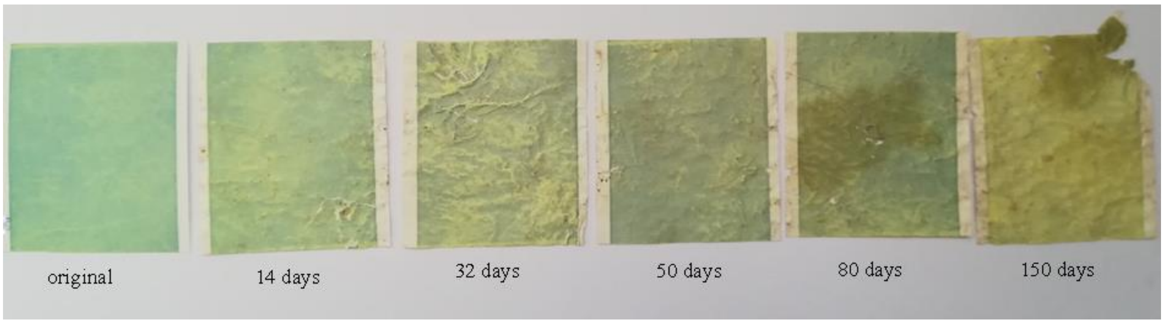

Figure 16. Visual observations; Wood free coated paper - print (WFC-GY) paper before and over 14, 32, 50, 80 and 150 days of biodegradation

The results of the prints colour change during biodegradation follow the results of the print adhesion strength, except in the case of print on the WFC paper. Specifically, optimal ink adhesion was obtained on the surface of 100R paper. The print on 100R paper shows the highest degradation, followed by prints on B and 33R paper and finally on S paper. Even though the lowest adhesion was obtained on the surface of the WFC paper, degradation of the print was the highest. Generally, better adhesion will result consequently in better degradation (except for print on WFC paper).

For the offset printed coated papers, separation of different ink components during ink setting and drying on coated paper may occur (Koivula et al., 2008; Pykönen et al., 2010). Oxidation of offset inks is normally based upon the reaction of alkyd resins and vegetable oils (Leach, 2007). During oxy-polymerization of the offset ink on the surface of paper, the cross-linking of the double bonds in the oil and alkyd resins occurs (Rousu et al., 2000; Koivula et al., 2008). Alkyd resins interacts with the coating pigment (kaolin or $CaCO_3$) and adsorbs on them (Rousu et al., 2000). Hydrophilic dispersed pigment surfaces of the coating act as sites for alkyd resins adsorption. This leads to separation of ink vehicle components and prevention of their mutual interactions, which can affect the ink drying. Because of it, the ink on WFC paper is not completely oxidised. Thus, the reaction of alkyd and vegetable oil is hampered, resulting in lower degree of ink oxy-polymerization. This behaviour can explain higher colour degradation of the WFC-GY print, because it is not oxidized and remains soft, the degree of polymerization is lower, allowing bacteria to degrade it better (*i.e.* microcapsules). For the print on synthetic paper, all the components of ink are present on the surface of paper. However, since there is no coating pigment present in the synthetic paper, interactions between pigment and alkyd will not appear, while reaction of alkyd and vegetable oil will exist and the print surface will have different properties compared to print on WFC paper. Due to higher amount of ink on the surface of synthetic paper, oxy-polymerization of ink will probably be slower compared to other prints since there is no penetration of the ink binder into the paper structure. In addition, this behaviour would explain the surface energy of the prints and its polarity. The highest values of dispersive components for both prints, S-GY and WFC-GY, originate from ink adsorbed on the surface of papers.

Polymerized vegetable oils harden on exposure to oxygen through the oxidation of double bonds to hydroperoxides (Shogren et al., 2004).

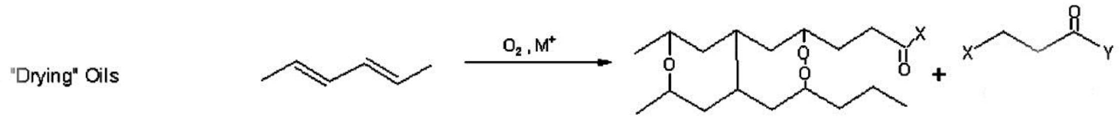

Figure 17. Representative chemical structure of cross-linking reactions. *M*$^+$ - drying catalyst; *X* and *Y* may be any functional group, commonly -H, -OH, -CH_3 or -OCH_3 (Shogren et al., 2004)

Simplified chemical structure of the product of the polymerization reaction is shown in *Figure 17.* It results in the formation of three-dimensional networks although some low molecular weight ketones, carboxylic acids, and alcohols are formed in the oxidative polymerization via decomposition of oil hydroperoxides. Polymerized oils are soft and sticky in some cases. According to Shogren et al., (2004) kraft paper coated with oxidatively polymerized soybean and linseed oil was 90%–100% converted to CO_2 after 65 days in soil at 30^0C. In our experiment, paper-prints degraded much more slowly. This may be due to slower degradation of classical yellow pigment and / or the addition of alkyd resins.

4.4.5. Weight loss measurements

Figure 18 shows the weight loss measurements of unprinted papers during biodegradation. For unprinted papers, it can be seen that the highest weight loss was obtained for WFC paper while the smallest was obtained for S paper. The rate of biodegradation increases in a row: 33R>B>100R.

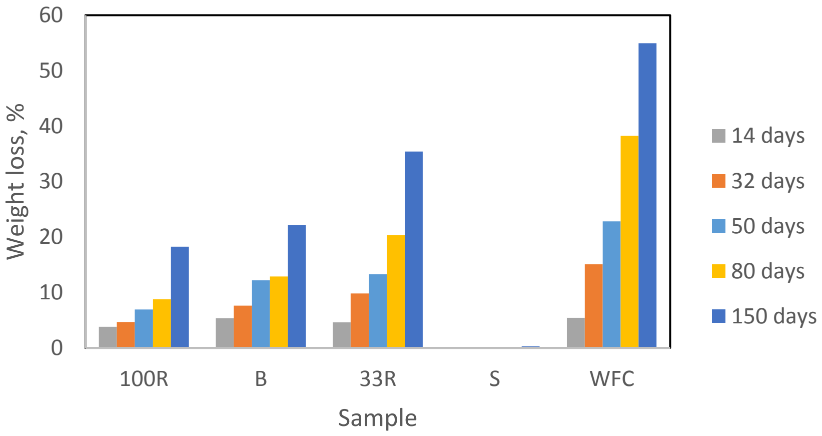

Figure 18. Weight loss measurements of unprinted papers during biodegradation

Figure 19 shows weight loss measurements of printed papers. For print on 100R paper, the best adhesion was measured. In this case, the rate of biodegradation for unprinted and printed paper slightly differ. The weight loss of samples points to degradation of paper and ink at the same time. In the case of printed B and 33R paper, the prints slow down the rate of biodegradation, somewhat more in the case of print on 33R paper. For the print on WFC paper, the print notably reduces the rate of biodegradation. Accordingly, the lowest adhesion will result in higher reduction of biodegradation rate. The highest rate of biodegradation (the highest weight loss) corresponds to samples where the optimum adhesion was achieved for 100R- GY. Even though the colour degradation was the highest in the case of WFC-GY print, the weight loss point mostly to degradation of microcapsules on the surface of the print. Probably other components of the ink present on the surface of coated paper are more likely difficult to degrade. Unprinted synthetic paper and print on synthetic paper shows almost no changes in weight during sampling time, most likely due to chemical composition of synthetic paper, *i.e.* polypropylene, since it is resistant to microbial attack (Arutchelvi et al., 2008; Leja and Lewandowicz, 2010).

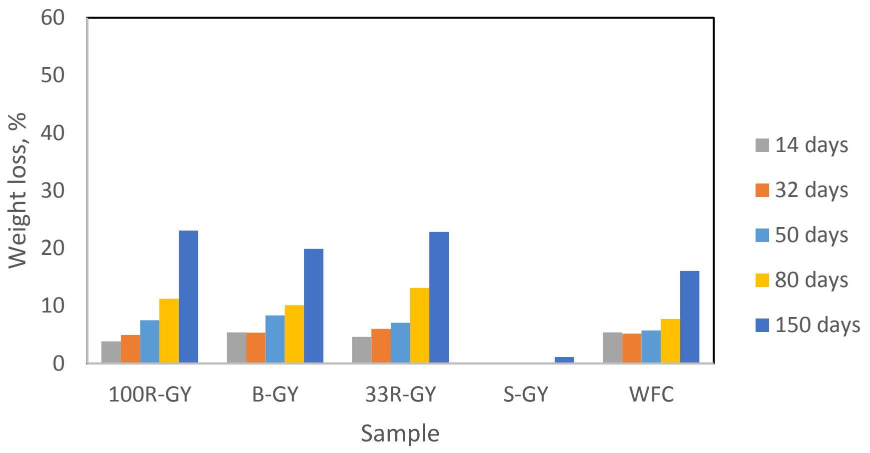

Figure 19. Weight loss measurements of papers with prints during biodegradation

Further evaluation of biodegradability aspect (SEM, FTIR, Microbial growth assay and colorimetric measurements) of thermochromic offset ink was evaluated on synthetic and 33% recycled paper (Paper IV).

4.4.6. SEM Microscopy

In the case of synthetic paper, the microcapsules are covered with a thick layer of binder that is why they are difficult to notice (*Figure 20*). For the print on synthetic paper, after biodegradation test, the most visible changes can be connected to the degradation of ink binder since no microcapsules can be detected (*Figure 21*). However, cracks with a diameter of about 0.1 µm are visible, where significant degradation of ink binder is possible and penetration of the bacteria to the microcapsules.

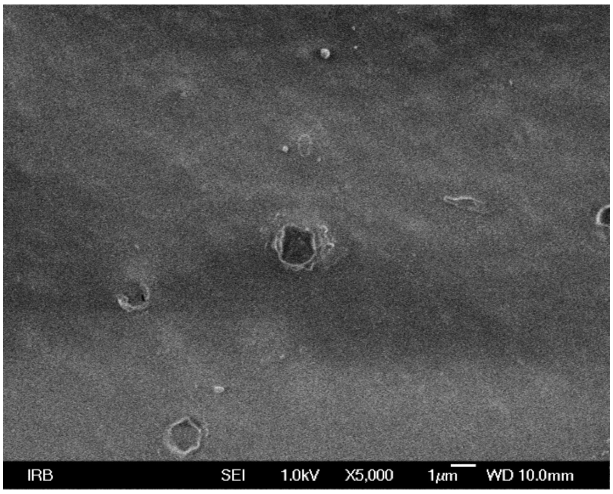

Figure 20. SEM micrograph of printed thermochromic offset ink on synthetic paper before biodegradation

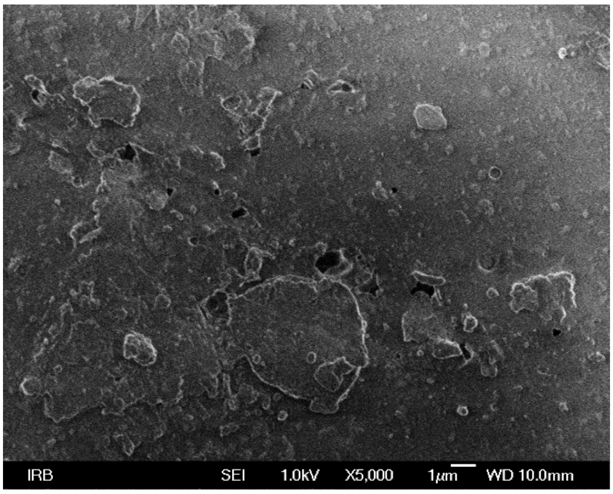

Figure 21. SEM micrograph of printed thermochromic offset ink on synthetic paper after 150 days of biodegradation

In the case of print on recycled paper, the microcapsules are visible, due to penetration of binder into the paper structure (*Figure 22*). The microcapsules are covered with a thinner layer of a binder. The sizes of the microcapsules are not uniform. Microcapsules of about 1 µm in diameter are visible, but also there are considerably smaller microcapsules noticed, which are located in the paper structure. Therefore, the penetration of microcapsules into the structure of recycled paper is possible. After 150 days of biodegradation, the changes in the shape of macrocapsueles for the print on recycled paper can be seen. Before biodegradation test (*Figure 22*), the microcapsules are in the form of regular circle forms, but after 150 days of biodegradation the SEM micrograph show that they are forming irregular forms or being flattened (*Figure 23*). However, no reduction in their number was noticed.

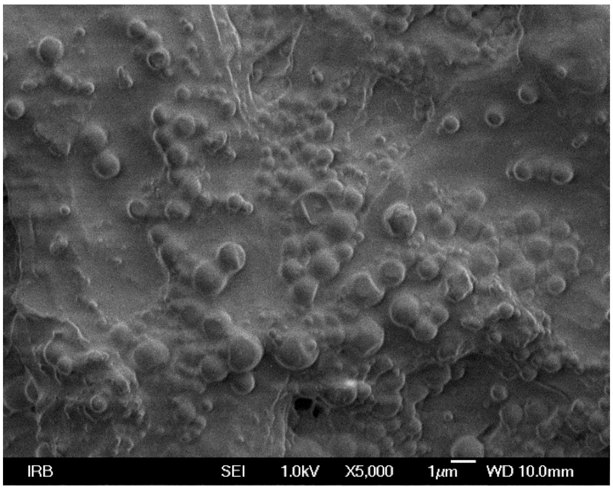

Figure 22. SEM micrograph of printed thermochromic offset ink on 33% recycled paper before biodegradation

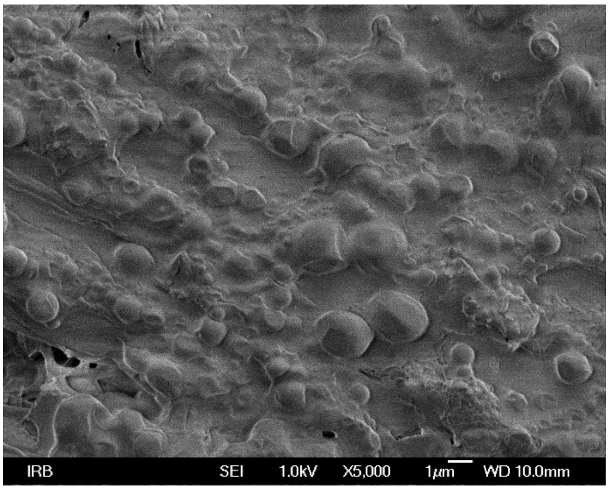

Figure 23. SEM micrograph of printed thermochromic offset ink on 33 % recycled paper after 150 days of biodegradation

The thicker the polymeric resin layer over the microcapsules is, they are more protected towards biodegradation. This means that the rate of microcapsule degradation is greater than the rate of biodegradation of the cross-linked oxidized binder (resins + oils). The higher the absorption of the ink vehicle into the paper is, the faster the rate of print degradation will be. In the case of WFC paper, microcapsules are probably protected with thicker layer of ink resin (vehicle, binder) but it is not completely oxidized and it is not cross-linked, resulting in soft resin, which is more easily for bacteria to degrade it. In the case of S-GY print microcapsules are covered with the thickest layer of the oxidised ink resin resulting in the smallest colour change.

4.4.7. Microbial growth assay

Table 17 shows the number of bacteria in the soil sample and on the samples of paper after 150 days of biodegradation, anaerobic bacteria and facultative anaerobes. For the 33% recycled paper, greater number of bacteria was observed compared to the soil sample. For the synthetic paper the number of bacteria is smaller. Synthetic paper remained unchanged on its unprinted side, while on the print small colour degradation was noticed. Therefore, there is also a small change in weight loss after 150 days of biodegradation (*Figure 19*). Weight loss for print on 33R paper is higher (*Figure 19*). This can be attributed to different chemical compositions of paper. In 33R paper, the bacteria penetrate from both sides of the paper, unprinted and printed, and use cellulose and print for their metabolism. In the case of synthetic paper the bacteria affect only the print but not the polypropylene since the polyolefins are resistant to microbial attack (Arutchelvi et al., 2008; Leja and Lewandowicz, 2010).

Table 17. Number of bacteria in soil and printed paper samples after 150 days of biodegradation

Sample	**log CFU/g**	
	Facultative anaerobes	**Anaerobes**
Soil	6.4±0.2	5.9±0.3
Synthetic paper - print	6.0±0.4	5.1±0.4
33% Recycled paper - print	8.0±0.1	7.8±0.2

4.4.8. FTIR spectroscopy of prints before and after biodegradation

The IR spectrum of the thermochromic ink was compared to the IR spectra of prints on the examined papers – before and after 50 and 150 days of biodegradation (*Figs 24 and 25*). In addition, the spectra of the unprinted papers were also presented.

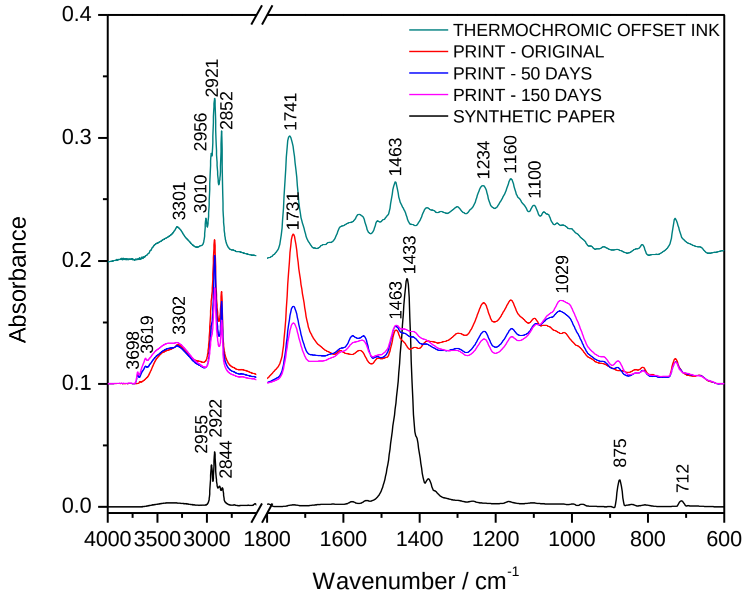

Figure 24. FTIR spectra of the thermochromic offset ink, neat S paper and prints of thermochromic offset ink on S paper before and after 50 and 150 days of biodegradation

In the IR spectra of the thermochromic ink print on both of the papers, the band at 3010 cm^{-1} was missing, most likely due to oxidative drying of the ink. This band was assigned to the C–H stretching of the *cis*-double bond (=C–H) in the vegetable oil (Gamage et al., 2009), for which was assumed to participate in reaction with atmospheric oxygen promoting polymerization during printing (HUBER Group, 2013). The IR spectra of the thermochromic ink on the recycled and synthetic paper were very similar, although the difference in intensity indicated a thinner layer of the thermochromic ink on the recycled paper when compared to the synthetic paper. Moreover, a significant contribution of the cellulose bands, especially in the 1450–1200 and 1160–1000 cm^{-1} range was obtained in the spectrum of the ink print on the recycled paper, which was in agreement with the proposed penetration of the ink into the recycled paper. The carbonyl stretching band of the thermochromic ink at 1741 cm^{-1} shifted towards 1731 cm^{-1} and 1732 cm^{-1} for the prints on the synthetic and recycled paper, respectively, implying ester oxidation. In the IR spectra of the ink prints buried in the soil, a slight broadening and increase in intensity of the O–H stretching band around 3300 cm^{-1} was observed, indicating formation of hydroxyl groups, most likely in the vegetable oil biodegradation products, such as glycerol.

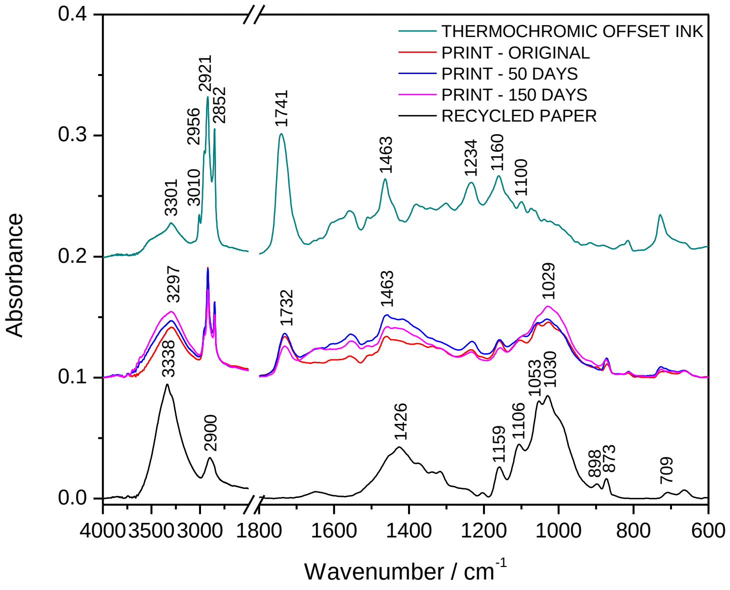

Figure 25. FTIR spectra of the thermochromic offset ink, neat 33R paper and prints of thermochromic offset ink on 33R paper before and after 50 and 150 days of biodegradation

The spectral changes were also observed around 1450 cm^{-1} and 1000 cm^{-1} for the degraded prints on both papers. The intensity increase of these broad bands in the spectra of the ink print on the recycled paper could be attributed to cellulose due to thinning of the ink layer on the paper surface, caused by long term degradation of the ink binder. Nevertheless, the same was observed for the prints on the synthetic paper, rather implying association of these bands with the biodegradation products. Thus the former band (~1450 cm^{-1}) was assigned to the alkyl CH_2 bending and the latter band (~1000 cm^{-1}) to the C–O stretching. Although to a lesser extent, silicates adsorbed on the paper from the soil could contribute to the broad band at 1029 cm^{-1}. The presence of silicates on the surface of the buried samples, was additionally indicated by weak bands at 3619 cm^{-1} and 3698 cm^{-1} in the spectrum of the ink printed on the synthetic paper (Tinti et al., 2015). However, bands in this spectral range could originate from the secondary oxidized products during biodegradation (Zahir et al., 2014). Since only very weak shoulders in the spectra of the ink on the recycled paper were observed, it could be assumed that that the vegetable oil in ink vehicle was more easily oxidized on the surface of the synthetic paper, then in the ink within the recycled paper structure.

4.4.9. Colorimetric measurements

Results of colorimetric values determined on blank (unprinted) paper samples as well as for thermochromic prints before and after biodegradation are presented in *Table 18*. Blank sample of recycled paper shows a shift of the *b** value towards the blue hue (due to presence of optical brighteners) and a lower *L** value. Therefore, the colour of blank recycled paper has a significant influence on prints colour reproduction. Hence, as the most accurate parameter, we can observe the change in the *a** value of prints on recycled paper. The sample of print on recycled paper before biodegradation is less green compared to the print on synthetic paper which can be attributed to a lower concentration of classic offset yellow ink and a lower concentration of blue microcapsules on the surface of recycled paper. During biodegradation of the prints, *a** values becomes more positive, and the change is more notable for the print on recycled paper. A remarkable change for the *b** value of the print on recycled paper after 150 days of biodegradation is observed, although this value is affected by the colour of the blank paper. In the case of the print on the recycled paper changes of colour from green to yellow is greater than with the print on the synthetic paper.

Table 18. Colorimetric properties of thermochromic offset prints at 23±2 °C before and after biodegradation and unprinted paper samples

Days of biodegradation	Synthetic paper				33 % Recycled paper			
	*L**	*a**	*b**	*ΔE*	*L**	*a**	*b**	*ΔE*
0	70.20±0.66	-15.41±0.25	-1.40±0.55	-	65.07±0.19	-13.19±0.23	-7.34±0.44	-
32	73.89±0.90	-15.09±0.55	6.11±0.68	8.37	64.07±0.43	-10.91±0.49	-2.12±0.81	5.78
50	72.42±1.01	-15.48±0.90	3.41±0.87	5.30	66.26±1.27	-11.52±0.53	-2.64±0.90	5.13
150	72.86±1.25	-13.65±1.76	5.02±0.98	7.49	76.89±1.02	-5.98±0.63	21.75±1.20	10.78
Blank untreated paper	95.09±0.08	-0.29±0.02	0.48±0.07	-	90.40±0.09	4.65±0.09	-17.41±0.12	-

The prints during biodegradation are becoming lighter green, and transforming to yellow due to degradation of blue microcapsules present in ink. The activation temperature of used thermochromic ink is 45ºC. Below activation temperature, the print was coloured in green and above its activation temperature the print was coloured in yellow. This behaviour can be explained by the formation of colorant - developer coloured complex in microcapsules (in this case blue coloured) on lower temperatures (below its activation temperature). On heating above the melting temperature of the solvent (above temperature of activation), the solvent goes in the liquid form and causes the breakdown of the colorant – developer coloured complex, the blue colour disappears while yellow colour of classic offset ink appears.

Thus, a shift of colour during degradation from green (combination of blue microcapsules and classical yellow offset ink) towards yellow indicates that deformation of microcapsules (diffusion of components from microcapsules) and / or degradation of the microcapsule occurred. The thicker the polymeric resin layer over the microcapsules is, makes them more protected towards biodegradation. This means that the rate of microcapsule degradation is greater than the rate of biodegradation of the crosslinked oxidized binder (resins + oils). The higher the absorption of the ink vehicle into the paper is, the faster the rate of print degradation will be. In the case of S-GY print, microcapsules are covered with the thickest layer of the oxidised ink resin, resulting in the smallest colour change.

In addition, in Paper V was concluded that microcapsules of the tested thermochromic offset ink contain polar functional groups, which interact with hydrogen bonding and therefore, it was assumed they are made from melamine resin that is biodegradable (El-Sayed et al., 2006).

4.5. Biodegradability of UV curable screen printing thermochromic ink on papers (Paper VII)

For the evaluation of biodegradability of thermochromic UV curable prints on papers, one leuco dye based, UV curable screen printing thermochromic ink was used (Chromatic Technologies, Inc.). The activation temperature of thermochromic ink is 31ºC. Below its activation temperature, the thermochromic UV curable screen print (hereinafter UV print) was coloured in purple and above its activation temperature the print was coloured in pink.

4.5.1. Optical Microscopy

Thermochromic ink is composed of blue microcapsules dispersed in pink conventional screen printing ink and due to that property, when the ink is exposed to temperatures above their activation temperature, the print changes its colour from purple to pink (*Figure 26*).

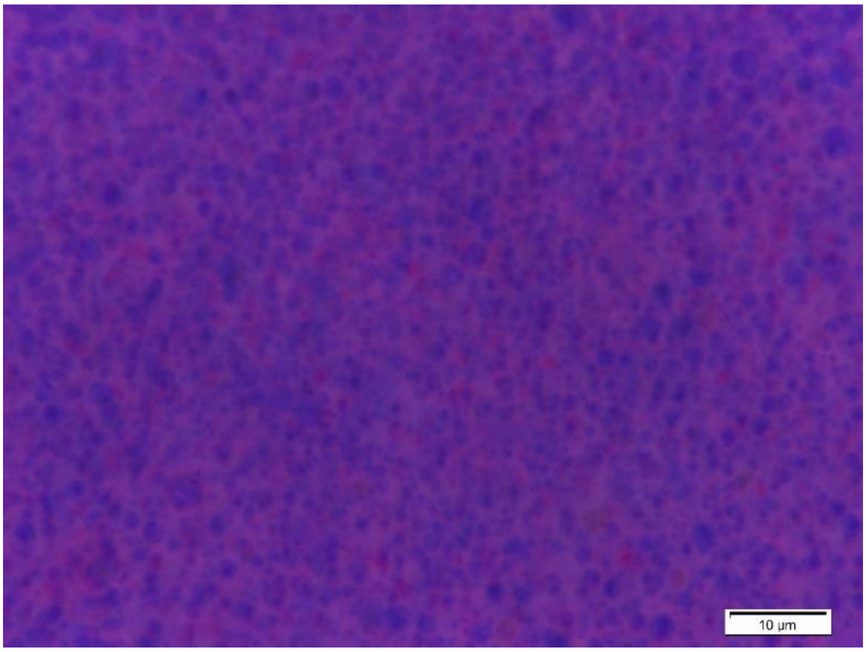

Figure 26. Optical microscopy image of thermochromic ink at 23°C

4.5.2. FTIR spectroscopy of thermochromic ink and papers

Figure 27 shows the FTIR spectra of the UV thermochromic ink which were measured in transmission mode at 25 °C and 50 °C, that is below and above its activation temperature. Even though temperature dependent measurements were accompanied by the thermally induced change in the sample colour, significant changes in the IR spectrum of the UV curable thermochromic ink upon heating were not observed. An exception was a weak band at 1382 cm^{-1}, obtained in the spectrum at the lower temperature and assigned CH bending vibrations of CH_2 and CH_3 groups, which was missing from the spectrum acquired at the higher temperature due to physical changes such as melting occurring during heating (*Figure 27 inset*). Few studies showed that IR spectral changes obtained during heating of the thermochromic composites indicated changes in the molecular structure of the components responsible for the colour change (Hajzeri et al., 2015; Panák et al., 2017; Raditoiu et al., 2016). The changes occurring during heating of the thermochromic system composed of a leuco dye, correspond to the symmetric and asymmetric stretching vibrations of COO^- groups which disappear by heating, while the C=O band, characteristic of the colourless lactone form, appears. However, in our case, these changes were not present. Given the similarity between the spectra obtained at both temperatures (*Figure 27*), the observed vibrational bands most likely originated from the thermochromic ink resin, and were not the result of the vibrational modes of the thermochromic composites within the microcapsules present in a significantly smaller amount. In addition, due to coverage of microcapsules with polymer resin, the vibrational bands of microcapsules wall material are probably covered and overlapped with vibrational bands of polymer resin that is present in higher amount.

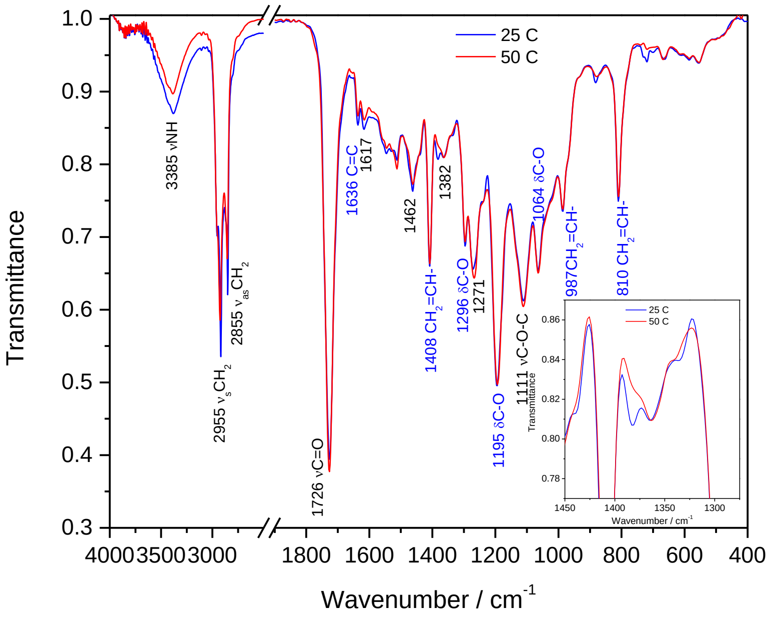

Figure 27. FTIR spectra of the UV curable screen printing thermochromic ink at 25 ºC and 50 ºC, measured in transmission mode

All typical vibrational bands of polyurethane, such as the bands at 3385 cm^{-1} (NH stretching), 2955–2855 cm^{-1} (symmetric and asymmetric CH$_2$ stretching), 1726 cm^{-1} (C=O stretching), 1365 cm^{-1} (C–N stretching) and 1111 cm^{-1} (C–O–C stretching) were obtained in the IR spectra, evidencing the existence of polyurethane in the UV thermochromic printing ink (Zhang et al., 2010). In addition to that, the bands at 810, 987 and 1408 cm^{-1}, attributed to the in-plane and out-of-plane deformation of the vinyl group (CH$_2$=CH–), as well as the band at 1636 cm^{-1}, associated with the double bond (C=C) stretching, pointed to the acrylate (Kim and Seo, 2004). Moreover, vibrational bands at 1064, 1195 and 1296 cm^{-1} could be assigned to vibrational modes of functionalities consisting of oxygen atom (C–O stretching), pointing to acrylates as well (Bénard et al., 2008). However, due to complexity of the obtained IR spectra some bands could not be unambiguously assigned. For instance, the sharp bands at 1617 and 1462 cm^{-1} could be associated with the ring stretching modes, implying presence of the phenyl moiety in the structure, most likely of polyurethane (Chalmers, 2007). Furthermore, the band at 1462 cm^{-1} could be also assigned to bending of the methylene groups present in both, polyurethane and acrylate, while the band at 1271 cm^{-1} could arise from the C–N stretching and C–O stretching in polyurethane and acrylate, respectively (Chalmers, 2007). Nevertheless, the IR spectra implied that the studied thermochromic printing ink was very likely composed of polyurethane acrylate.

Figure 28 shows the IR spectra of the unprinted papers. In the IR spectrum of the synthetic paper the obtained bands were associated with polypropylene (2960–2840 cm^{-1} (asymmetric and symmetric CH_2 and CH_3 stretching), 1433 cm^{-1} (CH_2 and CH_3 bending)) and calcium carbonate (875 and 712 cm^{-1} (asymmetric and symmetric CO_3^{2-} bending)), while beside calcium carbonate (873, 709 cm^{-1}) distinctive bands of cellulose (1426 cm^{-1} (in-plane HCH and OCH deformation), 1160–1000 cm^{-1} (C–O and C–C stretching, COH bending), 898 cm^{-1} (COC and CCO bending)) contributed to the IR spectrum of the recycled paper (*Fig 28*) (Proniewicz et al., 2002). The broad band around 3335 cm^{-1} in the spectrum of the recycled paper was assigned to the OH stretching, mostly originating from cellulose hydroxyl groups, though a weak broad band at 1650 cm^{-1} confirmed the presence of water too.

In the IR spectrum of bulky paper beside cellulose and calcium carbonate (873, 710 cm^{-1}), characteristic bands of lignin corresponding to phenyl ring vibrational modes at 1594 cm^{-1} (phenyl stretching), 1272 cm^{-1} (in-plane CH bending) and 812 cm^{-1} (out-of-plane CH bending) were observed (Derkacheva and Sukhov, 2008). Comparing the unprinted recycled and bulky paper, the higher intensity of the band assigned to the COC bending of β-(1→4)-glycosidic linkages, sensitive to the amount of the crystalline versus amorphous structure of cellulose and also called “amorphous” absorption band, indicated a higher degree of amorphous structure in the recycled paper (898 cm^{-1}) then in the bulky paper (899 cm^{-1}) (Ciolacu et al., 2011).

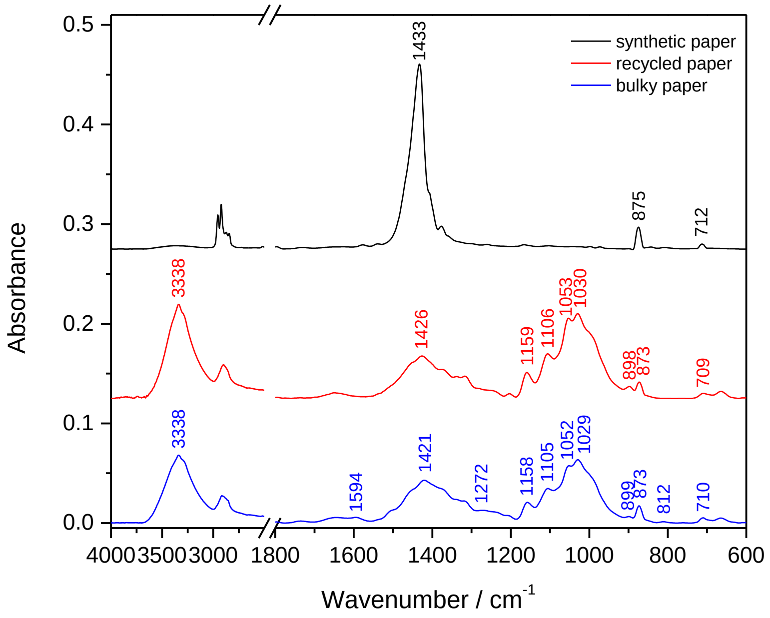

Figure 28. FTIR spectra of the unprinted papers measured in ATR mode.

4.5.3. Determination of thermochromic UV curable ink – paper interactions

Table 19 shows the surface free energies of papers and UV prints, while *Table 20* shows calculated adhesion parameters. The best adhesion performance is achieved if the following conditions are met: $\gamma_{12} = 0$, W_{12} = maximal and $S_{12} \geq 0$.

On the bulky paper the lowest γ_{12}, the highest W_{12} and better spreading were achieved, followed by recycled paper and then by synthetic paper. Bulky paper has the highest γ, but also it has the highest value of polar and dispersive component. Synthetic and recycled papers have similar values of γ. However, better adhesion property was achieved on the recycled paper, which contains higher value of polar component. The interactions between the thermochromic ink and the surface of the synthetic paper were achieved only by dispersion forces due to very small share of polar components on the surface of paper, which resulted in formation of the hydrophilic surface of the UV print due to presence of unbounded polar group of polyurethane acrylate resin. Based on the obtained results it can be concluded that the surface of the paper besides large surface free energy should have the optimal polarity in order to achieve better adhesion properties of used thermochromic ink.

Table 19. Surface energy of unprinted and printed samples and its components

Sample	Surface free energy γ (mJ m^{-2})		
	γ^d	γ^p	γ
Synthetic paper	22.99	0.11	23.10
Synthetic paper - UV print	27.18	4.93	32.11
Recycled paper	22.54	1.33	23.87
Recycled paper - UV print	35.21	1.09	36.30
Bulky paper	25.01	1.43	26.44
Bulky paper – UV print	34.58	0.86	35.44

Table 20. Adhesion parameters

Sample	Adhesion parameters / (mJ m^{-2})		
	γ_{12}	W_{12}	S_{12}
Synthetic paper - UV print	3.74	51.47	-12.75
Recycled paper - UV print	1.41	58.75	-13.84
Bulky paper – UV print	0.84	61.03	-9.84

4.5.4. SEM Microscopy

SEM micrographs of UV print on synthetic paper (*Figure 29*) show that microcapsules are covered with polymer resin (binder). After 180 days of biodegradation, the changes in the surface of UV print were observed (*Figure 30*). A noticeable biodegradation of the polymer resin can be seen, and the microcapsules become more visible. *Figure 30* shows heterogeneous degradation of the print. Microcapsules are in irregular shape, some are notched and some are hollow. In the case of UV prints on recycled and bulky paper (*Figs. 31*,*33*), it can be seen that microcapsules are covered with thinner layer of resin and thus, they are more visible. The number of microcapsules in UV prints is significant and they are in the regular circle forms, with around 1-2 µm in diameter. After biodegradation, the surfaces are visibly degraded, in UV print on bulky paper more than on UV print on recycled paper. UV print on recycled paper (*Figure 32*) shows a larger number of hollow microcapsules than UV print on synthetic paper (*Figure 30*), more deformation and higher number of irregular microcapsules. However, the number of microcapsules does not change much more than in the original printed recycled paper

(*Figure 31*). After 180 days of biodegradation of UV print on bulky paper destruction of almost all microcapsules is visible (*Figure 34*). In addition, in *Figure 34* there are also visible cellulose fibres, which indicate a thinning of the polymer resin layer on the surface of bulky paper, *i.e.*, greater biodegradation. In *Figure 34* it can be seen that few microcapsules between cellulose fibres, remain protected.

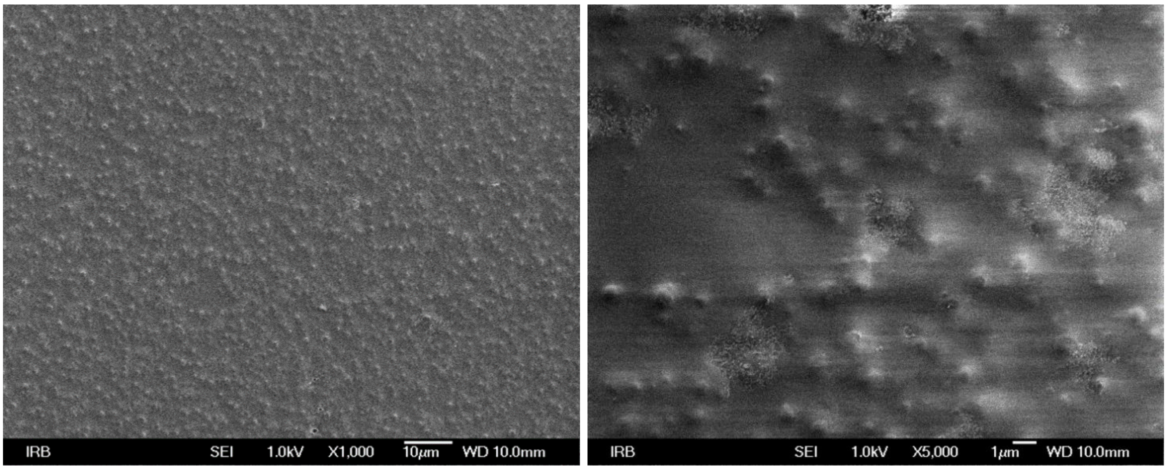

Figure 29. SEM micrograph of UV print on synthetic paper before biodegradation at different magnifications (1000x and 5000x)

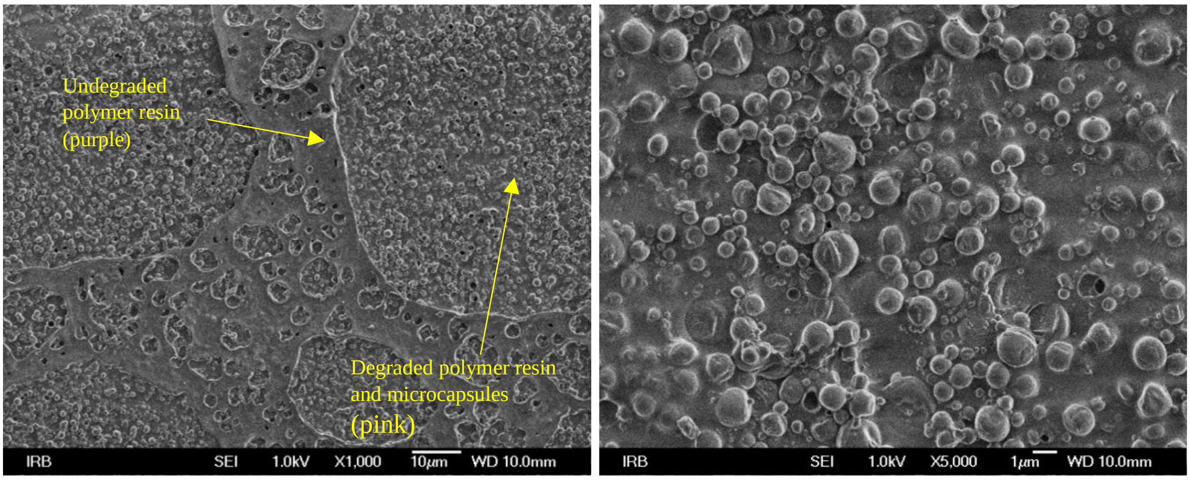

Figure 30. SEM micrograph of UV print on synthetic paper after 180 days of biodegradation at different magnifications (1000x and 5000x)

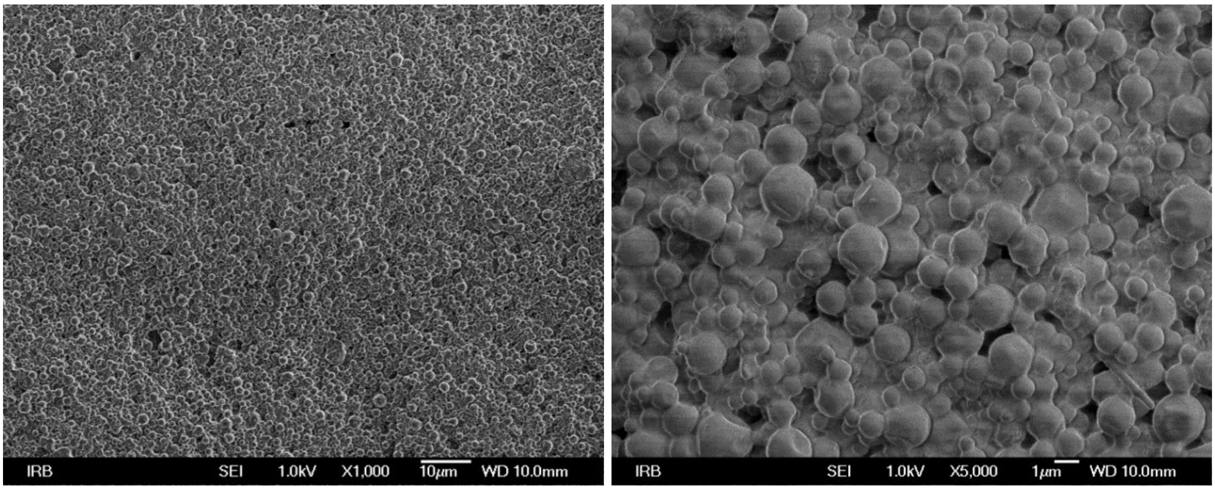

Figure 31. SEM micrograph of UV print on 33% recycled paper before biodegradation at different magnifications (1000x and 5000x)

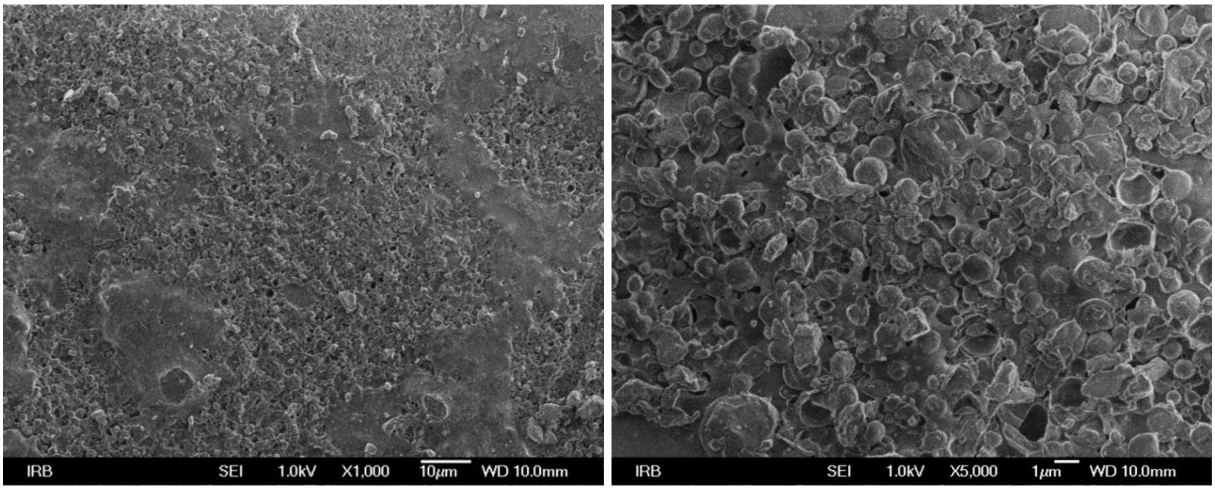

Figure 32. SEM micrograph of UV print on 33% recycled paper after 180 days of biodegradation at different magnifications (1000x and 5000x)

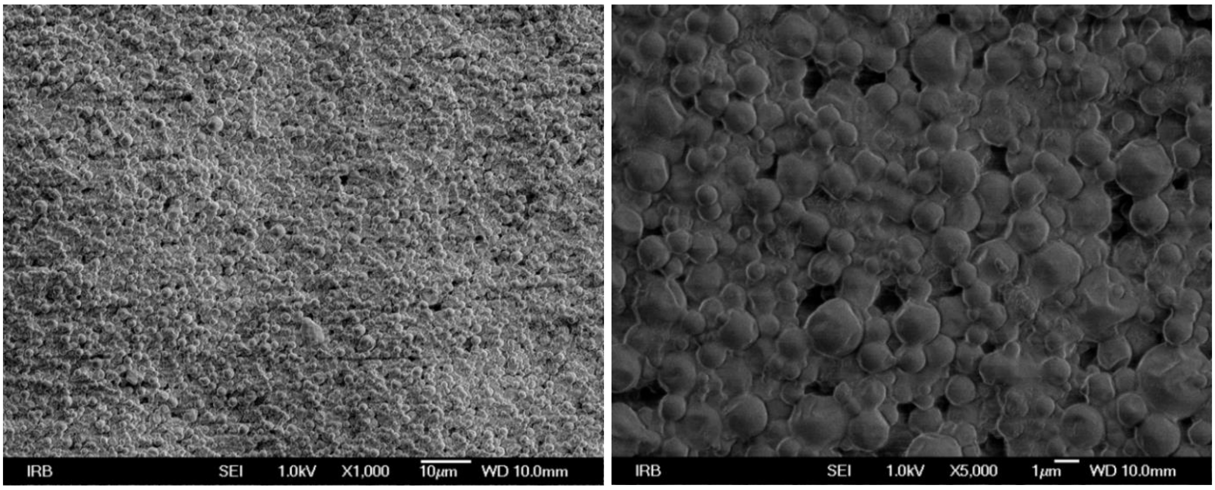

Figure 33. SEM micrograph of UV print on bulky paper before biodegradation at different magnifications (1000x and 5000x)

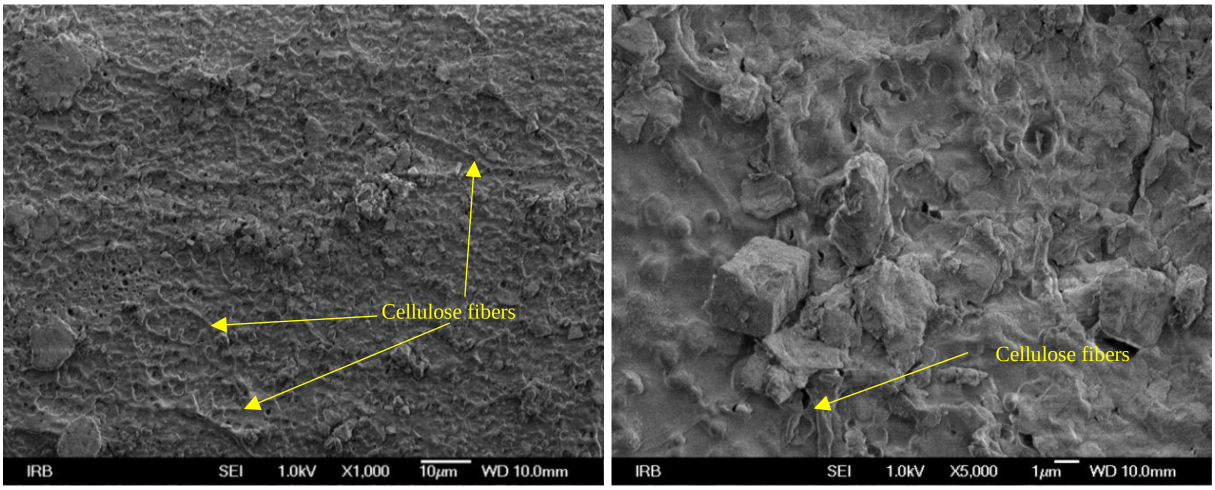

Figure 34. SEM micrograph of UV print on bulky paper after 180 days of biodegradation at different magnifications (1000x and 5000x)

4.5.5. Visual evaluation

Figure 35 and 36 shows the images used for visual evaluation of UV thermochromic prints before and after biodegradation. After 50 days of biodegradation, the UV prints on all papers show only slight changes in colour. After 180 days of biodegradation, it can be noticed that surface of UV print on synthetic paper is purple with pink areas, indicating a heterogeneous degradation of microcapsules. The UV print on recycled paper is mostly pink with a very small amount of purple coloration. Only a pink colour is visible for UV print on bulky paper. In the case of UV print on bulky paper it can be noticed that samples after 50 and 180 days were disintegrated into pieces, *i.e.* showing not only changes in colour, but in the structure as well. The changes in colour of the prints occurring during biodegradations are result of the microcapsules deformation and degradation. The greater the transition to pink colour is, the greater the destruction (deformation) of the microcapsule which was confirmed by SEM micrographs.

Figure 35. Visual evaluation of prints before and after 50 and 180 days of biodegradation

Comparing the unprinted sides of the prints (*Figure 36*), UV print on synthetic paper shows almost no changes in its visual appearance. For the UV print on recycled paper, some formation of spots can be noticed, but after 180 days of biodegradation, these spots present degradation of paper. However, these changes are smaller compared to unprinted side of UV print on bulky paper, whose visual appearance is very diverse from the original.

Figure 36 shows that unprinted sides of papers before degradation have some differences in colour, *i.e.* unprinted side of recycled paper is pink while unprinted side of bulky paper is more purple. That might be an indication that microcapsules altogether with polymer ink resin penetrate deeper in the structure of bulky paper and promote biodegradation. In the case of recycled paper, ink binder (altogether with classic pigment) penetrates into its structure. For the print on synthetic paper, there is no penetration of ink into to its structure. All components of ink remain on the surface of synthetic paper.

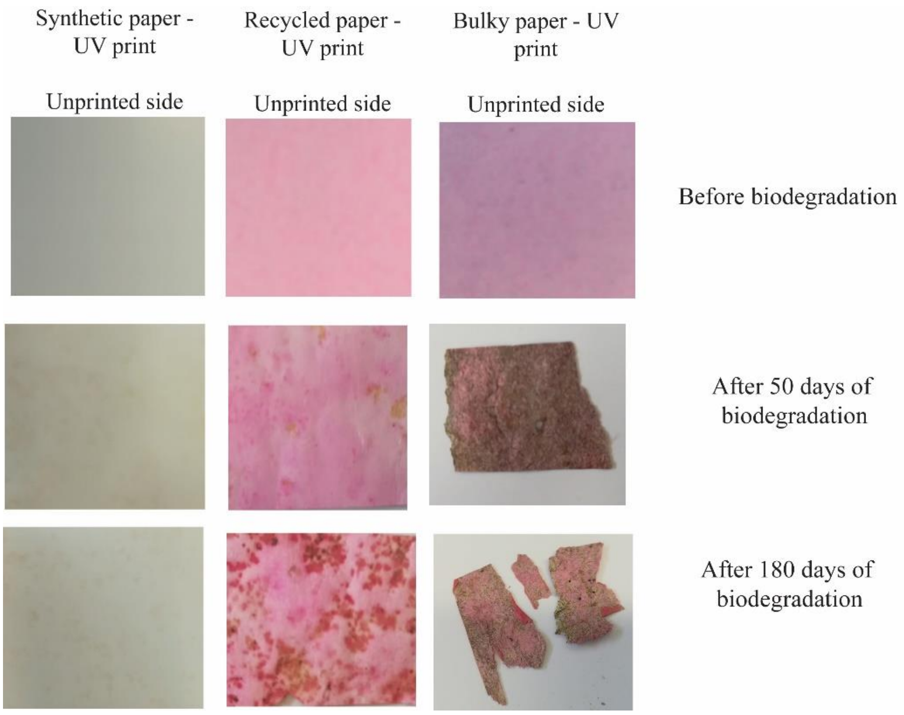

Figure 36. Visual evaluation of UV prints before and after 50 and 180 days of biodegradation – unprinted side

4.5.6. Microbial growth assay and weight loss measurement

Figure 37 shows the number of bacteria on the unprinted and printed-paper samples after 180 days of biodegradation in the soil. In the case of unprinted paper samples, the highest number of bacteria was noticed on recycled paper, followed by the bulky paper. The number of bacteria obtained on synthetic paper was the smallest and it was smaller compared to number of bacteria isolated from the soil. For this reason, synthetic paper shows no changes in weight after biodegradation period due to microbial attack resistance of polypropylene present in its structure (Arutchelvi et al., 2008; Leja and Lewandowicz, 2010). The weight loss measurement for unprinted recycled paper indicates higher biodegradation compared to bulky paper (*Table 21*). After 180 days of biodegradation, unprinted recycled paper was more than 90% degraded, while bulky paper was more than 25.8% degraded. Higher rate of recycled paper biodegradation compared to bulky paper, can be explained by the higher ratio of amorphous cellulose in recycled paper, which was confirmed by FTIR (*Figure 28*) and presence of shorter cellulose fibres resulting from process of recycling. Amorphous cellulose is more susceptible to degradation than the crystalline (Van Wyk and Mohulatsi, 2003). In addition, bulky paper contains lignin that interferes the paper biodegradation (Komilis and Ham, 2003).

The smallest number of bacteria was isolated on printed synthetic paper and it was almost the same as number of bacteria isolated from the soil, which resulted in a small weight loss (3%) after 180 days of biodegradation (*Table 21*). This can be mainly described by the UV print degradation rather than synthetic paper degradation since unprinted synthetic paper shows no changes in weight during biodegradation. It can be assumed that UV print is more biodegradable than synthetic paper. For the printed recycled paper an opposite behaviour was observed, *i.e.* notable reduction of biodegradation rate compared to unprinted recycled paper was noticed. With the application of thermochromic ink, the weight loss was five times lower. This behaviour can be explained by the polymer ink resin and pigment absorption. In the case of recycled paper, it is obvious that classic pigment that penetrates into its structure lowers the rate of biodegradation, which means that classic pigment is less degradable than recycled paper.

The highest change in the weight loss was obtained for the printed bulky paper. In this case, printed bulky paper degrades faster than unprinted bulky paper. Higher rate of printed bulky paper biodegradation compared to printed recycled paper can be due to better absorption of microcapsules. The deeper the penetration of the microcapsule into to structure of paper is, higher biodegradation occurring from the unprinted side is. Considering the fact that the weight loss measurement for printed sample is almost the same after 50 and 180 days of biodegradation, degradation of paper probably stopped after 50 days, but after that period only degradation of microcapsules occurred. Due to their small sizes and lower share in the thermochromic ink and printed sample, the weight loss reduction after 180 days was negligible. The similar number of bacteria obtained for unprinted and printed bulky paper can be explained by the fact that bacterial growth after 180 days of biodegradation of printed bulky paper was probably in decline due to destruction of almost all microcapsules (*Figure 34*) and reduction in biodegradation rate.

Thermochromic microcapsules are mostly composed of urea - formaldehyde or melamine - formaldehyde resins gelatine – gum arabic and epoxy resins (Aitken et al., 1996; Fujinami, 1996b; Seeboth and Lotzsch, 2008) which are biodegradable and during biodegradation can act as nitrogen sources (El-Sayed et al., 2006). Microcapsules can act as an active sites promoting biodegradation.

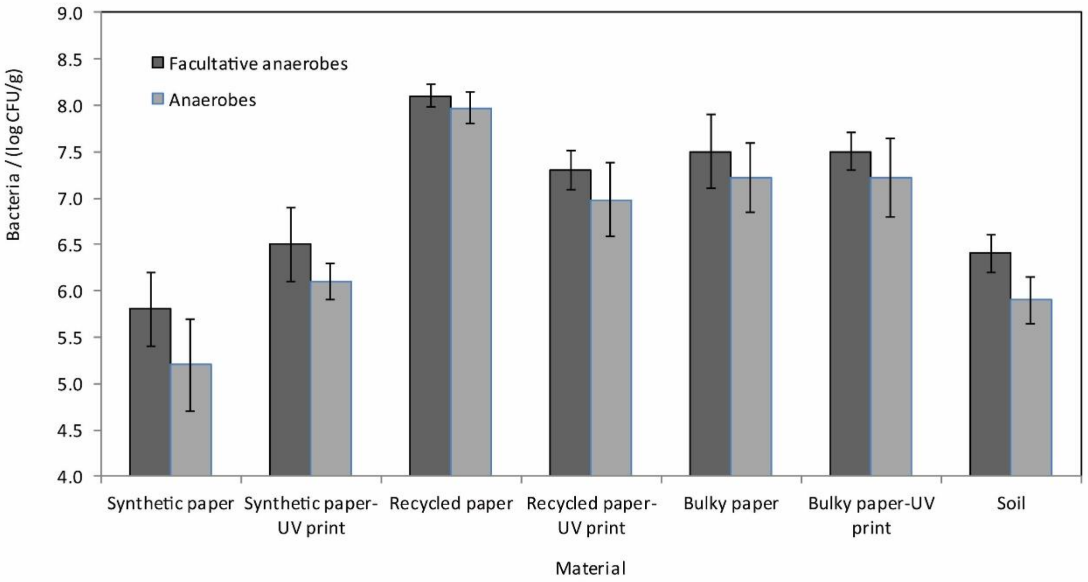

Figure 37. Number of viable bacteria on unprinted and printed-paper samples and in corresponding soil after 180 days of biodegradation

Table 21. Weight loss during soil burial

Sample	Weight loss / (%)	
	Days	
	50	180
Synthetic paper	0.0	0.0
Synthetic paper - UV print	0.6	3.0
Recycled paper	46.25	92.87
Recycled paper - UV print	6.8	17.8
Bulky paper	20.45	25.80
Bulky paper – UV print	49.2	50.2

4.5.7. FTIR spectroscopy of UV curable prints before and after biodegradation

The IR spectra of the thermochromic UV prints on the used papers before and after 50 and 180 days of biodegradation were shown in *Figures 38, 39* and *40*. In addition, the IR spectra of UV curable ink and unprinted papers have been presented in *Figures 38, 39* and *40*.

The IR spectra of the thermochromic prints on all paper samples: synthetic, bulky and recycled, measured in attenuated total reflectance (ATR) mode, were very similar. In comparison to the spectrum of the thermochromic UV curable ink, the bands at 1408, 1296, 1271, 1195 and 1064 cm^{-1} in the IR spectra of the prints were weaker and poorly defined. The intensity of these bands decreased due to polymerization of polyurethane acrylate during UV curing.

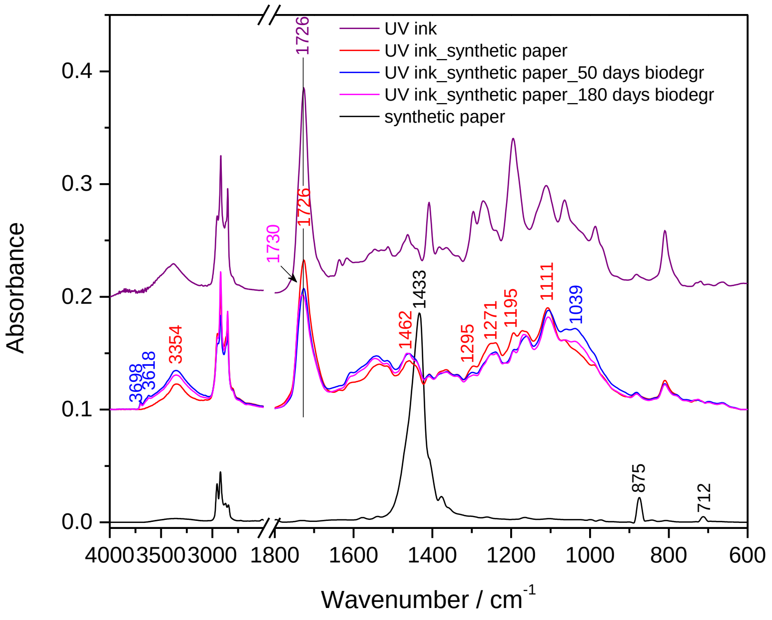

Figure 38. FTIR spectra of the UV thermochromic ink, the neat synthetic paper and the prints of the ink on the synthetic paper before and after 50 and 180 days of biodegradation, measured in ATR mode

A decrease of band intensities located in the 1100–1000 cm^{-1} range (attributed to the ester C-O stretching vibration), 1260 – 1200 cm^{-1} range (attributed to carbonyl oxygen linkage) and carbonyl peak around 1730 cm^{-1} were observed after degradation. The changes in those bands are present for all printed papers after biodegradation (*Figs 38, 39* and *40)* and very likely indicate the breaking down of the ester linkages, leading to the changes in the ester and urethane groups of polyurethane resin, *i.e.* changes in polymeric structure (Oprea et al., 2016; Oprea and Doroftei, 2011). In the ranges from 1100 – 1000 cm^{-1} and 1260 – 1200 cm^{-1}, the highest changes were observed for the print on bulky paper, followed by print on recycled paper. The smallest changes were observed for the synthetic paper. However, the changes in the spectral ranges from 1300 – 1800 cm^{-1} were observed only for the printed bulky paper.

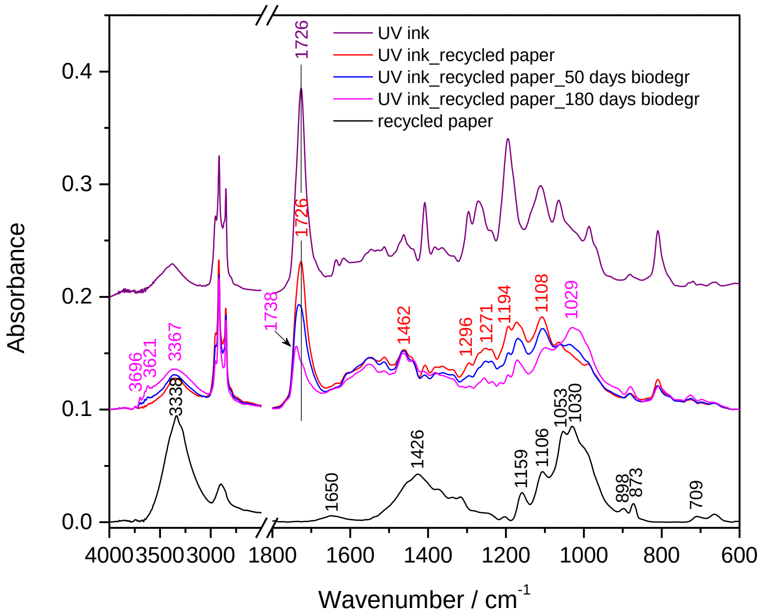

Figure 39. FTIR spectra of the thermochromic ink, the neat recycled paper and the prints of the ink on the recycled paper before and after 50 and 180 days of biodegradation, measured in ATR mode.

An appearance of the intense broad band at around 1030 cm^{-1} could be attributed to cellulose, due to thinning of the polymer resin on the surface of the bulky and recycled paper, which can be attributed to stretching of C–O in cellulose/hemicellulose molecules (Grilj et al., 2012). Interestingly, in the IR spectrum of the UV print on the bulky paper this band decreased after 180 days of biodegradation, if compared to the spectrum after 50 days, indicating cellulose degradation as well. This was supported by SEM micrographs (*Figs 33 and 34*). The intense cellulose like vibration bands (at 1030 cm^{-1}) were also obtained after 180 days of the UV print biodegradation on the recycled paper. Given that the spectral motif around 1030 cm^{-1} was obtained in the IR spectra of the UV print on all the papers after biodegradation, including the synthetic paper not consisting of cellulose, its origin could be also partially associated with silicates (Si–O stretching) adsorbed on the prints from the soil. The presence of silicates on the surface of the prints, was also indicated by the weak bands at 3698 and 3618 cm^{-1} assigned to O–H stretching in the Si–OH structural moieties located on the silicate surface (Das et al., 2013; Tinti et al., 2015). Since weak bands around 3696 and 3620 cm^{-1} correspond to the silicates OH groups were obtained in the IR spectra of the prints on all the papers, it was very likely that the band at 1039 cm^{-1} associated with the Si–O stretching in silicates was also present in the spectra of the prints on the recycled and bulky paper, but overlapped by the strong broad cellulose band.

Due to degradation of polyurethane, the formation of degradation products can be noticed and followed in the hydroxyl and NH group stretching range (3600–3100 cm^{-1}), whose intensity increased after biodegradation (Bénard et al., 2008; Huang et al., 2016; Oprea and Doroftei, 2011). Compared to the IR spectra before biodegradation, the band at around 3350 cm^{-1} was slightly stronger, wider and positioned at higher wavenumbers in the spectra of the buried prints (*Figs 38, 39* and *40*).

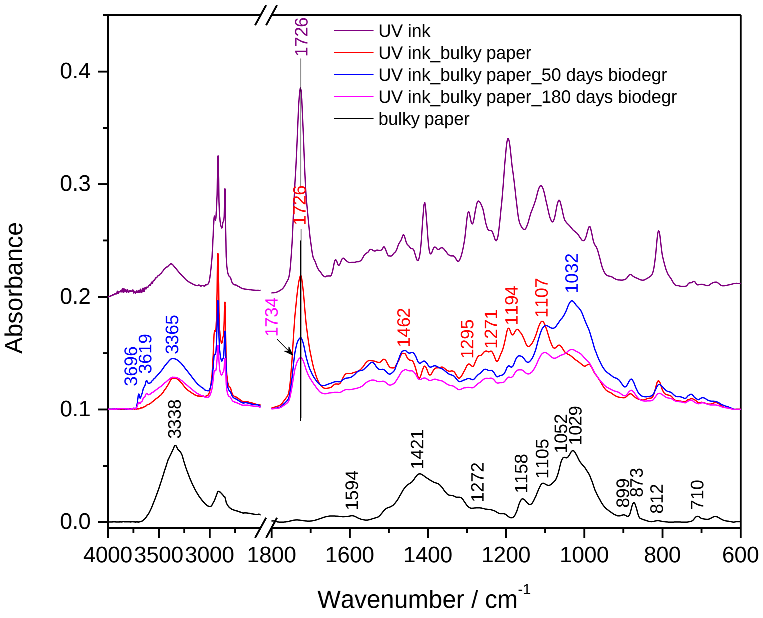

Figure 40. FTIR spectra of the thermochromic ink, the neat bulky paper and the prints of the ink on the bulky paper before and after 50 and 180 days of biodegradation, measured in ATR mode.

4.5.8. Colorimetric measurements

Results of colorimetric *a** and *b** values determined on UV thermochromic prints before and after biodegradation are presented in *Figure 41.* Due to the formation of polymer ink layer on the surface of all papers and its complete coverage of paper samples, the colour of unprinted papers does not have a significant influence on the colour reproduction of the UV prints. *Figure 41* shows that the colorimetric *a** and *b**values of original UV prints on bulky and recycled paper, measured below the activation temperature, have similar colorimetric properties. However, the UV print on bulky paper has slightly lower *a** and *b** values compared to UV print on recycled paper. This can be attributed to better absorption of microcapsules and classic pink pigment into a structure of bulky paper. Compared to UV prints on bulky and recycled paper, UV print on synthetic paper has higher *a** value, and smaller *b** value, due to higher concentration of ink on the surface of the paper.

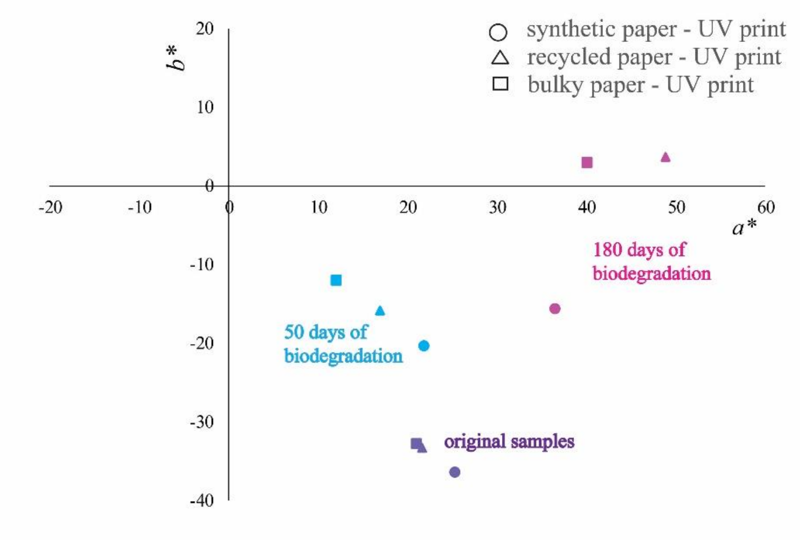

Figure 41. Colorimetric properties (*a** and *b** values) of UV prints measured at 20°C before (purple), after 50 days (blue) and 180 days (pink) of biodegradation (circle- UV print on synthetic paper, triangle – UV print on recycled paper, square – UV print on bulky paper)

Figure 41 shows the transition of prints colour from purple to pink. The *a** and *b** values of UV prints after 50 days of biodegradation are smaller than the initial values. The *a** value on bulky paper print shows the lowest positive values while the *b** value shows the smallest negative values, indicating the highest colour change. After 180 days of biodegradation, the *a**and *b** values of all samples, are more positive compared to the initial values. The smallest colour change was in the case of UV print on synthetic paper. After 180 days of biodegradation, the pink colour of print on bulky paper was lighter (smaller *a** value) compared to print on recycled paper, indicating higher colour change.

The TC system has memory, which is called hysteresis. It's colour hysteresis describes the colour of a TC sample as a function of temperature and should be presented in four-dimensional space or by two- dimensional graphs (Kulčar et al., 2010). The trajectory obtained by heating is not equal to one obtained by cooling. The area of the surface defined by the two trajectories shows the similarity (of the colour change) of the heating and cooling run. The reversible TC process can be presented by change of *L*, a** and *b** values as a function of temperature. When printed sample is heated, decolourization of microcapsules occurs above the activation temperature (TA). Therefore, the *b** values increase because only the pink colour of the classic pigment remains. The reverse process occurs during cooling at lower temperatures.

L(T)* hysteresis describes temperature dependence of *L** values. *Figure 42a* shows that all UV prints before biodegradation tests show similar values, *i.e.* similar reversibility of colour. UV prints on recycled and bulky paper show almost the same behaviour, while small differences can be noticed for UV print on synthetic paper. Due to higher amount of polymer resin containing pink classic pigment over the microcapsules present on the surface of the synthetic paper, the hysteresis is shifted to higher *L** values. After 50 days of biodegradation (*Fig 42b*), the initial *L** values of the UV prints on recycled and bulky paper are shifted to higher *L** values, similar to *L** value of UV print on synthetic paper. This indicates a higher concentration of classic pink pigment on their surface. The highest decrease of *L*(T)* hysteresis height was obtained on printed bulky paper, while the smallest change in *L*(T)* hysteresis height was obtained on printed synthetic paper, indicating that he highest destruction of colour was noticed on printed bulky paper. After 180 days of biodegradation (*Fig 42c*), the prints on recycled and bulky papers showed remarkable reduction of thermochromic effect. The reduction of thermochromic effect and changes occurring in *L*(T)* hysteresis are result of reduction in active microcapsules number, which was confirmed by the SEM micrographs. *L*(T)* hysteresis are substantially shifted toward higher *L** values suggesting greater concentration of classic pink pigment in relation to the concentration of microcapsules.

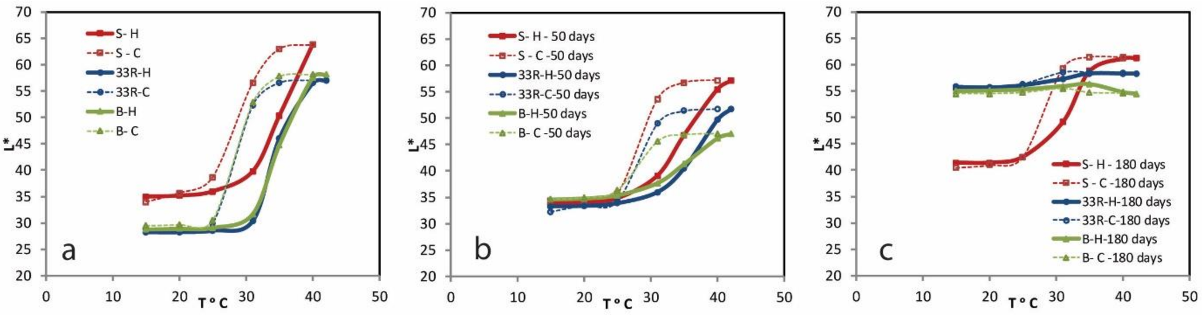

Figure 42. *CIELAB L** values of UV print on synthetic paper (S - red), recycled paper (33R - blue) and bulky paper (B - green) in dependence on temperature at heating (solid line) and cooling (open line) before biodegradation (a), after 50 days of biodegradation (b) and after 180 days of biodegradation (c).

In addition, the changes occurring in *b*(T)* hysteresis may also point to degradation of blue microcapsules (*Figs 43 a, b, c*). The smallest changes occurring in *b*(T)* hysteresis were obtained for UV print on synthetic paper. Interestingly, after 50 days of biodegradation, the final *b** values (at highest temperatures) are not approaching to zero by heating, but they are becoming positive (shift to the yellow area). In the case of UV prints on recycled and bulky paper, the *b** values are positive throughout the whole temperature range. After 180 days of biodegradation, the greatest shift to yellow area was obtained on printed synthetic paper, followed by printed recycled paper and printed bulky paper.

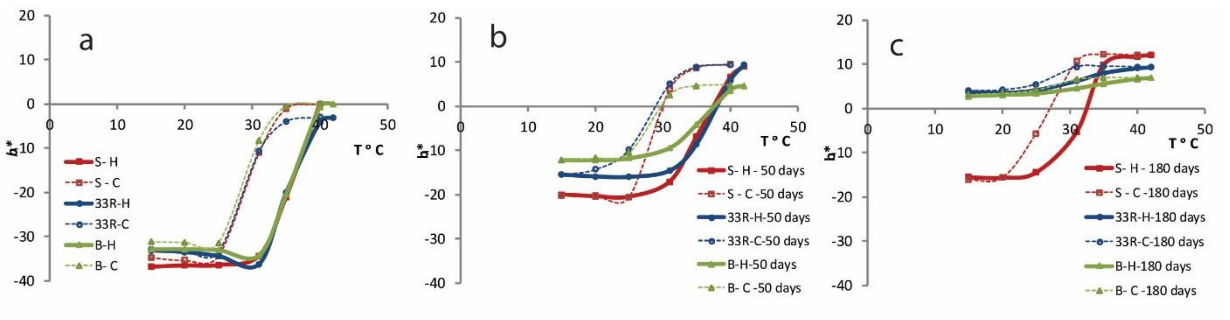

Figure 43. *CIELAB b** values of UV print on synthetic paper (S - red), recycled paper (33R - blue) and bulky paper (B - green) in dependence on temperature at heating (solid line) and cooling (open line) before biodegradation (a), after 50 days of biodegradation (b) and after 180 days of biodegradation (c).

The changes in the *a*(T)* hysteresis my point to degradation of classic pigment present in polymer ink resin (*Figs 44a, b and c).* After 180 days of biodegradation, the final *a** values (at highest temperatures) are the highest in the case of printed synthetic paper, slightly lower values are on printed recycled paper, and the smallest a* values are on printed bulky paper. Accordingly, the highest shift to yellow and red area obtained on the printed synthetic paper indicates the highest concentration of classic pink pigment. The smallest concentration of classic pink pigment was obtained on the printed bulky paper after 180 days of biodegradation. It can be assumed that classical pink pigment shows slower rate of biodegradation. In the case of printed bulky paper, in which the highest absorption of thermochromic ink was noticed, the active sites that bacteria use for their metabolism are the most accessible. If the smaller the effect of ink separation is, these sites are less accessible, so the rate of biodegradation is lower.

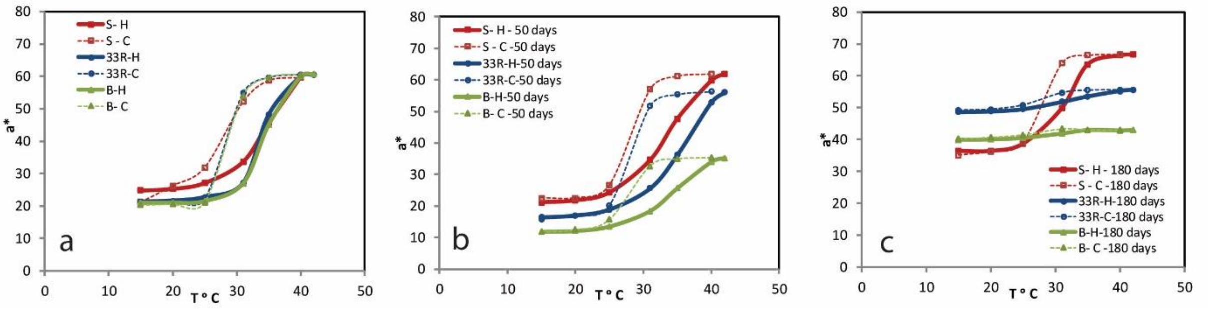

Figure 44. *CIELAB a** values of UV print on synthetic paper (S - red), recycled paper (33R - blue) and bulky paper (B - green) in dependence on temperature at heating (solid line) and cooling (open line) before biodegradation (a), after 50 days of biodegradation (b) and after 180 days of biodegradation (c).

4.6. Biodegradability of UV curable screen printing thermochromic ink on cardboard (Paper VIII)

Three different cardboard materials were used in biodegradability test. The used cardboards are representing different classes of cardboards (*Table 22*) according to their properties and quality.

Table 22. Cardboard classification

Cardboard samples	Abbreviation	Grammage, g/m^2	Classification
Lux Pack	LP	350	GC1
Propack	PP	350	GT2
Umca Color	UC	350	GD2

In the *Table 23* the obtained results for surface free energy of neat and printed cardboard samples are given. Neat cardboard samples have a large proportion of polar component in its SFE, as indicated by the γ^p and the dispersion index x^d. The highest polar character of surface is observed for UC sample (13.56 mJ m^{-2}), followed by LP (10.01 mJ m^{-2}), which is characteristic for the hydrophilic surface. Compared to UC and LP sample, PP sample has hydrophobic surface with the smallest polar component (1.44 mJ m^{-2}). By observing the SFE of prints, they are similar in all samples. SFE of prints on all samples mostly originate from its dispersive component, which is characteristic for hydrophobic surface. It is evident that LP-UV sample does not have hydrophilic molecules on the surface (γ^p = 0.00 mJ m^{-2}), and its total SFE is equal to its dispersive component. The other two printed cardboards (PP-UV and UC-UV) show the existence of polar components on their surface according to obtained SFE. From this it can be concluded that an adhesive bond between cardboard and ink is mostly provided by nonpolar interactions.

Table 24 shows the adhesion parameters for cardboards and prints. The largest adhesion is achieved on a UC-UV sample regardless to larger SFE of interphase (γ_{12}). In other two samples (PP-UV and LP-UV) the work of adhesion is similar but noticeably lower than in the UC-UV sample. This can be attributed to the large SFE of interphase (in the case of the LP-UV) and with different SFE of individual phases (in the case of PP-UV).

Cardboards with hydrophilic (polar) surface (LP and UC) show higher values of SFE of interphase. The high SFE of interphase can be explained by the existence of polar molecules on the surface of LP cardboard which creates resistance to print and thus preventing the binding and absorption of ink on the surface of cardboard. This resistance will result as a higher γ_{12}

value. Cardboard with hydrophobic surface (PP) shows the minimum value of SFE of interphase (3.41 mJ m^{-2}). Comparing these results to the results obtained on papers, it can be seen that cardboards show lower adhesion due to very high SFE of interphase, which can be interpret as high resistance of cardboards to ink, due to very high hydrophilic nature of cardboard.

Table 23. Surface properties

Sample	**Surface free energy (mJ m^{-2})** γ			x^d**(%)** (γ^d/γ)
	γ^d	γ^p	γ	
LP	17.22	10.01	27.23	63,24
PP	13.9	1.44	15.34	90,61
UC	20.58	13.56	34.14	60,28
LP-UV	30.43	0.00	30.43	100,00
PP-UV	29.19	0.18	29.37	99,39
UC-UV	32.91	2.12	35.03	93,95

Table 24. Adhesion parameters

Sample	**Adhesion parameters (mJ m^{-2})**	
	γ_{12}	W_a
LP - UV	11.88	45.78
PP - UV	3.41	41.30
UC - UV	6.40	62.77

In order to make a conclusion about biodegradability, changes in the appearance of sample surfaces were observed before and after biodegradation during the whole sampling time. Formation of holes, cracks and changes in colour were noticed. From *Figs 45, 46 and 47* it can be noticed that the highest changes on the surface of printed cardboard samples occur after 80 days. The biggest changes occur after 120 days of biodegradation for all samples. During the first 14 days of biodegradation test, no significant change in colour or on the surface of samples occurred. After 32 days in the LP-UV and UC – UV samples can be noticed the formation of cracks in the print, while in PP-UV sample it is visible after 80 days. In the LP-UV sample cracks in the print are the most visible but also detachment of ink layer from substrate can be observed. This can be attributed to the maximum value of SFE of interphase γ_{12} between the cardboard and ink (*Table 24*). As SFE of interphase increases in a row: PP-UV < UC-UV < LP-UV, the cracking and lamination of ink layer from the cardboard surface can be noticed. Thus, probably penetration of the bacteria occurs from all sides which resulted in higher color change.

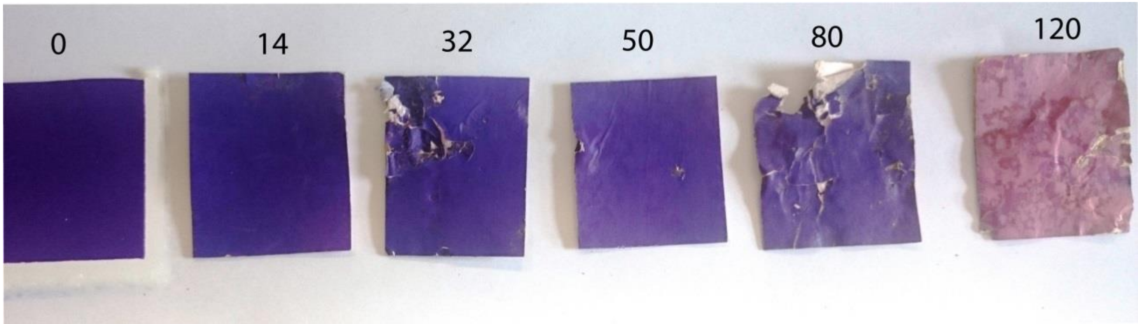

Figure 45. Biodegradation over 120 days for printed LP- UV cardboard

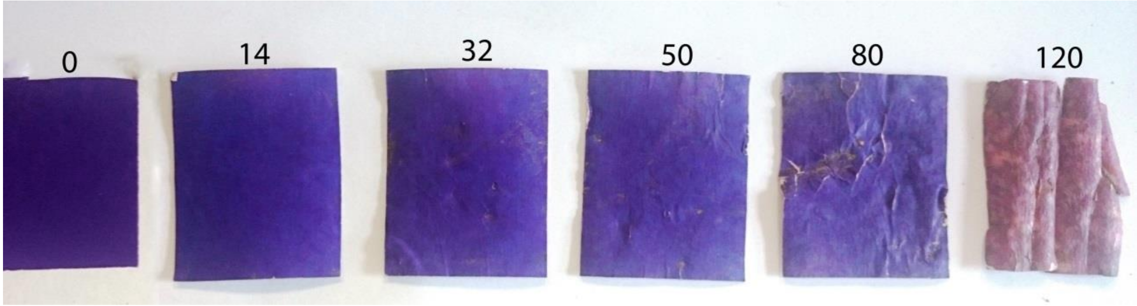

Figure 46. Biodegradation over 120 days for printed PP- UV cardboard

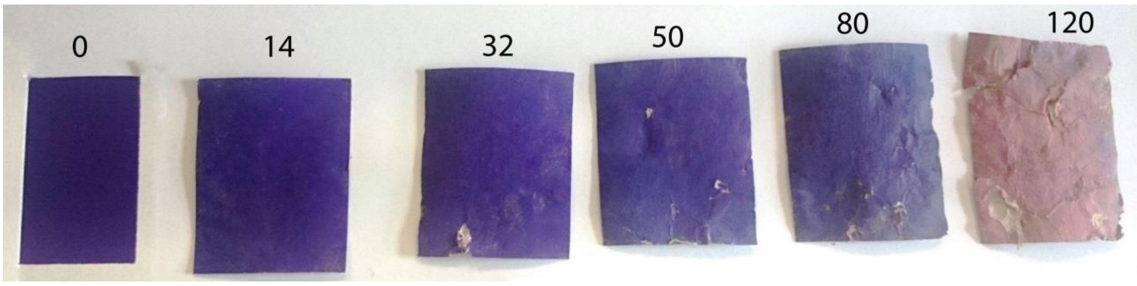

Figure 47. Biodegradation over 120 days for printed UC- UV cardboard

By observing the neat cardboard samples, the highest level of weight loss shows UC. After 120 days the total weight loss was about 38.4%, followed by the PP with 34.8%. The smallest weight loss has LP, with 31.5% after 120 days of biodegradation. Considering only the printed samples, it is obvious that the largest weight loss shows the sample LP – UV (31.7%), followed by the PP-UV (30.94%). The lowest weight loss was observed at the UC – UV sample (24.6%). The smallest changes in weight loss of all samples are in the first 50 days (*Figure 48*).

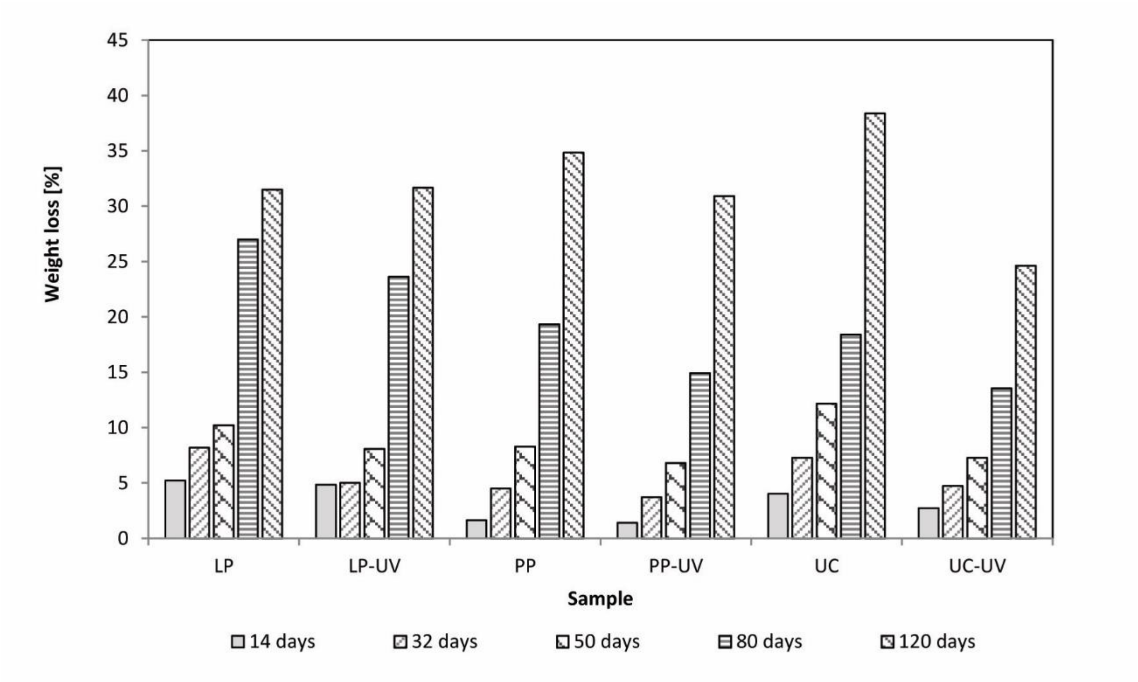

Figure 48. Biodegradation of samples through weight loss over 120 days

The highest change in colour (ΔE) was observed in the case of LP-UV cardboard while the lowest in the case of PP-UV cardboard (*Figure 49*). This could be associated with an SFE of interphase. The higher the SFE of interphase is, the greater the change in colour after 120 days can be noticed. Stronger bond between the ink and cardboard will result in better colour stability. The higher the value of SFE of the interface is, the forces of binding to the substrate are less, cracking and lamination of ink film during biodegradation occurs. Through the cracks and through the free spaces occurring between the cardboard and ink film bacteria can penetrate and degrade the ink film from all the sides. Lower rate of ink biodegradation results from lower surface free energy of interphase. The rate of printed cardboard degradation differs significantly from printed paper samples biodegradation.

It can be concluded that very high hydrophilic cardboard surface is not desirable for achieving the optimum adhesion, resulting in very high surface free energy of interphase which can affect printing quality as well.

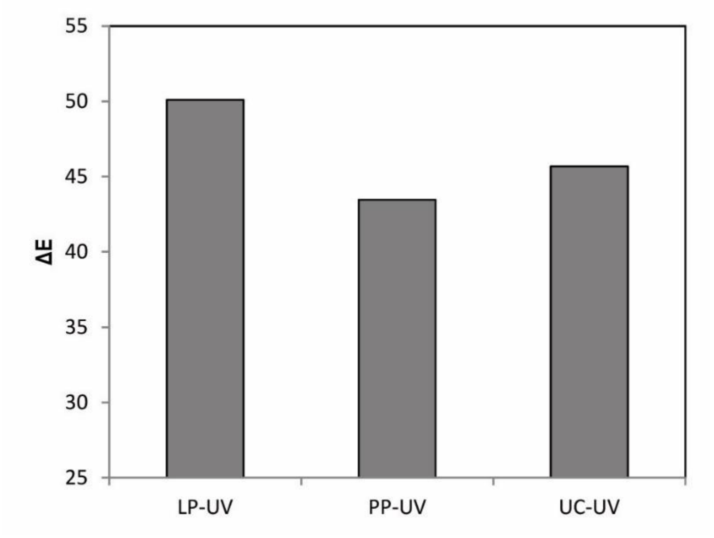

Figure 49. Total colour difference after 120 days of biodegradation

5. CONCLUSIONS

Based on the obtained results we may conclude that the tested thermochromic offset printing inks are poorly deinkable, due to very high adhesion to paper. Measurements of optical properties demonstrated the ineffectiveness of this method for the recycling of thermochromic ink prints, since only a small increase in deinked pulp brightness and whiteness was noticed. Moreover, image analysis showed that deinking flotation is not successful method for the elimination of disintegrated ink particles. A possible explanation of this could lie in the chemical composition of thermochromic inks and their ability to bond with examined paper substrate. Deinkability aspects of tested inks are influenced by good adhesion of inks to paper substrate and the existence of polar component in the printed ink film. It can lead to retention of the particles in pulp suspension due to weak adhesion onto the air bubbles. Due to poor deinkability, the retention of the ink particles in recycled pulp results in the presence of bisphenol A (BPA) and heavy metals. BPA originates from thermochromic ink. The reduction of only 50 % of BPA was noticed in the samples after flotation. According to new stricter limits of maximum permitted quantity of BPA, analysed samples failed the purity requirements, as both detected concentrations were above maximum permitted limits. The higher concentrations of Zn and Fe in all samples originate from printing substrate. The concentrations of Mn and Co in the DP handsheet and filtration froth originate from drying catalysts present in thermochromic inks. The growth of *Bacillus subtilis* and *Aspergillus niger* was not inhibited in all tested samples (B, UP, DP) indicating there was no release of toxic substances, despite the presence of BPA.

Besides the poor deinkability, recycling of thermochromic inks showed higher environmental impact in the terms of wastewater pollution due to their interactions with deinking solution, and thus the increase of organic pollution in the terms of TOC and COD.

Results showed that biodegradation of the thermochromic inks are dependent upon the penetration of ink binder into the structure of printing substrate. Thermochromic offset ink – paper interactions play an important role in the papers and prints biodegradation. In order to achieve the best adhesion properties, the paper should have surface free energy somewhat similar to ink, with optimum proportion of dispersive and polar forces. From the obtained results, it can be concluded that biodegradation of prints depends upon the adhesion, *i.e.* lower adhesion will result in reduction of biodegradation rate, while the strong adhesion will result in better paper degradation. During ink setting onto the paper, reactions between them will form different prints properties due to different affinity of paper for ink. In addition, the interactions between paper and ink as well as orientation of the molecules on the surface of the prints will affect the biodegradation. When the ink is applied on paper, the polar constituents of paper will react with polar constituents of ink. Smaller amount of polar components of paper will give a print with polar character. Thus, the paper surface participates in the organization and orientation of the molecules on the surface of the print. The optimum adhesion will influence the whole print (paper and ink) biodegradation.

Comparing the obtained prints, on non-absorbent paper the microcapsules are covered with thicker layer of binder making them more stable to biodegradation. In the case of absorbent papers, the binder and the microcapsules penetrate into the paper structure; the microcapsules on surface are covered with thinner layer of binder making them more susceptible to biodegradation.

Comparing the results of thermochromic inks biodegradation, it can be concluded that ink vehicle in offset ink (vegetable oil + resin) is more stable than the polymer resin present in UV curable screen printing thermochromic ink. SEM micrographs indicated a notably higher stability of offset ink binder and accordingly lower deformation of the microcapsules.

According to the obtained results, it may be concluded that organic recycling is better option for thermochromic prints disposal.

The scientific contribution of the proposed research was manifested through:

- Determination of optimal adhesion parameters between thermochromic ink and defining their role in material and organic recycling,
- Better understanding of thermochromic printing ink biodegradation mechanisms,
- Establishing more reliable and efficient methods of prints disposal, based on the results obtained.

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CURRICULUM VITAE

Marina Vukoje was born on December 21st 1987 in Slavonski Brod. She graduated in 2006 from Matija Mesić High School in Slavonski Brod with excellent success. In the same year, she enrolled in the study course of Environmental Engineering at the Faculty of Chemical Engineering and Technology. In 2009 she has completed undergraduate studies and in 2011 she completed a graduate study at the Faculty of Chemical Engineering and Technology, study course of Environmental Engineering with the thesis title "*Optimization of the preparation and characterization of biocatalysts for the oxido- reduction* ".

She worked as a senior environmental expert at the Department of Construction, Physical Planning and Environmental Protection of the City of Slavonski Brod from May 2012 until October 2012.

Since October 2012 she has been employed as an assistant at the Department of Environmental Protection, Faculty of Graphic Arts, University of Zagreb. In the same year she enrolled in the postgraduate study of graphic engineering and graphic design. She participates in teaching courses: Industry and the Environment, Environmental Science and Design, Design and Environment, Environmental Management Systems, Packaging and the Environment.

Since 1.10.2012. she has participated as a researcher on the scientific project "New Materials Formulation, Characteristics of Prints and Environmental Factors" (Project number 128-1281955-1953), under the supervision of assist. prof. Ivana Bolanča Mirković, PhD.

She has actively participated in the work of the European Cooperation in Science and Technology, COST Action FP 1003 "Impact of Renewable Materials in Packaging for Sustainability - Development of Renewable Fiber and Bio-Based Materials for New Packaging Applications. She is currently actively involved in the COST Action FP 1405 project "Active and intelligent fiber-based packaging - innovation and market introduction" as a MC Substitute Member.

In the year 2013 (07.09. - 29.09.) she completed scientific training at the Technical University of Dresden, Germany, Institute of Wood and Paper Technology, Professorship of Wood and Fibre Materials Technology, provided by the bilateral research project with the Germany "*Treatments of Fiber - based Materials for Improved Food Packaging*", under a supervision of assoc. prof. Branka Lozo, Ph.D.

In the year 2013 (11.12. - 13.12.) she completed scientific training at Grenoble INP PAGORA, France, within the international project COST FP 1003 BioMatPack (Winter Training School project - Use of nanopolysaccharides in packaging).

In the year 2014 (13.10. -15.10.) she completed scientific training at Packaging, Transport & Logistics Research Center (ITENE), Valencia, Spain, within the international project COST FP 1003 BioMatPack (Autumn Training School project - Innovation Management).

She participated as a researcher on "SuZ - Financial Support of Research:" Thermochromic inks, Light Stability (Molecular Changes) and Health Safety "(2014)," Organic Recycling of Recovered Paper and Packaging Waste "(2015)," The Influence of printing ink - paper Interactions on Classical and Organic Recycling "(2016), Modification of Convectional Graphic Materials by Nanoparticles and Chromogenic Materials (2017), and Modification of Conventional Graphic Materials by Nanoparticles and Chromogenic Materials and Their Health safety (2018) under the supervision of prof. Mirela Rožić, PhD.,

So far, she has published eight scientific papers in journals. Five of the published papers contain the results of her doctoral research. Ten scientific papers were published in internationally – reviewed conference proceedings. She also published three professional papers. All published scientific and professional papers are listed in Croatian National Bibliography under the number of scientists 337223.

LIST OF PUBLISHED SCIENTIFIC RESEARCH

Journal articles and review papers in CC journals

Jamnicki Hanzer, Sonja; Rožić, Mirela; **Vukoje, Marina**; Jukić, Mirela; Galić, Antonija Safety Evaluation of Deinked Pulp Containing Offset Thermochromic Inks. // BioResources, 13 (2018), 1; 678-690. doi:10.15376/biores.13.1.678-690 (international peer review, article, scholarly)

Bota, Josip; **Vukoje, Marina**; Brozović, Maja; Hrnjak-Murgić, Zlata Reduced water permeability of biodegradable PCL nanocomposite coated paperboard packaging. // Chemical and biochemical engeenering quartely, 31 (2017), 4; 417-424. doi:10.15255/CABEQ.2017.1126 (international peer review, article, scholarly)

Vukoje, Marina; Rožić, Mirela; Miljanić, Snežana; Pasanec Preprotić, Suzana Biodegradation of thermochromic offset prints. // Nordic pulp & paper research journal, 32 (2017), 2; 289-298. doi:10.3183/NPPRJ-2017-32-02-p289-298 (international peer review, article, scholarly)

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Rožić, Mirela; **Vukoje, Marina**; Kulčar, Rahela; Žužić, Ana Colorimetric properties of reversible thermochromic ink on different papers. // Proceedings of 8th international symposium on graphic engineering and design / Pavlović, Živko (ed.). Novi Sad: Grafički centar GRID, 2016. pp. 217-223 (lecture, international peer review, full paper, professional)

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Mikulić, Iva; **Vukoje, Marina** Continuous process for production of cellulose pulp from grass-like feedstock Miscanthus giganteus. // EFPRO - CEPI New ideas for the paper industry - Young researchers seminar Brussels: EFPRO - CEPI, 2014. (lecture, international peer review, pp slides, scholarly)

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APPENDICES

List of Publications summarized in the thesis

PRINTING INKS AND RECOVERY OF PAPER FOR RECYCLING - A REVIEW

(Subbmited to Cellulose Chemistry and Technology. It is under revision)

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Abstract

This review outlines the influence of printing inks on the efficiency of recovery processes of paper for recycling. Production of recycled fibres using conventional chemical flotation deinking process is the most used method worldwide and therefore, the most described. Poor deinkability of different prints can be overcome by using enzymes, ultrasound, and adsorbents in deinking methods, but their applications in paper recycling facilities are still limited. The poor deinkability of printing inks and their residuals in recycled pulp can cause problems related to health safety due to presence of toxic components. Collected paper for recycling is sometimes contaminated with food or it is wet, thus other methods are recommended, such as bioethanol production and organic recycling. In the last decade, paper for recycling is used for the production of cellulose derivatives. Energy recovery via pyrolysis, gasification and combustion are also recommended, but only in the case if the produced heat is used for other applications. However, in the literature, the influence of printing inks on the efficiency of these methods is poorly described. In order to choose the most effective waste management method, life cycle assessment (LCA) can be used, but in different studies, the main drawback is missing the information related to printing inks in paper for recycling.

Key words: paper for recycling, printing inks, material and organic recycling, recycled fibres, bioethanol, cellulose derivatives, energy recovery, life cycle assessment

1. Introduction

Municipal solid waste (MSW) is the most complex solid waste stream, consisted of food residues, paper and board, plastics and other components. Paper and board, altogether with kitchen waste, are one of the most common materials in municipal solid waste and waste material fraction with the highest recycling rates. In 2016, 72.5% of all paper consumed in Europe was recycled.[1] Recovered paper is today the most important raw material for the production of paper, paperboard and corrugated board. The packaging sector's production continued to increase whilst graphic paper (newsprint, printing and writing paper) maintained its recent decline. CEPI members produced 90.9 million tonnes of paper and board in 2016, while the utilisation of paper and board was 47.8 million tonnes, and the utilisation rate was 52.6%.[1] Not all paper is recycled in the same amounts: corrugated and kraft grades, as well as newspapers and magazines, constitute more than 70% of all the recovered paper in Europe (*Table* 1). Most of the paper based products mostly have a life span of a few days (*e.g.* newspapers) or a few weeks (*e.g.* packaging). Paper waste is not only discarded newspapers, office papers and packaging paper waste, but also production waste from the paper industry. Different processes in the pulp and paper industry (pulping, deinking unit operations and wastewater treatment) result in the formation of solid wastes and sludge. Their amount and composition depends mostly on the produced paper grades, used raw materials, applied process techniques and the paper properties which have to be fulfilled.[2] Generated paper mill and recycling sludge contains mainly short fibres, coatings, fillers such as kaolin, talc, calcium carbonate and clays that are added to improve finished properties of the paper product, additionally there are ink particles, extractive substances and de-inking additives.[3] Paper for recycling is mostly used as a raw material by the paper industry for the production of recycled paper and cardboard products. Sometimes, the quality of recycled paper is far poorer than that made from virgin pulps due to a shortening of the fibre length and reduction in tensile strength [4] but also the recycled pulp sometimes contains toxic substances originating from printing inks which are undesirable for health safety reasons.[5] The utilization of paper for recycling for production of valuable added materials such as bioethanol, different cellulose derivatives, biogas and eco-compositesis increasing all over the world in recent years and can provide an alternative to paper recycling and it may possibly address this issues arising from paper recycling.[6, 7]

Collected paper for recycling that needs to be recycled in some of the proposed ways is usually not clean and very often contains different impurities such as printing inks, coatings, or even residues of food when it comes to food packaging. Therefore, the aim of this paper is to provide an overview of the influence of the most significant paper for recycling components, printing inks, on the efficiency of paper for recycling management methods.

Table 1 CEPI Paper &Board Production and Consumption, Utilisation of Paper for Recycling by Sector in 2016 [1]

‘000 Tonnes			Grades of Paper for Recycling				Total use of paper for recycling	Utilisation by Sector %	Utilisation Rate %
Paper grades	Production	Consumption	Mixed	Corrugated and Kraft	Newspapers and Magazines	Other grades			
Newsprint	6.549	5.999	22	0	5.732	131	5.885	12.3	89.9
Other graphic papers	27.360	20.849	129	27	2.986	667	3.809	8.0	13.9
Total Graphic papers	33.909	26.849	151	27	8.719	797	9.694	20.3	28.6
Total Packaging Papers	45.671	39.802	8.351	22.541	492	2.248	33.632	70.4	73.6
Sanitary and Household	7.301	7.033	269	126	535	1.882	2.813	5.9	38.5
Other Paper and Board	4.050	3.716	245	1.044	190	132	1.611	3.4	39.8

2. Composition and quality of paper for recycling

Paper and paper products are made primarily of mechanical and/or chemical wood pulp, recycled fibres, non-fibrous components (minerals and additives) and water.[8] Fibres are made of cellulose, hemicellulose and lignin. Additives and fillers guarantee the particular use properties of the papers. Many papers are coated to improve the surface properties or partly varnished. As presented in the *Table 2,* different paper products will have different composition. Office paper contains lower amounts of lignin, compared too other types. Higher concentrations of metals (Al, As, Ca, Cd, Cr, Cu, Hg, Pb, Sb, Sn, Nd) in paper and cardboard waste may originate from printing inks and coatings [9–11], while C, H and Al originate from materials included in cardboard and paper composites (plastic and aluminium layers). The highest ash contents can be found in magazines, advertisement, and books that can be associated with higher Ca contents due to fillers (calcium carbonate and kaolin) in these fractions.

Table 2 Composition of paper for recycling

Sample*	**% (w/w) cellulose**	**% (w/w) hemicellulose**	**% (w/w) lignin**	**% (w/w) kaolin/calcium carbonate (ash)**	**Reference**
Copy paper	46	11.9	1	33	[12]
Office paper	84.9	12.3	1.4	1.4	[13]
Coated paper	42.3	9.4	15	-	[14]
Newspaper	48.5	9	23.9	-	[14]
Newspaper	41.02	24.85	23.07	5.99	[15]
Newspaper	68.5	13.1	23.4	3.9	[13]
Cardboard	56.9	10.7	17.8	12.8	[13]

**name given by the author*

Paper for recycling can also contain different materials such as staples, laminated covers, plastic wrapping, inks, thick adhesive layers, *etc.*.[16] In general, the printing inks are the most important non-fibres components that can be found in or be the part of paper for recycling. In addition to printing inks, lacquers or overprint varnishes, which are uncoloured forms of printing inks, used to give added gloss and protective properties to the print and substrate can be also found as non-paper components.[17] Paper based packaging contaminated with food is not desirable in paper recycling facilities due to cleaning difficulties, which leads to contamination issues.[18]

The quality of paper for recycling largely depends upon collection system, which is the first step in the recycling process, society's environmental awareness, sorting activities, the price for recovered paper and the impacts of printing and converting techniques.[19, 20] Besides these factors, the utilization of paper for recycling in the paper industry is affected by its price, processing costs, availability, the production of poorly recyclable products (influence of printing inks and adhesives) and lack of legislation and regulations.[19] The increased recycling rate and the use of commingled collection systems has reduced the quality of the collected paper and produced recycled paper.[21, 22] Increased use of non-fibre components can lead to increased difficulties in the later stages of the recycling processing chain.[8] During its lifecycle, paper is in contact with different materials, which results in numerus impurities, thus solid particles, moisture and dissolved substances can migrate from one waste material to another, which can have an enormous effect on material recycling. [23, 24] For example, the presence of Si, Ti, nutrients and halogens (N, S, Ca, K, Na, P, Cl and F) most likely originate from absorbed food scraps and dust.[24]

2.1. Printing inks

Printing inks are coloured complex mixtures, whose main task is to convey a message, provide protection and to give a decorative effect to the substrate to which they are applied. Mostly they are consisted of colorant (pigment or dyes), binder (resins, oils or solvents), solvent (oil or water-based) and additives (chelating agents, anti-oxidants, surfactants, biocides, etc.). Pigments are dispersed solids, insoluble in the support material and almost exclusively used in printing processes. Compared to pigments, dyes are soluble and have lower lightfastness and lower resistance to water. Resins used in printing inks contribute to the properties of hardness, gloss, adhesion and flexibility in an ink.[17] Mostly, resins or polymers are used as binders (phenolic resins, alkyd resins or synthetic resins (polyacrylates)). The ink binder is responsible for ink properties such as viscosity, drying properties, and surface energy.[25] Oils in printing inks may be drying, semi-drying or non-drying. Drying vegetable oils are glycerides or triglycerides of fatty acids, varying from those that are completely saturated (no double bonds) to those that contain three or more double bonds. Mineral oil in various forms is used as a binder in printing inks or as a solvent or diluent in the manufacture of ink binders. They consist of varying percentages of aromatic, naphthenic and paraffinic hydrocarbons, with a small sulphur content ranging up to 4%.[17] Solvents dissolve the binders and adjust the viscosity of the ink for the different printing processes. [26] Additives are used to improve the ink properties and they are added in ink formulations in amounts not exceeding 5%. These compounds include surfactants to reduce the surface tension and thereby the wetting problem. Adhesion promoters or wetting agents enhance the binding to the printing stock and biocides prevent microbiological degradation of the ink.[26] The main function of a plasticizer (expoxidized compounds, phthalates, polyesters, benzoates) is to make the dried ink flexible and driers help with the oxidative drying process and help to supply elasticity to an ink film. Driers are catalysts used to promote oxidation of the drying oils (inorganic salts and metallic soaps of organic acids). After application of printing ink onto the substrate, the binder dries and binds the colorant to the substrate under the press running conditions.[17] Ink drying can be achieved by physical and chemical means or a combination of both, depending by the chemical composition of printing inks.[17] Printing inks are formulated for individual printing processes, classic (offset, flexographic, screen, gravure) and digital (electrophotography, ink jet, laser). They must have certain rheological properties in order to be transferred to the printing plate and afterword from printing plate to the substrate (paper).

2.2. Paper – ink interactions

One of the main functions of printing inks is to adhere on the printing substrate and remain there for the whole lifespan of print. Adhesion of inks to paper plays an important role in many industrial applications and it can be characterized indirectly through thermodynamic analysis of the paper substrate, or directly through paper laminate or adhesion tape peel testing. [27, 28] The bond strength between the paper surface and polymer depends strongly on the physical and chemical structure of the two surfaces which are in contact. For example, the polymer polarity created by the carboxyl content of adhering polymers, would affect the adhesion strength of the cellulose-polymer bond, where peel strength increases when the carboxyl content increases. Also, the influence of critical surface free energy of paper and ink can have significant influence. Papers having critical surface free energies below that of inks can show the poor adhesion compared to those having critical surface free energies in excess of inks. Pure cellulose shows relatively high values (44-60 mN/m) of the critical surface free energy, while the values for lignin-containing and sized paper are lower. [27] Adhesion can be affected by inks formulation, *i.e.* upon colorants, solvents and vehicles. The influent of colourants on ink adhesion mostly depends upon their compatibility with the vehicle system, their type, percentage and degree of dispersion in the final ink. Adhesion is influenced by the degree of vehicle penetration on paper while for non-absorbent substrates, is controlled by the film-forming ability of the resin and the molecular affinity for the substrate. Adhesion of printing ink can be affected by solvents in two different ways, enchaining wettability and increasing penetration. Improvement of wetting is essential for good adhesion and flow-out of ink in order to give a continuous film. Improvement of ink penetration into the substrate can assist physical and chemical bonding. Adhesion can also be affected by adding additives in small amounts during manufacturing process in order to improve chemical bonding between printing substrate and ink. [17]

Borch (1991) and Forsström et al. (2005) explained that mechanisms controlling the adhesion between inks and printing substrate are:

- Thermodynamic characteristic. Surface energy has a central role as the wetting of cellulose by the ink is important for the final ink–cellulose interaction. Wetting is controlled by dispersion and polar interactions between paper and ink.
- Molecular contact area - surface topography (paper roughness). In electrophotography and thermal printing, decrease in toner adhesion occurs for rougher papers and similar behaviour is described for polymer coatings at low coating levels. The contact area governs interdiffusion and entanglement between the constituents of the ink with the amorphous part of the cellulose.
- Fusing temperature, time and pressure.

Surface interactions between printing ink and cellulose are of importance during printing, as well as during ink removal in paper recycling as a high adhesion between ink and cellulose might cause problems during ink detachment. [29] Surface energy studies can explain deinking effectiveness and fact that different compositions of printing inks may cause different problems due to differences in surface chemistry and mechanical dispersion properties [30]. For example, Vukoje et al. (2016a) explained the poor deinkability of thermochromic offset prints due to creation of very strong bonds resulting in high adhesion.[31] When it comes to adsorption deinking, the surface free energy of inks, paper and polymers used as adsorbents, structure and specific surface area of adsorbents can explain the ink detachment and recycling effectiveness. [32]

3. Paper for recycling and waste management methods

Reducing the amount of all kinds of produced waste streams has been presented through European laws, either by prevention, reusing or recycling. [33, 34] In order to improve recovery of waste, it should be collected separately if technically, environmentally and economically practicable and it should not be mixed with other waste or materials with different properties. In addition, member states should take measures to promote high quality recycling and set up separate collections of waste. Collecting of paper for recycling is very high in Europe, according to CEPI it was 56.406 million tonnes in 2016.[1]

Different waste management options for paper for recycling have been studied worldwide, due to different issues occurring. For example, poor deinkability of prints, contamination issues related to food, high moisture content of collected paper, *etc*. Despite the large percentage of use paper for recycling for production of recycled paper and board, different authors give various proposals, from incineration, production of bioethanol to biodegradation in aerobic and anaerobic environment. According to European law, waste management should be followed as presented at *Fig 1*. The most important is to prevent and to reduce the amount of all kinds of waste.[34] But, if the waste is produced, than it should be recycled (by means of material or organic recycling) or used for energy production.

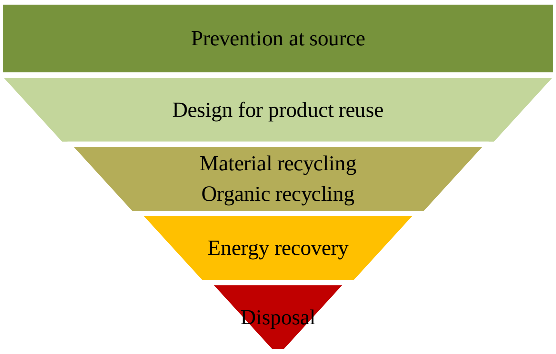

Fig. 1 Waste management hierarchy [35]

3.1. Material recycling

Recovery of paper for recycling from municipal solid waste is useful since it can be used for production of different valuable products. Production of recycled paper uses less energy (28-70% energy savings), reduces carbon dioxide emission, the volume and loading of effluent, compared to paper produced from virgin fibres.[20] Paper for recycling and paper industrial residues containing high cellulose content are also proved to be a promising source of low-cost, raw material for different cellulose derivatives production, as well as for other high value-added bio-conversion processes [36], such as ethanol [15, 37–42] and methane [13, 43]. Pendyala et al. (2013), Argun and Onaran (2016), Eker and Sarp (2017) have studied the potential of paper for recycling for hydrogen production, but they didn't describe the influence of prints on hydrogen yield production.[44–46]

3.1.1. Production of recycled fibres by deinking

Deinking is the most important process in the production of recycled paper and depends upon the quality of the collected paper for recycling, the type of printing process and properties of the printing inks, age of product and climatic conditions during its life cycle.[47–50] In order to achieve desirable properties of recycled pulp (optical and mechanical), improved deinkability of printed paper products has become essential and one of the most important key factors for a potential use of recovered paper in graphic papers production. Moreover, deinkability of packaging grades is of an importance lately due to the growing tendency to print certain products such as cardboard.[51] When the printing ink colloidal dissolves in the water and colours the entire pulp, a serious problem occurs in the case of graphic paper production, but it's not significant for brown paper production.[52] Packaging paper grades and mixed grades are commonly recycled without deinking and the main task is to disintegrate the packaging board into palpable suspension. Deinking process is common practice for graphic paper grades, except some high quality grades with little or no ink.[16] Recently the amount of paper based packaging products overcomes that of graphic products in the collection system. Mostly, corrugated boxes and folding boxboards have the largest share among paper based product categories and are normally quite easy to recycle in standard paper mills.[53] Researchers suggest that brown packaging, corrugated and paper boards should be collected separately and recycled separately from graphic paper grades due to unsatisfied recycled pulp properties. Iosip *et al.* (2010) showed that packaging paper and board from household collection, strongly affects the optical properties of deinked pulp, by decreasing brightness and by increasing the number and size of specks due to brown fibre flakes.[54]

Different deinking processes can be used for the production of recycled fibres, based on the quality of paper for recycling and desired quality and requirements of the produced pulp. The most common methods for ink removal use chemical approach, thus the proper selection of deinking chemicals is often a compromise between costs and performance.[55, 56]

Deinking by Flotation

Currently industrial processes dealing with paper recycling are mostly dealing with washing and flotation. Washing is most effective for removing small particles (<10 µm), flotation for the medium-sized particles (10–150 µm) range. Screening and centrifugal cleaners are used for removal of large ink particles (>100 µm).[56] Washing is used for removal of particles smaller than the mesh size of a filter cloth, mostly of fillers and coating particles, fines, microstickies and ink.[52]

Deinking by flotation is the most common practice for ink removal in paper recycling process, in which hydrophobic ink particles are removed from pulp suspension by adhesion to air bubbles, forming a froth, which can be separated from the pulp suspension. The efficiency of the deinking process depends on several factors such as fibre and ink properties (pigment size and type of solvent used), printing conditions, bubble size, collectors and calcium soaps formed from calcium ions and fatty acids and paper surface properties.[57, 58] For example, inks printed on coated paper surfaces detach more easily than inks printed directly on uncoated paper surfaces.[58]

The paper mills that produce recycled paper or cardboard have abundant cleaning systems (sorting machines and for graphic papers deinking systems). After defibrating, the suspension passes through several successive cleaning systems in which impurities are separated by their density, size or shape.[23] Recycling plants mostly can handle a certain amount of unwanted non-paper components but if the amount gets too high, the recycling process can become less economical. However, paper for recycling, which usually comes with different types of applied prints, will not always show positive deinkability tests (*Table 3*). Deinking by flotation is efficient mostly in the case of conventional offset and gravure printing inks where hydrophobic printing inks are present.[48, 52] According to Faul (2010), 81% of the offset prints, mostly newspapers and magazines, achieved a positive assessment of their deinkability, while the latter often occurs in the case of UV-cured prints.[16] Digital printing inks or water-soluble inks cannot be deinked, or only with great difficulty. Toner prints are usually well deinkable, if made by a dry toner process, but in the case of liquid toner prints the test fail, due to very high content of dirt particles in the deinked pulp.[59] Water-based flexographic inks present a particular problem to the de-inking process due to their small particle size (0.2-1.0 μm) after re-pulping, and they are too small for removal by flotation. In addition, these inks are hydrophilic and cannot be agglomerated. For the successfully removal of flexographic inks, recycling processes therefore incorporate aggressive washing stages which can lead to economically unacceptable yield losses.[30, 60]

Table 3 Deinkability of prints

Prints	Deinkability	Nature of ink particles	Problems	Reference
Offset	Good	Hydrophobic	After aging, bad ink detachment	[16, 48]
Gravure	Good	Hydrophobic	-	[16]
Flexographic	Poor	Hydrophilic	Small and hydrophilic nature of the ink particles which can't attach to the collectors in the flotation process	[16, 52]
Digital	Poor	Hydrophilic	Generating numerous ink particles above 100 µm	[48]
Inkjet	Poor	Hydrophilic	Ink may stain the fibre, formation of small particles	[30, 61, 62]
Hot melt based ink jet prints	Poor	Fused during drying – residual toner	Sticky deposits	[63]
Toner	Poor	Fused during printing	Formation of larger particles, flat and plate like particles	[30, 47]
Liquid toner	Poor	Too soft to pass the screens	Large visible inked film specks	[63]
UV curable	Poor	Formation of cross-linked films which are difficult to break down	Visible speck contamination by large flat and plate like particles	[30]

Also, deinkability problems can be noticed for UV curable coating due to visible speck contamination and for water based dye based prints due to low brightness or/and pronounced colour shade.[63] During digital printing (photocopy and laser-printing) toner particles are exposed to heat (200ºC), light and oxygen which results in the ink fusing with the paper and making it non-dispersible.[60, 64] During printing, the ink particles undergo the process of polymerization and oxidation with subsequent formation of peroxide bonds, resulting in strong chemical and physical bonding with cellulose fibres. During flotation deinking, these thermally fused ink particles and cellulose fibres will lead to formation of larger ink particle sizes resulting in poor deinkability. Besides polymerization, oxidation will create a greater polarity at the toner particle surface which can reduce the deinking efficiency.[47] Balea *et al.* (2017) showed that improvement in the removal of water based inks can be achieved by addition of cellulose nanofibers in combination with a cationic polyacrylamide.[65]

Deinking efficiency is also affected by the influence of light, temperature, moisture and storage time.[49, 50] The age of printed products mainly affects offset prints.[16] Pan and Nguyen (2007) showed that in the early stage after printing of offset ink, it is more difficult to detach mineral oil based ink than vegetable oil based ink but after thermal ageing the energy required for ink detachment is similar for both types of ink.[66]

In addition to conventional printing inks that have been used so far, development of new materials have increased and can affect the efficiency of recycling, regardless to the printing process which they have been made for. Small variations in their chemistry can affect their quality, printing quality as well their deinkability aspects. As the ink formulation is an essential factor in deinking, it is crucial to examine deinkability aspects of novel printing inks, which may differ from conventional inks in formulation, and size of colorants or additives. For example, information about the recycling of functional inks and smart printing inks is very limited. Aliaga et al., (2015) reported about the effects of the printed electronics on the paper recyclability. The analysis was based on a case study focussed on envelopes for postal and courier services provided with these intelligent systems. According to the results of the pilot scale recycling tests, the resistors (silicon-based electronic component) do not disintegrate in the pulping stage and they are retained in the screens and thus do not affect the quality of recycled paper. The results showed that nanosilver inks were dissolved in the pulp suspension and can affect both mechanical and optical properties of the recycled paper. In addition, the authors have emphasized that real impacts on industrial recycling are expected to be even significantly lower since the proportion of paper product with printed circuits in the current paper waste streams are much lower. However, they also point to the fact that further research on the treatment of printed electronics and smart labels is needed in parallel with innovation in these communicative devices.[67] The study of thermochromic offset printing inks showed they are very difficult to deink by flotation process which is successful method for conventional offset printing inks.[31] Some problems in recycling can be avoided by using enzymes or new methods for ink removal, such as ultrasound and adsorption deinking.

Enzymatic deinking

Enzymatic deinking have a valuable approach because of its high efficiency and environmental friendly nature.[68] Enzyme treatment can improve the physical properties of handsheets, decreases pollution of effluents, thus contributing to reduction of environmental pollution and lowering the waste water treatment cost.[69] According to Singh *et al.* (2012) the use of chemicals can be reduced to 50% to attain the same extent of brightness, whiteness by combination of enzymatic deinking and conventional deinking process.[69]

Cellulase, hemicellulase (*e.g.* xylanase), pectinase, lipase, laccase, *etc.*, are the enzymes employed in the deinking processes. Hemicellulase and cellulase can attack the components on the fibre surface. Detachment of ink from fibres takes place when these enzymes alter the fibre surface by modification of chemical bonds. Hemicellulases can result in the hydrolysis of hemicelluloses; starch based coating can be hydrolysed by amylolytic enzymes, lipase can degrade vegetable oil based ink binders and lignin is removed by the laccases.[70] The use of different enzymes is reported in literature, presented in *Table 4*. Depending on the used printing ink, printing process and paper type the proper enzyme in the enzymatic deinking process should be chosen. By the use of enzymatic deinking the increase of the recycled pulp optical properties (brightness, whiteness, ERIC), reduction of ink particle size, improved drainage and better mechanical properties can be achieved. Conventional deinking methods are not effective for removal of nonimpact printed mixed office wastepaper (MOW) (xerox and laser) due to strong adherence of toner ink particles to fibres.[68] These problems can be overcome by use of enzymes. Enzymatic deinking in the case of flexographic inks can be influenced by the presence of paper additives, and the highest inhibition was reported for calcium carbonate.[71]

Table 4 The use of enzymes in deinking processes

Prints/paper substrate*	**Enzyme**	**Reference**
Mixed office wastepaper	Enzyme extract (endoxylanase and endoglucanase) from fungus *Aspergillus terreus* and *Trichoderma viride*	72
Mixed office wastepaper (laser, inkjet and photocopy prints, photocopy paper)	Commercial endoglucanase, cellulase and xylanase	73
Inkjet-printed paper	Isolate from *Vibrio alginolyticus* bacteria	64
Mixed office wastepaper	Commercial endoglucanase, cellulase and xylanase	74
Laser printed office waste papers	Cellulase and hemicellulase from *Aspergillus niger*	75
Fresh and aged recycled newsprint/magazines	Cellulase	76
Old newsprint	Commercial hemicellulase with laccase-mediator system	77
Laser printed paper	Bacterial xylanase from *Bacillus sp.*	78
School waste paper	Xylano-pectinolytic enzymes from *Bacillus pumilus*	69
Old newsprint, magazines, laser, inkjet and Xerox	Bacterial laccase and xylanase from *Bacillus halodurans*	79
Laser printed paper; old newspaper (flexographic); photocopy paper (photocopy dry toner); glossy magazine paper ; bubble jet-printed waste paper	Commercial cellulase and hemicellulase	55
Photocopier waste papers (Xerox Black Toner)	cellulase and xylanase of newly isolated fungal strain *Trichoderma harzianum*	80
Flexographic inks	Fungal laccases from *Coriolopsis rigida and Myceliophthora thermophila,*	71
Laser printed paper	Lignocellulolytic enzyme from fungus *Penicillium*	81

	rolfsii	
Old newsprint	Cutinases from *Thermobifida fusca* and *Fusarium solani pisi*	82

**name given by the author*

Adsorption deinking

In adsorption deinking the ink particles are adsorbed on the surface of polymer blends (adsorbents) instead of air bubbles (in deinking flotation) at high stock consistencies of 15% and, at the same time, have a dispersing effect (ball mill effect); 90% less water needs to be pumped in the facility owing to the high stock consistency.[52] The efficiency of this method can be affected by concentration of calcium ions, used deinking chemicals, polymer blends used as adsorbents, used printing ink and paper [83]. Besides these factors, the efficiency of the method is affected by the surface free energy of inks, paper and used polymers, their structure and specific surface area.[32] Researchers have studied the possibility of using different polymers in adsorption deinking. Darwish *et al.* (2004) showed that polyethylene (PE) has a certain capability of removing toner particles while the wax-coated PE enhances the removal of toner particles beyond that obtained using only PE.[84] Liu *et al.* (2010) investigated the use of PET films in deinking of xerography wastepaper and obtained results showed that by choosing proper combinations of solvent, surfactant and toner can form viscous liquids that can be adsorbed on plastic films at ambient temperature and separated by a screen process.[85] Du *et al.* (2016) studied the potential of using chitosan as an adsorbent for removal of ink jet printing inks, which showed an increase of ISO brightness compared to standard deinking flotation procedure INGEDE method 11.[62] Petzold and Schwarz (2015) showed that efficiency of adsorption deinking is strongly influenced by the properties in suspension which depend on the type of paper.[86] Jamnicki *et al.* (2015) showed that adsorption deinking is more successful in the reduction of mineral oils in recycled pulp than the conventional flotation deinking method (INGEDE Method 11).[87] The main conclusion was that over 60% and up to 80% of mineral oils can be removed from paper for recycling by means of adsorption deinking.

Ultrasound deinking

Studies dealing with the ultrasonic deinking of paper for recycling mostly are related to the removal of digital print, which are not easily removed by conventional flotation methods. Ultrasound deinking uses cavitation to separate the printing ink particles from the fibres in high stock consistencies.[52] The cavitation occurs at frequencies between 20 and 100 kHz when ultrasound energy turns liquid into vapour at nucleating sites within the liquid. The produced bubbles grow in size before collapsing and releasing energy (implosion).[88] In the paper processing industry ultrasound can be used at different stages; enhancement of pulping, bleaching, depolymerisation of cellulose and treatment of wastepaper. The main advantage of using sonication resides in the fact that experiments can be carried out at ambient temperature under atmospheric pressure contrary to other advanced oxidation processes.[89] Tatsumi *et al.* (2000) also concluded that ultrasonic treatment can be effective for offset-printed newspaper and laser-printed office paper on commercially available paper for xerography, followed by conventional flotation.[90] The process, which consists of ultrasonic treatment for 1 min following flotation deinking, requires about 1.4 times as much energy as the conventional flotation deinking process, but it induced 20% improvement in brightness. Manning and Thompson (2004) have used high intensity ultrasound for removal of UV-curing screen printing ink. Exposure of pulps to high intensity ultrasound causes breakdown of the ink film under neutral pH conditions and detachment of significant proportion of UV cured ink particles from the pulp slurry.[88] According to Fricker *et al.* (2006) the ultrasound is effective in removal of indigo inks as well. It can remove almost 100 % of ink from pulp suspension because it causes the breakdown of ink particles into floatable sizes which can be successfully removed by flotation deinking.[91] The influence of temperature on an ultrasound-assisted ink removal process has been investigated by the Gaquere-Parker *et al.* (2009) and showed the effectiveness of ultrasound at any temperature tested (15–45 ºC), but brightness data and UV–vis absorbance indicated the optimum temperature was between 30 - 35 ºC.[89]

3.1.3. Toxity of effluents from paper recycling processes

Recycling paper mills produce effluents with different key pollutants than paper mills using virgin fibres (wood, agricultural residues). The processes of pulping and bleaching are the major sources of pollutants in paper industry effluents. [92] The type and quality of the raw material (wastepaper) used for recycling as well as pulping and deinking additives, mineral oils and other substances will affect the quality of effluents from paper recycling mills. [92]

Table 5 shows that different deinking processes (conducted in laboratory scale) and used raw materials (paper and prints obtained) will have different values of organic components in effluents. Current deinking processes depend upon the use of large amount of chemicals that produce toxic effluents and high chemical oxygen demand (COD) values. [69] In general, the most common used alkaline systems generate heavily loaded process water and thus neutral deinking could be better solution.[48] Sometimes, surfactants applied in neutral deinking may contribute to the increase of chemical oxygen demand (BOD) and COD values.[93] Enzyme deinking generally decreases the BOD and COD values of effluents, thus lowers the effluents treatment cost and environmental pollution. [68, 69, 94] However, in some cases the COD release appeared to be higher with the enzymatic treatments. This behaviour was described by the Magnin *et al.* (2002) during enzymatic deinking of mixed woodfree paper (offset, laser and copy) due to the hydrolytic property of the enzymes since they release soluble sugars from the pulp to the process water resulting in higher COD.[70] The COD of the pulp slurry effluent of the offset print is lower than that of the industrial newsprint/magazine furnish since the industrial raw material contain more soluble and colloidal contaminants than the offset print. [95]

Table 5 Organic pollution of effluents from paper recycling effluents generated in laboratory scale due to different deinking processes and samples used

Sample	Deinking process	Parameter		Reference
		COD / (mg/L)	BOD / (mg/L)	
Offset	Chemical - Alkaline	2650	-	48
Digital		4950	-	
Flexographic		2150	-	
Flexographic	Chemical - Neutral	1309	-	48
School wastepaper with blue ink	Chemical - Alkaline	3750	1136	69
	Enzymatic - xylano-pectinolytic	1056	368	
Toner	Chemical - Alkaline	270	122	80
	Enzymatic - commercial	148	85	
	Enzymatic - isolated	168	99	
Offset	Chemical - Alkaline	779	-	95
Newspaper / magazine		921	-	
Mixed - flexographic toner and offset	Chemical - Alkaline	409	240	93
	Chemical - Neutral	479	310	

Since different studies show different values obtained for COD and BOD values, in order to get more reliable data, the index of biodegradability (IB) should always be calculated according to *Eq 1*.[80, 93]

$$IB = \frac{BOD}{COD} \cdot 100 \ [\%] \qquad [1]$$

where: IB - biodegradability, % ; BOD - biochemical oxygen demand, COD - chemical oxygen demand.

Due to very high concentrations of organic compounds and the presence of toxic compounds resistant to biodegradation, the IB index in paperboard recycling plant effluent is usually below 0.15, which suggests that these effluents are resistant to biological treatment.[96] According to Birjandi *et al.* (2016) samples with IB smaller than 0.3 are not appropriate for biological degradation, as for complete biodegradation the effluent must present an index of at least 0.40.[97] This means biological treatments, as a stand-alone treatments are usually an ineffective methods for treatment of such industrial effluents.[96]

When it comes to paper recycling plants, studies show that effluents contain complex matrices containing a variety of toxic compounds. [98, 99] in addition, recycling paper mills generate an effluents that contain high concentrations of organic compounds such as lignin, cellulose and resins. [96] The quality of synthetic effluents derived from laboratory paper recycling, which contains only a limited number of toxic organic compounds are entirely different from real pulp and paper effluent chemistry and behaviour, due to the combination of various chemicals, suspended particles, nutrients and bacteria present. [99] In addition, *Table 6* shows the physical-chemical characterization of real effluents from paper recycling mills. COD and BOD values are are significantly higher than values obtained for laboratory deinking processes (*Table 5*). According to Muhamad *et al.* (2015) the six most important wastewater quality parameters, namely, COD, turbidity, ammonia (expressed as NH_3-N), phosphorus (expressed as PO_4^{3}-P), colour, and SS should always be monitored. [99] Besides these parameters, authors also found the preseance of other compound in effluents such as sulfate [100], AOX, metal ions such as Al, Fe, Ca [101], Si and Na [102].

Different studies showed the presence of wide range of various organic contaminants in effluents from paper recycling factories, receiving rivers and sediments such as Bisphenol A (BPA) [92, 98, 103], 2,4,7,9-tetramethyl-5-decyne-4,7-diol (TMDD) [92, 104], aromatic sensitizers [105], aryl hydrocarbons including chlorinated aryl ether (1600 mg L^{-1} and 190 mg g^{-1}) [106] . Some of those constituents are related to paper and graphic industry, such as photoinitiators, ink and thermal paper constituents. For example, 2,4,7,9-Tetramethyl-5-decyne-4,7-diol (TMDD) is a non-ionic surfactant used in printing inks. Concentrations of TMDD were found to be present in wastewater from factories processing recycled paper from 113 µg/L [104] up to 1700 g/L [92]. The preseance of BPA was found to be around 3400 g/L, respectively. [92] The isolated aryl hydrocarbons and aryl ether as well as aromatic sensitizers are chemicals used in thermal papers.[105, 106] Some of these compounds may affect vertebrate physiological and reproductive functions.[107] For example, adsorbable organic halides (AOX) may bioaccumulate in fish tissue, causing a variety of carcinogenic, endocrine, clastogenic, and mutagenic effects, which may then pose problems to humans consuming the contaminated fish. [99] TMDD can be harmful to fish and aquatic invertebrates only at high concentrations. [104] Resin acids and to a smaller extent, the unsaturated fatty acids can be toxic to fish.[98] BPA and some surfactants commonly present in paper recycling mills, are considered as endocrine-disrupting compounds that at low concentrations may potentially alter the normal hormone function and physiological status of animals.[98]

Due to very high concentrations of recalcitrant organic compounds and resins, before being discharged into the environment the effluents must be treated before. [96] Thus, the effluents should satisfy compliance levels such as chemical oxygen demand (COD), biochemical oxygen demand, (BOD), suspended solids (SS), and colour and residual organic matter consisting of potentially toxic chlorinated compounds.[99] Sometimes the effluents contain soluble organics and particulate matter that are not effectively degraded by traditional wastewater treatment technologies. [108] In order to achieve desirable parameters, different treatment process have been proved to be an efficient and appropriate technique for reduction of organic loads and enhancement of biodegradability. For example, aerobic sequencing batch reactors with granular activated carbon[99, 109], bench scale horizontal-flow anaerobic immobilized biomass (HAIB) reactor[110], coagulation process[111], ultrafiltration[112], electrochemical peroxidation process[96] In addition, if the paper recycling mill involves recirculating waters, the presence of organic components can have impact on paper machine and product quality.[98]

Table 6 Physical-chemical characterization of real wastewater from paper recycling mills

COD / (mg/L)	BOD / (mg/L)	Sulfate / (mg/L)	Ammonia / (mg/L)	Phosphate / (mg/L)	SS / (mg/L)	Turbidity / (TNU)	Colour Pt - Co	AOX	Refrence
1057	-	-	4.1	0.03	149	73	121	-	[99]
4300	535	-	-	-	-	1308	-	-	[96]
7820	3963	79	-	-	-	-	-	-	[100]
3523	940	50	-	73	260	873	-	-	[111]
1152	-	-	-	-	-	-	-	249	[113]
1500	563	-	0.17	-	2138	-	1002	-	[114]
780 - 800	150 - 200	-	170-200	-	-	-	-	-	[115]

3.1.4. Health safety of recycled paper

Recycling is supported for the sustainable use of materials, but on the basis of present toxicological assessments is often far beyond acceptable.[116] Pivnenko *et al.* (2015) showed that quality of the collected paper for recycling may ultimately decrease as more and more ‘‘marginal’’ paper fractions are collected for recycling and the contents of harmful substances in paper thereby increase.[5] In addition, they showed that paper for recycling might potentially contain a large number of hazardous chemical substances, while many of them can be associated with the printing industry. If the printing inks are not entirely removed during paper recycling, the recycled pulp and the product made of it may contain residues.[5, 117] Paper and cardboard, partly or fully produced from recycled fibres can be used in contact with dry foodstuff like flour, grain, sugar, salt, rice and pasta and as such must meet certain basic set of criteria concerning safety issues.

Different authors have studied the contaminants in recycled fibres, mineral oils hydrocarbons, phenols, phthalates, polychlorinated biphenyls, bisphenol A and toxic metals. [5, 117–121] In study of recycled paper containing thermochromic offset inks, Jamnicki Hanzer *et al.* (2018) showed the presence of Bisphenol A originating from thermochromic inks.[122] Vápenka *et al.* (2016) showed the preseance of 68 contaminants in packaging materials originating from paper pulp processing residues, printing inks or adhesives (photoinitiators, plasticizers, solvents), impregnation and coating (solvents, hydrocarbons).[123] Mertoglu-Elmas (2017) showed that coloured pigments are sources of heavy metals (Pb, Cd, Zn, and Cu) in recycled paper.[10] Most of the contaminants in paper packaging materials originated from materials used for modification of functional properties and/or residues from recycled pulp. Since recycled cardboard is made by disintegration of different materials mixture (newspaper, journals and cardboard) without ink removal, recycled pulp can contain mineral oil saturated hydrocarbons (MOSH) and mineral oil aromatic hydrocarbons (MOAH) mostly originating from printing inks in newspapers.[116] The mineral oil content could be reduced through the selection of the paper and board fed into the recycling process, by replacement of mineral oil containing inks with inks free of mineral oil (flexographic, digital, UV curing inks) and enable efficient deinking at the same time.[124]

3.1.5. Bioethanol production

Bioethanol derived from lignocellulosic biomass is a valuable renewable energy source recently used as a substitute for fossil fuels in road transport. Paper for recycling has relatively high carbohydrate content up to 80%, and a higher amount of cellulose than other lignocellulosic materials, which gives them considerable potential as feedstocks for bioethanol production.[37, 41] It has been estimated that an annual yield of 82.9 billion litres of cellulosic bioethanol could be derived from paper for recycling worldwide, replacing 5.36% of gasoline consumption with GHG emissions savings up to 86%.[37] Bioethanol production from paper consist of hydrolysis and fermentation. Steps can be accomplished in two stages (separate hydrolysis and fermentation—SHF) or in a single stage simultaneous saccharification and fermentation—SSF).[125] An enzymatic hydrolysis of paper for recycling is becoming a perspective way to obtain raw material for production of liquid biofuels, as presented by different authors. [37, 42, 126, 39, 127, 128] Besides paper for recycling, a sludge from pulp and paper production can also be useful for bioethanol production.[125, 129–131] The presence of printing inks, fillers and other additives make enzyme hydrolysis into fermentable sugars difficult, due to ineffective adsorption of enzyme to substrate due to possible binding of a proportion of the enzymes to impurities in the substrate (ink particles and paper fillers) or binding with lignin.[37, 132] According to Wang *et al.* (2012) enzyme activity is more affected by product inhibition (high lignin and glucose content) rather than ineffective adsorption caused by impurities such as fillers or inks.[37] Calcium carbonate inhibits cellulase activity remarkably as presented by Wang *et al.* (2011), Min and Ramarao (2017) and Schroeder *et al.* (2015).[125, 133, 134] According to Schroeder *et al.* (2015), enzyme activity also can be influenced by aluminium and silicon originating from the fillers used in the paper making process and metals from the printing inks.[125] Despite the fact that printing inks can inhibit enzyme reactions, and thus decrease the efficiency of bioethanol production, in the presented literature the influence of printing inks on the efficiency of bioethanol production is not taken into account. Only the Guerfali *et al.* (2015) have reported the importance of washing pretreatment process of paper for recycling in order to remove printing inks.[126] Enzyme inhibition problems can be avoided by using different pretreatment methods, such as ethylene glycol pretreatment, ultrasound in fermentation process, delignification alkali (NaOH) and enzymatic (ligninolytic) pretreatments of waste newspaper, or use of accelerants and hydrogen peroxide during the paper mill sludge conversion.[15, 130, 132, 135] Although the literature references mentions possible inhibition of enzyme activity by the various substances that may originate from the printing inks, there is no available information on how certain printing inks (*e.g.* offset, flexographic, UV curable, non-impact printing inks) affect the efficiency of bioethanol production from paper for recycling.

3.1.6. Production of Cellulose derivatives

Due to higher cost of recycled paper production and its lower quality, a number of studies have been conducted in order to find an alternative option for utilization of paper for recycling including, cellulose micro and nanocrystals, cyanoethyl and carboxymethyl cellulose synthesis and biocompatible cellulose aerogels as presented in *Table 7*. The quality of raw material used for production of cellulose derivatives can remarkably influence the quality of products and process yield.[136] The presence of residual ink, hemicellulose and lignin in paper for recycling are highly undesirable when it's used for production of cellulose derivatives, and thus these compounds should be removed.[6] According to literature presented in *Table 7*, pretreatment methods and deinking by flotation may ensure the removal of undesirable amorphous-type polymer components. Moreover, alkali treatment can disrupt hydrogen bonding in the network structure between different cellulose chains, improving the effectiveness of subsequent treatments like an acid hydrolysis process.[6, 137] With the inclusion of pretreatment process before acid hydrolysis, an increment in quality can be achieved, favouring the access of acid to cellulose. The main drawback of pretreatment methods is high chemical and energy consumption resulting in costs increases and the low process yield because of the high pretreatment losses.[136] Paper for recycling is an attractive potential feedstock for production of valuable cellulose derivatives and its utilization could decrease demand of competitive and conventional raw materials like cotton fibres and wood pulp for modified cellulosic products.[7] Despite the fact that authors emphasize the importance of printing inks removal from paper for recycling stream, in order to get higher efficiency of cellulose derivatives production, there is lack of information in the presented literature regarding to ink removal during conducted pretreatment methods and deinking. Also, most of studies are dealing with mixed office paper for recycling printed with non-impact printing technologies, which is generally known to be difficult to deink by conventional deinking by flotation. In addition, there is no present information about the influence of other printing inks on the efficiency of cellulose derivatives production. Due to different chemical formulations of printing inks, we suggest that in the future also some other printing inks and printing techniques should be taken into account when production of different cellulose derivatives from paper for recycling is studied.

Table 7 Production of cellulose derivatives from paper for recycling

Product	**Source***	**Pretreatment**	**Reference**
Rod-like cellulose nanofibers	Waste newspaper	Alkaline treatment and bleaching	138
Cellulose nanocrystals	Recycled pulp (1% lignin) produced from waste commercial wood pulp and used business papers	-	139
Cellulose nanocrystals	Wastepaper	Alkali and bleaching treatments	140
Cellulose nanocrystals	Old corrugated container fibre	Mechanical (pulping) and alkali pretreatment	141
Nanocrystalline cellulose (NCC)	Non-printed areas of recycled newspaper	Alkaline treatment and bleaching	142
Cellulose nanocrystals	Office waste paper (OWP)	Deinking and defibering by use of	4

		chemical agents and mechanical forces, proceeded by washing through a fine-mesh	
Cellulose Nanostructures	Primary paper residue	Mercerization followed by bleaching.	36
Cellulose Nanocrystals	Old newspapers and recycled newsprints	With and without alkali and bleaching treatments	136
Microcrystalline cellulose (MCC) powder	From three grades of waste paper: book, Ground- wood/Newsprint and paperboard	Deinking	143
Cellulosic aerogel from cellulose nanocrystals	Old newspaper	Alkali and bleaching treatments	144
Cellulose-based films	Waste newspapers	Alkali treatment and bleaching	145
Cyanoethyl cellulose	Office waste paper OWP (photocopier and computer printout papers)	Deinking by flotation	6
Carboxymethyl cellulose	Mixed office waste (MOW) photocopier and computer printout papers	Pulping and Deinking by flotation	7
Highly porous cellulose beads	Printed paper wastes	Pretreatment and maceration processes in alkali solution	146
Cello-oligomers	Printed paper wastes	Pulping and alkali treatment	147

**name given by the author*

3.2. Organic recycling

Even that most of collected paper for recycling will generally be recycled by means of recycled paper production; some of it will be contaminated with food or wet (about 40%). In these forms it's not suitable for conventional recycling methods but is suitable for organic recycling.[148, 149] Organic recycling is also considered as material recycling due to production of compost or biogas. But the main problem is that, as with incineration and bioethanol production, when paper is composted or digestated it disappears from the paper recycling chain.[148] During organic recycling, paper for recycling can be subjected to aerobic (composting), anaerobic or anaerobic–aerobic digestion. Digested and stabilized waste can be used for the reclamation of non-agricultural soils but first it should be examined by ecotoxicological tests in order to be sure that it doesn't contain any toxic substances which can be harmful to environment and human health.[150, 151] Biodegradation of paper products is mostly dependent upon the crystalline/amorphous ratio in cellulose and presence of lignin.[150, 152–154] Amorphous zones of cellulose are more susceptible to biodegradation than the crystalline regions. The relative content of these two components could also vary in the different paper materials making the process of biodegradation different.[155, 156] Different additives in paper are making biodegradation less effective through the inhibition of enzyme action.[155] Pinzari *et al.* (2010) showed that clay and aluminium can inhibit fungal development during biodegradation of paper more than $CaCO_3$.[157] During anaerobic biodegradation, excessive amounts of calcium can lead to precipitation of carbonate and phosphate, which can affect biomass activity, loss of buffer capacity. Heavy metals originating from printing inks or fillers in paper are not biodegradable and they can accumulate to potential toxic concentrations. They can disrupt the enzyme activity due to their potential of binding to different groups on protein molecules and replacing naturally occurring metals in enzyme prosthetic groups. When it comes from pulp and paper industry the most common inhibitors are sulphide, tannins, resin acids, LCFAs, and halogenated compounds.[158]

Based on the available literature and results different biodegradability of paper, depending on the biodegradation conditions can be seen. According to López Alvarez *et al.* (2009) the presence of paper in municipal solid waste (MSW) have inhibitory effect and interferes with the efficiency of composting plants while Zorpas *et al.* (2003) concluded that paper can accelerated the maturation of compost.[151, 159] The high C/ N of paper may limit its utilization in organic recycling and thus some studies are focused on their composting with different organic waste materials. During the composting process some undesirable products such as carbon dioxide, ammonia and VOC compounds can occur.[150, 160, 161] The emissions of gases during composting mostly depend upon substrates composition and the addition of components responsible for acceleration of composting process. Komilis and Ham (2006) showed that mixed paper waste (MXP) requires a relatively long time to approximate its full extent of decomposition due to relatively slow solids hydrolysis.[161] Pommier *et al.* (2008) also confirmed that substrate hydrolysis is the limiting step of the paper and cardboard aerobic biodegradation process.[162] Fonoll *et al.* (2016) presented the influence of paper for recycling replacement by food waste in the anaerobic digestion process.[163] Results showed that either replacing half of the paper for recycling by food waste or removing half of the paper for recycling have little impact on the reactor methane production. When the half of the paper for recycling was removed, methane production was sustained by a larger waste biodegradability. The replacement of all paper for recycling by food waste increased the reactor methane production (37%), while it was estimated that removing all paper for recycling would have reduced the methane production about 15%. Pretreatment methods can enhance anaerobic digestion of paper for recycling and cardboard, for example mechanical pretreatments, which are able to decrease the particle, size and reduce the crystallinity of the substrate. Sometimes these methods are high energy-use and do not have significant influence on anaerobic biodegradation. In order to avoid these problems, biological pretreatment can be used, resulting in low chemical and energy use.[13] Pommier *et al.* (2010) showed that shredding strongly affects the macrostructure of the waste but it doesn't significantly increase enzyme accessibility to cellulose as well as the surface bacterial colonization.[164] The positive effect of adding zeolite can be related to the immobilization of microorganisms which generated a biofilm and thus, develop a better environment, increasing its metabolism and improving the yield of the system, affecting the methane production rate.[165] Besides immobilization of microorganisms, natural zeolites have a great capacity for metal adsorption which is useful for removal of toxic materials that can inhibit the growth of microorganisms responsible for anaerobic processes.

Zheng *et al.* (2013) divided paper into two categories according to its lignin content: degradable paper with lignin content of <0.05 g g VS^{-1} (office paper and toilet paper), and refractory paper with lignin content >0.15 g g VS^{-1} (newspaper, coated paper and corrugated cardboard).[166] López Alvarez *et al.* (2009) showed that papers presented in *Table 8*, will never achieve the same level of biodegradation at 45 days compared to reference material, microcrystalline cellulose. According to the obtained results, cardboard, kraft paper, newspaper and tissue paper are not suitable for recycling while white paper (printing) and recycled are compostable.[159]

Table 8 Aerobic biodegradation of different paper based products under controlled composting conditions according to [159]

Type of paper*	C/N ratio	Biodegradation at 45 days, %	No. days for reaching 70 % of biodegradation
Microcrystalline cellulose	-	79.3	-
Printing and writing	177	65.2	65
Cardboard	173	51.7	133
Kraft	5630	36.0	994
Newspaper	422	43.3	309
Recycled	341	61.0	64
Tissue	324	50.1	142

**name given by the author*

As already presented and according to literature available in *Table 9,* most of the studies are related to organic recycling of paper products, but there is lack of knowledge about the biodegradation of printing inks and their influence on biodegradation efficiency of paper for recycling. In some studies the printing inks are only referred to only as the toxic components.[159, 167] According to López Alvarez *et al.* (2009) cardboard and newspaper are not biodegradable due to presence of certain chemical components (bleaching agents, printing ink and organic substances used in printing) which may inhibit the biodegradation process, but no result for this were presented. According to EuPIA (2013) the presence of print on a graphic product will not prevent it from complying with the biodegradation requirements and it won't have any major effect on the anaerobic degradability of printed matter in a landfill.[168] Stinson and Ham (1995) studied a decomposition of printed and unprinted newspaper. Based on the generated amount of methane, results indicated that printing ink did not inhibit the amount or affect the rate of methane production from cellulose in newspaper.[154] The biodegradation of thermochromic printing inks was conducted by Vukoje *et al.* (2016) and Vukoje *et al.* (2017).[169, 170] Printed cardboard samples with UV curable ink showed lower values of biodegradation, up to 36% reduction compared to unprinted cardboard samples after 120 days.[169] For the thermochromic offset print it was concluded that biodegradability of the prints mostly depends on the used paper substrates, penetration of the binder in the paper structure and therefore, the thickness of the ink print.[170] Studies of vegetable based polymers and binders, which are commonly used in printing inks, have been investigated by Erhan and Bagby (1995), Erhan *et al.* (1997) and Shogren *et al.* (2004). Erhan *et al.* (1997) studied the biodegradation of ink formulations (soy newspaper ink vehicle, hybrid soy oil newspaper ink vehicle and commercial petroleum newspaper ink vehicle with 18, 25, 27, and 9% by weight of black, yellow, red and blue pigment, respectively). Some differences were found in the abilities of the cultures (*Aspergillus fumigatus, Penicillium citrinum* and *Mucor racemos)* to degrade the different inks. The ink colour did not appear to affect the degradation rate soy oil inks or the hybrid soy ink but was a factor in the commercial petroleum ink.[173] Shogren *et al.* (2004) concluded that highly crosslinked triglycerides with non-degradable linkages (a conjugated system of double bonds) are not biodegradable to a significant extent while triglycerides (linseed or soybean oil) crosslinked with hydrolysable bonds (carboxylic acid or alcohols) such as esters remain biodegradable.[172] There are also available data on biodegradation of printed polymer films in which the reduction of biodegradation rate was noticed for printed samples.[174, 175]

From the presented literature review, it can be seen that the most of the studies are related to different paper types and the influence of different paper components on the efficiency of organic recycling, but almost nothing is known about the impact of printing inks and their behaviour in organic recycling. In addition, it can be concluded that biodegradability potential of paper for recycling products cannot be predicted since all presented results vary from study to study. Despite limited data, it can be sad that biodegradation efficiency of paper for recycling will be dependant upon the used paper substrates, but the influence of printing inks on biodegradation efficiency will be manifested through their chemical formulation, *i.e.* binder and presence of toxic metals.

Table 9 Biodegradation of paper for recycling

Source*	Waste treatment type	Influence of printing inks	Reference
Newspaper	Anaerobic degradation	Yes	154
newspaper, cardboard, magazines paper plastic paper	Aerobic degradation in compost pile	No	151
Hand towels, paper containing mechanical and chemical pulp, and high density paper	Aerobic - controlled composting and full-scale composting in a windrow	No	150
Paper bags	Anaerobic degradation – laboratory procedure	No	176
Old corrugated cardboard, printed office paper and old newsprint	Aerobic - Composting	No	160

Old corrugated cardboard, printed office paper and old newsprint	Aerobic -Composting	No	161
Waste paper	Anaerobic co-digestion		177
Copy (CP), news (NP) and box paper (BP)	Anaerobic degradation - batch testing conditions		178
Regular paper plates, Earthshell-made plates, and a commercial biogradable paper	Aerobic – composting in a pile	No	179
Waste paper and cardboard	Anaerobic degradation	No	164
Filter paper, office paper, newspaper, and cardboard	Anaerobic degradation	No	13
Paper	Anaerobic degradation	No	43
Newsprint, copy paper	Anaerobic degradation	No	152
Cardboard	Anaerobic soil environment	UV curable screen printing ink -thermochromic	169
Synthetic and recycled paper	Anaerobic soil environment	UV curable screen printing ink -thermochromic	170

**name given by the author*

3.3. Energy recovery

According to the European Commisssion (2008) the energy recovery of paper based products refers to generate energy through direct incineration with the recovery of heat. Thermal processes such as incineration with energy recovery, pyrolysis, gasification and supercritical water oxidation are being the purposed methods.[2] These methods can be used for materials which can't be recycled and for all kinds of paper products, graphic paper and paper based packaging, regardless to present inks, coatings, additives and adhesives that can generally cause problems in material and organic recycling. Most of the studies related to energy production from paper are related to wastes generated from paper production or recycling in paper mills.[3, 180–185] According to Vochozka *et al.* (2016) the fillers from paper hamper combustion.[186] Besides fillers, other additives (inks, PVC, PET, Al, polishes, and other finalizing products) often raise concerns about the combustion gases and about ash management. Thermal behaviour of paper and cardboard can be studied by thermogravimetric analysis (TGA) and Differential Scanning Calorimetry (DSC).[3, 187, 188] According to Méndez *et al.* (2009) TGA indicates that presence or mineral matter and degradation of cellulose significantly influences their pyrolysis behaviour.[180] In general, weight loss of paper mill waste materials started at lower temperatures than pure cellulose. In case of wastes from recycled paper, weight loss continues at temperatures highest than 500°C due to kaolinite dehydration and carbonates decomposition. Zhou *et al.* (2013) showed that CO_2 is mainly produced from early stage of printing paper and cardboard pyrolysis.[187] According to Zhou *et al.* (2015) printing paper (including blank printing paper and newspaper) with approximately 80% volatile and 10% ash content can be selected for waste-to-energy thermal conversion.[188] For example, Arenales Rivera *et al.* (2016) used thermogravimetric analysis (TGA) for characterization of three different simulating pyrolysis process, in which the first step (200–360 ºC) corresponds to cellulosic materials, the second step (360 and 530 ºC) is attributed to plastic materials and the third step (580 and 720ºC) belongs to additives of deinking sludge.[3] Based on the presented results, printing inks may influence the processes of energy recovery through inhibition of combustion, produced gasses and ash, but also, there is no available data about the influence of different printing inks on the process efficiency and quality of produced gasses and ash.

3.4. Landfilling

In the past century, landfilling was the main waste disposal method, but it is no longer desirable due to generation of greenhouse gases, leachate, soil contamination, etc. After disposal of waste in landfill, firstly the aerobic reactions are involved within the surface waste, which is in contact with the atmospheric air, but with time, the conditions become anaerobic.[162, 189] The aerobic reactions are highly exothermic and they lead to the development of higher temperatures (50 – 60°C), which are important for anaerobic biological activity. Initial conditions (temperature, substrate content) for anaerobic activity are influenced from the aerobic reactions kinetics.[162] Taking into account that in landfill, the presence of aerobic and anaerobic reaction is, we can say that the influence of printing inks on paper decomposition in landfill will be similar to those occurring in organic recycling. The fate of paper in a landfill is a very complex subject because large number of variables comes into connection (moisture, permeability of cover, temperature, pH and time). It may take a century or more for paper to decompose completely in a landfill. Different authors have studied decomposition of paper under landfill conditions or laboratory scale conditions, but there is no information about the influence of printing inks on paper decomposition in landfill.[190–193] All studies showed that paper containing lignin are less degradable than those made from bleached pulp. As well, diapers containing plastic and gels exhibited limited biodegradability.[193] Paper mill industries produce lots of wastes (deinking an paper mill sludge) which is mostly disposed by landfilling or incinerating.[2, 3] The problems associated with the landfilling of paper mill and recycling sludge are the large volumes involved and the possibility of hazardous substances leaking into the environment.[2]

4. Life Cycle Assessment methods

From an environmental point of view, the waste management hierarchy implies that some of the strategies are more appropriate than others, due to their environmental benefits and impacts. Life cycle assessment (LCA) is a methodological that analyses and evaluates the environmental impacts associated with products and processes throughout their whole life cycles: production, use and disposal by identifying and quantifying energy and materials as well as the wastes released into the environment.[194] The environmental impact of paper waste management has been studied extensively using the LCA method.[194–196] LCA can be useful tool for choosing desirable waste treatment option of paper waste but in order to get valuable and reliable results the system boundaries needs to be clearly defined, since it can influence results significantly.[196, 197] Villanueva and Wenzel (2007) presented in their literature review that large majority of analysed LCA scenarios conclude that paper recycling is a better option than landfilling or incineration.[198] Despite numerus research related to LCA of waste management options for paper waste, there is lack of research about LCA in which influence of printing inks in paper waste is taken into account. Most of them are related only to pulp and paper waste in general suggesting different waste management options such as energy recovery gasification biogas production, anaerobic digestion or recycling.[167, 196, 199–203]

Hermann *et al.* (2011) emphasized that drawbacks for the obtained LCA results studied for several waste management options for different materials, including paper. The main drawbacks were missing information about the influence of toxic compounds (printing inks) and ammonia emissions during composting, material lamination and thickness, water content and mixing of compost pile. Dahlbo (2005) only indicated that the printing conditions for all samples included in LCA study, remained unchanged.[203] An increase in the collection rate also led to an increase in the emissions, except for landfilling and material recycling, which differed from the others by having no energy recovery.[203] Iosip *et al.* (2012) showed that higher concentration of contaminants in paper for recycling will result in higher environmental impact due to the increase of energy consumption, volumes of generated waste and more emissions released into the air and water. [204]

Larsen *et al.* (2009) studied the LCA of generic printed matter produced by sheet fed offset printing. The results were used to quantify the possible importance of impact categories related to emissions of chemicals and showed that printing causes dominant environmental impacts with a contribution of 41% to the aggregated impact, (18% from ink emission at the printing company, and 17% from emissions of synthesis chemicals at upstream pigment production). Paper contributes 31% mainly due to emissions related to energy consumption. Eco toxicity and human toxicity were only included to a limited degree or not at all.[205] This study also emphasized that chemical emission-related impacts are generally poorly treated or completely excluded from LCA studies due to lack of inventory and/or impact assessment data. Larsen *et al.* (2009) also indicate that environmental impacts of chemicals related to printing inks and printing processes may change an energy-related impact profile significantly, at least for product systems with processes with considerable chemical emission (*e.g.* various types of printed matter and textiles).

From the studied literature related to LCA of waste management of paper for recycling options, it can’t be concluded what’s the best choice since all results significantly varies from data collected, definition of system boundaries, functional units, *etc*. In all studies, landfilling is the only option, which should be avoided. Despite the lack of information about printing inks when LCA were conducted, few studies indicated an importance of taking into account the presence of printing inks in order to get more reliable data about environmental impact of waste management options, since they can influence results remarkably. Therefore, a good knowledge of printing inks composition and behavior in waste management options is necessary.

5. Conclusion

Choosing a particular waste management technology depends upon the quality of the collected paper for recycling. Different waste management methods can be used, because each of them has a certain advantage and certain drawbacks, depending upon paper types and different prints applied. Methods of material recycling purposed for production of recycled paper and cellulose derivatives are mainly studied for graphic papers, while bioethanol production and organic recycling can be conducted for paper and paper based packaging which is wet and contaminated with different substances (mainly food), or even for wastes obtained during production and recycling of paper.

Printing inks applied on paper for recycling may notably influence quality of new materials produced, such as recycled paper. If the prints are not removed from pulp, recycled paper will not only have poor optical and mechanical properties, but also it can be problem due to presence of toxic substances. Thus, it is of great importance to provide a toxicological assessment of new materials, due to presence of different substances originating from printing inks. In order to avoid different problems, for the printing inks which are generally difficult to remove by classic deinking by flotation method, the use of other methods (enzymatic, adsorption and ultrasound deinking) or their combination with classis method can be conducted. During enzymatic deinking, different enzymes will degrade different prints. There is no unique enzyme, which will be effective for all kinds of prints. Considering that recycling of paper is the most studied method worldwide, the influence of different printing inks on the recycling efficiency is the most studied and well described in the literature. However, when dealing with other waste management methods for paper for recycling, there is lack of knowledge about the influence of printing inks on their efficiency. Since bioethanol production and organic recycling are dealing with biochemical reactions and living microorganisms, the only available information are the inhibition of enzymes activity by toxic substances present in printing inks (fillers, organics and heavy metals). Therefore, printing inks can reduce the efficiency of the processes, but it is unknown which printing inks can affect process more or the reduction of process efficiency would be equal, despite different chemical formulation of printing inks. In the last decade, the use of paper for recycling for the production of different cellulose derivatives has become a topic of many studies. The presence of printing inks may negatively affect the quality of new products, thus they must be removed. Most of the studs were only connected to mixed office paper that is printed by non-impact printing. For other types of printing inks there is no available data. Besides previous mentioned methods, thermal conversion with energy recovery like pyrolysis and gasification can be also useful. The presence of printing inks may disrupt the combustion and influence the quality of produced gases and ash, but the influence of different printing inks on process efficiency and to what extent it is still unknown. Paper for recycling is valuable material and thus, landfilling is the only method that is recommended to be avoided. LCA methods can be a useful tool for the selection of desirable waste management method, but only if the system boundaries are well defined. The main drawback of the LCA studies conducted up to now is the lack of information related to printing inks used for calculations of environmental impacts. Comparing the all-possible waste management methods for paper for recycling, the most significant influence of printing inks on process efficiency is known to be for classis recycling for the production of recycled paper, but when dealing with other methods there is lack of available data. In these methods (bioethanol production, organic recycling, and energy recovery) the efficiency of processes is mostly influenced by the types of paper substrates and their components (i.e. presence of lignin, fillers, *etc.*). Based on the literature presented, in all of these waste management methods, the printing inks play an important role, thus when researchers are dealing with some new recovery method, they always should take the presence of printing inks into account.

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Deinkability of thermochromic offset inks

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KEYWORDS: Thermochromic ink, Surface free energy, Adhesion, Recycling, Flotation deinking, Optical properties, Image analysis

SUMMARY: This paper evaluates the deinkability of thermochromic offset inks. For this purpose, three thermochromic inks were printed on white uncoated paper, in laboratory conditions. These prints were mixed in equal shares and recycled by means of chemical deinking flotation under defined conditions in the laboratory according to INGEDE method 11p. Deinkability is evaluated by calculating the flotation yield, pulp's brightness and whiteness increase and the colour properties, determination of residual ink area, as well as ash content elimination. The obtained results indicate that thermochromic prints are poorly deinkable. The image analysis shows that flotation deinking managed to eliminate only 12.8% of the total dirt area of thermochromic ink. Only a small increase in deinked handsheets brightness and whiteness (approx. 5% and 2%) is noticed. The results of surface properties determination showed that the adhesion of inks on the paper is high. Thermochromic inks can affect wastewater too, by affecting its colouration due to their interactions with deinking solution and/or as a result of their mechanical damage during defibration.

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Thermochromic printing inks are special chromogenic or colour changing inks which change colour under certain circumstances. They are temperature sensitive inks meaning that they exhibit a colour change with exposure to different temperatures. Thermochromic inks come in two forms: as liquid crystals or leuco dyes, with leuco dyes more commonly used in packaging applications. In their cool state, leuco dyes exhibit colour, and when heated, they become clear or translucent. The temperature range at which transition of coloured to colourless state occurs is commonly called the activation temperature (TA) or activation point. The change of colour may be irreversible or reversible (Kulčar et al. 2010). Moreover, some leuco dye thermochromic inks change from one colour to another, rather than changing from coloured to colourless state. This is achieved with an ink that combines a leuco dye with a conventional ink colorant formulation. For example, adding a blue leuco dye to a conventional yellow ink will result in a green ink formulation. In its cool state, the printed ink layer will be green, and once warmed above its activation temperature, it will revert to yellow as the leuco dye becomes clear or translucent (Homola 2003).

Both types of thermochromic inks are usually encapsulated to enable easier handling. Many thermochromic dyes are phenylmethane and fluoran derivates bearing a lactone ring moiety. In the lactone ring-closed state these leuco dyes are either colourless or coloured faintly yellow. On reaction with the developer an opening of the lactone ring occurs resulting in the formation of a zwitter-ionic structure – below activation temperature (Seeboth, Lötzsch, 2008). Colour developers are usually weak acids that assist opening the lactone ring of the leuco dye and stabilise the open form (MacLaren, White 2003). The most important commercial colour developers are Bisphenol A, laurylgallate, ethylgallate and p-hydroxybenzoic acid methyl ester (Bamfield 2001, Seeboth et al. 2007).

Thermochromic printing inks are a mixture of thermochromic microcapsules and vehicles (binders). The sizes of microcapsules used in printing inks are in the range of 3 to 5 µm which makes them at least ten times larger than the average pigment particle. The main disadvantage of organic microcapsules is their insufficient light stability and high sensitivity to environmental changes (Seeboth, Lötzsch, 2008, Rožić et al. 2015). Thermochromic inks are available for use on a variety of substrates, including metals, polypropylene, polyethylene, polyvinyl chloride, papers. Inks have been developed for many types of printing processes, such as screen, gravure and flexographic, and more recently the arrival of colorant formulations that are compatible with offset vehicles has extended the range of applications to offset lithography (Bamfield 2001).

Deinking flotation is the most common practice for ink removal in paper recycling process, in which hydrophobic ink particles are removed from pulp suspension by adhesion to air bubbles, forming a froth which can be separated from the pulp suspension. Flotation efficiency depends on ink particle size, bubble size, collectors and calcium soaps formed from calcium ions and fatty acids (van de Ven et al. 2001). Apart from flotation efficiency, ink removal from pulp suspension and the deinkability of printed products mostly depends upon the printing process used, the characteristics of inks and the age of printed products. The age of printed products mainly affects offset prints (Faul 2010). Paper and board are easily reusable after their manufacture but their conversion into other products undergoes different applications with non-paper components (coatings, varnishes, laminates, adhesives, etc.) which might affect their deinkability, economical efficiency or environmental impact (Faul 2010).

Paper surface energy and the ink's wetting properties can also significantly affect the deinkability properties of inks, due to adhesion of ink to paper (Forsström et al. 2005). Offset printing is a widely used printing technique and the majority of recovered paper is printed by this technique. Conventional offset inks are highly deinkable. According to different authors (Faul 2010, Dumea et al. 2009) the optimal deinkability for conventional offset prints is achieved under alkaline conditions.

Besides the deinkability aspects, it is crucial to determine the whole environmental impact of the thermochromic offset ink recycling process. Thus, effluent characteristics should be investigated as well. Effluents from paper recycling process can contain large numbers of toxic compounds which are mostly organic (Rigol et al. 2002, Terasaki et al. 2008). If there is a closed loop cycle of water circulation, contaminated water can also affect the equipment for the production of paper and the quality of the final product (Rigol et al. 2002, Moutinho et al. 2007).

As the ink formulation is an essential factor in deinking, the aim of this study was to determine the deinkability of thermochromic offset inks. Thermochromic offset inks differ from conventional inks in formulation and size of colorants due to the presence of the microcapsules that are much larger than conventional pigment particles. Hence, the objective of this study was to find out how this property will affect their deinkability. So far, no data on thermochromic ink recycling by flotation deinking have been reported.

Materials and Methods

Printing substrate

A white uncoated paper was used as a substrate in all printing trials. The characteristics of the chosen substrate are presented in *Table 1*.

Thermochromic inks

Three offset thermochromic inks were used for printing. One offset thermochromic ink was produced by CHAMELEON® and other two thermochromic inks were manufactured by CTI®. Thermochromic offset ink purchased from CHAMELEON® was coloured in blue below its activation temperature (TA=27 °C) and changed to colourless when was heated above the activation point (hereinafter BW). One CTI® thermochromic offset ink was coloured in green below its activation temperature (TA=45 °C) and changed to yellow above the activation point (hereinafter GY). Another CTI® thermochromic offset ink was coloured in burgundy below its activation temperature (TA=63°C) and changed to blue when heated above the activation point (hereinafter BB). The prints obtained with all three used inks started to fade (or to change to another colour) with increased temperature at approximately 4°C below their activation temperature. Also, the colour change was reversible, i.e. original colour was restored upon cooling. Ink producers recommended printing these inks onto uncoated, absorbent papers to achieve the best print quality. Also, a higher thickness of ink deposit than in conventional sheetfed offset process was required to gain a satisfactory result. Some properties of used thermochromic inks are presented in *Table 2*.

Printing

The printing trials were carried out using the Prüfbau Multipurpose Printability Tester. The quantity of 1.5 cm^3 of ink was applied on the distribution rollers while printing was carried out with the printing force of 600 N. For printing on Prüfbau Multipurpose Printability Tester45 mm wide paper strips were prepared. The papers were printed in full tone (*Fig 1*). About 74% of the total area of paper strip was covered with ink. Input material for deinking consisted of three sets of prints which were mixed in equal proportions. To an each printed strip one unprinted strip of paper was added in order to avoid too high grammage of applied ink in relation to the total mass of paper submitted to deinking. Thus the total area of print was 37% when compared to the total area of used paper.

Table 1 - Properties of paper substrate

	White uncoated paper	
Basis weight	(g/m^2)	140
Thickness	(mm)	0.159
Bulk	(cm^3/g)	1.14
Smoothness	(s)	12.3
CIE Whiteness	(%)	142.51
ISO Brightness	(%)	95.59
Opacity	(%)	96.95
$CaCO_3$	(%)	25.07

Table 2 - Characteristics of thermochromic offset printing inks

	Producer	
Property	**Chameleon®**	**CTI®**
Pigments ratio	30±1,5 %	No data
Pigments size	95% less than 6 µm	No data
Solid content	90%	79 %
Solvent	Mineral spirits	No data
Viscosity	150 – 180 Poise	180 – 300 Poise
Recommended printing substrate	Uncoated paper	Uncoated paper

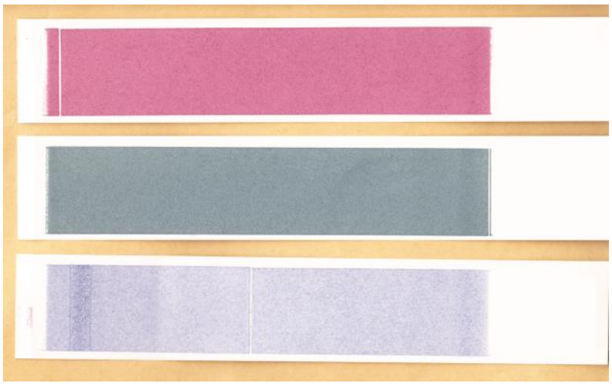

Fig 1 - Obtained thermocromic prints

Microscopy

In order to evaluate the presence of microcapsules in thermochromic inks and the residual ink particles in the froth and handsheets, microscopic images were taken using Olympus BX51 System Microscope. Images were taken under a magnification of 1000 x (*Fig 3, 4, 5*) and 50 x (*Fig 6, 7, 8*).

Flotation deinking

Flotation deinking of thermochromic prints was conducted in laboratory (scale) conditions, according to the INGEDE method 11p (*Fig 2*). The INGEDE method represents a procedure of evaluation of the deinkability of print products subsequent to flotation. The sample consisting of paper strips was recycled following the

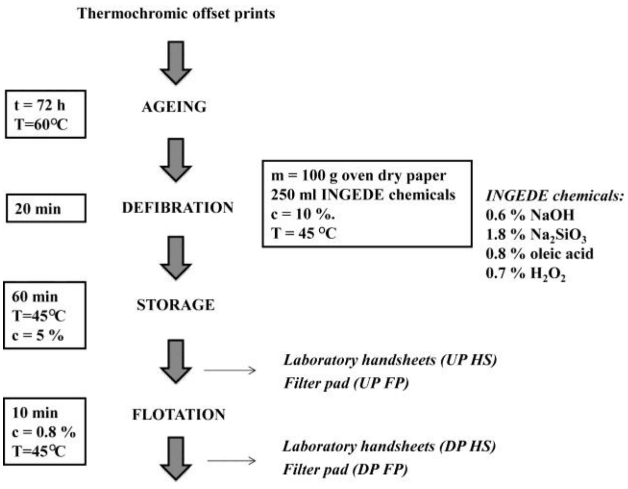

Fig 2 - Flow chart of the procedure for the assessment of printed product deinkability

standard procedure. Disintegration was conducted in the Enrico Toniolo desintegrator, while flotation was conducted in laboratory flotation cell. According to the INGEDE method 1, a certain amount of suspension with consistency 5% was separated in order to make undeinked pulp (UP) handsheets (HS). From pulp suspension after the flotation stage laboratory paper handsheets were prepared (hereinafter referred to as deinked pulp handsheets - DP) on Rapid-Köthen Sheet Machine, PTI. Besides the handsheets, filter pads (FP) were also prepared using the Buchner funnel, according to INGEDE method 1, as well. Basis weight of filter pads was set to 225 g/m^2, while all handsheets were prepared with a basis weight of 45 g/m^2. Handsheets and filter pads prepared from undeinked (UP) and deinked (DP) pulps were required to permit an optical evaluation. Also, handsheets and filter pads from blank paper samples were formed after the pulping (disintegration) of the original unprinted paper.

Determination of surface properties

The evaluation of surface free energy of paper and paper printed with inks were carried out by contact angle measurements on DataPhysics OCA 30 Goniometer, using the Sessile Drop method. Standard test liquids whose surface tensions are known (*Table 3*) are demineralized water, diiodomethane and glycerol. Measurements were performed at room temperature (23.0 ± 0.2)ºC. The volume of droplet was 1 µl. Contact angle was captured by CCD camera and measured 1–2 s after the droplet was formed. Average values of ten drops on different places of the same sample were taken and presented as mean±SD (*Table 4*).

Using the Owens Wendt calculation method the surface free energy of the paper samples was determined (Owens, Wendt 1969).

The surface free energy (γ_s) is the sum of dispersive (γ_s^d) and polar (γ_s^p) component. This calculation method is integrated in the software (SCA20, Version 2.01) and carried out automatically. The obtained surface free energy and its components are presented in the results section (*Table 5*).

Table 3 – Surface tensions (γ) of test liquids and their dispersive (γ^d) and polar (γ^p) components

Liquid	Surface tension (mJ/m^2)		
	γ	γ^d	γ^p
Water	72.80	21.80	51.00
Diiodomethane	50.80	50.80	0.00
Glycerol	63.40	37.00	26.40

Deinking evaluation

The efficiency of deinking process was evaluated by determination of flotation yield, ash content (%) elimination, determination of residual ink area (mm^2/m^2) and optical properties (CIE L*a*b*, ISO brightness, CIE whiteness).

For the determination of ash content a test specimen was ignited in a muffle furnace at 525 ± 25°C (T 211 om – 02). The data determined were expressed as the mean of five replicate determinations and presented as means±SD.

The dirt (residual ink) particle area on handsheets was determined by image analysis and data processing, using Spec Scan 2000 (Apogee Systems Inc.) according to ISO 15755. Handsheets were scanned with a resolution of 600 dpi. Threshold value was adjusted to 100 (manual) and 256 grayscale mode. Image analysis was performed on 0.001935 m^2 of each handsheet surface to detect particle size distribution. The total number and size of the residual ink particles, as well as their total area was determined (*Fig 9, Table 8*).

Undeinked (UP) and deinked pulp (DP) handsheets, as well as filter pads, were tested for their optical properties. All the measurements were carried out on Technydine Colour Touch 2 Spectrophotometer, according to standard methods. For the determination of ISO Brightness (ISO 2470) a measurement of diffuse blue reflectance factor (R_{457}) was conducted. Brightness is defined as the percentage reflectance of blue light only at a wavelength of 457 nm. CIE whiteness and colour components L*a*b* was measured according to ISO 11475. CIE whiteness was measured in conditions with and without UV-content of illumination. The data determined were expressed as the mean of ten replicate determinations. Results are presented in *Table 9, Fig 10* and *11*.

Filtrate characteristics

Effluents generated in laboratory paper recycling process were collected after the flotation process in order to determine their chemical characteristics in terms of total organic compound (TOC) and chemical oxygen demand (COD) values. Pulp suspension was filtrated through a Büchner funnel in order to remove residual pulp from effluent samples. Measurements were carried out according to the HACH method.

Digestion reactor block HACH DR 200 and HACH DR/890 colorimeter were used for TOC and COD concentration measurements (*Table 10*). Besides the investigation of organic contaminates in effluents after flotation process, the filtrate from froth was also investigated for absorbance due to visible colour change (*Fig 12*). Absorption value of froth filtrate was determined using a Konica Minolta CM-3600d spectrophotometer in the wavelength area between 360-740 nm.

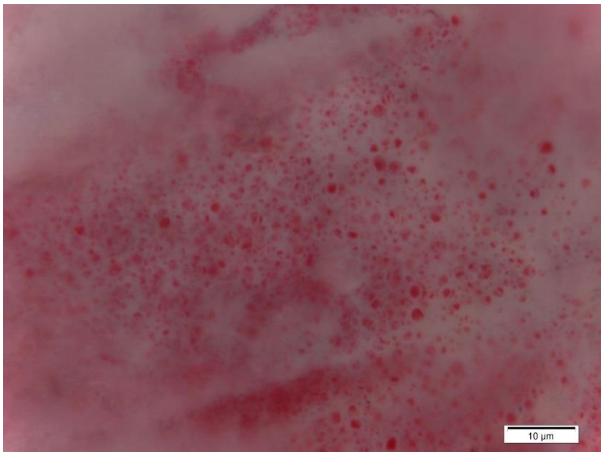

Fig 3 - Microscopic image of burgundy-blue (BB) thermochromic offset print

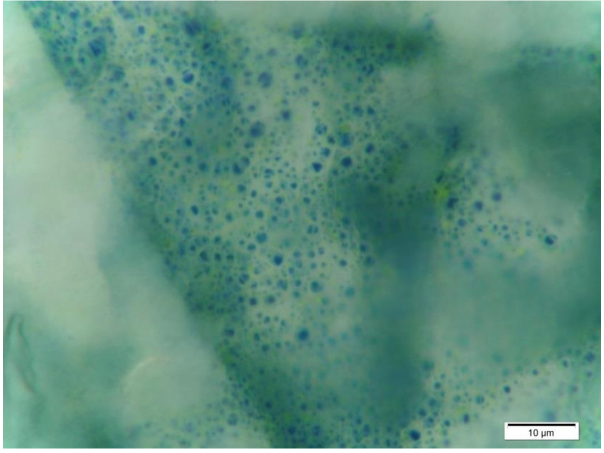

Fig 4 - Microscopic image of green-yellow (GY) thermochromic offset print

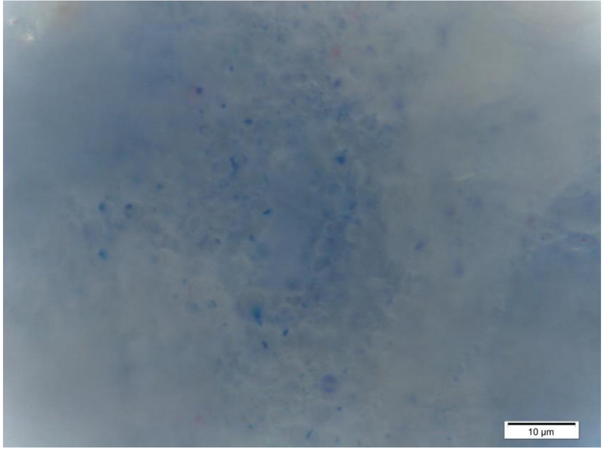

Fig 5 - Microscopic image of blue-white (BW) thermochromic offset print

Results and Discussion

For the determination of microcapsules and morphology of printed matter, the microscopic images were taken. From the presented *Figs 3- 5* it can be clearly seen that printed ink capsules had a size around 1µm in diameter.

Determination of surface properties

The removal of ink particles and other contaminants from pulp suspension during froth flotation deinking mostly depends on their different properties; differences in size, density and surface properties.

Table 4 - Contact angles measured on samples

	Contact angle [deg]		
	Water	**Diiodomethane**	**Glycerol**
Paper	102.0±4.9	72.0±5.8	108.6±5.2
BB	90.9±3.1	49.4±2.8	97.5±4.2
GY	92.6±3.5	49.9±1.5	85.6±3.4
BW	118.3±4.8	46.1±3.0	103.3±4.8

Table 5 - Surface parameters of paper, and paper with printed ink components calculated according to OW model

Sample	Surface free energy (mJ m^{-2})			x^d(%)
	γ	γ^d	γ^p	(γ^d/γ)
Paper	17.47	16.66	0.81	95.36
BB	28.03	26.90	1.13	95.97
GY	31.58	30.62	0.96	96.96
BW	34.78	33.07	1.71	95.08

In order to evaluate the wetting properties of paper and ink prints, contact angle measurements were performed. If fine particles have adequate hydrophobicity they may attach to air bubbles (Chipfunhu et al. 2011).Obtained contact angles presented in *Table 4* show mostly hydrophobic surface properties of paper and of ink prints. According to obtained contact angles it is evident that the greatest hydrophobic surface has a BW ink print, followed by unprinted paper. Similar hydrophobic surfaces have GY and BB ink prints but their measured contact angle values are smaller than BW ink print and paper. These properties can strongly influence deinkability aspects of inks due to their hydrophilic/hydrophobic property.

Different authors have presented that froth flotation and ink detachment can also be strongly affected by surface properties and its components, and a greater polarity of surface makes flotation more difficult (Nie et al. 1998, Forsström et al. 2005).

From *Table 5* it can be observed that a predominant component of surface free energy of paper and ink deposits is the dispersive component and an adhesive bond between solid and ink is provided by nonpolar interactions. The lowest value of total surface free energy obtained for paper can be described due to high additives content. The highest polar character of surface is observed for BW print (1.71 mJ m^{-2}). Besides the greatest polar component, the smallest dispersive index is observed (95.08%). The existence of polar groups in the ink surface can lead to better bonding with polar molecules in deinking solution and thus dissolving in it.

Adsorption theory, according to the Dupré approach, presenting the thermodynamic work of adhesion W_{12} (*Eq 1*) between two phases is equal to (Zenkiewicz, 2007):

$$W_{12} = \gamma_1 + \gamma_2 - \gamma_{12} \qquad [1]$$

where the subscript refers to surface free energy of the each solid, in our case paper and ink print, and the γ_{12} denotes their surface free energy of the interphase. Owens-Wendt model includes the assumption according to which both the dispersive and polar interactions between two phases are equal to the geometric mean expression of surface free energy of the individual phase which are in contact with each other, according to equation 2 (Zenkiewicz 2007):

$$\gamma 12 = \gamma_1 + \gamma_2 - 2(\gamma_1^d \gamma_2^d)^{0.5} - 2(\gamma_1^p \gamma_2^p)^{0.5} \qquad [2]$$

The adhesion of ink to the paper substrate depends on the intermolecular interaction between them. The obtained results show that the interaction between all tested thermochromic inks and printing substrate are strong. The work of adhesion is the highest for paper - BW ink print (49.30 mJ m^{-2}), despite the highest surface free energy of its interphase (2.95 mJ m^{-2}) (*Table 6*). This can only be explained by the largest surface free energy (γ_2) of BW ink print (*Table 5*). The obtained works of adhesion are in the range of the work of adhesion for toner formulations, ranging from 41.2 to 62.4 mJ m^{-2} that are known to be very difficult to deink by conventional flotation process (Thompson et al. 2000).

Microscopy of froth and handsheets

Fig 6 presents a microscopic image of removed froth (sludge collected during flotation). As seen, the froth mostly contains ink particles originating from GY and BB prints, while the BW ink particles are observed in a smaller amount. The largest ink particles originate from the GY ink prints while the smallest come from the BW ink prints. *Fig 7* shows undeinked pulp (UP) handsheet in which only BB and GY ink particles can be observed. Deinked pulp (DP) handsheet (*Fig 8*) is cleaner but also contains mainly BB and GY ink particles. As there are small amounts of BW ink residues, it can be assumed that microcapsules of BW ink have retained in water solution, despite the poor wetting properties of BW ink print **(***Table 4*) and the highest work of adhesion (*Table 6*). Polar component (*Table 6*) can contribute to this, too.

Another explanation may lay in the fact that the inks have been manufactured by different ink producers which most likely resulted in a different formulation of the chemicals used in inks. The largest work of adhesion that is evident for printed BW ink may be explained by different chemical composition of BW ink in comparison to the other two inks (GY and BB). It is possible that the difference in formulation of ink vehicle affects the surface properties of the print in a different manner (*Table 4*). The components present in the vehicle of BW ink may be more reactive with deinking solution, causing ink frag-mentation into very small particles and probably sub-sequent release of the microcapsules from the print. Thus, the BW ink particles in the undeinked and deinked pulp are very hard to detect. In this case, small fragments of BW ink print can remain in suspension and can hardly be removed from it by flotation.

Flotation yield

The yield of the deinking process is presented in *Table 7*, as well as the ash content of tested paper and filter pad samples. Obtained flotation yield was 95.8%. From result of ash content determined in froth filter pad (45.9%) it is further possible to calculate the total loss of the fibres during the flotation deinking, which is, in this case, quite small amount of only 2.27%. Ash content elimination, calculated from the ash balance of the undeinked and deinked pulp samples shows that the ash content was reduced for 8.3% by flotation.

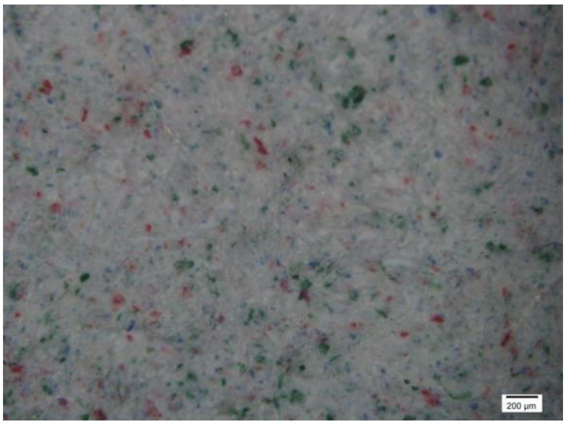

Fig 6 - Microscopic image of removed froth

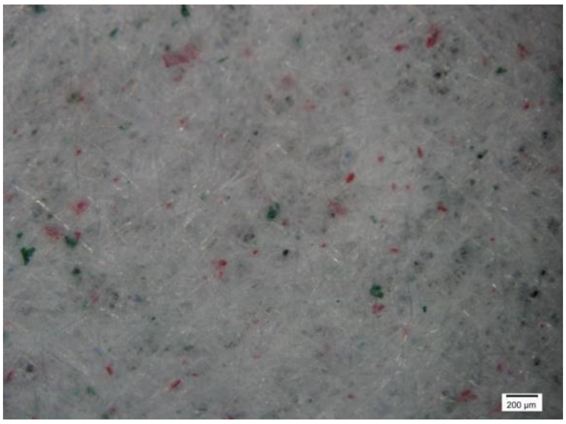

Fig 7 - Microscopic image of undeinked pulp (UP) handsheet

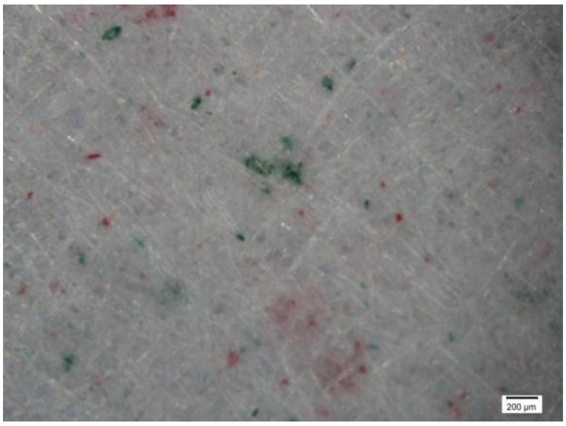

Fig 8 - Microscopic image of deinked pulp (DP) handsheet

Table 6 - Adhesion parameters of components

Sample	Adhesion parameters (mJ m^{-2})	
	Surface free energy of interphase γ_{12}	Work of adhesion W_{12}
Paper –BB	1.25	44.25
Paper –GY	2.11	46.94
Paper –BW	2.95	49.30

Table 7 - Yield of deinking process

Sample		Value
Flotation yield, %		95.80
Ash content, %	Froth filter pad	45.90±0.67
	Original paper	25.38±1.81
	Blank filter pad	25.23±0.87
	UP filter pad	25.50±2.45
	DP filter pad	23.39±1.43

Table 8 -Total area of dirt particles (ISO 15755)

Sample	Total area of dirt particles [mm²/m²]
Undeinked pulp	908.5
Deinked pulp	792.2

Table 9 - Colorimetric values of recycled handsheets

Sample	*L**	*a**	*b**
Original paper	95.30±0.03	2.88±0.02	-12.14±0.07
Blank handsheet	95.03±0.04	2.57±0.03	-12.53±0.21
UP handsheet	89.70±0.08	2.64±0.04	-11.41±0.05
DP handsheet	90.34±0.08	2.87±0.09	-11.41±0.24

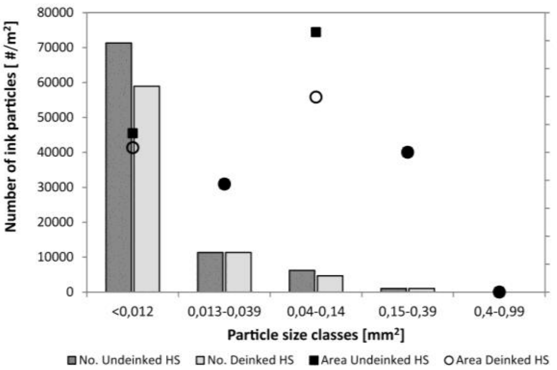

Fig 9 - Ink particle size distribution (ISO 15755)

Determination of dirt particle measurements and optical properties

The results of the image analysis are presented in *Fig 9*. During the recycling process, ink is disintegrated mainly into very small fragments (*Figs 6-9*). The largest number of particles on both, undeinked (UP) and deinked pulp (DP) handsheets can be found in the particles of the size class less than 0.012 mm^2, followed by other, very small particles, ranging from 0.013 to 0.039 mm^2. The results show that deinking flotation reduced the number of disintegrated ink particles smaller than 0.012 mm^2 for 17%, while those in particle size range of 0.04–0.14 mm^2 were reduced for 25%. However, in particle size classes of 0.013-0.039 mm^2 and 0.15-0.39 mm^2 no reduction in number was noticed. No particles larger than 0.4 mm^2 were detected. A reduction of ink area was also noticed. For ink particles that fall within the range of 0.04–0.14 mm^2, a reduction of dirt area was 25%, while for ink particles smaller than 0.012 mm^2, a decrease in the ink area of 9% was determined. The total area of dirt particles has been reduced for only 12.8% (*Table 8*).

As explained earlier, it can be assumed that the smallest particles (<0.012 mm^2) originate from BW ink, while larger derive from GY and BB inks which is further confirmed by microscopic images (*Figs 7-8*). It is known that the optimal particle size range for flotation deinking is from 10 to 150 µm (Jiang et al. 2000). In this case, printed ink film is broken into very small fragments, making flotation more difficult.

Very small percentage of removed dirt particles contributes to the poor optical properties of the pulp (*Table 8*). Small particles that are not removed from the pulp by flotation reduce the brightness and influence the paper colour properties.

Results of colorimetric values determined on undeinked (UP) and deinked (UP) pulp handsheets are presented in *Table 9*. The obtained results are compared to the target values measured on a blank handsheet. In the CIE L*a*b* colour space the value L* represents the lightness of the colour, the value +a* represents redness, –a* represents greenness, +b* represents yellowness while the value –b* represents blueness (Kipphan 2001). The obtained results show that L* values are slightly lower than the target value and similar to each other. Only a small increase in the lightness of the pulp was observed after the process of flotation. a* values are very similar to the target value and b* values are the same in both, undeinked and deinked handsheets, but are slightly more positive if compared to the target value. The changes of the value b* could be attributed to unstable BW ink print and its microcapsules which retained in suspension.

The efficiency of deinking process is further evaluated through brightness and whiteness increase which is calculated as follows:

Brightness increase (%) = DP brightness (%) – UP brightness (%) [3]

Whiteness increase (%) = DP whiteness (%) – UP whiteness (%) [4]

Fig 10 presents the results of ISO brightness determinations conducted on handsheets and filter pads of undeinked (UP) and deinked (DP) pulps as well as on the blank samples. Brightness and whiteness values measured on blank handsheet and filter pad samples are considered to be the pulp's target values (ideally, the level that we want to achieve through deinking). Results of brightness measurements indicate that flotation managed to improve brightness only slightly, as the brightness increase of only 4.2% and 4.8 % was detected on handsheets and filter pads, respectively (*Eq 3*).

If the values of deinked pulp's brightness (measured on handsheets) are compared to the brightness target values (HS blank) it can be seen that the levels of deinked pulp's brightness deviate from the target brightness values for 9.7%. Comparing the filter pads in the same manner, a deviation of 8.8% is noticed.

Fig 11 presents the results of CIE whiteness measurements conducted on handsheets and filter pads of undeinked (UP) and deinked (DP) pulps as well as on the blank samples. The results of CIE whiteness determination with and without included UV-content of illumination (*Fig 11*) show an even smaller increase in pulp's whiteness after flotation when compared to brightness increase evaluation. The whiteness increased after flotation for only 1.2% and 1.9%, on handsheets and filter pads, respectively, under UV-content of illumination (*Eq 4*). The results furthermore show large deviations from target whiteness values of 13.4% in case of handsheets and of 11.5% in case of filter pads.

The measurements conducted without UV-content of illumination show an increase of only 1% determined on handsheets and of 1.4% measured on filter pads (*Eq 4*). The obtained results indicate slightly smaller deviations from target whiteness values; deinked pulp whiteness measured on handsheets deviates from target values for 11.1% and for 8.5% when measured on filter pads.

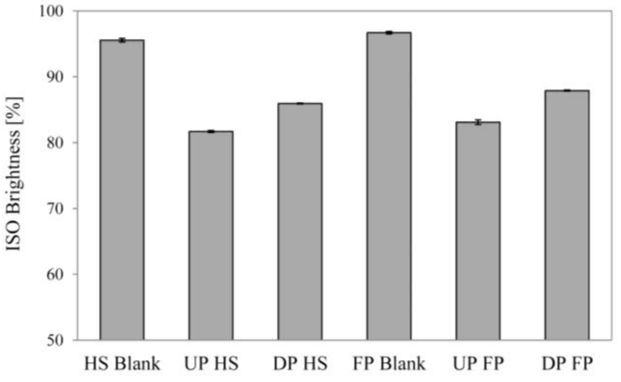

Fig 10 - Brightness of blank samples and undeinked (UP) and deinked (DP) pulps

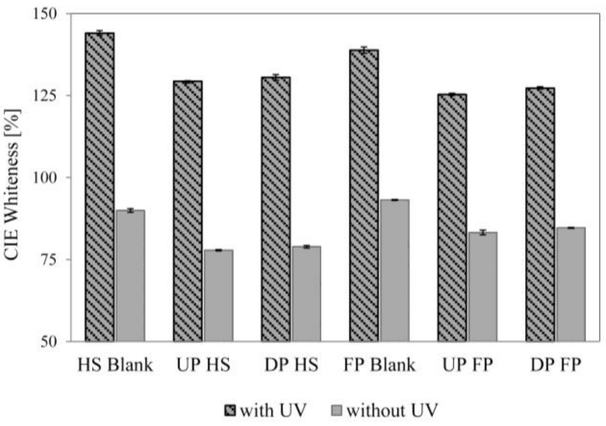

Fig 11 - CIE Whiteness with and without UV-content of illumination

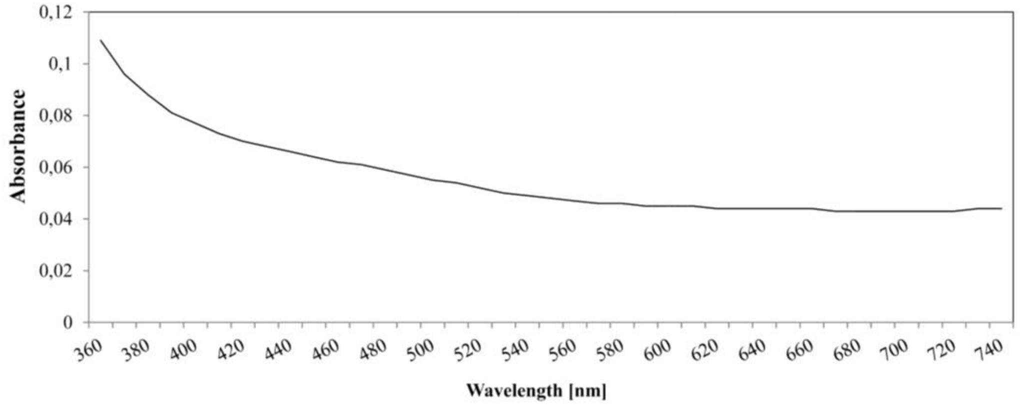

Fig 12 - Absorbance spectra of froth filtrate

Table 10 - TOC and COD values in effluents after flotation

Parameter [mg/L]	Value	
	Blank	After deinking
TOC	92	176
COD	69	155

Filtrate characteristics

In order to obtain the whole environmental impact of thermochromic inks, the filtrate of suspension after flotation was analysed in the terms of TOC and COD values which can relate to the biodegradability aspects. The effluents obtained in paper recycling can be strongly influenced by raw materials and chemicals used for the deinking process. Compared to obtained results in previous research in which the deinkability of newspaper (standard offset ink) was studied (Vukoje et al. 2014), thermochromic inks have greater environmental impact due to higher TOC and COD values, possibly due to ink interactions with the deinking solution (*Table 10*). Comparing the presented results from effluents generated from blank and after flotation, it is evident that inks contribute to the effluent TOC and COD.

The filtrate from froth was analysed for absorbance due to visible colour change (*Fig 12*). The absorbance spectra show the yellow coloration of filtrate obtained from the froth derived from the flotation process and it is assumed that this colouration comes from the BW thermochromic ink, as residues of this ink weren't found in UP and DP handsheets, due to its chemical composition and polar component. The solvent in the BW ink is a mineral spirit. A mineral spirit can destroy the capsule wall by increasing the pores and permeability. Hence, a froth filtrate is coloured in yellow. Ketones, diols and aldehydes must be minimized as solvents in thermochromic inks, as well as most mineral spirits (Highberger, Small 1996). The lower the amounts of these compounds are, the better the performance of the thermochromic ink and the longer the shelf life of the product. Many thermochromic dyes are phenylmethane and fluoran derivates bearing a lactone ring moiety. In the lactone ring-closed state (below activation temperature) these leuco dyes are either colourless or coloured faintly yellow (Seeboth, Lötzsch 2008).

Conslusions

Based on the obtained results we may conclude that the tested thermochromic offset printing inks are poorly deinkable despite its hydrophobic properties and low surface free energy. Measurements of optical properties demonstrated the ineffectiveness of this method for the recycling of thermochromic ink prints, since only a small increase in deinked pulp brightness and whiteness was noticed. Moreover, image analysis showed that flotation deinking is not successful method for the elimination of disintegrated ink particles. A possible explanation of this could lie in the chemical composition of thermochromic inks and their ability to bond with examined paper substrate. Deinkability aspects of tested inks are influenced by good adhesion of inks to paper substrate and the existence of polar component in printed ink film.

It can lead to retention of the particles in pulp suspension due to weak adhesion onto the air bubbles. Besides the poor deinkability, recycling of thermochromic inks showed higher environmental impact in the terms of wastewater pollution due to their interactions with deinking solution. Further research into development of more effective deinking chemicals is needed. Another approach would be a different recycling method for thermochromic offset prints.

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Safety Evaluation of Deinked Pulp Containing Offset Thermochromic Inks

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Evaluating the safety of thermochromic inks for offset lithography in deinked pulp samples is a major area of investigation. In this study, three offset inks were analyzed – one that dries by absorption and two that dry by oxypolymerization of vegetable oils. Inks were printed separately on strips of white uncoated paper, and the prints were recycled by chemical deinking flotation. Thermochromic inks, handsheets, filter pads, and process waters obtained from deinking were tested for the presence of heavy metals, while concentrations of bisphenol A (BPA), total organic compounds, and antimicrobial agents were examined in handsheets and filter pads. The concentration of heavy metals cations was determined from ashes of undeinked and deinked pulp handsheets as well as from ashes of blank paper, flotation froth, and process water filtrates. BPA originates from thermochromic inks, and a 50% reduction of BPA was noticed in the samples after flotation. Considering the results, deinked pulp is undesirable due to the presence of BPA. Despite the presence of BPA, there was no release of toxic components from deinked pulp.

Keywords: Recycled paper; Thermochromic inks; Heavy metals; Bisphenol A; TOC; Antimicrobial properties

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INTRODUCTION

Recycled paper is an important source of fibers for paper production. The quality of recycled pulp decreases as the collection rate of recovered paper increases and as more "marginal" paper fractions are collected (Bobu *et al*. 2010; Pivnenko *et al*. 2015). Most white recovered paper grades are recycled by deinking flotation. Using surface-active substances, hydrophobic printing ink particles are removed from pulp suspensions by adhesion to air bubbles, forming a froth that can be easily separated from the suspension (Blanco *et al.* 2013). The deinkability of printed products mostly depends on the printing process used, the ink characteristics, and the age of printed products (Faul 2010).

Studies on paper-based food packaging materials have identified a wide range of substances that may be present in recycled pulp (Boccacci Mariani *et al.* 1999; Summerfield and Cooper 2001; Jamnicki *et al.* 2012; Pivnenko *et al.* 2015; Vápenka *et al.* 2016), which mostly originate from printing and converting processes undertaken in the previous use of the paper. Those substances remain in the solid matrix during paper recycling and thereby end up in new products based on recycled fibers. Binderup *et al.* (2002) cited a large list of potentially harmful substances found in recycled paper, including phthalates, solvents, azocolorants, diisopropyl naphthalenes, primary aromatic amines, polycyclic aromatic hydrocarbons, and benzophenone. Moreover, certain paper and board fractions in recovered paper derived from households contain relatively high concentrations of chemicals such as mineral oil hydrocarbons, phthalates, phenols, polychlorinated biphenyls, and toxic metals (Cd, Co, Cr, Cu, Ni, and Pb) (Pivnenko *et al*. 2016). In order to maintain the high paper recycling rates with satisfactory quality of recycled pulp, the presence of chemicals should be taken into account, and it is crucial that paper recycling processes are highly effective in ink and toxic component removal. Some harmful substances can be removed from recycled pulp with new deinking methods. Jamnicki *et al*. (2015) showed that adsorption deinking is more successful in the reduction of mineral oils than conventional flotation deinking.

If recycled paper is used in food packaging, it must comply with many specific requirements proposed by the European legislation (EC 2004, 2006). These requirements refer to the control and analysis of contaminants in recycled paper and board such as heavy metals, plasticizers, aromatic amines, poly-aromatic hydrocarbons, benzophenone, and BPA (Mohammadpour *et al*. 2016).

In the printing industry, many different types of inks and printing processes are used. Even though all printing inks are composed of four main ingredients (colorant, vehicle or binder, solvent, and additives), they differ in chemical composition. In order to satisfy the market innovations, there is a greater demand for traditional and functional printing inks, such as thermochromic printing inks.

Thermochromic printing inks are temperature-sensitive inks that exhibit color change at different temperatures. They come in two forms: liquid crystals or leuco dyes. In the cool state, leuco dyes exhibit color, and when heated, they become clear or translucent. The temperature of the color change transition is called the activation temperature (TA) (Homola 2008). Moreover, some leuco dye thermochromic inks change from one color to another, rather than changing from colored to colorless state. This is achieved with an ink that combines a leuco dye with a conventional ink colorant formulation. Commercially available thermochromic printing inks based on leuco dyes consist of microencapsulated leuco dye–developer–solvent systems and a resin binder (Tang and Stylios 2006; Seeboth and Lotzsch 2013). The thermochromic effect is caused by the formation of leuco dye–developer complexes in a reversible equilibrium redox reaction between leuco dye and developer (Seeboth *et al.* 2007). The most common dyes are phenylmethane and fluoran derivatives bearing a lactone ring moiety. In the lactone ring-closed state, these leuco dyes are either colorless or weakly yellow colored. Leuco dye–developer–solvent systems are colored in the solid state and become transformed on heating above the melting temperature of the solvent into a colorless liquid (Seeboth and Lotzsch 2008). Color developers are usually weak acids (bisphenol A, octyl phydroxybenzoate, methyl p-hydroxybenzoate, 1,2,3-triazoles, and 4-hydroxycoumarin derivatives) that assist opening the lactone ring of the leuco dye and stabilize the open form, while long-chain alkyl alcohols, esters, and acids are commonly used as solvents (White and LeBlanc 1999; MacLaren and White 2003). Vinković *et al.* (2017) found the presence of bisphenol A and benzophenone in commercially available thermochromic printing inks.

Deinkability of three different offset thermochromic inks printed on white uncoated paper was described in Vukoje *et al*. (2016), which was part of our previous research, and it was evaluated by calculating the flotation yield, pulp's brightness and whiteness increase and the color properties, determination of residual ink area, as well as ash content elimination. The obtained results indicate that thermochromic prints are poorly deinkable because only 12.8% of the total dirt area of thermochromic ink was removed by deinking flotation and small increases in deinked handsheets brightness and whiteness (approx. 5% and 2%) were noticed. Although the classic offset prints are generally highly deinkable, poor deinkability of thermochromic offset prints was explained by high adhesion of inks onto the paper, which was similar to observations for toner formulations that are known to be very difficult to deink by conventional flotation process (Vukoje *et al.* 2016).

Due to poor deinkability of thermochromic offset prints and the presence of different harmful substances in their structure, the objective of this study was to evaluate the safety aspect of the deinked pulp made from paper printed with thermochromic inks, *i.e.*, its possible use in food contact applications. As paper material is considered safe to be brought in direct contact with foods only if it is free from any substances that have toxic potential, aim of this study was, thus, to determine the concentration of heavy metals and BPA, total organic compound (TOC), total carbon (TC) in recycled pulp containing thermochromic inks, as well as transfer of antimicrobial constituents from the recycled paper. Where it was possible, the concentrations of determined chemicals were compared with the proposed limits set out in Industry Guideline for the Compliance of Paper and Board Materials and Articles for Food Contact developed by the European paper and board food packaging chain (CEPI/CITPA/CEFIC/FPE 2012).

EXPERIMENTAL

Materials

Paper

A white uncoated paper was used as a substrate for printing. The characteristics of this substrate are presented in Table 1.

Table 1. Properties of Paper Substrate

White Uncoated Paper							
Basis weight (g/m^2)	Thickness (mm)	Bulk (cm^3/g)	Smoothness (sec)	CIE Whiteness (%)	ISO Brightness (%)	Opacity (%)	$CaCO_3$ (%)
140	0.159	1.14	12.3	142.51	95.59	96.95	25.07

Thermochromic inks

Three offset thermochromic inks, which differed in their activation temperature, color, and chemical composition were used for printing (Table 2).

Table 2. Offset Thermochromic Inks

Thermochromic Ink	Producer	Abbreviation	Activation Temperature	Drying Mechanism
Blue to Colorless	CHAMELEON®	BW	27 °C	Absorption
Green to Yellow	CTI®	GY	45 °C	Oxypolymerization
Burgundy to Blue	CTI®	BB	63 °C	Oxypolymerization

All thermochromic inks had the ability to change their color above the mentioned activation temperatures (TA). For example, thermochromic offset ink (GY) was green-colored below its activation temperature (63 °C) and changed to yellow above its activation point. The color change was reversible, *i.e.*, the original color was restored upon cooling.

Methods

Offset printing

The printing trials were carried out using a Prüfbau Multipurpose Printability Testing System (MZ II, Peissenberg, Germany) as described in Vukoje *et al*. (2016). For each print, the same printing parameters were used, *i.e.*, the same amount of ink was applied on the rollers, and the printing force was 600 N. For printing on the Prüfbau Multipurpose Printability Tester, 45 mm wide paper strips were prepared. The papers were printed in full tone. About 74% of the total area of paper strip was covered with ink. Input material for deinking consisted of three sets of prints, which were mixed in equal proportions. To each printed strip one unprinted strip of paper was added in order to avoid too high grammage of applied ink in relation to the total mass of paper submitted to deinking. Thus the total area of print was 37% when compared to the total area of used paper.

Flotation deinking

Deinking flotation of thermochromic prints was conducted under laboratory conditions, according to the INGEDE method 11p as previously described (Vukoje *et al.* 2016). Handsheets and filter pads of blank (B), undeinked pulp (UP), and deinked pulp (DP) were prepared according to INGEDE method 1. Blank paper (B) samples were formed after the pulping of the original unprinted paper. Samples from undeinked pulp (UP) were formed after pulping of printed paper samples (without conducting flotation process), while deinked samples (DP) were formed after pulping and flotation of printed paper samples.

Determination of heavy metal content using atomic absorption spectroscopy (AAS)

The concentrations of heavy metals (Pb, Cd, Cu, Zn, Fe, Mn, Ni, Cr, Co, As) were determined in thermochromic printing inks, samples obtained from deinking process, and water filtrate by the AAS method. The concentrations of heavy metal cations were determined from ashes of undeinked (UP) and deinked pulp (DP) handsheets as well as from ashes of blank paper sample (B) and flotation froth. First, 5 g of sample was burned in a porcelain pot by slowly heating the electric hot plate and burner until it was completely carbonized. The “black” sample in porcelain pot was afterwards placed into the muffle furnace and heated to 540 °C until the ash achieved a light grey-white color. The ash content in the porcelain pot was dissolved in 2 mL of 6 M HCl and filtrated through double filter paper into a 50 mL volumetric flask. Before the measurements, three different known concentrations of tested metals were prepared to make calibration curves. Results were recorded by the Varian SpectrAA 220 atomic absorption spectrometer (Mulgrave, Victoria, Australia). The heavy metals concentration in process water filtrates were determined by the same procedure but without ignition pretreatment.

Determination of Bisphenol A concentrations

Bisphenol A was determined in filter pad samples made from undeinked (UP) and deinked pulp (DP) as well as in blank paper samples (B). Paper samples were cut in pieces, and 50 mL of solvent (methanol:water = 1:1) was added to 1 g of sample. The extraction was performed in Soxtherm (O.I. Analytical, College Station, TX, USA) for 4 h.

Determination of total organic compound (TOC) and Total carbon (TC)

Total organic compound (TOC) and total carbon (TC) were determined in filter pad samples using TOC-VCSH analyzer with unit for solid samples SSM-5000A (Shimadzu, Kyoto, Japan).

Determination of the transfer of antimicrobial constituents

The handsheets obtained from the deinking process (B, UP, DP) were tested for their effect on the growth of bacteria *Bacillus subtilis* and fungus *Aspergillus niger*. The test determined whether the paper samples release antimicrobial constituents in quantities that inhibit the growth of the bacteria and fungus, which represents the toxicity of tested papers. Paper samples were cut to a shape of discs having 6 mm in diameter. Microbiological tests were performed according to HR EN 1104 (2002), in two ways:

1. *Bacillus subtilis* suspension (1 mL at 10^4 cell/mL) was transferred to three Petri dishes and flushed with nutrient agar (NA). The paper disc was placed in the middle of the dish. The same procedure was repeated for *Aspergillus niger* (10^5 cell/mL) with malt agar (MA) as the growing media.
2. In three Petri dishes containing nutrient agar (NA), 0.1 mL of *Bacillus subtilis* suspension (10^5 cell/mL) was added and homogenized with a Drigalski spatula. The paper disc was placed in the middle of the dish. The same procedure was repeated for *Aspergillus niger* (10^6 cell/mL) with malt agar (MA) as the growing media. Dishes were incubated for 3 to 5 days at 37 °C for bacteria and at 28 °C for fungus.

After incubation, an inhibition zone (in the growth of flora) indicated the release of antimicrobial constituents. A *Bacillus subtilis* penicillin sensitivity test was performed to confirm the results.

RESULTS AND DISCUSSION

Determination of Heavy Metals

Table 3 shows the obtained concentrations of heavy metals in the tested thermochromic inks. BW ink contained the highest concentration of Fe (20 mg/kg). In printing inks, iron is used in the form of iron oxide yellows (yellow pigment). Exceptional heat resistance makes them suitable for use in printed furniture surfaces and other high light specifications (Leach *et al.* 2007). The GY ink exhibited the highest concentrations of Co (500 mg/kg) and Mn (950 mg/kg). The GY ink contains vegetable oil as ink vehicles (Vukoje *et al*. 2017). Co and Mn salts are used as catalysts (siccatives) for oxypolymerization drying of vegetable oil. Moreover, in GY ink, notably lower concentrations of Fe (7.90 mg/kg) and Zn (3.80 mg/kg) were observed. In printing inks, Zn is used as white pigment and extender in the form of zinc white (ZnO) and zinc sulphide (ZnS). ZnO is a strong UV absorber and self-fungicidal. It discolors with copper compounds, and it becomes yellow when hot or white when cold. It is used as a white extender in many inks (Leach *et al.* 2007). GY ink had the highest concentration of Cr (0.26 mg/kg). Concentrations of other cations were less than 1 mg/kg of ink. In the BB ink, the highest concentrations of Co (700 mg/kg) and Mn (1100 mg/kg) were measured. Zn and Fe were present at concentrations of 1.80 and 10.0 mg/kg, while other cations were present at concentrations lower than 1 mg/kg. Thermochromic offset printing inks contain remarkably lower amounts of heavy metals than digital offset printing inks (Barbaric-Mikocevic *et al*. 2004).

Table 3. Concentration of Heavy Metals in Used Thermochromic Offset Inks

Heavy Metals (mg/kg)	Thermochromic Printing Inks		
	BW	**GY**	**BB**
Pb	0.20	0.20	< 0.10
Cd	< 0.01	< 0.01	< 0.10
Cu	0.53	0.45	0.45
Zn	1.60	3.80	1.80
Fe	20.0	7.90	10.0
Mn	0.35	950	1100
Ni	1.30	0.34	0.44
Cr	0.12	0.26	0.14
Co	0.03	500	700
As	0.01	0.01	< 0.01

According to Rožić *et al.* (2005), certain cations present in paper can cause problems in paper usage or in paper recycling. Metal (Fe, Cu, and Mn) hydroxides/oxides in various additives catalyze paper acidification. During paper recycling, multivalent metal cations reduce swelling of fiber, due to reduction of electrostatic double layer at surfaces within the fiber microstructure. Reduced swelling inhibits bonding of fibers to each other and therefore paper sheets become weak. Taking into account that additives for paper production are not of high chemical purity, it is possible that some elements are introduced as impurities in calcium carbonate, which is used as filler (Rožić *et al.* 2005). Mertoglu-Elmas (2017) showed that presence of heavy metals in recycled corrugated board papers originates from chemical additives used in the process of pulp and paper manufacturing, as well as the finishing operations of paper, such as Pb, Cd, Zn, and Cu derived from colored pigments.

Table 4 shows the obtained concentrations of heavy metals in handsheet ashes of blank (B), before (UP) and after (DP) flotation, flotation froth, and process water filtrates that originated from blank (paper + deinking chemicals) and after flotation samples. The B sample contained the highest concentrations of Zn (144 mg/kg) and Fe (78.2 mg/kg), while the concentration was 7.10 mg/kg for Co and 12.2 mg/kg for Mn. Due to very high concentrations of Zn and Fe in B sample, it may be concluded that printing substrate is the main source of these metals. The high concentration of Zn can be explained by the Zn-based compounds used in paper production as fillers for the enchainment of some optical properties of paper such as opacity (Mertoglu-Elmas 2017). The UP sample contained slightly higher concentrations of Zn (165 mg/kg), Mn (16.2 mg/kg), Ni (0.87 mg/kg), and Co (11.7 mg/kg) than the DP sample. Larger concentrations of these cations are the result of thermochromic inks. The Pb, Cd, Cu, and Fe concentrations were lower in the UP and DP samples than in the B sample. Zn, Fe, Mn, and Co concentrations were reduced in the obtained handsheet after flotation (DP). However, in this sample (DP), the concentrations of Zn, Ni, Mn, and Co were greater than in the B sample due to print particles retention (*i.e.*, poor deinkability). Moreover, the determined quantities of Pb and Cd metals in the B, UP, and DP samples were all below maximum permitted limits in the CEPI/CITPA/CEFIC/FPE Industry Guideline. Even though current EU legislation on paper and board food contact materials, at the moment, does not provide specific migration limits for other determined heavy metals, the authors believe that the levels of determined heavy metals (Cu, Zn, Fe, Mn, Ni, Cr, Co, As) could be of potential threat especially if recycled paper is to be brought in direct contact with moist and/or fatty food.

In our previous research, microscopic imaging revealed that flotation froth mostly contained ink particles originating from GY and BB prints, while the BW ink particles were observed in a smaller amount. Undeinked pulp (UP) handsheet contained mostly BB and GY ink particles while deinked pulp (DP) handsheet was cleaner but also contained mainly BB and GY ink particles. Since only small amounts of BW ink residues were present in all samples, their poor visibility was due to deformation and because of their mechanical damage during pulping. It was also assumed that BW ink particles (microcapsules) were retained in aqueous suspension (Vukoje *et al.* 2016). As deinking froth contained mainly short fibers, fillers, ink particles, and deinking additives, the highest concentrations of Zn, Mn, and Co that were found in GY and BB inks, were also present in filtration froth filter pad. A high concentration of Zn cations in filtration froth filter pad may originate from additives present in paper.

Determined concentrations of cations in process waters show that deinking does not affect heavy metals release from thermochromic inks. In process water filtrates, Zn and Fe were present in very low concentrations, while the concentration of other heavy metals was negligible (Table 4). Since thermochromic ink particles are difficult to separate from the pulp suspension, the release of heavy metals in process water is minimal.

Table 4. Concentration of Heavy Metals in Handsheets (B, UP, DP) and Process Water Filtrates Obtained from Blank and After Flotation

Heavy Metals (mg/kg)	Maximum Permitted Quantity* (mg/kg)	Samples Obtained from Deinking Process				Process Water Filtrate	
		Blank (B)	Undeinked pulp (UP)	Deinked pulp (DP)	Filter pad – flotation froth	Blank (chemicals and paper)	After flotation
Pb	3.0 **	2.60	1.70	1.60	4.20	0.01	<0.01
Cd	0.5 **	0.12	0.09	0.09	0.23	<0.01	<0.01
Cu	not established	2.60	2.40	2.50	4.90	0.01	0.01
Zn	not established	144	165	147	458	0.15	0.33
Fe	not established	78.2	75.9	71.2	142	0.08	0.17
Mn	not established	12.2	16.2	15.4	32.1	0.02	0.02
Ni	not established	0.67	0.87	0.79	1.75	<0.01	<0.01
Cr	not established	1.85	1.90	1.85	3.80	<0.01	<0.01
Co	not established	7.10	11.7	10.7	24.7	0.01	0.02
As	not established	<0.01	<0.01	0.01	0.01	<0.01	<0.01

* Purity requirements set out in the CEPI/CITPA/CEFIC/FPE Industry guideline.
** The concentration of these metals is usually determined in an aqueous extract according to EN 12498. Also, the materials are subjected to tests only if, in normal circumstances, the end use of the paper and board is known to be for contact with moist and/or fatty food.

Results imply that printing substrate is the main source of heavy metals concentrations (Fe, Zn) in the process waters produced by deinking flotation. In addition to this conclusion, it can also be assumed that Fe concentrations in process water may be result of BW thermochromic ink residues present in pulp suspension as described in previous research by Vukoje *et al.* (2016). Concerning the low concentrations of heavy metals in process water, it can be reused and returned into the recycling process.

Determination of BPA, TOC, and TC Content

Table 5 shows the concentrations of BPA, TOC, and TC in filter pad samples. Because no BPA was found in the blank sample, it was concluded that the BPA originated from the thermochromic printing inks. A relatively large reduction in BPA concentration was observed. Filter pads obtained after flotation contained 50% less BPA than the undeinked filter pads. Vinković *et al.* (2017) examined the BPA concentrations in commercially available printing inks where, among others, they also analyzed the same inks we used in this research. Their results showed that BPA was present only in BW thermochromic ink, while GY and BB inks did not contain any BPA.

A slight reduction of TOC and TC in filter pads after flotation compared with those obtained before flotation indicated a very slight decrease in the organic content. From the obtained results it can be concluded that TOC in samples originates from paper, *i.e.* cellulose, while only a small percentage is related to thermochromic printing inks. Small amount of inorganic carbon results from fillers (calcium carbonate) in paper. In our previous study, process water filtrates were examined in terms of TOC and chemical oxygen demand (COD). The obtained values for process water after flotation showed higher organic matter loads than the blank (Vukoje *et al*. 2016).

Table 5. Concentration of BPA, TOC, and TC in Obtained Filter Pads

Filter Pad Sample	BPA (mg/kg)	TOC (%)	TC (%)
Blank (B)	0	35.8	40.0
Undeinked pulp (UP)	15	37.2	40.8
Deinked pulp (DP)	7.5	36.1	40.2

Purity requirements set out in the CEPI/CITPA/CEFIC/FPE Industry guideline specify the limit value for BPA, which is shown in Table 6. However, the latest risk assessment by the European Food Safety Authority (EFSA) on the use of BPA (Bolognesi *et al.* 2015) stimulated the European Commission to strengthen the regulation on the use of BPA in food contact materials (FCMs). A draft regulation by the European Commission's (EC) Directorate-General for Health and Food Safety (DG SANTE) concerning the regulation of BPA in FCMs lowers the specific migration limit (SML) for food contact plastics from 0.6 mg/kg to 0.05 mg/kg (EC 2016). Because the existing SML value for BPA as stated in Industry guideline is derived from the current Regulation EC) 10/2011 on plastics FCMs, it is assumed that new lower SML values for BPA will also be adopted in the paper and board FCM regulations.

The conversion of BPA concentrations to the proposed limits presented in Table 6 was done by taking into account the actual grammage of analyzed filter pads (225 g/m^2) according to Eq. 1.

$$Qa = (Qm \times G)/100000 \qquad (1)$$

where *Qa* is the concentration of substance in paper expressed as mg/dm², *Qm* is the concentration of substance in paper expressed as mg/kg, and *G* is the grammage of paper as expressed as g/m². *Qa* is the maximum quantity of the contaminant allowed in the packaging, if it is assumed that 100% of it will migrate into the food. The BPA content of the analyzed filter pads expressed as mg/dm^2 of material is presented in Table 6.

Table 6. Purity Requirements for BPA in Food Contact Paper and Board and Concentrations of BPA in Filter Pads Obtained from Deinking Process

Substance	**Limit in Food**	**Tested in Paper and Board**	**Filter Pad Sample Measured concentrations of BPA** (mg/dm^2)		
	SML (mg/kg food)	Limit (mg/dm^2)	Blank (B)	Undeinked pulp (UP)	Deinked pulp (DP)
BPA	0.6	0.1	0.0	0.034	0.017
New reduced limit for BPA (from draft regulation)	0.05	0.008			

The converted results indicated that the BPA in the analyzed filter pads obtained before and after deinking flotation were below the existing limits as set in Industry Guideline and current Regulation (EC) 10/2011 on plastics FCMs. However, under the stricter and likely new regulation limits, both analyzed filter pads failed, as the detected concentrations were above the permitted limits (Table 6). The results also showed that deinking flotation did not sufficiently eliminate the BPA content from the pulp to meet the draft regulation's new purity requirements. The presence of BPA in recycled pulp can be of major concern if the paper printed with thermochromic ink is used for production of paperboard where only pulping of paper is conducted, without performance of flotation process. Based on the obtained results for undeinked pulp (UP), it would mean even greater concentrations of BPA that would be left in recycled pulp. Based on the obtained results, in order to improve removal of thermochromic prints residues and toxic compounds, other recycling methods should be investigated.

Determination of Antimicrobial Properties

Components present in paper as fillers (Zn oxide, titanium oxide, heavy metals) or components of thermochromic inks (bisphenol A, heavy metals) may show antimicrobial activities (Munoz-Bonilla and Fernández-García 2012; Lemire *et al.* 2013). In order to examine release and possible transfer of the antimicrobial constituents from recycled paper pulp, microbiological tests were performed.

The total number of sporadic *Aspergillus niger* (Fig. 1a) was determined by counting in a Thomson Chamber and was 1.3×10^7 cell/mL. The total number of *Bacillus subtilis* cells in 1 mL was 1.4×10^9 cell/mL (Fig. 1b). The exposure of *Bacillus subtilis* to penicillin resulted in the formation of a 4-cm diameter inhibition zone (Fig. 1c).

Samples of B, UP, and DP were tested with *Bacillus subtilis* (Fig. 2) and *Aspergillus niger* (Fig. 3). There were no inhibition zones around the paper discs, indicating that the samples did not inhibit microbial growth and that there was no release of any toxic substances from recycled paper pulp. On malt agar, almost no discs were observed because of fungus overgrowth (Fig. 3).

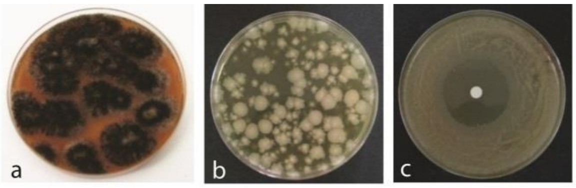

Fig. 1. Growth of fungus *Aspergillus niger* (a) and bacteria *Bacillus subtilis* (b); inhibition of *Bacillus subtilis* by penicillin (c)

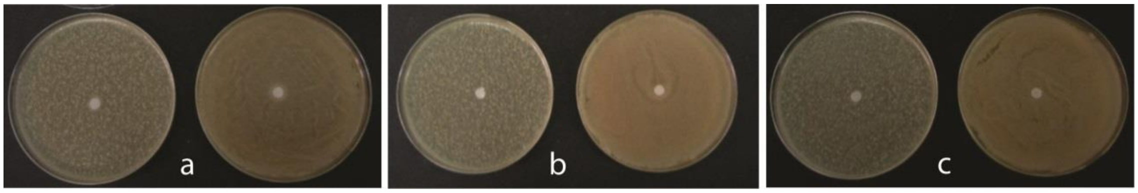

Fig. 2. Sensitivity test for bacteria *Bacillus subtilis* in samples B (a), UP (b), and DP (c). In each panel: (left) 1 mL of suspension flushed with s NA; (right): 0.1 mL of suspension homogenized with a Drigalski spatula

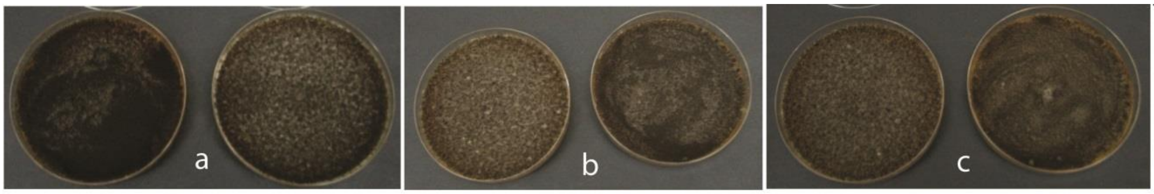

Fig. 3. Sensitivity test for the fungus *Aspergillus niger* in samples B (a), UP (b), and DP (c). In each panel: (left) 1 mL of suspension flushed with s NA; (right): 0.1 mL of suspension homogenized with a Drigalski spatula

CONCLUSIONS

1. Thermochromic printing ink dried by absorption (BW) contained only Fe in higher concentrations, while the other two oxypolymerization drying inks (GY and BB) contain notably higher concentrations of Co and Mn (that originate from their drying catalysts or siccatives).
2. The higher concentrations of Zn and Fe in all samples (B, UP, DP and process water filtrates) originate from printing substrate. The concentrations of Mn and Co in the DP handsheet and filtration froth originate from drying catalysts present in GY and BB inks.
3. Considering very low concentrations of heavy metals in process waters, they can be reused in recycling process.
4. BPA originated from BW thermochromic ink. The reduction of only 50% of BPA was noticed in the samples after flotation, which can be explained due to poor deinkability of thermochromic inks.
5. According to new stricter limits of maximum permitted quantity of BPA in FCMs, both analyzed samples failed the purity requirements, as both detected concentrations were

above maximum permitted limits.

6. The growth of *Bacillus subtilis* and *Aspergillus niger* was not inhibited in all tested samples (B, UP, DP), indicating that there was no release of toxic substances, despite the presence of BPA.

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Biodegradation of thermochromic offset prints

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KEYWORDS: Thermochromic offset ink, Biodegradation, Synthetic paper, Recycled paper, SEM, FTIR

ABSTRACT: In this study, biodegradability aspect of thermochromic leuco dye print on two different paper materials were studied using the soil burial test under anaerobic conditions. Printed paper samples were evaluated for changes by visual examination, weight loss measurements, FTIR spectroscopy, SEM, microscopic images, and colorimetric measurements. SEM micrographs indicated that microcapsules on non-absorbent synthetic paper are covered with thicker layer of ink binder, which was also confirmed by the IR spectra. Therefore, the microcapsules on SEM micrograph aren't visible. SEM analysis shows significant penetration of the binder in the structure of absorbent recycled paper, making the microcapsules more visible even though they are covered with a thinner layer of a binder. Colour degradation of the print on the recycled paper is significant – the colour changes from green to yellow – green. The SEM micrograph shows certain deformation of the microcapsules for the print on recycled paper. Lower degradation was noticed for the print on synthetic paper for which the obtained SEM micrograph indicates destruction of the binder and possible interactions of bacteria with microcapsule at a place of resulting cracks. FTIR spectra show that vegetable oil in ink vehicle was oxidized on all prints during biodegradation test.

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Introduction

Smart polymers or stimuli-responsive polymers undergo large reversible changes, either physical or chemical, in their properties as a consequence of small environmental variations, such as temperature, optical wavelength, absorbed gas molecules or pH values (Larrucea and San Roman 2014). One of the examples of smart polymers is thermochromic materials. Thermochromic materials have a wide range of applications, and their development is still in progress. Each of these applications requires a specific set of material properties and deeper understanding of the physical and chemical background. In thermochromic materials, light can interact with materials in the form of reflection, absorption or scattering (Seeboth and Lotzsch 2013). In thermochromic leuco dye–developer–solvent system thermochromic effects are based on changes of absorption caused by molecular interactions of the incorporated functional dye within its microenvironment (Aitken et al. 1996; White, LeBlanc 1999; MacLaren et al. 2003; Seeboth et al. 2007). Leuco dye–developer–solvent systems consist of a chromogenic compound (leuco dye), developer and solvent. The thermochromic effect is caused by the formation of leuco dye–developer complexes in a reversible equilibrium redox reaction between leuco dye and developer. The reaction is triggered by interactions between the complex and the solvent during the melting or crystallization process (Seeboth et al. 2007). The most common electron-donating chromogenic compounds are phenylmethane and fluoran derivatives bearing a lactone ring moiety. In the lactone ring-closed state these so-called leuco dyes or colour formers are either colourless or weakly yellow coloured. Leuco dye–developer–solvent systems are coloured in the solid state and transform on heating above the melting temperature of the solvent into a colourless liquid (Seeboth and Lötzsch 2008). Colour developers are usually weak acids (bisphenol A, octyl phydroxybenzoate, methyl p-hydroxybenzoate, 1,2,3-triazoles, and 4-hydroxycoumarin derivatives) while long – chain alkyl alcohols, esters, and acids are commonly used as solvents (White,LeBlanc 1999; MacLaren et al. 2003).

Thermochromism can appear in all different classes of polymers: thermoplastics, duroplastics and gels, as well as thermochromic colouring agents for toys, temperature indicators for plastic and printing inks, for paints, etc.

Printing still plays an important role in everyday life. There is an increasing demand for printing inks, as well as for traditional and for functional printing inks, such as thermochromic printing inks (Robert 2015).

Commercially available thermochromic printing inks based on leuco dyes are consisted of microencapsulated leuco dye–developer–solvent systems and a resin binder (Tang and Stylios 2006; Seeboth and Lötzsch 2013). The microencapsulated thermochromic pigments usually have medium particle size of a few micrometres, which is about ten times larger than the particle size of conventional pigment particles (Seeboth and Lötzsch 2013). Microcapsules are dispersed in a binder. For example, adding microcapsules with a blue leuco dye–developer complex to a conventional yellow ink will result in a green ink formulation. In its cooled state, the printed ink layer will be green, and once warmed above its activation temperature (TA), it will revert to yellow as the leuco dye becomes clear or translucent (Homola 2008). The most widely used system for micro-encapsulation of thermochromic and photochromic inks involves urea or melamine and formaldehyde systems (Aitken et al. 1996), gelatine–gum arabic and epoxy resins (Fujinami 1996).

Printing inks can contain different chemical additives for the improvement of their performance, such as catalysts, antioxidants, adhesion promoters, amine stabilizers, antifoam agents, biocides, chelating agents, dispersing agents, siccatives for optimized drying, flow agents, gallants, ink stabilizers, optical brighteners, photoinitiators, waxes, UV stabilizers, wetting agent. Biocides are needed for aqueous inks to control microbial growth, but in offset letterpress technology can be used in fountain solutions as well (Leach et al. 2007; Pekarovicova and Husovska 2016). The use of biocides can affect microbial degradation of printed products.

As the amount of waste increases; it becomes one of the major environmental problems. Paper based products are one of the basic components of the municipal solid waste. As the organic recycling increases over past years as a potential method in waste management, thus it is crucial to examine it for new materials (COST Action FP1003 - BioMatPack 2015). Due to the increasing use of thermochromic materials in smart packaging applications and other graphic products, it is necessary to examine the possibility of their waste disposal.

Biodegradation is defined as a complex process, where decomposition of organic substances is carried out by the action of microorganisms and/or abiotic factors. This action leads to the recycle of carbon, the mineralisation (CO_2, H_2O and salts) of organic compounds and the generation of new biomass and/or energy. Biodegradation consists of three stages: biodeterioration, biofragmentation and assimilation (Lucas et al. 2008). In the past decade, it becomes the subject of research as a method of waste disposal.

As the previous research showed that thermochromic offset printing inks are very difficult to recycle by conventional chemical deinking method (Vukoje et al. 2016a), the anaerobic soil burial experiments were conducted in order to test their biodegradability and to explore their possibility for organic recycling. When it comes to unprinted paper samples, the few studies showed that paper products are anaerobic biodegradable in laboratory-scale landfill reactors (De la Cruz et al. 2014; Wang et al. 2015) or aerobically by composting (Venelampi et al. 2003; López Alvarez et al. 2009). There is lack of information about influence of printing inks on biodegradation of paper. Stinson and Ham (1995) studied a decomposition of printed and unprinted newspaper. Based on the generated amount of methane, obtained results indicate that the printing ink did not inhibit the amount or affect the rate of methane production from cellulose in newspaper. Previous studies about thermochromic inks mainly investigated only the chemical composition of the leuco dyes in the microcapsules and their changes (Hajzeri et al. 2015; Raditoiu et al. 2016; Panák et al. 2017). For the commercially available thermochromic printing ink a different studies have been conducted for the purpose of their colorimetric properties and UV stability (Kulčar et al. 2010; Kulčar et al. 2011; Friškovec et al. 2013; Rožić et al. 2015). There are no available data on the biodegradation of thermochromic prints or thermochromic materials in general. In addition to this study, a biodegradation survey of UV screen printing ink on cardboard was conducted. Research has shown that applied thermochromic UV inks reduces the degree of cardboard biodegradation (Vukoje et al. 2016b).

Materials and Methods

Printing substrate and printing ink

Two different paper substrates (synthetic and recycled) printed with offset thermochromic ink were exposed to anaerobic soil conditions. Synthetic paper (Yupo) is extruded from polypropylene pellets. This type of paper is commonly used for different graphic products such as posters and book covers or in packaging application. Recycled paper (Mondi) containing 33 % of recycled cellulose fibres was also used. These two papers were selected due to their different absorption capacity, which was determinate with the air permeability measurements explained in the next section.

For the printing of paper samples one leuco dye based thermochromic offset printing ink was used (Chromatic Technologies, Inc.). The activation temperature of thermochromic ink is 45ºC. Below its activation temperature, the print was coloured in green and above its activation temperature the print was coloured in yellow (GY). Used ink was vegetable oil-based. The printing trials were carried out using Prüfbau Multipurpose Printability Tester. The quantity of 1.5 cm^3 ink was applied on the distribution rollers while printing was carried out with the printing force of 600 N. All the samples were printed in the full tone.

Air permeability measurements of paper samples

The air permeability measurements were conducted using Frank Bendtsen Roughness Tester device. Average values of ten measurements are presented as mean±SD. The device registers the amount of air that comes out of the ring into the atmosphere per time unit [mL / min].

Soil burial experiments

Laboratory soil burial experiments were conducted at room temperature 25±2 °C by placing the printed paper substrates (size 4 x 5 cm) horizontally in field soils in in 2L volume laboratory glass containers. The paper substrates were buried for 32, 50 and 150 days. The water content of the soil was adjusted to 40 % of its maximum water retention capacity. The commercial available reagent *Anaerocult A* (*Merck*) was used in order to allow the development of anaerobic conditions.

Visual evaluation

A method of visual evaluation can be used in order to describe biodegradation as a first indication of microbial activity in the terms of visible surface changes such as formation of holes or cracks, de-fragmentation or changes in colour but it does not prove the existence of biodegradation process in terms of metabolism (Shah et al. 2008). Photos of paper samples were taken from the containers in sampling times in order to visually evaluate the prints degradation over time.

Microbial growth assay

The total number of microorganisms in the sample which could have the ability to degrade and deteriorate studied printed paper samples were determined by the defibering method and expressed as number of colony forming units (CFU) per 1 g of a sample. A nutrient agar media was used for bacterial growth. The growth of bacteria was evaluated over 7 days, at 37 °C. Average values of five measurements are presented as mean±SD. The total number of anaerobic bacteria and facultative anaerobes in the samples after 150 days of biodegradation in the soil was determined.

Weight loss measurement

Samples degradation was monitored by measuring the weight of printed paper samples before and after incubation in the soil containers. The samples were taken out and rinsed with distilled water to remove soil particles from the surface. Then they were dried on air and weighed. The weight loss percentage was calculated according to *Eq 1*:

$$W = \frac{m_0 - m_1}{m_0} \cdot 100\% \qquad [1]$$

where, m_0 is the initial weight of the sample, m_1 is the final weight of the sample after degradation.

Scanning electron microscopy

The printed thermocromic surface on synthetic and recycled paper before and after 150 days of biodegradation was monitored using a FE-SEM Jeol 7000 field emission scanning electron microscope.

Fourier transform infrared (FTIR) spectroscopy

Infrared spectra in transmission and attenuated total reflectance (ATR) mode were measured using a Bruker Equinox 55 interferometer. The transmission IR spectra of the thermochromic printing ink were obtained at 25 °C and 50 °C from the sample smeared in a thin layer on the surface of the KBr pellet. For the temperature dependent measurements a Bruker heating device with a temperature controller type A599 was used. The IR spectra were recorded in the spectral range between 4000 and 400 cm^{-1} at 4 cm^{-1} resolution and averaged over 32 scans. In the final spectrum the baseline was corrected.

The ATR spectra of the paper samples printed with the ink before and after the soil burial were measured using the PIKE MIRacle ATR sampling accessory with a diamond/ZnSe crystal plate. The spectra were taken in the single reflection mode, over the spectral range 4000-600 cm^{-1} at 4 cm^{-1} resolution. Thirty two scans were averaged for the final spectrum, which was also corrected using the ATR correction function within the OPUS 6.0 program.

Microscopy

Microscopic images of thermochromic prints before and after biodegradation tests were taken using Olympus BX51 System Microscope under a magnification of 2000x.

Colour measurement

The colour measurement was carried out using Konica Minolta Spectrophotometer CM – 3600d at temperature of 23±2 °C in spectral range from 360 – 740 nm in 10 nm steps. The colour of prints before and after biodegradation test was determined according to the CIE *L*a*b** system. The reflection d/8° geometry, D50 illuminant and 2° standard observer were used in these calculations. Colour differences were calculated using *Eq 2*:

$$\Delta E = [(L_2 - L_1)^2 + (a_2 - a_1)^2 + (b_2 - b_1)^2]^{0.5} \qquad [2]$$

Results and Discussion

Determination of air permeability of tested samples

Table 1 shows the air permeability of the paper samples and prints. Results show that synthetic paper is not absorbent, unlike recycled and thus ink can penetrate into the structure of recycled paper but it cannot penetrate into the synthetic paper. Application of print onto the surface of recycled paper resulted in the reduction of his permeability from which it may be concluded that the diameter of pores decreases. Therefore, penetration of binder into the structure of the recycled paper is possible.

Visual evaluation

Fig 1 shows the thermochromic prints before and after biodegradation. Print on synthetic paper, although not significantly degraded, shows a small change of colour, showing yellow colour. Print on recycled paper is visibly degraded after 150 days and becomes yellow – green.

Microbial growth assay

Table 2 shows the number of bacteria in the soil sample and on the samples of paper after 150 days of biodegradation, anaerobic bacteria and facultative anaerobes. In the recycled paper, greater number of bacteria was observed compared to the soil sample. In the synthetic paper the number of bacteria is smaller.

Synthetic paper remained unchanged on its unprinted side, while on the print small colour degradation was noticed. Therefore, there is also a small change in weight loss after 150 days of biodegradation (*Table 3*). Weight loss for print on recycled paper is higher (*Table 3*). This

Table 1 - Air permeability of the paper samples.

Sample	mL/min
Synthetic paper	0.0±0.0
Synthetic paper - print	0.0±0.0
Recycled paper	619.0±22.0
Recycled paper-print	129.0±8.6

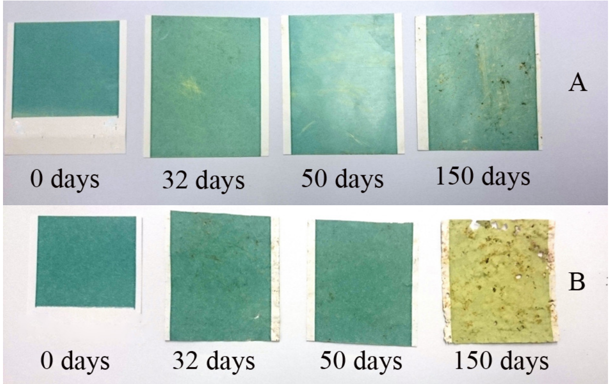

Fig 1 - Visual observations; Synthetic paper - print before and over 32, 50,and 150 days of biodegradation (a) ; Recycled paper - print paper before and over 32, 50 and 150 days of biodegradation (b).

Table 2 – Number of bacteria in soil and printed paper samples after 150 days of biodegradation.

Sample	**log CFU/g**	
	Facultative anaerobes	**Anaerobes**
Soil	6.4±0.2	5.9±0.3
Synthetic paper - print	6.0±0.4	5.1±0.4
Recycled paper - print	8.0±0.1	7.8±0.2

Table 3 – Weight loss during soil burial.

Sample	**Weight loss, %**		
	Days		
	32	**50**	**150**
Synthetic paper - print	0.00	0.17	0.35
Recycled paper - print	6.02	7.04	25.24

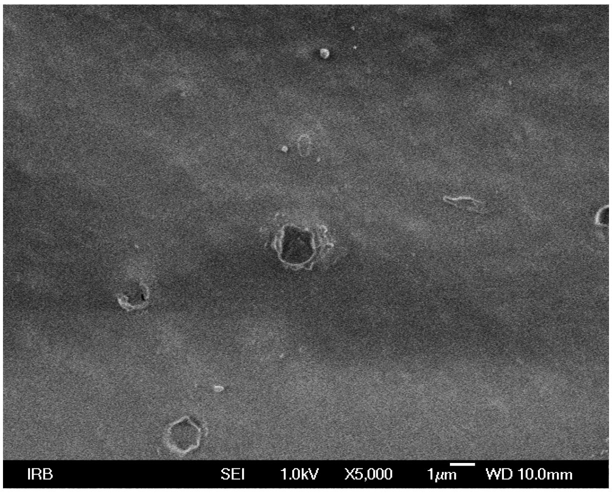

Fig 2 - SEM micrograph of printed thermochromic ink on synthetic paper before biodegradation.

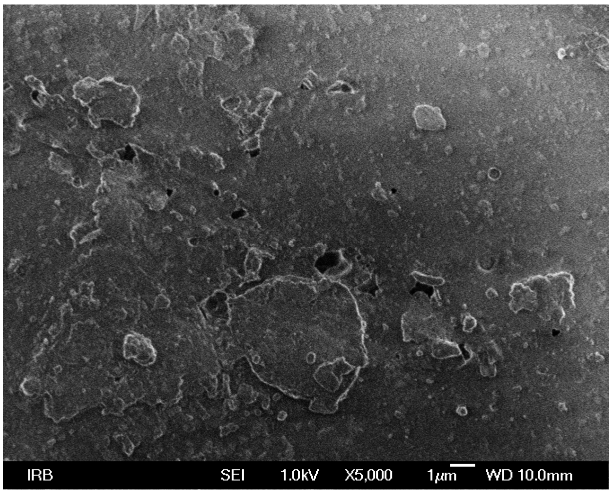

Fig 3 - SEM micrograph of printed thermochromic ink on synthetic paper after 150 days of biodegradation.

can be attributed to different chemical compositions of paper. In recycled paper, the bacteria penetrate from both sides of the paper, unprinted and printed, and use cellulose and print for their metabolism. In the case of synthetic paper the bacteria affect only the print but not the polypropylene since the polyolefins are resistant to microbial attack (Arutchelvi et al. 2008; Leja and Lewandowicz 2010).

Table 3 shows the weight loss measurements for 32, 50 and 150 days after soil burial. Synthetic paper shows almost no changes in weight, less than 0.5 %. For the recycled paper 25.2 % reduction in weight was noticed after 150 days.

SEM

In the case of synthetic paper, the microcapsules are covered with a thick layer of binder which is why they are difficult to notice (*Fig 2*).

For the print on synthetic paper, after biodegradation test, the most visible changes can be connected to the degradation of ink binder since no microcapsules can be detected (*Fig 3*). However, cracks with a diameter of

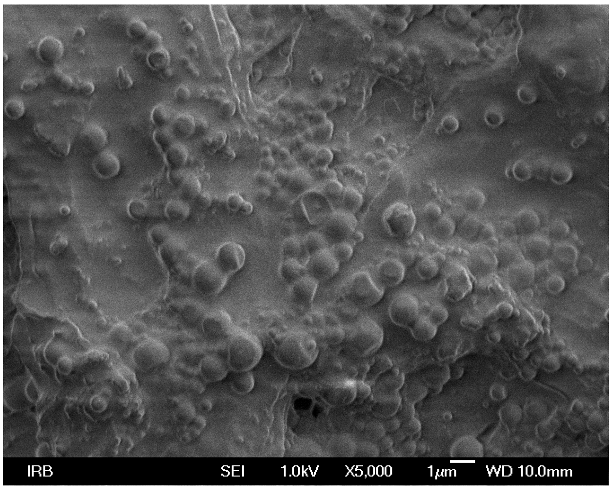

Fig 4 - SEM micrograph of printed thermochromic ink on recycled paper before biodegradation.

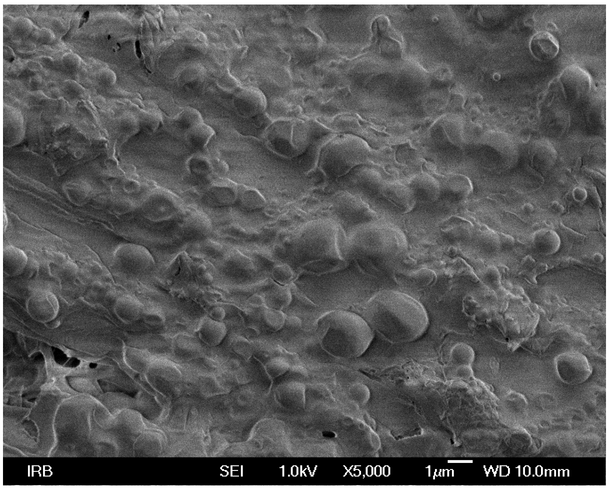

Fig 5 - SEM micrograph of printed thermochromic ink on recycled paper after 150 days of biodegradation.

about 0.1 μm are visible, where significant degradation of ink binder is possible and penetration of the bacteria to the microcapsules.

In the case of print on recycled paper, the microcapsules are visible, due to penetration of binder into the paper structure (*Fig 4*). The microcapsules are covered with a thinner layer of a binder. The sizes of the microcapsules are not uniform. Microcapsules of about 1 μm in diameter are visible, but also there are considerably smaller microcapsules noticed, which are located in the paper structure. Therefore, the penetration of microcapsules into the structure of recycled paper is possible.

After 150 days of biodegradation, the changes in the shape of macrocapsueles for the print on recycled paper can be seen. Before biodegradation test (*Fig 4*), the microcapsules are in the form of regular circle forms, but after 150 days of biodegradation the SEM micrograph show thaht they are forming irregular forms or being flattened (*Fig 5*). However, no reduction in their number was noticed.

FTIR spectroscopy

The FTIR spectra of the thermochromic ink were measured at 25 °C and 50 °C (*Fig 6*). Though temperature dependent measurements were followed by the thermally induced change in the sample colour, significant spectral changes in the IR spectrum upon heating were not observed, implying that the obtained vibrational bands did not originate from the thermochromic system. Namely, by heating the thermochromic composites, the IR spectral changes indicate changes in the molecular structure of the components responsible for the colour change (Hajzeri et al. 2015; Raditoiu et al. 2016; Panák et al. 2017). Hence in the IR spectrum of the thermochromic system composed of a leuco dye, bands corresponding the COO^- groups (symmetric and asymmetric stretching vibrations) disappear, while the C=O band, characteristic of the colourless lactone form, appears (Hajzeri et al. 2015; Raditoiu et al. 2016; Panák et al. 2017).

Given the similarity between the spectra obtained at both temperatures, the observed vibrational bands most likely originated from the thermochromic ink binders, and were not the result of the vibrational modes of the thermochromic composites within the microcapsules. Although the number of microcapsules is not insignificant (*Fig 4*), the FTIR analysis only shows vibrational modes characteristic for the surface layer, in this case it is the layer of ink binder.

In the IR spectra, bands characteristic of vegetable oils, common components of the ink binders, were observed (Vlachos et al. 2006; Gomez et al. 2016). The bands at 3010, 2956, 2921 and 2852 cm^{-1} were assigned to the stretching modes of CH, CH_2, and CH_3 groups in aliphatic chains of fatty acids, while the carbonyl stretching band at 1741 cm^{-1} accompanied by the bands at 1234, 1160 and 1100 cm^{-1} pointed to the ester group. A broad band in the 3500–3100 cm^{-1} range was attributed to the OH stretching.

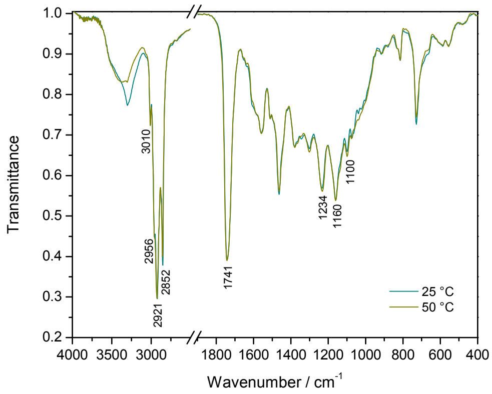

Fig 6 - FTIR spectra of the thermochromic offset ink at 25 ºC and 50 ºC.

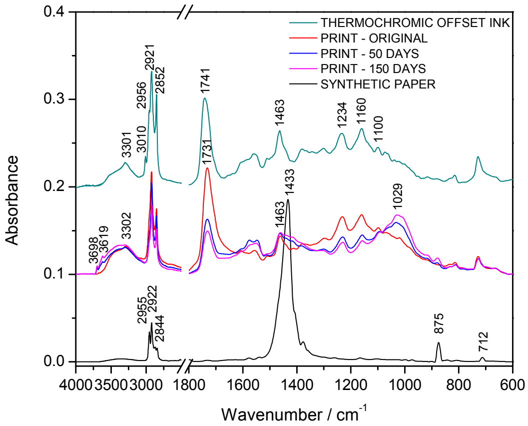

Fig 7 - FTIR spectra of the thermochromic ink, neat synthetic paper and prints of thermochromic ink on synthetic paper before and after 50 and 150 days of biodegradation.

The IR spectrum of the thermochromic ink was compared to the IR spectra of prints on the examined papers – before and after 50 and 150 days of biodegradation (*Fig 7 and 8*). Also the spectra of the unprinted papers were also presented.

In the IR spectrum of the synthetic paper (*Fig 7*) the obtained bands were associated with the polypropylene (2960–2840, 1433 cm^{-1}) and calcium carbonate (875, 712 cm^{-1}), while beside calcium carbonate (873, 709 cm^{-1}) distinctive bands of cellulose (1426, 1160–1000, 898 cm^{-1}) contributed to the IR spectrum of the recycled paper (*Fig 8*) (Proniewicz et al. 2002). The broad band around 3335 cm^{-1} in the spectrum of the recycled paper were assigned to the OH stretching mostly of hydroxyl groups in cellulose, while a weak broad band at 1642 cm^{-1} confirmed also the presence of water.

In the IR spectra of the thermochromic ink print on both of the papers, the band at 3010 cm^{-1} was missing, most likely due to oxidative drying of the ink. This band was assigned to the C–H stretching of the *cis*-double bond (=C–H) in the vegetable oil (Gamage et al. 2009), for which was assumed to participate in reaction with atmospheric oxygen promoting polymerization during printing (HUBER Group 2013). The IR spectra of the thermochromic ink on the recycled and synthetic paper were very similar, although the difference in intensity indicated a thinner layer of the thermochromic ink on the recycled paper when compared to the synthetic paper. Moreover, a significant contribution of the cellulose bands, especially in the 1450–1200 and 1160–1000 cm^{-1} range was obtained in the spectrum of the ink print on the recycled paper, which was in agreement with the proposed penetration of the ink into the recycled paper. The carbonyl stretching band of the thermochromic ink at 1741 cm^{-1} shifted towards 1731 cm^{-1} and 1732 cm^{-1} for the prints on the synthetic and recycled paper, respectively, implying ester oxidation.

In the IR spectra of the ink prints buried in the soil, a slight broadening and increase in intensity of the O–H stretching band around 3300 cm^{-1} was observed, indicating formation of hydroxyl groups, most likely in the vegetable oil biodegradation products, such as glycerol. The spectral changes were also observed around 1450 cm^{-1} and 1000 cm^{-1} for the degraded prints on both papers. The intensity increase of these broad bands in the spectra of the ink print on the recycled paper could be attributed to cellulose due to thinning of the ink layer on the paper surface, caused by long term degradation of the ink binder. Nevertheless, the same was observed for the prints on the synthetic paper, rather implying association of these bands with the biodegradation products. Thus the former band (~1450 cm^{-1}) was assigned to the alkyl CH_2 bending and the latter band (~1000 cm^{-1}) to the C–O stretching. Although to a lesser extent, silicates adsorbed on the paper from the soil could contribute to the broad band at 1029 cm^{-1}. The presence of silicates on the surface of the buried samples, was additionally indicated by weak bands at 3619 cm^{-1} and 3698 cm^{-1} in the spectrum of the ink printed on the synthetic paper (Tinti et al. 2015). However, bands in this spectral range could originate from the secondary oxidized products during biodegradation (Zahir et al. 2014). Since only very weak shoulders in the spectra of the ink on the recycled paper were observed, it could be assumed that that the vegetable oil in ink vehicle was more easily oxidized on the surface of the synthetic paper, then in the ink within the recycled paper structure.

Microscopy

Microscopic images showed that the printed thermochromic ink is composed of blue microcapsules dispersed in classic yellow offset ink. It is also evident that the amount of the microcapsules is greater in the print on the synthetic paper since it is not absorbent, while in the print on the recycled paper thermochromic ink absorbs into its structure, so the thermochromic microcapsules partly penetrate and they are partially covered with the cellulose fibres.

Fig 9a and *9b* shows the microscopic image of thermochromic print on papers before biodegradation, while *Fig 10 – 12* shows prints after 32, 50 and 150 days of biodegradation.

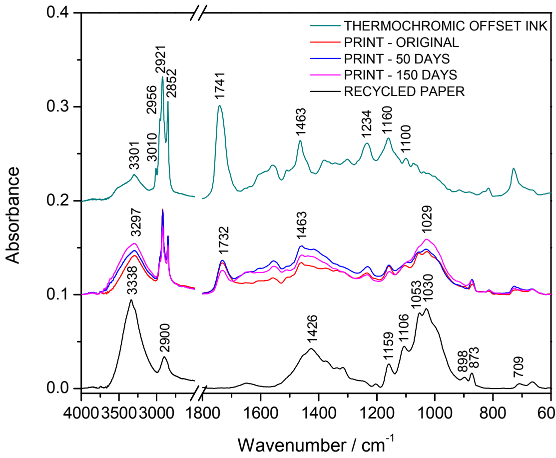

Fig 8 - FTIR spectra of the thermochromic ink, neat recycled paper and prints of thermochromic ink on recycled paper before and after 50 and 150 days of biodegradation.

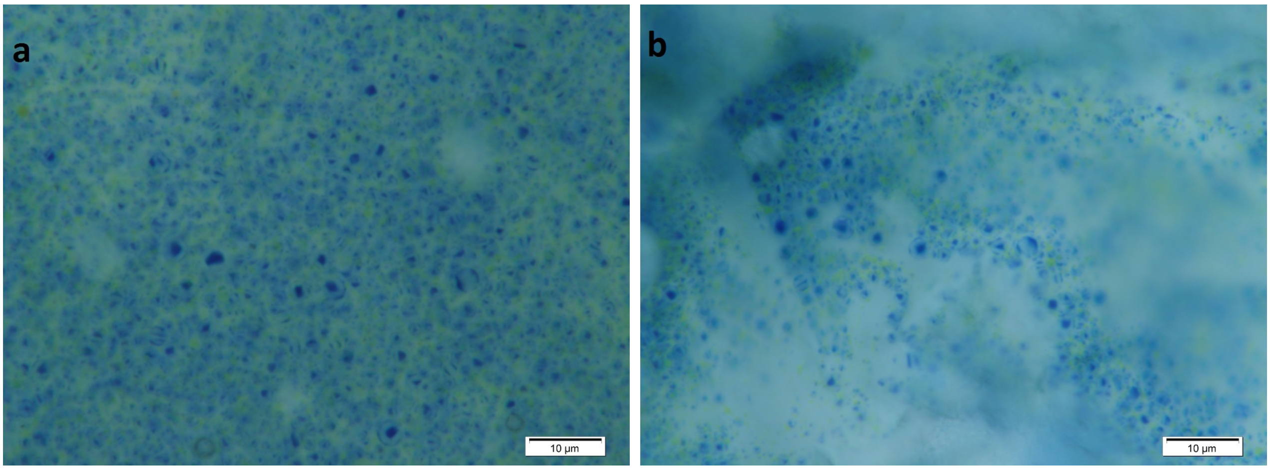

Fig 9 - Microscopic image of thermochromic prints on synthetic (a) and recycled paper (b) before biodegradation.

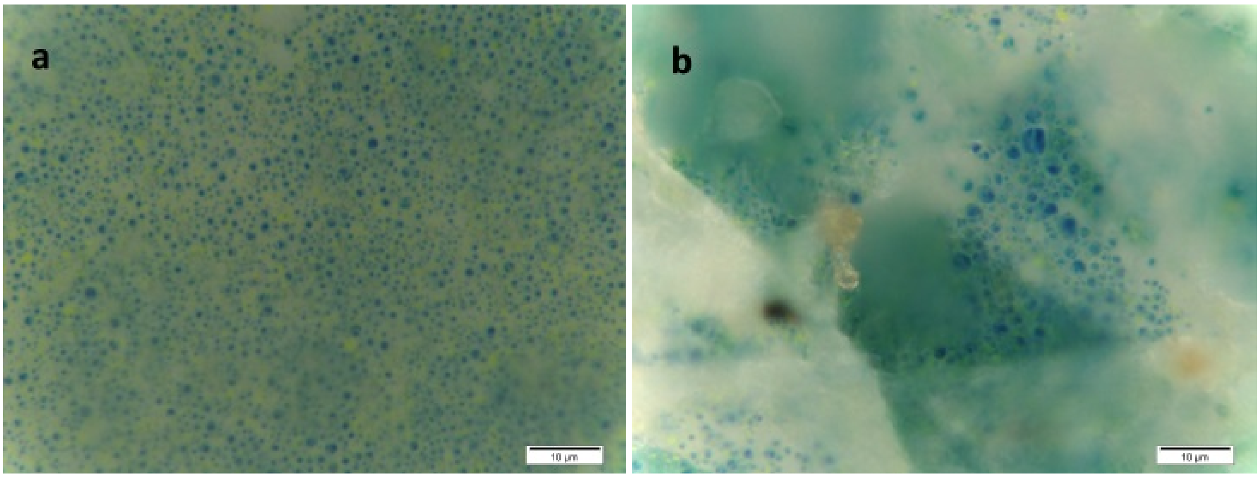

Fig 10 - Microscopic image of thermochromic prints on synthetic (a) and recycled paper (b) after 32 days of biodegradation.

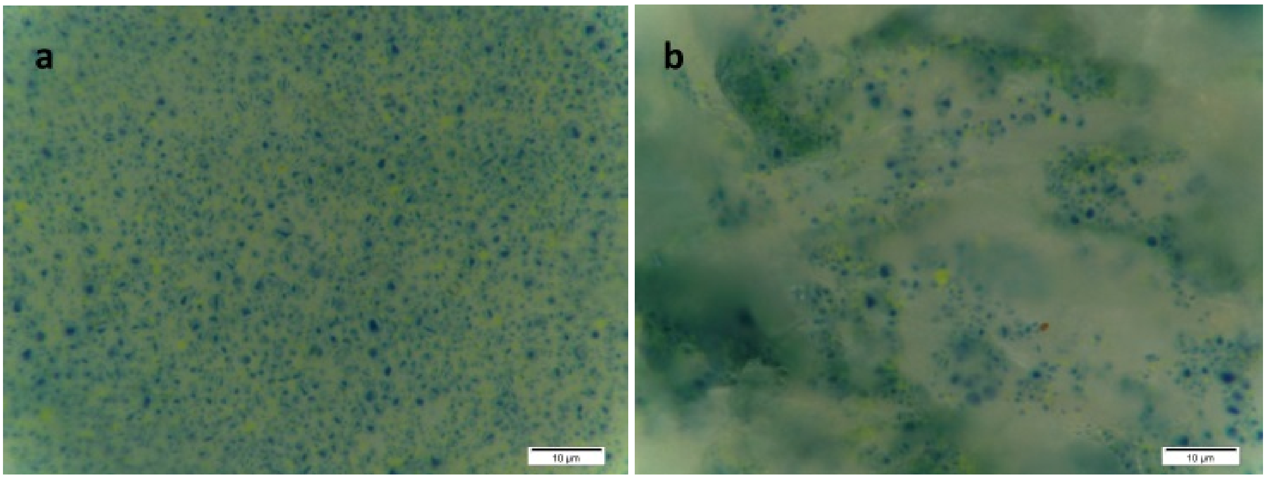

Fig 11 - Microscopic image of thermochromic prints on synthetic (a) and recycled paper (b) after 50 days of biodegradation.

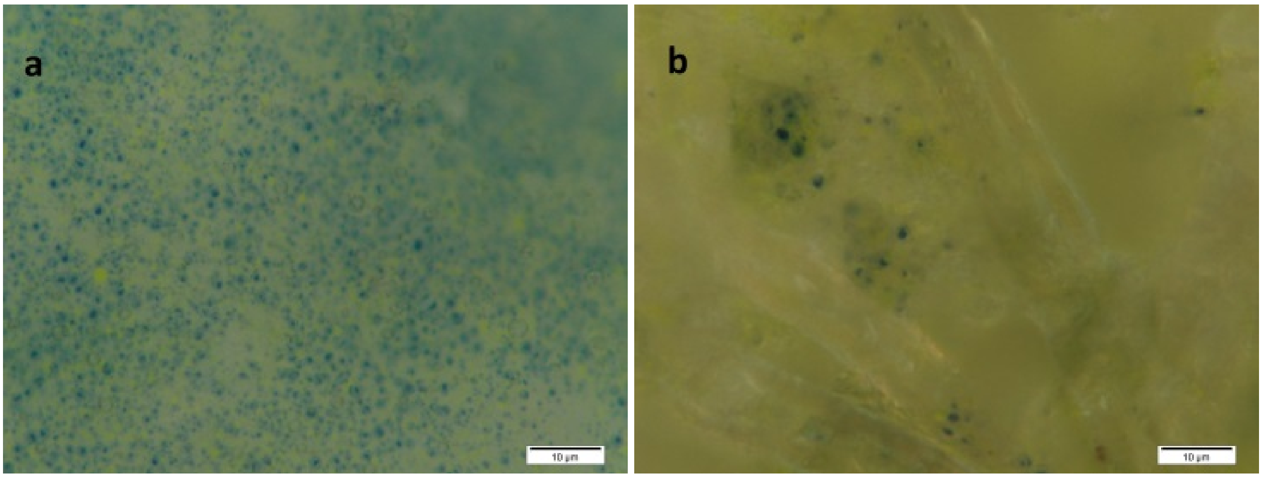

Fig 12 - Microscopic image of thermochromic prints on synthetic (a) and recycled paper (b) after 150 days of biodegradation.

Fig 12b shows significant changes in the colour of the print on the recycled paper after 150 days of biodegradation. This behaviour can be connected due to changes in the shape of the microcapsules, which was confirmed by SEM micrographs (*Fig 5*). Microscopic image shows smaller number of coloured microcapsules; however the other (colourless) microcapsules aren't visible. From this it can be assumed that a certain change in the thermochromic composite within the microcapsule has occurred. Therefore, the sample of thermochromic print on the recycled paper shows a smaller intensities in green colour and higher intensities in yellow colour. The observed colour degradation of print on the synthetic paper is less notable. There is a slight reduction in the number of blue coloured microcapsules and a smaller shift to the yellow area. The colour of prints can be confirmed by the results of colorimetric measurements.

Table 4 - Colorimetric properties of thermochromic prints at 23±2 °C before and after biodegradation and unprinted paper samples.

Days of biodegradation	Synthetic paper				33 % Recycled paper			
	*L**	*a**	*b**	*ΔE*	*L**	*a**	*b**	*ΔE*
0	70.20±0.66	-15.41±0.25	-1.40±0.55	-	65.07±0.19	-13.19±0.23	-7.34±0.44	-
32	73.89±0.90	-15.09±0.55	6.11±0.68	8.37	64.07±0.43	-10.91±0.49	-2.12±0.81	5.78
50	72.42±1.01	-15.48±0.90	3.41±0.87	5.30	66.26±1.27	-11.52±0.53	-2.64±0.90	5.13
150	72.86±1.25	-13.65±1.76	5.02±0.98	7.49	76.89±1.02	-5.98±0.63	21.75±1.20	10.78
Blank untreated paper	95.09±0.08	-0.29±0.02	0.48±0.07	-	90.40±0.09	4.65±0.09	-17.41±0.12	-

Colorimetric measurements

Results of colorimetric values determined on blank (unprinted) paper samples as well as for thermochromic prints before and after biodegradation are presented in *Table 4*. In the CIE L*a*b* colour space the value L* represents the lightness of the colour, the value +a* represents redness, –a* represents greenness, +b* represents yellowness while the value –b* represents blueness.

Blank sample of recycled paper shows a shift of the b* value towards the blue hue (due to presence of optical brighteners) and a lower L* value. Therefore, the colour of blank recycled paper has a significant influence on prints colour reproduction. Hence, as the most accurate parameter, we can observe the change in the a* value of prints on recycled paper. The sample of print on recycled paper before biodegradation is less green compared to the print on synthetic paper which can be attributed to a lower concentration of classic offset yellow ink and a lower concentration of blue microcapsules on the surface of recycled paper. During biodegradation of the prints, a* values becomes more positive, and the change is more notable for the print on recycled paper. A remarkable change for the b* value of the print on recycled paper after 150 days of biodegradation is observed, although this value is affected by the colour of the blank paper. In the case of the print on the recycled paper changes of colour from green to yellow is greater than with the print on the synthetic paper.

Conclusions

A smaller number of bacteria determined on the print on synthetic paper compared to the print on recycled paper were obtained due to low affinity of bacteria to polypropylene. The bacteria only use a print for their metabolism, while in the case of the recycled paper they use both, the paper and the print, which results in different weight loss. Comparing both prints, on synthetic paper the microcapsules are covered with thicker layer of binder making them invisible by SEM analysis. In the case of print on recycled paper, the binder and the microcapsules penetrate into the paper structure. The microcapsules are covered with thinner layer of binder, therefore they are more visible. The SEM micrograph of prints after 150 days of biodegradation showed a certain deformation of microcapsules which probably resulted in significant colour degradation of the print on recycled paper, implying that a change in the thermochromic composite within the microcapsule has occurred. However, the SEM micrograph doesn't show the reduction in their number. The colour degradation of print on synthetic paper was less. SEM micrograph showed only cracks with a diameter of about 0.1 µm, where significant degradation of ink binder is possible and penetration of the bacteria to the microcapsules. The obtained FTIR spectra implied that the ink binder contains vegetable oil. The difference in the intensity of the IR spectra indicated a thinner layer of the thermochromic print on the recycled paper which was also confirmed by the SEM micrographs. The changes in the IR spectra during biodegradation were attributed to the degradation of the ink binder on the surface of the papers. The obtained microscopic images show a smaller number of coloured microcapsules; however the other (colourless) microcapsules aren't visible. A significant reduction of visible coloured microcapsules is noticed after 150 days in thermocromic print on recycled paper. Only a slight reduction of coloured microcapsules was noticed for print on synthetic paper. This behaviour is confirmed by colorimetric measurements. Colour degradation of the print on the recycled paper is significant – the colour changes from green to yellow green – while lower colour degradation was observed for print on synthetic paper. Based on the obtained results, it can be sad that biodegradability of the prints mostly depends on the used paper substrates, penetration of the binder in the paper structure and therefore, the thickness of the ink print.

Acknowledgements

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Solvents interactions with thermochromic print

ABSTRACT

In this study, the interactions between different solvents (benzene, acetone, cyclohexanone, various alcohols and water) and thermochromic printing ink were investigated. Thermochromic printing ink was printed on metal surface. Components of thermochromic printing inks are polymeric microcapsules and classic yellow offset printing ink. Below its activation temperature, dye and developer within the microcapsules form a blue coloured complex. Therefore, thermochromic print is green. By heating above the activation temperature, blue colour of the complex turns into the leuco dye colourless state and the green colour of the prints turns into the yellow colour of the classic offset pigment. The results of the interaction with various solvents show that the thermochromic print is stable in all tested solvents except in ethanol, acetone and cyclohexanone. In ethanol, the green colour of the print becomes yellow. SEM analysis shows that microcapsules are dissolved. In acetone and cyclohexanone, the green colour of the print turns into blue, and the microcapsules become significantly more visible. Thus, the yellow pigment interacts with examined ketones. Based on the obtained interactions it can be concluded that the microcapsules have more polar nature than the classical pigment particles. Solvent-thermocromic print interactions were analysed using Hansen solubility parameters that rank the solvents based on their estimated interaction capabilities.

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thermochromic ink, solvent, microcapsules, interactions

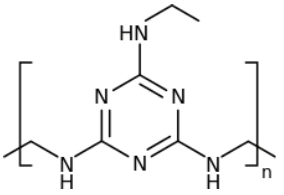
Introduction

The thermochromic ink composition includes a thermochromic microcapsules and an ink vehicle. Thermochromic microcapsules usually consist of at least three components – the colorant, colour developer and solvent. In order to achieve desired effect, the components are mixed in precisely determined proportions and encapsulated in a polymer envelope in order to protect him against external influences (Kulčar et al., 2010).

The thermochromic effect in thermochromic leuco dye-developer-solvent systems is caused by the formation of leuco dye-developer complex. Formation between the colorant (leuco dye) and developer predominates on lower temperatures. Organic solvent at lower temperatures is in solid state, and with the increase of temperature it becomes liquid. The solvent in liquid state causes destruction of the colorant – developer complex resulting in separation of both components. When the thermochromic complex cools again, the solvent becomes solid, and the developer and colorant blend again and the colour returns to its original state (Kulčar et al., 2010; Aitken et al., 1996). The solvent component of reversible thermochromic systems determines the switching temperature of the colour change. Paraffin, long chain alcohols, alkyl amides and alcanoic acids are solvents typically used. Most solvents contain a long hydrocarbon chain (Kulčar et al., 2010; Bamfield, 2010; Seeboth et al., 2007; Christie & Bryant, 2005; Lee et al., 2007).

Colour developers are weak organic acids which act as proton donors. The phenols – bisphenol A (BPA), laurylgallate (LG), ethylgallate (EG) and p-hydroxybenzoic acid methyl ester – are typical developers for reversible thermochromic leuco dye-developer-solvent systems (Seeboth et al., 2007).

Encapsulation with melamine resin is a common method widely described in the literature. Only a few examples of encapsulation with epoxy resin have been reported (Seeboth et al., 2007; Bamfield, 2010). Melamine resin or melamine formaldehyde (also shortened to melamine) is a thermosetting plastic material made from melamine and formaldehyde by polymerization (Figures 1 and 2). Melamine resin capsules have a core-shell geometry. Melamine formaldehyde is very hard and will not break down at high temperature (Bamfield, 2010). Epoxy resins possess better temperature stability in comparison to melamine resins. The term “epoxy”, “epoxy resin”, refers to a broad group of compounds that are characterized by the presence of an oxirane or epoxy ring shown in Figure 3. This is represented by a three-member ring containing an oxygen atom that is bonded with two carbon atoms already united in some other way (Thompson, 2004). Despite the rapid development of instrumental analytical methods, classic analytical approaches still have their place. Solvent precipitation techniques are often used in the first stages of ink analysis to affect separation of an ink into its major component. With regards to the type of printing ink, it is often necessary to choose a solvent that will interact with the individual components of ink. The resulting fractions can be examined using some appropriate identification techniques (Leach & Pierce, 1999).

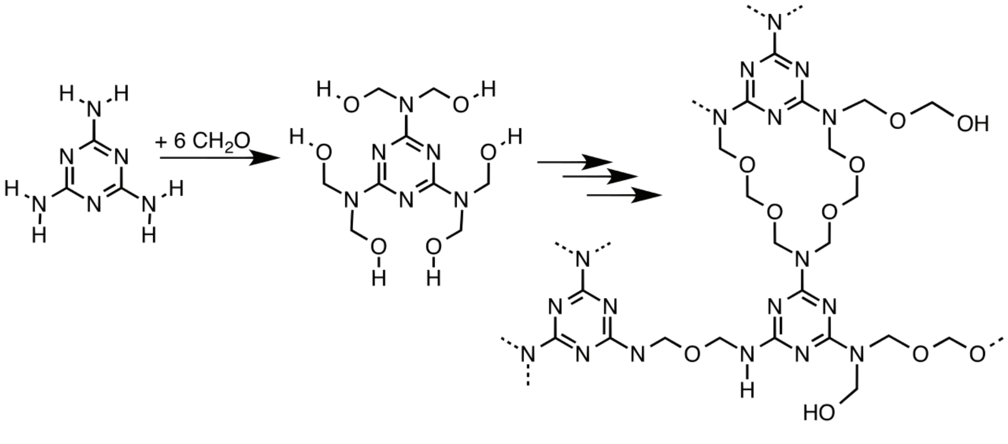


» **Figure 1:** *Structure of melamine resins*

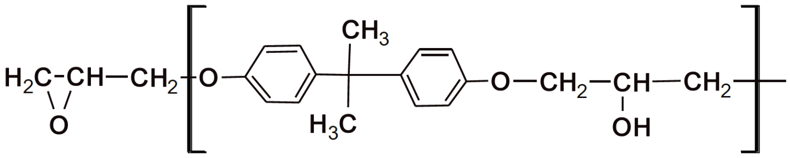
In this study, preliminary studies of interactions between thermochromic printing ink and various solvents have been carried out. The data obtained can be used to determine the ink extraction scheme.

Experimental

One leuco dye based thermochromic offset printing ink was used (Chromatic Technologies, Inc.). The activation temperature of thermochromic ink is 45 °C. Below its activation temperature, the print was coloured in green and above its activation temperature the print was coloured in yellow. Used ink was oil-based containing leuco dye system as colorant. In preparation of the experiment metal plate were used as printing substrate. The printing trials were carried out using



» **Figure 2:** *Chemical reactions leading to melamine-formaldehyde resin*



» **Figure 3:** *Epoxy resin structure*

Prüfbau Multipurpose Printability Tester. The quantity of 1.5 cm^3 ink was applied on the distribution rollers while printing was carried out with the printing force of 600 N. All the samples were printed in the full tone.

After printing, the metal plate was cut into several smaller tiles of 1x1 cm. Plates were immersed in glasses containing 20 cm^3 of solvent. The following solvents were used: acetone, cyclohexanone, ethanol, benzene, cyclohexanol, butanol, pentanol, hexanol, isobutanol, propan-2-ol, ethylene glycol and water. Samples were soaked in solvents for 2 days.

When the samples were dried, the colour measurements were carried out using Konica Minolta spectrophotometer at temperatures of 23 and 50 ±2 °C (below and above its activation temperature). After heating at 50°C, the samples were cooled again at 23 °C in order to examine the preservation of the colour reversibility.

Each print sample was heated by the Full Cover water block (EK Water Blocks, EKWB; Slovenia). The temperature of the copper plate surface was varied by circulation of thermostatically controlled water in channels inside the water block, which was assured to be up to 1 °C accurate in the applied temperature region. The colour of prints was determined according to the CIE L*a*b* system.

The thermocromic surfaces were monitored using a FE-SEM Jeol 7000 field emission scanning electron microscope too.

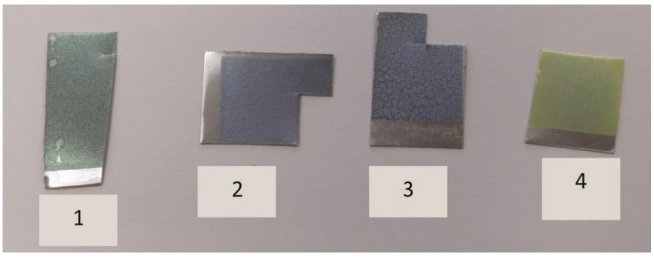
Results and discussion

Photos of samples were taken in order to visually evaluate the prints. Figure 4 shows visual evaluation. Thermochromic prints are stabile in all solvents besides acetone, cyclohexanone and ethanol (Figure 4a). The colour of the print turned from green into yellow after interaction with ethanol. After interaction with acetone and cyclohexanone the colour of the print was changed to blue.

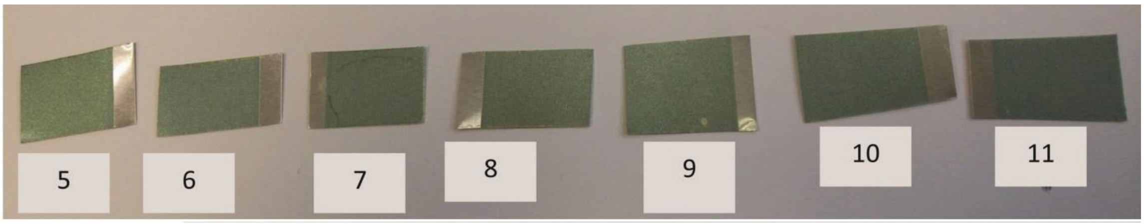
SEM micrograph (Figure 5) shows that microcapsules in thermochromic ink after printing stay more or less covered by the binder.

After interaction with acetone the microcapsules become more visible (Figure 6). Since the colour of the print was changed to blue, it can be assumed that a yellow pigment (or yellow offset ink) was dissolved in acetone.

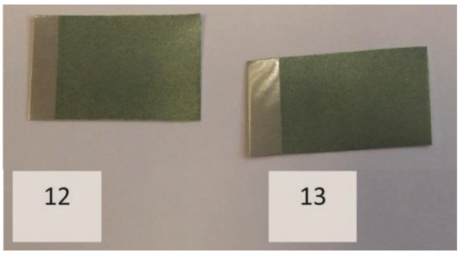
After interaction with cyclohexanone microcapsules become more visible (Figure 7). The diameter of the microcapsules ranges from 1 to 3 µm.



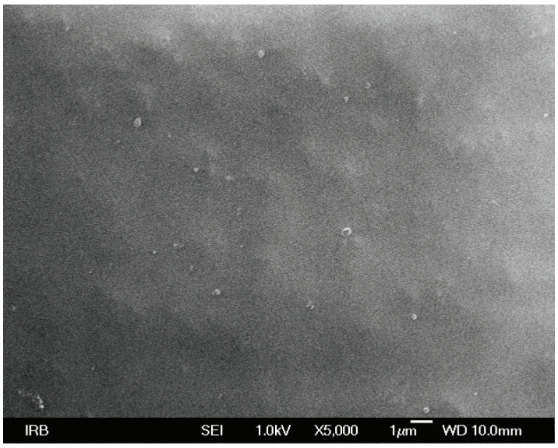
» **Figure 4a:** *Thermochromic prints: 1-orginal sample and after interaction with 2-acetone, 3-cyclohexanone, 4-ethanol*



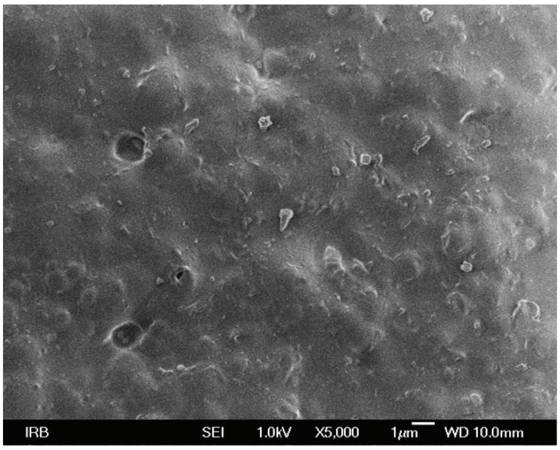
» **Figure 4b:** *Thermochromic print after interaction with: 5-benzene, 6-cyclohexanol, 7-butanol, 8-pentanol, 9-hexanol, 10-isobutanol, 11-propan-2-ol*



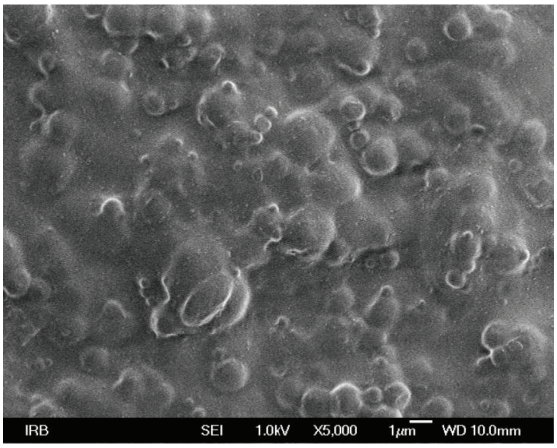
» **Figure 4c:** *Thermochromic print after interaction with: 12-ethylene glycol, 13-distilled water*



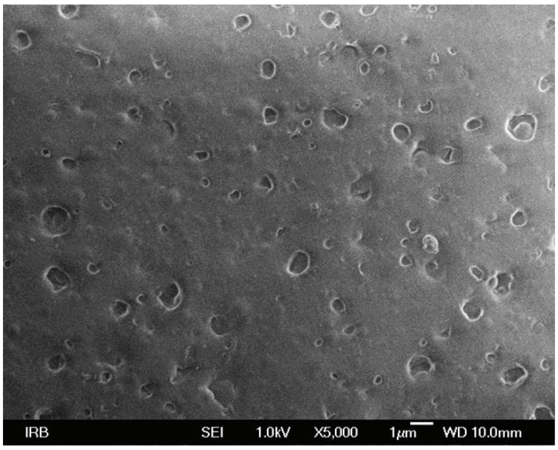
» **Figure 5:** *SEM micrograph of original green thermochromic print (magnification 5000x)*



» **Figure 6:** *SEM micrograph of green thermochromic print after interaction with acetone (magnification 5000x)*



» **Figure 7:** *SEM micrograph of green thermochromic print after interaction with cyclohexanone (magnification 5000x)*

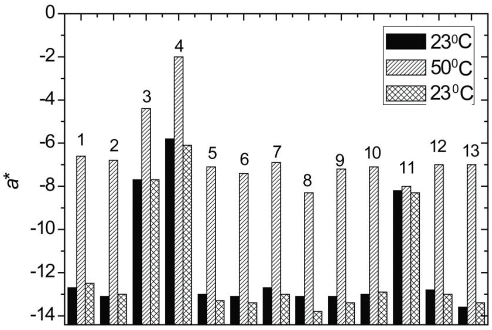


» **Figure 8:** *SEM micrograph of green thermochromic print after interaction with ethanol (magnification 5000x)*

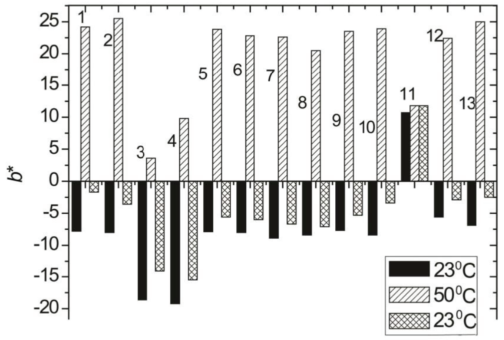
After interaction with ethanol, cracks with a diameter of about 1 µm are formed, so it can be assumed that microcapsules have dissolved in those places (Figure 8).

When a colour is expressed in CIELAB, a* denotes the red/green value. A colour measurement movement in the-a direction depicts a shift toward green. After interaction with solvents, the prints retained the reversibility of the colour change (Figure 9). At the initial temperature of 23 °C all prints except the prints interacting with acetone, cyclohexanone and ethanol have approximately the same a* values. Print samples which have interacted with acetone, cyclohexanone and ethanol have more positive a* values, while the greatest change in a* value was obtained after interaction with cyclohexanone.

Along the b* axis,-b movement represents a shift toward blue, and +b toward yellow. b* values at the initial temperature of 23 °C are practically the same for all samples except for samples interacting with acetone, cyclohexanone and ethanol (Figure 10).



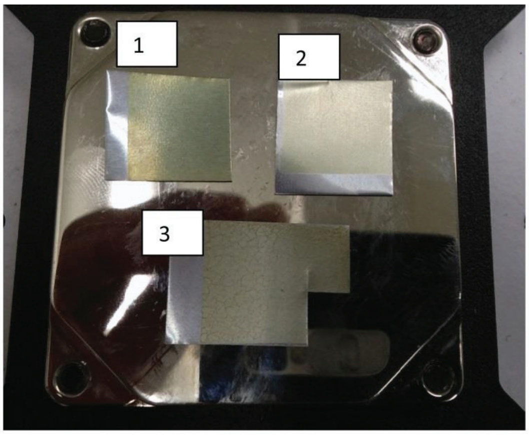
» **Figure 9:** *a* values of the prints at temperatures 23, 50 and repeated cooling to 23 °C (1-orginal and after interaction with: 2- benzene, 3-acetone, 4-cyclohexanone, 5-propan-2-ol, 6-isobutanol, , 8-pentanol, 9-hexanol, 10-cyclohexanol, 11-ethanol, 12-ethylene glycol, 13-water)*



» **Figure 10:** *b* values of the prints at temperatures 23, 50 and repeated cooling to 23 °C (1-orginal and after interaction with: 2- benzene, 3-acetone, 4-cyclohexanone, 5-propan-2-ol, 6-isobutanol, , 8-pentanol, 9-hexanol, 10-cyclohexanol, 11-ethanol, 12-ethylene glycol, 13-water)*

The samples interacting with acetone and cyclohexanone have more negative b* value (greater shift to blue area), while the sample interacting with ethanol has a positive b* value (greater shift to yellow area). After the interaction with acetone, the b* value is slightly more positive compared to interaction with cyclohexanone. A greater shift to the blue area was obtained after interaction with the cyclohexanone. This was also confirmed with SEM micrographs (Figures 6 and 7).

By heating to 50 °C, b* values become positive (shift to yellow area). The prints which were in contact with acetone and cyclohexanone also change their colour in yellow, but the shift to the yellow area was smaller compared to those obtained for samples interacting with other solvents (Figures 10 and 11). This arises from partial but not completely dissolution of yellow pigment in acetone and cyclohexanone.



» **Figure 11:** *The samples of thermochromic prints after interaction with 1) ethanol, 2) acetone and 3) cyclohexanone at 50°C*

The print which was in interaction with ethanol at 50 °C becomes yellow. With repeated cooling at 23 °C, the b* value of the prints (except for the print soaked in ethanol) were much more positive compared to those obtained at the initial temperature which was also 23 °C (Figure 10). It is possible that the microcapsules by heating change their shape, i.e. they spread and need to be cooled.

Varied classification systems were developed to rank the solvents based on their estimated interaction capabilities. Solvatochromic scale base on the solvent properties. The Reichardt's scale, the Snyder scale, Hildebrand and Hansen scale, Abraham scale, COSMO-RS approach are included in solvatochromic scale base (Lesellier, 2015; Hansen, 2000).

Snyder suggested three parameters, x_e, x_d and x_n respectively describing hydrogen bond basicity, hydrogen bond acidity and the solvent dipolarity. This scale is a polarity scale and does not include the dispersive interactions. The sum of the parameters (x_i) is equal to 1 (Lesellier, 2015).

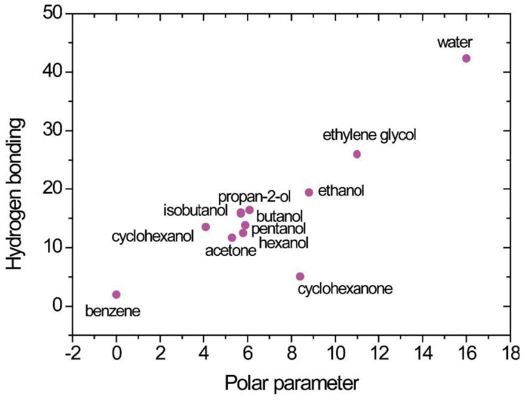
Hansen solubility parameters (HSP) were developed by Charles M. Hansen as a way of predicting if one material will dissolve in another and form a solution. They are based on the idea that "like dissolves like" where one molecule is defined as being 'like' another if it bonds to itself in a similar way. Hansen suggested that the solubility parameter was the sum of dispersive (δ_d), polar (δ_p) and hydrogen bonding (δ_h) (donor and acceptor). Compared to the Snyder scale, Hansen scale includes dispersive interactions, and joined the hydrogen bond acidity and basicity. Hansen solubility parameters can be treated as vector for a point in three dimensions also known as the Hansen space. The nearer two molecules are in this three dimensional space, the more likely they are to dissolve into each other (Hansen, 2000).

Table 1

Hansen solubility parameters (HSP)
(Lesellier, 2015; Hansen, 2000)

Solvent	**δ_d**	**δ_p**	**δ_h**
Benzene	18.4	0	2.00
Cyclohexanone	17.8	8.4	5.08
Acetone	15.5	5.3	11.7
Propan-2-ol	15.8	6.1	16.4
Isobutanol	15.1	5.7	16
Cyclohexanol	17.4	4.1	13.5
Hexanol	15.9	5.8	12.5
Pentanol	15.9	5.9	13.8
Butanol	16.0	5.7	15.8
Ethanol	15.8	8.8	19.4
Ethylene glycol	17	11	26
Water	15.6	16.0	42.3

Table 1 shows Hansen solubility parameters of tested solvents, while Figure 12 presents the relationship between hydrogen and polar interactions of tested solvents. Benzene interacts with dispersion interactions. Other tested solvents interact with hydrogen and polar interactions. In cyclohexanone, the polar interactions are stronger than hydrogen bonding while other solvents have higher share of hydrogen bond interactions. Cyclohexanone interacts in a larger proportion with dispersion interactions. It can be concluded that the yellow pigment, since it is soluble in cyclohexanone, is not non-polar but it contains functional groups which interact with polar interactions but the proportion of dispersion interactions is higher which can be attributed to the structure of the coloured organic compounds. The proportion of hydrogen bonded interactions is small (Figure 12). Acetone interacts with stronger hydrogen bonds, but weaker dispersion forces and polarity than cyclohexanone, and therefore the yellow pigment is less soluble in it.



» **Figure 12:** *Relation between hydrogen bonding and polar parameters of tested solvents*

Alcohols interact by hydrogen and dispersion interactions. Alcohols with larger molecular weight (cyclohexanol, hexanol, pentanol) are coupled with stronger dispersion interactions and weaker hydrogen interactions. The lower molecular weight alcohols (propan-2-ol, isobutanol and ethanol) are coupled with stronger hydrogen bonds and weaker dispersion interactions. Due to the lowest molecular weight, ethanol interacts with the strongest hydrogen interactions and relatively weak dispersion interactions. Polar alcohol interactions are small except for ethanol whose molecules are associated with stronger polar interactions. Compared to the cyclohexanone, dispersion interactions of alcohols are weaker and the hydrogen interactions are stronger. Polar interactions are considerably lower compared to dispersion and hydrogen interactions. Due to dissolution of microcapsules in ethanol, the surface of the microcapsules is certainly more polar than the surface of the yellow pigment or it contains more polar functional groups. Ethylene glycol and especially water molecules are coupled to the highest degree by hydrogen bonds and in a lower degree by dispersion interactions, so they do not interact with the microcapsules.

Conclusions

Microcapsules of the tested thermochromic printing ink contain polar functional groups which interact with hydrogen bonding. Therefore, it could be assumed they are made from melamine resin (Figures 1 and 2). They dissolve in ethanol, but not in the other examined alcohols, due to stronger polar and hydrogen bonds interactions of ethanol. Because it's a polymer, dispersion interactions are also important. Yellow pigment interacts primarily through dispersion interactions and in a lower degree by polar interactions. Therefore it dissolves in cyclohexanone. The obtained results can be used for characterization of thermochromic inks and determination of the solvents sequence used in sequential analysis. They also indicate which solvents should not be used in the formulation of thermochromic inks.

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Thermochromic offset ink – paper interactions and print biodegradation

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Abstract:

This study examines the adhesion and interactions between thermochromic offset ink and different papers as well their role in papers and prints biodegradation. Obtained results show that biodegradation of prints depends upon the adhesion, *i.e.* lower adhesion will result in reduction of biodegradation rate, while the strong adhesion will result in better paper degradation. Reactions between paper and thermochromic ink will form different prints properties due to different affinity of paper for ink while interactions between them will affect the prints biodegradation. When the ink is applied on paper, the polar constituents of paper will react with polar constituents of ink. Smaller amount of polar components of paper will give a print with polar character.

Key words:

Thermochromic offset ink, paper – ink interactions, adhesion, biodegradation

1. Introduction

Printing inks are coloured complex mixtures, liquids or pastes, mostly consisted of colorant, binder (resins), solvent and additives. Additives are often different chemical substances for the improvement of printing ink performance, such as catalysts, antioxidants, adhesion promoters, amine stabilizers, antifoam agents, biocides, chelating agents, dispersing agents, siccatives for optimized drying, flow agents, gallants, ink stabilizers, optical brighteners, photoinitiators, waxes, UV stabilizers, and wetting agent. Biocides are needed for aqueous inks to control microbial growth, but in offset letterpress technology can be used in fountain solutions as well (Leach, 2007; Pekarovicova and Husovska, 2016). Chemical composition of printing inks and their physical property mostly differs due to printing process that they are intended for. When they are applied to substrate, the ink must be converted to solid state. The binder dries and binds the colorants to the substrate. The drying of printing inks must be achieved as quickly as possible and it can be performed by physical (evaporation) and chemical (oxidation, radiation-induced curing) means or a combination of both (Leach, 2007). Sheet-fed offset inks set by oxidative polymerisation of the drying oils and alkyds. Drying is commonly accelerated using oxidative metal-ions or absorbing oils in the ink formulation to concentrate the ink faster, or by the use of IR or UV drying (Rousu *et al.*, 2000).

One of the main functions of printing inks is to adhere on the printing substrate and remain there for the whole lifespan of print. Adhesion is the interatomic and intermolecular interaction at the interface of two surfaces. It is a multi-disciplinary topic which includes surface chemistry, physics, rheology, polymer chemistry, stress analysis, polymer physics and fracture analysis (Awaja *et al.*, 2009). Adhesion of printing inks onto the printing substrate depends upon colorants, solvents and binders. The influence of colorants on ink adhesion mostly depends upon their compatibility with the binder system, their type, percentage and degree of dispersion in the final ink. Adhesion is influenced by the degree of binder absorption on absorbent (paper) while for non-absorbent substrates, is controlled by the film-forming ability of the binder and the molecular affinity for the substrate. Solvents can influence wettability and absorption of printing ink. Adhesion can also be affected by adding additives in small amounts during manufacturing process in order to improve chemical bonding between printing substrate and ink (Leach, 2007). The bond strength between the paper surface and polymer depends strongly on the physical and chemical structure of the two surfaces that are in contact. For example, the polymer polarity created by the carboxyl content of adhering polymers, would affect the adhesion strength of the cellulose-polymer bond, where peel strength increases when the carboxyl content increases. Thus, polarity of polymer and cellulose substrate affects the strength (Borch, 1991).

Surface properties of paper (surface energy, absorption, roughness and porosity) of the paper may affect printability of functional inks (Öhlund *et al.*, 2012; Bollström *et al.*, 2013; Dogome, Enomae and Isogai, 2013). In addition, appropriate matching of surface energy to ink surface tension (adhesion) becomes important or the print definition and conductivity of functional inks (Öhlund *et al.*, 2012). Ink-paper interactions, including the ink transfer, setting and drying processes, have an important role in print production, since they influence both print quality and runnability (Pykönen *et al.*, 2010). Surface interactions between printing ink and paper are of importance during printing, as well as during ink removal in paper recycling as a high adhesion between ink and cellulose might cause problems during ink detachment (Thompson, Manning and Lane, 2000; Forsström, Eriksson and Wågberg, 2005; Vukoje, Jamnicki and Rožić, 2016).

Thermochromic printing inks undergo changes in colour because of small environmental variations, such as temperature. Thermochromic printing inks have a wide range of applications, and their development is still in progress. Each of these applications requires a specific set of material properties and deeper understanding of the physical and chemical background. Commercially available thermochromic printing inks based on leuco dyes are consisted of microencapsulated leuco dye–developer–solvent systems and a resin binder (Tang and Stylios, 2006; Seeboth and Lotzsch, 2013). The microencapsulated thermochromic pigments usually have medium particle size of a few micrometres, which is about ten times larger than the particle size of conventional pigment particles (Seeboth and Lotzsch, 2013). Microcapsules are dispersed in a binder. The most widely used system for microencapsulation of thermochromic and photochromic inks involves urea or melamine and formaldehyde systems (Aitken *et al.*, 1996), gelatine–gum arabic and epoxy resins (Fujinami, 1996). In thermochromic leuco dye–developer–solvent system thermochromic effects are based on changes of absorption caused by molecular interactions of the incorporated functional dye within its microenvironment (Aitken *et al.*, 1996; White and LeBlanc, 1999; MacLaren and White, 2003; Seeboth *et al.*, 2007). Leuco dye–developer–solvent systems consist of a chromogenic compound (leuco dye), developer and solvent. The thermochromic effect is caused by the formation of leuco dye–developer complexes in a reversible equilibrium redox reaction between leuco dye and developer. The reaction is triggered by interactions between the complex and the solvent during the melting or crystallization process (Seeboth *et al.*, 2007). The most common electron-donating chromogenic compounds are phenylmethane and fluoran derivatives bearing a lactone ring moiety. In the lactone ring-closed state these so-called leuco dyes or colour formers are either colourless or weakly yellow coloured. Leuco dye–developer–solvent systems are coloured in the solid state and transform on heating above the melting temperature of the solvent into a colourless liquid (Seeboth and Lotzsch, 2008). Colour developers are usually weak acids (bisphenol A, octyl phydroxybenzoate, methyl p-hydroxybenzoate, 1,2,3-triazoles, and 4-hydroxycoumarin derivatives) while long – chain alkyl alcohols, esters, and acids are commonly used as solvents (White and LeBlanc, 1999; MacLaren and White, 2003).

The aim of the study was to investigate the influence of thermochromic ink – paper interactions on prints biodegradation. Thermocromic ink used in this study is based on vegetable oil polymer resin (Vukoje *et al.*, 2017) with Co and Mn salts used as catalysts (siccatives) for oxypolymerization drying of vegetable oil (Jamnicki Hanzer *et al.*, 2018). Microcapsules present in printing ink have polar nature than the classical pigment particles which was confirmed by solvent-thermocromic print interactions using Hansen solubility parameters that rank the solvents based on their estimated interaction capabilities (Rožić *et al.*, 2017).

2. Materials and Methods

2.1. Printing substrate and printing ink

In preparation of the experiment, five different paper samples were used: synthetic, 33% recycled, 100% recycled, bulky and wood free-coated (Table 1). These papers were selected due to their different chemical composition and absorption capacity.

Table 1. Papers used in experiment

Paper type	Abbreviation	Producer	Grammage	Description
Synthetic paper	S	Yupo	73 g/m^2	Extruded from polypropylene pellets
33% recycled paper	33R	Mondi	80 g/m^2	Containing 33% of recycled cellulose fibres
100% recycled paper	100R	Evercopy +Clairefontaine	80 g/m^2	Containing 100% of recycled fibres,
Bulky paper	B	Munken Print White	80 g/m^2	Containing wood free pulp and more than 10% mechanical wood pulp
Wood free coated	WFC	Maxi satin	115 g/m^2	High quality coated paper

For the printing of paper, samples one leuco dye based thermochromic offset printing ink was used (Chromatic Technologies, Inc.). The activation temperature of thermochromic ink is 45ºC. Below its activation temperature, the print was coloured in green and above its activation temperature the print was coloured in yellow (hereinafter GY). Thermochromic ink is composed of blue microcapsules dispersed in classic yellow offset ink (Vukoje *et al.*, 2017). The printing trials were carried out using Prüfbau Multipurpose Printability Tester. The quantity of 1.5 cm^3 ink was applied on the distribution rollers while printing was carried out with the printing force of 600 N. All the samples were printed in the full tone.

2.2. Determination of surface properties of paper samples

Evaluation of surface free energy of paper and paper printed with ink were carried out by contact angle measurements on DataPhysics OCA 30 Goniometer, using Sessile Drop method. By measuring contact angles of standard test liquids (demineralized water, diiodometane and glycerol) whose surface tensions are known (Table 2) it is possible to determine the total solid surface energy and it’s dispersive and polar component. Measurements were performed at room temperature (23.0 ± 0.2) ºC. The volume of droplet was 1 µL. Contact angle was captured by CCD camera and measured 2 s after the droplet was formed. Average values of ten drops on different places of the same sample were taken.

Table 2 Surface tensions (γ) of test liquids and their dispersive (γ^d) and polar (γ^p) components

Liquid	**Surface tension / (mJ/m^2)**		
	γ	$\gamma^{\mathbf{d}}$	$\gamma^{\mathbf{p}}$
Water	72.80	21.80	51.00
Diiodomethane	50.80	50.80	0.00
Glycerol	63.40	37.00	26.40

The Owens, Wendt, Rabel and Kaelble (OWRK) calculation method was applied to the contact angle data of test liquids in order to evaluate the parameters of surface free energy *(γ)*

and its dispersive (γ^d) and polar (γ^P) components (*Table 4*). Conducted calculation method is integrated in the software (SCA20, Version 2.01) and automatically carried out. From the obtained γ, adhesion parameters (surface free energy of the interphase (γ_{12}), work of adhesion (W_{12}) and wetting coefficient (S_{12})) were calculated (*Table 5*). Owens-Wendt model includes the assumption according to which both the dispersive and polar interactions between two phases are equal to the geometric mean expression of γ of the individual phase which are in contact with each other, according to *Eq. (1)* (Żenkienwicz, 2007):

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\sqrt{\gamma_1^d \gamma_2^d} - 2\sqrt{\gamma_1^p \gamma_2^p} \tag{1}$$

where the subscript refers to surface free energy of the each solid, in our case paper and ink print, and the γ_{12} denotes their γ of the interphase. Adsorption theory, according to the Dupré approach, which presents the thermodynamic work of adhesion W_{12} between two phases is equal to *Eq. (2)* (Żenkienwicz, 2007):

$$W_{12} = \gamma_1 + \gamma_2 - \gamma_{12} \tag{2}$$

The wetting coefficient S_{12} is equal to *Eq. (3)* and indicates that an ink will spontaneously wet and spread on the solid surface if the value is positive or equal to zero, while the negative value implies the lack of spontaneous wetting.

$$S_{12} = \gamma_1 - \gamma_2 - \gamma_{12} \tag{3}$$

2.3. Soil burial experiments

Laboratory soil burial experiments were conducted at room temperature (25±2°C) by placing the printed and unprinted paper substrates horizontally in field soils in laboratory glass containers. The paper substrates were buried for 14, 32, 50, 80 and 150 days. The water content of the soil was adjusted to 40% of its maximum water retention capacity. The commercial available reagent *Anaerocult A* (*Merck*) was used in order to allow the development of anaerobic conditions.

2.4. Visual evaluation

A method of visual evaluation can be used in order to describe biodegradation as a first indication of microbial activity in the terms of visible surface changes such as formation of holes or cracks, de-fragmentation or changes in colour but it doesn’t prove the existence of biodegradation process in terms of metabolism (Shah *et al.*, 2008). Paper samples were taken from the containers in sampling times and photos of them were taken, in order to visually evaluate the prints degradation over time.

2.5. Colorimetric measurements

The colorimetric properties of thermochromic samples were described in the *CIELAB* colour space. Temperature-dependent colorimetric properties were measured using Ocean Optics USB2000+ spectrophotometer and Ocean Optics Spectra Suite software for the calculation of the *CIELAB* values *L*, a*, b** from measured reflectance in the spectral range of 400-700 nm (in 1 nm steps). The D50 illuminant and 2° standard observer were applied in these calculations. Each sample was thermostated by the Full Cover water block (EK Water Blocks, EKWB; Slovenia) at 23°C. The temperature of the copper plate surface was varied by circulation of thermostatically controlled water in channels inside the water block, which was assured to be up to 1°C accurate in the applied temperature region.

2.6. Weight loss measurements

Samples degradation was monitored by measuring the weight of printed-paper samples before and after incubation in the soil containers. The samples were taken out and rinsed with distilled water, in order to remove soil particles from the surface. Then they were dried on air and weighed. The weight loss percentage (w) was calculated according to *Eq 4*:

$$w = \frac{m_0 - m_1}{m_0} \cdot 100 \ [\%] \tag{4}$$

where, m_0 is the initial weight of the sample, m_1 is the final weight of the sample after biodegradation.

3. Results

3.1. Determination of surface free energy

All used paper substrates show hydrophobic surface (water contact angle is greater than 90º) (*Table 3*). The highest hydrophobicity shows bulky paper (120°) due to the presence of lignin in paper (Hubbe, Venditti and Rojas, 2007), while the lowest hydrophobic character was achieved for 33% recycled paper (91°).

Comparing the characters of thermochromic prints, it can be seen that prints on B, 100R, 33R and WFC papers are hydrophobic while for the print on S, obtained water contact angle (83.19°) indicates a hydrophilic surface. Different prints surface properties can be attributed to the absorption of inks into the paper structure. Synthetic paper is not absorbent, and all the components of the printing ink remain on the surface. Smaller water contact angle on the WFC (94.0°) also points to more polar surface. The used thermochromic printing ink is offset, and her main characteristic is hydrophobic property. In addition, the used ink is based on vegetable oil, as confirmed by Vukoje *et al.*, (2017), and contains Co and Mn salts as catalysts (siccatives) necessary for oxypolymerization drying of vegetable oil (Jamnicki Hanzer *et al.*, 2018). In reaction with oxygen from the air, vegetable oils and alykids, dries by oxypolymerization resulting in formation of polymers with R-O-O-R structure, where R represents alkyl groups.

Table 3. Contact angles measurements

Sample	Contact angle / (°)		
	Water	Glycerol	Diiodomethane
S	102.98	109.51	57.15
B	120.24	118.38	55.84
100R	119.59	119.99	48.94

33R	91.89	104.91	55.60
WFC	100.34	118.95	61.81
S-GY	83.19	97.056	47.75
B-GY	108.26	113.17	50.97
100R-GY	104.59	111.17	53.38
33R-GY	110.47	120.11	57.24
WFC-GY	94.0	81.62	38.99

Figure 1 provides the calculated values of the surface free energy (γ) of unprinted and printed samples. Unprinted papers can be divided into two categories- absorbent (100R, B, 33R) and non-absorbent (S and WFC). Comparing the γ values of absorbent papers, it can be seen that 100% recycled paper has the highest value (29.42 mJ m^{-2}), followed by bulky (26.44 mJ m^{-2}) and 33% recycled paper (23.87 mJ m^{-2}). Synthetic paper (23.10 mJ m^{-2}) and WFC paper (18.84 mJ m^{-2}) have slightly smaller values of γ.

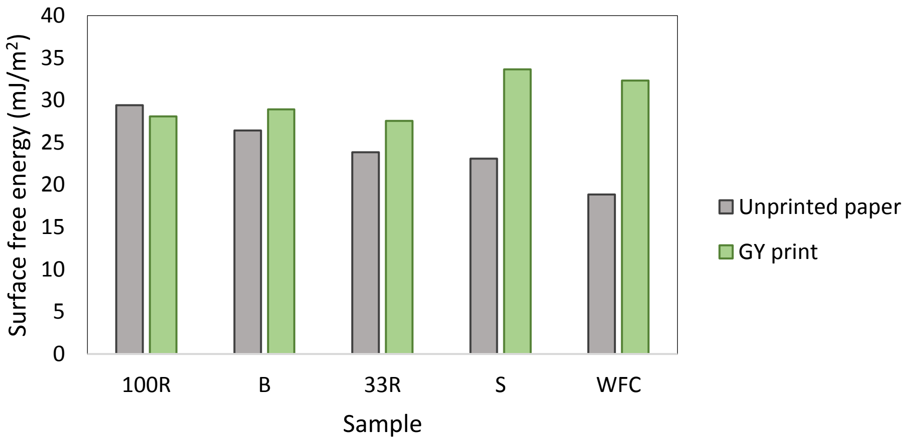

Figure 1. Surface free energy of unprinted papers and prints

Only print on 100R paper has lower γ compared to unprinted paper. The prints on other papers have higher value of γ. The highest differences in γ can be noticed for prints on S and WFC papers. This results point that the best ink adhesion was obtained on the surface of 100R paper. Molecules present on the surface of 100R paper have the highest γ and thus they have the highest tendency to reduce it in the interaction with molecules. It can be concluded that in this case, the adhesion forces are higher than the forces of cohesion. In other cases, the surfaces of papers have too low γ, so the forces of cohesion between the molecules of ink are greater than the adhesion forces. In this case, it can be concluded that ink has poor wettability of surfaces.

Specific surface energy of all unprinted paper samples mostly originate from its dispersive component as evident from the *Figure 2*. The smaller surface free energy (γ) of paper will result in its smaller dispersive component (γ^d) (a slight deviation occurs with S paper). All the prints show higher values of γ^d compared to unprinted paper samples. The highest values of prints γ^d were obtained on non-absorbent papers (S-GY and WFC-GY). For the 100R-GY, the value of γ^d was almost the same as for unprinted 100R paper. In the case of B-GY and 33R-GY, the value of γ^d was slightly higher compared to unprinted papers.

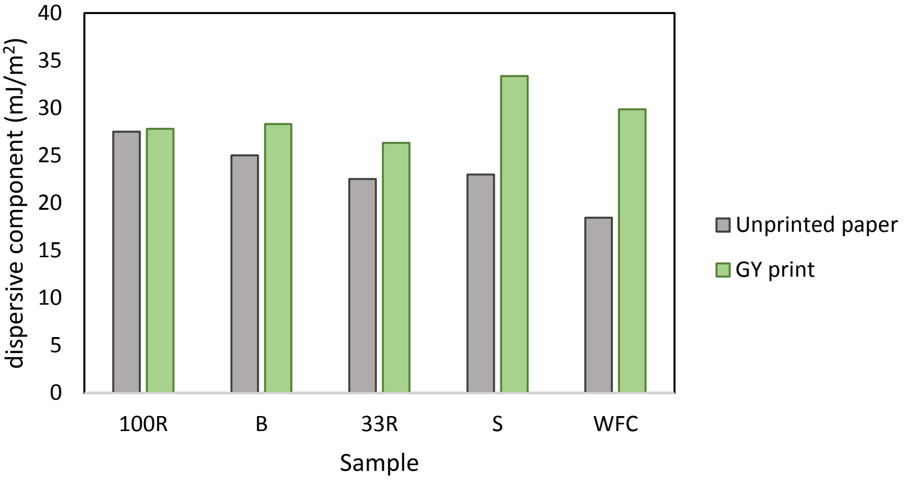

Figure 2. Dispersive component of surface free energy of unprinted papers and prints

Surface free energy of 100R, B and 33R papers have small values of polar components (γ^p), but still higher than polar component of S and WFC paper (*Figure 3*). 100% recycled paper has the highest value of polar component than other papers (1.91 mJ m^{-2}).

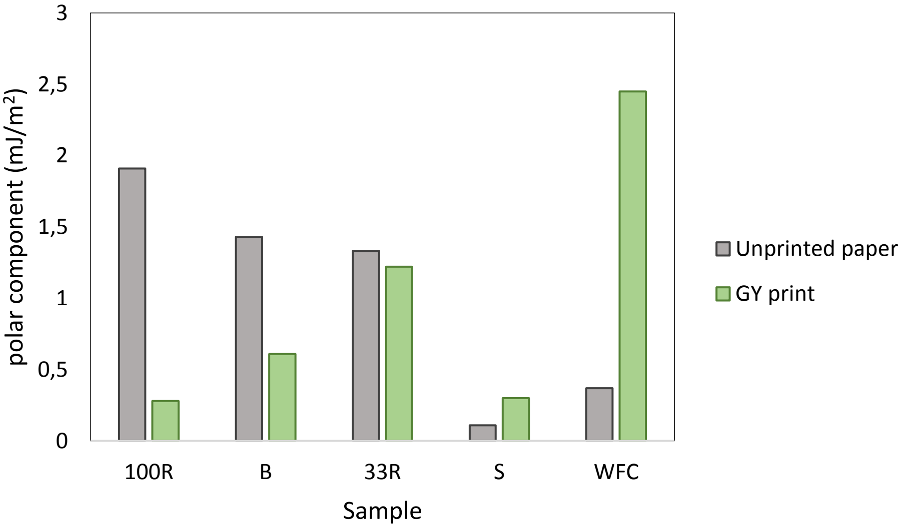

Figure 3. Polar component of surface free energy of unprinted papers and prints

In the case of 100R, B and 33R papers, the polar components of the prints are smaller compared to polar components of the unprinted papers. Even though surface free energies of paper as well as dispersive components of γ do not reduce in contact with print, the polar components do (*Figs 1, 2, 3*). The highest reduction of polar components was in case of 100R paper. This can mean that between 100R, B and 33R paper and thermochromic ink are the most important polar interactions. The polar interactions are the highest with the surface of 100R paper, while the lowest are in the case of 33R paper. In the case of S and WFC papers, the polar interactions are higher compared to unprinted papers, which, together with the previous conclusions, indicate a poor adhesion.

Figure 4 shows the calculated values of adhesion parameters. The calculated adhesion parameters can be used to predict the optimal adhesion at the interface. The conditions for the optimal adhesion at the interface between paper and thermochromic printing ink are achieved if the following conditions are met: $\gamma_{12} = 0$, W_{12} = maximal and $S_{12} \geq 0$. The adhesion of ink components to the substrates can be expressed as the sum of works of adhesion for polar and dispersive interaction, giving as a result the overall thermodynamic work of adhesion (Repeta, 2013). *Figure 4* shows that optimum adhesion was achieved in the case of 100R and thermochromic ink interface. The lowest adhesion was achieved in the case of WFC paper and thermochromic ink.

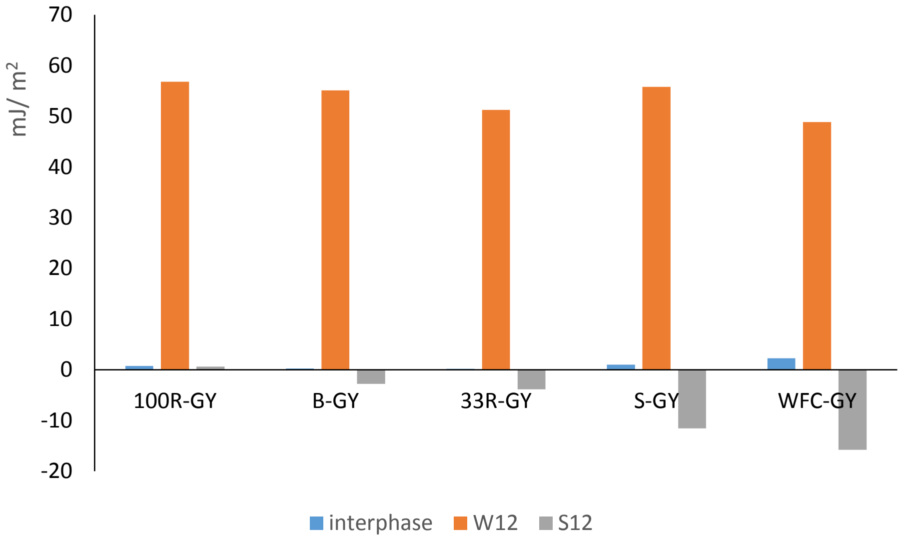

Figure 4. Surface free energies of interphase, work of adhesion (W_{12}) and spreading (S_{12})

3.2. Visual evaluation

From *Figs 6 – 10* visual appearance after prints biodegradation can be seen. All the prints show differences in colour, especially after 150 days of biodegradation. From the *Figs 8 and 9* it can be seen that the prints on S and WFC paper are damaged during sampling (stretch marks) which points to non-crosslinked network and non-oxidized ink (other samples were not damaged in this way). Moreover, the print on WFC paper shows the most heterogeneous print degradation, which can also be the result of non-crosslinked and non-oxidized ink on the surface of paper.

Results of a^* colorimetric values determined on thermochromic prints before biodegradation are presented in *Figure 5*. In the *CIELAB* colour space the value $-a^*$ represents greenness. The lowest a^* value has thermochromic print on S paper, probably due to highest concentration of ink on the surface. The highest a^* values (more positive) are in the cases of 100R and B paper probably due to best adhesion.

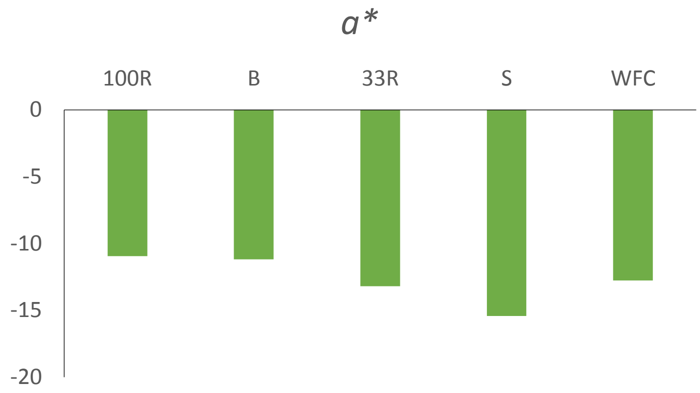

Figure 5. Initial *a** colorimetric values of prints

All samples, besides print on S paper, show noticeable degradation not only of the print colour, but the whole sample (paper) as well, especially after 50 and 180 days of biodegradation. Formation of brown spots can be seen which point to significant degradation, and formation of cracks. The prints during biodegradation are becoming lighter green, and transforming to yellow due to degradation of blue microcapsules present in ink (Vukoje *et al.*, 2017). The activation temperature of used thermochromic ink is 45ºC. Below activation temperature, the print was coloured in green and above its activation temperature the print was coloured in yellow. This behaviour can be explained by the formation of colorant-developer coloured complex in microcapsules (in this case blue coloured) on lower temperatures (below its activation temperature). On heating above the melting temperature of the solvent (above temperature of activation) the solvent in liquid form, causes the breakdown of the colorant – developer coloured complex, the blue colour disappears while yellow colour of classic offset ink appears.

Thus, the shift of colour during degradation from green (combination of blue microcapsules and classical yellow offset ink) towards yellow indicates that deformation of microcapsules (diffusion of components from microcapsules) and / or degradation of the microcapsule occurred (Vukoje *et al.*, 2017).

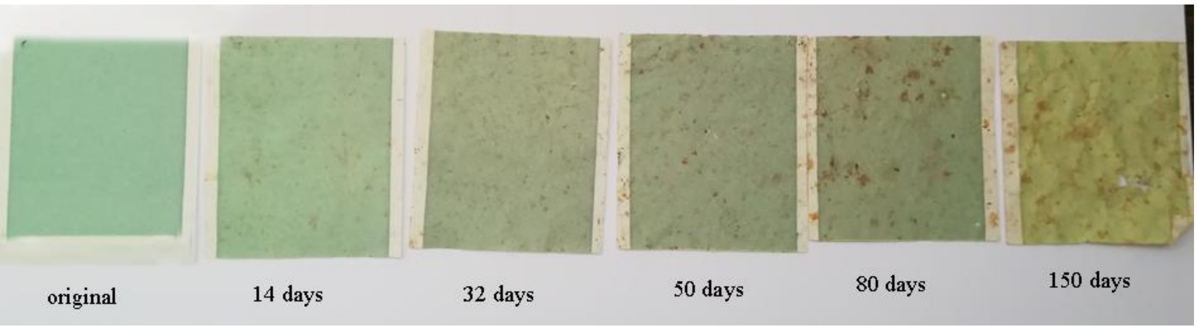

Figure 6. Visual evaluation; 100% recycled paper - print (100R-GY) before and over 14, 32, 50, 80 and 150 days of biodegradation

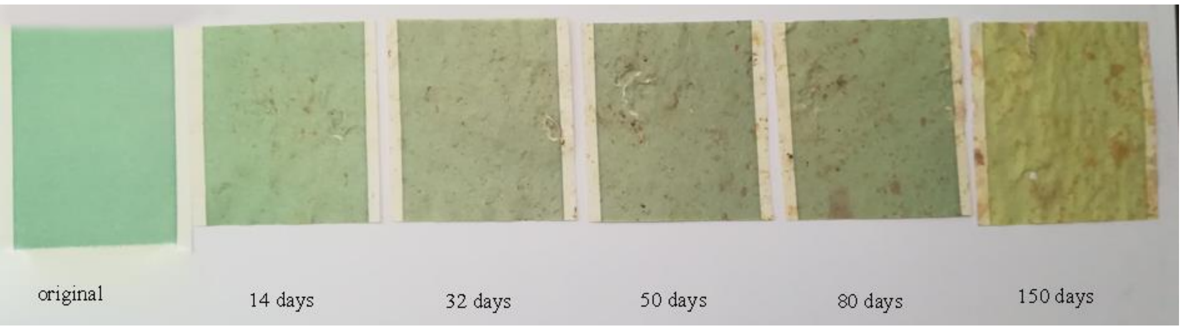

Figure 7. Visual evaluation; Bulky paper - print (B-GY) before and over 14, 32, 50, 80 and 150 days of biodegradation

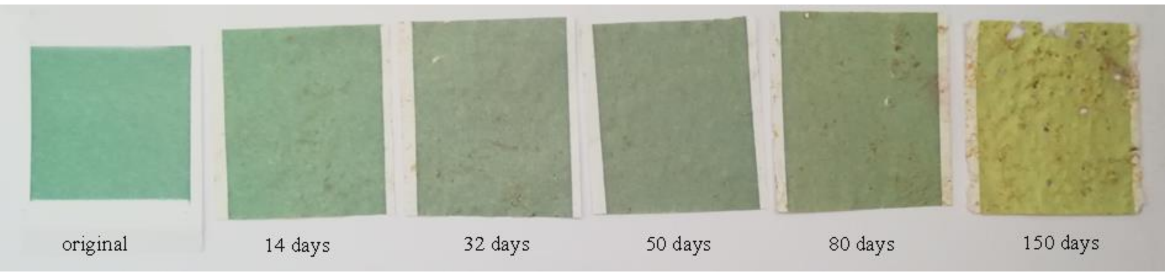

Figure 8. Visual evaluation; 33 % Recycled paper - print (33R-GY) paper before and over 14, 32, 50, 80 and 150 days of biodegradation

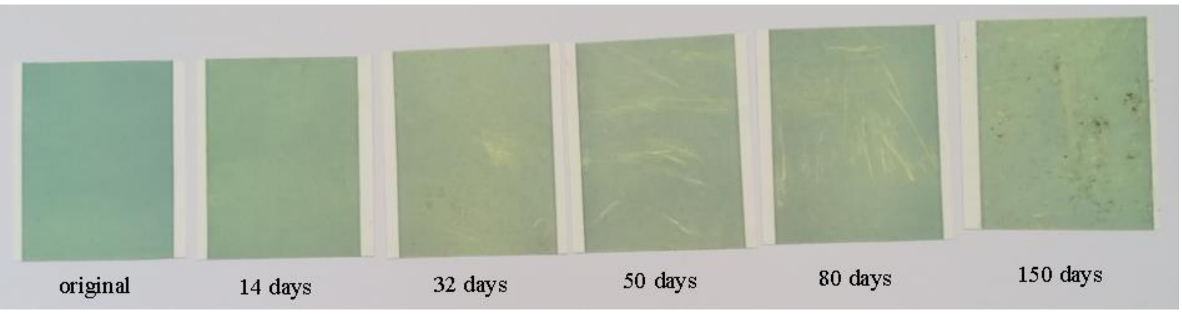

Figure 9. Visual evaluation; Synthetic paper - print (S-GY) before and over 14, 32, 50, 80 and 150 days of biodegradation

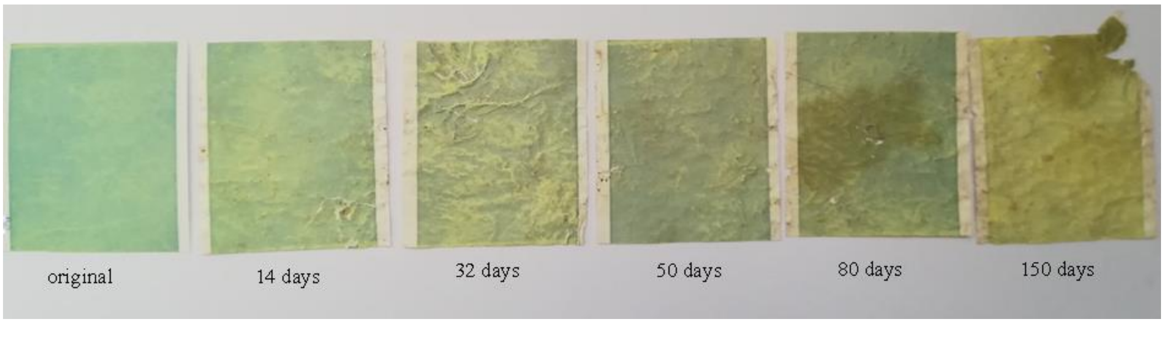

Figure 10. Visual evaluation; Wood free coated paper - print (WFC-GY) paper before and over 14, 32, 50, 80 and 150 days of biodegradation

The results of the prints colour change during biodegradation follow the results of the print adhesion strength, except in the case of print on the WFC paper. Specifically, optimal ink adhesion was obtained on the surface of 100R paper (*Figure 4*). The print on 100R paper shows the highest degradation, followed by prints on B and 33R paper and finally on S paper. Even though the lowest adhesion was obtained on the surface of the WFC paper, degradation of the print was the highest. Additionally, better adhesion will result consequently in better degradation (except for print on WFC paper).

Polymerized vegetable oils harden on exposure to oxygen through the oxidation of double bonds to hydroperoxides (Shogren *et al.*, 2004).

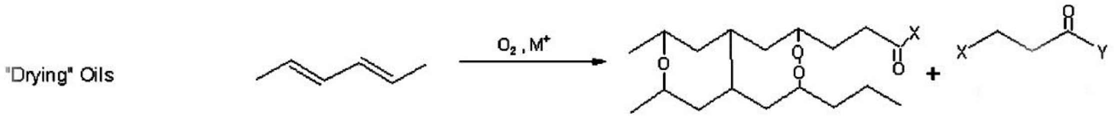

Figure 11. Representative chemical structure of cross-linking reactions. M^+ - drying catalyst; X and Y may be any functional group, commonly -H, -OH, $-CH_3$ or $-OCH_3$ (Shogren *et al.*, 2004)

Simplified chemical structure of the product of the polymerization reaction is shown in *Fig. 11*. It results in the formation of three-dimensional networks although some low molecular weight ketones, carboxylic acids, and alcohols are formed in the oxidative polymerization via decomposition of oil hydroperoxides. Polymerized oils are soft and sticky in some cases. According to Shogren *et al.*, (2004), kraft paper coated with oxidatively polymerized soybean and linseed oil was 90%–100% converted to CO_2 after 65 days in soil at 30^0C. In our experiment, paper-prints degraded much more slowly. This may be due to slower degradation of classical yellow pigment and / or the addition of alkyd resins.

For the offset printed coated papers, separation of different ink components during ink setting and drying on coated paper may occur (Koivula *et al.*, 2008; Pykönen *et al.*, 2010). Oxidation of offset inks is normally based upon the reaction of alkyd resins and vegetable oils. (Leach, 2007). During oxypolymerization of the offset ink on the surface of paper, the cross-linking of the double bonds in the oil and alkyd resins occurs (Rousu et al., 2000; Koivula et al., 2008). Alkyd resins interacts with the coating pigment (kaolin or $CaCO_3$) and adsorbs on them (Rousu *et al.*, 2000). Hydrophilic dispersed pigment surfaces of the coating act as sites for alkyd resins adsorption. This leads to separation of ink vehicle components and prevention of their mutual interactions, which can affect the ink drying. Because of it, the ink on WFC paper is not completely oxidised. Thus, the reaction of alkyd and vegetable oil is hampered, resulting in lower degree of ink oxypolymerization. This behavior can explain higher color degradation of the WFC-GY print, because it is not oxidized and remains soft, the degree of polymerization is lower, allowing bacteria to be better degraded it (*i.e.* microcapsules). For the print on synthetic paper, all the components of ink are present on the surface of paper. However, since there is no coating pigment present in the synthetic paper, interactions between pigment and alkyd will not appear, while reaction of alkyd and vegetable oil will exist and the print surface will have different properties compared to print on WFC paper. Due to higher amount of ink on the surface of synthetic paper, oxypolymerization of ink will probably be slower, compared to other prints since there is no penetration of the ink binder into the paper structure. In addition, this behaviour would explain the surface energy of the prints and its polarity. The highest values of dispersive components for both prints, S-GY and WFC-GY, originate from ink adsorbed on the surface of papers.

The changes in the colour of the prints, probably occurs due to degradation and deformation of the thermochromic microcapsules present in ink as confirmed earlier in the study by (Vukoje *et al.*, 2017). The thicker the polymeric resin layer over the microcapsules is, makes them more protected towards biodegradation, as demonstrated in the previous study by Vukoje *et al.*, (2017). This means that the rate of microcapsule degradation is greater than the rate of biodegradation of the cross-linked oxidized binder (resins + oils). For this reason, the rate of biodegradation of the print on 100R paper surface is the highest. The higher the absorption of the ink vehicle into the paper is, the faster the rate of print degradation will be. In the case of WFC paper, microcapsules are probably protected with thicker layer of ink resin (vehicle, binder) but it is not completely oxidized and it is not cross-linked, resulting in soft resin, which is more easily for bacteria to degrade it. In the case of S-GY print microcapsules are covered with the thickest layer of the oxidised ink resin resulting in the smallest colour change.

3.3. Weight loss measurements

Figure 12 shows the weight loss measurements of unprinted papers during biodegradation. For unprinted papers, it can be seen that the highest weight loss was obtained for WFC paper while the smallest was obtained for S paper. The rate of biodegradation increases in a row: 33R>B>100R.

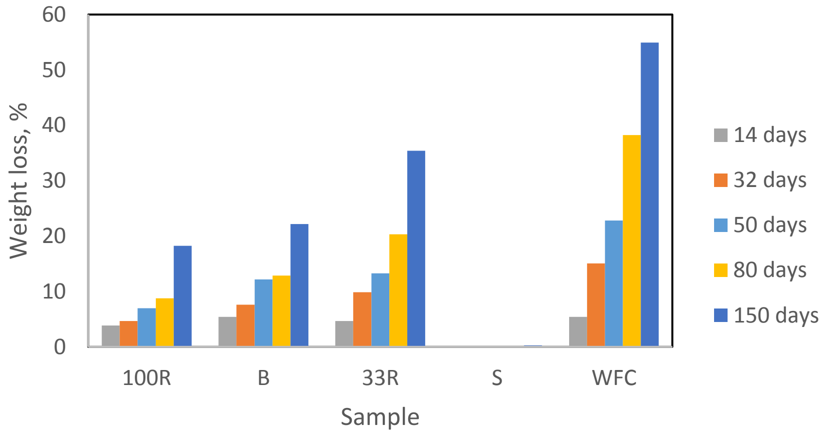

Figure 12. Weight loss measurements of unprinted papers during biodegradation

Figure 13 shows weight loss measurements of printed papers. For print on 100R paper, the best adhesion was achieved. In this case, the rates of biodegradation for unprinted and printed paper slightly differ. The weight loss of samples points to degradation of paper and ink at the same time. In the case of printed B and 33R paper, the prints slow down the rate of biodegradation, somewhat more in the case of print on paper 33R. For the print on WFC paper, the print notably reduces the rate of biodegradation. Accordingly, the lowest adhesion will result in higher reduction of biodegradation rate. The highest rate of biodegradation (the highest weight loss) corresponds to samples where the optimum adhesion was achieved for 100R- GY. Even though the colour degradation was the highest in the case of WFC-GY print, the weight loss point mostly to degradation of microcapsules on the surface of the print. Probably other components of the ink present on the surface of coated paper are more likely difficult to degrade. Unprinted synthetic paper and print on synthetic paper shows almost no changes in weight during sampling time, most likely due to chemical composition of synthetic paper, *i.e.* polypropylene, since it is resistant to microbial attack (Arutchelvi *et al.*, 2008; Leja and Lewandowicz, 2010).

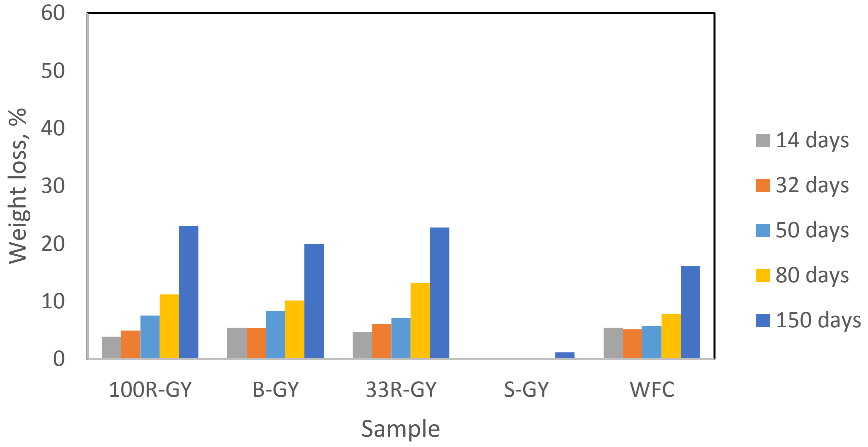

Figure 10. Weight loss measurements of papers with prints during biodegradation

4. Conclusion

Thermochromic offset ink – paper interactions play an important role in the papers and prints biodegradation. In order to achieve the best adhesion properties, the paper should have surface free energy somewhat similar to ink, with optimum proportion of dispersive and polar forces. From the obtained results, it can be concluded that biodegradation of prints depends upon the adhesion, *i.e.* lower adhesion will result in reduction of biodegradation rate, while the strong adhesion will result in better paper degradation. During ink setting onto the paper, reactions between them will form different prints properties due to different affinity of paper for ink. In addition, the interactions between paper and ink as well as orientation of the molecules on the surface of the prints will affect the biodegradation. When the ink is applied on paper, the polar constituents of paper will react with polar constituents of ink. Smaller amount of polar components of paper will give a print with polar character. Thus, the paper surface participates in the organization and orientation of the molecules on the surface of the print. The optimum adhesion will influence the whole print (paper and ink) biodegradation.

5. References

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Thermochromic ink – paper interactions and their role in biodegradation of UV curable prints

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Abstract:

In this study, biodegradability aspects of UV thermochromic leuco dye print on three different paper materials (synthetic, recycled, and bulky) were studied using the soil burial test under anaerobic conditions. Biodegradation of UV curable thermochromic prints were evaluated for changes by visual examination, microbial growth assay, weight loss measurements, Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy and colorimetric measurements. Results showed a better absorption of ink into the bulky paper structure, followed by recycled paper. Synthetic paper is not absorbent. The ink binder altogether with classic pigment and microcapsules penetrates into the structure of bulky paper. Recycled paper absorbs ink binder mostly with classic pigment. Better adsorption of binder into the bulky paper structure results in thinner layer of ink binder on the paper surface. On non-absorbent synthetic paper, microcapsules are covered with thicker layer of ink binder. In the case of bulky paper, the highest rate of biodegradation was observed, resulting in a higher number of bacteria, higher weight loss, higher changes in colour (destruction of almost all microcapsules) and reduction in thermochromic effect of the prints. Results show that microcapsules, which penetrate into the structure of bulky paper, are promoting the rate of bulky paper biodegradation. The opposite behaviour was noticed for the penetration of classic pigment into the structure of recycled paper, which resulted in remarkable reduction of recycled paper biodegradation rate. The thicker layer of ink binder (containing classic pigment) on the surface of microcapsules on recycled paper resulted in slower rate of microcapsules degradation and smaller colour change of the print. The thickest layer of ink binder and classic pigment on synthetic paper surface causes the slowest rate of biodegradation of print.

Keywords: thermochromic ink, paper ink interactions, biodegradation, bacteria, SEM, FTIR

Introduction

Printing inks are coloured complex mixtures, liquids or pastes, mostly consisted of colorant (pigments or dyes), binder (resins), solvent (organic or water based) and additives (chelating agents, anti-oxidants, surfactants, biocides, etc.). Their composition and physical property mostly differs due to printing process that they are intended for. When they are applied to substrate, the ink must be converted to solid state. The binder dries and binds the colorants to the substrate. The drying of printing inks must be achieved as quickly as possible and it can be performed by physical (evaporation) and chemical (oxidation, radiation-induced curing) means or a combination of both (Leach 2007). Radiation-induced drying includes ultraviolet radiation, infrared, electron beam, microwave and radio frequency. The volatile organic compounds (VOC) evaporation from solvent based inks and their emission into the atmosphere during printing can be overcome by the use of water based and UV-cured inks. Besides better environmental appearance, the UV curable printing inks are especially suited for printing on non-absorbent surfaces due to quick drying (Robert 2015). Radiation curing inks are formulated as other inks, consisting of pigments, binder, solvent and additives. In UV curable printing inks the binders are generally acrylates (epoxy, polyurethane and polyester acrylates). The solvents in these systems are low-viscosity monomers while the additives can be waxes, surfactants, photoinitiators (*e.g.* benzophenone) and photoactivators (*e.g.* amines), inhibitors and in some cases additives to improve printability. Photoinitiators are required in order to achieve solid state of ink after printing, in the presence of UV light by free radical, cationic or hybrid reaction (Leach 2007). The UV curable printing inks have some drawbacks such as contamination of packaging by residual reactive diluents and photoinitiators which remain in the ink after printing (Robert 2015), as well as problems during recycling of paper (Carré et al. 2005).

In the last decade, there is an increasing demand for inks in packaging resulting in the growing of the printing ink market by 3% per year which leads to an increasing demand for traditional as well as new printing inks (Robert 2015). Recently, smart polymers, such as thermochromic printing inks can be found for application in different products. Thermochromic printing inks change their colour by the heat. Commercially available thermochromic printing inks instead of classic pigments contain microencapsulated leuco dye–developer–solvent systems (Tang and Stylios 2006; Seeboth and Lotzsch 2013). The microencapsulated thermochromic pigments usually have medium particle size of a few micrometres, which is about ten times larger than the particle size of conventional pigment particles (Seeboth and Lotzsch 2013). The thermochromic effect is caused by the formation of leuco dye–developer complexes in a reversible equilibrium redox reaction between leuco dye and developer (Seeboth et al. 2007). The reaction is triggered by interactions between the complex and the solvent during the melting or crystallization process. Leuco dye–developer–solvent systems are coloured in the solid state and transform on heating above the solvent melting temperature (activation temperature TA) into a colourless liquid (Homola 2008). The most widely used system for microencapsulation of thermochromic inks involves urea - formaldehyde, melamine - formaldehyde , gelatine–gum arabic and epoxy resins (Aitken et al. 1996; Fujinami 1996; Seeboth and Lotzsch 2008). Melamine - formaldehyde resins are biodegradable and during biodegradation can act as carbon and nitrogen sources (El-Sayed et al. 2006).

In order to reduce the generation of municipal solid waste on landfills, different material recycling potentials for paper-based products have been purposed during last decade. Material recycling by flotation deinking is the most studied method for graphic papers, purposed for production of recycled fibres. Sometimes, this method is not suitable. For example for products contaminated with food (Monte et al. 2009). Besides this problems, some problems related to health safety of recycled paper due to residual printing inks in recycled pulp are of major concerns (Pivnenko et al. 2015). In order to avoid these problems, potentials of organic recycling should also be examined for new materials that can be found on the market. UV inks are generally known to cause problems during paper recycling resulting in residual ink in recycled pulp. The use of thermochromic printing inks is growing and they are being used for different applications, due to their attractive visual effects.

One of the main functions of printing inks is to adhere on the printing substrate and remain there for the whole lifespan of print. Adhesion of printing inks depends upon colorants, solvents and binders. The influence of colorants on ink adhesion mostly depends upon their compatibility with the binder system, their type, percentage and degree of dispersion in the final ink. Adhesion is influenced by the degree of binder absorption on absorbent (paper) while for non-absorbent substrates, is controlled by the film-forming ability of the binder and the molecular affinity for the substrate. Solvents can influence wettability and absorption of printing ink. Adhesion can also be affected by adding additives in small amounts during manufacturing process in order to improve chemical bonding between printing substrate and ink (Leach 2007). Adhesion of printing inks to paper plays an important role in many industrial applications and it can be characterized indirectly through thermodynamic analysis of the paper substrate (by measuring static and dynamic contact angle of liquid drops), or directly through paper laminate or adhesion tape peel testing. The bond strength between the paper surface and polymer depends strongly on the physical and chemical structure of the two surfaces which are in contact. For example, the polymer polarity created by the carboxyl content of adhering polymers, would affect the adhesion strength of the cellulose-polymer bond, where peel strength increases when the carboxyl content increases. Thus, polarity of polymer and cellulose substrate affects the strength (Borch 1991). Surface interactions between printing ink and paper are of importance during printing, as well as during ink removal in paper recycling as a high adhesion between ink and cellulose might cause problems during ink detachment (Thompson et al. 2000; Forsström et al. 2005; Vukoje et al. 2016).

Biodegradability aspect of paper and paper based products was the subject of many studies (Venelampi et al. 2003; López Alvarez et al. 2009; De la Cruz et al. 2014; Wang et al. 2015). However, there is lack of knowledge about the biodegradation of printing inks and their influence on paper based products biodegradation. In some studies the printing inks are only referred to only as the toxic components (López Alvarez et al. 2009; Hermann et al. 2011). Stinson and Ham (1995) studied a decomposition of printed and unprinted newspaper and based on the generated amount of methane the obtained results indicate that the printing ink did not inhibit the amount or affect the rate of methane production from cellulose in newspaper.

Studies of vegetable based polymers and binders biodegradation, which are commonly used in printing inks, have been investigated by few researches (Erhan and Bagby 1995; Erhan et al. 1997; Shogren et al. 2004) and also there are few available data on biodegradation of printed polymer films in which the reduction of biodegradation rate was noticed for printed samples (Hoshino et al. 2003; Bardi et al. 2014).

Our previous research has shown that biodegradation of thermochromic offset prints which dries by oxypolymerization of vegetable oil depends mostly upon physico-chemical properties of used paper substrates and absorption of ink binder into the paper structure (Vukoje et al. 2017).

Since several studies (Erhan and Bagby 1995; Erhan et al. 1997; Shogren et al. 2004) showed that differences in biodegradation of printing inks binders depends even upon small changes in their chemical composition, our goal was to investigate the differences in biodegradation of UV curable screen printing inks since they have different composition compared to offset inks.

Materials and Methods

Printing substrate and printing ink

Three different paper substrates (synthetic, 33% recycled, and bulky), unprinted and printed with screen thermochromic ink were exposed to anaerobic soil conditions. Synthetic paper (Yupo, 73 g/m^2) extruded from polypropylene pellets, recycled paper (Mondi, 80 g/m^2) containing 33% of recycled cellulose fibres and bulky paper (Munken Print White, 80 g/m^2) containing wood free pulp and more than 10% mechanical wood pulp, were used. These papers were selected due to their different chemical composition and absorption capacity.

For the printing of paper samples one leuco dye based, UV curable screen printing thermochromic ink was used (Chromatic Technologies, Inc.). The activation temperature of thermochromic ink is 31ºC. Below its activation temperature, the thermochromic UV curable screen print (hereinafter UV print) was coloured in purple and above its activation temperature the print was coloured in pink. The printing ink was screen printed using the screen printing device (Holzschuher K.G., Wuppertal) employing 60/64 mesh. All the samples were printed in the full tone. The printed samples were dried under the UV irradiance (30 W/cm) using Technigraf Aktiprint L 10-1 device.

Air permeance (porosity) of paper samples

The air permeance (porosity) measurements were conducted using Frank Bendtsen Roughness Tester device according to the ISO 5636/3 standard method (Thompson 2004). Average values of ten measurements are presented as mean±SD.

Determination of paper and print thickness

Thickness of unprinted paper samples was determined according to ISO 534:2005 standard using Enrico Toniolo DGTB001 Thickness Gauge. Print thickness values were obtained by subtracting the measured values of the thickness of unprinted paper from the measured values of thickness of paper with print. Average values of twenty measurements are presented as mean±SD.

Determination of surface free energy γ

Evaluation of surface free energy of paper and paper printed with ink were carried out by contact angle measurements on DataPhysics OCA 30 Goniometer, using Sessile Drop method. By measuring contact angles of standard test liquids (demineralized water, diiodometane and glycerol) whose surface tensions are known (*Table 1*), it is possible to determine the total solid surface free energy and its dispersive and polar component (Cyras et al. 2007; Zhao and Kwon 2010; Moutinho et al. 2011; Tkalčec et al. 2016; Bota et al. 2017). Measurements were performed at room temperature 23.0±0.2 ºC. The volume of droplet was 1 μL. Contact angle was captured by CCD camera and measured 2 s after the droplet was formed. Average values of ten drops on different places of the same sample were taken and presented as mean±SD.

Table 1 Surface tensions (γ) of test liquids and their dispersive (γ^d) and polar (γ^p) components

Liquid	**Surface tension (mJ/m^2)**		
	γ	γ^d	γ^p
Water	72.80	21.80	51.00
Diiodomethane	50.80	50.80	0.00
Glycerol	63.40	37.00	26.40

The Owens Wendt calculation method was applied to the contact angle data of test liquids in order to evaluate the parameters of surface free energy *(γ)* and its dispersive (γ^d) and polar (γ^P) components (*Table 4*) (Cyras et al. 2007; Zhao and Kwon 2010; Moutinho et al. 2011). Conducted calculation method is integrated in the software (SCA20, Version 2.01) and automatically carried out. From the obtained *γ*, adhesion parameters (surface free energy of the interphase (γ_{12}), work of adhesion (W_{12}) and wetting coefficient (S_{12})) were calculated (*Table 5*)(Zhao and Kwon 2010; Bota et al. 2017). Owens-Wendt model includes the assumption according to which both the dispersive and polar interactions between two phases are equal to the geometric mean expression of *γ* of the individual phase which are in contact with each other, according to Eq. (1) (Żenkienwicz 2007):

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\sqrt{\gamma_1^d\gamma_2^d} - 2\sqrt{\gamma_1^p\gamma_2^p} \qquad (1)$$

where the subscript refers to surface free energy of the each solid, in our case paper and ink print, and the γ_{12} denotes their *γ* of the interphase. Adsorption theory, according to the Dupré approach, which presents the thermodynamic work of adhesion W_{12} between two phases is equal to Eq. (2) (Żenkienwicz 2007):

$$W_{12} = \gamma_1 + \gamma_2 - \gamma_{12} \qquad (2)$$

The wetting coefficient S_{12} is equal to Eq. (3) and indicates spontaneously wetting and spreading on the solid surface if the value is positive or equal to zero, while the negative value implies the lack of spontaneous wetting.

$$S_{12} = \gamma_1 - \gamma_2 - \gamma_{12} \qquad (3)$$

Soil burial experiments

Laboratory soil burial experiments were conducted at room temperature 25±2 °C by placing the unprinted and printed papers horizontally in the forest field soils (containing humus) in glass containers. They were buried for 50 and 180 days, two samples of each. The water content of the soil was adjusted to 40 % of its maximum water retention capacity. The commercial available reagent *Anaerocult A* (*Merck*) was used in order to allow the development of anaerobic conditions.

Scanning electron microscopy

The printed thermochromic surface before and after 180 days of biodegradation was monitored using a FE-SEM Jeol 7000 field emission scanning electron microscope. The micrographs were taken under a magnification of 1000x and 5000x.

Optical Microscopy

Microscopic image of thermochromic ink was taken using Olympus BX51 System Microscope under a magnification of 2000x.

Visual evaluation

A method of visual evaluation can be used in order to describe biodegradation as a first indication of microbial activity in the terms of visible surface changes such as formation of holes or cracks, de-fragmentation or changes in colour but it does not prove the existence of biodegradation process in terms of metabolism (Shah et al. 2008). Paper samples were taken out from the containers in sampling times and photos of them were made in order to visually evaluate the prints degradation over time. All the images were taken using Huawei camera under the same lighting conditions (resolution 3968x2976, CMOS BSI sensor, f/2.2, with a camera stand).

Fourier transform infrared (FTIR) spectroscopy

Infrared spectra in transmission and attenuated total reflectance (ATR) mode were measured using a Bruker Equinox 55 interferometer. The transmission IR spectra of the UV thermochromic printing ink were obtained at 25 °C and 50 °C from the sample smeared in a thin layer on the surface of the KBr pellet. For the temperature dependent measurements a Bruker heating device Eurotherm 2216e was used. The IR spectra were recorded in the spectral range between 4000 and 400 cm^{-1} at 4 cm^{-1} resolution and averaged over 32 scans. The baseline was corrected in the final spectrum. The ATR spectra of the paper samples, unprinted as well as printed with the ink before and after the soil burial, were measured using the PIKE MIRacle ATR sampling accessory with a diamond/ZnSe crystal plate. The spectra were taken in the single reflection mode, over the spectral range 4000–600 cm^{-1} at 4 cm^{-1} resolution. Thirty two scans were averaged for the final spectrum, which was afterwards corrected using the ATR correction function within the OPUS 6.0 program. Each ATR spectrum shown in figures is the average of three ATR spectra acquired per a sample.

Microbial growth assay

Number of viable bacteria on studied paper samples and corresponding soil was determined after 180 days of soil burial experiments. Paper samples were gently rinsed with sterile distilled water, placed into 9 mL of sterile saline, macerated and vortexed prior to decimal dilution in sterile saline. Number of both facultatively anaerobic and obligately anaerobic bacteria was determined on Nutrient agar (*Biolife*) after incubation at 22°C/3 days in aerobic and anaerobic (*Anaerocult A, Merck*) atmosphere, respectively. Number of viable bacteria was expressed as log CFU (colony forming units) per 1 g of paper sample or wet soil.

Weight loss measurement

Samples degradation was monitored by measuring the weight of paper samples and prints before and after incubation in the soil containers. The samples were taken out and rinsed with distilled water to remove soil particles from the surface.

Then they were dried to constant weight and weighed. The weight loss percentage (w) was calculated according to Eq. (4):

$$w = \frac{m_0 - m_1}{m_0} \cdot 100 \qquad / (\%) \qquad (4)$$

Where, m_0 is the initial weight of the sample, m_1 is the final weight of the sample after degradation.

Colour measurement

Colorimetric properties of printed samples before and after biodegradation were measured using the Ocean Optics USB2000+ spectrophotometer and Ocean Optics SpectraSuite software for the calculation of the *CIELAB* values L^*, a^*, b^* from measured reflectance in the entire spectral range (380-730 nm in 1 nm steps). The D50 illuminant and 2° standard observer were applied in these calculations. All the samples were thermostated by the Full Cover water block (EK Water Blocks, EKWB, Slovenia). The temperature of the copper plate surface was varied by circulation of thermostatically controlled water in channels inside the water block, which was assured to be up to 1 °C accurate in the applied temperature region. All the samples were heated (cooled) and measured at seven different temperatures: 15, 20, 25, 31, 35, 40 and 42 °C.

Results and Discussion

Determination of air permeance of tested samples and increase in thickness due to UV print

Table 2 shows the air permeance of the paper samples and increase in thickness of the samples due to UV print. Results show that synthetic paper is not absorbent (air permeance is 0 µm/Pas), unlike recycled and bulky paper. Bulky paper shows the highest values of air permeance (almost 2 times higher compared to recycled paper). Application of UV printing ink onto the surface of recycled and bulky paper completely reduces theirs air permeance. The increase in thickness of printed bulky paper is the smallest while for synthetic paper is the highest. The measured values of thickness increase due to UV print presented in *Table 2* may suggest that different ink amount was applied on papers, but since printing was carried out under the same conditions, these values are result of different ink absorption into the paper structure resulting from physio-chemical composition of paper substrates.

Table 2 Air permeance of the samples and increase in thickness of the samples due to UV print

Sample	**Air permeance / (µm/Pas)**	**Thickness of the paper / (µm)**	**Increase in thickness due to UV print / (µm)**	**Mass ratio ink to paper / (%)**
Synthetic paper	0.0±0.0	96±1	-	
Synthetic paper - UV print	0.0±0.0	-	13±1	25.2
Recycled paper	6.99±0.25	108±1	-	
Recycled paper- UV	0.0±0.0	-	7±1	25.1

print				
Bulky paper	13.66±0.90	125±1	-	
Bulky paper – UV print	0.0±0.0		5±1	25.3

FTIR spectroscopy of thermochromic ink and papers

Figure 1 shows the FTIR spectra of the UV thermochromic ink were measured in transmission mode at 25 °C and 50 °C, that is below and above its activation temperature. Even though temperature dependent measurements were accompanied by the thermally induced change in the sample colour, significant changes in the IR spectrum of the UV curable thermochromic ink upon heating were not observed. An exception was a weak band at 1382 cm^{-1}, obtained in the spectrum at the lower temperature and assigned CH bending vibrations of CH_2 and CH_3 groups, which was missing from the spectrum acquired at the higher temperature due to physical changes such as melting occurring during heating (*Fig 1 inset*). Few studies showed that IR spectral changes obtained during heating of the thermochromic composites indicated changes in the molecular structure of the components responsible for the colour change (Hajzeri et al. 2015; Raditoiu et al. 2016; Panák et al. 2017). The changes occurring during heating of the thermochromic system composed of a leuco dye, corresponding the symmetric and asymmetric stretching vibrations of COO^- groups which disappear by heating, while the C=O band, characteristic of the colourless lactone form, appears. However, in our case, these changes were not present. Given the similarity between the spectra obtained at both temperatures (*Fig 1*), the observed vibrational bands most likely originated from the thermochromic ink resin, and were not the result of the vibrational modes of the thermochromic composites within the microcapsules present in a significantly smaller amount. In addition, due to coverage of microcapsules with polymer resin, the vibrational bands of microcapsules wall material are probably covered and overlapped with vibrational bands of polymer resin that is present in higher amount.

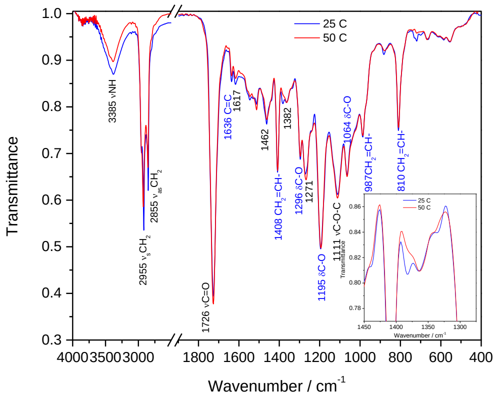


Fig 1. FTIR spectra of the UV thermochromic ink at 25 ºC and 50 ºC, measured in transmission mode

All typical vibrational bands of polyurethane, such as the bands at 3385 cm^{-1} (NH stretching), 2955–2855 cm^{-1} (symmetric and asymmetric CH_2 stretching), 1726 cm^{-1} (C=O stretching), 1365 cm^{-1} (C–N stretching) and 1111 cm^{-1} (C–O–C stretching) were obtained in the IR spectra, evidencing the existence of polyurethane in the UV thermochromic printing ink (Zhang et al. 2010). In addition to that, the bands at 810, 987 and 1408 cm^{-1}, attributed to the in-plane and out-of-plane deformation of the vinyl group (CH_2=CH–), as well as the band at 1636 cm^{-1}, associated with the double bond (C=C) stretching, pointed to the acrylate (Kim and Seo 2004). Moreover, vibrational bands at 1064, 1195 and 1296 cm^{-1} could be assigned to vibrational modes of functionalities consisting of oxygen atom (C–O stretching), pointing to acrylates as well (Bénard et al. 2008). However, due to complexity of the obtained IR spectra some bands could not be unambiguously assigned. For instance, the sharp bands at 1617 and 1462 cm^{-1} could be associated with the ring stretching modes, implying presence of the phenyl moiety in the structure, most likely of polyurethane (Chalmers 2007). Furthermore, the band at 1462 cm^{-1} could be also assigned to bending of the methylene groups present in both, polyurethane and acrylate, while the band at 1271 cm^{-1} could arise from the C–N stretching and C–O stretching in polyurethane and acrylate, respectively (Chalmers 2007). Nevertheless, the IR spectra implied that the studied thermochromic printing ink was very likely composed of polyurethane acrylate.

Figure 2 shows the IR spectrum of the unprinted papers. In the IR spectrum of the synthetic paper the obtained bands were associated with polypropylene (2960–2840 cm^{-1} (asymmetric and symmetric CH_2 and CH_3 stretching), 1433 cm^{-1} (CH_2 and CH_3 bending)) and calcium carbonate (875 and 712 cm^{-1} (asymmetric and symmetric CO_3^{2-} bending)), while beside calcium carbonate (873, 709 cm^{-1}) distinctive bands of cellulose (1426 cm^{-1} (in-plane HCH and OCH deformation), 1160–1000 cm^{-1} (C–O and C–C stretching, COH bending), 898 cm^{-1} (COC and CCO bending)) contributed to the IR spectrum of the recycled paper (*Fig 2*) (Proniewicz et al. 2002). The broad band around 3335 cm^{-1} in the spectrum of the recycled paper were assigned to the OH stretching, mostly originating from cellulose hydroxyl groups, though a weak broad band at 1650 cm^{-1} confirmed the presence of water too. In the IR spectrum of bulky paper beside cellulose and calcium carbonate (873, 710 cm^{-1}), characteristic bands of lignin corresponding to phenyl ring vibrational modes at 1594 cm^{-1} (phenyl stretching), 1272 cm^{-1} (in-plane CH bending) and 812 cm^{-1} (out-of-plane CH bending) were observed (Derkacheva and Sukhov 2008). Comparing the unprinted recycled and bulky paper, the higher intensity of the band assigned to the COC bending of β-(1→4)-glycosidic linkages, sensitive to the amount of the crystalline versus amorphous structure of cellulose and also called "amorphous" absorption band, indicated a higher degree of amorphous structure in the recycled paper (898 cm^{-1}) then in the bulky paper (899 cm^{-1}) (Ciolacu et al. 2011).

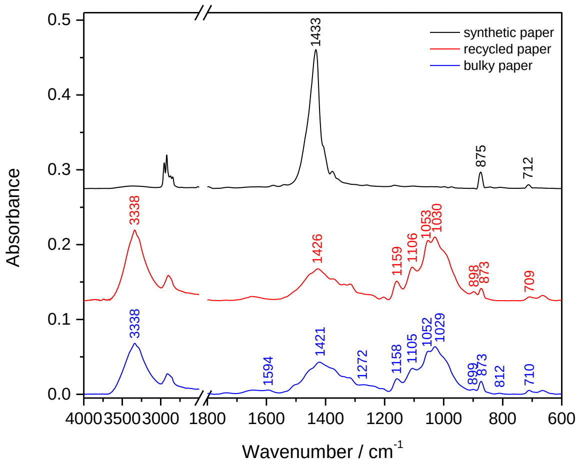


Fig 2. FTIR spectra of the unprinted papers measured in ATR mode. The spectra of the papers are vertically displaced for visual clarity.

Optical Microscopy

Thermochromic ink is composed of blue microcapsules dispersed in pink conventional screen printing ink and due to that property, when the ink is exposed to temperatures above their activation temperature, the print changes its colour from purple to pink (*Fig 3*).

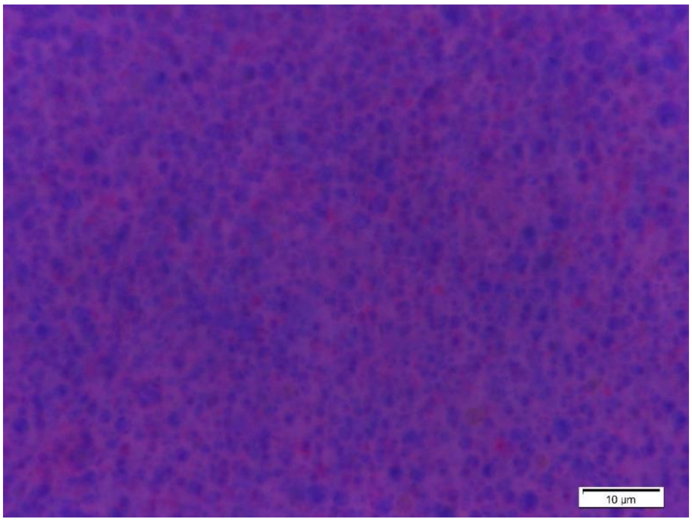


Fig 3. Optical microscopy image of thermochromic ink at 23°C

Determination of surface free energy

All used paper substrates show hydrophobic surface (water contact angle is greater than 90º) (*Table 3*). The highest hydrophobicity shows bulky paper (120°) due to the presence of hydrophobic lignin in paper (Hubbe et al. 2007), while the lowest hydrophobic character was achieved for recycled paper (91°). Comparing the characters of UV prints, it can be seen that UV print on recycled and bulky paper are hydrophobic while for the UV print on synthetic paper, obtained water contact angle (73°) indicates an hydrophilic surface. Different prints surface properties can be attributed to the absorption of ink into the paper structure. Synthetic paper is not absorbent, and all the components of the printing ink remain on the surface. Due to the hydrophilic character of the polyurethane acrylate remaining on the surface of synthetic paper, the hydrophilic properties of the UV print on synthetic paper are greater. Due to heterogeneous surface of samples in the chemical and physical meaning, a greater deviation of contact angels can be seen.

Table 3 Contact angles measurements

Sample	Contact angle / (°)		
	Water	Glycerol	Diiodomethane
Synthetic paper	102.98±4.83	109.51±4.00	57.15±2.36
Synthetic paper - UV print	73.29±4.48	97.80±4.71	38.00±3.67
Recycled paper	91.89±3.80	104.91±4.48	55.60±4.89
Recycled paper - UV print	109.86±4.93	110.95±3.99	28.47±1.03
Bulky paper	120.24±2.28	118.38±4.35	55.84±3.52
Bulky paper – UV print	107.10±4.70	112.10±4.09	28.07±2.16

Table 4 provides the calculated values of the surface free energy (γ) of unprinted and printed samples and its components. The γ values of unprinted paper samples are approximately the same, especially for recycled (23.87 mJ m^{-2}) and synthetic paper (23.10 mJ m^{-2}), slightly higher value has bulky paper (26.44 mJ m^{-2}). γ of all unprinted paper samples mostly originate from dispersive component, which is the highest in the case of bulky paper. Surface free energies of recycled and bulky papers have small values of polar components, but still higher than polar component of synthetic paper due to its chemical structure. Bulky paper has slightly higher polar component than recycled paper.

Comparing the results of γ for printed samples, it can be seen that the highest value of polar component is on UV print on synthetic paper, followed by UV print on recycled paper. The smallest polar component was obtained on UV print on bulky paper. Accordingly, the larger the polar component of the paper, the smaller the polar component of the print is.

This can be explained by the fact that polar component of the thermochromic printing ink and the surface of paper form polar interactions. The polyurethane acrylate is partially hydrophilic due to the presence of C=O and N-H groups. By increasing the polar component of the paper, the attractive polar interactions between the paper and the polyurethane acrylate resin also increase.

Table 5 shows the calculated adhesion parameters. The best adhesion performance is achieved if the following conditions are met: $\gamma_{12} = 0$, W_{12} = maximal and $S_{12} \geq 0$. The adhesion can be expressed as the sum of works of adhesion for polar and dispersive interaction, giving as a result the overall thermodynamic work of adhesion (Repeta 2013).

On the bulky paper the lowest γ_{12} , the highest W_{12} and better spreading (wettability) were achieved, followed by recycled paper and then by synthetic paper. Bulky paper has the highest γ, but also it has the highest value of polar and dispersive component. Synthetic and recycled papers have similar values of γ. However, better adhesion property was achieved on the recycled paper, which contains higher value of polar component. The interactions between the thermochromic ink and the surface of the synthetic paper were achieved only by dispersion forces due to very small share of polar components on the surface of paper, which resulted in formation of the hydrophilic surface of the UV print due to presence of unbounded polar group of polyurethane acrylate resin. Based on the obtained results it can be concluded that the surface of the paper besides large surface free energy should have the optimal polarity in order to achieve better adhesion properties of used thermochromic ink.

Table 4 Surface energy of unprinted and printed samples and its components

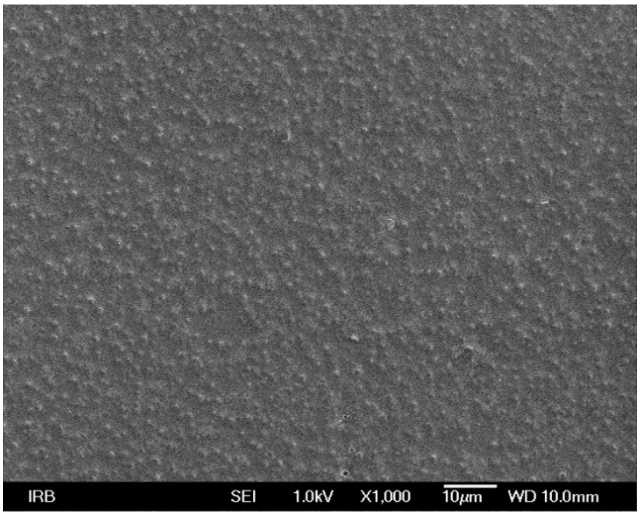
Sample	**Surface free energy γ (mJ m^{-2})**		
	γ^{d}	γ^{p}	γ
Synthetic paper	22.99	0.11	23.10
Synthetic paper - UV print	27.18	4.93	32.11
Recycled paper	22.54	1.33	23.87
Recycled paper - UV print	35.21	1.09	36.30
Bulky paper	25.01	1.43	26.44
Bulky paper – UV print	34.58	0.86	35.44

Table 5 Adhesion parameters

Sample	Adhesion parameters / (mJ m^{-2})		
	γ_{12}	W_{12}	S_{12}
Synthetic paper - UV print	3.74	51.47	-12.75
Recycled paper - UV print	1.41	58.75	-13.84
Bulky paper – UV print	0.84	61.03	-9.84

SEM

SEM micrographs of UV print on synthetic paper (*Fig 4*) show that microcapsules are covered with polymer resin (binder). After 180 days of biodegradation, the changes in the surface of UV print are observed (*Fig 5*). A noticeable biodegradation of the polymer resin can be seen, and the microcapsules become more visible. *Figure 2* shows heterogeneous degradation of the print. Microcapsules are in irregular shape, some are notched and some are hollow. In the case of UV prints on recycled and bulky paper (*Figs. 6,8*), it can be seen that microcapsules are covered with thinner layer of resin and thus, they are more visible. The number of microcapsules in UV prints is significant and they are in the regular circle forms, with around 1-2 μm in diameter. After biodegradation, the surfaces are visibly degraded, in UV print on bulky paper more than on UV print on recycled paper. UV print on recycled paper (*Fig. 7*) shows a larger number of hollow microcapsules than UV print on synthetic paper (*Fig. 5*), more deformation and higher number of irregular microcapsules. However, the number of microcapsules does not change much more than in the original printed recycled paper (*Fig. 6*). After 180 days of biodegradation of UV print on bulky paper destruction of almost all microcapsules is visible (*Fig. 9*). In addition, in *Figure 9* there are also visible cellulose fibres, which indicates a thinning of the polymer resin layer on the surface of bulky paper, *i.e.*, greater biodegradation. From *Figure 9* it can be seen that few microcapsules between cellulose fibres, remains protected. Comparing the results to our previous research where the biodegradation of thermochromic offset ink was studied (Vukoje et al. 2017), results indicated that ink vehicle (vegetable oil + resin) in thermochromic offset ink are more stable than the polymer resin present in UV curable screen printing thermochromic ink. SEM micrographs indicated a notably higher stability of offset ink binder and accordingly lower deformation of the microcapsules.



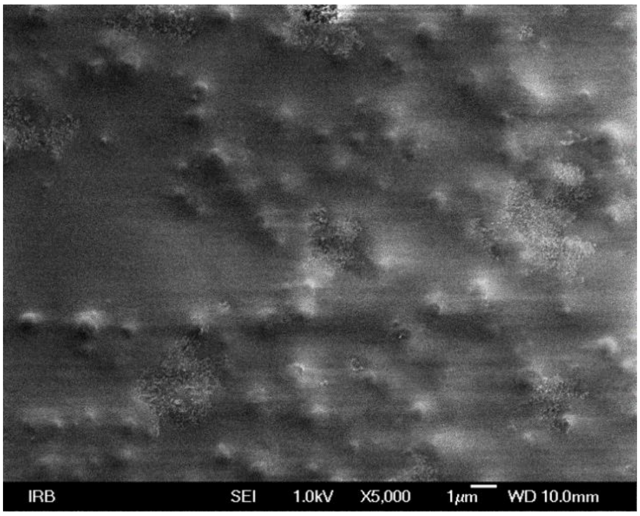


Fig 4. SEM micrograph of UV print on synthetic paper before biodegradation under different magnifications (1000x and 5000x)

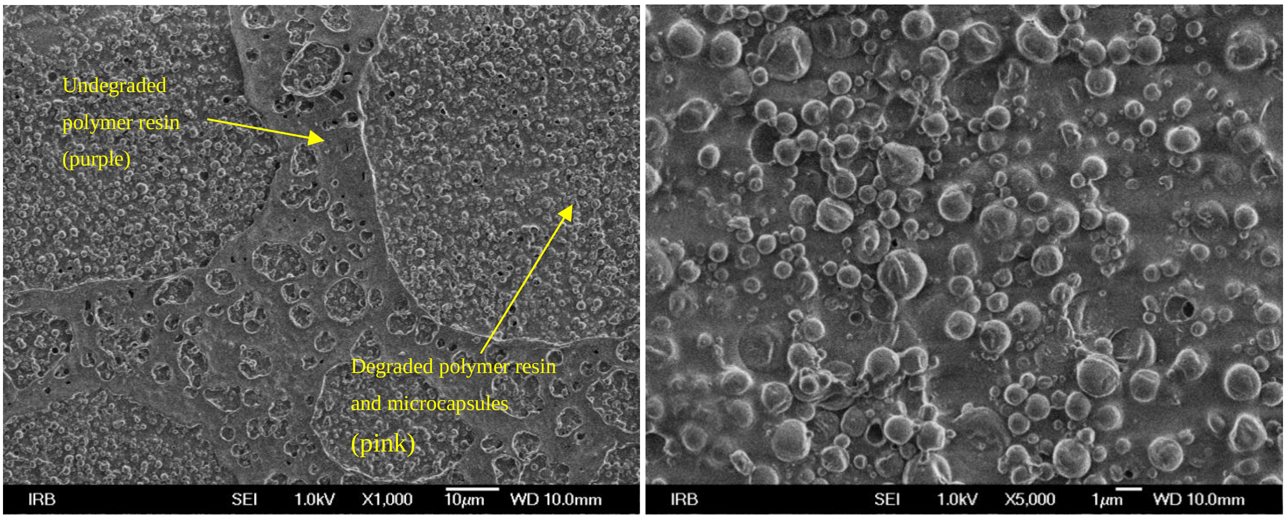


Fig 5. SEM micrograph of UV print on synthetic paper after 180 days of biodegradation under different magnifications (1000x and 5000x)

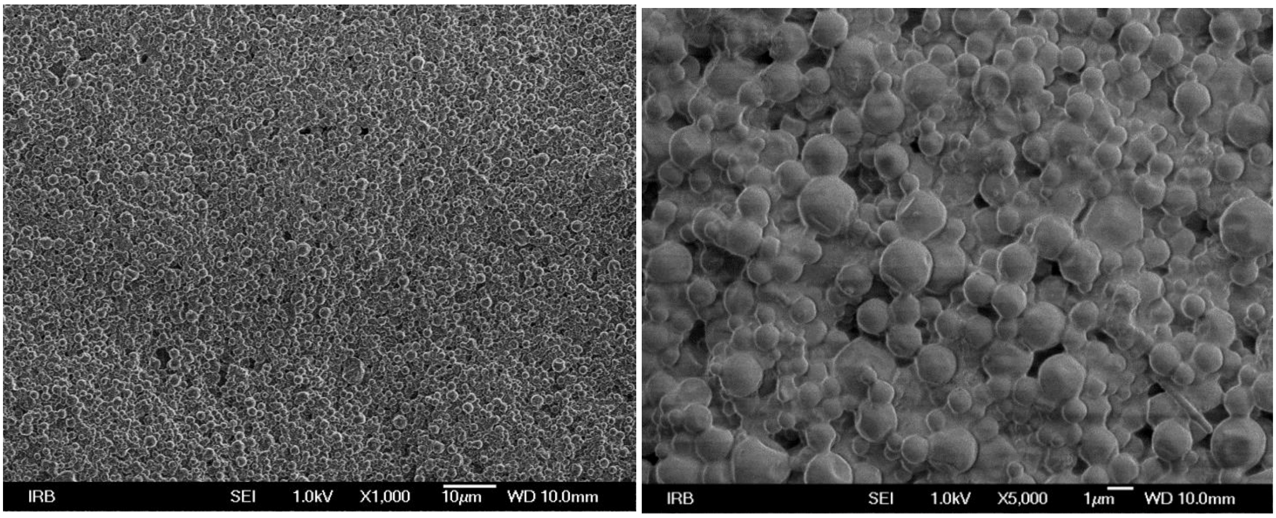


Fig 6. SEM micrograph of UV print on 33% recycled paper before biodegradation under different magnifications (1000x and 5000x)

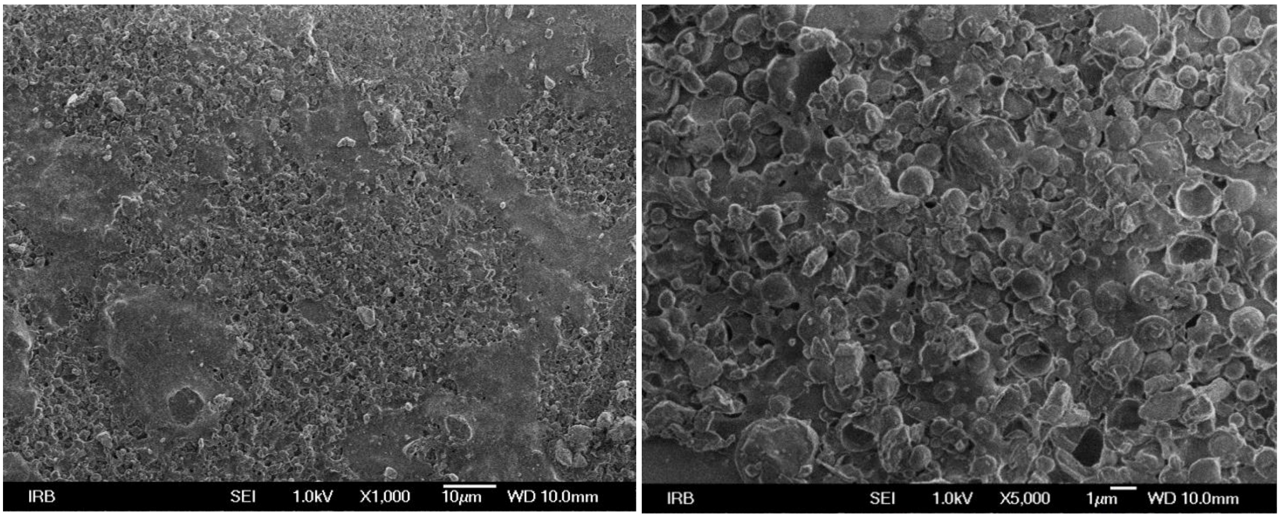


Fig 7. SEM micrograph of UV print on 33% recycled paper after 180 days of biodegradation under different magnifications (1000x and 5000x)

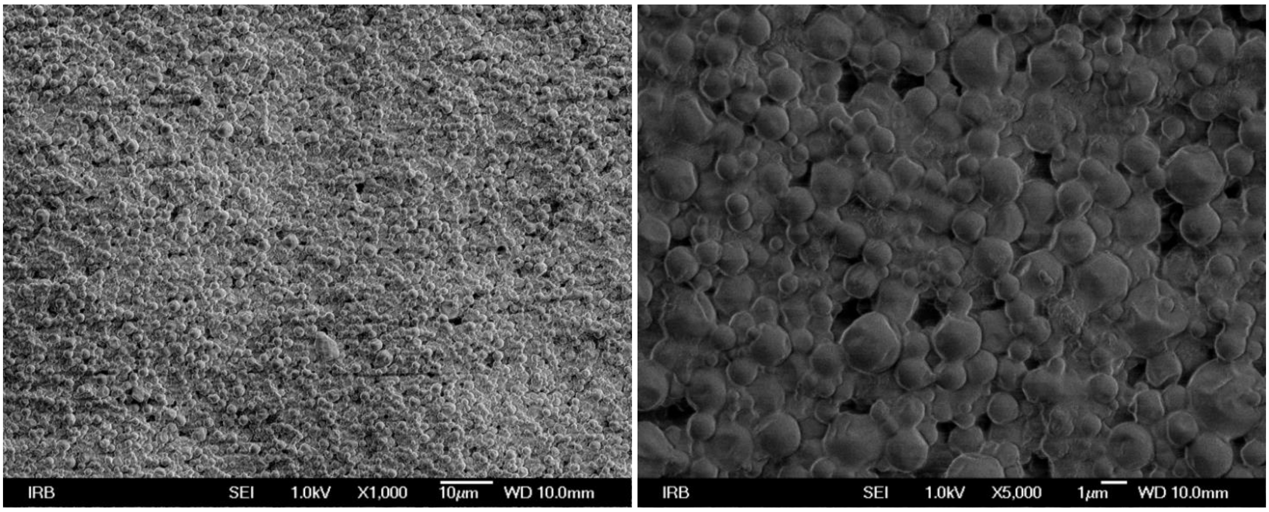


Fig 8. SEM micrograph of UV print on bulky paper before biodegradation under different magnifications (1000x and 5000x)

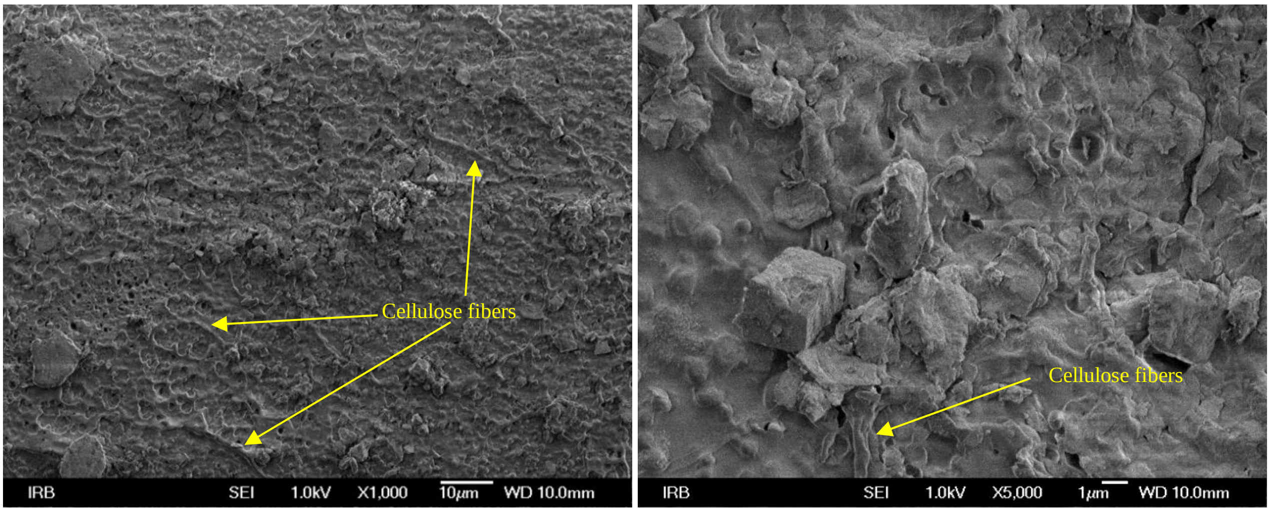


Fig 9. SEM micrograph of UV print on bulky paper after 180 days of biodegradation under different magnifications (1000x and 5000x)

Visual evaluation

Fig 10 and 11 shows the visual evaluation of UV thermochromic prints before and after biodegradation. After 50 days of biodegradation, the UV prints on all papers show only slight changes in colour. After 180 days of biodegradation, it can be noticed that surface of UV print on synthetic paper is purple with pink areas, indicating a heterogeneous degradation. The UV print on recycled paper is mostly pink with a very small amount of purple coloration. Only a pink colour is visible for UV print on bulky paper. In the case of UV print on bulky paper it can be noticed that samples after 50 and 180 days were disintegrated into pieces, *i.e.* showing not only changes in colour, but in the structure as well. The changes in colour of the prints occurring during biodegradations are result of the microcapsules deformation and degradation. The greater the transition to pink colour is, the greater the destruction (deformation) of the microcapsule which was confirmed by SEM micrographs.

Fig 10. Visual evaluation of prints before and after 50 and 180 days of biodegradation

Comparing the unprinted sides of the prints (*Fig 11*), UV print on synthetic paper shows almost no changes in its visual appearance. For the UV print on recycled paper, some formation of spots can be noticed, but after 180 days of biodegradation, these spots present degradation of paper. However, these changes are smaller compared to unprinted side of UV print on bulky paper, whose visual appearance is very diverse from the original.

Fig. 11 shows that unprinted sides of papers before degradation have some differences in colour, *i.e.* unprinted side of recycled paper is pink while unprinted side of bulky paper is more purple. That might be an indication that microcapsules altogether with polymer ink resin penetrate deeper in the structure of bulky paper, promoting biodegradation. In the case of recycled paper, ink binder (altogether with classic pigment) penetrates into its structure. For the print on synthetic paper, there is no penetration of ink into to its structure. All components of ink remain on the surface of synthetic paper.

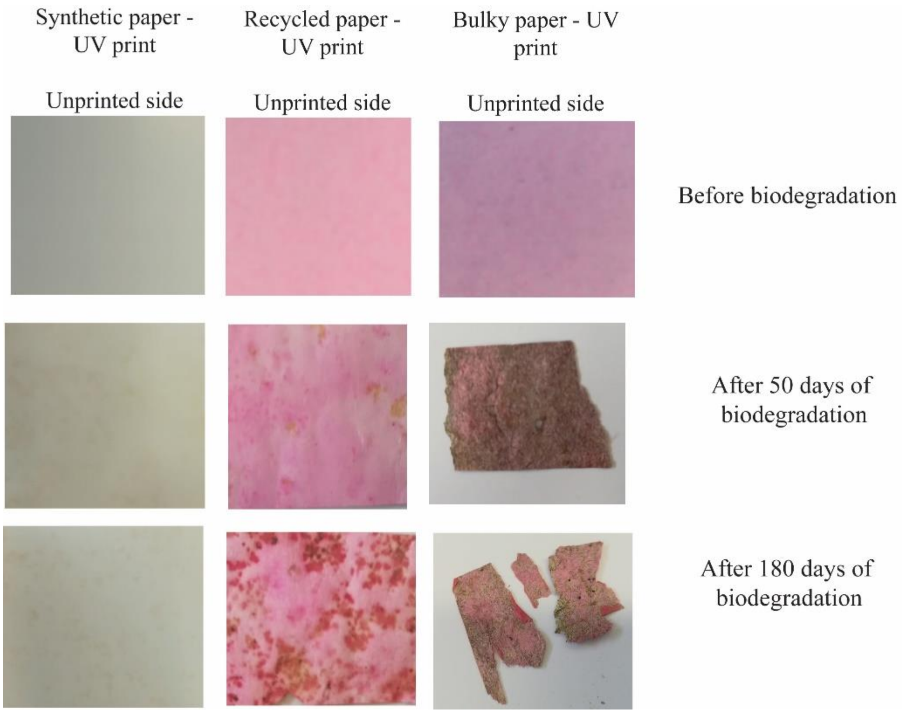


Fig 11. Visual evaluation of prints before and after 50 and 180 days of biodegradation – unprinted side

Microbial growth assay and weight loss measurement

Figure 12 shows the number of bacteria on the unprinted and printed-paper samples after 180 days of biodegradation in the soil. In the case of unprinted paper samples, the highest number of bacteria was obtained on recycled paper, followed by the bulky paper. The number of bacteria obtained on synthetic paper was the smallest and it was smaller compared to number of bacteria isolated from the soil. For this reason, synthetic paper shows no changes in weight after biodegradation period due to microbial attack resistance of polypropylene present in its structure (Arutchelvi et al. 2008; Leja and Lewandowicz 2010). The weight loss measurement for unprinted recycled paper indicates higher biodegradation compared to bulky paper (*Table 6*). After 180 days of biodegradation, unprinted recycled paper was more than 90% degraded, while bulky paper was more than 25.8% degraded. Higher rate of recycled paper biodegradation compared to bulky paper, can be explained by the higher ratio of amorphous cellulose in recycled paper, which was confirmed by FTIR (*Fig. 2*) and presence of shorter cellulose fibres resulting from process of recycling. Amorphous cellulose is more susceptible to degradation than the crystalline (Van Wyk and Mohulatsi 2003). In addition, bulky paper contains lignin that interferes the paper biodegradation (Komilis and Ham 2003).

The smallest number of bacteria was isolated on printed synthetic paper and it was almost the same as number of bacteria isolated from the soil, which resulted in a small weight loss (3%) after 180 days of biodegradation (*Table 6*). This can be mainly described by the UV print degradation rather than synthetic paper degradation since unprinted synthetic paper shows no changes in weight during biodegradation. It can be assumed that UV print is more biodegradable than synthetic paper. For the printed recycled paper an opposite behaviour was observed, *i.e.* notable reduction of biodegradation rate compared to unprinted recycled paper was noticed. With the application of thermochromic ink, the weight loss was five times lower. This behaviour can be explained by the polymer ink resin and pigment absorption. In the case of recycled paper, it is obvious that classic pigment that penetrates into its structure lowers the rate of biodegradation, which means that classic pigment is less degradable than recycled paper.

The highest change in the weight loss was obtained for the printed bulky paper. In this case, printed bulky paper degrades faster than unprinted bulky paper. Higher rate of printed bulky paper biodegradation compared to printed recycled paper can be due to better absorption of microcapsules. The deeper the penetration of the microcapsule into to structure of paper is, higher biodegradation occurring from the unprinted side is. Considering the fact that the weight loss measurement for printed sample is almost the same after 50 and 180 days of biodegradation, degradation of paper probably stopped after 50 days, but after that period only degradation of microcapsules occurred. Due to their small sizes and lower share in the thermochromic ink and printed sample, the weight loss reduction after 180 days was negligible.

The similar number of bacteria obtained for unprinted and printed bulky paper can be explained by the fact that bacterial growth after 180 days of biodegradation of printed bulky paper was probably in decline due to destruction of almost all microcapsules (*Fig 9*) and reduction in biodegradation rate.

Thermochromic microcapsules are mostly composed of urea - formaldehyde or melamine -formaldehyde resins gelatine – gum arabic and epoxy resins (Aitken et al. 1996; Fujinami 1996; Seeboth and Lotzsch 2008) which are biodegradable and during biodegradation can act as nitrogen sources (El-Sayed et al. 2006). Microcapsules can act as an active sites promoting biodegradation.

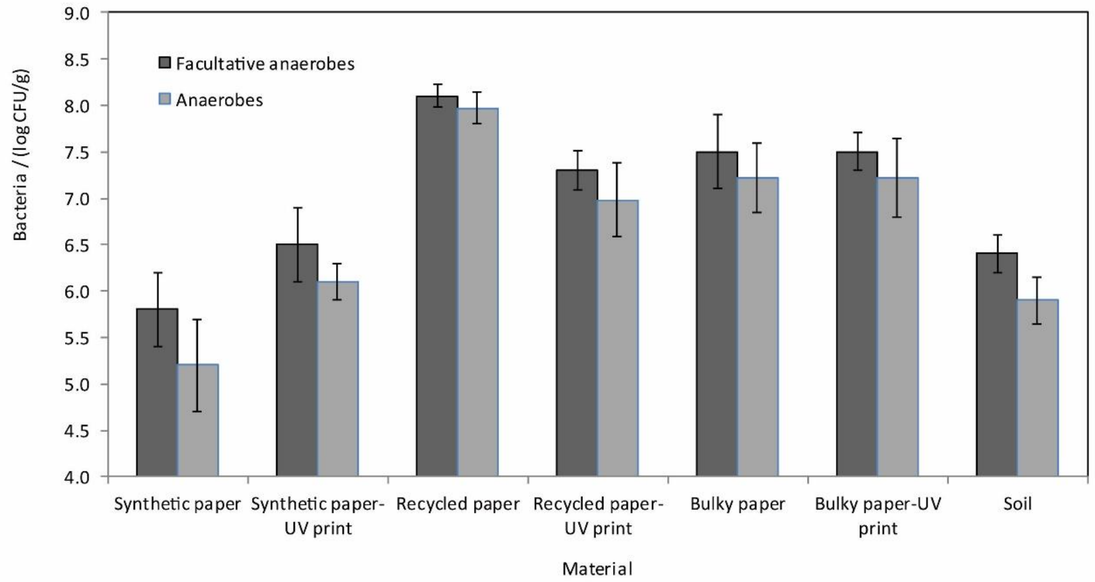


Fig 12. Number of viable bacteria on unprinted and printed-paper samples and in corresponding soil after 180 days of biodegradation

Table 6 Weight loss during soil burial

Sample	Weight loss / (%)	
	Days	
	50	180
Synthetic paper	0.0	0.0

Synthetic paper - UV print	0.6	3.0
Recycled paper	46.25	92.87
Recycled paper - UV print	6.8	17.8
Bulky paper	20.45	25.80
Bulky paper – UV print	49.2	50.2

FTIR spectroscopy of prints before and after biodegradation

The IR spectra of the thermochromic prints on all paper samples: synthetic, bulky and recycled, measured in attenuated total reflectance (ATR) mode, were very similar (*Fig 13*). In comparison to the spectrum of the thermochromic UV curable ink, the bands at 1408, 1296, 1271, 1195 and 1064 cm^{-1} in the IR spectra of the prints were weaker and poorly defined. The intensity of these bands decreased due to polymerization of polyurethane acrylate during UV curing.

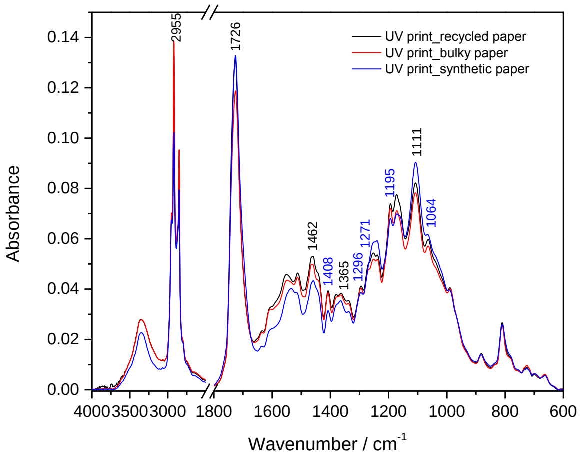


Fig 13. FTIR spectra of the UV thermochromic print on the recycled, bulky and synthetic paper before biodegradation, measured in ATR mode

The IR spectra of the thermochromic UV prints on the used papers before and after 50 and 180 days of biodegradation were shown in *Figures 14,15* and *16*. In addition, the IR spectra of UV curable ink and unprinted papers have been presented in *Figures 12, 13* and *14*.

A decrease of band intensities located in the 1100–1000 cm^{-1} range (attributed to the ester C-O stretching vibration), 1260 – 1200 cm^{-1} range (attributed to carbonyl oxygen linkage) and carbonyl peak around 1730 cm^{-1} were observed after degradation. The changes in those bands are present for all printed papers after biodegradation (*Figs 14, 15 and 16)* and very likely indicate the breaking down of the ester linkages, leading to the changes in the ester and urethane groups of polyurethane resin, *i.e.* changes in polymeric structure (Oprea and Doroftei 2011; Oprea et al. 2016). In the ranges from 1100 – 1000 cm^{-1} and 1260 – 1200 cm^{-1}, the highest changes were observed for the print on bulky paper, followed by print on recycled paper. The smallest changes were observed for the synthetic paper. However, the changes in the spectral ranges from 1300 – 1800 cm^{-1} were observed only for the printed bulky paper.

An appearance of the intense broad band at around 1030 cm^{-1} could be attributed to cellulose, due to thinning of the polymer resin on the surface of the bulky and recycled paper, which can be attributed to stretching of C–O in cellulose/hemicellulose molecules (Grilj et al. 2012). Interestingly, in the IR spectrum of the UV print on the bulky paper this band decreased after 180 days of biodegradation, if compared to the spectrum after 50 days, indicating cellulose degradation as well. This was supported by SEM micrographs (*Figs 8 and 9*). The intense cellulose like vibration bands (at 1030 cm^{-1}) were also obtained after 180 days of the UV print biodegradation on the recycled paper. Given that the spectral motif around 1030 cm^{-1} was obtained in the IR spectra of the UV print on all the papers after biodegradation, including the synthetic paper not consisting of cellulose, its origin could be also partially associated with silicates (Si–O stretching) adsorbed on the prints from the soil. The presence of silicates on the surface of the prints, was also indicated by the weak bands at 3698 and 3618 cm^{-1} assigned to O–H stretching in the Si–OH structural moieties located on the silicate surface (Das et al. 2013; Tinti et al. 2015). Since weak bands around 3696 and 3620 cm^{-1} corresponding to the silicates OH groups were obtained in the IR spectra of the prints on all the papers, it was very likely that the band at 1039 cm^{-1} associated with the Si–O stretching in silicates was also present in the spectra of the prints on the recycled and bulky paper, but overlapped by the strong broad cellulose band.

Due to degradation of polyurethane, the formation of degradation products can be noticed and followed in the hydroxyl and NH group stretching range (3600–3100 cm^{-1}), whose intensity increased after biodegradation (Bénard et al. 2008; Oprea and Doroftei 2011; Huang et al. 2016). Compared to the IR spectra before biodegradation, the band at around 3350 cm^{-1} was slightly stronger, wider and positioned at higher wavenumbers in the spectra of the buried prints (*Figs 14, 15 and 16*).

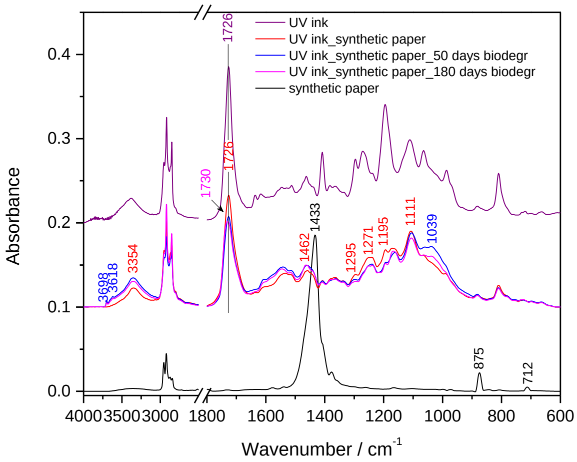


Fig 14. FTIR spectra of the UV thermochromic ink, the neat synthetic paper and the prints of the ink on the synthetic paper before and after 50 and 180 days of biodegradation, measured in ATR mode. The spectra of the ink, the paper and the prints are vertically displaced for visual clarity.

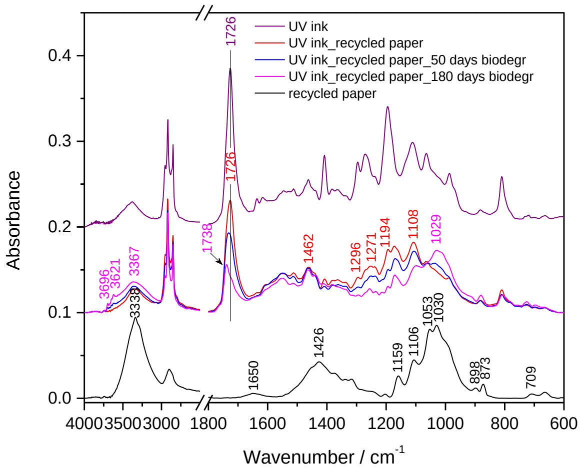


Fig 15. FTIR spectra of the thermochromic ink, the neat recycled paper and the prints of the ink on the recycled paper before and after 50 and 180 days of biodegradation, measured in ATR mode. The spectra of the ink, the paper and the prints are vertically displaced for visual clarity.

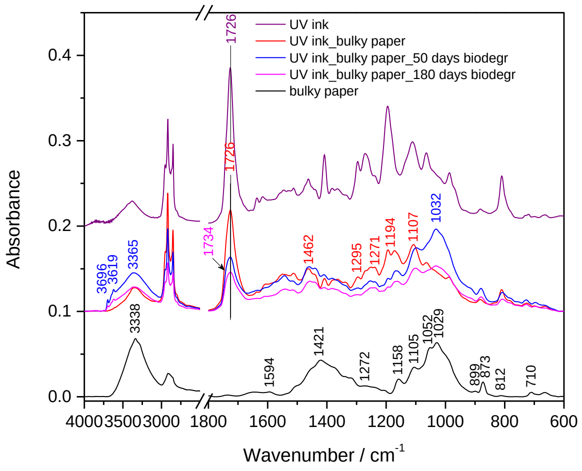


Fig 16. FTIR spectra of the thermochromic ink, the neat bulky paper and the prints of the ink on the bulky paper before and after 50 and 180 days of biodegradation, measured in ATR mode. The spectra of the ink, the paper and the prints are vertically displaced for visual clarity.

Colorimetric measurements

Results of colorimetric *a** and *b** values determined on UV thermochromic prints before and after biodegradation are presented in *Figure 17.* In the *CIELAB* colour space the value *L** represents the lightness of the colour, the value *+a** represents redness, *–a** represents greenness, *+b** represents yellowness while the value *–b** represents blueness. Due to the formation of polymer ink layer on the surface of all papers and its complete coverage of paper samples, the colour of unprinted papers does not have a significant influence on the colour reproduction of the UV prints. *Figure 17* shows that the colorimetric *a** and *b**values of original UV prints on bulky and recycled paper, measured below the activation temperature, have similar colorimetric properties. However, the UV print on bulky paper has slightly lower *a** and *b** values compared to UV print on recycled paper. This can be attributed to better absorption of microcapsules and classic pink pigment into a structure of bulky paper. Compared to UV prints on bulky and recycled paper, UV print on synthetic paper has higher *a** value, and smaller *b** value, due to higher concentration of ink on the surface of the paper. *Figure 17* shows the transition of prints colour from purple to pink. The *a** and *b** values of UV prints after 50 days of biodegradation are smaller than the initial values. The *a** value on bulky paper print shows the lowest positive values while the *b** value shows the smallest negative values, indicating the highest colour change. After 180 days of biodegradation, the *a**and *b** values of all samples, are more positive compared to the initial values. The smallest colour change was in the case of UV print on synthetic paper. After 180 days of biodegradation, the pink colour of print on bulky paper was lighter (smaller *a** value) compared to print on recycled paper, indicating higher colour change.

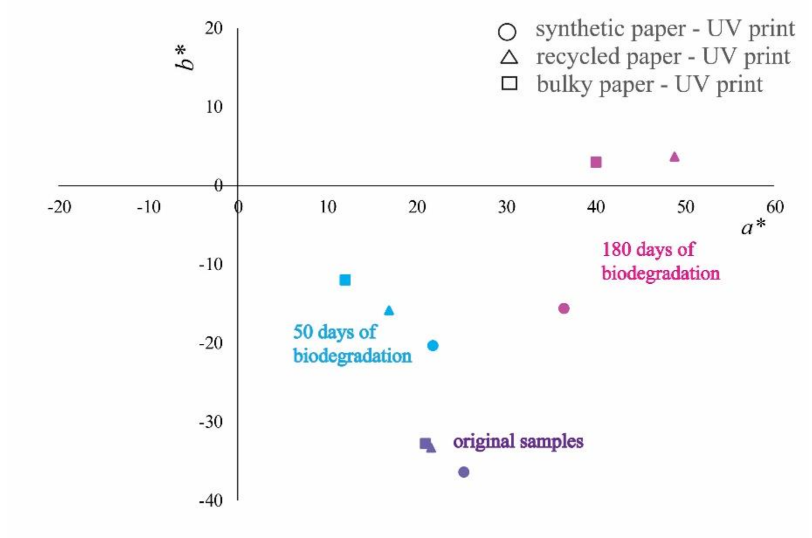


Fig. 17. Colorimetric properties (*a** and *b** values) of UV prints measured at 20°C before (purple), after 50 days (blue) and 180 days (pink) of biodegradation (circle- UV print on synthetic paper, triangle – UV print on recycled paper, square – UV print on bulky paper)

The TC system has memory, which is called hysteresis. It’s colour hysteresis describes the colour of a TC sample as a function of temperature and should be presented in four-dimensional space (*i.e.* whose three dimensions represent colour values *L**, *a**, *b**, while the fourth dimension illustrates temperature (T)) or by two- dimensional graphs (Kulčar et al. 2010). The trajectory obtained by heating is not equal to one obtained by cooling. The area of the surface defined by the two trajectories shows the similarity (of the colour change) of the heating and cooling run.

The reversible TC process can be presented by change of *L**, *a** and *b** values as a function of temperature. When printed sample is heated, decolourization of microcapsules occurs above the activation temperature (TA). Therefore, the *b** values increase because only the pink colour of the classic pigment remains. The reverse process occurs during cooling at lower temperatures.

L(T)* hysteresis describes temperature dependence of *L** values. *Figure 18a* shows that all UV prints before biodegradation tests show similar values, *i.e.* similar reversibility of colour. UV prints on recycled and bulky paper show almost the same behaviour, while small differences can be noticed for UV print on synthetic paper. Due to higher amount of polymer resin containing pink classic pigment over the microcapsules present on the surface of the synthetic paper, the hysteresis is shifted to higher *L** values. After 50 days of biodegradation (*Fig 18b*), the initial *L** values of the UV prints on recycled and bulky paper are shifted to higher *L** values, similar to *L** value of UV print on synthetic paper. This indicates a higher concentration of classic pink pigment on their surface. The highest decrease of *L*(T)* hysteresis height was obtained on printed bulky paper, while the smallest change in *L*(T)* hysteresis height was obtained on printed synthetic paper, indicating that he highest destruction of colour was noticed on printed bulky paper. After 180 days of biodegradation (*Fig 18c*), the prints on recycled and bulky papers showed remarkable reduction of thermochromic effect. The reduction of thermochromic effect and changes occurring in *L*(T)* hysteresis are result of reduction in active microcapsules number, which was confirmed by the SEM micrographs. *L*(T)* hysteresis are substantially shifted toward higher *L** values suggesting greater concentration of classic pink pigment in relation to the concentration of microcapsules.

In addition, the changes occurring in *b*(T)* hysteresis may also point to degradation of blue microcapsules (*Figs 19 a, b, c*). The smallest changes occurring in *b*(T)* hysteresis were obtained for UV print on synthetic paper. Interestingly, after 50 days of biodegradation, the final *b** values (at highest temperatures) are not approaching to zero by heating, but they are becoming positive (shift to the yellow area). In the case of UV prints on recycled and bulky paper, the *b** values are positive throughout the whole temperature range. After 180 days of biodegradation, the greatest shift to yellow area was obtained on printed synthetic paper, followed by printed recycled paper and printed bulky paper.

The changes in the *a*(T)* hysteresis my point to degradation of classic pigment present in polymer ink resin (*Figs 20 a, b and c).* After 180 days of biodegradation, the final *a** values (at highest temperatures) are the highest in the case of printed synthetic paper, slightly lower values are on printed recycled paper, and the smallest a* values are on printed bulky paper. Accordingly, the highest shift to yellow and red area obtained on the printed synthetic paper indicates the highest concentration of classic pink pigment. The smallest concentration of classic pink pigment was obtained on the printed bulky paper after 180 days of biodegradation. It can be assumed that classical pink pigment shows slower rate of biodegradation. In the case of printed bulky paper, in which the highest absorption of thermochromic ink was noticed, the active sites that bacteria use for their metabolism are the most accessible. If the smaller the effect of ink separation is, these sites are less accessible, so the rate of biodegradation is lower.

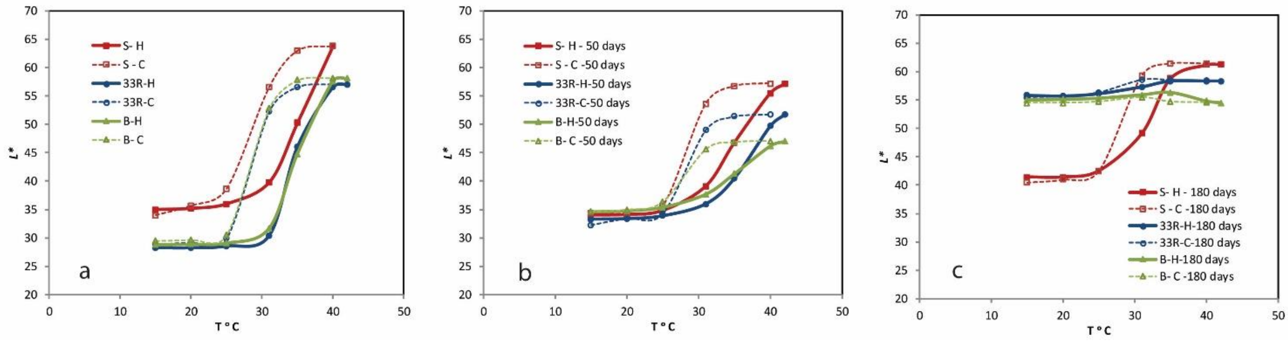


Fig 18. *CIELAB L** values of UV print on synthetic paper (S - red), recycled paper (33R - blue) and bulky paper (B - green) in dependence on temperature at heating (solid line) and cooling (open line) before biodegradation (a), after 50 days of biodegradation (b) and after 180 days of biodegradation (c).

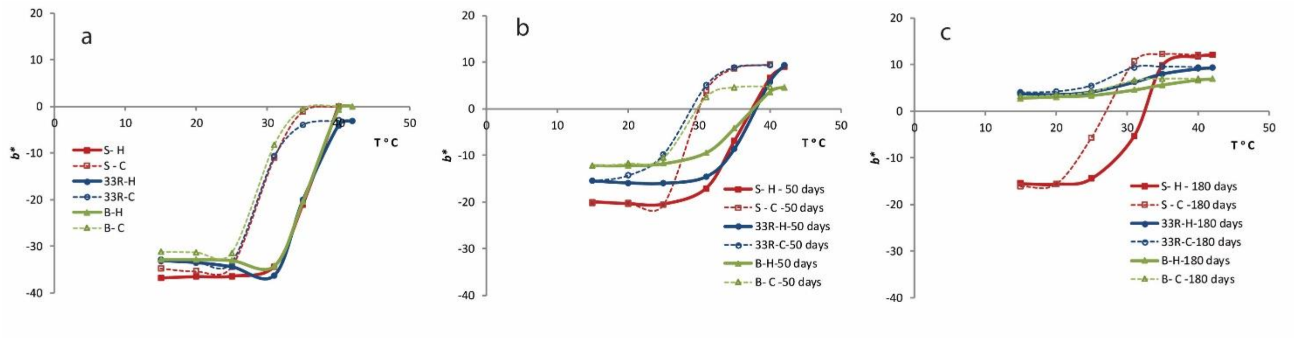


Fig 19. *CIELAB b** values of UV print on synthetic paper (S - red), recycled paper (33R - blue) and bulky paper (B - green) in dependence on temperature at heating (solid line) and cooling (open line) before biodegradation (a), after 50 days of biodegradation (b) and after 180 days of biodegradation (c).

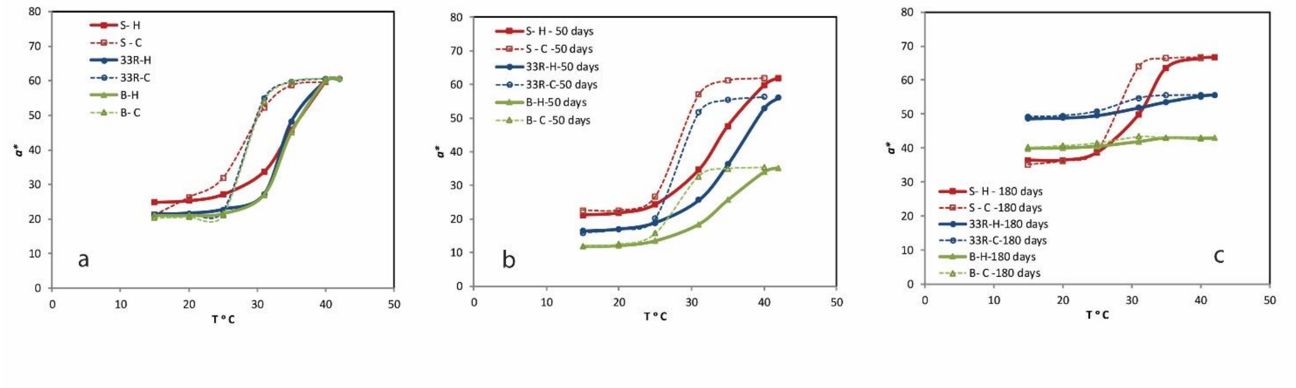


Fig 20. *CIELAB a** values of UV print on synthetic paper (S - red), recycled paper (33R - blue) and bulky paper (B - green) in dependence on temperature at heating (solid line) and cooling (open line) before biodegradation (a), after 50 days of biodegradation (b) and after 180 days of biodegradation (c).

Conclusions

The ink penetration into the paper structure is very important property. Results show that the best absorption of ink was in case of bulky paper structure, followed by recycled paper. In the case of synthetic paper, there is no ink penetration into its structure. The results show that the print obtained on paper that absorbs more biodegradable thermochromic ink, shows higher rate of biodegradation. If the microcapsules are more exposed to bacteria, *i.e.* covered with a thinner layer of ink polymer resin, the higher rate of biodegradation will be. On synthetic paper, the microcapsules are covered with thicker layer of polymer resin making them less exposed to bacteria. The obtained FTIR spectra implied that the ink binder is polymer resin containing polyurethane acrylate. The highest changes in the IR spectra during biodegradation were obtained for UV print on bulky paper followed by UV print on recycled paper. The smallest changes were obtained for the UV print on synthetic paper. In addition, the SEM micrograph indicated degradation of almost all microcapsules after 180 days of biodegradation on UV print on bulky paper. The SEM micrograph of prints on recycled paper after 180 days of biodegradation showed a certain deformation and degradation of microcapsules. In the case of UV print on synthetic paper, in the SEM micrograph only degradation of polymer resin was observed. However, deformation of microcapsules can be noticed but not in the whole area as for UV print on recycled paper. Some of the microcapsules remain protected by the polymer resin hence biodegradation occurred as spots, thus the colour degradation of print after 180 days of biodegradation was less comparable to other samples on bulky and recycled paper. Based on the obtained results, it can be said that in the case of the used thermochromic UV ink, the polymer resin, pigment and the microcapsules are biodegradable in the anaerobic soil environment.

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THE ROLE OF ADHESION ON THERMOCHROMIC PRINTED CARDBOARD BIODEGRADATION

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Abstract: As the packaging industry is growing lately and the amount of packaging waste increases, it becomes one of the major environmental problems. Packaging waste comprising about one-third of all municipal solid waste, mainly plastic and paper based. Anaerobic degradation is one of the most environmentally friendly methods for solid organic waste treatment and widely applied for bio-energy production. In this study, the influence of screen print thermochromic ink on biodegradability aspect of three different cardboard materials (UmcaColor - UC, Propack - PP, Lux Pack - LP) were studied using the soil burial test under anaerobic conditions. Neat and printed cardboard samples were evaluated for changes over 4 months by visual examination, weight loss measurements, volatile solids reduction and surface properties. The surface free energy (SFE) and adhesion parameters were determined for all samples, and showed a very high binding of ink to all cardboard samples. Thermochromic ink reduces the biodegradation of cardboard due to strong ink adhesion on cardboard. If a large SFE interphase is, separation of ink from the substrate occurs. The highest reduction of biodegradation for printed samples was noticed for UC sample. After 120 days the total weight loss for all three neat cardboard samples was similar (about UC 38.4%, PP 34.8%, LP31.5%). Printed samples showed lower values of biodegradation, up to 36 % reduction compared to neat samples after 120 days.

Keywords: surface free energy, adhesion, biodegradation, cardboard, thermochromic ink

INTRODUCTION

Municipal solid waste continues to be a major environmental problem. Biodegradable municipal waste consists mostly of organic fraction, paper, wood and textiles. Existing methods of waste management include processing and recycling, incineration, composting or aerobic digestion, anaerobic digestion and landfilling. Anaerobic digestion occurs in landfilling sites as natural process but produced methane can be collected or flamed. Paper is mostly recycled by conventional methods like deinking. 40% of paper is wet and is not suitable for recycling but is suitable for composting or digestion (Murphy and Power 2006). Even though paper based materials are often recycled by means of deinking flotation, not all products are suitable for it. Paper based packaging contaminated with food is not desirable in paper recycling facilities due to cleaning difficulties, which leads to contamination issues (Twede, Diana; . Selke, Susan; l Kamdem and Shires, David ; Pira 2015).Besides food contaminants, in the classic flotation deinking process a certain types of prints can cause problems as well. It is known that classic offset prints are easy deinkable by conventional process, but flexographic and UV curing inks can hardly be removed from recycled pulp (Faul 2010). The quality of the waste paper may ultimately decrease as more and more "marginal" paper fractions are collected for recycling and the contents of harmful substances in paper thereby increase (Pivnenko et al. 2015). Study conducted on deinkability aspect of thermochromic inks showed they are very difficult to deink by conventional deinking process (Vukoje et al. 2016). Thus it is crucial to find an alternative method to classic recycling process, such as composting or anaerobic digestion.

Anaerobic digestion (AD) is a promising technology which is widely used in the treatment of various organic wastes, mostly for the treatment of the rapidly biodegradable municipal solid waste, agro-wastes, sewage sludge, etc. It is a natural process where anaerobic bacteria existing in an oxygenfree environment degrade organic matter releasing biogas that primarily contains methane (CH_4) and carbon dioxide (CO_2). Anaerobic process, if properly applied, can have more advantages than other processes like high degree of waste stabilization, low production of waste biological sludge, low nutrient requirements, no oxygen requirements and useful energy end product – methane (Ismail and Abderrezaq 2007).

Even there are numbers of different methods for biodegradation examination; the soil burial test is one of the simplest methods. The soil beds containing the samples are incubated at a constant temperature for between 28 days and 12 months. The moisture content is normally set at 20–30%, although it is better calculated as a percentage (40–50%) of the soil's maximum water holding capacity (Chandra 1998).

Variety types of paper and board can be used in packaging applications. Cardboard can either be a single or a multi-layer material. It can be made of more than one type of pulp and it often incorporates a recycled fibres. In multi layered cardboards, the inner layers are usually made of from lower quality pulp than the outer layers. In order to improve printability, the cardboard can contain clay or other coating on one or both surfaces. Cardboard is often classified by its thickness, ranging from 410 to 610 µm (Twede, Diana; . Selke, Susan; l Kamdem and Shires, David ; Pira 2015).Cardboards can be classified using a brief description consisting of two letters and a number, for example GC1; where G represents coated, C- chromo and 1- low quality.

Thermochromic inks are temperature sensitive materials which change colour with heat. In their cool state, they exhibit colour, and when heated, they become clear or translucent. The temperature range at which transition of coloured to colourless state occurs is commonly called the activation temperature (TA). The change of colour may be irreversible or reversible (Homola 2008). The reversible inks microcapsule consists of leuco dye, solvent and colour developer. The main disadvantage of organic microcapsules is their insufficient light stability and high sensitivity to environmental changes (Rožić et al. 2015). Thermochromic inks are available for use on a variety of substrates and they have been developed for many types of printing processes, such as screen printing, gravure and flexography, and more recently for applications in offset lithography (Bamfield, P, Hutchings 2010).

Many studies have reported the degradation of paper based materials in various environments such as aerobic and anaerobic (Yen and Brune 2007; Wang et al. 2015; Fonoll et al. 2016), but there is lack of studies about influence of printing inks on biodegradation, especially for thermochromic inks.

METHODS

Materials

Three different cardboard materials were used in biodegradability test. The used cardboards are representing different classes of cardboards (Table 1) according to their properties and quality.

Table 1 – Cardboard classification

Cardboard samples	Abbreviation	Grammage, g/m^2	Classification
Lux Pack	LP	350	GC1
Propack	PP	350	GT2
UmcaColor	UC	350	GD2

All cardboard samples were analysed in the terms of thickness, moisture, ash and $CaCO_3$ content. Thickness of all samples was determined according to T411 standard. Moisture content was determined according to T412 om-94, while ash content was determined according to T413 (combustion at 900°C). Alkalinity of paper as calcium carbonate was determined according to T533.

All three cardboard samples were printed with thermochromic ink in order to examine how it affects the process of biodegradation. One leuco dye based, screen-printing UV curable thermochromic ink produced by CTI®was used for printing. The thermochromic ink was coloured in purple below its activation temperature (TA=31 °C) and changed to pink above the activation point. The biodegradation of neat (UC, LP, PP) and printed cardboard (UC-UV, LP-UV, PP-UV) samples was studied using the soil burial test under anaerobic conditions as it will be described in the text.

Printing

The printing trials were carried out using the Siebdruckgeräte von Holzschuher K.G., Wuppertal. The cardboards were printed in full tone, under the same conditions. The printed samples were dried under the UV irradiance (30 W/cm) using TechnigrafAktiprint L 10-1 device.

Determination of surface properties

The evaluation of surface free energy (SFE) of neat and cardboard printed with thermochromic ink was carried out by measuring contact angle of standard liquids. Measurements were conducted on DataPhysics OCA 30 Goniometer, using the Sessile Drop method. Standard test liquids whose surface tensions are known (Table 2) were demineralized water, diiodomethane and glycerol. Measurements were performed at room temperature of 23.0 ± 0.2ºC. The volume of droplet was 1 µL. Contact angle was captured by CCD camera and measured 1s after the droplet was formed. Average values of ten drops on different places of the same sample were taken and presented as mean±SD in Table 4.

Table 2 – Surface tensions (γ) of test liquids and their dispersive (γ^d) and polar (γ^p) components

Liquid	Surface tension (mJm^{-2})		
	γ	γ^d	γ^p
Water	72.80	21.80	51.00
Diiodomethane	50.80	50.80	0.00
Glycerol	63.40	37.00	26.40

Using the Owens Wendt calculation method the surface free energy (γ) of the samples was determined as well as their dispersive (γ^d) and polar (γ^p) components. This calculation method is integrated in the software (SCA20, Version 2.01) and carried out automatically. The obtained surface free energy and its components are presented in the results section (Table 5). From the obtained SFE, adhesion parameters were calculated. Thermodynamic work of adhesion W_a between two phases was calculated according to (Eq. 1) (Żenkienwicz 2007).

$$W_{12} = \gamma_1 + \gamma_2 - \gamma_{12} \qquad [1]$$

where the subscript refers to surface free energy of the each solid, in our case cardboard and ink print, and the γ_{12} denotes their surface free energy of the interphase. Using the Owens-Wendt model the surface free energy of the interphase was determined according to Eq.2 (Żenkienwicz 2007).

$$\Gamma_{12} = \gamma_1 + \gamma_2 - 2\sqrt{\gamma_1^d \gamma_2^d} - 2\sqrt{\gamma_1^p \gamma_2^p} \qquad [2]$$

Soil burial experiments

Soil was sieved to less than 2 mm particle size. Large plant materials, stones, and other inert materials were removed. Laboratory soil burial experiments were conducted at room temperature 25±3°C by placing the neat and printed cardboard samples horizontally in laboratory glass containers filled with soil. Samples were cut in 4 x 5 cm. All the samples were buried for 14, 32, 50, 80 and 120 days in glass containers filled with the soil. The water content of the soil was adjusted to 60% of its maximum water retention capacity. The commercial available reagent was used in order to allow the development of anaerobic conditions. The existence of anaerobic conditions was proved with Anaerotest (Merck) strips.

Visual observation of surface appearance change

Changes in the appearance of sample surfaces were observed before and after biodegradation. Photos of all samples were taken in order to visually evaluate the substrate degradation over time. A method of visual evaluation can be used in order to describe biodegradation as a first indication of any microbial activity in the terms of visible surface changes (formation of holes or cracks, de-fragmentation, changes in colour)(Shah et al. 2008).

Weight loss measurement and Volatile solids (VS) determination

After the soil burial test, biodegradability was measured through weight loss and volatile solids (VS) reduction. After the incubation in the soil containers, the samples were taken out and rinsed with distilled water to remove soil particles from the surface. Then were dried to constant weight and weighed. The weight loss percentage was calculated according to Eq.3.

$$\% W = \frac{m_0 - m_1}{m_0} \cdot 100 \qquad [3]$$

where, m_0 is the initial weight of the sample, m_1 is the final weight of the sample after degradation.
The volatile solids (VS) were determined by ignition of material in muffle furnace at 550 °C during 2 h. All the samples were tested for VS.

Colour measurement

The colour measurement was carried out using X-Rite i1Pro spectrophotometer at temperature of 23±2°C. The colour of original printed cardboards and printed samples after biodegradation was determined according to the CIE L*a*b* system. The average of ten values of those measurements was presented in Result section (Table 8). The total colour difference ΔE*Lab was determined according to the Equation 4 and presented in Figure 11.

$$\Delta E = \sqrt{(L_2 - L_1)^2 + (a_2 - a_1)^2 + (b_2 - b_1)^2} \qquad [4]$$

RESULTS AND DISCUSSION

Due to the different constitution materials and quality properties the cardboard samples were examined for some basic properties such as thickness, moisture, ash and $CaCO_3$ content and results are presented in Table 3. All the samples have similar moisture content. The lowest amount of ash content was found in LP sample, followed by UC and PP. The amount of $CaCO_3$ increases in a series of: PP < LP < UC. This value can originate from fillers as well as from coatings. All samples differ in thickness, which grows in a row: UC < PP <LP. Due to different degrees of wetting, the thickness of TC UV print is different for all samples, and increases in a row: PP < UC < LP.

Table 3: Properties of used cardboards

	moisture, %	ash, %	$CaCO_3$, %	Thickness, mm	Thickness of TC UV print, mm
LP	4.63	9.67	13.09	0.563	0.010
PP	4.28	18.51	12.56	0.494	0.003
UC	4.51	16.25	15.28	0.453	0.005

In order to obtain surface free energy (SFE) of all samples and adhesion parameters, the samples were examined for contact angle measurements with different liquids. Results of contact angle determination are presented in Table 4, while results of SFE determination and adhesion parameters are presented in Tables 5 and 6.

Table 4: Contact angle measurements

Sample	Contact angle Θ		
	Water	Diiodomethane	Glycerol
LP	68.4±3.48	56.9±3.59	105.9±2.90
PP	98.5±7.39	73.0±2.98	58.2±5.17
UC	58.2±4.40	48.1±3.01	97.8±2.29
LP-UV	103.0±4.48	46.8±1.70	99.1±1.95
PP-UV	96.6±4.51	44.7±1.73	101.1±1.93
UC-UV	114.8±4.48	32.7±1.67	119.3±2.23

Obtained contact angles presented in Table 4 show mostly hydrophilic surface properties of cardboard except for PP which shows hydrophobic surface. The highest hydrophilic surface is noticed for UC sample. All samples of prints show hydrophobic surface (UC-UV > LP-UV > PP-UV).

In the Table 5 the obtained results for surface free energy of neat and printed cardboard samples are given. Neat cardboard samples have a large proportion of polar component in its SFE, as indicated by the γ^p and the dispersion index x^d. The highest polar character of surface is observed for UC sample (13.56 mJ m^{-2}), followed by LP (10.01 mJ m^{-2}), which is characteristic for the hydrophilic surface. Compared to UC and LP sample, PP sample has hydrophobic surface with the smallest polar component (1.44 mJ m^{-2}). SFE of neat cardboard samples increases in a row: PP<LP <UC. By observing the SFE of prints, they are similar in all samples. SFE of prints on all samples mostly originate from its dispersive component, which is characteristic for hydrophobic surface. It is evident that LP-UV sample does not have hydrophilic molecules on the surface (γ^p = 0.00mJ m^{-2}), and its total SFE is equal to its dispersive component. The other two printed cardboards (PP-UV and UC-UV) show the existence of polar components on their surface according to obtained SFE. From this it can be concluded that an adhesive bond between cardboard and ink is mostly provided by nonpolar interactions.

Table 6: Adhesion parameters

Sample	Adhesion parameters (mJ m^{-2})	
	γ_{12}	W_a
LP - UV	11.88	45.78
PP - UV	3.41	41.30
UC - UV	6.40	62.77

Table 6 shows the adhesion parameters for cardboards and prints. Optimum adhesion can be achieved when the following conditions are fulfilled: W_a = maximum, γ_{12} = minimal, and $\gamma_1 = \gamma_2$. As these conditions are satisfied, adhesion will be optimal. Considering these conditions, it can be concluded that the greatest adhesion is achieved on a UC-UV sample (W_a = largest, SFE of both phases are almost equal) regardless to larger SFE of interphase (γ_{12}). In other two samples (PP-UV and LP-UV) the work of adhesion is similar but noticeably lower than in the UC-UV sample. This can be attributed to the large SFE of interphase (in the case of the LP-UV) and with different SFE of individual phases (in the case of PP-UV). The obtained results show that the interaction between all tested cardboards and TC ink are strong. The work of adhesion is the highest for UC-UV sample (62.77 mJ m^{-2}) (Table 6). The smallest work of adhesion is observed for the PP-UV sample (41.30 mJ m^{-2}) due to largest differences in SFE of individual phases.

The adhesion of ink onto the cardboard substrate depends on the intermolecular interactions between them. Cardboards with hydrophilic (polar) surface (LP and UC) show higher values of SFE of interphase. The highest SFE of interphase is observed for the LP-UV sample (11.88 mJ m^{-2}). In this case the adhesion is provided only by the dispersive bond due to absence of polar components in the print. The high SFE of interphase can be explained by the existence of polar molecules on the surface of LP cardboard which creates resistance to print and thus preventing the binding and absorption of ink on the surface of cardboard. This resistance will result as a higher γ_{12} value. Cardboard with hydrophobic surface (PP) shows the minimum value of SFE of interphase (3.41 mJ m^{-2}). Furthermore, SFE of interphase also affects the thickness of print on the cardboard surface. The greater the SFE of interphase, the thickness of the print on the cardboard higher is (Table 3 and 6). Thus, LP-UV results in the thickest print, followed by UC-UV, and PP-UV with a minimum thickness of the print. Due to maximum absorbency of ink on PP cardboard, the smallest is the difference in the contact angles of neat and printed PP cardboard (Table 4). In order to make a conclusion about biodegradability, changes in the appearance of sample surfaces were observed before and after biodegradation during the whole sampling time. Samples were taken out from the soil containers in different sampling periods (14, 32, 50, 80 and 120 days). Formation of holes, cracks and changes in colour were noticed.

From Figure 1, 2 and 3 it can be noticed that the biggest changes on the surface of neat cardboard samples occur after 80 days. During the 14, 32 and 50 days, the biggest changes are reflected in the change of color, ie. they tend to yellow. The biggest changes occur after 120 days of biodegradation for all samples. Also, changes in the coating can be noticed, due to formation of wrinkles and cracks.

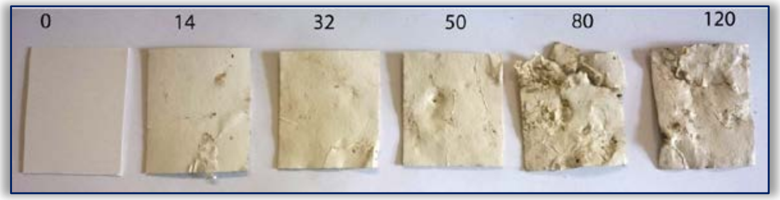

Figure 1: Biodegradation over 120 days for neat LP cardboard

Figure 2: Biodegradation over 120 days for PP neat cardboard

Figure 3: Biodegradation over 120 days for neat UC cardboard

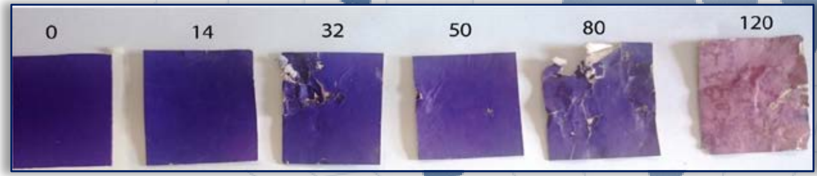

Figure 4: Biodegradation over 120 days for printed LP - UV cardboard

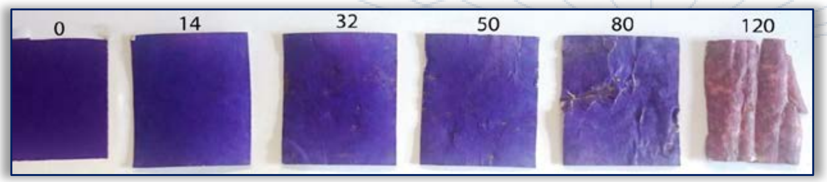

Figure 5: Biodegradationover 120 days for printed PP - UV cardboard

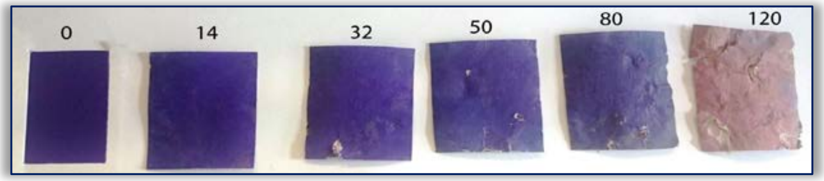

Figure 6: Biodegradation over 120 days for printed UC - UV cardboard

Observing the printed cardboard samples (Figures 4, 5 and 6), the most significant changes are in the colour of the print after 120 days. The print is much lighter on all printed samples. During the first 14 days of biodegradation test, no significant change in colour or on the surface of samples occurred. After 32 days in the LP-UV and UC – UV samples can be noticed the formation of cracks in the print, while in PP-UV sample it is visible after 80 days. In the LP-UV sample cracks in the print are the most significant but also detachment of ink layer from substrate can be observed. This can be attributed to the maximum value of SFE of interphase γ_{12} between the cardboard and ink (Table 6). As SFE of interphase increases in a row: PP-UV< UC-UV< LP-UV, the cracking and lamination of ink layer from the cardboard surface can be noticed.

By observing the neat cardboard samples, the highest level of weight loss shows UC. After 120 days the total weight loss was about 38.4%, followed by the PP with 34.8%. The smallest weight loss has LP, with 31.5% after 120 days of biodegradation. This sequence can be attributed to the thickness of cardboard – the thinner the cardboard, better degradation is. Considering only the printed samples, it is obvious that the largest weight loss shows the sample LP – UV (31.7%), followed by the PP-UV (30.94%). The lowest weight loss was observed at the UC – UV sample (24.6%). The smallest changes in weight loss of all samples are in the first 50 days. After 80 days, there is a significant change in the weight loss of samples, particularly evident for the LP and LP-UV pattern. As with other samples, the biggest changes were observed after 120 days.

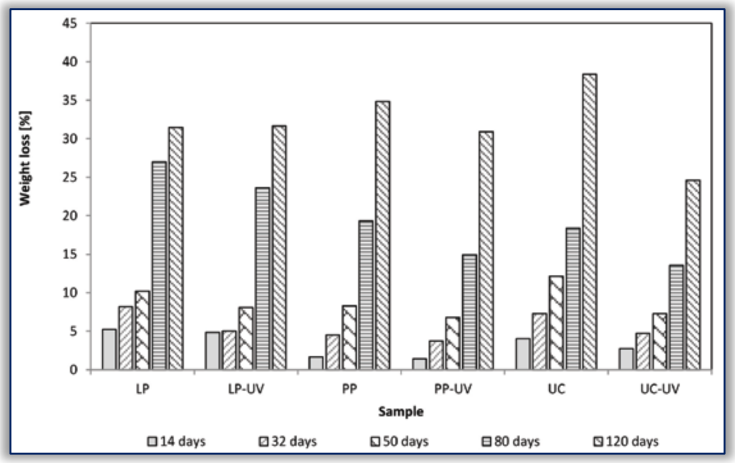

Figure 7: Biodegradation of samples through weight loss over 120 days

Table 7: The influence of thermochromic ink on the reduction of biodegradation over time, compared to neat cardboard

	Time (days)				
	14	32	50	80	120
PP/PP-UV	14.38 %	17.50 %	14.65 %	14.65 %	11.21 %
LP/LP-UV	7.00 %	38.78 %	20.72 %	12.45 %	0.00 %
UC/UC-UV	31.85 %	35.07 %	40.23 %	26.29 %	35.80 %

Thermochromic ink significantly influence the degree of cardboard biodegradation. Although sometimes ink can serve as a food source for the microorganisms and thus improve the degree of biodegradation (Lucas et al. 2008), here the different trend was observed. Degree of biodegradation was observed through weight loss, in all printed samples compared to neat cardboard. The total weight loss of PP – UV after 120 days was reduced by about 11% compared to the neat cardboard. The greatest impact of thermochromic ink on biodegradation was observed in UC-UV sample. The total degradation after 120 days compared to neat sample was reduced by 35%. This can be attributed to the high adhesion of ink to the substrate. The sample UC-UV has the greatest adhesion of TC ink to the substrate (62.77 mJ m^{-2}). During all the time interval of biodegradation, printed samples were reduced by about 26 - 40% (Table 7). As in the PP-UV and UV-LP samples the obtained work of adhesion is quite the same (Table 6), reduction of weight loss in the samples was lower than in UC-UV sample. In addition, it can also be attributed to SFE of interphase between the ink and the substrate. LP-UV pattern has the highest SFE of interphase, and during the 120 days the reduction of weight loss differed and cannot be observed by a specific rule. The SFE of interphase in the UC-UV sample was double less than in LP- UV sample and it can be seen that there is less variation in the weight loss reduction during the sampling time, and varies from 26 to 40%. Due to lowest SFE of interphase in PP-UV, the regular reduction of weight loss vs. sampling time (14 ± 3%), or with very small deviations, can be observed.

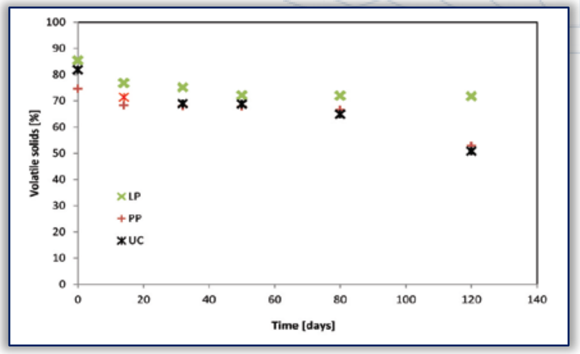

Figure 8: Reduction of volatile solids over time for neat cardboard

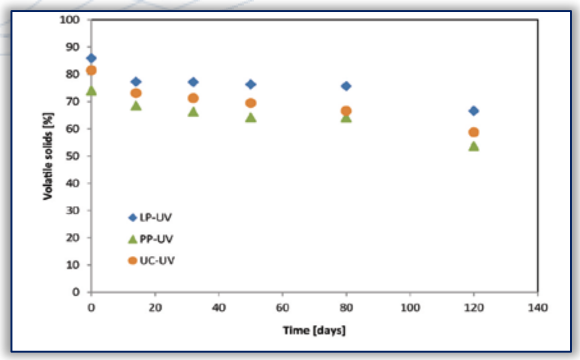

Figure 9: Reduction of volatile solids over time for printed cardboard

Concerning the percentage of ash in neat samples (Table 3), it is expected that the LP sample will have the largest share of VS. Observing neat samples (Figure 8), after 120 days the highest percentage reduction in VS was observed at UC (37.9%), followed by PP (27.6%) and LP (16.1%) compared to the initial share of VS in all samples. These results confirm the results of the weight loss determination. For all printed cardboard samples (Figure 9), percentages of VS decrease are very similar. After 120 days, for UC-UV a reduction of VS was around 27.9%, for PP-UV 27.6% and for LP-UV 22.48%. In the printed samples decrease of VS originate from cardboard and from ink degradation. From this it can be concluded that weight losses during 120 days originates not only from decomposition of organic matter but also from defragmentation and washout of coatings and fillers.

Table 8 shows that all samples over time bright, ie their colour start to fade. The a* value is reduced to almost half of its value but still remains in the red area of L*a*b* colour space, while the value of b* changes from negative to positive values. This means that the blue thermocromic microcapsules are biodegradable during conducted degradation process. Blue thermocromic microcapsules in the formulation of the print are responsible for the purple coloration of the print (Figure 10). By mixing blue leuco dye to a conventional pink ink will result in a purple ink formulation.

Table 8: Colorimetric properties of thermochromic ink at 23±2°C

DAYS	LP-UV			PP-UV			UC-UV		
	L*	a*	b*	L*	a*	b*	L*	a*	b*
0	34.70	40.47	-35.34	34.70	37.67	-33.95	35.66	45.12	-25.51
14	37.29	30.65	-31.81	37.14	30.13	-32.35	36.37	31.37	-27.76
32	36.39	26.11	-29.98	38.43	28.59	-28.99	42.15	24.44	-22.26
50	39.74	24.81	-27.15	38.31	23.03	-26.33	42.46	21.57	-20.05
80	41.75	23.19	-19.93	43.92	26.35	-21.15	46.62	20.21	-12.63
120	57.79	33.25	8.50	50.34	24.63	4.43	59.40	25.41	8.16

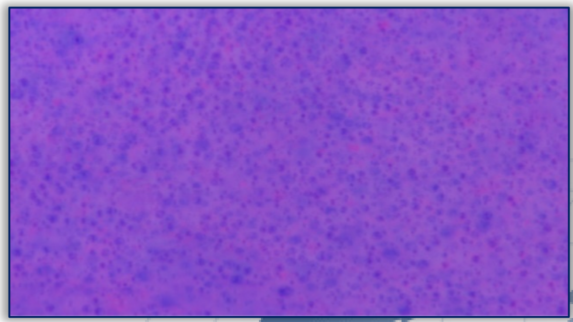

Figure 10: Blue microcapsules in ink formulation (original sample) at magnification of 2000x

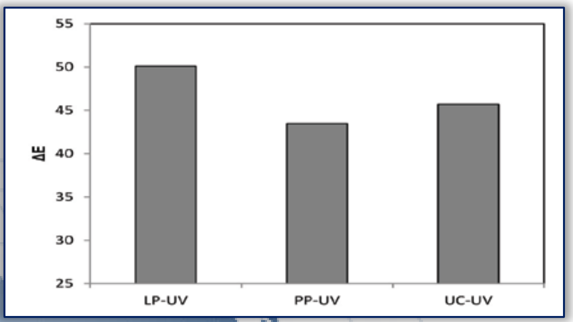

Figure 11: Total colour difference after 120 days of biodegradation

Figures 4, 5, 6, 11 and Table 8 shows that the print was mostly discoloured after 120 days. In the period to 80 days, changes in colour were not so significant. The highest change in colour (ΔE) was observed in the case of LP-UV cardboard while the lowest in the case of PP-UV cardboard (Figure 11). This could be associated with an SFE of interphase. The higher the SFE of interphase is, the greater the change in colour after 120 days can be noticed. As the γ_{12} increases in a row: PP-UV < UC-UV < LP-UV; the difference in colour (ΔE) increases in a series of PP-UV < UC-UV< LP-UV. Stronger bond between the ink and cardboard will result in better colour stability. The higher the value of SFE of the interface is, the forces of binding to the substrate are less.

CONCLUSION

Thermochromic ink reduces the biodegradation of cardboard. The greatest role plays the ink adhesion on cardboard, but also its SFE of interphase. The greater the adhesion of ink on the surface will result in lower weight loss, i.e. lower degree of biodegradation. If a large SFE of interphase is, separation of ink from the substrate occurs. This can improve the biodegradation of the sample.

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Note

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