

# Struktura i površinska svojstva te postojanost materijala za trodimenzijski tisak

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UNIVERSITY OF ZAGREB  
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**STRUCTURE, SURFACE AND  
PERMANENCE PROPERTIES OF THREE  
DIMENSIONAL PRINTING MATERIALS**

DOCTORAL THESIS

Zagreb, 2010

UNIVERSITY OF ZAGREB  
FACULTY OF GRAPHIC ARTS  
(SVEUČILIŠTE U ZAGREBU  
GRAFIČKI FAKULTET)

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STRUCTURE, SURFACE AND PERMANENCE PROPERTIES OF THREE  
DIMENSIONAL PRINTING MATERIALS  
(STRUKTURNA I POVRŠINSKA SVOJSTVA TE POSTOJANOST MATERIJALA ZA  
TRODIMENZIJSKI TISAK)

DOCTORAL THESIS  
(DOKTORSKA DISERTACIJA)

Supervisor: assist. prof. Branka Lozo, PhD  
(Mentor: doc. dr. sc. Branka Lozo)

Zagreb, 2010

## SUMMARY

3D printing is classified as an additive, powder-based, solid freeform fabrication technique. The method researched can be also regarded as a novel and propulsive form of digital printing, creating finished objects in three dimensions. It is based on conventional ink jet technology, using powder material instead of a substrate and liquid binder, clear or coloured, as an ink.

As 3D printing materials and 3D prints properties have been only periodically researched from the view of standard graphic technology, the thesis offers a comprehensive study using the existing and customized characterization methods usually employed in the graphic and material science and other related industries. The work explains the variety of characteristics of 3D materials and prints, including the structure, colour reproduction and methodology, permanence and colour stability, effects of accelerated aging and mechanical properties, as well as provides the general research models and defines the methodology.

The goal of the research was to characterize the structure and to define permanence and stability of 3D printing materials and prints by applying selected microscopic, spectrophotometric methods, image analysis methods, surface evaluation methods, mechanical testing and permanence testing methods. These were performed with compiled existing and newly acquired knowledge during the interdisciplinary research and optimal solutions and methods were discussed.

The thesis outcomes are specifically in the following, verification of the selected characterization methods as suitable for 3D printing materials and prints properties research; definition of methods and procedures, for research of 3D prints structure, surface, colorimetric and colour stability characteristics; contribution to the development of methodology for valorisation of 3D prints colour permanence, with emphasis on light fastness of 3D prints under natural and accelerated aging conditions; systematic presentation and analysis of quantitative and qualitative data regarding the 3D prints specific properties.

Keywords: 3D ink-jet printing, Structure, Surface, Reproduction, Colour, Light stability



## SAŽETAK

3D tisak klasificiran je kao aditivna, bazirana na prahu, solid freeform fabrication tehnika. Istraživana metoda može se također smatrati novom i propulzivnom vrstom digitalnog tiska koja proizvodi trodimenzionalne objekte (“otiske“). Tehnika se temelji na konvencionalnom ink jet tisku, koristeći materijal u obliku praha umjesto tiskovne podloge i tekuće vezivo kao tiskovnu boju.

Svojstva materijala za 3D tisak samo su periodično istraživana sa gledišta standardne grafičke tehnologije. Stoga, teza nudi cjelovitu studiju svojstava osnovnih materijala i samih otisaka, koristeći postojeće i modificirane metode karakterizacije koje se koriste u grafičkoj industriji, strojarstvu i ostalim srodnim industrijama. Istraživanje objašnjava raznolika svojstva materijala za 3D tisak i 3D otisaka, uključujući strukturalna svojstva, reprodukciju boje, postojanost boje, utjecaje ubrzanog starenja, mehanička svojstva, te nudi općenite modele istraživanja i definira metodologiju.

Cilj teze je karakterizacija strukture i definicija trajnosti i stabilnosti materijala i otisaka u 3D tisku upotrebom odabranih mikroskopskih metoda, spektrofotometrijskih metoda, metoda slikovne analize, metoda za evaluaciju površinske strukture, metoda mehaničkog ispitivanja te metoda za starenje i određivanje postojanosti materijala. U evaluaciji i karakterizaciji korištena su prikupljena i novo stečena znanja tijekom interdisciplinarnog istraživanja, te su diskutirana optimalna rješenja i metode.

Rezultati teze su specifično u slijedećem, verifikaciji odabranih metoda za karakterizaciju kao pogodnih za istraživanje svojstava materijala i otiska u 3D tisku; definiciji metoda i procedura ispitivanja strukturalnih, površinskih i kolorimetrijskih svojstava, te svojstava postojanosti i stabilnosti boje 3D otisaka; doprinos razvoju metodologije za valorizaciju postojanosti 3D otisaka, s naglaskom na postojanost prema svjetlu u uvjetima ubrzanog i prirodnog starenja; sistematski prikaz i analiza kvantitativnih i kvalitativnih podataka vezano uz specifična svojstva 3D otisaka.

Ključne riječi: 3D ink-jet tisak, Struktura, Površina, Reprodukcija, Boja, Postojanost prema svjetlu

## PREFACE

The idea of the presented thesis has been a topic of interest and researched during 2007-2010. The need for the comprehensive study about 3D printing materials and 3D prints, which would be done as a graphic technology based research, was originally raised by the 3D printing industry itself. As preliminary results have shown the high potential, the research topics were broadened. 3D printing being a novel field of application for printing industry, and as the research continued, the situations which need to be researched, described and defined were often discovered. In the same time, the methods which were not originally developed for printing technology research, have shown good applicability in the conventional printing materials research and the potential of their use in 3D printing needed to be explored further. It was recognized from the beginning that the field of 3D printing is of interdisciplinary nature and therefore, a fruitful cooperation with the colleagues from the fields of material characterization, design, wood science, chemistry and mechanical engineering was developed.

The thesis research is supported within the frames of Croatian national project “Innovative Printing Materials”, principal investigator assist. prof. Branka Lozo, the supervisor for the presented thesis. Also, the preliminary research and research in the course of thesis work has been done in collaboration with a number of colleagues from various universities and research institutes, such as University of Ljubljana, Slovenia; UWE, UK; VTT, Finland; Abo Akademi, Finland; Helsinki University of Technology, Finland; PFI, Norway, KCPK, Netherlands. 3D material and printing was supplied by Ib-procadd, Ljubljana, Slovenia. X-Rite (Gretag Macbeth) colour measuring equipment was supplied by HSH, Ljubljana, Slovenia.

I am grateful for all the help, advice and support to Edo Sternad, Andrej Žužek, Kristijan Celec, Roman Satošek and Kaja Antlejš, Ib-Procadd, Slovenia; Tadeja Muck, Diana Gregor Svetec and Aleš Hladnik, Faculty of Natural Sciences and Engineering, University of Ljubljana, Slovenia; Nina Knešaurek, Faculty of Graphic Arts, University of Zagreb, Croatia; Gary Chinga, PFI, Norway; Juha Saari, Kemira, Finland; Mari Nurmi and Jonas Asplund, Abo Akademi, Finland; Tapani Vuorinen, Rita Hatakka and Antti Kivioja, Helsinki University of Technology, Finland; Roman Habicht, HSH, Slovenia; Jeff Cunningham, ZCorporation, USA; Peter J. Walters, Carinna Parraman and David Huson, Centre for Fine Print Research, University of West of England, UK. I would also like to thank all the

members of Committee for their time and for helpful comments and advice on making of this thesis. I am also thankful to my colleagues at University of Zagreb, Faculty of Graphic Arts and big thank you goes to my boss, Arie Hooimeijer, for giving me time and patience to finish this thesis.

I would like to personally and professionally say the biggest thank you to my dear supervisor Branka Lozo, who was the one that introduced me to 3D printing and who I can thank for it becoming the subject of my thesis, for all the support, serious and fun discussions and talks and lots of laughs, early morning and sometimes late night telephone calls and e-mails :) and all that we shared, including lots and lots of coffees and chocolates :) during the course of this PhD. It was a true pleasure and joy to be in this together and it will stay as a very dear memory and I am always grateful to her for being my supervisor.

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Thank you all for helping me to make this PhD possible!

Maja Stanić

Zagreb, October 2010

## LIST OF PUBLICATIONS

The thesis is based on the following publications, which are included in the thesis:

- I. Lozo, Stanić, Muck, Jamnicki, Mahović Poljaček: “Three-Dimensional Ink-jet Prints: Impact of Infiltrants“, *Journal of Imaging Science and Technology*, 52/5, IS&T, USA, 2008
- II. Stanić, Lozo, Walters: “Reproduction in Three-Dimensional Ink-jet Printing”, *Journal of Imaging Science and Technology*, 2010 (accepted for publication)
- III. Stanić, Lozo, Gregor Svetec: “Colorimetric Properties and Stability of 3D Prints”, *Rapid Prototyping Journal*, 2010 (accepted for publication)
- IV. Stanić, Lozo: “Permanence and Color Stability in 3D Ink-jet Printing”, submitted to *Journal of Imaging Science and Technology*, 2010
  
- V. Lozo, Stanić, Jamnicki, Muck: “3D Printing as a Function of 2D Printing”, *International Conference Digital Fabrication 2007 (collocated with Non-impact Printing 23)*, Anchorage, AK, USA, 2007
- VI. Stanić, Lozo, Muck, Jamnicki, Kulčar: “Color Measurements of Three-dimensional Ink-jet Prints”, *International Conference Non-impact Printing 24 (collocated with Digital Fabrication 2008)*, Pittsburgh, PA, USA, 2008
- VII. Stanić, Walters, Lozo: “Image Analysis of Surface Elements Reproduction Quality in 3D Ink-jet Printing”, *International Conference Digital Fabrication 2009 (collocated with Non-impact Printing 25)*, Louisville, KY, USA, 2009
- VIII. Stanić, Lozo: “Color and Permanence Issues in 3D Ink-jet Printing”, *33rd International Convention MIPRO 2010*, Opatija, Croatia, 2010
- IX. Stanić, Lozo: “Permanence and Color Stability in 3D Ink-jet Printing”, *International Conference Digital Fabrication 2010 (collocated with Non-impact Printing 26)*, Austin, TX, USA, 2010

The papers are later mentioned in the text by their corresponding roman numerals.

The author's contribution to the joint publications included in the thesis:

Papers I and V

Maja Stanić defined the research plan together with the co-author, performed a part of the experimental work related to 3D prints production and mechanical testing, surface and cross-cuts experimental work and analysis, analyzed and discussed the corresponding results, and wrote the manuscript.

Papers II, III, IV, VI, VII and IX

Maja Stanić defined the research plan, performed the entire or major part of the experimental work, analyzed and discussed the corresponding results, and wrote the manuscript.

Paper VIII

Maja Stanić defined the research plan, performed literature review, and wrote the manuscript.

# CONTENTS

INTRODUCTION .....	10
BACKGROUND .....	11
OBJECTIVES AND HYPOTHESES.....	13
RESEARCH OUTLINE, MATERIALS AND METHODOLOGY .....	14
LITERATURE REVIEW .....	18
3D INK-JET PRINTING.....	19
3D INK-JET PRINTS SURFACE AND MECHANICAL PROPERTIES – IMPACT OF INFILTRANTS AND PROCESS PREFERENCES .....	25
REPRODUCTION IN 3D INK-JET PRINTING.....	26
COLOUR MEASUREMENTS AND PROPERTIES OF 3D INK-JET PRINTS .....	28
COLOUR STABILITY AND PERMANENCE IN 3D INK-JET PRINTING.....	31
EXPERIMENTAL.....	37
MATERIALS AND METHODS .....	38
3D INK-JET PRINTS SURFACE AND MECHANICAL PROPERTIES – IMPACT OF INFILTRANTS AND PROCESS PREFERENCES .....	38
REPRODUCTION IN 3D INK-JET PRINTING.....	46
COLOUR MEASUREMENTS AND PROPERTIES OF 3D INK-JET PRINTS .....	62
COLOUR STABILITY AND PERMANENCE IN 3D INK-JET PRINTING.....	67
RESULTS AND DISCUSSION.....	75
3D INK-JET PRINTS SURFACE AND MECHANICAL PROPERTIES – IMPACT OF INFILTRANTS AND PROCESS PREFERENCES .....	76
REPRODUCTION IN 3D INK-JET PRINTING.....	103
COLOUR MEASUREMENTS AND PROPERTIES OF 3D INK-JET PRINTS .....	114
COLOUR STABILITY AND PERMANENCE IN 3D INK-JET PRINTING.....	126
CONCLUSIONS.....	143
SCIENTIFIC CONTRIBUTION.....	147
REFERENCES.....	148
EXTENDED ABSTRACT .....	156
APPENDICES .....	176
CURRICULUM VITAE.....	177
LIST OF FIGURES .....	183
LIST OF TABLES.....	188

# **INTRODUCTION**

## **BACKGROUND**

By rapid development of new technologies, novel methods and materials, primarily belonging to the process and mechanical engineering, became available. Within the last decade, new production technologies and respective novel materials, based on the conventional ink jet printing have been developed and have entered the industry. One of them is the three-dimensional printing. 3D printing process being researched uses powder material instead of two dimensional substrate and liquid binder as an ink. In recent years, the opportunity of colour 3D prints has been made possible. In a 3D colour printer, the colorants make part of the binder solution and the colour is reproduced on the basis of conventional ink-jet printer. Due to the interdisciplinary nature, methods and materials mentioned display a wide range of characteristics which need to be defined both qualitatively and quantitatively, using the knowledge from various industry and scientific fields. Partly due to their native technology field, the 3D printing materials and prints have not been adequately researched from the view of graphic technology.

By using the knowledge and experience gained during the research of conventional ink jet printing and basic materials (papers, polymer substrates, coatings, inks), it is possible to apply the existing solutions in order to study and characterize the relevant properties of 3D printing materials and prints. In the same time, the measuring methods which have not been originally developed for the graphic technology based research, if they are modified to some extent, can be successfully used. They present the new opportunities and perspectives for research. Based on the stated, it is presumed that the identified problems can be adequately solved by applying the existing knowledge of graphic technology and by using some non traditional methods to define the procedures to study both 3D printing materials and prints in terms of their characteristics, structure and permanence.

3D printing itself has been a topic of interest in a number of research studies, scientific and technical articles and some theses in the last decade, mainly in the field of rapid prototyping and advanced engineering. Topics researched include, among other, general overview of technology and future outlooks, achievable accuracy, mechanical properties, bioprinting, benchmarking to competing rapid prototyping technologies. Until a couple a years ago, there were a limited number of scientific articles dealing with the 3D printing colour capabilities, and not from a graphical technology point of view. The most of the existing research conducted was from a field of process engineering, dealing mainly with determination and



benchmarking of 3D prints and various processes applicability. Other large field of research is bioprinting and application of 3D prints in biomedical applications. Colour properties of 3D prints have recently been a scope of interest in some of the research papers, with the majority of research in the definition of potential areas of use of 3D colour prints, requirements and basic parameters of introducing colour to RP and colour reproduction and design of pre-visualization aids.

Therefore, after the initial literature research, it has been realized that the proposed subject of the thesis has not been adequately or at all researched, as based on the current and existing research projects and individual papers. This is partly due to the novelty of 3D printing materials and 3D printing process itself, and 3D printing being an interdisciplinary process which needs to be researched from different points of view. Due to the nature of 3D printing process, graphic technology is one of the fields in which the research of 3D printing should be performed. It has also been defined that there are areas of 3D printing process and materials which need to be defined from the graphic technology point of view as there are no viable alternative procedures in the process and mechanical engineering field. Such topics primarily include, but are not limited to, colour reproduction, colour appearance, colour stability and colour measurements methodology.

The idea of the proposed thesis has been a topic of preliminary research for over 2 years. The need for the comprehensive study about 3D printing materials and 3D prints, which would be done as a graphic technology based research, was originally raised by the 3D printing industry itself. As preliminary results have shown the high potential, the research topics were broadened. 3D printing being a novel field of application for printing industry, and as the research continued, the situations which need to be researched, described and defined were often discovered. In the same time, the methods which were not originally developed for printing technology research, have shown good applicability in the conventional printing materials research and the potential of their use in 3D printing needed to be explored further (Lozo, 2005; Holmstad *et al.*, 2003; Holmstad, 2004; Muck, 2002; Reme and Kure, 2000; Vikman, 2004; Vikman and Sipi, 2003). It was recognized from the beginning that the field of 3D printing is of interdisciplinary nature and therefore, the techniques and methods from various technology fields and industries that are included add to the comprehensiveness of the performed research, assuring that all relevant aspects are covered and all relevant issues addressed.

## **OBJECTIVES AND HYPOTHESES**

The goal of the research is to characterize the structure and to define permanence and stability of 3D printing materials and prints by applying selected microscopic, spectrophotometric methods, image analysis methods, surface evaluation methods, mechanical testing and permanence testing methods.

The main hypothesis is that by using the above mentioned methods, with their advantages and limits respected, it is possible to comprehend the changes in structure, colour and permanence of 3D printing materials and prints.

The final aim is to compile the existing and newly acquired knowledge during the interdisciplinary research in order to define the optimal solutions and methods.

## **RESEARCH OUTLINE, MATERIALS AND METHODOLOGY**

The methodology of the research was developed in order to permit the achievement of the set goals and verification of the hypothesis. Knowledge and experience gained through the literature survey and research formed a base for the theoretical part of the thesis and contributed to the research framework for the practical part of the thesis. After determining the main and supporting presumptions for the research work, the acquired knowledge and experience were classified in order to serve as a basis upon which, together with the discussion of the research results, the conclusion and recommendations were defined and proposed.

Literature survey and research of the existing scientific work serves as a framework for determination of the appropriate methods and procedures which are conducted in the research. The materials which form the samples for the experimental part of the research work are defined. In addition to the main methods and procedures needed for the research, the introductory measurement methods for the material characterization are defined as well. The research results were processed and served as the basis for the discussion. The conclusions are defined and appropriate optimal solutions and recommendations are proposed. The work was afterwards compiled in the thesis and presented.

As it was noticed during the literature survey and research and preliminary measurements, there exists a broad area of research within the frames of 3D printing which requires interdisciplinary approach, with the emphasis on graphic technology based research, in order to characterize various important properties of the novel materials for 3D printing and 3D prints. The defined issue is even more in need of comprehensive research as it offers the possibility of using traditional graphic technology methods, some non-traditional methods which have proved as useful in graphic technology based research and the synthesis of the existing and acquired knowledge and experience in order to both determine the applicability of the mentioned methods and define the properties of 3D printing materials and 3D prints.

In this context, the research incorporates certain microscopic, spectroscopic, spectrophotometric, profilometric and newly developed image analysis procedures and routines in order to characterize the basic materials for 3D printing, define the detrimental process parameters that define the final structure of the prints. In addition, some of the methods are used for a comprehensive study of the permanence, stability and aging

behaviour of 3D prints. In order that the methods and procedures can be proven as adequate for the research of 3D printing materials and 3D prints, the measurements results obtained by them are cross compared and compared with the results from the existing research in similar applications and fields.

The main thesis research topics are defined as follows:

- Study of the 3D ink-jet prints surface and mechanical properties in relation to the variations in printing and finishing process.
- Study of reproduction in 3D ink-jet printing in relation to the variations in printing process preferences by using conventional graphic technology and other applied methods.
- Definition of colour measuring methodology, colour measurements and properties of 3D ink-jet prints in relation to the variations in printing and finishing process.
- Study of the colour stability and permanence in 3D ink-jet printing by using natural and accelerated aging procedures and conventional graphic technology and other applied methods.

The samples for the research and experimental part were performed on the materials as follows:

- Basic materials for 3D printing
  - i. Inorganic and organic materials in the shape of powder
  - ii. Liquid binders (inks)
  - iii. Finishing agents (infiltrants)
- Prints produced by 3D printing method

Besides the materials on which the research was performed, the research includes the materials needed for the certain measurements, such as resins, coatings, conductors.

Within the thesis research work, the following measurement methods and procedures have been used, depending on the properties and changes monitored and information that was wanted to be gained:

#### Microscopy methods

- Optical microscopy, with CMOS or CCD camera, for imaging of the surface and cross-section structures
- SEM (Scanning Electron Microscopy)
- Stereo SEM of the surface structures
- SEM of the cross-sections
- Image analysis of the images acquired by optical microscope, with CMOS or CCD camera, and by SEM microscope with ImageJ program built-in and custom developed routines

#### Spectroscopy and spectrophotometry methods

- FTIR spectroscopy
- Spectrophotometry
- i. Spherical ( $d/8^\circ$  or  $8^\circ/d$ ) geometry
- ii.  $0^\circ/45^\circ$  or  $45^\circ/0^\circ$  geometry

#### Aging procedures

- Natural aging under set conditions with/without the exposure to the light
- Accelerated aging with/without the exposure to the light on Xenotest weathering apparatus

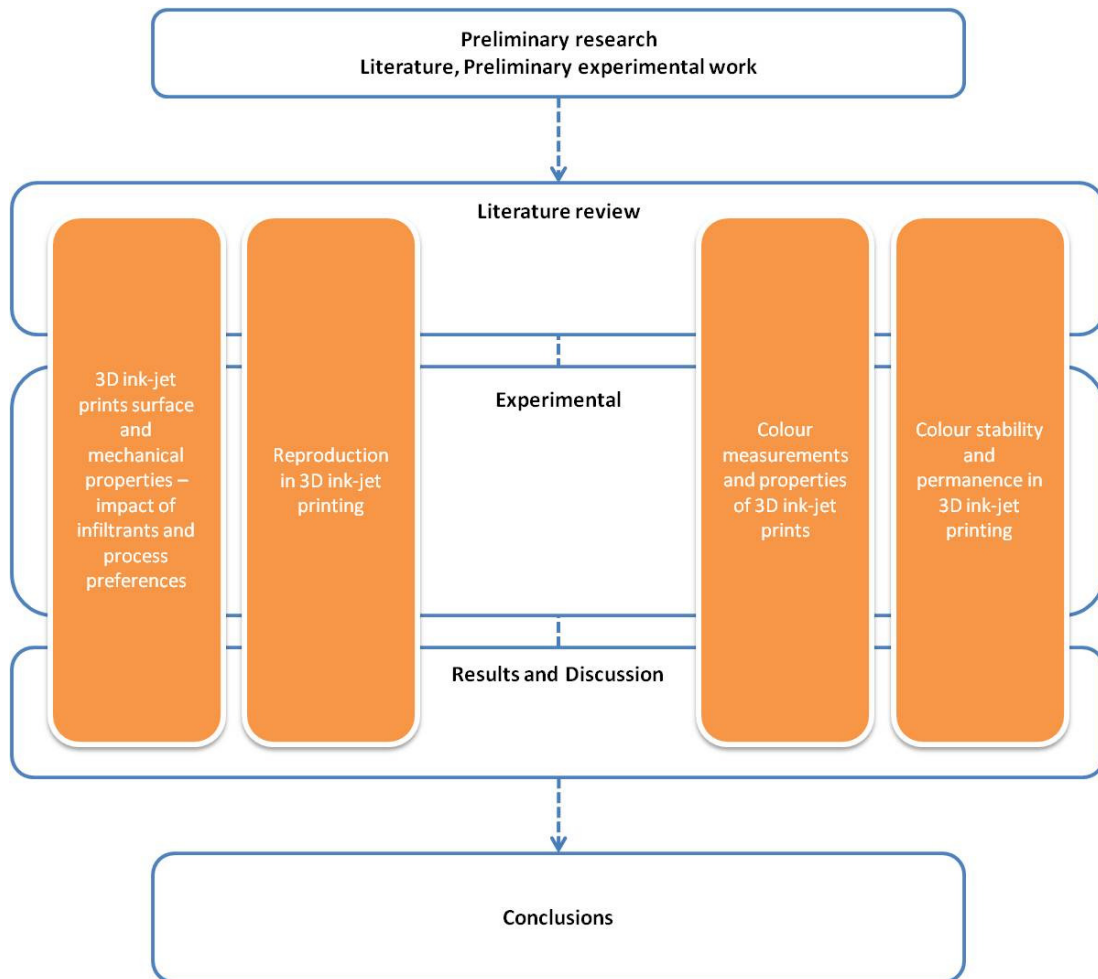
#### Mechanical measurements

- Universal tensile machine
- Hardness measurements, ball indentation method
- Impact measurements, Un-notched Charpy method

#### Other methods

- Scanning methods
- Laser profilometry
- Mechanical profilometry, with stylus based instrument

Basic scheme of research, with separate parts of thesis and defined areas of research is graphically presented below.

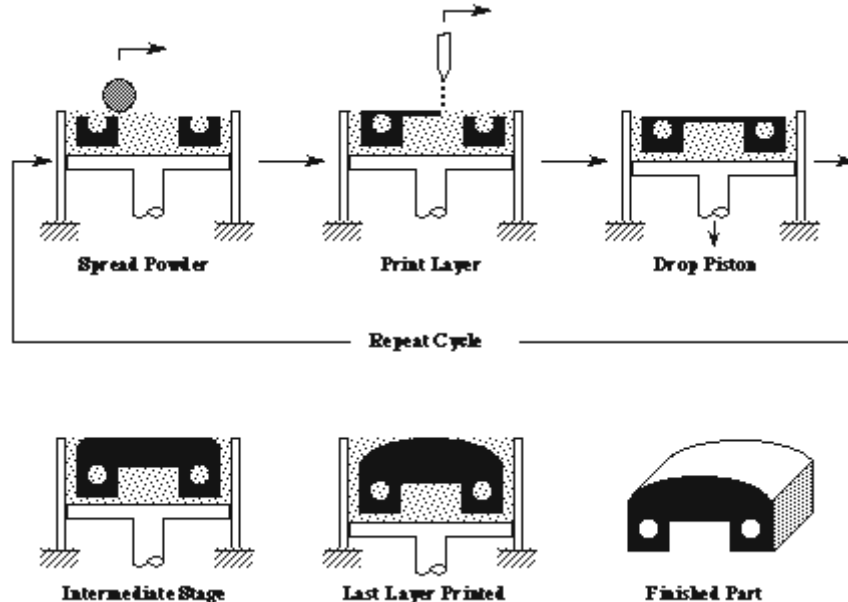


# **LITERATURE REVIEW**

## 3D INK-JET PRINTING

Rapid prototyping (RP) is a general term describing technologies that can produce physical objects from CAD data (Cooper, 2001). It is often also called solid-freeform-fabrication (SFF) and additive manufacturing (AM). RP can be used in a wide range of industries and technologies and in a number of applications. It is a pervasive, versatile and powerful technology (Grimm, 2004) and been growing in use in the last two decades.

Three-dimensional ink-jet printing (3D printing) is a RP process which describes technologies using a variety or the principle of conventional ink-jet printing technology to produce objects. It is classified as additive layered manufacturing technology, with the basic materials of powder and binder. The process itself is based on ink-jet printing, with the powder being deposited in consecutive layers which are selectively joined by ink jetting the binder (Grimm, 2003; Upcraft and Fletcher, 2003). 3DP™ core technology has been developed and patented by the Massachusetts Institute of Technology (MIT) in the 1990s (Cima *et al.*, 1995) and licensed to various companies in diverse fields of use.



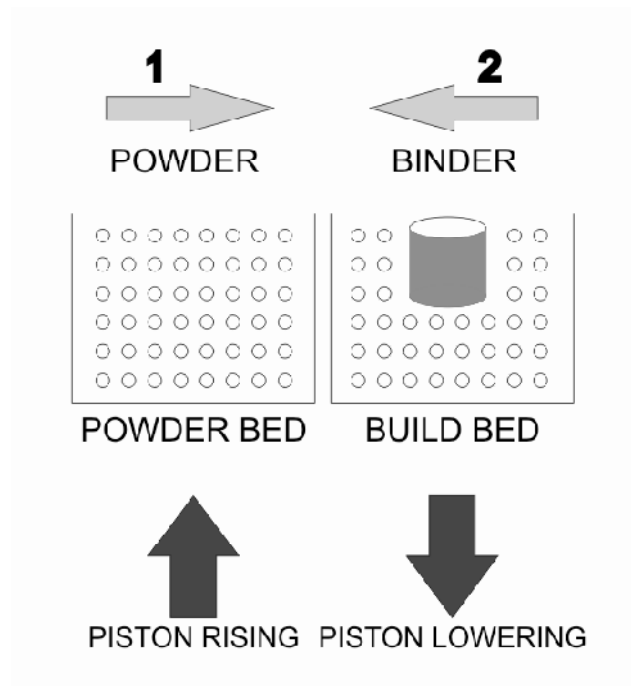
**Figure 1.** Scheme of 3D printing process, patented by MIT ©3DPTM Laboratory, MIT

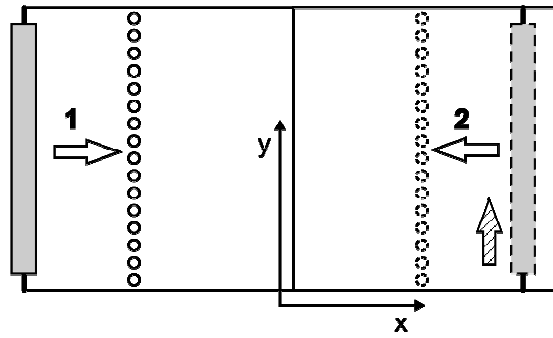
One of the licensees was Z Corporation which focused on appearance parts and concept modelling. In 2008, Z Corporation was second largest producer of machines, by number of installations of their 3D printing system worldwide (Wohlers, 2009). 3D printing technology



was further developed by incorporating colour (Gibson and Ming, 2001), and by using coloured binders it offered rapid production of full spectrum colour 3D objects.

The patents which describe the generic 3D ink-jet printing process are US6146567, US5851465, US5807437, US5387380, US5204055. The process technology itself is based on ink-jet printing; it employs a similar method of jetting the binder material in a form of controlled droplets which join the powder particles together. 3D printing process functions by building parts in layers, which have been sliced in cross-sections of defined thickness by computer algorithms from the CAD model of the desired object. For the each layer production, the powder particles are evenly distributed over the printing surface and selectively joined by employing a binder material. The support piston is then lowered and the next layer of powder is applied, followed by the binder material. This process is repeated until the desired object is finished. Figure 2 shows the scheme of powder being distributed by roller in the arrow 1 direction, while the binder is applied from the printheads in the return motion, arrow 2 direction. The printing starts in the striped arrow direction.





**Figure 2.** Scheme of 3D printing process, side view (upper figure) and top view (bottom figure) of three-dimensional printing process, powder is distributed by the roller in the arrow 1 direction, while the binder is applied from the printheads in the return motion, arrow 2 direction. The printing starts in the striped arrow direction.

The patents that are relevant for the specific application of 3D ink-jet printing process to the technology used by Z Corporation, plaster based powder and water based binder which are described in this thesis are US5902441, US6416850B1, US7435368B2, US7795349B2, US7550518B2, US7332537B2, US7087109B2, US6989115B2, US6610429B2, US6375874B1, US6007318, US20080187711A1.

The first step in the 3D object creation process is a of 3D computer model, obtained by modelling in the 3D CAD software or acquisition of an existing object with a 3D scanner. The 3D computer model is then sliced in software in a number of layers and the information is sent to the 3D printer. Each virtual layer is the being built from the basic materials, in this case in a form of plaster based powder and binders, which are water-based solutions. The powder is deposited and spread by a roller system, while the binders are applied from the print heads, very similar to the ink application in classic 2D ink-jet printing. In 3D colour ink-jet printing, colour is produced with a combination of CMY or CMYK binders, in addition to the clear binder. In coloured binders, the colorants are a part of the binder solution. An example of a 3D colour print is shown in Figure 3.



**Figure 3.** Example of a 3D colour print, model of a house, ©ZCorporation

The scheme of the building principle for the previous generation printer model, ZPrinter 510, can be described as in following. A thin layer of powder is deposited by spreading forward across the build platform from the powder bed. In newer versions of ZCorp. printers, such as in ZPrinter 650, the difference is in the powder deposition method, as the powder is spread from a chamber instead from the powder bed. The printing system then moves across the layer of powder, depositing binders in the pattern of cross-cut or layer of the 3D computer model. The powder and binder react, creating a (partially) solid layer. The piston below the build chamber then lowers the build bed for a thickness of a layer. The cycle is repeated until the model is finished (ZCorp., 2009). The powder that was not printed with is left dry, thus supporting the model being built. This means that, unlike in some other RP systems, there is no need for special support structures that need to be build along with the object. The printed 3D object are then cleaned from the loosed powder and in most cases finished with the appropriate agent. Infiltrants are e.g. cyanoacrylate-based, epoxy resins, polyurethane-based, wax etc. and are applied by either dipping, pouring, with a brush or with an air-gun. Infiltrants provide the needed mechanical stability of the 3D prints and enhance colours.

For 3D colour prints, 3D computer model can have colour applied in several ways: surfaces can be coloured directly or colour can be applied as a part of the texture. The 3D digital data also needs to be saved as a type of file that can, in addition to the geometry information, contain the colour information, for instance as a .VRML, .3DS, .PLY, or ZCorp. proprietary .ZPR file. Other than in 3D CAD software, colour can also be applied in ZPrint, or more specifically in ZEdit Pro, ZCorporation proprietary 3D printing software, also by direct colouring of the surfaces or by texture application. If colours are applied directly, either in 3D CAD software or in ZPrint, they are selected from a palette or by their specific coordinates, most often in a RGB colour space. 3D computer model can have colour applied

on several ways; surfaces can be coloured directly or colour can be applied as a part of the texture (image file, usually a JPEG or TIFF file type). Due to the several operational and cost efficiency factors, coloured binders are printed on the approximately last 10 layers of an object.

Three-dimensional printing is currently among the fastest RP technologies available. Other than that, it is capable of adapting to newly developed materials and compositions. This is due to its flexibility in material handling and the fact that it uses different print heads for different materials, which makes it able to tailor locally the material composition. Furthermore, it has no limitations in terms of geometry of the designed part (MIT, 1989-2000). Nowadays, 3D printing is used in various fields and areas, such as architecture, engineering, medicine, product development, concept modelling, direct casting, fine art, etc. In addition, use of 3D printing in design practice has been studied in doctoral thesis by Evans (Evans, 2002). Three-dimensional printing is considered one of the emerging application fields of standard ink-jet printing (Le, 1998), and in consideration of the technological progress both in printing technology and materials research, it is one of the most dynamic RP processes.

There are several relevant characteristics that are known to affect the three-dimensional printing accuracy and definition. Some of those are: selected layer thickness, amount of saturation of the binder (powder/binder ratio), bleed control, relative position in the build bed, etc. Of most interest here are the shell saturation level, which determines the amount of binder to be applied and is expressed as percentage, relative to the default 100%; bleed control, which compensates for the seepage of binder into the powder layer, surface orientation and position in the build bed. The absorption of binder in the surrounding and non-printed areas leads to potential accuracy and definition loss. The amount of binder seepage and specific surface orientation are relevant for the underside surfaces as it causes poorer surface finish by potential additional bleeding of the binder into the surrounding non-printed powder (Hackney, 2003). This was also studied in more detail in doctoral thesis by Hackney (Hackney, 2007).

Although 3D printing is basically a RP process, the general principle of objects production via ink-jetting the binder on layers of powder and its colour capabilities raise the need for the research from the printing industry perspective. The 3D colour printing is based, as conventional printing techniques are, on subtractive colour mixing process and digital

halftoning, meaning the primary cyan, magenta and yellow inks are printed to form a combination of unique colours. In 3D printing the inks are basically coloured binders, with the colorants making part of the binder solution, with the addition of clear binder to prints “whites”. Recently, a 3D printing system that incorporates black binder was introduced. 3D printing process by Z Corporation uses Hewlett-Packard printheads for application of the binder, which is water-based and similar to the conventional ink-jet ink, with specific alterations in the composition. Addition of colour to 3D printing opened up a whole array of application areas other than its original field of use, such as the use in AEC and GIS, for printing of architectural (Gibson *et al.*, 2002) and landscape models, in preservation of cultural heritage, for digitalization of works of art such as statues and reliefs, and printing of replicas and, quite recently, in fine arts, where artists use 3D technology to create digitally based works of art. These new application areas raised the need to study in more detail the colour properties of 3D prints and to address the permanence and colour stability issues. This kind of research would define the possibilities of 3D colour printing in terms of the colour output, introduce better control over the 3D colour reproduction process and examine the factors influencing the 3D prints permanence and colour stability.

**3D INK-JET PRINTS SURFACE AND MECHANICAL PROPERTIES –  
IMPACT OF INFILTRANTS AND PROCESS PREFERENCES**

A three-dimensional (3D) printing process is a novel and propulsive way of digital fabrication. By employing the well developed technique of ink jetting one type of material onto the other type and thus fusing them together, it enables the fast and accurate production of complex three-dimensional objects. The process itself is remarkably similar to standard 2D ink jet printing, both in the technology of dispersing the binder onto the powdered material and in the use of almost conventional ink jet ink as a binder. Having in mind the advantages of the discussed technology, we concentrated our investigation mainly on the characteristics of the objects produced. Printing resolution is still considerably lower than that of the standard ink jet printing; printed objects have a relatively rough surface and are somewhat heavily textured. Consequently, their mechanical properties are limited prior to finishing.

Since 3D prints are almost always postprocessed, the infiltration of printed objects is routinely done. Epoxy resin, cyanoacrylate, and polyurethane agents are commonly used. Since mechanical (Grimm, 2004) and surface characteristics of the finished prints are highly dependent on the finishing agent used, the impact of the type of infiltrant on the selected properties of final prints was studied.

## **REPRODUCTION IN 3D INK-JET PRINTING**

The 3D printing process functions on the basis of the conventional ink-jet printing and it can produce objects in full colour, using C, M, Y, K coloured binders and a clear binder. The basic process principle, the ink-jet printing, and its colour capabilities are the reason why it is also a topic of interest for the graphic technology based research. The image processing methods have been investigated as the methods for practical measurements, providing data about, for example, particles and shape identification, and size distribution (Igathinathane *et al.*, 2008). In graphic technology, the need for effective print quality assessment of ink-jet printing has continued as printer technology has developed, and particular attention has been paid to methods based on image analysis. These methods use microscope in conjunction with a digital camera to capture the print target image or are scanner-based (Barker *et al.*, 1999). Line quality, text quality, dot quality, colour reproduction, ink dot size and various surface coverage characteristics are just a few of the many elements that can be characterized in detail by such systems (Wolin *et al.*, 1998; Bergman *et al.*, 2005; Tse, 2007). Dot quality can be influenced by the printer mechanism, the characteristics of the ink and the properties of the substrate. The dot quality test provides information about the spatial and morphological variations of the dots (Kipman, 1998).

The scope of the work presented in this part is to obtain basic information about reproduction of the surface elements in relation to different printing preferences and object position in three-dimensional ink-jet printing, and to study the application of image analysis as a technique for objective evaluation.

Image analysis is a computer-aided technique which is often used in a large number of industries and research areas. It is versatile and easily adaptable to different uses. In papermaking and printing, it is frequently used for various inspections of paper products' characteristics during and after production and converting and evaluation of the interactions between inks and substrates during printing processes, as well as for print quality evaluations. In ink jet printing, there exists the need for effective print quality assessment with particular attention to the automatic methods based on image analysis. Microscope, in conjunction with a digital camera, is often used to capture the print target image or the methods are scanner-based (Barker *et al.*, 1999). Line quality, dot quality, colour

reproduction and various surface coverage characteristics are just a few of the many elements that can be characterized in detail by such systems (Wollin *et al.*, 1998).

As previously mentioned, there are several relevant characteristics that are known to affect the 3D print accuracy and definition, such as: selected layer thickness; amount of saturation of the binder (powder/binder ratio); bleed control, which compensates for the seepage of binder into the powder layer (Hackney, 2003), etc. These printing preferences have been varied in order to observe their potential impact on the quality of surface reproduction. Other specific characteristic of 3D printing process of importance here is relative position in the build bed (in xyz space). The position of the test plates has been varied as well in order to observe its potential impact on the characteristics of surface reproduction.



## PAPER VI

### **COLOUR MEASUREMENTS AND PROPERTIES OF 3D INK-JET PRINTS**

3D printing is a rapid prototyping method which functions on the basis of the conventional ink-jet printing. It is currently the only RP method which is capable of producing objects in full colour. Although being a RP process, its basic principle of objects production and colour capabilities are the reason why it is a topic of interest for the graphic technology based research. 3D printing itself has been a topic of interest in a number of articles in the last few years, mainly in rapid prototyping and advanced engineering journals. Topics researched include, among other, general overview of technology and future outlooks, achievable accuracy, mechanical properties, bioprinting, benchmarking to competing rapid prototyping technologies. However, there are only a limited number of scientific articles dealing with the 3D printing colour capabilities, which raises the need to assess this topic in greater detail.

The scope of the work in this part is to obtain basic information about reproduction of colour in three-dimensional ink-jet printing as well as to research the methodology of 3D colour measurements and analysis.

There have been a certain number of publications (Gibson and Ling, 1999; Ling and Gibson, 1999; Gibson and Ming, 2001; Wang *et al.*, 2007) regarding the colour RP technology, mainly discussing recent advantages; applications and specific issues; new solution for producing coloured objects. The reproduction, measurement and control in 3D colour printing have also been researched, but only recently using the solutions and procedures of standard colour printing technologies (Parraman *et al.*, 2008; Walters *et al.*, 2009). This is in accordance with the fact that, until the year 2000, there was no RP system fully capable of building colour 3D models. Current technology from ZCorp. is using, as mentioned before, colour ink-jet printing technique to directly produce full colour.

Incorporating colour directly into the RP process offers the application of 3D models in various research areas, industries and arts, as well shifting the focus from functional models to the visualization of complex models and creation of concept models. Colour also plays a crucial role in further developing of rapid prototyping as a communication media, as the fully coloured model contains information on both, the picture and the object. This makes RP more appealing to a larger audience, adding value to the visualization process.

The possibility of direct production of colour 3D models is or will be especially important in application areas such as concept modelling, direct manufacturing, art, design, and architecture. There are several factors, such as hardware, materials, and software issues, which need to be respected in the development and use of colour RP (Rees, 1998).

As mentioned previously, 3D ink-jet printing process described here is the one by ZCorporation, with basic materials being in form of powder and liquid binder. It is the only RP method that can produce physical models in full colour, by using subtractive colour mixing and digital halftoning, much like in conventional colour ink-jet printing, realized through the application of coloured binders in addition to the clear binder. This enables creation of various models that are useful in solutions for e.g. visualization, concept modelling, Finite Element Analysis (FEA), presentation models, packaging, AEC, industrial design, fine arts, bio-medical research, geospatial, entertainment and retail (ZCorp., 2010).

Three-dimensional physical models, in addition to the virtual reality (VR) technology models and solutions, are often used for visualization and data analysis, providing, among others, a haptic experience. Used in different research areas, applications and industries, physical models can have certain advantages when compared with VR models and can lead to a new quality in visualization and better insight into the forming process (Rase, 2009).

3D models are especially important in research, application and education in mechanical engineering. They allow better visualization of parts and enhance the geometric interpretation and spatial analysis of mechanical parts, which are important in machine design and manufacturing processes evaluation (Santos *et al.*, 2005).

The visualization of architectural and GIS models is also one of the application areas where RP models are used. Although VR was adopted and widely used for spatial visualization of object, and provide more visual information, a physical model is still often requested by developers and users. They are often also requested at key stages of design or as a tool to communicate the visual appearance of the design concept. It has also been noted that RP model making process offers an opportunity of melding the digital with the analogue (Gibson *et al.*, 2002). Choice of the RP technology to be used in architecture and GIS applications depends on a number of factors; with colour being an interesting option. However, the current possibilities and limitations of colour RP systems need to be taken into account.

Another area of application of colour RP models for visualization is medical scientific research and medicine. An example of this is using colour RP as visualization tools in diffusion-tensor MRI analysis. They provide a useful tool, in addition to the VR applications, for doctors and surgeons, enabling them to both visualize and feel the different aspects of brain data. RP has also been used in visualization of molecular models for test assembly possibilities and in creating physical models of the human brain surface. Colour RP models offer more complete representation of multi-variate medical data, respecting the colour issues and reproducibility of RP (Acevedo *et al.*, 2004).

Colour 3D printing, as a part of RP, has undergone, until recently, only limited research (Gibson and Ming, 2001). Colour reproduction, colour measurements, colour consistency and colour permanence are some of the issues that are an integral part of both graphic technology research, and the printing industry. The methodology of quantifying, judging and controlling the colour output has been well researched and is constantly developing further. The question which is raised here is can the methodology developed for dealing with conventional ink-jet printing colour issues, and to what extent, can it be applied to the 3D colour printing. Colour issues in 3D ink-jet printing include 3D colour reproducibility, colour constancy and control, achievable range of colours and the effect of materials and process properties, 3D prints surface characteristics and colour measurements, etc. (Cunningham, 2010).

## **COLOUR STABILITY AND PERMANENCE IN 3D INK-JET PRINTING**

As mentioned, due to the emerging application areas of colour 3D prints, permanence and colour stability of 3D prints has recently started to be an issue. In such applications, 3D prints are expected to last for specific amount of time, with their properties, including mechanical, surface and thus colour, remaining acceptable to all relevant users. The open questions are the colour reproduction possibilities of 3D colour printing, possible better control to obtain maximum of achievable colour output and, most recently, 3D prints permanence, especially lightfastness and colour stability, including the development of the appropriate measurements methodology, description of aging mechanism and characterization of properties of 3D prints. The evident nature of 3D prints, the fact they are three-dimensional also leads to the possible issue of colour appearance being different on various sides and geometry of the object and varying colour stability, as the amount of light intensity which specific sides of the object are being exposed to could lead to them not reaching the same level of fading.

An example of these application areas is production of architectural, landscape and especially city models for display purposes, usually in places like city halls, museums and other various public spaces. 3D prints here serve as semi-permanent or permanent models which need to maintain the required appearance for specific duration of time. One of these examples is the city of Zagreb, Croatia, whose area has been digitalized and 3D virtual model was created using photogrammetric mapping of rooflines and Digital Terrain Model (DTM). The centre urban area was then printed as a 3\*3 meters large colour 3D model, Figure 4, which was procured by the Zagreb government for their department of spatial and urban planning and was publicly displayed, in transparent casing with open top, in the Zagreb City hall. The model which is currently exhibited consists of 120 panels, which are a part of about 500 panels that were made (Franic *et al.*, 2009). The model is intended to be further broadened by assembling together printed panels of other areas of the city and should be exhibited in one of museums. This example covers some of the mentioned issues with colour and stability of 3D prints, such as the variation of colour output, which infiltrant has been used, based on achieving adequate mechanical and best available colour and permanence properties, under what conditions, light, casing, temperature, humidity will the model be display, at what time span will the additional panels be added to the original model and for how long is it expected that the model will be used.



**Figure 4.** 3D printed model of city of Zagreb, ©Ib-procadd

Other example of using 3D prints as public display models is the model of the Sečovlje Salina, Slovenia, which is one of the largest such models in the world. The 3D model was printed from the digital model based on digital relief model (DMR) and digital orthophoto (DOF) of saline, and is 4.5\*3.5 meters in dimension, assembled from 172 panels, Figure 5. It was finished with epoxy based infiltrant, and later further protected by employing polyurethane-based UV varnish on top. The 3D model is displayed, un-covered, as a central object in Multimedia Centre in Sečovlje. Other than the large 3D model, a smaller model, measuring 1.05\*1.25 meters in dimension, for visually impaired people was also produced, containing Braille's writing (Ib-procadd, 2009-1). This is of possible interest since the model is therefore going to be more handled by visitors, introducing another element to the issue of durability.



**Figure 5.** 3D printed model of Sečovlje Salina, ©Ib-procadd

Other example of this kind is also the 3D model of settled part of Šaleška Valley, Slovenia. The 3D digital model was created on the basis of digital panoramic photographs, digital relief models and other archival written documentation and images, measures 1.5\*1.5 meters in dimension and contains 30 panels. The 3D colour printed models was as well infiltrated with epoxy-based finishing agent and glazed with polyurethane-based varnish, mounted on a vertical board and is publicly displayed outdoors, near the hayrack in town Gaberke in Šaleška Valley (Ib-procadd, 2009-2), Figure 6. The displayed model is placed in glass casing, and turned in such position that it is not under the impact of direct sunlight. This application of 3D models is interesting due to the fact that the 3D printed object is displayed outdoors.



**Figure 6.** 3D printed model of Šaleška Valley, displayed at the site near town of Gaberke, ©Ib-procadd

Colour, permanence and stability are potentially also relevant to the application of 3D prints in preservation of cultural heritage, especially for reproduction of replicas of specific works of art and other artefacts, which could be used for either presentation or education purposes. This application already uses the 3D scanning and its use is further increasing as a method for digitalization of objects for preservation, so 3D printing of such obtained digital models could be the next step. Other application area is fine arts and design, where the 3D printed objects are regarded as an author works of art and are often exhibited in galleries, museums, various exhibition places and in some cases could also be displayed in open places. The question which is additionally raised here is how important is permanence as the object could be easily reproduced again when it changes in its properties above the specific end point. But, if digital methods of object production are regarded as just a mean of expression

and creation, it could be said that reproducing the object again interferes with that concept, although it is up to the author to decide on how to treat this production process.

When material and prints properties are concerned, 3D prints are, in addition, most often infiltrated, with the infiltrant being usually present either just in the surface area of specific depth or penetrating through the whole print structure. Colour 3D ink-jet prints which are discussed here can be considered as a system comprising of powder, binder, with the colorants making part of the binder, specific infiltrant and additional varnish or coating that can sometimes be applied on top. Therefore, research of both colour and permanence of 3D prints opens the questions of defining the adequate measurement methodology and determining the specific prints properties.

When talking about conventional printed matter, both traditional and digital, prints permanence and lightfastness issues have been continuously a topic of research. This is especially relevant to the photographic images industry, which has been long focused on permanence, currently with the emphasis on digitally printed photographs, with ink-jet and “dye-sub” printers covering the majority of market, and to the conservation industry, where there is a question of preserving the printed matter and works of art in museums, libraries, collections etc. There are number of studies published in the field of conventional prints permanence, with the work done by Wilhelm Imaging Research (Wilhelm *et al.*, 2009; Wilhelm, 2004-1; Wilhelm, 2004-2) offering most comprehensive research in stability and preservation of traditional and digital colour photographs and prints. Other notable research institutions include The Image Permanence Institute (IPI, 2009) and Aardenburg Imaging & Archives (McCormick-Goodhart, 2007).

High-intensity fluorescent and xenon arc lights are two types of light that are nowadays recommended as radiation sources for accelerated aging procedures. For a number of years the printing and photographic industry permanence research has been done by utilizing the fluorescent lights for accelerated aging procedures, with xenon arc light based instruments, in accordance with the light sources other industries are using, being used in some recent research (Wilhelm *et al.*, 2009). Xenon arc light sources, when used with the appropriate optical interference cut-off filters, simulate the ultraviolet (UV) and visible global daylight spectrum much better, especially for the window filtered daylight (Schulz, 2009; Wypych, 2008). As the radiation in the UV wavelength range is mainly responsible for photochemical

processes, the UV irradiance needs to be adjusted and controlled to be constant in accelerated aging and artificial weathering devices (Boxhammer, 2001).

Light induced changes and degradation of printed matter are influenced by the properties of colorant, medium or substrate and light composition itself. There are also other relevant factors that influence stability behaviour such as area being solid or half-tone, colour density, properties of coating if is present (ASTM, 2009). In the case of 3D prints, the system is further broadened by the use of infiltrants, which are usually applied as finishing agents in order the prints obtain their final mechanical, but also colorimetric properties. Two main mechanisms responsible for light induced degradation of conventional ink-jet prints are photolytic degradation, photo-oxidation and photo-reduction, and photo-catalysis (Vogt, 2001; Jürgens, 1999). Colour changes that usually take place during exposure of multi-colour prints to various factors are addressed as colorants fading, which, if they fade at the same rate lead to overall fade of image, and if one of the colorants fades at a different rate than the others, hue shifts, as migration of colorants and as the change of the substrate (IPI, 2009).

As for the evaluation of changes of colour for storage and keeping of ink-jet prints in specific, it is recognized that the dark stability of prints should be assessed under the conditions that are in accordance with the end use application in question (ASTM, 2006).

The colour stability of 3D colour prints has recently been brought up as a research topic, as 3D colour prints have entered application areas such as AEC, preservation of cultural heritage and fine arts. Such examples are production of architectural and especially urban landscape models (Franic *et al.*, 2009) as display models for exhibition purposes in e.g. town halls, museums; production of replicas of historical objects and pieces and voluminous works of art in cultural heritage preservation; and creation of fine arts (Reid, 2009; Walters and Davies, 2010). In these applications, the permanence of colour, as well as the other properties such as mechanical and surface, is important since the printed output is not there longer regarded as a prototype or concept model, but rather as an object with a specific purpose which needs to be maintained, and whose integral parts are image and colour. To answer the open question of 3D colour prints colour stability and hence longevity, further research should be performed on the subject of the behaviour of colour during aging, depending on the material, printing and environmental parameters (Cunningham, 2010). This is the main objective for the research performed, which serves as a starting point for a



broader discussion and introduces some of the initial measurements of colour stability to both xenon-based light source accelerated exposure and natural aging in display and storage specific conditions. The idea of the research is to simulate exposure of 3D prints to various display, in window-filtered daylight and artificial light, and storage, both sealed and not covered, conditions. The research work is performed for basic evaluation of colour stability behaviour in application purposes in which the prints would be displayed e.g. in showrooms, window displays, under glass casings in public places and/or shown in offices and other indoor display spaces such as galleries and museums or stored under different conditions.

# **EXPERIMENTAL**

## **MATERIALS AND METHODS**

### **PAPERS I AND V**

#### **3D INK-JET PRINTS SURFACE AND MECHANICAL PROPERTIES – IMPACT OF INFILTRANTS AND PROCESS PREFERENCES**

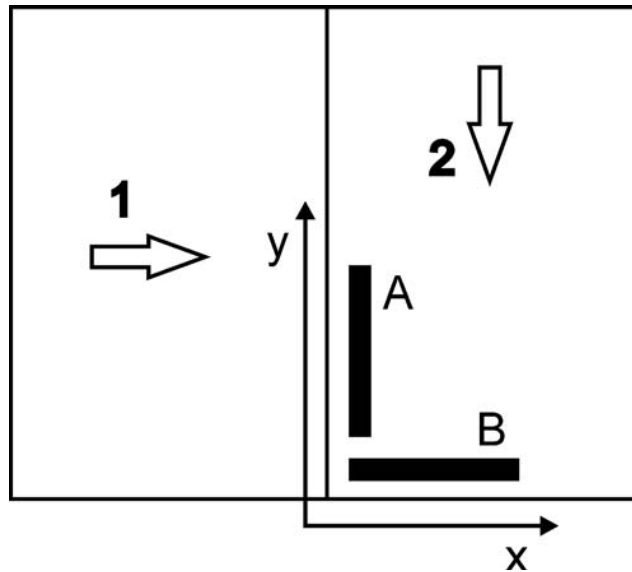
##### **Mechanical Properties**

Characteristics addressed in this part of work were tensile strength, impact, and hardness of 3D print materials. The combination of current plaster-based powder and water-based binder was chosen, and testing of mechanical properties was performed. In addition to testing of unfinished samples, three infiltrant agents were used. Properties of finished samples were then determined.

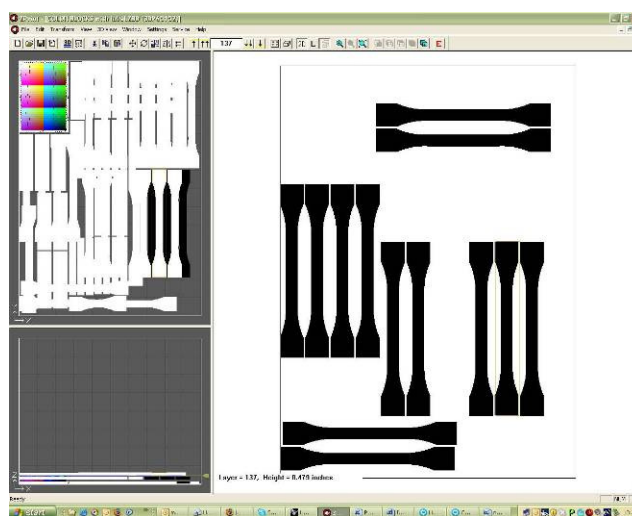
The standard sized samples needed for testing were printed on the Z Corporation/Context Spectrum Z510/Cx printer. The prints were made with the Zp130 high performance composite material (MSDS zp130, 2005) and Zb58 binder (MSDS zb58 2005), with the layer thickness set to 0.0035 in. Printed samples were divided into four groups and handled in the following manner: first group samples were left untreated, second group samples were finished with an ultralow viscosity cyanoacrylate infiltrant (Z-Bond 101, manufactured by the Z Corporation, USA), third group samples were finished with the medium viscosity epoxy infiltrant (Z-Max, manufactured by the Z Corporation, USA), and fourth group samples were finished with the low viscosity polyurethane-based infiltrant (Protektin, manufactured by the Samson Kamnik, Slovenia). Additionally, three more subgroups of samples for the tensile properties test were made; one printed in the x-y direction of printing, Figure 7, one printed in additive synthesis black colour (Table of Abbreviations), and one baked at approximately 60°C for 30 min. Set-up for x and y direction printed samples is shown in pre-print software ZPrint as well, Figure 8. All three subgroups were later finished with the cyanoacrylate infiltrant and tested, Figure 9. A summary of the samples and the abbreviations used to designate them is given in Table 1. The pre-print, printing and finishing procedure is shown in Figure 10 to Figure 16.

**Table 1.** Table of Abbreviations

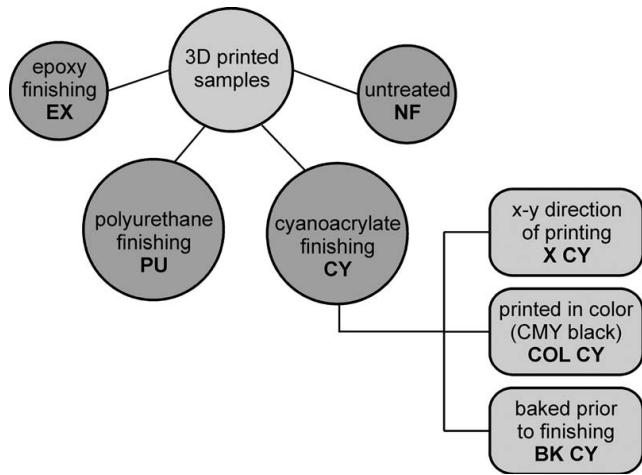
<b>NF</b>	<b>Not finished, green</b>
<b>CY</b>	<b>Cyanoacrylate finishing</b>
<b>EX</b>	<b>Epoxy finishing</b>
<b>PU</b>	<b>Polyurethane-based finishing</b>
<b>CY COL</b>	<b>Colour (R 0 G 0 B 0)</b>
<b>CY X</b>	<b>x-y direction of printing</b>
<b>CY BK</b>	<b>Baked prior to finishing, for 30 min at</b>



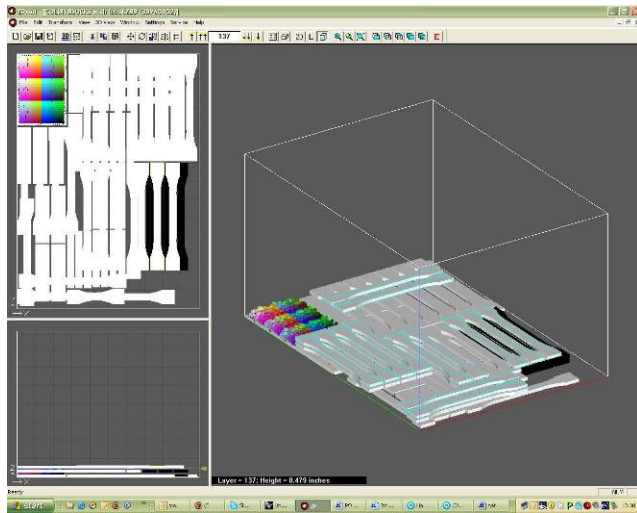
**Figure 7.** Flat view (z axis not shown) of the samples printed in x-y and y-x directions. The powder is distributed in a layer in the arrow 1 direction onto the print area. In the return direction, the binder is ink jetted onto the layer of powder. The ink jetting of the binder is in the arrow 2 direction. Bar A shows orientation of prints printed in x-direction, bar B in the x-y direction.



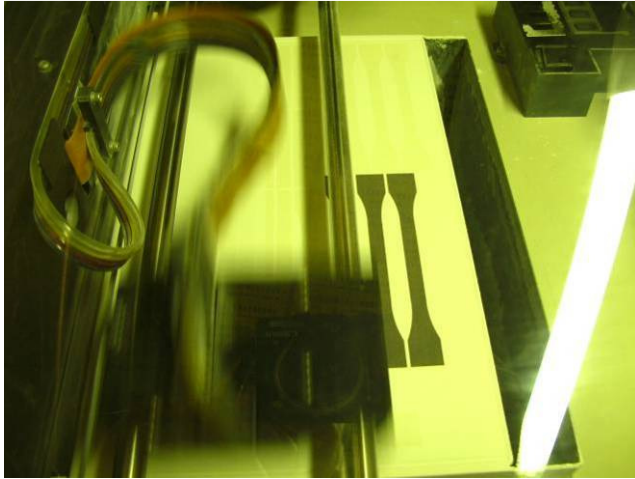
**Figure 8.** Graphical representation of the samples set up for printing



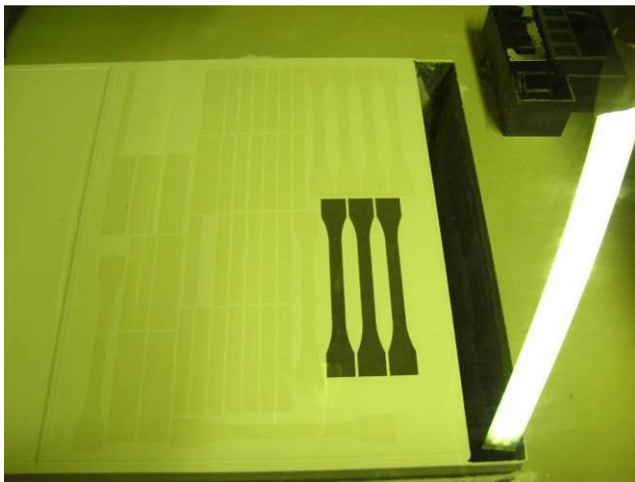
**Figure 9.** Workflow of the material mechanical testing sample production



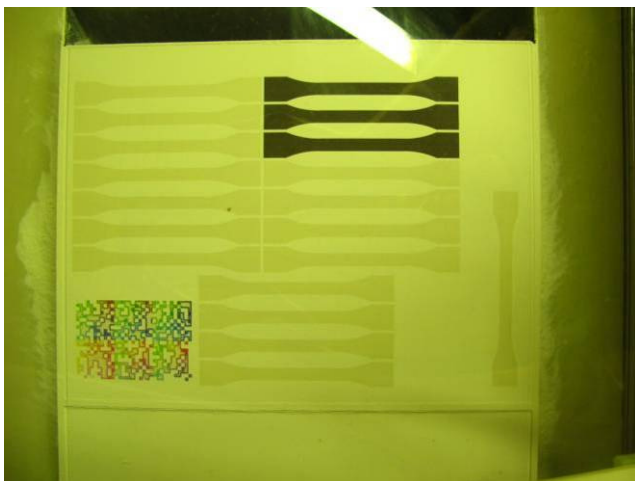
**Figure 10.** Samples set up in pre-print software, ZPrint



**Figure 11.** Printing, print carriage in motion, ZPrinter 510



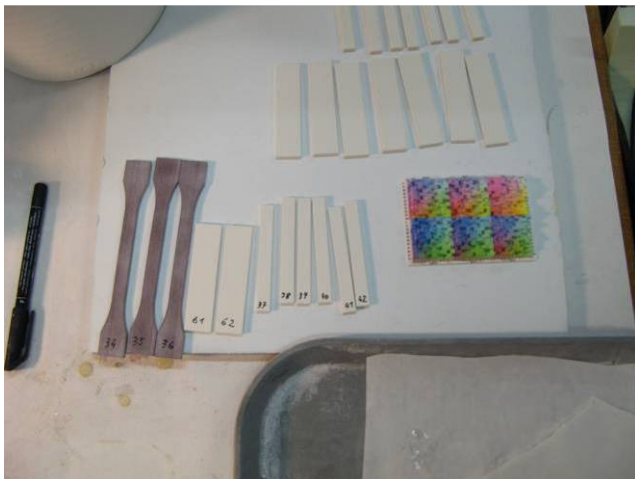
**Figure 12.** Printing, process in progress, ZPrinter 510



**Figure 13.** Printing, process in progress, top view, ZPrinter 510



**Figure 14.** Post-processing, gross de-powdering, ZPrinter 510



**Figure 15.** Printed and de-powdered prints, prior to infiltration



**Figure 16.** Post-processing, example of finishing by dipping in infiltrant

All infiltrant agents were applied onto the samples by dipping them completely into the infiltrant fluid for the following amounts of time: 2 sec in the case of cyanoacrylate agent, 2.5 min in the case of the epoxy agent, and 2 min in the case of the polyurethane agent. The amount of infiltrant was quantified gravimetrically.

In order to test physical and mechanical characteristics of nonfinished 3D prints, as well as those finished by the infiltrants, the selected tests were conducted. Tensile properties were tested on the universal tensile testing machine in accordance with ISO 527-1:1996 and the ISO 527-2:1996 standards (ISO 527, 1996), on type 1A samples and are expressed as tensile strength at break. The measurement scale of the machine was set to 0–950 N, with a load speed of 7 mm/min. Impact strength was tested on the Charpy type impact apparatus, on the unnotched standard sized sample, in accordance with ISO 179-1:2000 (E) (Charpy) standard (ISO 179-1, 2001). Hardness of materials was tested by the ball indentation method (Brinell), in accordance with ISO 2039-1:2001 (E) standard (ISO 2039-1, 2003). The hardness measurements employed a ball 5 mm in diam at a pressure of 5 kP (NF, CY, PU samples) or 13.5 kP (EX sample); results are shown for  $t=30$  sec as established by the standard. In accordance with the aforementioned standards, for each type of prints, the measurements were done on five samples for tensile and impact properties tests and on 10 locations of two samples for the hardness test.



## Surface and Cross-Sectional Images

Besides testing of the mechanical properties, all samples were observed visually in order to check the appearance of their surfaces: 3D print surfaces were inspected visually using an optical light microscope and by means of a scanning electron microscope, SEM JEOL JSM-6060 LV; the magnification factors were 30X and 200X, respectively. In order to observe depth of infiltrants upon penetration, cross sections of samples were observed with the scanning electron microscope with a magnification factor of 20X and with the optical light microscope Leica EZ4D with a magnification factor of 25X. Samples for SEM scanning were prepared by coating with sequential layers of carbon and gold. All the images were acquired at 10 kV. Optical light microscope images were captured with the microscope manufacturer's proprietary software Leica Application Suite.

In order to visualize the surface differentiation among the range of infiltrants and the penetration depth of infiltrant agents, image analysis software ImageJ (Rasband, 2010) was used. ImageJ is free, open-source software, which works in Java and is highly customizable through various macros and plug-in functions. ImageJ's built-in surface plot function was used for the purpose of clearer representation of the SEM images. Penetration depth was estimated using the set scale and straight line functions in ImageJ.

The surface stereo pair was obtained using a Hitachi S-3000 VPSEM, in low vacuum mode. The accelerating voltage was 10 kV, the working distance was 10 mm and the magnification was 100x. The size of the digital image was 2560x1920 pixels using 256 grey levels. The corresponding resolution was 0.5 mm/pixel. After image acquisition the stereo pair was aligned with the TurboReg plugin (Thevenaz, 1998) using a simple translation approach.

A new plugin for ImageJ was implemented for surface reconstruction, i.e. the StereoJ plugin. The height map is generated by finding the best match between a local predefined window on the right image and a local window of the left image. The predefined window on the right image is used for scanning the right image on the same y-position. As the processing time is proportional with the width of the left image and the dimensions of the predefined window, the length for scanning and the dimensions of the searching window can be predefined. The predefined window on the right image scans the left image within a predefined distance in the x-direction, calculating the cross-correlation coefficient for each step. The cross-correlation coefficient ( $r$ ) is given by:

$$r = \frac{\sum_{i=1}^{N_x'} \sum_{j=1}^{N_y'} (f_{ij} - \bar{f})(g_{ij} - \bar{g})}{N_x' N_y' \sigma_f \sigma_g} \quad (1)$$

where  $N_x'$  and  $N_y'$  are the local dimensions of the searching window,  $f$  and  $g$  are the local greylevels at the local position  $(i,j)$ ,  $\bar{f}$  and  $\bar{g}$  are the mean greylevels and  $\sigma_f$  and  $\sigma_g$  are the standard deviations of the greylevels on the left and right local images respectively.

The highest cross-correlation coefficient, within the scanning distance, defines the best match between the local region of the right and left images. The local x-positions on the right and left images were thus used for the local height calculation according to Eq. 2. The local height ( $z_{ij}$ ) is calculated according to Eq. 2 (see e.g. Ammann and Bouchaud, 1998; Hein, 2001; Cheng et al., 2000):

$$z_{ij} = \frac{x_{left} - x_{right}}{2M \sin\left(\frac{\Delta\phi}{2}\right)} \quad (2)$$

where  $x_{left}$  and  $x_{right}$  are the local positions at the left and right images respectively,  $M$  is the pixel size and  $\Delta\phi$  is the total tilting angle.

If the cross-correlation coefficient for a given height value was lower than a predefined acceptance level the height value was considered invalid and marked for correction. The final height map, containing valid and invalid height values, was filtered with a local median filter. The filter replaced only the invalid height values with the median height of the surrounding valid values.

In addition to generating an anaglyph based on the stereo pair, the StereoJ plugin also generates a correlation map showing the local cross-correlation coefficient at each local position. This is valuable information for verifying the reliability of the generated height map.

## REPRODUCTION IN 3D INK-JET PRINTING

### Example 1

#### Test Plates Preparation and Printing

A test target file was created and prepared in order to monitor the reproduction in three-dimensional ink-jet printing, Figure 17. The test target was prepared in Adobe Illustrator software and saved as a tiff type file. It was then imported, positioned and placed as a texture on the 3 cm by 3 cm x 0.3 cm plate in ZCorporation proprietary ZEdit software, Figure 18. The test target consisted of various geometrical elements and letters; circles of two different diameters (5 mm and 10 mm), vertical, horizontal and angled lines with the stroke width of 2 pt and capital Times New Roman letter E in two different sizes (12 pt and 24 pt). The test target was constructed in magenta colour only, in a way to secure that there will be no deposition of two or three binders for obtaining the specified colour.

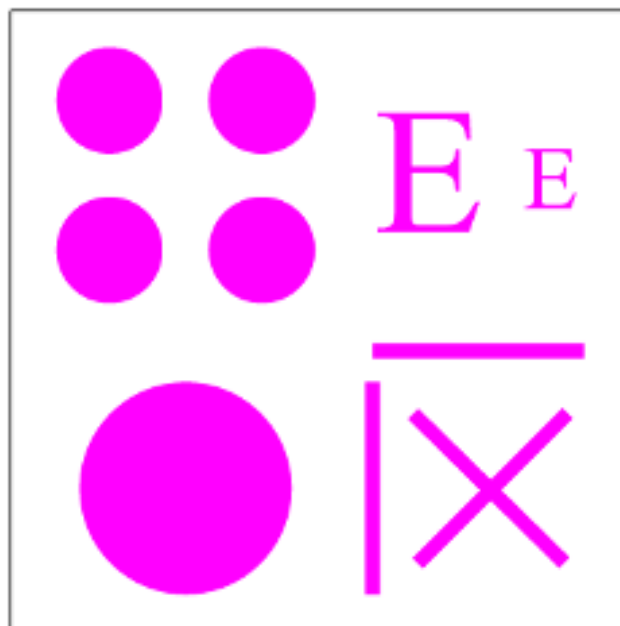
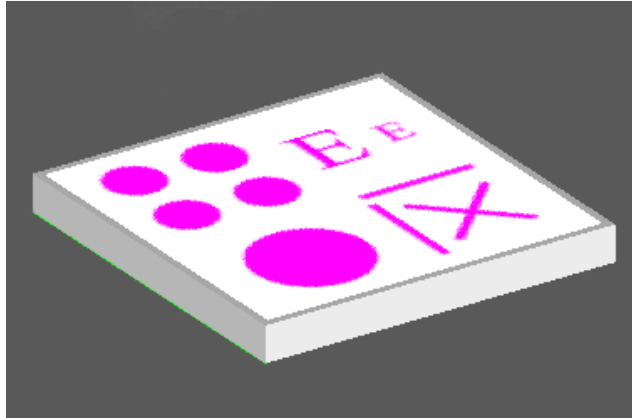
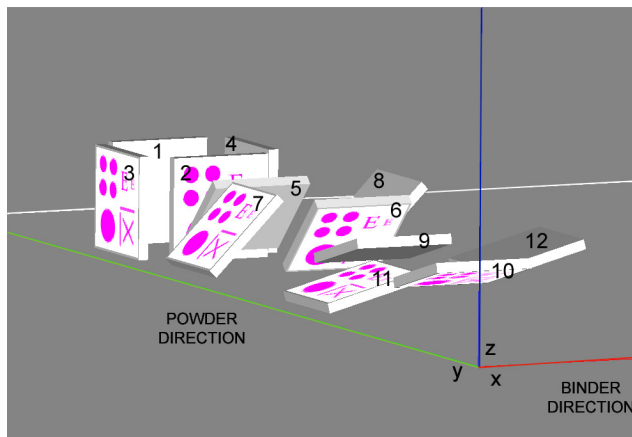


Figure 17. Designed test plate with elements



**Figure 18.** Prepared test target file was applied as a texture on a test plate, visualization of the test plate in ZPrint software

The test target plates were then placed in specified positions and/or printed with the specified printing preferences. Table 2 and Table 3 present the specified printing preferences set up. First group of samples was set up in such a way that the printing preferences were the same and samples were placed in different positions within the xyz space in the build bed, Figure 19. This group of samples was prepared in order to show the possible changes in the surface reproduction depending on the relative position in the build bed. All the samples from the first group were printed with the layer thickness set to 0.1 mm, 100% shell saturation and bleed control off.



**Figure 19.** Graphical representation of the second group of samples set up, different positions in the build bed, numbers correspond to the labels in Table 2.

**Table 2.** Printing set up, same printing preferences, different xyz positions

Label	Position
1	xz, binder direction, last
2	xz, binder direction, first
3	yz, powder direction, first
4	yz, powder direction, last
5	xz, binder direction, inclined at 45°, facing up
6	xz, binder direction, inclined at 45°, facing down
7	yz, powder direction, inclined at 45°, facing up
8	yz, powder direction, inclined at 45°, facing down
9	xz, binder direction, inclined at 75°, facing up
10	xz, binder direction, inclined at 75°, facing down
11	yz, powder direction, inclined at 75°, facing up
12	yz, powder direction, inclined at 75°, facing down

Second group of samples was printed with different printing preferences. It was prepared in order to monitor the surface reproduction depending on the printing preferences, namely the facing direction (up or down), layer thickness, shell saturation and bleed control.

**Table 3.** Printing set up, different printing preferences

Label	Position	Layer thickness	Saturation	Bleed
A_D	Down	0.1 mm	100%	ON
A_U	Up	0.1 mm	100%	ON
B_D	Down	0.1 mm	100%	OFF
B_U	Up	0.1 mm	100%	OFF
C_D	Down	0.1 mm	150%	OFF
C_U	Up	0.1 mm	150%	OFF
D_D	Down	0.1 mm	75%	OFF
D_U	Up	0.1 mm	75%	OFF

The printing was done on the ZCorporation Spectrum Z510 printer. It is a colour printer, with resolution of 600 x 450 pixels, build size 10 x 14 x 8 inches, build speed of 2-4 layers per minute, user selectable layer thickness between 0.0035-0.004 inches (0.0875-0.100 mm). Its printing head system comprises of four printheads (one for the each of the C, M, Y colour ink binders and one for the clear binder) with 1216 jets in total. Materials used were high performance composite zp131 powder and zb60 binders (cyan, magenta, yellow, clear). The zp131 powder is plaster based powder, with additional components added in smaller percentages. Zb60 binders are based on standard water-based ink-jet fluids, comprising mainly of water, colorants and other additives.

After the printing was finished, the samples were removed from the printing bed and cleaned from the remaining loose powder. The elements which are analyzed, shown and discussed in this paper are: a circle with the 5 mm diameter and characters “E”. Circle was selected as an example element on which the image analysis procedures and the reproduction in three-dimensional printing were researched. As image analysis as a technique has yet not been extensively or at all used on three-dimensional prints, the example element was analyzed and used as a starting point in researching the application specific issued. The reproduction of characters “E” was shown for the samples that were placed in different xyz position in the print bed, to show if the nature of the three-dimensional printing process leads to potentially visually noticeable differences in reproduction.

## Image Capturing and Analysis

After printing and post-processing, the samples were captured using Leica EZ4D stereomicroscope equipped with integrated 3-megapixel CMOS sensor digital camera. The capturing was done using 12.5 x magnification rate. Image size was 2048 x 1536 pixels. The magnification rate used was chosen based on the element size that were captured in order to obtain the highest level of detail. The microscope images were used for detailed observations of the reproduction of elements, and due to the practical reasons, as the procedures studied would be of potential use in industry, scanned images were used for observations as well. The samples were therefore scanned, in reflective mode, on HP ScanJet G4010 flat-bed scanner, at resolution of 1200 dpi. All the captured samples were saved as tiff type files.

The ImageJ software (Rasband, 2010) was used for image processing and analysis. ImageJ is free and open source software, working in Java environment. It was selected as the tool for performing image analysis predominantly since it can be upgraded and fit to specific uses, by the use and development of customized macros and plug-ins. ImageJ has a built-in function for particle analysis, with user defined set of measurements analyzed and provided in the output results, such as number of particles, area and total area, perimeter, percentage of coverage, best fitting ellipse axes, circularity, roundness (Igathinathane *et al.*, 2008). Images were uploaded to ImageJ, pre-processed and later analyzed by using the built-in Analyze Particles function. The measurements parameters of the analyzed circle elements which were calculated are total area, perimeter, circularity, Feret diameter, Major and Minor. Feret diameter denotes the longest distance between any two points along the selection boundary, also known as caliper length. Major and Minor denote the primary and secondary axis of the best fitting ellipse. Circularity is one of the measurement parameters in ImageJ that can be used to describe how different is the element from the ideal circle ( $C=1$ ). Circularity is directly dependant on the relationship between the area and the perimeter of the element, and was calculated using the formula:

$$C = 4 \Pi * (\text{area}/\text{perimeter}^2) \quad (3)$$

In order that images can be analyzed by ImageJ Analyze Particles function, the regions of interest (ROI) need to be segmented from the background. The segmentation divides the image into specific and separate regions. There are a number of segmentation methods, one of which is based on the histogram thresholding (Navon *et al.*, 2005). The segmentation is done based on intensities' differences of the ROI and background, and the threshold values defined separate the pixels with intensity below the lower and above the higher threshold

values from the pixels with intensity above the lower and below the higher threshold value. Once threshold is applied, the image is transformed to a binary image (Baecker, 2009).

In the presented research, the images were thresholded using the Threshold Colour plug-in (Landini, 2009) which deals with colour images, as separate threshold values for each channel (in the Threshold Colour the channels are either R,G,B; H,S,V; CIE L,a,b; and Y,U,V) can be selected and passed/stopped. The images are segmented by selecting the threshold values for selected or all channels at which the ROI elements are separated from the background. They can then be binarised if necessary, by using Make Binary function. Other than using specific threshold values for each channel in the image, the grayscale thresholding could be used as well, with or without image pre-processing, and with automated or manual selection of the threshold values.

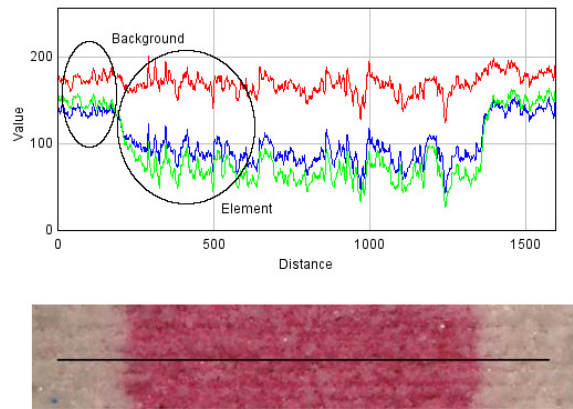
```
// Colour Thresholding v1.9-----
// Autogenerated macro, single images only!
// G Landini 2/Feb/2008.
// This only works with Black background and White foreground!
// You will probably have to uncomment the following 2 lines if
// the settings in ImageJ are not so:
//run("Colors...", "foreground=white background=black selection=yellow");
//run("Options...", "iterations=1 black count=1");
//
min=newArray(3);
max=newArray(3);
filter=newArray(3);
a=getTitle();
run("RGB Stack");
run("Convert Stack to Images");
selectWindow("Red");
rename("0");
selectWindow("Green");
rename("1");
selectWindow("Blue");
rename("2");
min[0]=147;
```



```

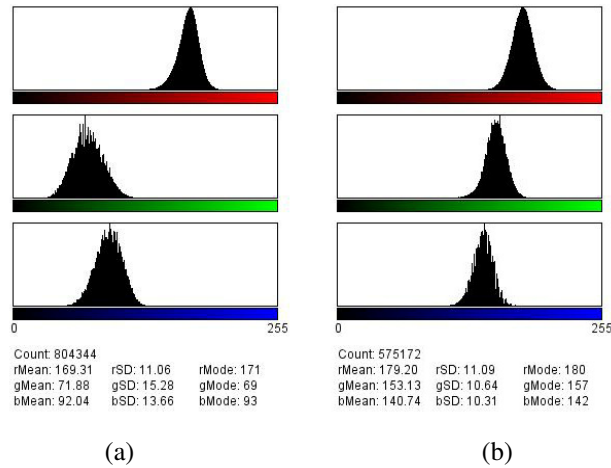
max[0]=237;
filter[0]="pass";
min[1]=25;
max[1]=132;
filter[1]="pass";
min[2]=40;
max[2]=190;
filter[2]="pass";
for (i=0;i<3;i++){
    selectWindow(""+i);
    setThreshold(min[i], max[i]);
    run("Make Binary", "thresholded remaining");
    if (filter[i]=="stop") run("Invert");
}
imageCalculator("AND create", "0","1");
imageCalculator("AND create", "Result of 0","2");
for (i=0;i<3;i++){
    selectWindow(""+i);
    close();
}
selectWindow("Result of 0");
close();
selectWindow("Result of Result");
rename(a);
// Colour Thresholding-----
run("Invert");

```



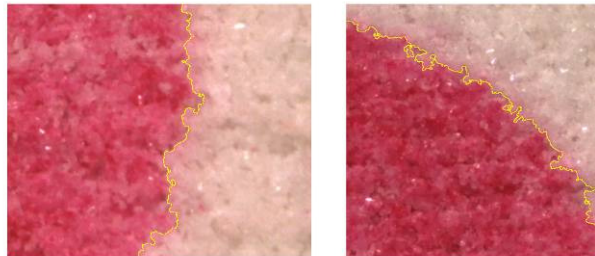
**Figure 20.** RGB profile of a sample microscope image of a 5 mm circle and its background, showing the difference in values of channels for the element and the background; the bottom image shows the line of the RGB profile

Figure 20 shows the RGB profile of the selected part (line selection) of a sample image. The RGB profile shows the differences in values of R, G and B channels for the background and the element. This facilitates the selection of threshold values for colour thresholding since it shows if and in which channels there is a distinctive difference between values of the ROI and the background pixels. In this research, the colour thresholding was done by blocking the specific values, belonging to the background pixels, in G channel, as it was most clearly differentiated for the ROI and the background pixels. The thresholding could be done by blocking the specific values of the background pixels in the B channel as well, although the separation of the G channel values was adequate. Figure 21 shows the same differences in a form of a RGB histogram, showing separate histograms for each of the channel, presented from the sample image rectangular selections of the area of the element and the background. The RGB profile was made by using real-time RGB profiler plug-in (Mutterer, 2009). The RGB histograms were made using Color Histogram plug-in (Prodanov, 2009).



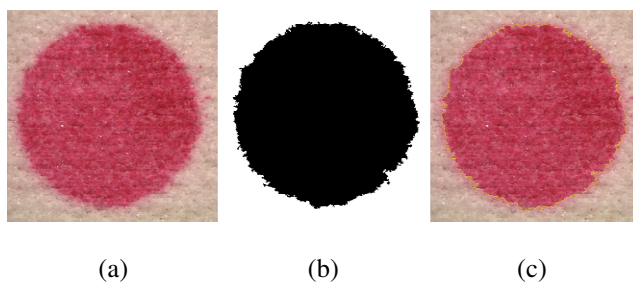
**Figure 21.** RGB histograms of element (a) and background (b) of the sample image of a 5 mm circle, showing differences in channels; R channel histogram top, G channel histogram middle, B channel histogram bottom

Figure 22 shows the close up of the image of the outline which is the border of the element that was obtained by using the colour thresholding procedure for processing and thresholding of the original microscope images, captured at 12.5x magnification. The image of the outline is overlaid on the original image in order to see the fitting of the outline of the binary image obtained by the described procedure.



**Figure 22.** Close up of the samples images, border (outline) obtained by applying threshold overlaid on the original microscope image

Figure 23 shows the processing and image analysis procedure on an example image, from the original image captured by the microscope, 12.5x magnification, to the mask of the character, showing the area which was analyzed by image analysis. As it can be seen, the image analysis procedure was set to disregard the particles which are not the part of the analyzed element but were included in the thresholded image based on their intensities level being in the selected specific threshold range.



**Figure 23.** Image analysis procedure, illustration; original microscope image (a), mask of analyzed element (b), outline of analyzed element overlaid on the original microscope image (c)

## Example 2

### Test Plates Preparation and Printing

The test target was prepared as an image in order to be analyzed by image analysis procedure, Figure 24. The image was prepared in Adobe Illustrator software and saved as a tiff type file. In ZEdit software the file was placed as a texture on a 50 mm by 50 mm x 3 mm plate, previously constructed in Solidworks software, Figure 25.

The image file consisted of various geometrical elements and characters; circles of five different diameters (5, 4, 3, 2, 1 mm) in C, M, Y, K, R, G, B colours; horizontal lines with the stroke of 2 pt, C, M, Y, K colours; capital Times New Roman letter E in six different sizes (24, 18, 14, 12, 10, 8 pt), M colour; three blocks consisting of two colours, in K/Y, C/Y, M/Y colour combinations. The test target was prepared in such a way to ensure that only the desired binders are actually applied during printing, to prevent the unwanted colour mixing, depending on a specific colour that needs to be obtained.

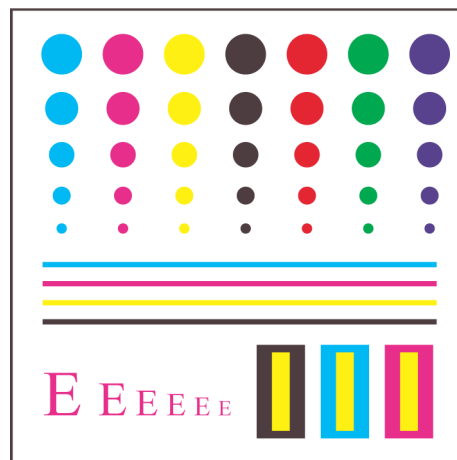


Figure 24. Designed test plate with elements

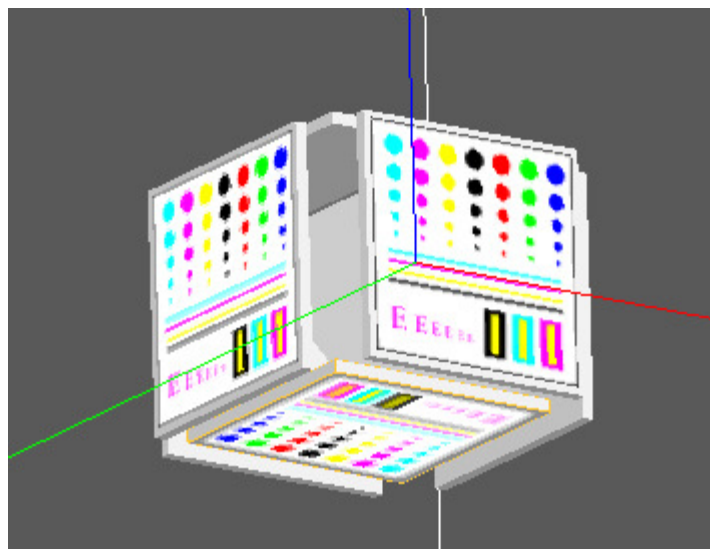


**Figure 25.** Image of the constructed test plate, with test elements on its surface

In ZPrint software the constructed test plates were placed in specified positions in the print bed, xyz space. Table 4 and Figure 26 present the different positions set up.

**Table 4.** Set up of the test plates in the build bed

Label	Position
1	xy, facing top
2	xy, facing bottom
3	xz, binder direction, first
4	xz, binder direction, last
5	yz, powder direction, first
6	yz, powder direction, last
7	xy, powder direction, tilted 45°, facing up



**Figure 26.** Graphical presentation of the test plates set up in the build bed

The samples were printed with zp131 powder, zb60 binders, with the layer thickness set to 0.1 mm, 100% shell and core saturation and bleed compensation off. The zp131 powder is plaster based powder, with additional components added in smaller percentages. Zb60 binders are based on standard water-based ink-jet fluids, comprising mainly of water, colorants and other additives. After the printing, the samples were removed from the printing bed and cleaned from the excess powder. An example of printed and post-processed test plate is presented in Figure 27.

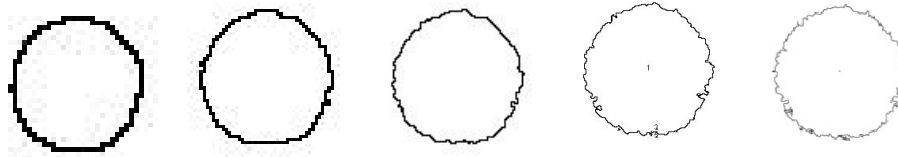


**Figure 27.** Example of printed and post-processed test plate

Due to the limited space, only several elements of the test form have been discussed in this paper; the magenta circles in various dimensions (5, 4, 3, 2, 1 mm in diameter). Magenta coloured elements have been chosen as they are, due to the contrast between the region of interest and the background, easier to separate, which was important for the visual control of the threshold selection while converting into binary images.

## Image Capturing and Analysis

After printing and post-processing, the samples were captured using Hewlett Packard G4010 flat bed scanner, using reflection mode. The capturing was done using 200, 300, 600, 1200 and 2400 dpi, from which the most adequate scanning resolution was decided on. Figure 28 shows the effect of scanning resolution on the achieved level of details, as seen on the obtained outlines of the analyzed elements. By comparing the achieved outline of the scanned images with the visual appearance of the samples, it was decided that the ones scanned on 1200 dpi present the optimum solution regarding the speed of scanning, the level of scanner noise included and the level of details captured.



**Figure 28.** Effect of scanning resolution on the obtained outline of the analyzed elements; resolutions 200, 300, 600, 1200, 2400 dpi, from left to right

Software ImageJ (Rasband, 2010) was used for image processing and analysis. ImageJ is free and open source Java environment software. It has been widely used in different research and industry areas. It is easily adaptable and can be upgraded to fit various uses by user-developed macros and plug-ins. Selected plug-ins and custom developed macro routines were used in the presented work as well. Images were uploaded to ImageJ, processed and analyzed by using Analyze Particles routine. The measurements parameters of analyzed elements which are discussed here are total area, perimeter and circularity. Before the analysis, the images need to be thresholded, or transformed in binary, black and white images, thus separating the elements of interest from the background. In a binary image, black can represent the element of interest and white the background or vice versa. In order to transform the RGB scanned images into binary images, they first need to be converted to 8-bit. Then the threshold is set, based on some of the automated procedures or manually selected, and applied, separating the print elements (here value 0) from the background (here value 1). For this purpose, the Otsu (Otsu, 1979) thresholding technique was used, as it was decided as the most appropriate method of automated analysis. For the most of the samples, the automated thresholding was used as the starting point for manual selection of threshold values for finer adjustments. The whole image processing and analysis routine was written in a form of a macro, which facilitated the procedure, by making it fast (the whole procedure is

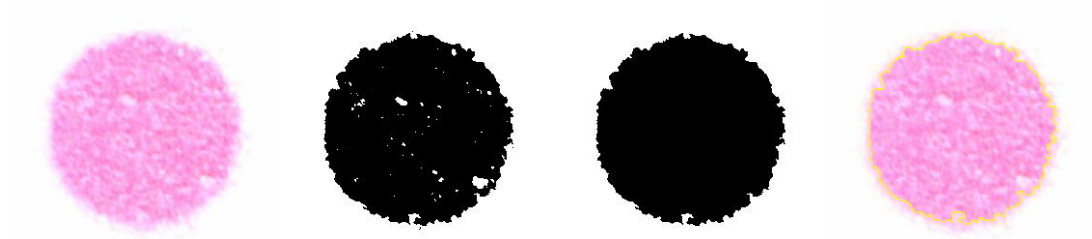


finished in under a second), fit to user needs and repeatable. In the same time, the developed macro allows the user to calibrate the image by selecting the scanning resolution, select the area on the scan that needs to be analyzed and perform the manual thresholding, if needed. The developed macro routine is presented below.

```
//3D scanned elements analysis
requires("1.39r");
saveSettings();
Dialog.create("Inputs");
Dialog.addNumber("Dpi: ", 1200);
Dialog.show();
Dpi = Dialog.getNumber();
parseFloat("Dpi");
run("Set Scale...", "distance="+Dpi+" known=25.4 pixel=1 unit=mm global");
Dialog.create("Select Area Dimensions to Evaluate");
Dialog.addNumber("Width (px):", 1100);
Dialog.addNumber("Height (px):", 300);
Dialog.show();
w = Dialog.getNumber();
q = Dialog.getNumber();
ImageID = getImageID();
makeRectangle(0, 0, q, w);
ID1 = getImageID();
setTool(0);
beep();
waitForUser("Select Area to Analyze");
if (selectionType () !=0)
exit("Please select rectangle!");
selectImage(ImageID);
run("Copy");
run("Internal Clipboard");
run("8-bit");
setAutoThreshold("Otsu");
//run("Threshold...");
beep();
```

```
waitForUser("Select Threshold");  
run("Convert to Mask");  
run("Analyze Particles...", "size=0.2-Infinity circularity=0.00-1.00 show=Outlines display  
exclude  
clear include summarize");  
restoreSettings();
```

Figure 29 shows the processing and image analysis routine of a print element, in this case circle with the diameter of 5mm, from the original scanned image captured, at 1200 dpi, to the mask of the character showing the area which was analyzed by image analysis. As it can be seen, the image analysis procedure was disregards the small residual particles that are not the part of the analyzed element. On the last image, the outline of the analyzed element obtained by image analysis procedure is superimposed on the original image in order to see the effect of image processing and analysis procedure.

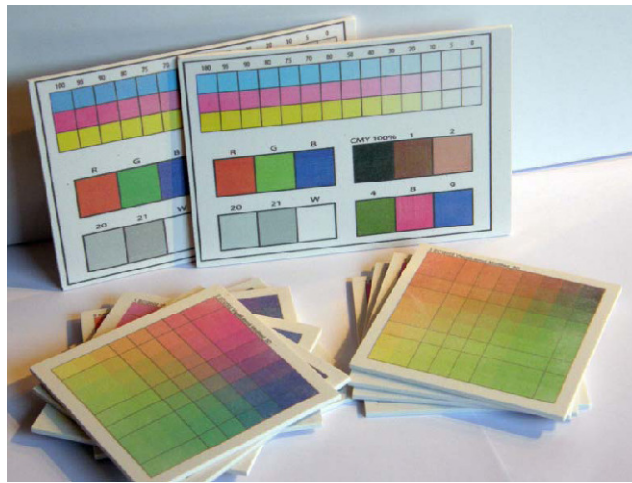


**Figure 29.** Image processing and analysis routine

## COLOUR MEASUREMENTS AND PROPERTIES OF 3D INK-JET PRINTS

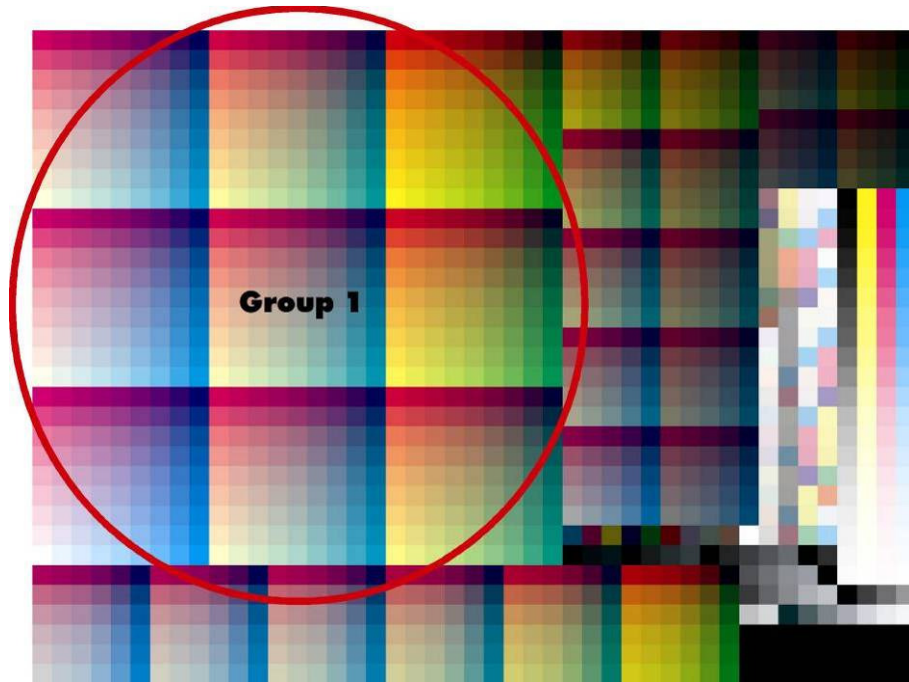
### Test Targets File Preparation

Two kinds of colour test targets were constructed and printed, marked ECI 2002 3D and CMY+, Figure 30, for characterization of colour capabilities of 3D printing process and observing the reproduction of basic colours. Both colour test targets were used for the creation of test plates, custom prepared for the research.

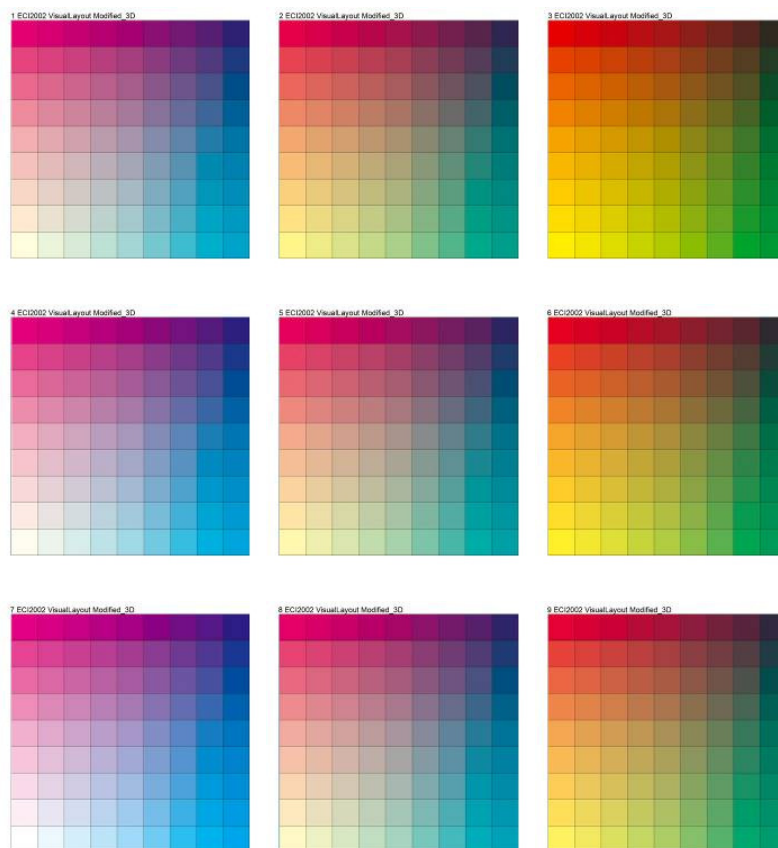


**Figure 30.** 3D prints used for measurements, non-infiltrated sample presented

ECI 2002 3D target was used for characterization of colour capabilities of 3D printing process. Group 1 portion of ECI 2002 Visual Layout test target (ECI, 2008) was used. Group 1 belongs to the profiling part of the ECI 2002 V test target and it consists of 729 patches, Figure 31. The patches are constructed of varying percentages of cyan, magenta and yellow colours. Due to the material surface characteristics and measuring equipment specifications, single patch of at least 1 cm in length and 1 cm in width was needed. Therefore, Group 1 patches were separated into nine equal squares and prepared as nine single tiff images. Images were fitted onto 10 cm by 10 cm plates (0.5 cm of white space on every end of the plate), measuring 3 mm in height, in ZEdit software, Figure 32.

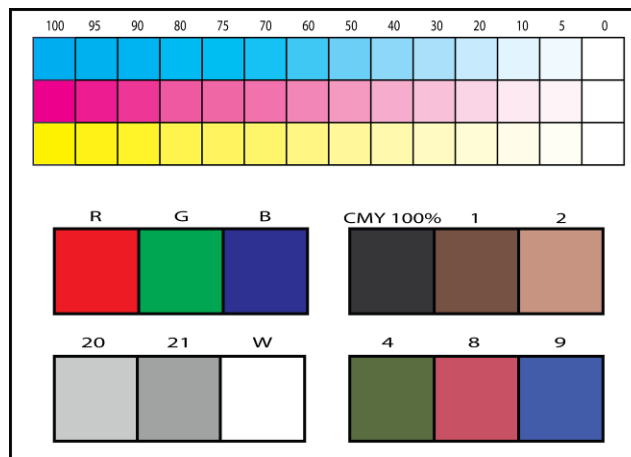


**Figure 31.** The ECI 2002 V test target, with Group 1 patches circled



**Figure 32.** Images from the ECI 2002 V test target which were fitted onto the sample plates

For observing the reproduction of basic colours, user defined target, CMY+ target, was created in Adobe Illustrator software and saved as a tiff image. Following patches from the test target were used in this work, their labels marked in parenthesis: 100% coverage of cyan, magenta and yellow colours in 1 cm by 1 cm patches (C, M, Y); 100% coverage of red, green and blue colours in 2 cm by 2 cm patches (R, G, B); “black” patch consisting of 100% of cyan, magenta and yellow, 2 cm by 2 cm (CMY); and “white” patch, clear binder, 2 cm by 2 cm (W). Image of user defined CMY+ target is presented in Figure 33.



**Figure 33.** Image of the CMY+ target, with the before described patches

## **Printing and Finishing**

The printing was done on the ZCorporation Spectrum Z510 printer. It is a colour printer, with resolution of 600 x 450 pixels, build size 10 x 14 x 8 inches, build speed of 2-4 layers per minute, user selectable layer thickness between 0.0035-0.008 inches (0.0875-0.203 mm). Material options are high performance composite, elastomeric and direct casting materials. Its printing head system comprises of four printheads (C, M, Y colour ink binders and clear binder) with 1216 jets total. Z510 printer uses HP thermal ink-jet printheads, with the continuous supply binder containers. Materials used were high performance composite zp131 powder and zb60 binders (cyan, magenta, yellow, clear). The zp131 powder is plaster based powder, with additional components added in smaller percentages. Zb60 binders are based on standard water-based ink-jet fluids, comprising mainly of water, colorants and other additives (humectants, buffer solution). Layer thickness was 0.004 inch (0.100 mm) for all the printed samples.

The printed samples were removed from the printing bed and cleaned from the remained powder. The samples were divided into three subgroups in accordance to the finishing process that followed, first group was left un-treated, second group was finished with Z-Bond 101 infiltrant and third group with Z-Max Epoxy infiltrant. Z-Bond 101 infiltrant is cyanoacrylate based infiltrant. It is ultra low viscosity finishing agent, which bonds in seconds. Z-Max infiltrant is epoxy resin based infiltrant, comprising of two components, the resin and the hardener, which have to be mixed together prior to use. It is medium viscosity finishing agent (ZCorp., 2007). Infiltration methods used were: pouring for ZBond infiltrant and continuous brushing for Z-Max infiltrant.

## Colour Measurements

Colour measurements were made with the X-Rite (Gretag Macbeth) Coloreye XTH sphere spectrophotometer. Some comparing measurements were made with the X-Rite 528 spectrodensitometer. Microsoft Excel software was used for the calculations and representation of data. Gretag Macbeth ProfileMaker 5.0 tools MeasureTool, ProfileMaker and ProfileEditor as well as open source software ICCView 2.0 (ICCView, 2008) were used for the assessment of colorimetric data. XTH sphere spectrophotometer has the following characteristics: pulsed xenon as the light source and diffuse 8°, Ø 38 mm integrating sphere as the optical configuration. The XTH spectrophotometer is presented in Figure 34. The following measurement characteristics were set and used in the colorimetric assessment: D65 illuminant, 10° observer, SPI, SAV (aperture Ø 5 mm illuminated, Ø 2 mm measured). Results of the measurements were recorder in the form of the CIE L\*a\*b\* and CIE L\*C\*h values were later computed. After the completion of the measurements, several analysis and comparisons were made. Colour differences  $\Delta E$  between different finishing types and non-infiltrated and finished prints were calculated and discussed. The colour difference formulas used were  $\Delta E_{2000}$  and  $\Delta E_{cmc\ 2:1}$ . Differences in L\*, C\* and H\* between the differently infiltrated samples and between the non-infiltrated versus infiltrated samples were calculated as well. Gamuts of the 3D prints, dependant of the finishing agent used, were assessed as well.



**Figure 34.** Coloreye XTH (© X-Rite)

**COLOUR STABILITY AND PERMANENCE IN 3D INK-JET PRINTING**

In the case of lightfastness of printed matter, it is understood that it is dependant on parameters such as the area printed, meant here as solid or half-tone, and initial colour density, type of substrate, type of colorant, type and thickness of the coating. The lightfastness is naturally also dependant on the spectral-power distribution of the light source to which the printed matter is exposed, as recognized in ASTM Standard Practice for Evaluating the Relative Lightfastness and Weatherability of Printed Matter (ASTM, 2009). The mentioned standard also notes that xenon-arc lamp, when used with the appropriate cut-off filter system provides spectral-power distribution corresponding more to the daylight than carbon-arc lamp. ASTM Standard Practice for Determining the Relative Lightfastness of Ink Jet Prints Exposed to Window Filtered Daylight Using a Xenon Arc Light Apparatus notes that two criteria which are used for assessing lightfastness are colour change, expressed instrumentally and change in optical density (ASTM, 2005).

Therefore, for the experimental part the test plates were designed to contain patches with different colours, different area coverage and were left untreated or finished with two different infiltrants. Colour change was used as a factor for discriminating the lightfastness of the prints and was calculated by using two colour difference formulae. Table 5 presents list of the abbreviations used.

**Table 5.** List of Abbreviations

<b>Label</b>	<b>Description</b>
<b>Coloured patches</b>	
C	Cyan
M	Magenta
Y	Yellow
R	Red, containing magenta, yellow inks
G	Green, containing cyan, yellow inks
B	Blue, containing cyan, magenta inks
K	Black, containing cyan, magenta, yellow inks
W	White, un-printed
<b>Finishing method</b>	
NF	Untreated
CY	Finished with cyanoacrylate based infiltrant
EX	Finished with epoxy resin based infiltrant

The experimental set up consisted of the following steps: design and construction of custom test chart and test plate, printing and finishing; initial colorimetric measurements, accelerated



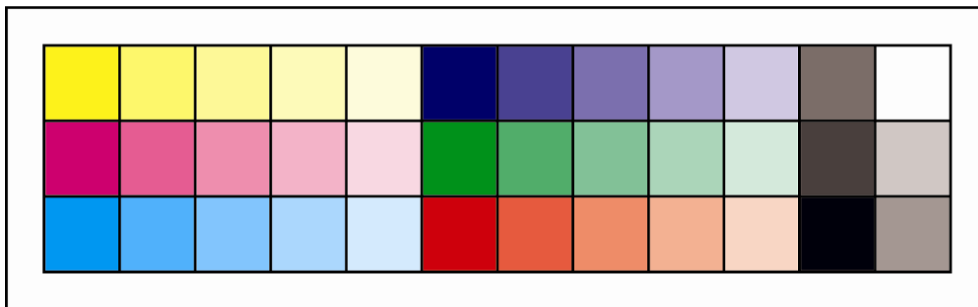
exposure of test plates in Xenotest weathering apparatus and colorimetric measurements after exposure to light; assessment of spectral data, conversion of spectral data, computing and analysis of colour differences.

## Production of Colour 3D Prints

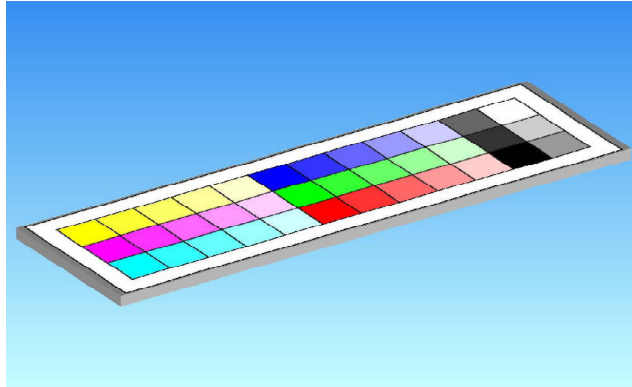
In order to observe the change in colorimetric properties of 3D prints, custom test plates were prepared. Custom test chart was constructed in Adobe Illustrator software and saved as a tiff file type. The test chart was designed to include the patches, 10 mm by 10 mm in dimension, of specific basic colours in varying range of percentage of ink coverage and in such way that only the needed colours were printed on the specific patches. In proprietary ZEdit software, test chart was placed as a texture on one of the surfaces of a 130 mm by 40 mm x 3 mm test plate, constructed in SolidWorks software. Table 6 describes the specific patches of test chart, presented in Figure 35, and Figure 36 shows the pre-view of the designed test plate, after the test chart was placed as a texture in printing and editing software ZPrint (ZEdit).

**Table 6.** Colour and percentage of area coverage of specific patches of test chart

Test plate colour patches set-up											
Y 100%	Y 80%	Y 60%	Y 40%	Y 20%	B 100%	B 80%	B 60%	B 40%	B 20%	K 60%	W
M 100%	M 80%	M 60%	M 40%	M 20%	G 100%	G 80%	G 60%	G 40%	G 20%	K 80%	K 20%
C 100%	C 80%	C 60%	C 40%	C 20%	R 100%	R 80%	R 60%	R 40%	R 20%	K 100%	K 40%



**Figure 35.** Test chart designed and used as a texture



**Figure 36.** Test plate designed for colour and stability measurements

Test plates were then printed, with printing preferences set to layer thickness 0.1 mm, 100% core and shell saturation and bleed control on. Printing was done on ZCorp. Z510 printer, using Zp131 plaster-based powder and Zb60 C, M, Y binders. Printed test plates were later removed from the printing bed and cleaned from the excess powder by air pressure and light brushing. Printed test plates were divided into three groups, depending on the finishing method, and were left untreated, finished with cyanoacrylate infiltrant or epoxy resin based infiltrant. Infiltrants used were Neostik CN105/I cyanoacrylate from Belinka Kemostik, Slovenia and two part epoxy based resin from Iridia/PPG Industries, Italy/UK, comprising of Selemix 7-410 Epoxy topcoat (2 parts) and Selemix 9-011 Fast Epoxy hardener (1 part), which were mixed at sight and stirred for 2 minutes prior to infiltration. Both Neostik infiltrant and Selemix epoxy resin based infiltrant were applied by dipping the test plates for 5 seconds in the case of Neostik infiltrant and 60 seconds for Selemix infiltrant. Finished test plates were then left to air dry until completely set.

## **Lightfastness Procedure**

Printed and finished samples were placed in test chamber Xenotest Alpha apparatus and were exposed simultaneously to a light source under specified conditions for 72 hours. The Xenochrome 320 filter system was used, simulating the solar radiation behind window glass, generally in accordance with standards ASTM F2366 – 05, ASTM D3424 – 09 and ISO 11341:2004, with selected irradiance of 42 W/m<sup>2</sup> in the range of 300-400 nm. The exposure conditions used were test Chamber Temperature – CHT = 35°C, Black Standard Temperature – BST = 50°C, RH = 35%, turning mode, number of phases = 1, duration of phases = 60 min. The colour stability to light of the samples was evaluated by colorimetric comparison, i.e. colour change of the exposed samples to the unexposed initial samples.

## Colour Measurements Methodology

Colorimetric properties of the initial and exposed colour test plates were measured using the GretagMacbeth (X-rite) XTH sphere spectrophotometer. The spectrophotometer is a device that uses the light source to illuminate the sample and records the spectral reflectance, or intensity as function of wavelength. The measuring preferences were: D65 illuminant, 10° standard observer, standard area of view (10 mm illuminated, 7 mm measured). The CIE standard D65 illuminant represents daylight at 6504 K. The spherical geometry spectrophotometer was used opposed to the 0°/45° or 45°/0° due to the relatively rough and uneven surface of 3D prints. Specific patches spectral values were compared in terms of  $\Delta L$ ,  $\Delta C(ab)$ ,  $\Delta H(ab)$ , colour shifts and colour difference,  $\Delta E$ , in X-Rite Gretag Macbeth ProfileMaker 5.0 MeasureTool software. Two colour difference formulas were used,  $\Delta E_{CMC}$  (Green and MacDonald, 2002; AATCC, 2009), with lightness and chroma weights for perceptibility measurements, and  $\Delta E_{2000}$  (Green and MacDonald, 2002; Luo *et al.*, 2000). The measured spectral data was converted in  $L^*a^*b^*$  values, with  $L^*$ ,  $a^*$  and  $b^*$  being the colour coordinates in CIELAB colour system (Ohno, 2000), where  $L^*$  denotes the lightness (from luminance) value and  $a^*$  (redness-greenness plane) and  $b^*$  (yellowness-blueness plane) denote the chromatic value of the colour (Schanda, 2007). Comparisons were done between same colours of untreated and differently finished samples, between same colours with different percentage of ink coverage for all samples and between different colours for all samples, with specific percentage of ink coverage, as well.

The stability of colour on natural aging of 3D prints was evaluated under different environmental conditions, which were chosen to reflect the potential uses and/or storage of the printed objects. The exposure was for 6 months, or precisely 25 weeks, from February to July. The conditions are listed in Table 7.

**Table 7.** Exposure conditions for natural aging in display and storage set-up

<b>Label</b>	<b>Description</b>
<b>Exposure conditions</b>	
UMLG	Display conditions, mixed natural/artificial lighting, under glass cabinet Samples were exposed in typical showroom environment, placed in glass cabinet. Light was a mixture of daylight behind window and artificial light, average low light present
UOML	Office/display conditions, mixed artificial/natural lighting, no coverage Samples were exposed to typical office/print room environment, not covered. Light was a mixture of predominantly artificial and not direct and in small amount daylight behind window light; samples were mostly exposed to light for the duration of work hours
UNSL	Display conditions, sunlight behind window, no coverage, north facing Samples were exposed to direct natural light, sunlight behind window, north facing
USSL	Display conditions, sunlight behind window, no coverage, south facing Samples were exposed to direct natural light, sunlight behind window, south facing
SE	Storage conditions, no coverage Samples were stored in basement type room, in shallow box, not covered, minimum amount of mixed light present
SS	Storage conditions, sealed Samples were stored in basement type room, in sealed padded envelope, dark storage

The environmental parameters of temperature and humidity were measured once a week, making it 25 measurement points in total, and were in showroom average  $T = 24.65\text{ }^{\circ}\text{C}$ ,  $T_{\text{max}} = 27\text{ }^{\circ}\text{C}$ ,  $T_{\text{min}} = 21.7\text{ }^{\circ}\text{C}$ ,  $\text{StDev} = 1.55$ ; average  $\text{RH} = 31.96\%$ ,  $\text{RH}_{\text{max}} = 50\%$ ,  $\text{RH}_{\text{min}} = 18\%$ ,  $\text{StDev} = 10.85$ ; in office/print room average  $T = 25.85\text{ }^{\circ}\text{C}$ ,  $T_{\text{max}} = 33\text{ }^{\circ}\text{C}$ ,  $T_{\text{min}} = 22\text{ }^{\circ}\text{C}$ ,  $\text{StDev} = 2.76$ ; average  $\text{RH} = 28.48\%$ ,  $\text{RH}_{\text{max}} = 40\%$ ,  $\text{RH}_{\text{min}} = 18\%$ ,  $\text{StDev} = 7.33$ ; in storage room average  $T = 21.96\text{ }^{\circ}\text{C}$ ,  $T_{\text{max}} = 26.3\text{ }^{\circ}\text{C}$ ,  $T_{\text{min}} = 19\text{ }^{\circ}\text{C}$ ,  $\text{StDev} = 1.71$ ; average  $\text{RH} = 37.96\%$ ,  $\text{RH}_{\text{max}} = 65\%$ ,  $\text{RH}_{\text{min}} = 19\%$ ,  $\text{StDev} = 15.11$ . The parameters for UOML and UNSL conditions were not able to be monitored, but they were both standard office room conditions.

The custom test plate that was created and used was the one also used for accelerated exposure to xenon-arc light research and is described previously. For the experimental part, two patches, 100% and 40% area coverage were monitored. The printed test plates were finished differently; one set was left untreated (marked NF), one set was finished with cyanoacrylate based infiltrant (marked CY) and one set was finished with polyurethane based infiltrant (marked PU).

The test plates were set up in ZPrint software, prepared for printing and printed on ZCorp. Z510 printer. Materials used were Zp131 plaster-based powder and Zb60 C, M, Y binders. Printing setting were layer thickness 0.1 mm, bleed control on, one group of samples 100% shell saturation and one group of samples 115% shell saturation, 100% core saturation for both groups. Samples from both groups were printed for all three types of finishing. Test plates were cleaned from the excess powder and left untreated or infiltrated accordingly. Infiltrants used were ZBond cyanoacrylate, ZCorp., USA (ZCorp., 2005) and polyurethane

based mixed Protektin, Belinka/Samson Kamnik, Slovenia (Samson Kamnik). Finished test plates were then left to air dry until completely set.

Lightfastness is usually addressed in terms of either density loss or colour changes of initial and aged or exposed samples. In this work, the stability was determined by instrumentally assessed colour change of initial and exposed samples, and it was expressed using  $\Delta E_{2000}$  colour difference formulae. The samples were measured with GretagMacbeth (X-rite) XTH sphere spectrophotometer prior and after the exposure under selected conditions. The colour measurement settings were: D65 illuminant, 10° standard observer, standard area of view (10 mm illuminated, 7 mm measured). Measured initial and exposed values were compared using X-Rite Gretag Macbeth ProfileMaker 5.0 MeasureTool software. The assessment was done on both measured spectral data and L\*a\*b\* values that were calculated in the software.

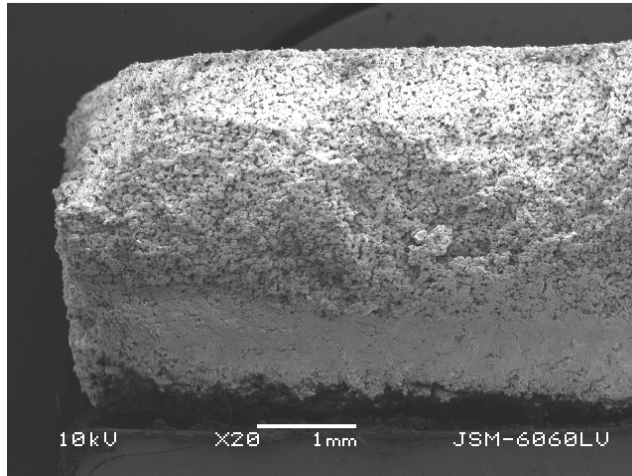
# **RESULTS AND DISCUSSION**



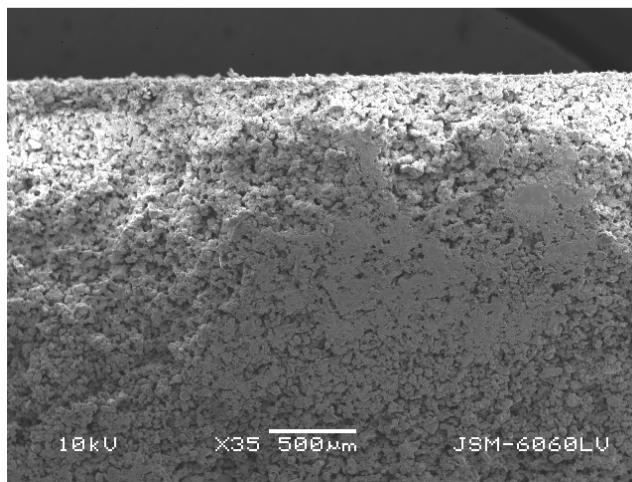
### **3D INK-JET PRINTS SURFACE AND MECHANICAL PROPERTIES – IMPACT OF INFILTRANTS AND PROCESS PREFERENCES**

#### **Mechanical Properties**

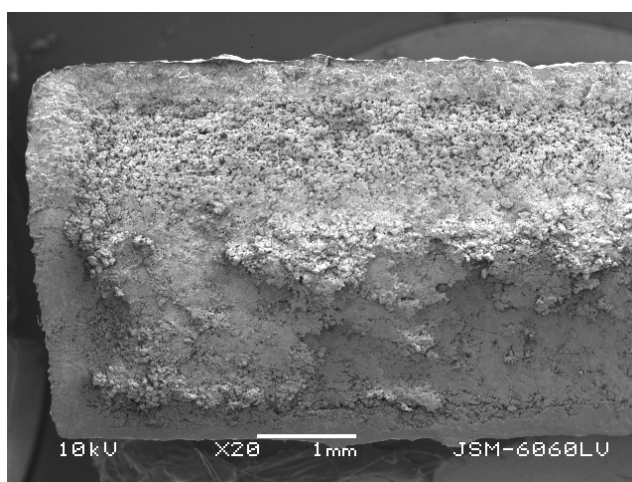
Gravimetric measurements of samples show that their weight increased for 21% after being finished with the epoxy agent, 12% with the cyanoacrylate agent, and 7% with the polyurethane agent. This variation is most probably due to the physical characteristics and penetration depth of infiltrants. The penetration depth of infiltrants and changes in appearance of prints can be seen in the cross sections of printed samples. Sections of the samples were evaluated visually, with the optical microscope and with the SEM. SEM images of NF, CY, EX and PU samples, taken at 20X and 35X magnification rates can be seen in Figure 37 to Figure 44, respectively. LM surface cross sections images of NF, CY, CY BK, EX and PU samples are presented in Figure 45 to Figure 49, respectively. The height of samples printed for mechanical properties testing was 4 mm. Epoxy infiltrant penetrates from around 5 mm up to 10 mm in depth and cyanoacrylate infiltrant from around 0.5 mm up to 3 mm (ZCorp., 2007), thus, the amount of epoxy agent absorbed is higher than of cyanoacrylate agent. The epoxy agent penetrated through the whole cross section of printed samples. Cyanoacrylate agent penetrates up to a certain depth in a matter of seconds and further penetration is thereby made impossible. Depth of infiltration is dependent on variables and conditions in printing and postprinting stages; for instance, on baking/drying the prints prior to infiltration. An example of this can be seen in Figure 46 and Figure 47, which depict the difference in penetration depth of CY and CY BK samples. Approximate penetration depth, calculated by image analysis from figures, of CY sample is 0.42 mm and of CY BK sample is 0.57 mm. Polyurethane-based infiltrant penetrated through the whole cross section of samples, but due to the fact that a high percentage of it evaporates during the hardening stage, the increase in weight is smaller than for the other two infiltrants. From the gravimetric measurements of the samples, it was observed that the samples finished with the epoxy infiltrant vary the most in weight and that the amount of the infiltrant absorbed increases with the weight of the initial sample.



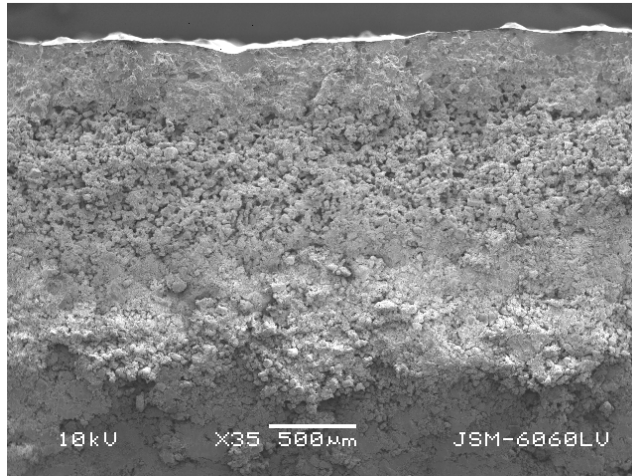
**Figure 37.** SEM image of NF sample cross section (20X)



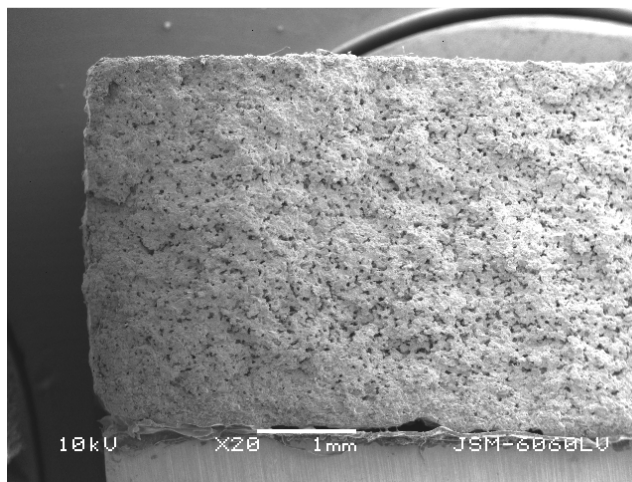
**Figure 38.** SEM image of NF sample cross section (35X)



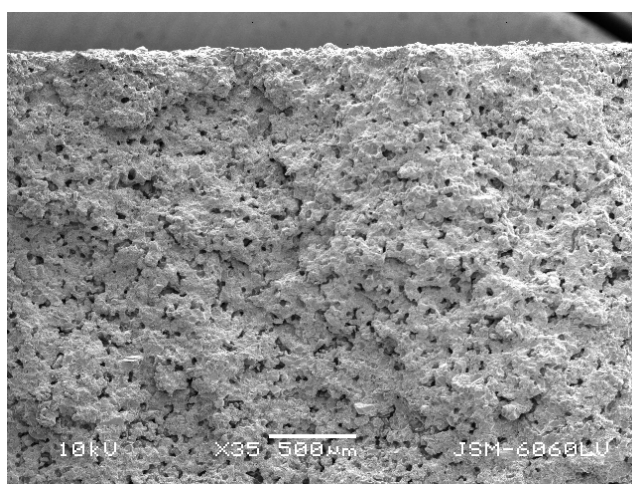
**Figure 39.** SEM image of CY sample cross section (20X)



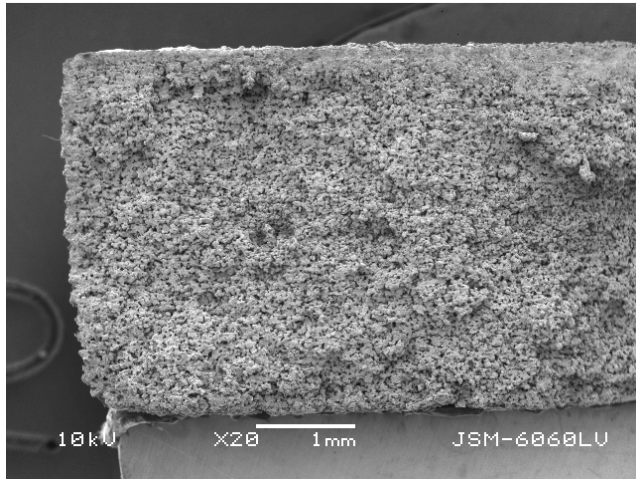
**Figure 40.** SEM image of CY sample cross section (35X)



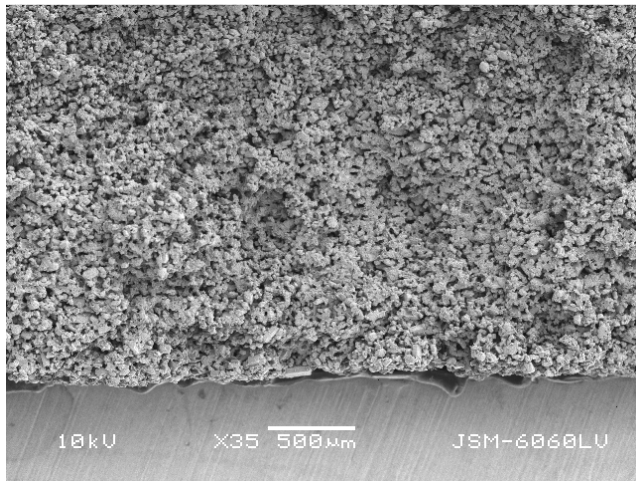
**Figure 41.** SEM image of EX sample cross section (20X)



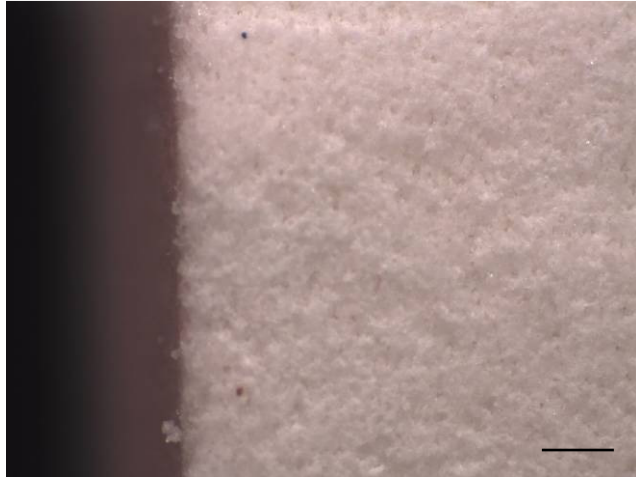
**Figure 42.** SEM image of EX sample cross section (35X)



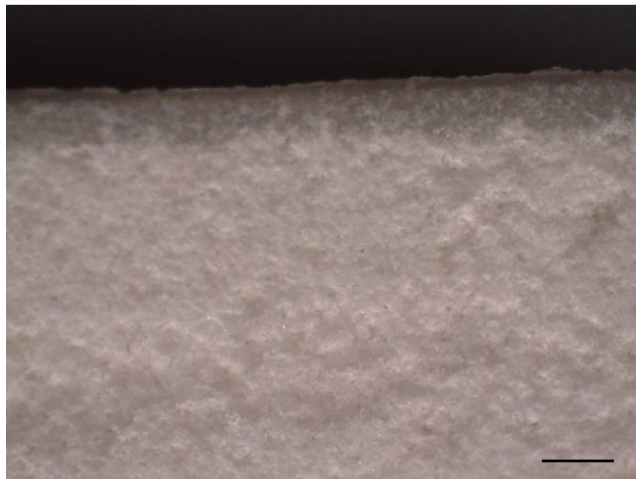
**Figure 43.** SEM image of PU sample cross section (20X)



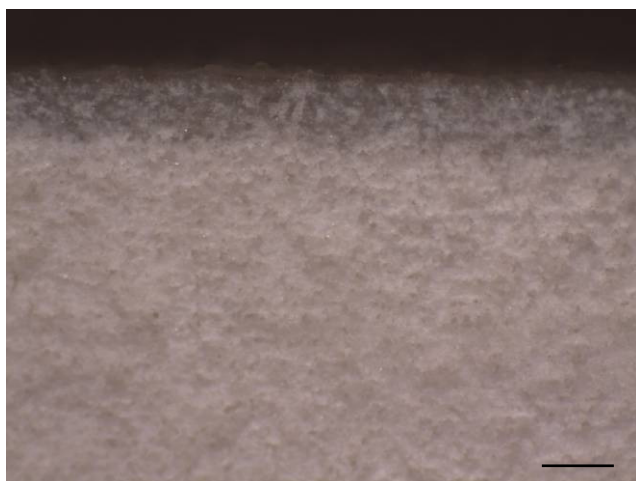
**Figure 44.** SEM image of PU sample cross section (35X)



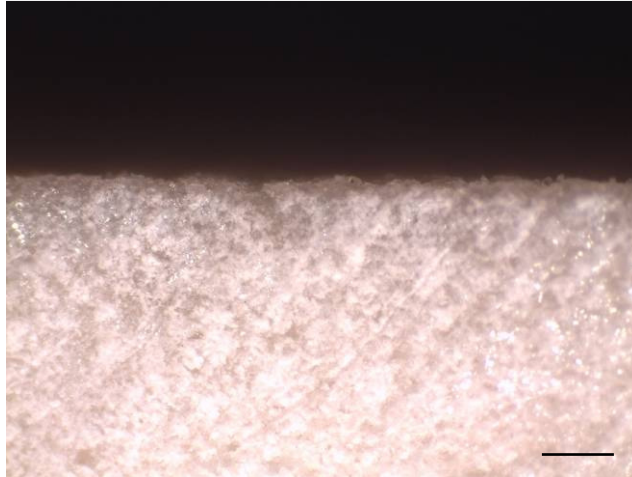
**Figure 45.** Optical microscope image of NF sample surface cross section (25X), bar denotes 0.5 mm



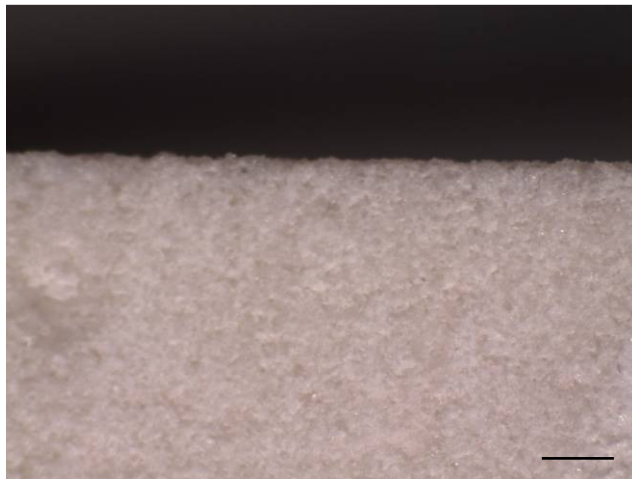
**Figure 46.** Optical microscope image of CY sample surface cross section (25X), bar denotes 0.5 mm



**Figure 47.** Optical microscope image of CY BK sample surface cross section (25X), bar denotes 0.5 mm



**Figure 48.** Optical microscope image of EX sample surface cross section (25X), bar denotes 0.5 mm



**Figure 49.** Optical microscope image of PU sample surface cross section (25X), bar denotes 0.5 mm

Figure 50 shows that the EX sample endures the highest force before breaking into two pieces, followed by the CY sample, PU sample, and NF sample, respectively. When comparing NF sample with the corresponding finished samples, finishing by epoxy agents improves tensile strength 5.23 times, by the cyanoacrylate agent 2.77 times, and by the polyurethane agent 2.32 times. It is presumed that the various printing preferences such as colour or direction of printing may have an effect on the finished sample tensile characteristics. The CY samples were divided in four groups of samples, according to different printing and finishing preferences. The CY sample, which was baked as prescribed by the manufacturer of the material and then finished with the agent, show the highest tensile strength among the CY group of samples. The improvement in strength is 1.28 times when comparing CY BK and CY sample. CY X sample compared to CY sample shows a small degradation in tensile properties by 5.98%, which is consistent with the expectation that

poorer mechanical properties of untreated samples printed in x-y versus y-x direction are almost completely obscured when the samples are finished by the infiltrant. The CY COL, on the other hand, was printed in y-x direction of printing, as was the CY sample, but its measurement result showed 6.52% degradation. This is possibly related to the fact that the sample was printed in colour.

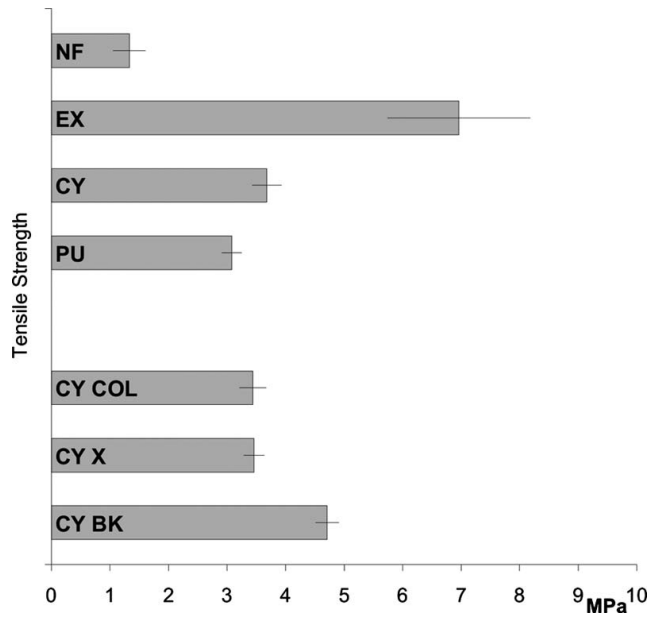


Figure 50. Tensile strength plot

The plot of the results for impact properties of samples is shown in Figure 51. Again, EX samples showed the highest impact strength and were followed by the CY samples, PU samples, and NF samples, respectively. The finishing by the epoxy agent increases impact strength 3.86 times, by the cyanoacrylate agent 2.22 times, and by polyurethane agent 1.65 times when compared to the NF sample measurement result.

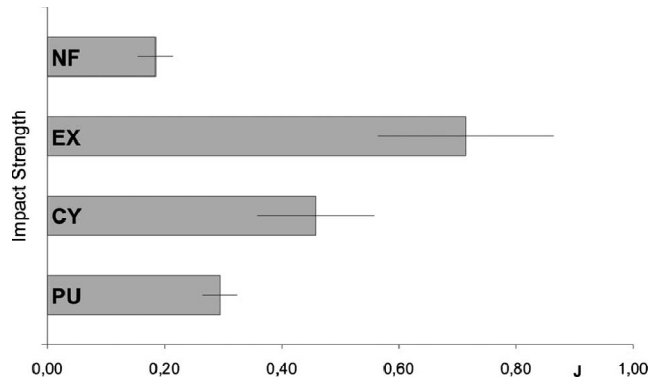
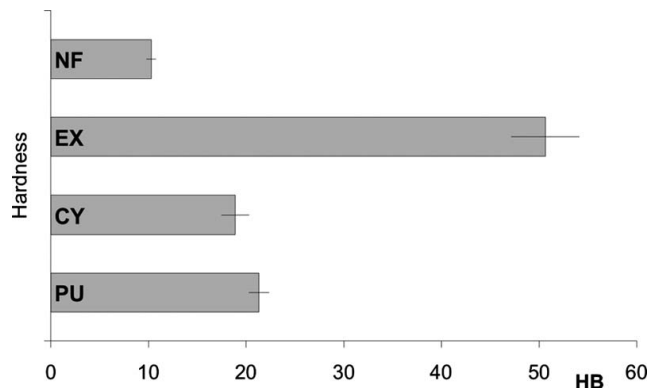


Figure 51. Impact strength plot

Figure 52 shows the plot for the results of Brinell hardness measurements. The EX sample shows the highest hardness, followed by PU, CY, and NF sample in descending order. When comparing the hardness measurements of the NF sample with the finished samples, the finishing of the original sample by the epoxy agent improved hardness 5.2 times, by the polyurethane agent 2.06 times, and by the cyanoacrylate agent 1.86 times.

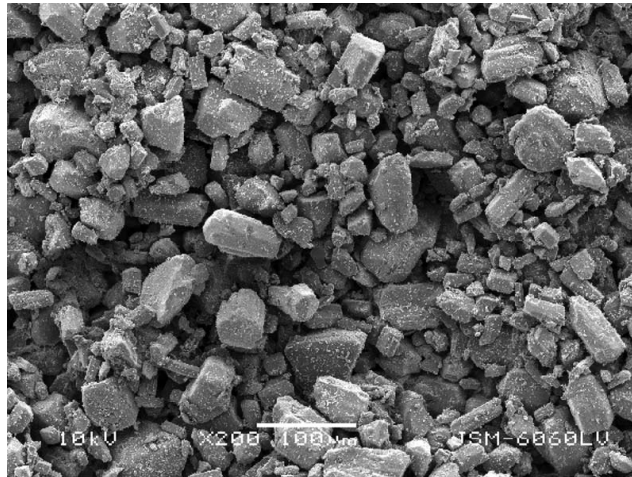


**Figure 52.** Brinell hardness plot

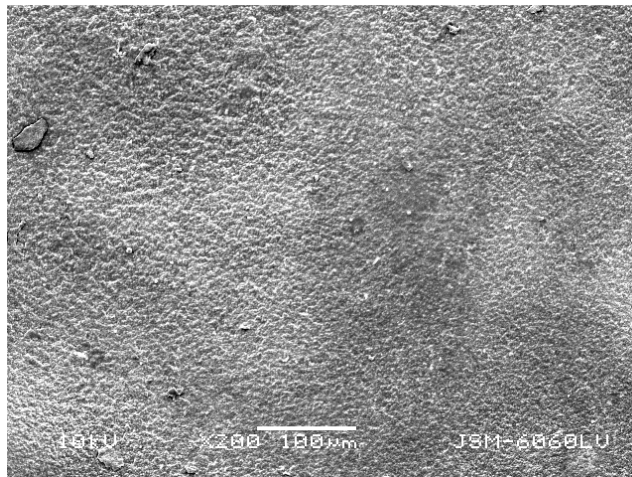


## Surface Properties

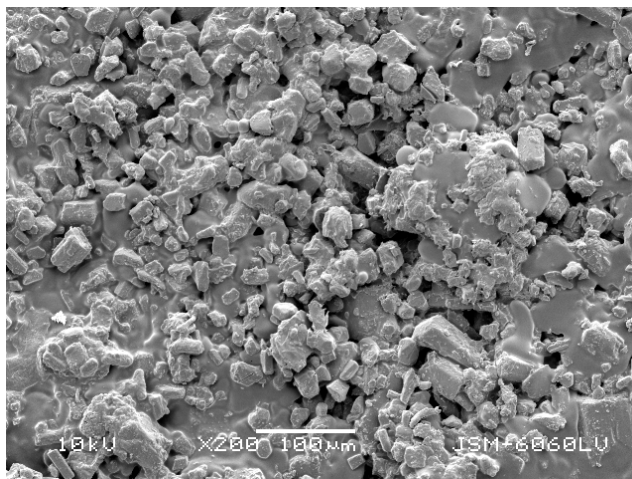
Samples surface acquired by SEM, at 200X magnification are shown in Figure 53 to Figure 57. Figure 56 shows an example of difference between surfaces of EX samples on parts of surface that were filled in with infiltrant, as it was previously discussed and are due to the characteristics of epoxy infiltrant.



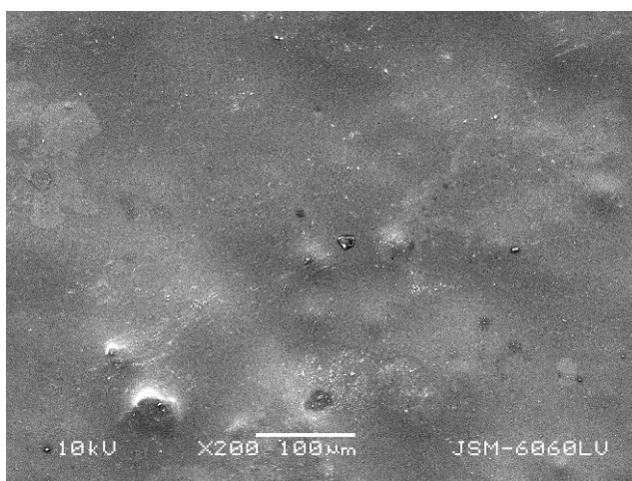
**Figure 53.** SEM image of NF sample surface (200X)



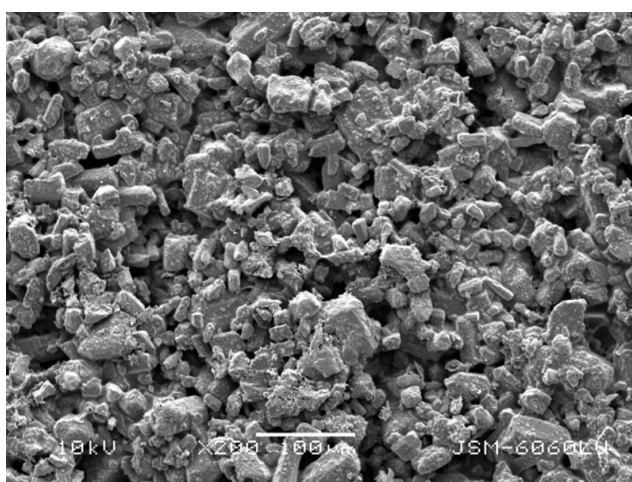
**Figure 54.** SEM image of CY sample surface (200X)



**Figure 55.** SEM image of EX sample surface (200X)

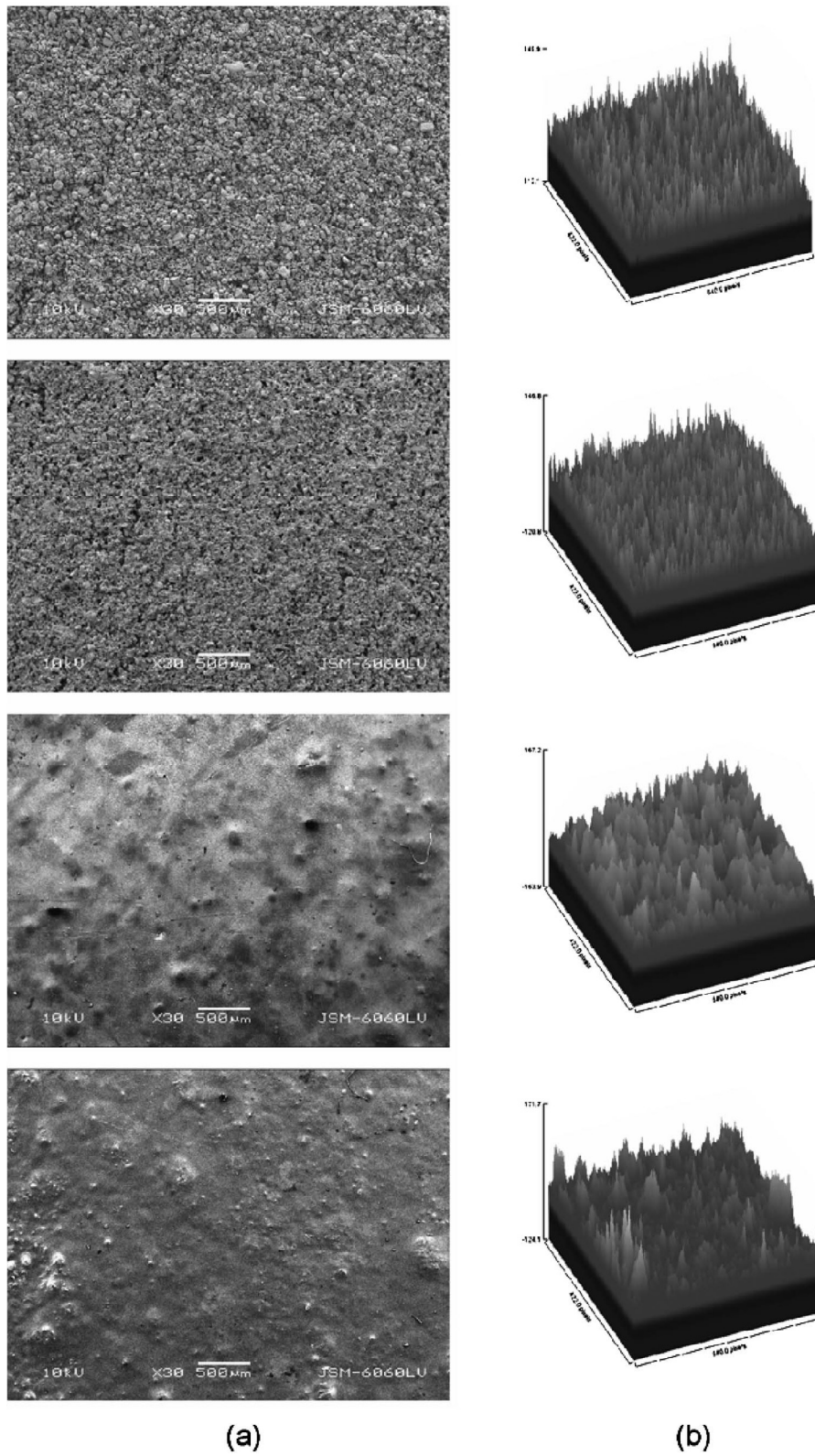


**Figure 56.** SEM image of EX sample surface (200X), example of filled in surface



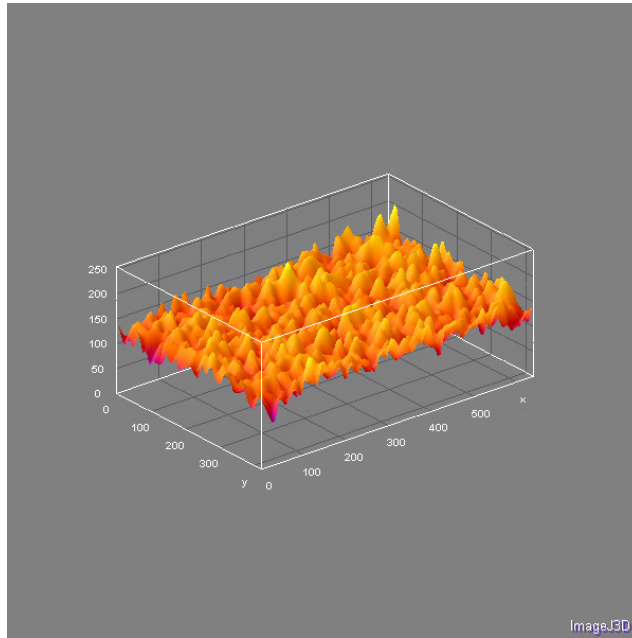
**Figure 57.** SEM image of PU sample surface (200X)

Surface of prints was evaluated visually, with the optical microscope and with the SEM. Lower magnification SEM images of all the samples, Figure 58(a), were used for visualization of differences in surface structure among differently finished samples. Observations of the surface of the samples show noticeable differences among both unfinished versus finished samples, as well as between samples finished by different infiltrants. Finishing with the cyanoacrylate and epoxy agents produces prints with generally smoother surfaces. As the cyanoacrylate agent bonds in seconds and the penetration of the infiltrant is stopped after a certain depth is reached, the surface of prints is smoothed by the hardened agent that does not penetrate further. This leaves a more uniform surface, but very fine structures could be filled and possibly blocked. As for the epoxy finished samples, it was observed that they can have traces of the leftover epoxy agent on some areas of the surface. A small amount of infiltrant sometimes does not penetrate completely but remains on the surface and, thus, has a slight influence on the dimensional stability of the prints. This effect can be controlled to a point by careful and more time consuming infiltration process, e.g., by carefully brushing layer after layer of the infiltrant agent onto the surface of the print. As the previous layer is absorbed, another layer is applied and the procedure is continued until the prints cannot absorb any more infiltrant. Surfaces of the samples finished with the polyurethane-based agent resemble more the surfaces of the unfinished samples, and individual powder particles, although coated in infiltrant, can be distinguished. The SEM images of NF, EX, CY, and PU samples surface, Figure 58(a), show the effect of different infiltrants on surface. In surface SEM image of the NF sample, individual powder particles are clearly seen. The PU sample shows a surface similar in structure to the NF sample, but the effect of infiltration is somewhat visible and contributes to a smoother surface characteristic. In the CY and EX samples, the high level of infiltrant on the surface of the prints is visible. The individual powder particles are for the most part not seen as they are covered with the infiltrant, and larger structures are noticed. To aid the visualization of differentiation among infiltrated samples surfaces, surface plot views of samples are shown in Figure 58(b). They represent the SEM images from Figure 58(a), with the z-axis of the graph corresponding to the gray value of a pixel.

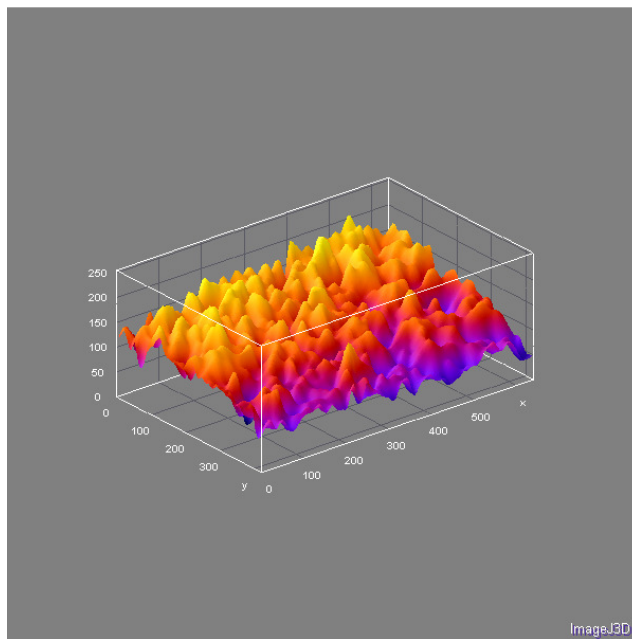


**Figure 58.** (a) SEM images of samples NF, PU, CY, EX; from top to bottom image, respectively (30X); (b) surface plots of samples NF, PU, CY, EX; from top to bottom image, respectively

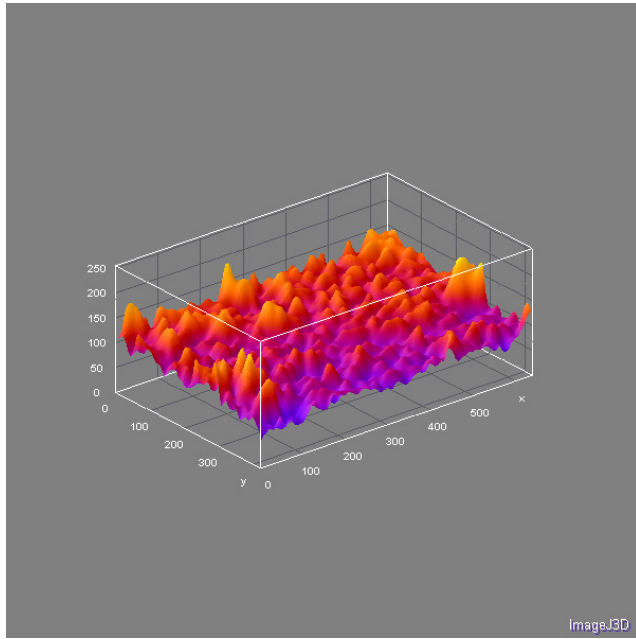
Samples surface plots visualized by ImageJ 3D Surface Plot plugin are shown in Figure 59 to Figure 62.



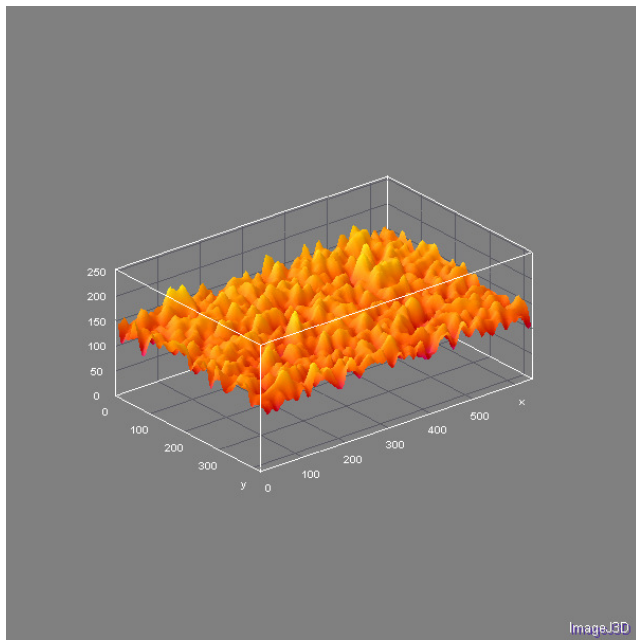
**Figure 59.** Surface plots of sample NF



**Figure 60.** Surface plots of sample CY



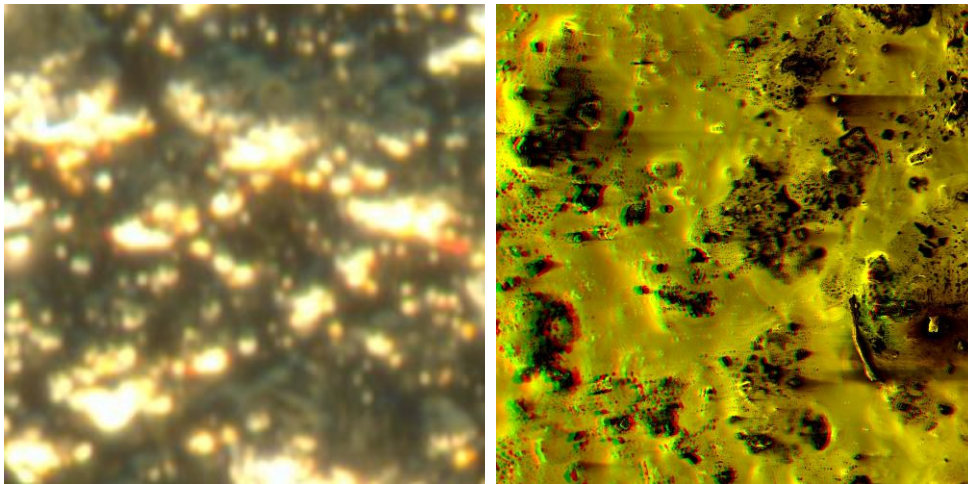
**Figure 61.** Surface plots of sample EX



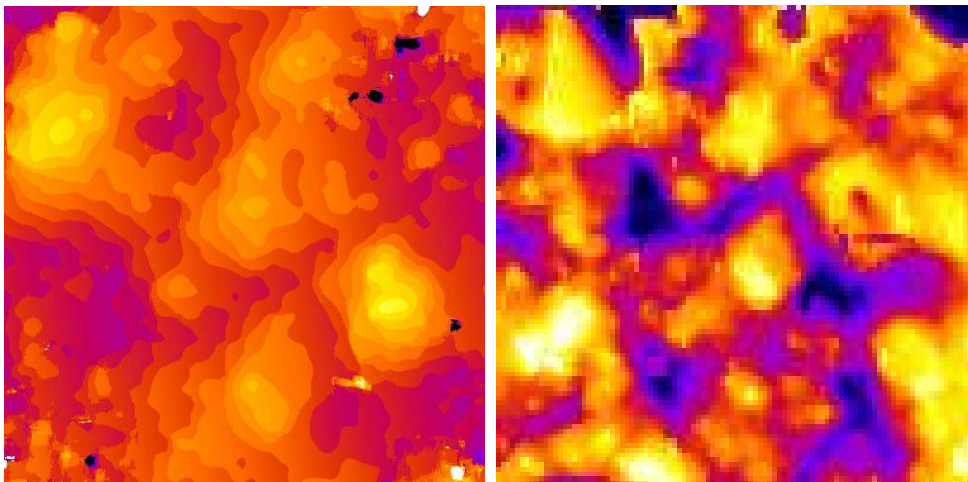
**Figure 62.** Surface plots of sample PU

## Surface Roughness

The surfaces of any material can be assessed with several methods. The suitability of a given surface assessment method for characterising a given material depends on i) the z-direction sensitivity of the applied instrument, ii) the size of the assessed area and iii) the required lateral resolution. In this study several surface assessment methods were applied for verifying the appropriateness of each method and for revealing the corresponding advantages and disadvantages. Fig. XX presents example images of the same surface as described by desktop scanners, scanning electron microscopy and laser profilometry.

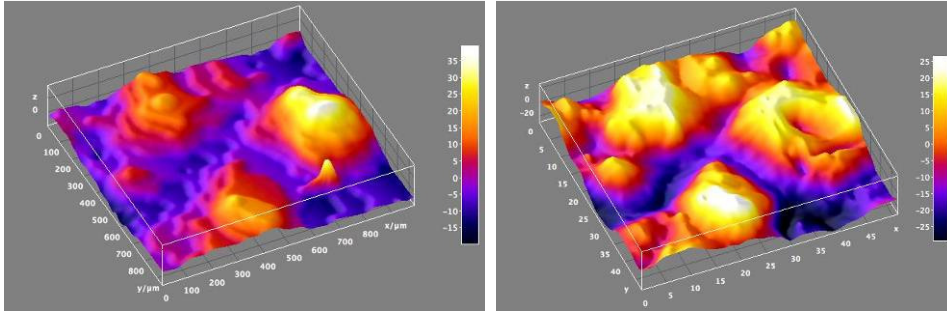


**Figure 63.** Scanner (left), SEM Stereo (right)



**Figure 64.** SEM Stereo, height map (left), Laser profilometry (right)

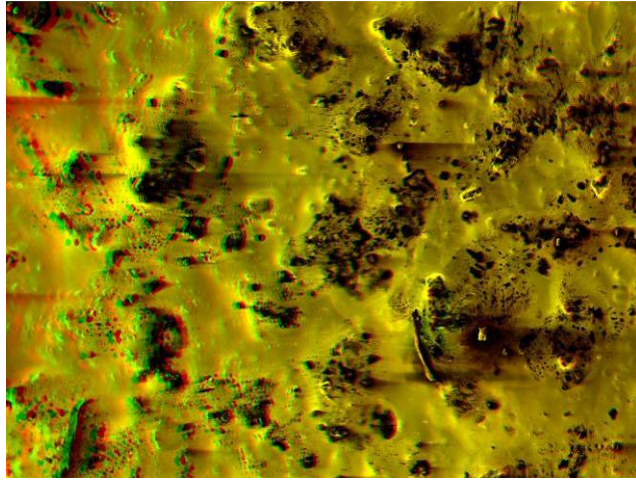




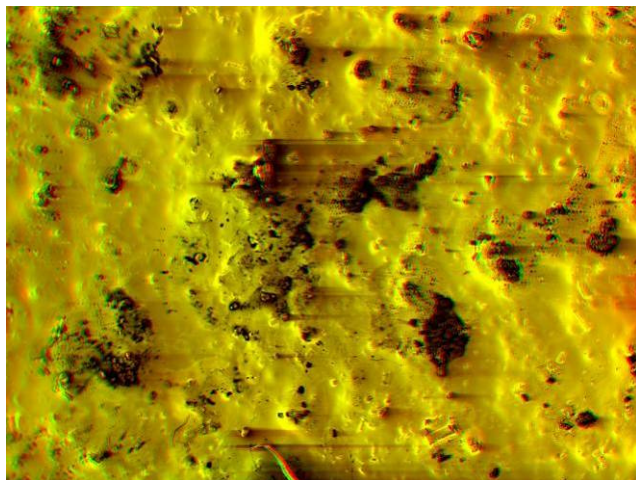
**Figure 65.** Surface plots from the same areas as measured on the SEM stereo images (left) and laser profilometry (right)



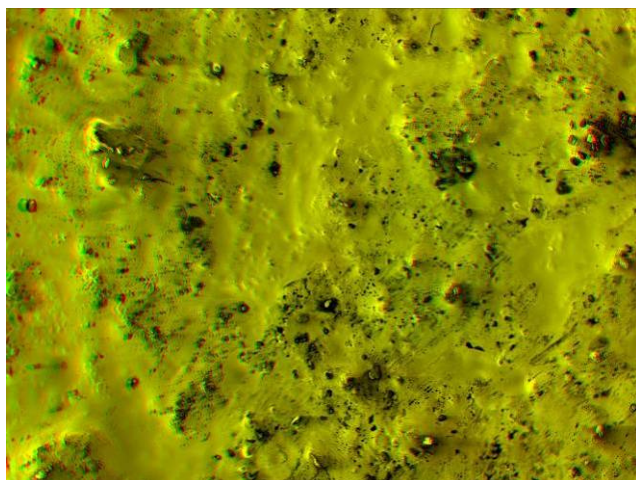
Samples surface acquired by stereo SEM procedure are presented in Figure 66 to Figure 97.



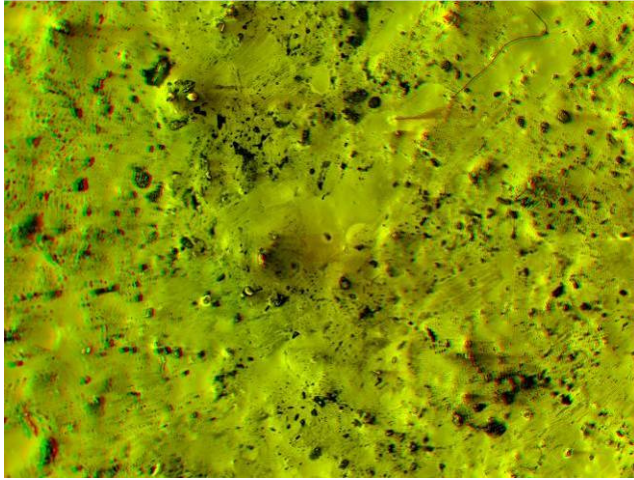
**Figure 66.** Stereo SEM image of ZB1\_01



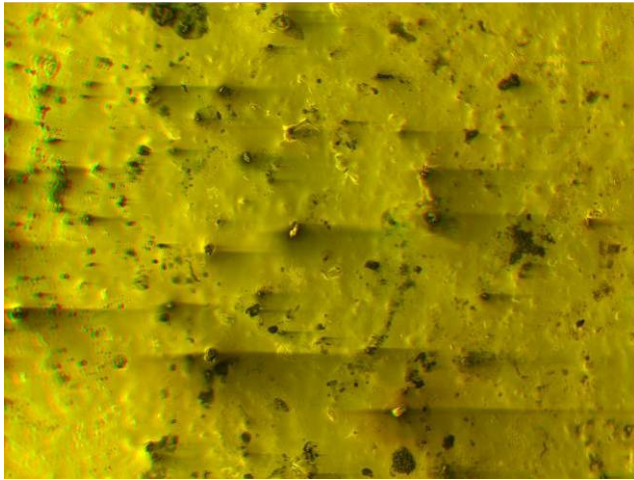
**Figure 67.** Stereo SEM image of ZB1\_02



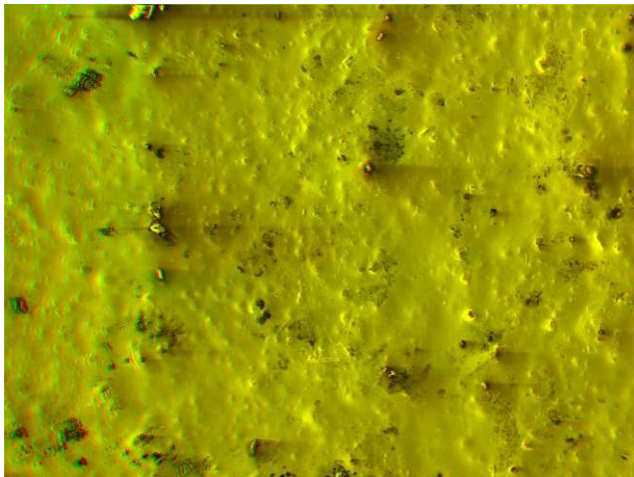
**Figure 68.** Stereo SEM image of ZB2\_01



**Figure 69.** Stereo SEM image of ZB2\_02

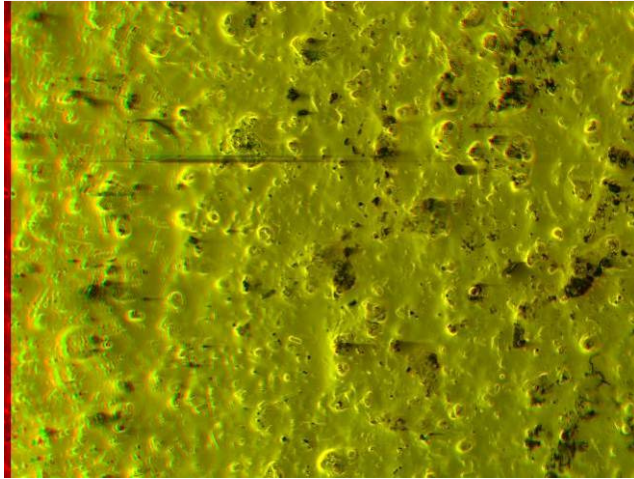


**Figure 70.** Stereo SEM image of ZB3\_01

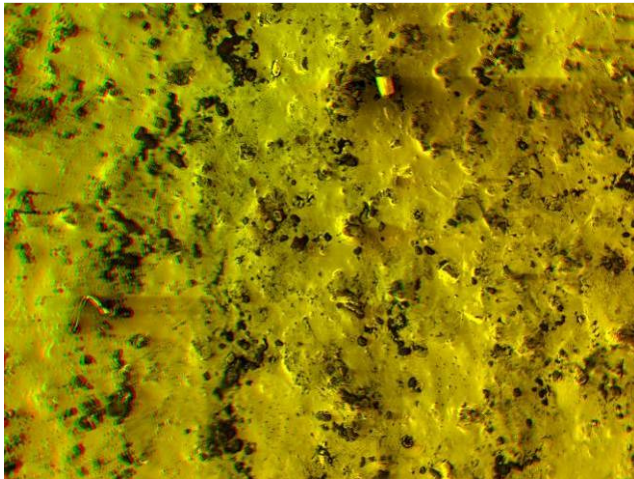


**Figure 71.** Stereo SEM image of ZB3\_02

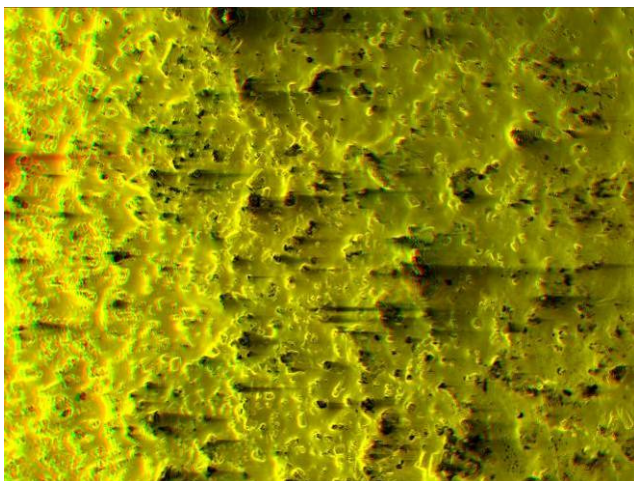




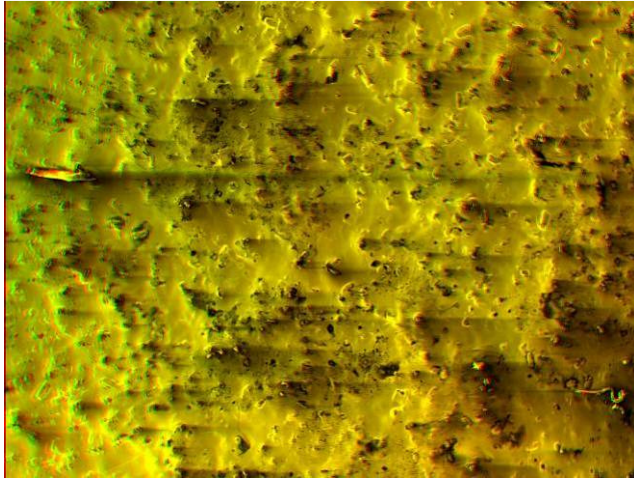
**Figure 72.** Stereo SEM image of ZB4\_01



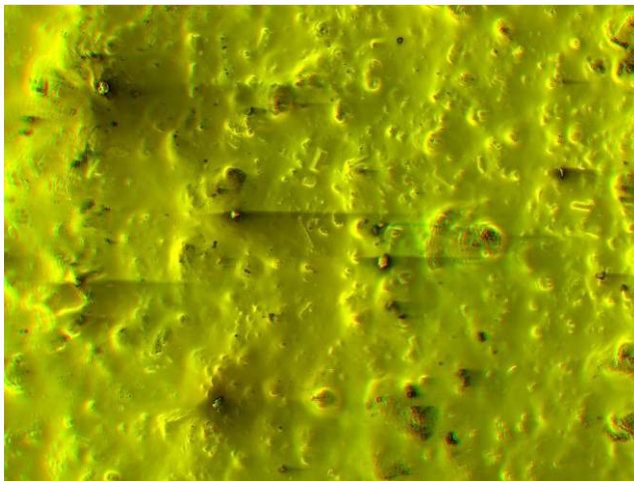
**Figure 73.** Stereo SEM image of ZB4\_02



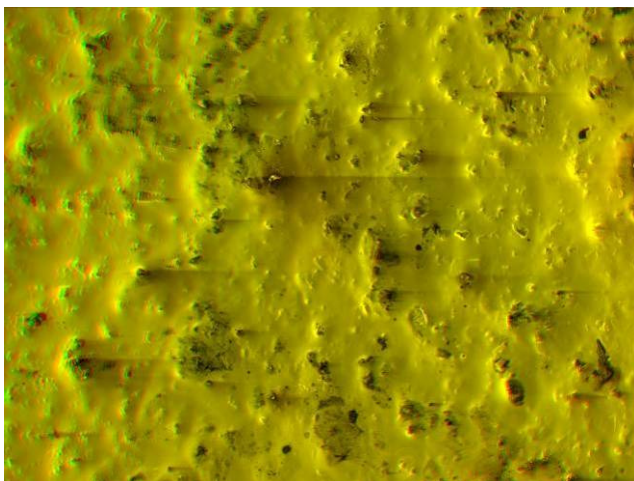
**Figure 74.** Stereo SEM image of ZB5\_01



**Figure 75.** Stereo SEM image of ZB5\_02

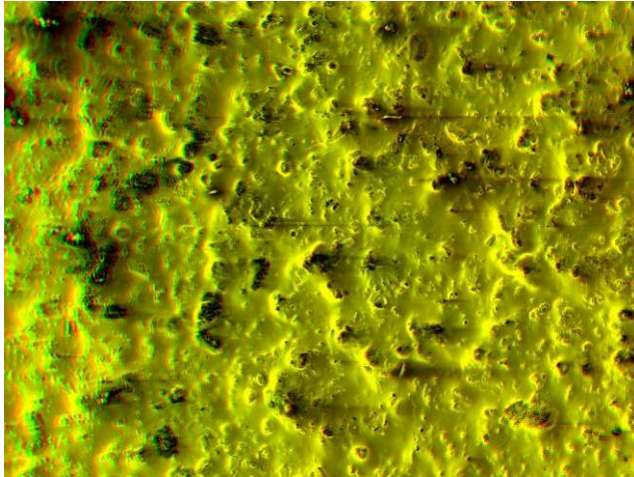


**Figure 76.** Stereo SEM image of ZB6\_01

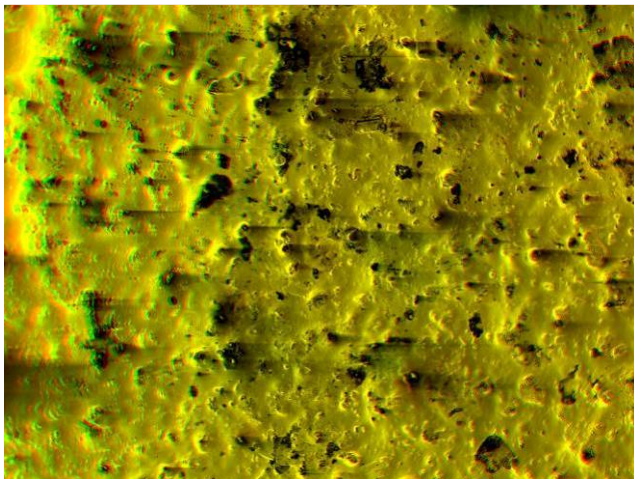


**Figure 77.** Stereo SEM image of ZB6\_02

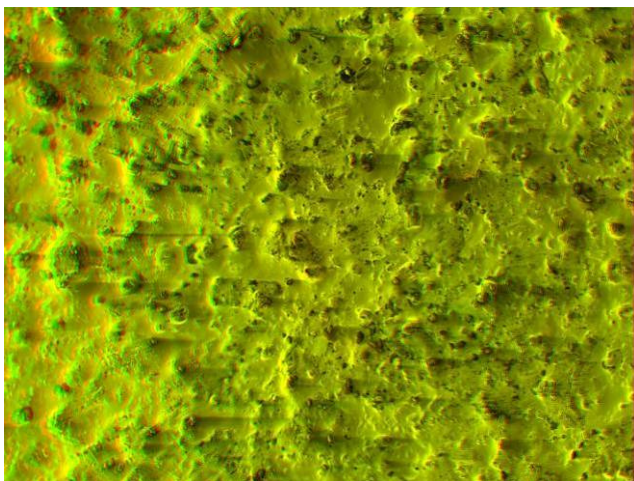




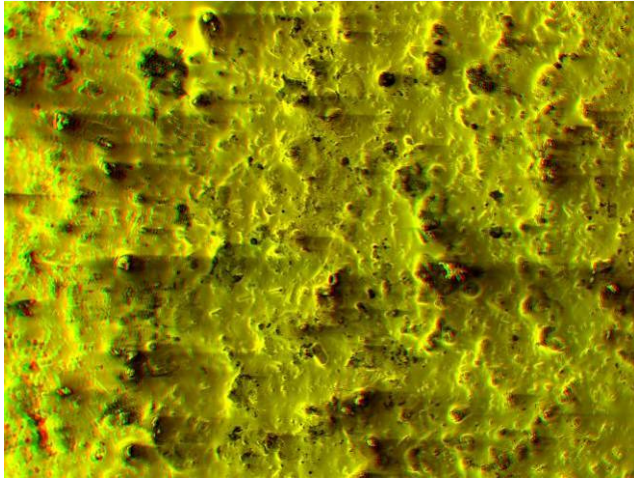
**Figure 78.** Stereo SEM image of ZB7\_01



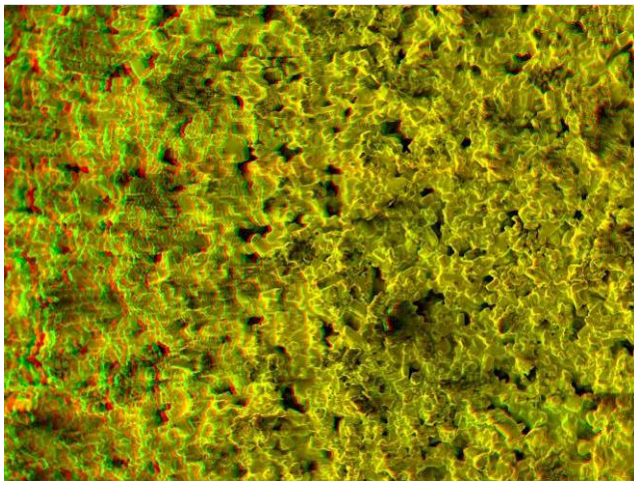
**Figure 79.** Stereo SEM image of ZB7\_02



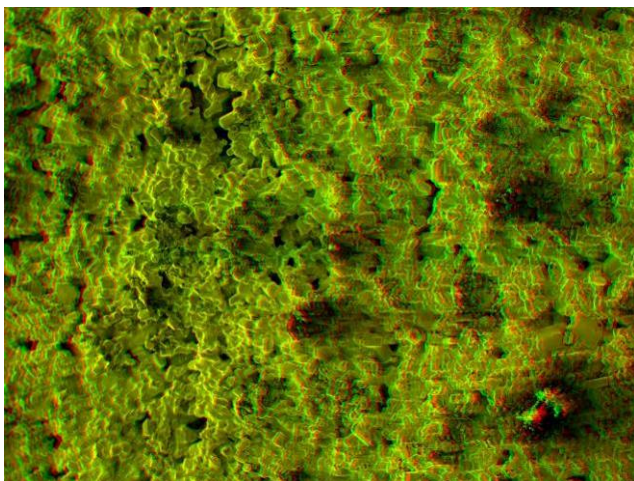
**Figure 80.** Stereo SEM image of ZB8\_01



**Figure 81.** Stereo SEM image of ZB8\_02

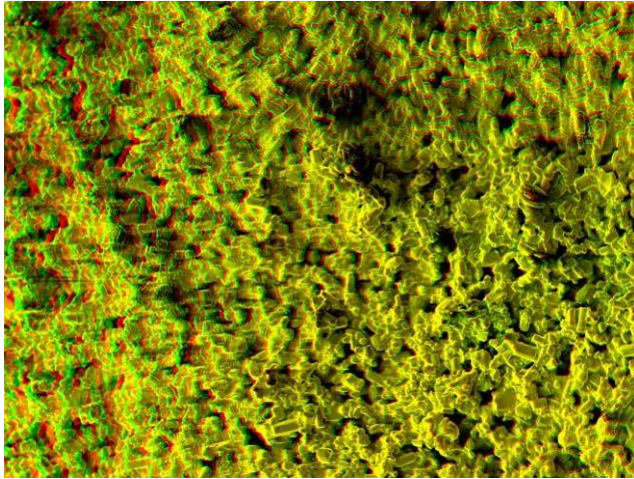


**Figure 82.** Stereo SEM image of BB1\_01

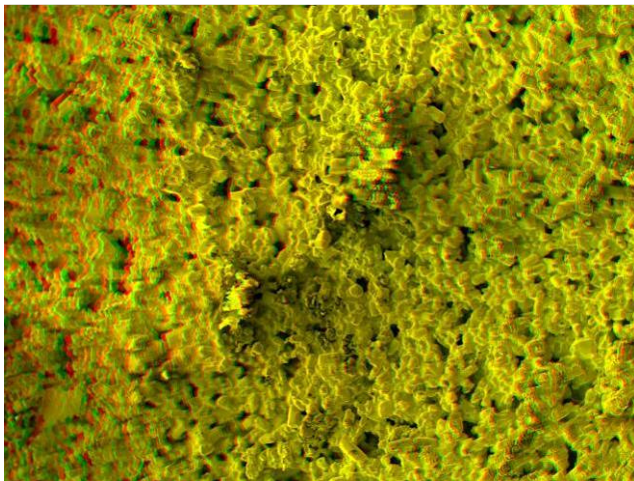


**Figure 83.** Stereo SEM image of BB1\_02

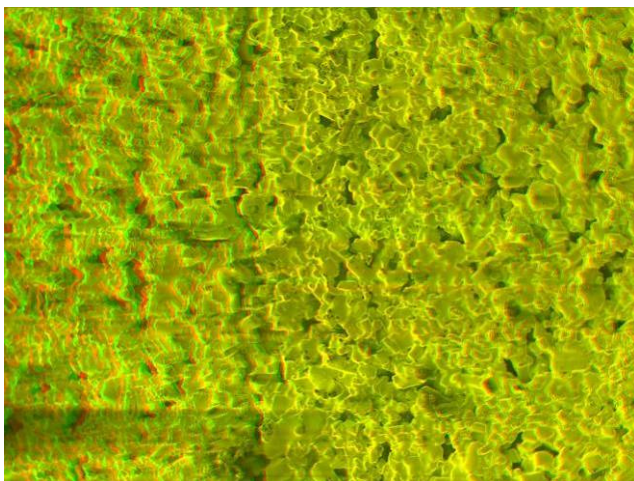




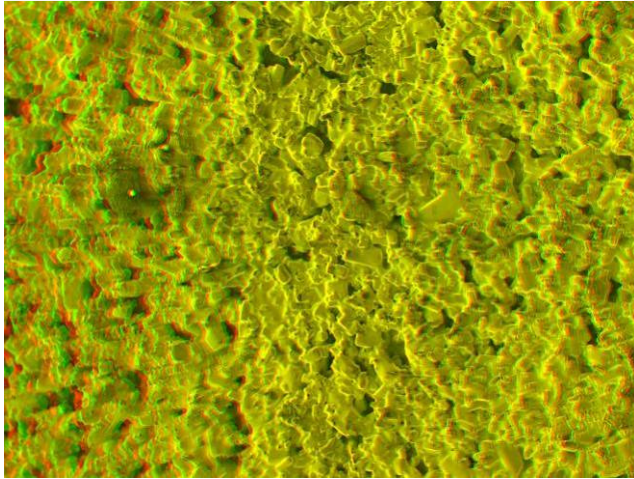
**Figure 84.** Stereo SEM image of BB2\_01



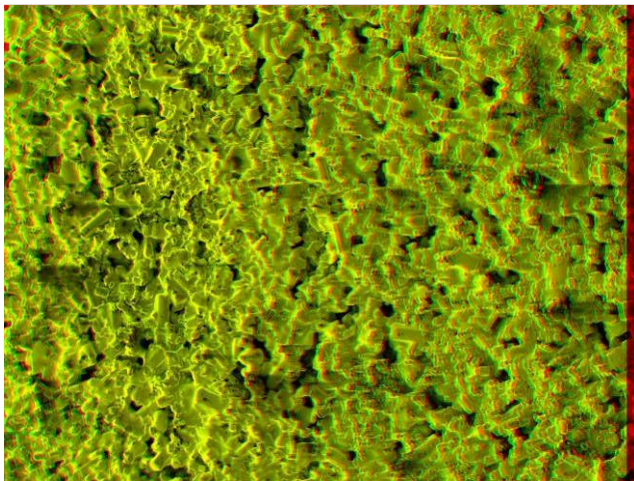
**Figure 85.** Stereo SEM image of BB2\_02



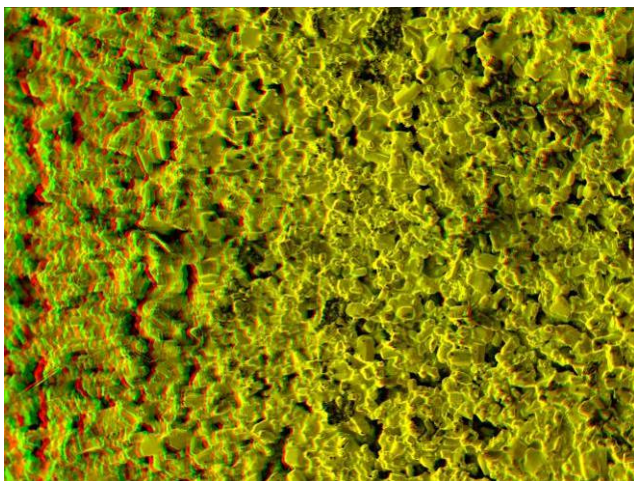
**Figure 86.** Stereo SEM image of BB3\_01



**Figure 87.** Stereo SEM image of BB3\_02

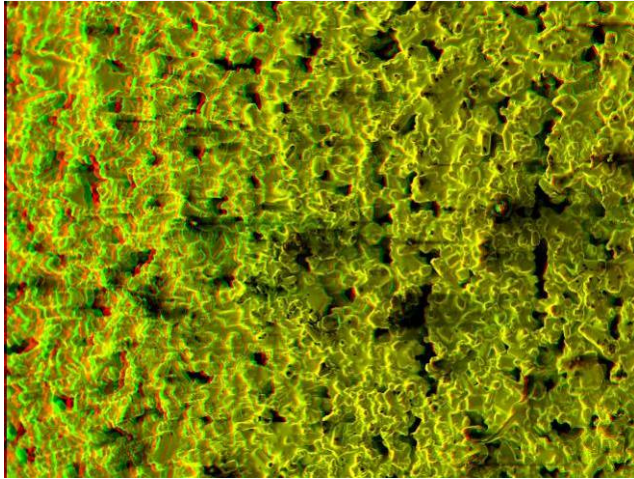


**Figure 88.** Stereo SEM image of BB4\_01

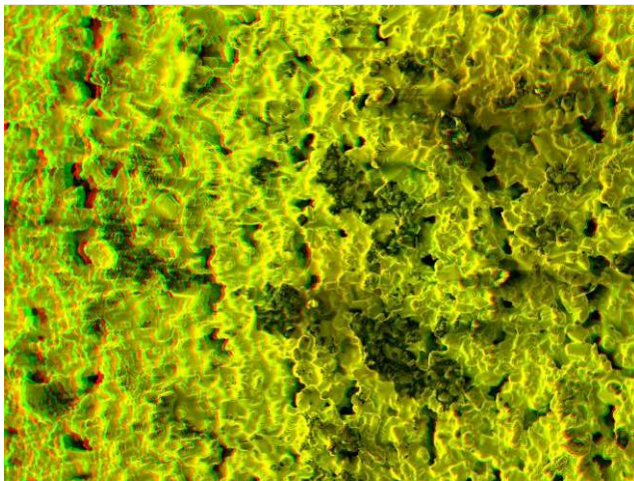


**Figure 89.** Stereo SEM image of BB4\_02

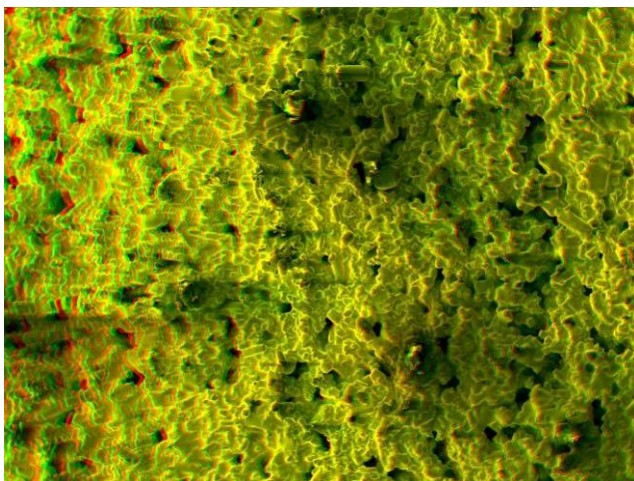




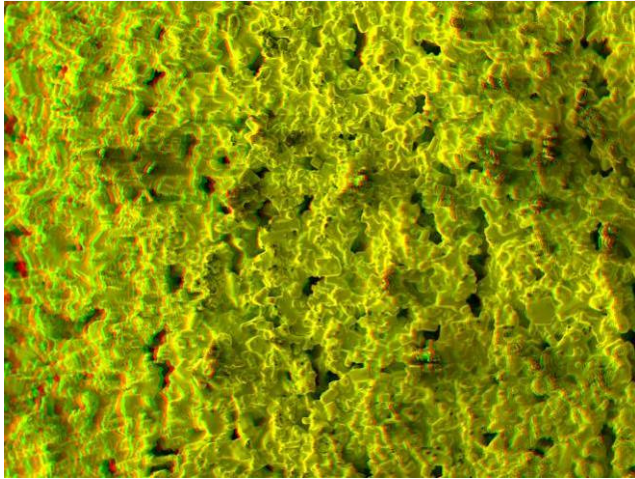
**Figure 90.** Stereo SEM image of BB5\_01



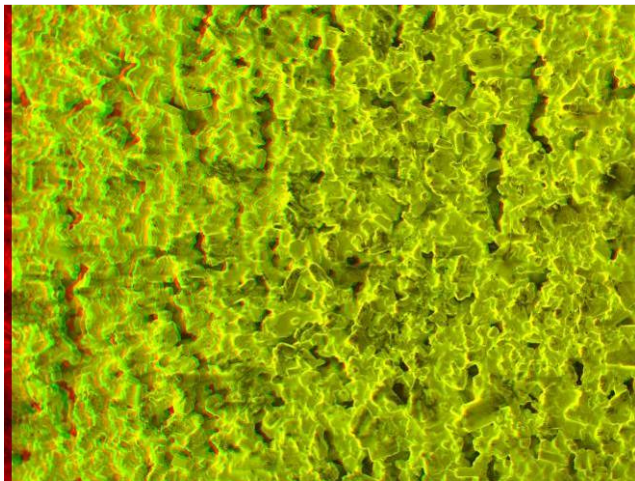
**Figure 91.** Stereo SEM image of BB5\_02



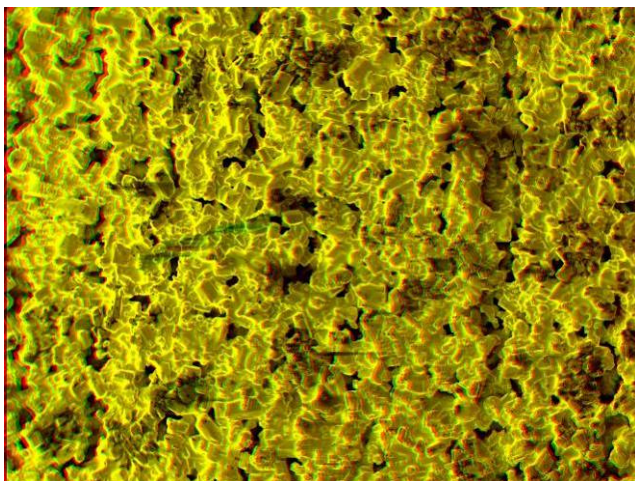
**Figure 92.** Stereo SEM image of BB6\_01



**Figure 93.** Stereo SEM image of BB6\_02

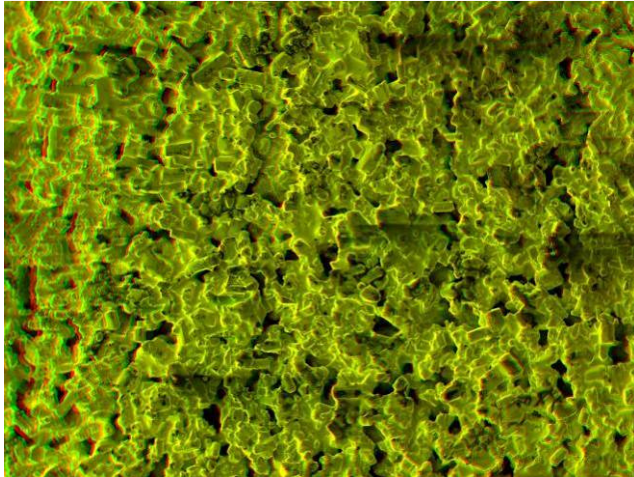


**Figure 94.** Stereo SEM image of BB7\_01

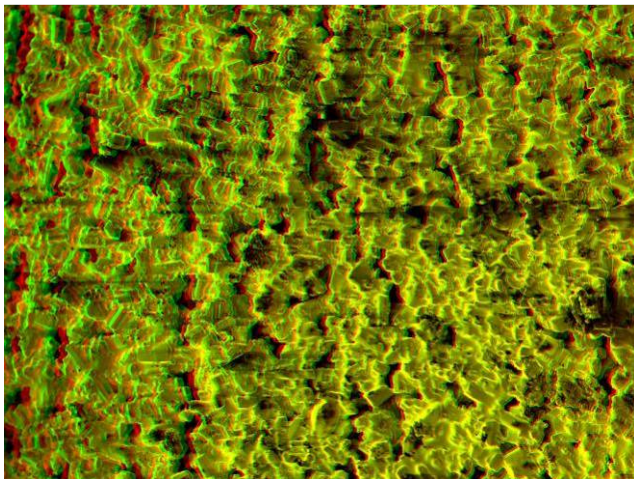


**Figure 95.** Stereo SEM image of BB7\_02





**Figure 96.** Stereo SEM image of BB8\_01



**Figure 97.** Stereo SEM image of BB8\_02

## **REPRODUCTION IN 3D INK-JET PRINTING**

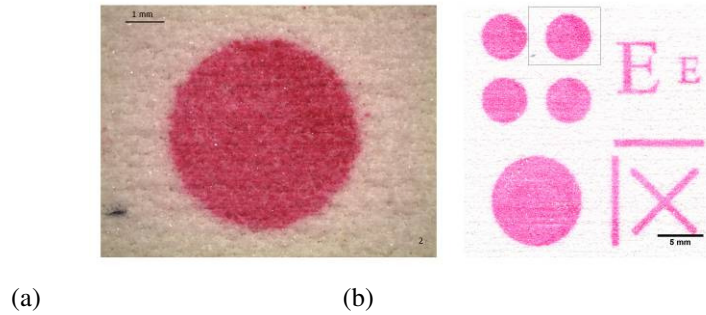
### **Example 1**

#### **Image Analysis**

The objective evaluation by image analysis depends on obtained images reliable quantitative data (Miriello and Crisci, 2006). The issues in application of image analysis for print reproduction in 3D printing mostly arise from the structures of 3D prints surfaces. When compared to evaluation of ink-jet prints on substrates such as papers, the surface of 3D prints is much rougher and uneven, due to the “substrate” material being in the shape of powder. This causes problems in segmentation of the images, especially the ones captured from microscope, as selection of adequate threshold value at which the pixels belonging to the ROI are clearly separated from the background is, in some cases, difficult. The structures in surfaces caused from unbound powder, visible layers, cracks etc. that are in the proximity of the printed areas can cause difficulties during segmentation, both by gray-scale or colour histogram thresholding. The histogram thresholding does not take into account the spatial details and can be difficult to perform on images without distinctive histogram peaks and valleys (Bergman *et al.*, 2005). The selection of different threshold values that are next to each other for the same image can cause differences in the results of obtained thresholded images of e.g. perimeter, and therefore circularity, values and makes development of automated segmentation procedures possibly challenging.

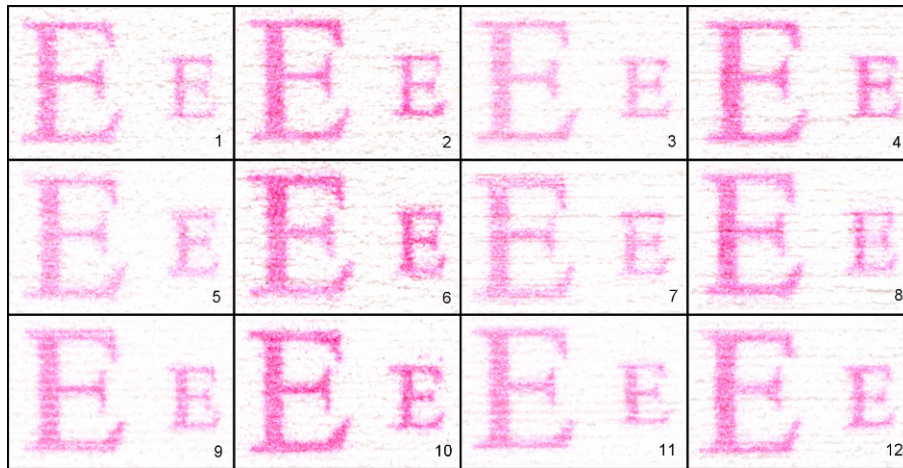
## Analysis of Reproduction

Figure 98 shows the sample element from the first group of samples printed in different positions in the xyz space. The microscope capture is shown on the left and the same area is marked on the scanned image on the right.



**Figure 98.** Images showing the sample element, 5 mm circle, captured by microscope (a) and the same area marked on the scanned image of the test plate surface (b)

Figure 99 shows the 12 pt “E” character reproduction on the samples printed in different relative position in xyz space. The differences in reproduction of characters depending on the position of the surface can be visually observed. Note the differences in, for example, characters reproduction on samples 1 and 2, which have been placed in the same x-z position, but with a different position relative to the application of the binder; sample 2 was placed first relative to the application of binder and sample marked 1 on the end of the binder application. Further, the differences in characters reproduction between samples placed in the same position relative to the direction of powder and binder application (samples 1, 5 and 9; 2, 6 and 10; 3, 7 and 11; 4, 8 and 12) but inclined at different angles, 0°, 45°, 75° respectively, can also be observed.



**Figure 99.** Reproduction of character “E”, from the first group of samples, printed in different relative xyz positions in the print bed, scanned images, sample num marked in the bottom right corner

Table 8 shows the results of image analysis of sample element characteristics, 5 mm circle for samples printed in different relative xyz positions in the print bed.

**Table 8.** Results of image analysis, sample element characteristics, 5 mm circle, samples printed in different relative xyz positions

Label	Total Area (mm <sup>2</sup> )	Perimeter (mm)	Circularity	Feret (mm)	Major (mm)	Minor (mm)
1	18.20	34.53	0.19	5.15	4.85	4.77
2	18.12	33.50	0.20	5.07	4.82	4.79
3	18.76	36.08	0.18	5.44	4.94	4.83
4	17.99	26.61	0.32	5.18	4.82	4.75
5	18.98	44.41	0.12	5.40	4.94	4.89
6	19.31	34.80	0.20	5.28	5.05	4.87
7	19.04	39.62	0.15	5.26	5.01	4.84
8	19.63	39.78	0.16	5.30	5.12	4.88
9	18.14	33.76	0.20	5.10	4.84	4.77
10	17.87	29.09	0.27	5.03	4.78	4.76
11	19.03	35.54	0.19	5.26	4.94	4.90
12	19.03	31.27	0.24	5.14	4.95	4.90

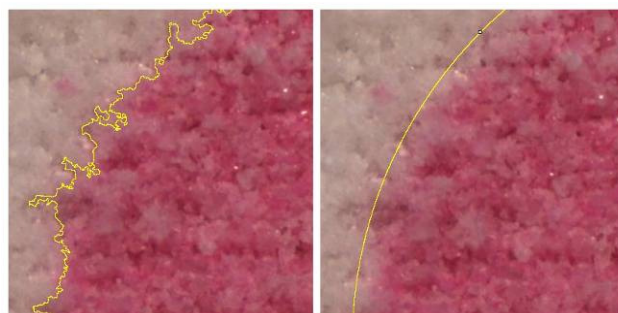
The apparent differences in reproduction of surfaces of first group of samples can be due to the nature of the three-dimensional printing process. As the powder is distributed from one direction and binder in perpendicular direction, the surfaces that are placed in different positions relative to the direction of powder and binder application are possibly influenced by the process characteristics. The angle of inclination of the surface also contributes to the surface reproduction. Potentially pronounced striping effect is often visible on inclined surfaces in all the manufacturing techniques that use layers as the basic process element<sup>1</sup>. The visibility of the “stripes” is influenced by characteristics of materials and surfaces, and

layer thickness. In three-dimensional printing process, “stripes” are sometimes visible on the vertical surfaces as well, especially on the large coloured areas, and are, among others, caused by just printed layer being slightly pushed by the following layer being printed, contributing to the rougher surface. In addition to the reproduction of elements, this also affects colour reproduction (Parraman *et al.*, 2008). The results of sample elements of first group of samples are comparable to the B marked samples from the second group as the same printing preferences were used, and potential differences resulting from different positions in xyz space can be observed. Results of image analysis of sample element characteristics for samples printed with different printing preferences, for a 5 mm circle are presented in Table 9.

**Table 9.** Results of image analysis, sample element characteristics, circle with diameter of 5 mm, samples printed with different printing preferences

Label	Total Area (mm <sup>2</sup> )	Perimeter (mm)	Circularity	Feret (mm)	Major (mm)	Minor (mm)
A_D	18.12	29.82	0.26	5.08	4.89	4.72
A_U	18.41	32.56	0.22	5.13	4.87	4.81
B_D	19.24	47.60	0.11	5.72	5.08	4.83
B_U	19.25	37.82	0.17	5.24	4.97	4.93
C_D	21.21	48.32	0.11	5.60	5.21	5.18
C_U	20.19	35.54	0.20	5.50	5.10	5.04
D_D	18.39	41.03	0.14	5.23	4.85	4.83
D_U	17.83	32.98	0.21	5.11	4.81	4.72

The example of outline obtained by the image analysis routine of the analyzed element can be seen in the left side, and the ideal circle overlaid on the three-dimensional printed element shown in the right side of Figure 100.



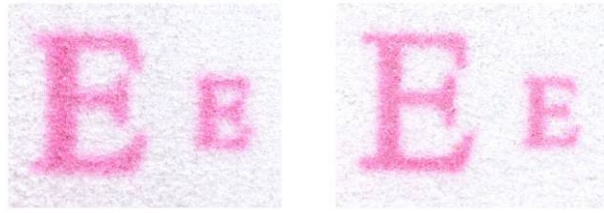
**Figure 100.** Image showing close up of the outline of the thresholded element (right) overlaid on the original microscope image and the outline of an “ideal” circle with the diameter of 5 mm (left)

The A sample elements, Table 9, are generally reproduced with smallest distortions. When comparing results of image analysis of A and B samples elements, which have been printed with the bleed control on and off respectively, the effect of bleed compensation is visible in monitored characteristics as A samples have smaller total area, which was expected, but also show smaller perimeter and higher circularity. This shows the efficiency and effect on the reproduction of the print element of bleed control in the three-dimensional printing process. Bleed compensation is set up in such a way that it takes into account the expected spreading of the print areas into the surrounding un-printed areas and offsets the print areas from the designed size inwards (Hackney, 2003).

The elements from the C samples (printed with higher shell saturation or amount of binder applied), have the highest total area, Table 9, which is directly related to the highest amount of binder that was applied during printing. Results show that other characteristics, perimeter, circularity and Feret diameter, have relatively similar values for B and C samples elements. This is an important parameter for the three-dimensional printing process as it shows that the elements are somewhat similarly reproduced, apart from element total area that is directly related to the amount of binder applied. The B sample elements compared to D sample, printed with lower shell saturation) elements show the effect of printing with smaller amount of binder. The resulting total area of D sample elements is smaller and the circularity is relatively higher.

The reproduction of surfaces facing downwards and upwards can be seen if comparing the samples marked *\_D* and *\_U*, Table 9. The differences are due to the printing process, as the objects are created from the lowest layer first and built upwards. That means the bottom downwards object planes are being built first and are observed to potentially show rougher surface, more bleeding to the unprinted powder (Hackney, 2003), especially with higher shell saturation, more saturated and darker colours, which show differences in relation to the surface orientation (Walters *et al.*, 2009), etc. Figure 101 shows the differences in reproduction on the example of samples printed with higher amount of binder, scanned images. The areas of E characters in 24pt and 12 pt on surface that was facing downwards is 17.58 mm<sup>2</sup> and 5.77 mm<sup>2</sup> and on surface facing upwards 13.7 mm<sup>2</sup> and 4.21 mm<sup>2</sup>, respectively.





(a)

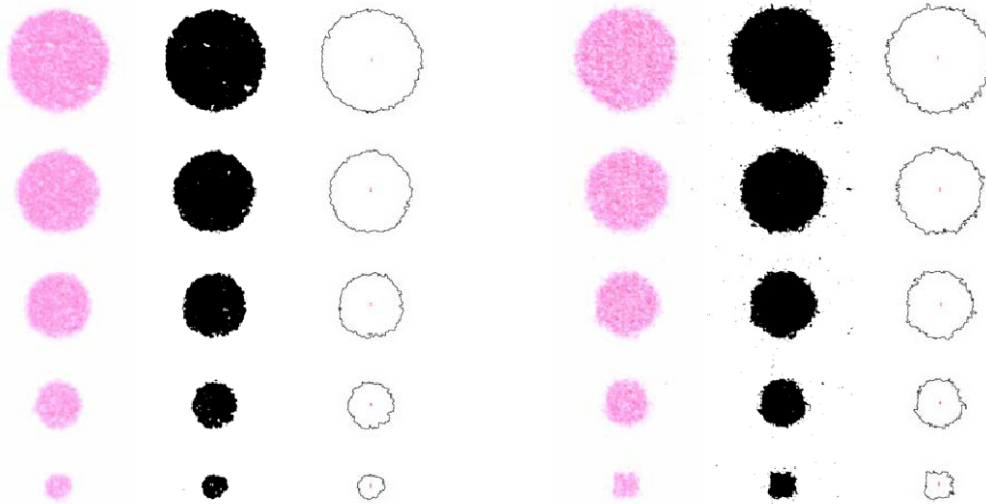
(b)

**Figure 101.** Reproduction of characters “E”, 24 pt and 12p, downwards and upwards facing surfaces; C\_D sample (a), C\_U sample (b), scanned images, 1200 dpi

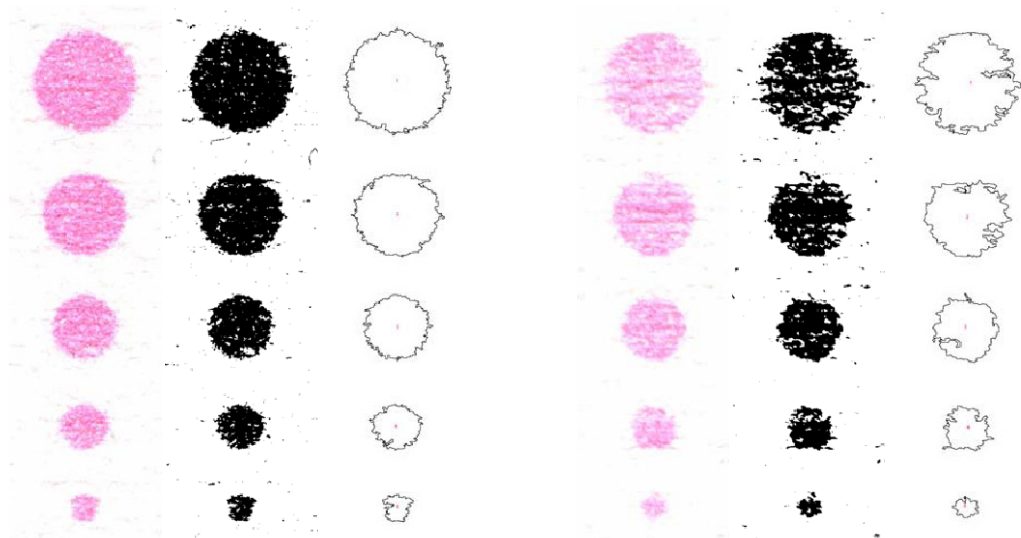
## Example 2

### Image Analysis

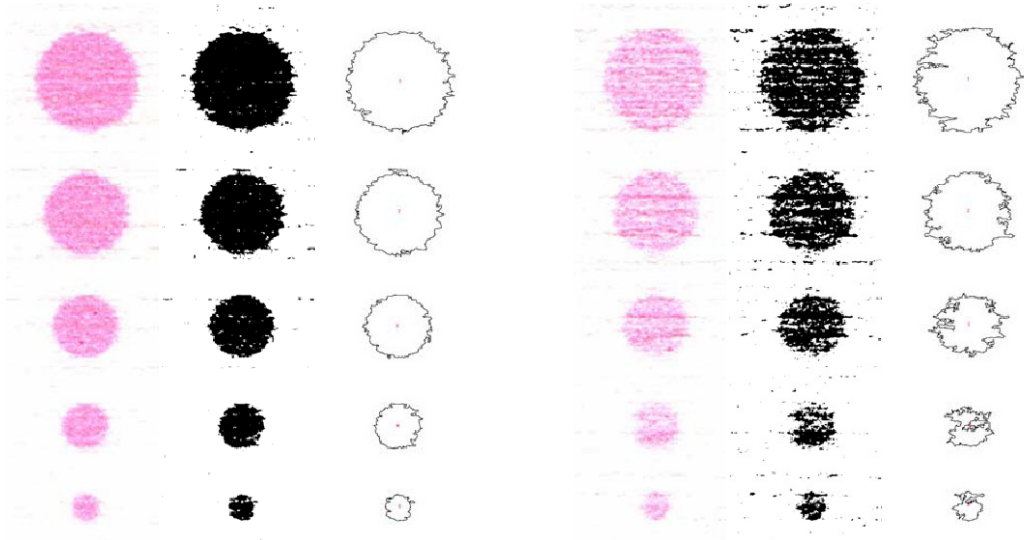
Figures 102 to Figure 108 show the results of the processing and image analysis, by presenting the original image scanned on 1200 dpi, binarized masks of the elements and outline of the elements that were analyzed.



**Figures 102. and 103.** Original scan, binarized mask and outlines of the analyzed elements from test plates 1 and 2, left and right



**Figures 104. and 105.** Original scan, binarized mask and outlines of the analyzed elements from test plates 3 and 4, left and right



**Figures 106. and 107.** Original scan, binarized mask and outlines of the analyzed elements from test plates 5 and 6, left and right



**Figure 108.** Original scan, binarized mask and outlines of the analyzed elements from test plate 7

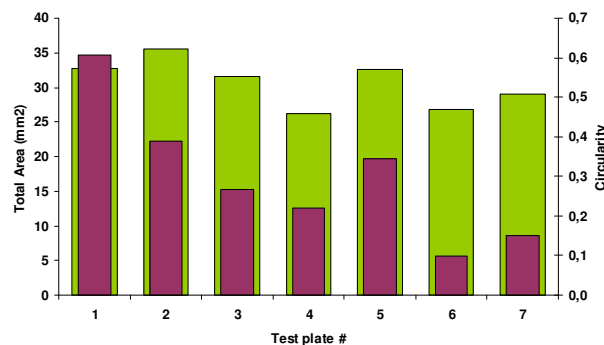
## Analysis of Reproduction

Visual results show there are noticeable differences between different plates. Layering is the most pronounced effect, leading to distortions in the structure of elements. The outlines show the effect of visible layers on the analyzed element; increasing its perimeter and, in some cases, distorting the circular shape to a high degree. Plates 1, 2, 3 and 5 show less distortion, with elements retaining their circular shape. On the other hand, plates 4, 6 and 7 show more distortions, with some of the elements losing the shape almost completely.

Figure 109 shows the graphical representation of numerical results of analysis of above presented elements. As mentioned, the measurements parameters of analyzed elements which were analyzed are total area, perimeter and circularity. Circularity is calculated as:

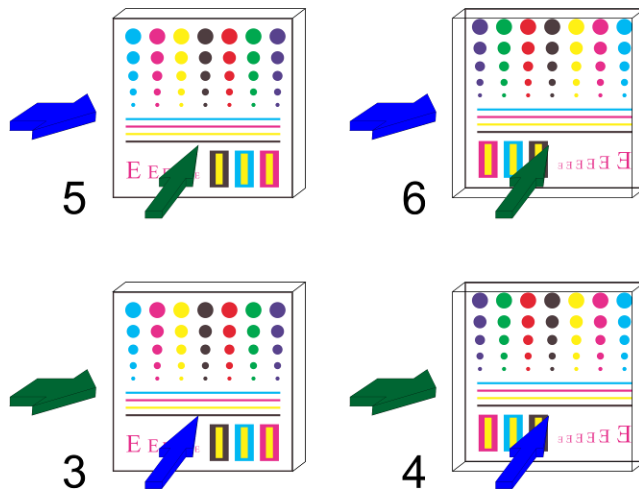
$$C = 4\Pi*\text{area}/\text{perimeter}^2 \quad (4)$$

Higher circularity denotes an element that is closer to an ideal circle ( $C=1$ ). As it can be seen on Figure 109, numerical results are in accordance with the visual observations. Plate 1 elements have overall highest circularity, followed by plates 2, 5, 3, 4, 7 and 6 respectively. Total area of all the elements on the plates is highest on plate 2, followed by plates 1, 5, 3, 7, 6 and 4 respectively. This confirms the visual observation of elements on plate 2 as being the “fullest”, showing the effect of facing surfaces downwards. Those surfaces are in the same time in the print bed for the longest period of time, pressed by the other layers for the duration of printing and lying in the print bed after the object is finished and show the effect of bleeding of the binder in the surrounding area.



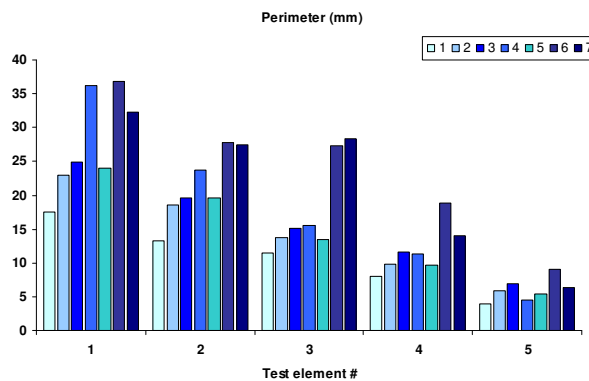
**Figure 109.** Total area ( $\text{mm}^2$ ) of all elements on test plates, green columns; average circularity of all elements on test plates, purple columns

The lower circularity of elements on plates 4 and 6 when compared to elements on plates 3 and 5 respectively is interesting since those plates were positioned in the same binder/powder direction, with the only difference being in different order of applying binder/powder, Figure 110. The analysis showed that the elements on surfaces on which the binder/powder was applied first, plates 3 and 5, are less distorted.



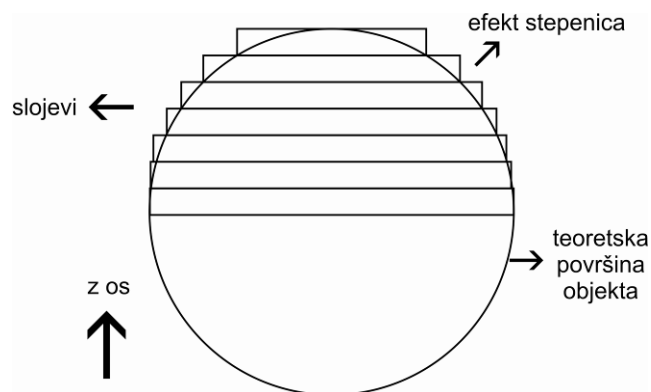
**Figure 110.** Diagram showing the direction of application of powder (green arrow) and binder (blue arrow) on test plates 3, 4, 5 and 6

Figure 111 shows separately the perimeter of all the elements on all the test plates. The analysis showed that the elements on test plates 6 and 7 have the largest perimeter, followed by test plates 3 and 4, 1 and 2. Large perimeter generally shows the high distortions of elements, both from uneven distribution of binder in all directions (like wicking) and from the effect of layers. For the complete analysis of shape, perimeter ought to be analyzed together with the area of the shapes. That is analyzed here as circularity.



**Figure 111.** Perimeter (mm) of all elements on test plates

“Staircase” effect is analogue to the appearance of lines that are not parallel to the substrate edges in standard ink jet printing. The cause for these lines different apparent reproduction is in small movements of printing system in direction of  $x$  and  $y$  axes, while in 3D printing there is additional issue of surfaces that are not parallel with the  $z$  axis being interpreted as a discrete movements rather than smooth transitions between layers, and is dependant on the thickness of the layer itself and the basic build materials. As 3D printing, and all rapid prototyping processes also, builds objects layer by layer, the object produces in such manner should theoretically show, on all surfaces except the ones parallel to the main axes  $x$ ,  $y$  and  $z$ , the “staircase” effect. As the layer thickness is smaller, or as the layers are finer, and depending on the used material properties, this effect diminishes and does not have to be apparent. “Staircase” effect is graphically shown in Figure 112.



**Figure 112.** Diagram showing the “staircase” effect in processes that used layers as basic element (slojevi = layers; efekt stepenica = staircase effect; teoretska površina objekta = theoretical area of object;  $z$  os =  $z$  axis)

The test plate 7 was placed in a position tilted to the  $xy$  plane, at  $45^\circ$ . Due to the “staircase” effect, that is the layers being more visible on the surfaces not parallel with  $xy$ ,  $xz$  and  $yz$  planes, it was expected that the reproduction of surface elements on the test plate will be the worst when compared to the other plates. However, both by visual observations and results from image analysis, the reproduction of elements on test plates 7 was at least comparable to the elements on test plate 6 and 4. The results of image analysis are in accordance with visual observances. Differences in values of measured parameters can be explained by the influence of printing preferences and printing system parameters. In this work, the position of test plates or surfaces with the test elements in the  $xyz$  space has showed to have measurable effect on the final reproduction.

## PAPER VI

### COLOUR MEASUREMENTS AND PROPERTIES OF 3D INK-JET PRINTS

#### Colour Measurements Methodology

Due to the surface of the 3D prints being far rougher than the ink-jet prints on paper substrates, it was presumed that the instrument based on most commonly used measurement geometry in graphic technology, the  $45/0^\circ$  or  $0/45^\circ$ , will not always produce repeatable and credible results. Thus, some preliminary measurements were done with the X-Rite 528 spectrodensitometer, which uses  $45/0^\circ$  geometry. Same trial patches were measured with the X-Rite XTH sphere spectrophotometer. Sphere spectrophotometers are commonly used when measuring colour on textured surfaces such as textiles and fabrics, canvas, plastics, etc. The  $d/8^\circ$  measuring geometry proved to be more reliable in interpreting the colours than the  $45/0^\circ$  geometry. The use of standard graphic arts spectrophotometer was found to be dubious for this purpose since the measurements result depends on the actual material reflectance characteristics and the topography feature that the incident light hits when measuring the spectral reflectance of the surface. Thus, the measurements with the devices with  $45^\circ/0^\circ$  or  $0^\circ/45^\circ$  measuring geometry can work well on smooth and fairly uniform 3D prints surface (for instance with the filled up and smooth surface areas of the Z-Bond infiltrated samples), but give diverse readings if the surface is uneven in topography, which is often the case with 3D prints. 3D prints not only vary in surface topography between differently infiltrated samples, but in the same sample surface as well. The 3D printer prints colour binder on the approximately last ten layers (up to app. 1 mm), meaning that the colour is in sort of under layer and the ink binder is always combined with powder. In addition, the samples are most commonly infiltrated and can have a thin layer of the finishing agent on the top, depending on the infiltrant agent used and its absorbance and hardening behaviour. The surface gloss of the 3D prints depends on the infiltrant used. The cyanoacrylate based agents generally contribute to more glossy surfaces than the epoxy based ones, bearing in mind that the term glossy needs to be relatively taken. As the used spectrophotometer allows simultaneous readings with specular included (SPI) or excluded (SPE) initial measurements were done with the specular component (gloss) included and excluded. The differences were generally very small and not noticeable on all evaluated samples.

### 3D Prints Colour Characteristics

The results of measurements of selected colours of CMY+ test target of non-infiltrated, cyanoacrylate and epoxy based infiltrated samples are presented in Table 10a) to c) respectively. Differences between the non-infiltrated versus infiltrated samples are presented in Table 11a) to Table 10b). Differences in L\*, C\* and H\*, as well as colour differences  $\Delta E_{2000}$  and  $\Delta E_{cmc\ 2:1}$ , between differently infiltrated samples are presented in Table 11c).

**Table 10. a) to c)** Measured and calculated 3D colour data

Table 10a) non-infiltrated

	L*	a*	b*	C*	h/°
C	72,59	-9,53	-22,64	24,56	247,17
M	65,09	35,30	-6,46	35,89	349,63
Y	86,13	-5,20	57,29	57,53	95,19
R	64,88	26,78	21,18	34,14	38,34
G	73,02	-29,64	23,40	37,76	141,71
B	59,16	2,73	-23,99	24,14	276,49
CMY	59,12	-2,20	-0,45	2,25	191,56
W	92,02	3,18	-3,36	4,63	313,42

Table 10b) cyanoacrylate (Z-Bond)

	L*	a*	b*	C*	h/°
C	57,51	-10,76	-29,88	31,76	250,20
M	49,75	47,58	-4,75	47,82	354,30
Y	77,52	-2,33	72,41	72,45	91,84
R	47,26	40,23	28,38	49,23	35,20
G	56,58	-40,45	29,07	49,81	144,30
B	39,72	4,89	-31,16	31,54	278,92
CMY	38,32	-2,06	-2,01	2,88	224,30
W	85,36	3,66	-0,59	3,71	350,84

Table 10c) epoxy resin based (Z-Max)

	L*	a*	b*	C*	h/°
C	55,54	-10,54	-26,10	28,15	248,01
M	46,07	40,74	-3,15	40,86	355,58
Y	68,70	-0,70	59,38	59,38	90,68
R	44,28	32,15	21,47	38,66	33,74
G	51,32	-37,34	25,15	45,02	146,04
B	37,53	2,58	-25,48	25,61	275,78
CMY	35,84	-3,67	-0,64	3,73	189,89
W	79,37	2,95	-0,24	2,96	355,35



**Table 11. a) to c)** 3D prints colour differences

Table 11a) non-infiltrated to Z-Bond

	$\Delta L^*$	$\Delta C^*$	$\Delta H^*$	$\Delta E_{00}$	$\Delta E_{CMC}$
C	-15,08	7,19	1,47	12,77	7,10
M	-15,34	11,93	3,38	14,71	8,49
Y	-8,61	14,92	3,77	7,35	6,63
R	-17,62	15,09	2,25	17,31	10,23
G	-16,44	12,05	1,96	14,19	8,34
B	-19,44	7,40	1,17	19,60	9,23
CMY	-20,80	0,63	1,43	20,74	9,02
W	-6,66	-0,92	2,66	4,93	4,24

Table 11b) non-infiltrated to Z-Max

	$\Delta L^*$	$\Delta C^*$	$\Delta H^*$	$\Delta E_{00}$	$\Delta E_{CMC}$
C	-17,05	3,58	0,38	14,29	6,84
M	-19,02	4,98	3,97	18,08	8,35
Y	-17,43	1,86	4,60	12,75	6,79
R	-20,60	4,52	2,92	19,82	9,01
G	-21,70	7,26	3,11	18,77	9,08
B	-21,63	1,47	0,31	21,46	9,16
CMY	-23,28	1,48	0,08	22,93	10,00
W	-12,65	-1,67	2,65	8,71	5,85

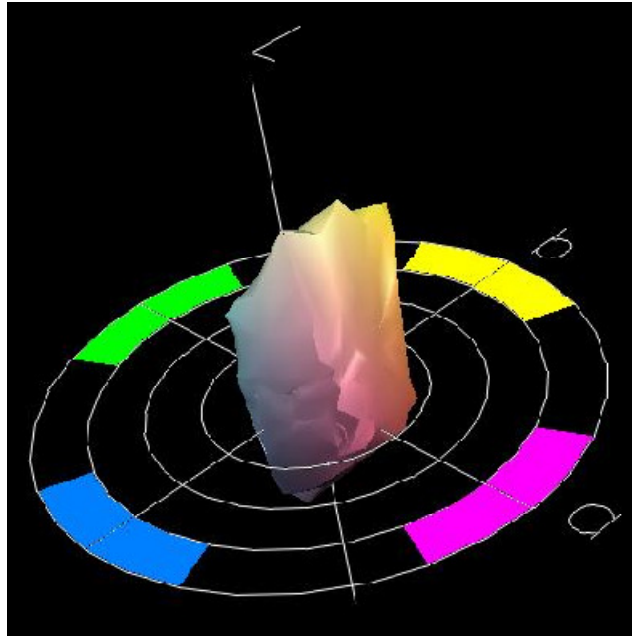
Table 11c) Z-Bond to Z-Max

	$\Delta L^*$	$\Delta C^*$	$\Delta H^*$	$\Delta E_{00}$	$\Delta E_{CMC}$
C	-1,97	-3,61	1,14	2,35	2,11
M	-3,68	-6,95	0,99	4,34	3,29
Y	-8,82	-13,06	1,34	7,40	5,49
R	-2,98	-10,57	1,12	4,62	4,47
G	-5,26	-4,79	1,44	5,34	3,03
B	-2,19	-5,93	1,56	2,65	3,37
CMY	-2,48	0,85	2,56	4,24	4,11
W	-5,99	-0,75	0,26	4,15	2,34

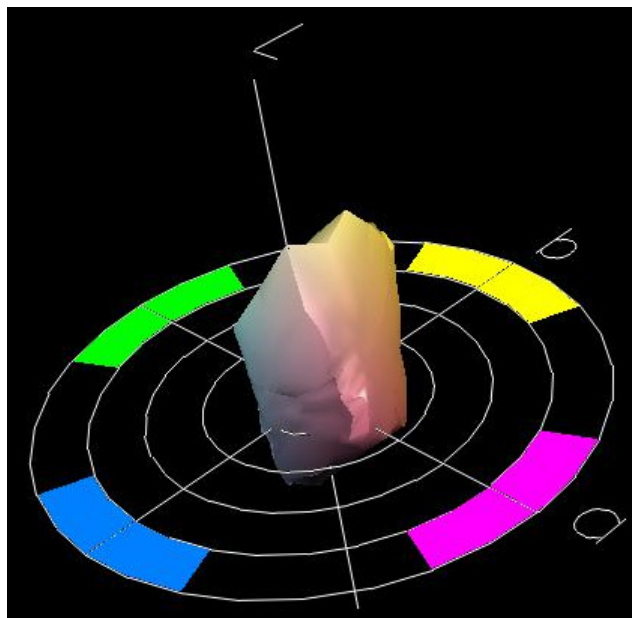
From the Table 11a) and Table 11b) it can be seen that infiltration has a positive effect on chroma values, which are increased more by the cyanoacrylate agent than the epoxy based agent. The lightness values are decreased. For the chromatic colours, the colour hue changes in much less amount than the chroma.  $\Delta E$  differences are from ~ 4-7 in white and yellow patches to ~ 9-20 (depending on the formula used) in cmy, red and blue patches. They follow the same trend for both infiltrant agents. Table 11c) present colour differences between the samples infiltrated with two types of agents. Chroma values are again changed more than hue values. The lightness values do not change much.  $\Delta E$  differences range from ~ 2 for cyan patch to ~ 5-7 (depending on the  $\Delta E$  formula used) for yellow patch.

### Display of 3D prints gamut

The gamut of the 3D prints, depending on the infiltrant used, is presented in Figure 113 and Figure 114.

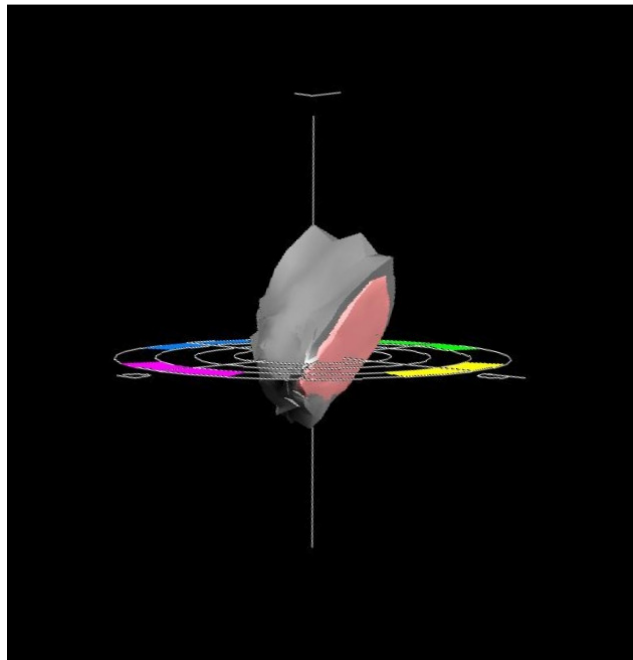


**Figure 113.** Gamut representation of 3D prints infiltrated with cyanoacrylate agent (Z-Bond)

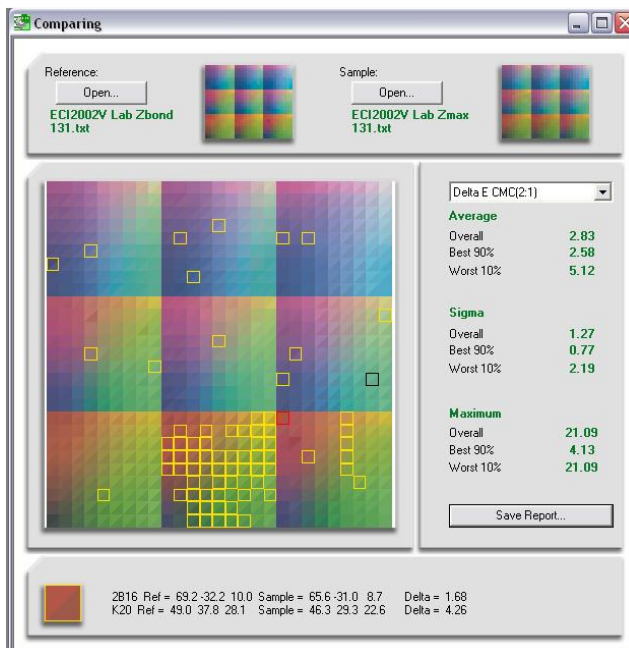


**Figure 114.** Gamut representation of 3D prints infiltrated with epoxy-based agent (Z-Max)

ECI 2002 3D targets measurement results were used for the characterization of the 3D printing colour capabilities and gamut representation as based on the colours from the used test target. The gamut of prints infiltrated with the cyanoacrylate agent is larger than of corresponding prints infiltrated with the epoxy based agent. This result was expected since the cyanoacrylate infiltrated samples had higher chroma and lightness colour values than epoxy infiltrated ones. Differences are mostly pronounced in the range from red to yellow-green colours, in the upper part of the gamut. There are areas containing colours that are very similarly reproduced, irrespective of the infiltrant used. They are mainly located in the bottom part of gamut in the range from cyan to darker green-yellows, as presented in Figure 115 and Figure 116.



**Figure 115.** Some similarly represented colours of both gamuts, Z-Bond gray, Z-Max pink



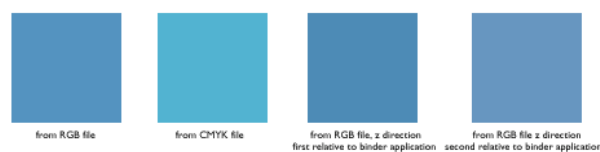
**Figure 116.** Differences in reproduction between samples finished with two infiltrants, patches with highest  $\Delta E$  marked

## Colour monitoring, measurement and control

The possibility of creating coloured objects with RP techniques, in basic colours (the colours of e.g. basic polymer build materials) or full spectrum colours, as in 3D ink-jet printing by ZCorp. has been introduced in the last decade. Although conventional colour ink-jet printing has been developed and researched for a long time, the incorporation of the colour in the 3D ink-jet process has specific, materials and process dependant, issues. They can be identified as the prints surface and colour appearance, colour gamut dependant on the printing and finishing materials, “bleed” on all dimension of the objects, positioning of the printed surfaces and the effect on the resulting object colour etc.

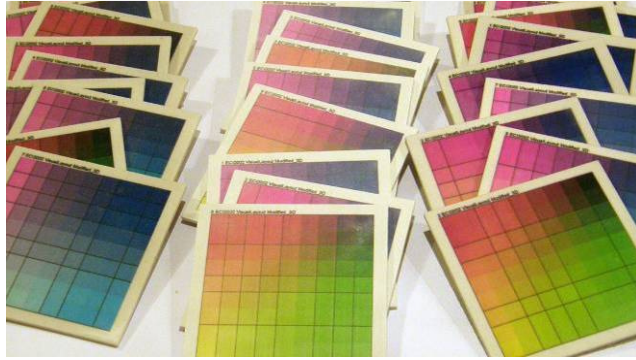
The surface of 3D prints differs in degree of roughness and has a specific granular texture as well, due to the principle of object build, printing mechanism and the basic material used, which is in the shape of powder.

Different positions of the printed surfaces relative to the x, y and z axes also have an effect on the reproduction of colours. This is due to the principle of the object build and the layered approach, or the fact that horizontal surfaces are printed differently than other, vertical, angled and curved surfaces, so the “staircase” effect and visible layering can be an issue. Some of these effects can be dealt with during finishing. An example of measured C colour from different CMY+ plates is presented in Figure 117, screen visualization.

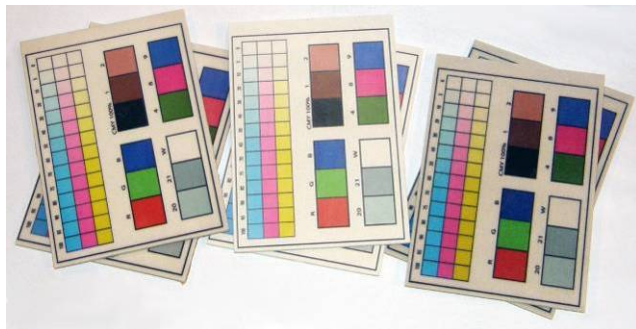


**Figure 117.** Screen visualization of measured C colour from various CMY+ test plates

There is also a certain difference in colour between variously finished prints, dependant on the specific optical, chemical and physical characteristics of the infiltrants and the resulting surfaces of the prints. Figure 118 and Figure 119 show an example of two differently finished 3D printed test charts and non-finished colour test charts; observe the colour difference, mostly in saturation and lightness components.



**Figure 118.** Printed sample test plates from ECI 2002 V, Z-Max (left), non-infiltrated (centre), Z-Bond (right) respectively



**Figure 119.** Custom colour charts, infiltrated with cyanoacrylate (left), non-infiltrated (middle), infiltrated with epoxy resin (right)

Another issue is the selection of the appropriate measuring apparatus, due to the prints surface structure and characteristics. Thus, in our research on 3D prints colour properties and colour permanence, we have used sphere spectrophotometer ( $d/8^\circ$  measuring geometry). Sphere spectrophotometers are commonly used in textile and fabric, paint, plastic and automotive industries, i.e. wherever the colour measurements of specific surfaces, differing in texture or gloss, are needed.

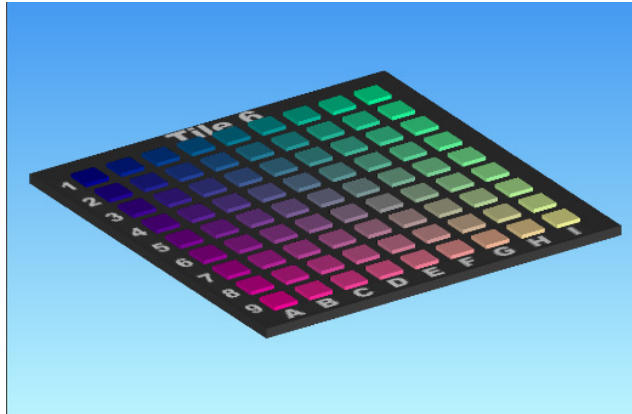
In order to describe the colour capabilities, monitor and control the colour output of a 3D printer, colour test charts or objects are used, together with a necessary measurement equipment and software. Colour test charts can be generic, such as Sample Color Chart from ZCorporation or can be custom developed. Custom developed charts and object can be of a specific design and size and can feature colours of interest. Colour test charts can be in a form of a flat plate, which is useful in some applications, since they are much more suitable for spectrophotometric measurements. Some of custom designed and printed test colour charts in the form of plates are shown in Figure 120.



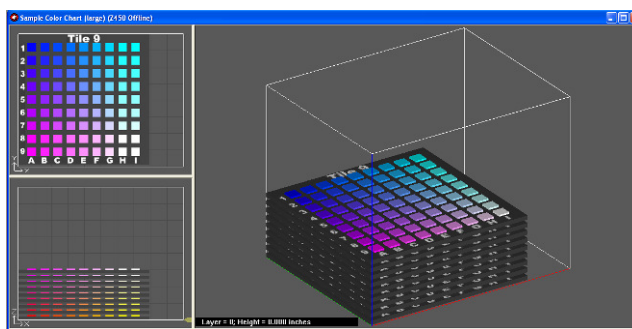
**Figure 120.** Example of custom designed and printed test colour charts in the form of plates

Colour charts can also be in a form of 3D objects, which are useful for observing and monitoring the colour reproduction on flat, angled and curved surfaces, for specific applications. The colour charts could also serve as visualization aids, allowing the users to correctly pre-view the colour as it will look on the printed and finished prints. They can also be used as a tool, like a 3D colour swatch-book, which could be used to select the desired colours.

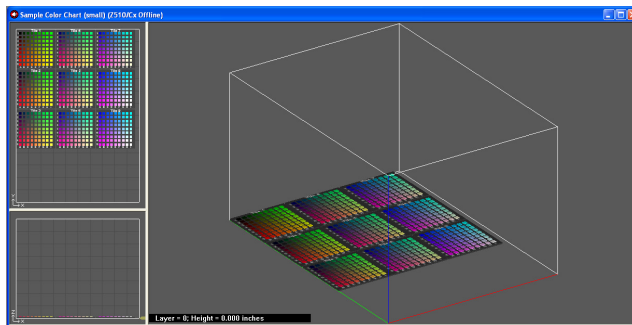
Colour test charts can be used to observe and monitor colour reproduction, colour gamut, colour differences or as colour visualization aids and can be universal, e.g. a Sample Color Chart from ZCorporation, or custom developed, depending on the application. 3D colour charts can be flat plates or complex 3D objects. Flat plates can be used for general applications, monitoring the reproduction of selected colours or for studying the colour differences. Flat plates, if well designed, are also easier to use when performing the spectrophotometric measurements. The Universal ZCorporation Sample Color Chart, Figure 121 to Figure 123 consists of 9 tiles with a total of 729 colour patches. For specific applications, custom colour charts can be developed, as they can contain specific number of patches and feature the selected colours. Some of custom designed and printed test colour charts in the form of plates are shown in Figure 120. Flat test plates can also, for instance, be placed in different positions relative to the x, y and z axes, so the reproduction of colours on horizontal, vertical or angled surfaces can be observed, which is an issue in 3D colour printing.



**Figure 121.** ZCorp. Sample Color Chart, example tile, preview



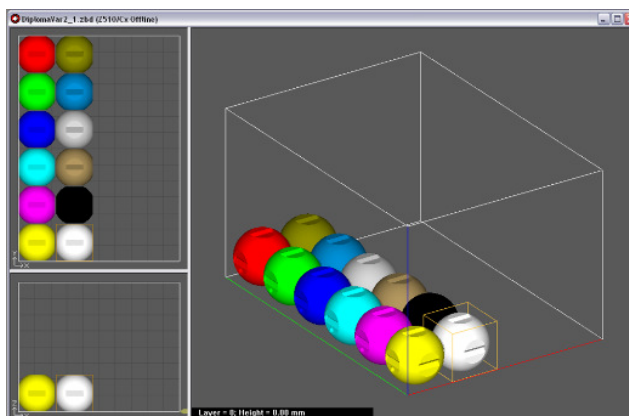
**Figure 122.** ZCorp. Sample Color Chart, option with large tiles, preview



**Figure 123.** ZCorp. Sample Color Chart, option with small tiles, preview

Complex 3D colour test objects can be used for observing and examining the colour reproduction on both flat and curved surfaces, depending on their design. An example of one custom designed 3D object is presented in Figure 124. The object can be coloured in the desired colour, some of which (R, G, B; C, M, Y, earth, sky, silver, gold, black, white) are shown. Printed objects can be infiltrated with different finishing agents, for e.g. showing the impact of the finishing agent on reproduced colours and the size of the object can be also scaled.





**Figure 124.** Custom designed 3D colour test object, preview

The colour charts can, in addition to their technical aspect of use, also be used as visualization aids for 3D technology users, such as designers and artists, allowing them to correctly pre-view the colour as it will look on the printed and finished prints. If the colour charts and objects have colour information (names, marks or colour coordinates) attached to the specific colour, they can also be used as a tool which enables the users to select colour based on the obtained output, in a sort of colour reverse – engineering process. Examples of some of the custom designed 3D colour test objects, as based on GretagMachbeth ColorChecker, are presented in Figure 125 and Figure 126.



**Figure 125.** Example of printed custom designed 3D colour test object, with the respective GretagMachbeth ColorChecker patches shown (Walters, XX)



**Figure 126.** Example of custom designed colour test object, 3D printed colour test blocks (Walters, XX)

## **COLOUR STABILITY AND PERMANENCE IN 3D INK-JET PRINTING**

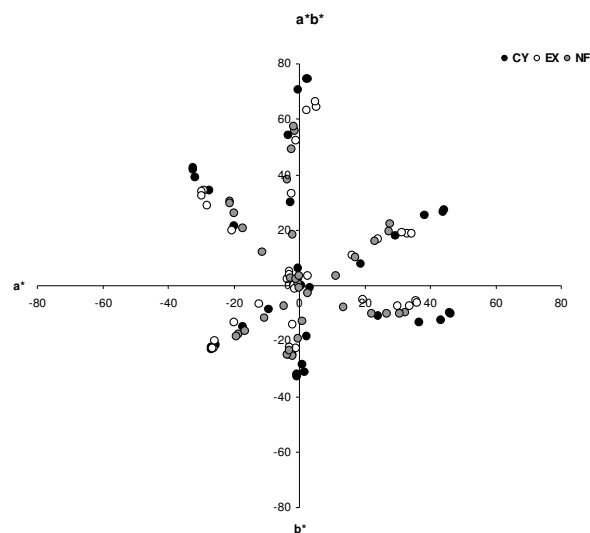
### **Colour stability and permanence under accelerated aging**

New areas of application of 3D printing have opened discussion about permanence, colour and in general, and colour stability of 3D prints. This question is of special interest to the developers and users of the RP technology in the areas such as art and design, for printing works of art, and GIS, architecture and spatial planning, for printing models of landscapes, city models and architectural objects for e.g. public display. As the colour is the integral part of the print, it is expected to last for a specific duration of time. Colour longevity and stability depend on a number of factors, such as light, humidity, temperature, ozone and gas to which the prints could be exposed. Graphic technology, printing industry and colour science have developed and use a variety of standard and established methods for research and prediction of permanence and colour stability of standard prints, especially in the area of ink-jet printed photographs and fine art ink-jet prints. Could this methodology be used in the research of 3D prints, what are the actual mechanisms of colour aging, depending on the materials and exposure conditions and how long do the prints last are some of the open questions that we are currently researching.

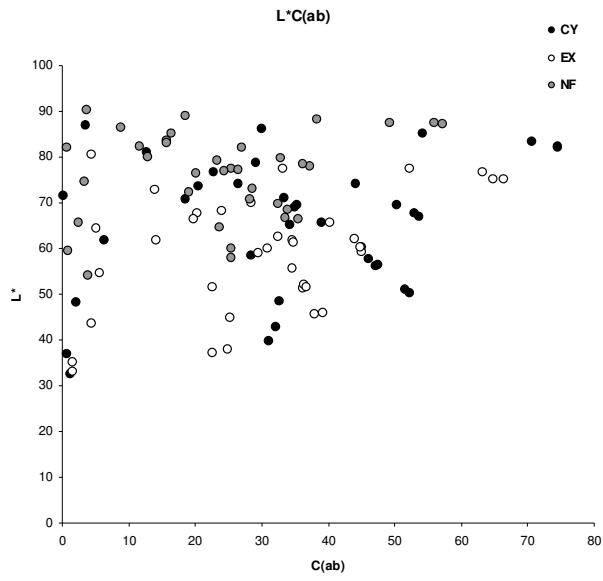
The research about permanence and colour stability of 3D prints is focused on defining the appropriate methodology to conduct real-time and accelerated exposure of 3D prints to various environmental conditions, such as light, temperature and humidity and on comparative research on the aging and colour behaviour of differently infiltrated 3D prints. Custom colour charts for colour permanence research, with a number of patches of defined colour and coverage, have also been developed and used.

As, for the most part, 3D prints printed with commercially available and recommended materials are further post-processed to ensure the desired mechanical, surface finish and colour properties are achieved, selected finishing agents are used. As various finishing agents usually used have specific chemical, optical and other characteristics, they contribute to different final properties of finished 3D prints. Change in colour appearance can be observed when 3D prints are post-processed, bearing in mind that the 3D prints are supposed to obtain final colour properties when appropriate infiltrants are used, as they, in addition to contributing to mechanical properties, also enhance colour saturation (Z Corporation, 2009).

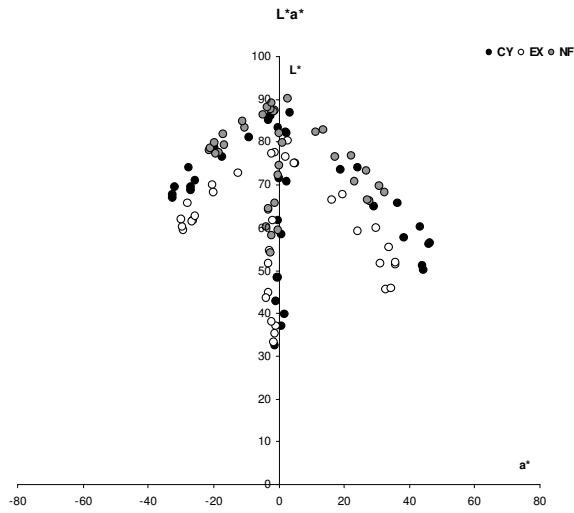
Figure 127 shows the CIELab  $a^*b^*$  plot, or the chromatic values, of all the coloured patches from NF, CY and EX samples. When comparing the position of the marks of NF with marks from infiltrated samples (CY, EX) a positive shift in chroma or saturation can be visible, which also, when combined with the shift in lightness values ( $L^*$ ), Figure 128, contributes to differences in gamut of untreated and infiltrated 3D prints. Gamut is here comprehended as a total volume of colours that can be reproduced in a given system. Small shifts in hue (angle) direction are also noticeable for some colours with higher chroma, e.g. magenta or red, while the lightness decreases for all colours. When comparing different infiltrants, it is visible that infiltration with the cyanoacrylate based agent contributed to higher chroma, and to some degree, higher lightness values.



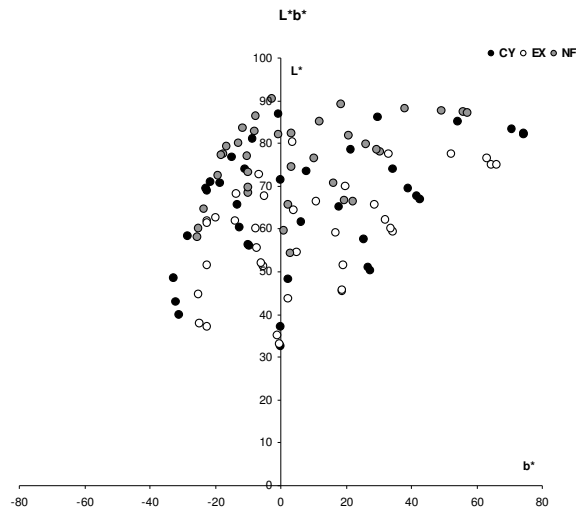
**Figure 127.** CIELab plot of NF, CY and EX samples coloured patches



**Figure 128.** L\*C(ab) plot of NF, CY and EX samples coloured patches

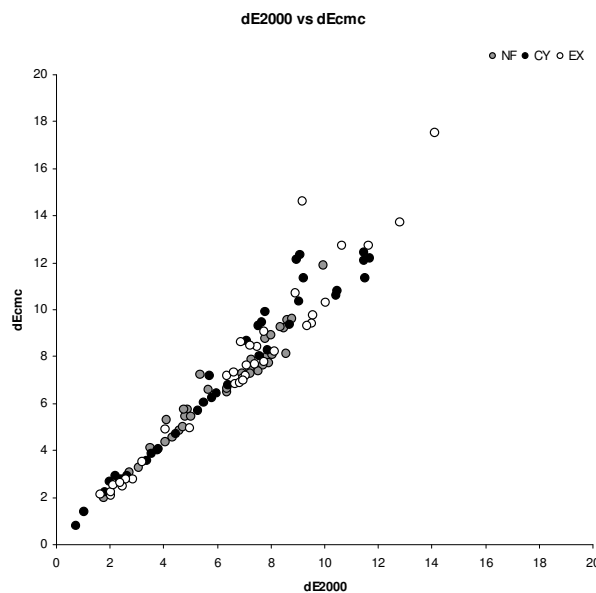


**Figure 129.** L\*a\* plot of NF, CY and EX samples coloured patches



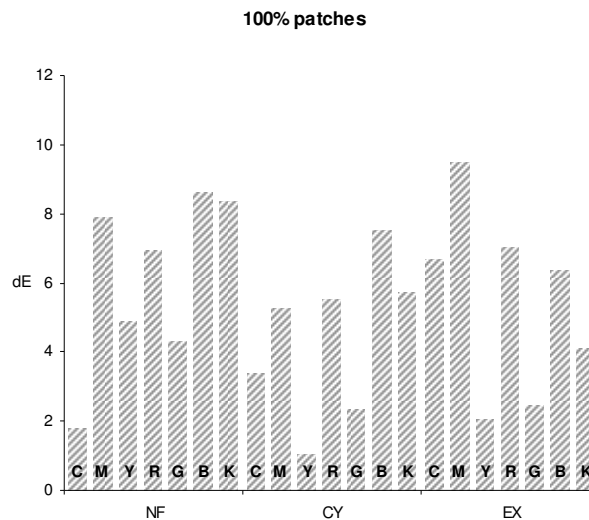
**Figure 130.** L\*a\*b\* plot of NF, CY and EX samples coloured patches

Following results show the effect of accelerated light exposure on spectral and colorimetric properties of selected colours of 3D prints. As described previously, both  $\Delta E_{2000}$  and  $\Delta E_{cmc}$  colour differences were computed, and their observed values are, up to  $\Delta E$  values of approximately 10, linearly correlated. They follow the same trend, with  $\Delta E_{2000}$  values slightly lower than  $\Delta E_{cmc}$  values. Comparison of  $\Delta E_{2000}$  and  $\Delta E_{cmc}$  colour differences are presented in Figure 131.



**Figure 131.**  $\Delta E_{2000}$  values compared to  $\Delta E_{cmc}$  values plot of NF, CY and EX samples coloured patches

Figure 132 shows  $\Delta E_{2000}$  values of 100% ink coverage colour patches of all samples. If the primary printing colours, C, M and Y patches are observed, it is visible that M colour patches have the highest  $\Delta E$  values, meaning the magenta colours show biggest differences when compared with the initial samples. For the NF samples, M colour patch is followed by Y and then C colour patches, while for the infiltrated samples, CY and EX, M colour patch is followed by C and then Y colour patches. Consequently, when the secondary inks, R, G and B, are observed, it is visible that the highest  $\Delta E$  values are observed in B and R inks colour patches, with the G colour patches showing smallest differences. This is attributed to the observed colour differences in C, M and Y colour patches, as blue colour is obtained by printing with C and M inks, red colour is obtained by printing with M and Y inks and green colour is obtained by printing with C and Y inks. For instance, as magenta colour has highest differences, all of the secondary colours obtained by printing with magenta ink will also be impacted by its colour change.



**Figure 132.**  $\Delta E$  values of 100% ink coverage colour patches for NF, CY and EX samples

Figure 133 to Figure 135 show the  $\Delta E_{2000}$  colour difference for all the test plates, shown depending on the percentage of ink coverage. If  $\Delta E$  values for the untreated samples, Figure 133, are observed, it is visible that the differences between respective percentages of ink coverage are less prominent. When the finished samples, Figure 134 and Figure 135, are observed, the  $\Delta E$  values decrease as the ink concentration is increased, with the lowest values for 100% ink coverage colour patches.

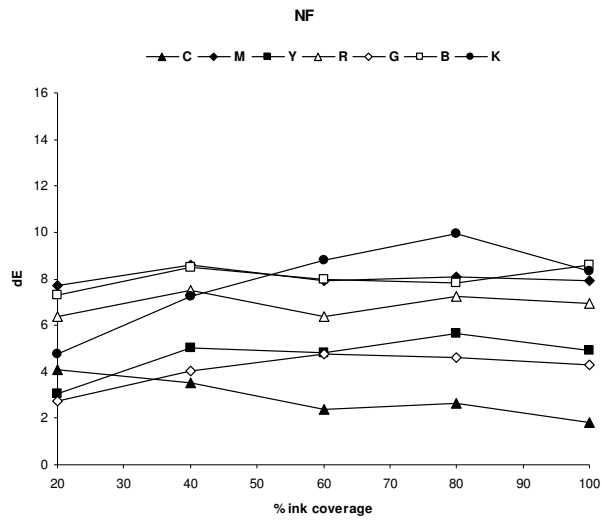


Figure 133. ΔE colour difference, NF sample, by the percentage of ink coverage

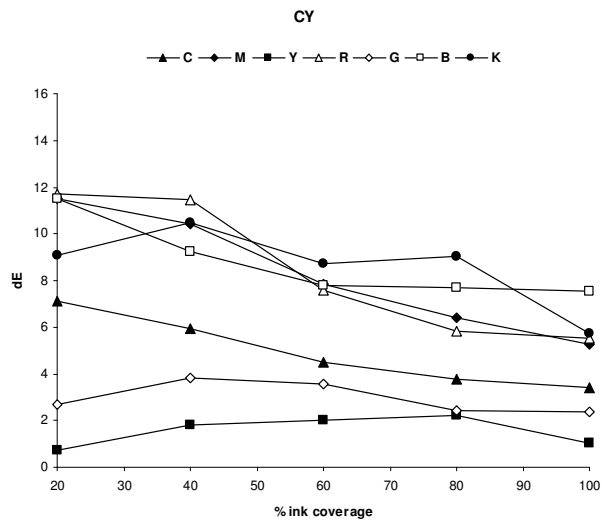
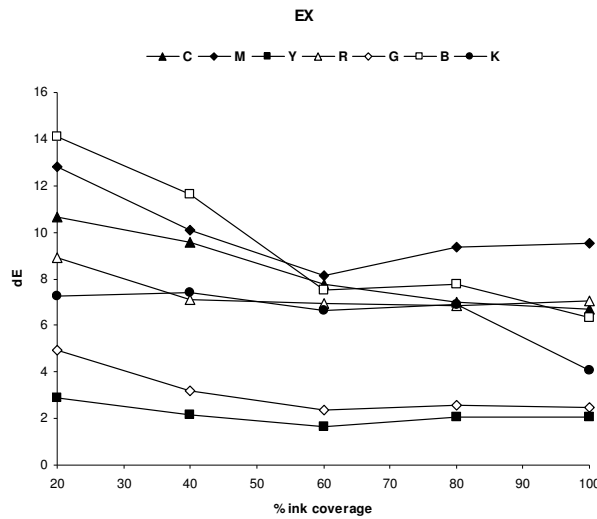


Figure 134. ΔE colour difference, CY sample, by the percentage of ink coverage





**Figure 135.**  $\Delta E$  colour difference, EX sample, by the percentage of ink coverage

As the  $\Delta E$  calculations show the overall visually noticeable difference in colour, it is useful to analyze the change in specific colorimetric parameters such as difference in lightness,  $\Delta L$ , difference in chroma or saturation,  $\Delta C$  and difference in hue,  $\Delta H$ , of the colours. It has to be noted that  $\Delta H$  is not geometrical difference in hue angle,  $h$ , but the difference in hue parameter of two respective colours. Such analysis enables the specific colorimetric parameters relative impact on overall noticeable difference in colour to be evaluated. Figure 136 to Figure 138 show the values of  $\Delta L$ ,  $\Delta C$  and  $\Delta H$  for colour patches of all samples. The calculated values for  $\Delta L$  and  $\Delta C$  are expressed here as absolute values for better distinction, denoting how much the respective parameter is changed, irrespective of its direction, which is further analyzed in text. For the untreated sample, Figure 136, the changes are predominantly in chroma parameter. The only exception is the B patch, which has showed some shifts in hue. When the corresponding  $\Delta E$  values are analyzed (Figure 133), colour patch B values are among the relatively highest ones. For the CY finished sample, Figure 137, the changes are again mostly in the chroma parameter. Some differences in hue parameter, which is the most prominent change, can also be visible in C and consequently B colour patches. For the EX finished samples, Figure 138, the results show that there is no single distinctive parameter which showed the most differences for all the colour patches. B colour patch again has most changes attributed to the hue parameter, visible as colour shifts, which can be compared to the hue shifts in C and M colour patches as well. The chroma values are generally decreased for all the chromatic colours, for all the samples, when compared to the respective initial samples. All differences in the lightness parameter, for all the samples irrespective of the type of finishing, are in the positive direction, as samples

exposed to light have higher lightness values, as the colours are becoming less saturated and are fading.

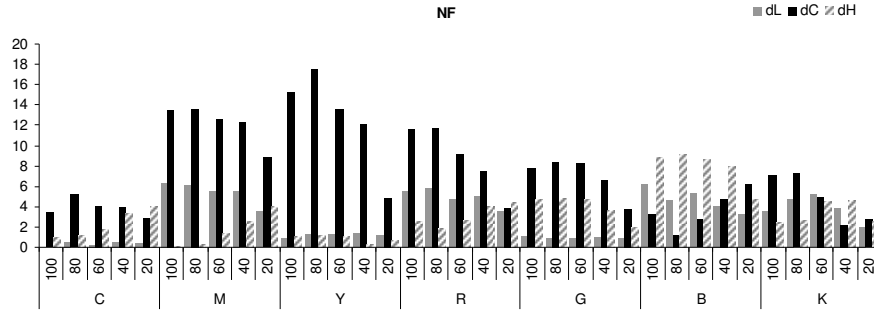


Figure 136.  $\Delta L$ ,  $\Delta C$  and  $\Delta H$  parameters, NF sample

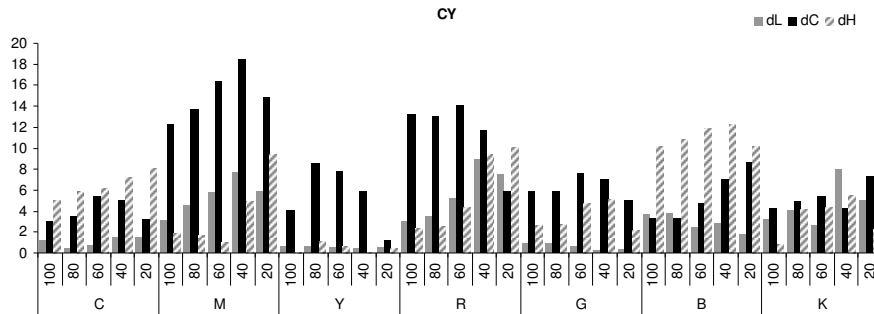


Figure 137.  $\Delta L$ ,  $\Delta C$  and  $\Delta H$  parameters, CY sample

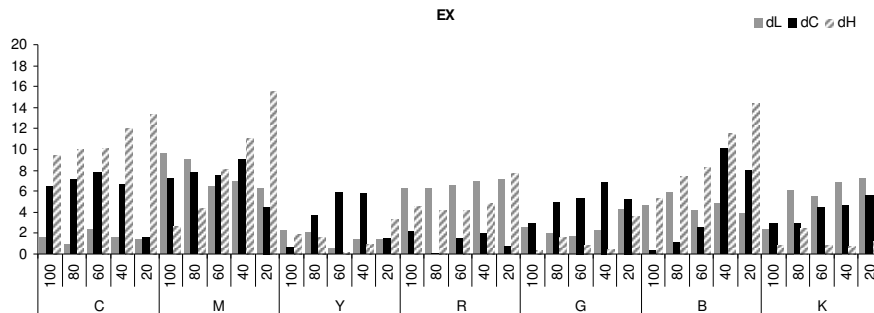
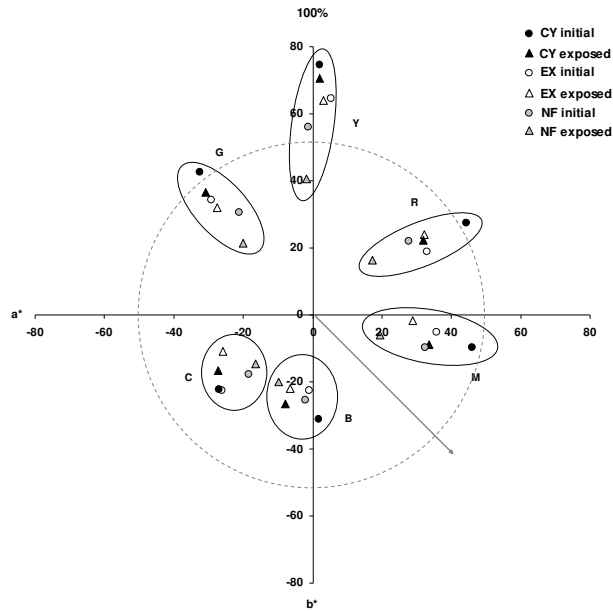


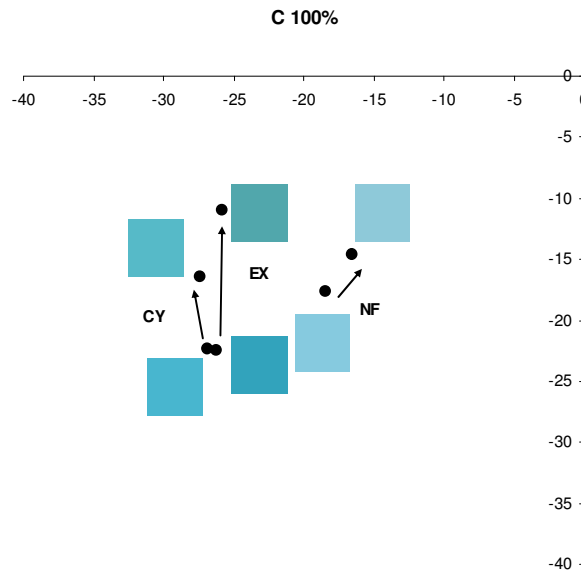
Figure 138.  $\Delta L$ ,  $\Delta C$  and  $\Delta H$  parameters, EX sample

The breakdown of apparent colour changes to changes in a specific parameter, such as chroma or hue, can also be analyzed together with the CIELAB  $a^*$  and  $b^*$  values plotted against each other, as they further show the direction of chromatic changes. The  $a^*b^*$  plot, Figure 139, shows the 100% ink coverage colour patches values. The mentioned changes in

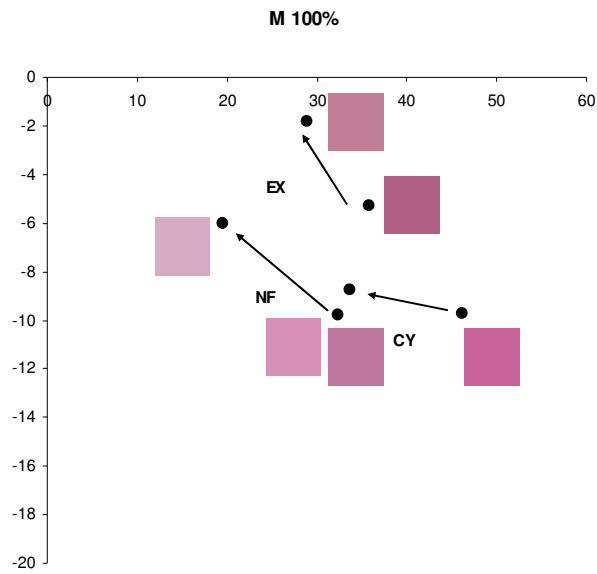
chroma and hue of specific colour patches can also be visible, together with the direction of changes, arrow for chroma and circle for hue changes are added for aided visualization (Schanda, 2007).



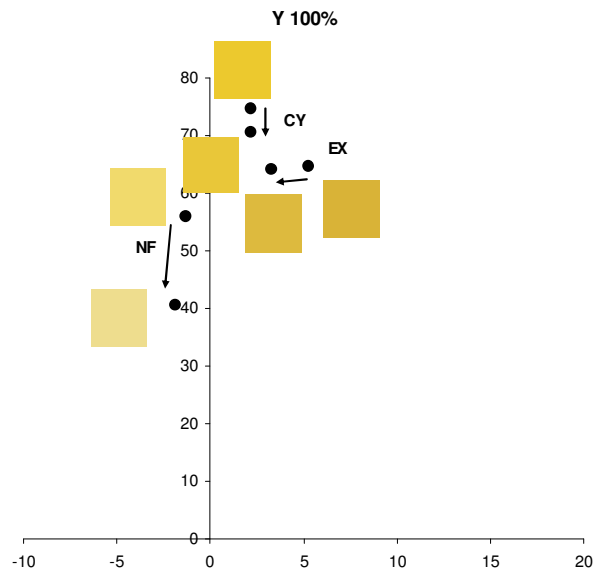
**Figure 139.** 100% ink coverage colour patches, changes in chroma (increases from centre towards edge, as shown e.g. in the direction of the arrow) and hue (angles are changed along the sample circle, dotted line)



**Figure 140.** a\*b\* plot of initial and exposed colour patch, C 100% ink coverage, visualization of patch also shown, for NF, CY and EX samples

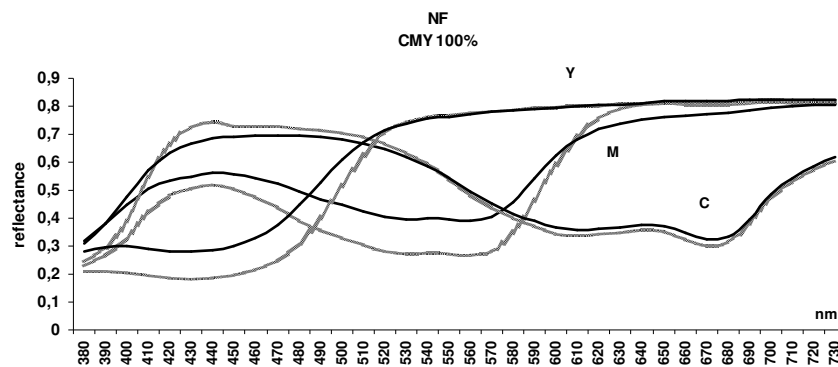


**Figure 141.** a\*b\* plot of initial and exposed colour patch, M 100% ink coverage, visualization of patch also shown, for NF, CY and EX samples

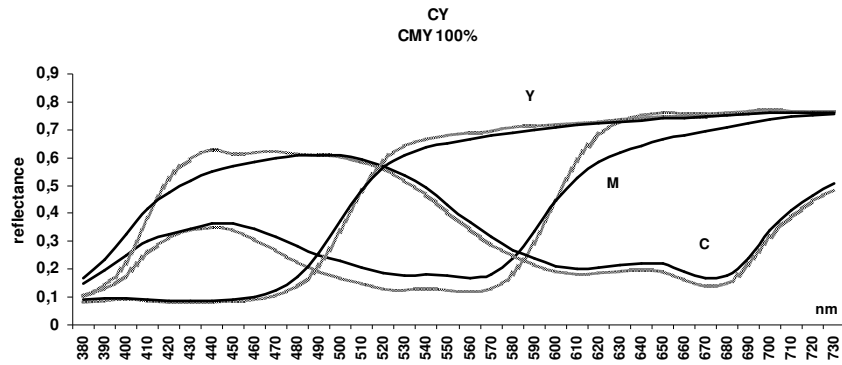


**Figure 142.** a\*b\* plot of initial and exposed colour patch, Y 100% ink coverage, visualization of patch also shown, for NF, CY and EX samples

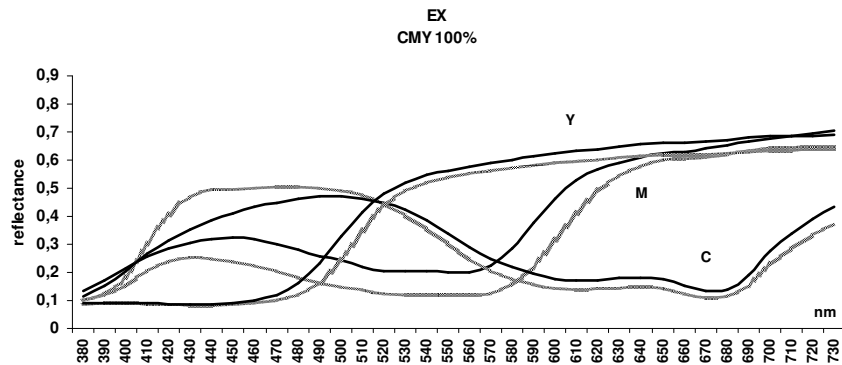
Spectral curves, displayed as reflectance versus wavelength, were also plotted in order to better comprehend the observed differences in chromatic values of colours. Figure 143 and Figure 145 show examples of such spectral curves, for C, M and Y colour patches of NF, CY and EX test plates, respectively. The changes in colour appearance are here visible as the changes in reflectance, and thus absorbance, of the specific wavelengths. The samples exposed to light generally show higher reflectance, and are perceived as overall lighter, or fading. The degree of change in reflectance is, confirming the colorimetric results, highest for the magenta colour. Smaller or larger changes in reflectance of initial and exposed samples relative to the specific wavelength area is also noticed, for example in lower wavelengths area (blue part of the spectrum) for the CY sample C colour patch, where it can be observed that the reflectance was decreased after the aging procedure, thus less light was reflected in the blue region. The analysis of spectral curves further confirmed the results in terms of specific CIELAB parameters values.



**Figure 143.** Example of spectral reflectance curves, C, M and Y colour patches, NF sample; dotted line initial sample values, full line sample after exposure values

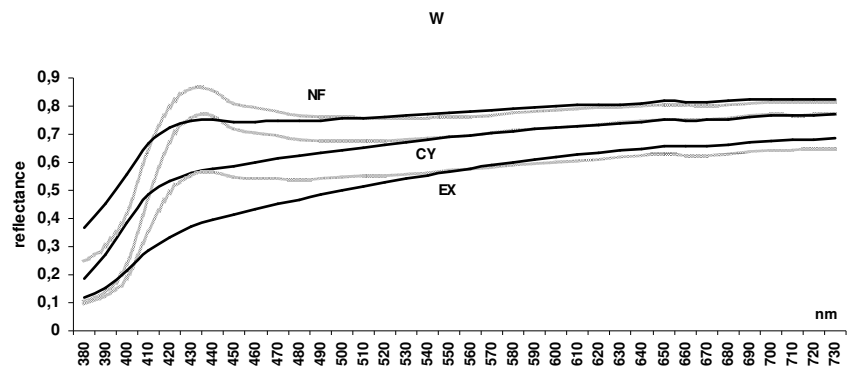


**Figure 144.** Example of spectral reflectance curves, C, M and Y colour patches, CY sample; dotted line initial sample values, full line sample after exposure values



**Figure 145.** Example of spectral reflectance curves, C, M and Y colour patches, EX sample; dotted line initial sample values, full line sample after exposure values

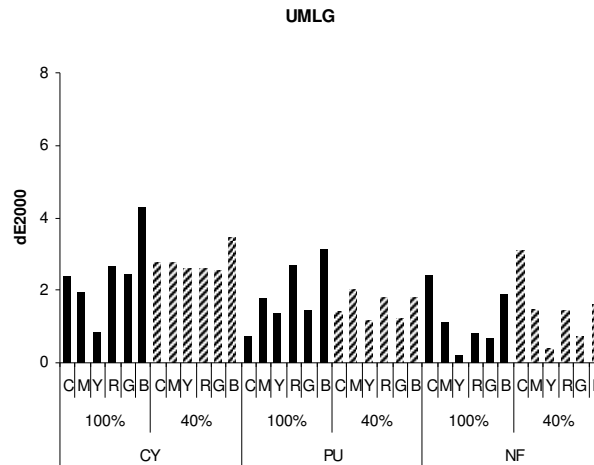
The colour changes in non-printed, W, patch were also analyzed, as they show the aging behaviour of powder-binder system in the case of NF sample and powder-binder-infiltrant system in the case of CY and EX samples. It was observed that the colour is generally shifting upwards in yellowness-bluesness plane, towards the yellow part of the spectrum, especially in the case of EX sample. The spectra of the W patch, Figure 146, also show that the reflection in the part of blue wavelengths is decreased after the exposure to light, and more for infiltrated, CY and EX, samples.



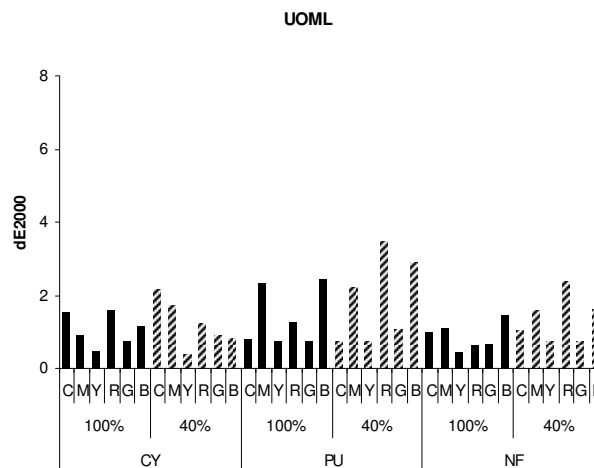
**Figure 146.** Spectral reflectance curves of W patch, NF, CY and EX samples; dotted line initial sample values, full line sample after exposure values

## Colour stability and permanence under natural aging

The results of colour difference between initial and exposed samples are presented in Figure 147 to Figure 152, for specific environmental conditions respectively.



**Figure 147.** Display conditions, mixed natural/artificial lighting, under glass cabinet

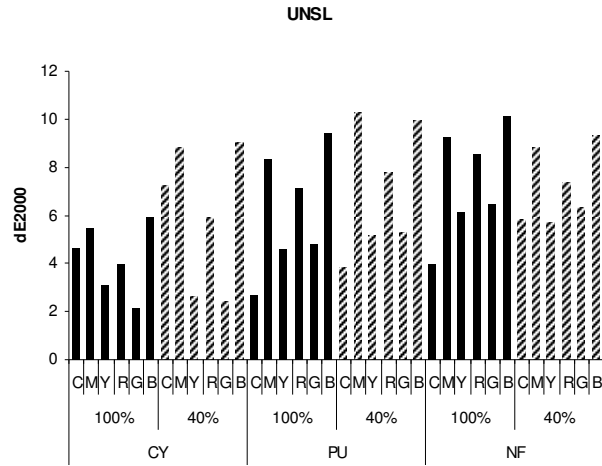


**Figure 148.** Office/display conditions, mixed artificial/natural lighting, no coverage

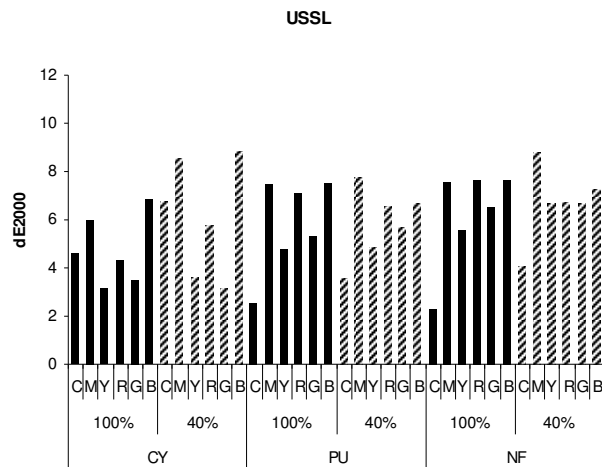
Samples marked UMLG were placed in a display type environment, in glass casing which was located in the far side of a showroom, turned towards the windows. The light that the samples were exposed was a mixture of low level natural daylight behind window and artificial lightning present in the room. Samples marked UOML were placed in typical office/print room environment, backed up on a wall, left uncovered, in far end of the room



and facing window. The light was mixture of low level natural daylight and artificial lightning that was on for the majority of working days.

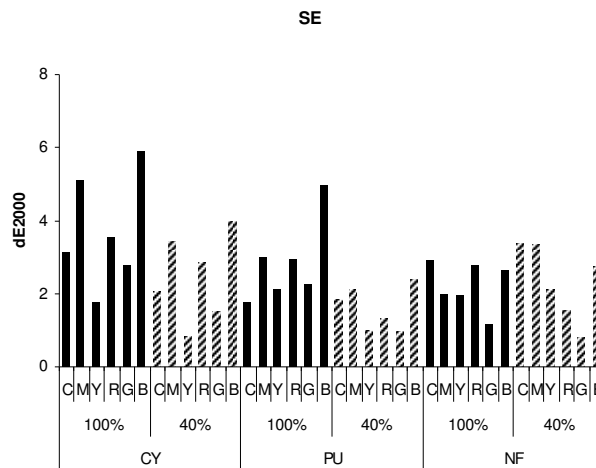


**Figure 149.** Display conditions, sunlight behind window, no coverage, north facing

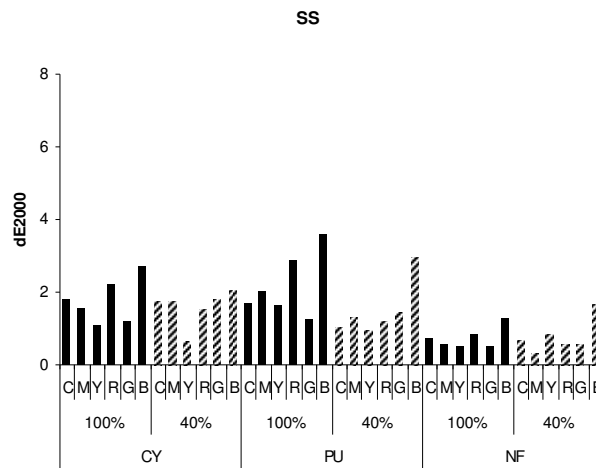


**Figure 150.** Display conditions, sunlight behind window, no coverage, south facing

Samples marked UNSL and USSL were placed in a display type environment, and exposed to sunlight behind window, no coverage, north and south facing respectively. The samples were fixed onto holders, in upright position, placed on the shelf directly in front the window and turned towards the glass.



**Figure 151.** Storage conditions, no coverage



**Figure 152.** Storage conditions, sealed

Samples marked SE were placed in a storage type environment, in shallow box, no coverage, which was placed on a shelf in basement type room, with minimum amount of mixed natural and artificial light present. Samples marked SS were placed in sealed padded envelope, which consisted of layers of plastic and paper, and placed in the same environment.

Comparative research has done using instrumentally assessed colour change of initial and aged samples. The research has been done on selected basic colours patches, C, M, Y, R, G and B, with two different percentages of ink coverage, 40% and 100%. The differences that were monitored and compared for samples were between finishing method/infiltrant type and the amount of binder present on the patches, respectively.

Regarding the samples exposed under display conditions colour differences, highest  $\Delta E$  values have been observed in filtered daylight exposed samples, UNSL and USSL, and smallest  $\Delta E$  changes in mixed light display cabinet/office non-covered exposed sample, UOML. For the sample UMLG, highest  $\Delta E$  changes were noticed in the CY infiltrated samples, especially for the 40% coverage patches. Average colour changes are round  $\Delta E$  2, with several patches with changes up to  $\Delta E$  4. Regarding the specific colours, C and M patch have undergone more changes than Y patch on average, resulting thus in higher changes in especially B and R patches, lower for G patch. For the sample UOML,  $\Delta E$  changes were round  $\Delta E$  1 on average. The trends for less area coverage and specific colours colour changes were as described in previous sample. For the samples UNSL and USSL, colour changes were on average round  $\Delta E$  4, with maximum round  $\Delta E$  8 in some cases. Regarding the specific colours, the trends are as described, C and M colour patches have undergone more changes on average, though more changes have been noticed in Y colour patches for some samples. For the secondary colours, more changes have again been observed in B and R patches, respectively compared to G patch. Lower area coverage patches have changed slightly more on average, though the differences are not distinct.

Regarding the samples exposed in storage conditions colour differences, higher  $\Delta E$  values have been observed in open exposed sample, SE (very low/no light conditions), while smaller  $\Delta E$  changes noticed in sealed samples, SS. Regarding the SE and SS samples, the trends for specific colour patches and higher and lower area coverage patches are following the previous results, with more changes in C and M patches, thus resulting in higher changes in R and B patches, while it has been noticed that infiltrated samples have undergone more changes than non-finished samples.

It can be concluded that material and process parameters that influence the colour stability and behaviour of 3D ink-jet prints are type of finishing, exposure and environmental conditions.

# **CONCLUSIONS**

The thesis showed a comprehensive study of 3D ink-jet materials and prints specific properties using the existing and customized characterization methods usually employed in the graphic and material science and other related industries. The work explained the variety of characteristics of 3D ink-jet materials and prints, including the structure, colour reproduction and methodology, permanence and colour stability, effects of accelerated aging and mechanical properties, as well as provides the general research models and defines the methodology.

Considering the 3D prints structure, mechanical and surface properties it has been shown that type of infiltrant agent used for postprocessing of the ink-jet based 3D prints greatly contributes to the investigated properties of the final prints. Finishing with an epoxy agent resulted in the highest tensile and impact strength and hardness. A cyanoacrylate agent ensured better tensile strength and impact properties of the finished prints than did the polyurethane-based agent. A polyurethane-based agent, on the other hand, contributed to higher hardness measurement on the final prints. Surface inspection showed that polyurethane-based finished samples have similar surface characteristics as unfinished samples, whereas epoxy and cyanoacrylate infiltrants produced more uniform surfaces. The impact of these two infiltrant agents on dimensional change, as well as possible blocking of fine cavity and relief details of final prints must be taken into account.

Considering the reproduction in 3D ink-jet printing, it was evaluated for several possibly influencing printing and material preferences on a number of sample elements. The effect of different printing preferences and placement of printed surfaces in different positions in the build bed on the reproduction has been presented and morphological characteristics of the test elements, as analyzed by the described routines, have been discussed. Image analysis was studied as a tool for objective evaluation of the surface elements. The research of image analysis as a technique for objective reproduction analysis showed it can be a valuable tool, acknowledging the specific issues that arise from application in the evaluation of reproduction in three-dimensional ink-jet printing. The presented results discuss and give perspective to the interaction of materials and define the factors that influence the reproduction in the specific area of three-dimensional ink-jet printing. They are of importance as they show how the principles of the three-dimensional printing, with process specific parameters such as orientation of the objects and surfaces, bleed control and saturation levels, influence, and in what amount, the surface elements reproduction and appearance of 3D prints.

Regarding the colour reproduction in 3D ink-jet printing, current colour capabilities and colour application areas in RP and more specifically in 3D ink-jet printing have been described. Colour measurements methodology, colour properties, issues in colour reproduction and control have been discussed. Due to the colour characteristics and surface topography of 3D prints, sphere spectrophotometer ( $d/8^\circ$  measuring geometry) was used. The finishing of 3D prints, influenced by the infiltrant agent used, was found to decrease the lightness values and increase the chroma values. The hue angle does not significantly change. Infiltration with the cyanoacrylate agent, compared to the epoxy agent, contributes to the higher chroma values, while lightness and hue values do not differ much. Consequently, the gamut of cyanoacrylate finished 3D prints is larger than the epoxy infiltrated, although there are areas of the gamut that are reproduced very similarly. The research has shown that developed, existing standardized methods for colour measurement, monitoring and control, used in graphic technology, printing and colour science can, to some extent, be applied to issues arising in the novel field of colour 3D ink-jet printing. It has also been identified that further research is still needed, especially in the areas such as control of the colour process and the colour stability for different applications.

Considering the colour stability and permanence of 3D ink-jet prints, research was performed upon exposure to xenon-arc based accelerated aging procedure and natural aging. The research concentrated on obtaining basic comparative data on untreated 3D prints and 3D prints finished with two selected infiltrants. Based on the methodology used, the analysis has shown the changes in colour appearance of differently finished 3D prints, which were mostly attributed to chroma, or saturation, and lightness variations. Accordingly, the gamuts of untreated and finished 3D prints, as based on the selected colours, will differ. The colour stability analysis of samples after being subjected to xenon-arc based light exposure for 72 hours has shown that the finishing method has noticeable influence on the obtained colour. The  $\Delta E$  colour differences among untreated and differently finished 3D prints were discussed, along with changes in specific parameters, lightness, chroma and hue, and spectral curves. The colour stability of samples studied was noticed to vary and is dependant on colour, percentage of ink coverage and finishing method. Regarding the natural aging of 3D prints, the impact of process and material 3D prints properties and selected environmental conditions on colour stability was evaluated. The work used methodology derived from standard ink-jet prints measurements. Regarding the samples exposed under display conditions, highest colour differences values have been observed in filtered daylight exposed

samples, and smallest changes in mixed light display cabinet/office non-covered exposed sample. Regarding the samples exposed in storage conditions colour differences, higher colour differences values have been observed in open exposed sample (very low/no light conditions), while smaller changes noticed in sealed samples. The studied material and process parameters that have potential influence on the colour stability and behaviour of 3D ink-jet prints are type of finishing, exposure and environmental conditions. The issue of colour and stability of 3D ink-jet prints will potentially become important as 3D printing emerges into new application areas, in which the object properties will need to be maintained for certain amount of time. On the basis of the presented and discussed, open research issues of 3D prints colour stability and permanence can be defined, and include the development of adequate standardized methodology for studying colour and permanence, including natural and accelerated aging; predictive test, with reciprocity failure defined; further explanations of aging mechanisms and characterization of properties of 3D prints.

The goal of the research was to characterize the structure and to define permanence and stability of 3D printing materials and prints by applying selected microscopic, spectrophotometric methods, image analysis methods, surface evaluation methods, mechanical testing and permanence testing methods. These were performed with compiled existing and newly acquired knowledge during the interdisciplinary research and optimal solutions and methods were discussed.

It can be concluded that the main hypothesis set, by using the above mentioned methods, with their advantages and limits respected, it is possible to comprehend the changes in structure, colour and permanence of 3D printing materials and prints, was proven.

## **SCIENTIFIC CONTRIBUTION**

Scientific contribution of the thesis is primarily in a comprehensive study of 3D ink-jet materials and prints selected structure, surface, colour and permanence properties using the existing and customized characterization methods employed in the graphic and material science and other related industries. This is of importance as there was no thorough research available up to this point, covering these specific issues which have proved to be relevant for existing and emerging applications of 3D ink-jet prints.

Scientific contribution of the thesis is specifically in the following:

Proposed characterization methods were proved to be verified as suitable for three dimensional printing materials and three dimensional prints properties research.

Methods and procedures for research, within the graphic technology and related fields, of three-dimensional structure and colorimetric surface characteristics were studied and defined.

Methodology and definition of optimal procedures for valorisation of three dimensional prints colour permanence, with emphasis on light fastness of three dimensional prints under natural and accelerated aging conditions were set.

Quantitative and qualitative data regarding the three dimensional prints colour characteristics and colour permanence mechanism was systematically presented and analysed.

The scientific contribution is as well in contribution to generation of standards for surface structure and permanence testing procedures of three dimensional prints.



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# **EXTENDED ABSTRACT**

## PRELIMINARNA ISTRAŽIVANJA

Brzim razvojem novih tehnologija, nove metode i materijali, koji primarno pripadaju u procesno inženjerstvo i strojarstvo, postali su dostupni. Unutar posljednje dekade, nove proizvodne tehnologije i sukladno tome, novi materijali, bazirani na standardnom ink jet tisku, razvijene su i pojavile su se na tržištu. Jedna od novih tehnologija je i tro-dimenzionalni ink jet tisak. Proces 3D tiska koji se istražuje koristi materijal u obliku praha umjesto dvo-dimenzionalne podloge i tekuće vezivo kao tiskarsku boju. Posljednjih godina se pojavila i mogućnost 3D tiska u boji. Kod 3D printera u boji, koloranti se nalaze u otopini veziva, a boja se reproducira kao i kod standardnih printera. Zbog interdisciplinarnosti prirode, opisane metode i materijali pokazuju široki raspon karakteristika koje je potrebno definirati, kako kvalitativno, tako i kvantitativno, koristeći znanje iz različitih znanstvenih disciplina. Djelomično i zbog njihovog osnovnog polja tehnologije, materijali za 3D tisak nisu adekvatno istraženi s pogleda grafičke tehnologije. Koristeći znanja i iskustvo stečena tijekom istraživanja standardnih ink jet otisaka i osnovnih materijala (papira, polimernih podloga, premaza, tiskarskih boja), moguće je primijeniti postojeća rješenja kako bi se istražilo i karakteriziralo relevantna svojstva materijala u 3D tisku i 3D otisaka. U isto vrijeme, mjerne metode i postupci koji nisu originalno potekli iz grafičke tehnologije, mogu se uspješno koristiti, ukoliko se do nekog stupnja izmjene i prilagode. Oni predstavljaju nove mogućnosti i perspektive istraživanja. Na osnovi navedenog, moguće je pretpostaviti da se identificirana pitanja mogu adekvatno istražiti koristeći postojeće znanje iz grafičke tehnologije, te koristeći neke ne-tradicionalne metode kako bi se definirale procedure za proučavanje i materijala za 3D ink jet tisak i samih otisaka, u smislu njihovih karakteristika, strukture i trajnosti.

Tema 3D tiska bila je tema relativno velikog broja istraživanja, znanstvenih i stručnih članaka i nekoliko disertacija, većinom u polju brze izrade prototipova i mehaničkog inženjerstva. Teme koje su istraživane uključuju, između ostalog, općeniti pregled tehnologije i perspektive u budućnosti, preciznost i točnost, te mehanička svojstva otisaka, biotisak, usporedba sa konkurentskim tehnologijama brze izrade prototipova. Do unazad nekoliko godina svega se nekoliko znanstvenih radova bavilo problematikom 3D tiska s aspekta mogućnosti obojenja, a nijedan od njih to područje nije proučavao s grafičkog aspekta. Većina spomenutih radova bila je orijentirana na procesno inženjerstvo, baveći se uglavnom definiranjem i klasificiranjem 3D otisaka i različitim primjenama. Drugo značajno područje vezuje se uz bio-tisak i primjenu 3D tiska za biomedicinske primjene.

Svojstva boja 3D otisaka bila su predmet izučavanja u radovima kolega s Univeristy of the West of England, Faculty of Creative Arts, gdje je većina istraživanja posvećena reprodukciji boja i kreiranju pred-tiskovnih rješenja.

Stoga se, nakon početnog proučavanja literature, uvidjelo da predložena tema doktorske disertacije nije do sada bila istražena ili nije bila dovoljno istražena u javno dostupnim istraživačkim projektima i objavljenim radovima. Jedan od razloga za takvu situaciju je inovacija koju predstavljaju 3D materijali i sama tehnologija 3D tiska, kao i činjenica da je 3D tisak interdisciplinarnan proces kojeg je potrebno proučavati s više aspekata. Upravo zbog načina otiskivanja, smatra se 3D tisak treba proučavati kroz prizmu grafičke tehnologije. Također je činjenica da se pojedina područja procesa 3D tiska moraju proučavati iz perspektive grafičke tehnologije budući da ne postoji adekvatna alternativa ni u procesnom ni u mehaničkom inženjerstvu. Takva područja prvenstveno uključuju, no nisu limitirana samo na njih, reprodukciju boja, karakteristike obojenja, stabilnost boje i metodologiju mjerenja boje.

Osnovna ideja predložene doktorske disertacija bila je predmetom preliminarnih istraživanja u protekle dvije godine. Potreba za detaljnom analizom 3D materijala i otisaka koja bi se provodila kao istraživanja bazirana na grafičkoj tehnologiji, u osnovi je potekla iz industrije 3D tiska. Budući da su preliminarna ispitivanja pokazala veliki potencijal, teme istraživanja su proširene. S obzirom da je 3D tisak inovativna metoda s primjenom u grafičkoj tehnologiji i kako su istraživanja napredovala, simultano su se otkrivala područja koja je trebalo istraživati, opisivati i definirati. Istovremeno se pokazalo da se neke od metoda istraživanja, koje nisu bile originalno razvijene za primjenu u grafičkoj tehnologiji, mogu adekvatno primijeniti u istraživanjima konvencionalnih grafičkih materijala i da predstavljaju potencijal za primjenu u istraživanjima 3D materijala, te ih treba koristiti i u daljnjim ispitivanjima (Lozo, 2005; Holmstad et al., 2003; Holmstad, 2004; Muck, 2002; Reme and Kure, 2000; Vikman, 2004; Vikman and Sipi, 2003). S obzirom da se u slučaju 3D tiska zaista radi o interdisciplinarnom području, od prvih preliminarnih istraživanja razvija se bliska suradnja s institucijama i kolegama iz područja ispitivanja materijala, oblikovanja, drvne tehnologije, kemije i strojarstva. Sve to zajedno doprinosi razumijevanju predložene teme, osiguravajući istovremeno da se tema prouči sa svih relevantnih aspekata i da sva relevantna područja budu ispitana.

## **CILJEVI I HIPOTEZA**

Cilj disertacije je strukturna karakterizacija i definicija otpornosti i stabilnosti materijala za 3D tisak i 3D otisaka primjenom odabranih mikroskopskih i spretrofotometrijskih metoda, primjenom metoda slikovne analize, metoda za ispitivanje površinskih i mehaničkih svojstava, te metoda za ispitivanje trajnosti i otpornosti materijala.

Hipoteza disertacije je da je primjenom spomenutih metoda, uzimajući u obzir njihove mogućnosti i ograničenja, moguće razumjeti strukturne promjene, te postojanost i stabilnost boje materijala za 3D tisak i 3D otisaka.

Konačna svrha disertacije sadržana je u upotpunjavanju postojećih i stjecanju novih spoznaja tijekom interdisciplinarnog istraživanja kojima bi se definirao optimalan izbor metoda ispitivanja određenih svojstava 3D otisaka.

## **PRIKAZ ISTRAŽIVANJA, MATERIJALI I METODOLOGIJA**

Metodologija istraživanja predložene disertacije razvijena je na način da omogućiti ispunjavanje zadanih ciljeva i verifikaciju postavljene hipoteze. Znanje i iskustvo prikupljeno tijekom istraživanja literature tvorilo je podlogu za teoretski dio disertacije i pridonijeti će u definiranju okvira istraživanja za eksperimentalni dio. Nakon određivanja glavnih i sporednih pretpostavki istraživačkog rada, stečena znanja i iskustva su kako bi poslužila kao baza na kojima se, nakon diskusije rezultata istraživanja, temelje definicije zaključaka i predloženih rješenja.

Istraživanje literature i proučavanja postojećih znanstvenih radova poslužilo je kao okvir za određivanje mogućih prikladnih metoda i postupaka koje će biti provedene u istraživanju. Definirani su materijali koji tvore uzorke za eksperimentalni dio rada. Uz glavne metode i postupke potrebne u istraživanju, također su definirane uvodne mjerne metode za karakterizaciju materijala. Rezultati istraživanja obrađeni su i poslužili su kao temelj za diskusiju. Definirani su zaključci i optimalna rješenja, te su predložene smjernice. Cjelokupan rad je na kraju prikupljen u tezu i predstavljen.

Nakon istraživanja literature i postojećih istraživanja, te preliminarnih mjerenja, uočeno je da postoji široko područje unutar okvira 3D tiska koje zahtijeva interdisciplinarni pristup, s naglaskom na istraživanje s gledišta grafičke tehnologije, kako bi se karakterizirala važna svojstva novih materijala za 3D tisak i 3D otisaka. Definirana je potreba za cjelovitim istraživanjem s obzirom da postoje standardne istraživačke metode grafičke tehnologije, neke ne-tradicionalne metode koje su se pokazale izuzetno korisnima u istraživanjima u polju grafičke tehnologije, te će se njihovom sintezom s postojećim i znanjima koja su bila tek stečena određena je prihvatljivost navedenih metoda, te definirana determinatna svojstva materijala za 3D tisak i 3D otisaka.

U navedenom kontekstu, istraživanje je uključilo mikroskopske, spektroskopske, spektrofotometrijske, profilometrijske i novo razvijene postupke slikovne analize kako bi se karakterizirali osnovni materijali za 3D tisak, definirali određujuće procesne parametre koji definiraju strukturu otisaka. Neke od navedenih metoda korištene su za cjelovitu studiju trajnosti, stabilnosti i mehanizama starenja 3D otisaka. Kako bi se korištene metode i postupci mogli dokazati kao adekvatni za istraživanje materijala za 3D tisak i 3D otisaka,

rezultati mjerenja koji su njima bili dobiveni uspoređeni su međusobno i sa rezultatima postojećih istraživanja sličnog karaktera i područja primjene.

Glavne teme istraživanja definiraju se kako slijedi:

- Studija mehaničkih svojstava i unutarnje strukture 3D otiska ovisno o varijacijama u postupcima tiska i dorade.
- Studija strukture površine 3D otisaka ovisno o varijacijama u postupcima tiska i dorade koristeći konvencionalne metode grafičke tehnologije, te ostale primijenjene metode.
- Definiranje metodologije mjerenja boje, karakterizacija svojstava boje ovisno o postupcima tiska i dorade, te reprodukcija boje u 3D tisku.
- Studija trajnosti, stabilnosti i tijeka starenja svojstava boje 3D otiska, koristeći postupke prirodnog starenja, ubrzanog starenja te konvencionalne metode grafičke tehnologije i ostale primijenjene metode.

Uzorci za istraživanje i eksperimentalni dio definiraju se kao slijedeći materijali:

- Osnovni materijali za 3D tisak
  - i. Anorganski i organski materijali u obliku praha
  - ii. Tekuća veziva (tiskarske boje)
  - iii. Sredstva za doradu (infiltranti)
- Otisci dobiveni metodom 3D tiska

Uz definirane materijale na kojima se provodilo istraživanje, uključeni su bili i pomoćni materijali potrebni za određena mjerenja, kao što su smole, premazi, vodiči.

Unutar istraživačkog rada u disertaciji, koristile su se slijedeće mjerne metode i postupci, ovisno o svojstvima i promjenama koje se prate i informacijama koje je moguće njima dobiti.

Mikroskopske metode

- Optička mikroskopija, sa CMOS ili CCD kamerom, za promatranje površinskih struktura i presjeka
- SEM (skenirajuća elektronska mikroskopija)
- Stereo SEM površinskih struktura
- SEM presjeka

- Slikovna analiza slika dobivenih optičkom mikroskopijom, sa CMOS ili CCD kamerom, te SEM mikroskopijom, koristeći ImageJ program i ugrađene i posebno razvijene postupke

#### Spektroskopske i spektrofotometrijske metode

- FTIR spektroskopija
- Spektrofotometrija
- i. Sferna ( $d/8^\circ$  ili  $8^\circ/d$ ) geometrija
- ii.  $0^\circ/45^\circ$  ili  $45^\circ/0^\circ$  geometrija

#### Postupci za određivanje trajnosti i tijeka starenja

- Prirodno starenje pod određenim uvjetima, s/bez izlaganja svjetlu
- Ubrzano starenje, s/bez izlaganja svjetlu na Xenotest uređaj

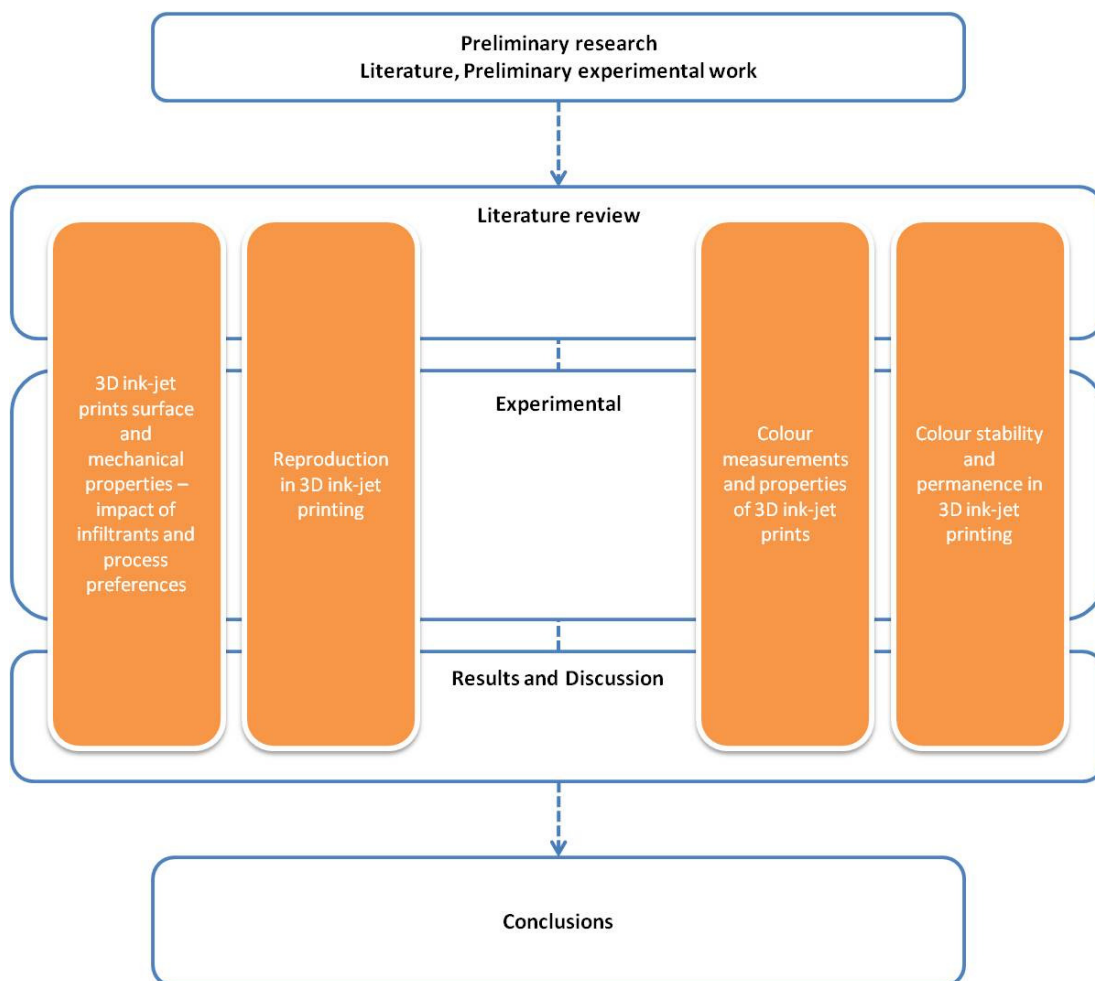
#### Mehanička ispitivanja

- Vlačna čvrstoća
- Tvrdća, metoda sa utiskivanjem kuglice
- Udarna čvrstoća (žilavost), Charpy metoda, bez ureza

#### Ostale metode

- Skenerske metode
- Laserska profilometrija
- Mehanička profilometrija, uređaj s ticalom

Osnovna shema istraživanja, sa pojedinim dijelovima i definiranim područjima istraživanja grafički je prikazana ispod.

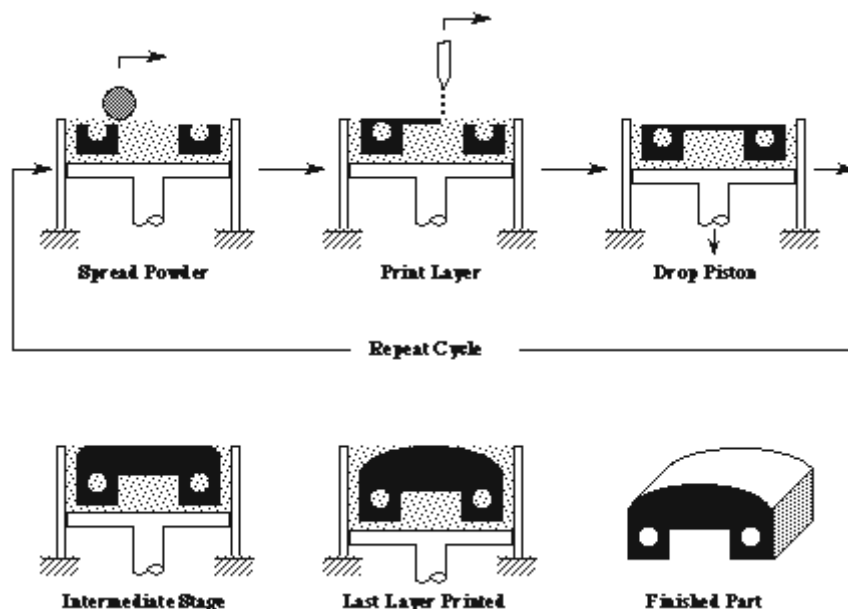




### 3D INK-JET TISAK

Brza izrada prototipova (RP) je generički izraz koji opisuje tehnologije kojima se mogu proizvesti fizički, realni objekti iz CAD podataka, tj. datoteka (Cooper, 2001). Pojmovi proizvodnja tijela čvrste slobodne forme (SFF) i aditivna proizvodnja također su često u upotrebi. RP se može koristiti u velikom broju industrija i tehnologija, te u brojnim aplikacijama. RP je snažna tehnologija u razvoju, koja se može koristiti u razne svrhe (Grimm, 2004) te njezina upotreba raste u posljednja dva desetljeća.

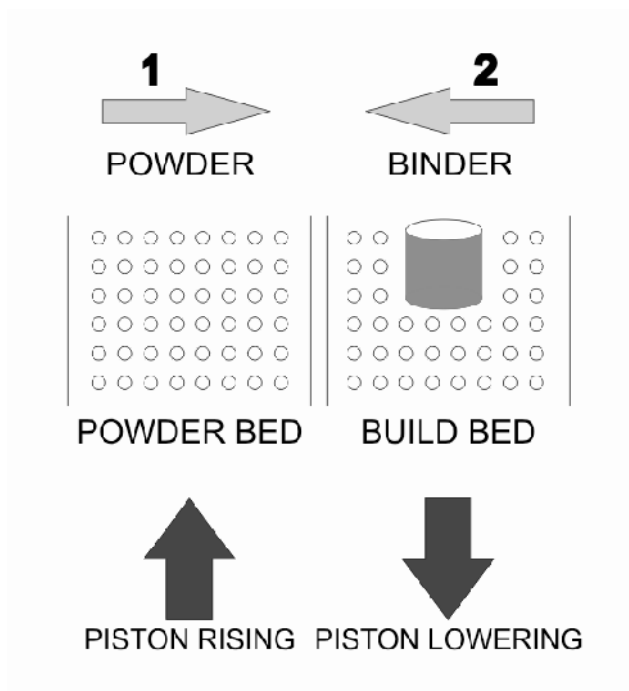
Trodimenzijski ink-jet tisak (3D tisak) jedan je od procesa brze izrade prototipova (RP), koji opisuje tehnologije koje koriste razne principe konvencionalnog ink-jet tiska kako bi proizvele fizičke objekte. Klasificira se kao tehnologija aditivne proizvodnje, s osnovnim materijalima u obliku praha i veziva. Sam proces baziran je na ink-jet tisku, gdje se prah nanosi u uzastopnim slojevima koji su selektivno spojeni („sljepljeni“) vezivom koje se nanosi ink-jet tehnikom (Grimm, 2003; Upcraft and Fletcher, 2003). 3DP™ temeljna tehnologija razvijena je i patentirana od strane Massachusetts Institute of Technology (MIT) u 1990-ima (Cima *et al.*, 1995) te licencirana određenim tvrtkama u raznolikim područjima uporabe.

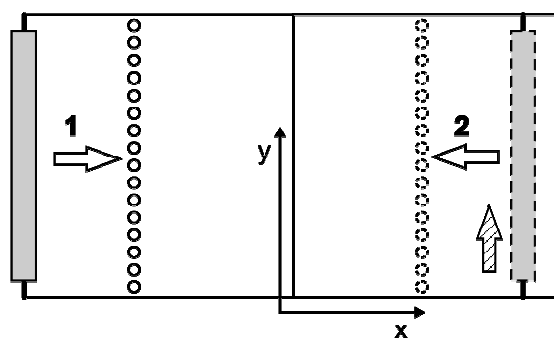


Slika 153. Shema proces 3D tiska, patentiranog od strane MIT-a ©3DP™ Laboratory, MIT

Jedna od tvrtki koje su preuzele licencu na korištenje je Z Corporation, čiji je fokus bio na konceptnim modelima i proizvodnji vizualnih modela. Godine 2008. Z Corporation je bio drugi najveći proizvođač strojeva za 3D tisk, po broju instalacija na svjetskoj razini (Wohlers, 2009). Tehnologija 3D tiska dalje je razvijana putem uključivanja boje, (Gibson and Ming, 2001), te korištenjem veziva u boji koja su omogućila i ponudila brzu izradu 3D modela u punom spektru boja.

Patenti koji opisuju generički proces 3D ink-jet tiska su US6146567, US5851465, US5807437, US5387380, US5204055. Procesna tehnologija je sama bazirana na ink-jet tisku, stoga što koristi sličnu metodu brizganja vezivnog materijala u formi kontroliranih kapljica, koje spajaju („sljepljuju“) čestice praha. Proces 3D tiska funkcionira tako da gradi objekte u slojevima, koji su poprečni presjeci definirane debljine dobiveni računalnim algoritmima iz CAD modela željenog objekta. Za proizvodnju svakog sloja, čestice praha su jednoliko nanosene na tiskovnu površinu te su selektivno spojene („sljepljene“) korištenjem vezivnog materijala. Potporni klip se zatim spušta, te se nanosi slijedeći sloj praha, praćen vezivnim materijalom. Proces se ponavlja dok željeni objekt nije završen. Slika 2 pokazuje shemu praha koji se nanosi putem sistema valjaka u smjeru strelice 1, dok se vezivo nanosi kroz tiskovne glave u povratnom pokretu, smjer strelice 2. Tisak počinje u smjeru prugaste strelice.





Slika 154. Shema procesa 3D tiska, pogled sa strane (slika gore) i pogled od gore (slika dolje) procesa trodimenzijskog tiska, prah se nanosi sistemom valjaka u smjeru strelice 1, a vezivo se nanosi kroz tiskovne glave u povratnom pokretu, smjer strelice 2. Tisak počinje u smjeru prugaste strelice.

Patenti koji su relevantni za specifične aplikacije 3D ink-jet procesa tiska za Z Corporation tehnologiju, za prah na bazi gipsa i vezivo na bazi vode, opisanu u ovoj disertaciji su US5902441, US6416850B1, US7435368B2, US7795349B2, US7550518B2, US7332537B2, US7087109B2, US6989115B2, US6610429B2, US6375874B1, US6007318, US20080187711A1.

Prvi korak u procesu kreacije 3D objekta je 3D računalni model, dobiven modeliranjem u 3D CAD software-u ili 3D skeniranjem postojećih objekata. 3D računalni model zatim je razrezan u software-u na specifičan broj slojeva, te je ta informacija poslana u 3D printer. Svaki pojedini virtualni sloj gradi se od osnovnih materijala, u ovom slučaju od praha na bazi gipsa i veziva, koja su otopine na bazi vode. Prah se nanosi i poravnava sistemom valjaka, dok se vezivo nanosi kroz tiskovne glave, jako slično kao što se nanosi boja u klasičnom 2D ink-jet tisku. U 3D ink-jet tisku u boji, boja se producira kombinacijom CMY ili CMYK veziva, uz dodatak prozirnog veziva. U vezivima u boji, koloranti su dio otopine veziva. Primjer 3D otiska u boji prikazan je na Slici 3.



Slika 155. Primjer 3D otiska u boji, model kuće, ©ZCorporation

Shema principa izrade za prethodnu generaciju modela printera, ZPrinter 510, može se opisati kao slijedeća. Tanki sloj praha nanosi se širenjem preko tiskovne platforme iz spremnika praha. U novijim verzijama ZCorp. Printera, kao u npr. Zprinter650, razlika je u načinu depozicije praha, zbog toga što se prah nanosi iz komore umjesto iz spremnika praha. Tiskovni sistem se tada pomiče preko sloja praha, nanoseći vezivo u uzorku poprečnog presjeka sloja 3D računalnog modela. Prah i vezivo reagiraju, tvoreći (djelomično) tvrdi sloj. Klip ispod tiskovne platforme tada spušta spremnik praha za debljinu sloja. Ciklus se ponavlja dok model nije gotov (ZCorp., 2009). Prah koji nije bio otisnut ostaje suh, te time podupire model koji se izrađuje. To znači da, za razliku od nekih drugih RP sistema, nema potrebe za specijalnim potpornim strukturama koje se grade uz model. Otisnuti 3D modeli se tada čiste od slobodnog praha i u većini slučajeva, završavaju s odgovarajućim sredstvom. Infiltranti su npr. Na bazi cijanoakrilata, epoksi smola, na bazi poliuretana, voska itd. i apliciraju se bilo uranjanjem, lijevanjem, četkom ili zračnim pištoljem. Infiltranti omogućavaju potrebnu mehaničku stabilnost 3D otisaka i unaprijeđuju boje.

Za 3D otiske u boji, 3D računalni model može imati boju naneseu na nekoliko načina: površine mogu biti direktno obojane ili boja može biti naneseu kao dio teksture. 3D digitalni podaci također moraju biti spremljeni kao tip datoteke koja, uz informaciju o geometriji, sadrži i informaciju o boji, na primjer kao .VRML, .3DS, .PLY, ili ZCorp. vlastita .ZPR datoteka. Osim u 3D CAD software-u, boja također može biti nanešena u ZPrint programu, ili specifično u ZEdit Pro programu, ZCorporation vlastitom software-u za tisak, također direktnim obojanjem površina ili aplikacijom teksture. Ako se boje nanose direktno, u 3D CAD software-u ili u ZPrint programu, odabiru se iz palete ili putem njihovih specifičnih koordinata, najčešće u RGB prostoru boja. 3D računalni model može imati boju naneseu na nekoliko načina, površine mogu biti direktno obojane ili boja može biti

nanesena kao dio teksture (slikovna datoteka, uobičajeno JPEG ili TIFF tip datoteke). Radi nekoliko operacionalnih faktora i faktora efikasnosti troškova, vezivo u boji se printa na otprilike posljednjih 10 slojeva objekta.

Trodimenzijski tisak je trenutno među najbržim RP tehnologijama koje postoje. Osim toga, sposoban je adaptirati se prema novo razvijenim materijalima i kompozicijama. To je omogućeno zbog fleksibilnosti procesa u prihvaćanju materijala i zbog činjenice da koristi različite tiskovne glave za različite materijale, što čini mogućim lokalnu kontrolu kompozicije materijala. Nadalje, u procesu gotovo ne postoje limitacije u geometriji dizajniranog dijela (MIT, 1989-2000). Danas je 3D tisak korišten u različitim poljima i područjima, kao u arhitekturi, inženjerstvu, medicini, razvoju proizvoda, konceptnom modeliranju, direktnom lijevanju, umjetnosti, itd. Također, korištenje 3D tiska u dizajnerskoj praksi proučavano je u doktorskoj disertaciji Evansa (Evans, 2002). Trodimenzijski tisak smatra se jednim od razvijajućih polja aplikacije standardnog ink-jet tiska (Le, 1998), i uzimajući u obzir tehnološki razvitak i u tehnologiji tiska i u razvoju materijala, jedan je od najdinamičnijih RP procesa.

Postoji nekoliko relevantnih karakteristika koje su poznate da utječu na preciznost tiska trodimenzijskog tiska. Neke od tih su: odabrana debljina sloja, količina zasićenja veziva (eng. powder/binder ratio), kontrola razlijevanje (eng. bleed control), relativna pozicija u spremniku za građenje, itd. Najinteresantije ovdje su razina zasićenja vanjske ovojnice (shell saturation level), koja određuje količinu veziva koja će biti nanescena i izražena je kao postotak, relativno prema standardnoj 100% kontroli razlijevanja, koja kompenzira za rasipanje veziva u sloj praha, orijentaciju površine i poziciju u spremniku za građenje. Absorpcija veziva u okolinu i neotisnute površine dovodi do potencijalnih gubitaka preciznosti i definicije. Količina rasipanja veziva i specifična orijentacija površine relevantne su za površine okrenute prema dolje zbog toga što uzrokuje lošiji izgled površina potencijalnim dodatnim razlijevanjem veziva u neotisnuti prah u okolini (Hackney, 2003). Ovo je također bilo proučeno u više detalja u doktorskoj disertaciji od Hackneya (Hackney, 2007).

Iako je 3D tisak u osnovi RP proces, generalni princip produkcije objekata putem brizganja veziva na slojeve praha i njegove mogućnosti boje stvorili su potrebu za istraživanjem s perspektive grafičke industrije. 3D tisak u boji bazira se, kao i konvencionalne tiskarske tehnologije, na suptraktivnom procesu miješanja boje i digitalnom rastriranju, što znači da se

primarne tiskarske boje cijan (eng. cyan), purpurna (eng. magenta) i žuta (eng. yellow) tiskaju tako da tvore kombinaciju jedinstvenih boja. U 3D tisku tiskovne boje su bazično veziva u boji, s kolorantima kao dijelovima otopine veziva, s dodatkom prozirnih veziva za tisak „bijeće“. U posljednje vrijeme, 3D sistemi koji uključuju i crno vezivo su predstavljeni. 3D proces tiska od Z Corporation koristi Hewlett-Packard tiskovne glave za nanošenje veziva, koje je na bazi vode i slično konvencionalnoj tiskarskoj boji za ink-jet tisak, sa specifičnim izmjenama u kompoziciji. Dodatak boje u 3D tisak otvorio je cijeli niz novih područja aplikacija izvan njegovog originalnog polja upotrebe, kao što su AEC i GIS, za tisak arhitekturnih (Gibson *et al.*, 2002) i modela krajolika, u zaštiti kulturne baštine, za digitalizaciju umjetnina kao što su kipovi i reljefi, za tisak replika i, relativno nedavno, u umjetnosti, gdje umjetnici koriste 3D tehnologiju za stvaranje umjetnina na bazi digitalnih objekata. Ova nova područja aplikacija stvorila su potrebu za istraživanjem svojstava boje 3D otisaka i otvorenih pitanja trajnosti i stabilnosti boje. Ova vrsta istraživanja definirala bi mogućnosti 3D tiska u boji, u odnosu na reprodukciju boja, uvela bi bolju kontrolu procesa reprodukcije u 3D tisku i proučila faktore koji utječu na trajnost i stabilnost boje 3D otisaka.

## **EKSPERIMENTALNI DIO**

Materijali i metode obuhvaćaju metodološki prikaz i opisuju sve osnovne materijale korištene u istraživanju, kao i testne forme i otiske i uzorke na kojima se provodilo ispitivanje, opisani su i kompjuterski programi koji su se koristili u istraživanju i obradi podataka, sve to u standardnim oblicima ili posebno proizvedeno ili prilagođeno za istraživanje u okviru disertacije. Rezultati i diskusija rezultata opisuju analizu rezultata, diskutiraju ih i identificiraju područja koja zahtijevaju daljnja istraživanja bazirana na dometima rezultata provedenih u okviru disertacije. U ovom poglavlju se također detaljno opisuju primijenjene i korištene metode za karakterizaciju različitih svojstava materijala za 3D tisak i 3D otisaka i s obzirom na specifičnosti materijala opisuju se mogućnosti primjene tih metoda i naglašavaju se njihova ograničenja.

Disertacija je razdijeljena u četiri područja istraživanja, prikazana objedinjenim sadržajem objavljenih radova temeljnih postavki disertacije. Područja su logičke cjeline i obuhvaćaju specifične teme istraživanja, u odnosu na svojstva i karakteristike 3D otisaka koja se proučavaju. Disertaciju čine navedena područja: Površinska i mehanička svojstva 3D ink-jet otisaka – utjecaj infiltranata i procesnih parametara; Reprodukcijska svojstva u 3D ink-jet tisku; Kolorimetrijska svojstva 3D ink-jet otisaka; Stabilnost boje i postojanost 3D ink-jet otisaka.

Površinska i mehanička svojstva 3D ink-jet otisaka – utjecaj infiltranata i procesnih parametara

S obzirom na strukturu 3D otisaka i njihova mehanička svojstva kao i svojstva površine, ispitivanja su fokusirana na utjecaj pojedine vrste infiltranta koji se koristi u postprocesiranju gotovih otisaka, kao što su fokusirana i na procesne parametre koji utječu na spomenute karakteristike. Neinfiltrirani uzorci otisaka kao i oni infiltrirani različitim sredstvima, kao što su cijanoakrilati, ili sredstva na bazi poliuretaana i epoksi smola, podvrgnuti su ispitivanjima mehaničkih i površinskih svojstava. Primijenjene su različite metode za ispitivanje mehaničkih svojstava, skenirajuća elektronska mikroskopija, optička mikroskopija, profilometrija i slikovna analiza, te se provelo vrednovanje i primjenjivost pojedine metode u karakterizaciji definiranih svojstava.

Reprodukcija u 3D ink-jet tisku

U pogledu reprodukcije u 3D tisku, istraživanje je bilo usmjereno na vrednovanje utjecaja više postavki vezanih uz tisak i materijale i njihov utjecaj na reprodukciju površinskih

elemenata 3D otisaka. Upotrijebljena je prilagođena i za potrebe ispitivanja proizvedena testna forma s razrađenim geometrijskim oblicima i slovima, te je podvrgnuta ispitivanjima metodama slikovne analize, uz posebno razvijene procedure ispitivanja. Na taj način je osigurano objektivno vrednovanje površinskih pojavnosti 3D otisaka. Za potrebe kvantificiranja utjecaja na konačnu reprodukciju u 3D tisku i vidljivu pojavnost tiskovnih elemenata, prilikom pripreme za tisak i samog tiska varirale su pojedine opcije procesa, kao npr. razlijevanje boje, ili količina zasićenosti bojom itd.

#### Kolorimetrijska svojstva 3D ink-jet otisaka

Vezano uz reprodukciju 3D otisaka u boji, istraživanje je provedeno na osnovi mogućnosti reprodukcije, definirajući metodologiju za kvantificiranje kolorimetrijskih svojstava 3D otisaka u boji, te uz identifikaciju utjecaja koji utječu na tu reprodukciju i kontrolu boje u 3D tisku. Također, u ovom poglavlju su opisane i nove i nadolazeće mogućnosti primjene 3D otisaka u boji. Za mjerenja su korištene standardne i posebno razvijene testne forme. Ispitani su neinfiltrirani uzroci kao i uzorci infiltrirani dvjema vrstama infiltranata, onih na bazi cijanoakrilata i epoksi smola, te su prikazane razlike u reprodukciji boja s obzirom na njih. Primjenom standardnih mjernih metoda u području grafičke tehnologije i u području analize grafičke reprodukcije definirana su ograničenja korištenja takvih metoda za uzroke 3D otisaka u boji. Time je određen smjer daljnjih ispitivanja reprodukcije na uzorcima 3D tiska u boji.

#### Stabilnost boje i postojanost 3D ink-jet otisaka

Stabilnost i postojanost 3D otiska u boji verificirana je podvrgavanjem uzoraka ubrzanom starenju uz primjenu xenonskog izvora svjetla, kao i procesu prirodnog starenja s različitim parametrima izloženosti uzoraka. Uzorci koji su proizvedeni, tj. otisnuti u boji za ovo specifično ispitivanje sadržavali su polja otisnuta različitim postotcima pokrivenosti površine boje, odnosno svake od boja, dizajniranih prema testnoj formi koji se koristi u testiranju standardnih ink-jet otisaka. Rezultati ispitivanja prikazuju usporedne vrijednosti za neinfiltrirane 3D otiske u odnosu na one infiltrirane sredstvima na bazi cijanoakrilata i epoksi smola. Stabilnost otiska u boji proučavana je ovisno o tonu boje, postotku pokrivenosti površine boje na otisku i načinu infiltracije otisaka. Značaj Također, u ovom dijelu detaljno je prikazana aplikativnost samih rezultata u područja primjene 3D otisaka u različitim područjima djelatnosti za koje je stabilnost boje otiska kao i postojanost prema svjetlu od iznimnog značaja, te tim više čini provjeru primjenjivosti standardnih mjernih metoda u ovoj domeni potrebnom bilo da se radi o prirodnom ili ubrzanom starenju otisaka.



## ZAKLJUČCI

Disertacija je pokazala cjelovitu studiju specifičnih svojstava 3D ink-jet materijala i otisaka koristeći postojeće i prilagođene metode karakterizacije uobičajeno korištene u grafičkoj znanosti i znanosti o materijalima i drugim povezanim industrijama. Rad je objasnio razne karakteristike 3D ink-jet materijala i otisaka, uključujući strukturu, reprodukciju boje, postojanost i stabilnost boje, efekte ubrzanog starenja i mehanička svojstva, kao što je uz to i ponudio generalne modele istraživanja te definirao metodologiju.

Što se tiče strukturnih, mehaničkih svojstava i svojstava površine 3D otisaka, pokazano je da vrsta sredstva za infiltraciju koje je korišteno za završnu obradu 3D ink-jet otisaka u velikoj mjeri doprinosi istraživanim svojstvima krajnjih otisaka. Završna obrada sa epoksi sredstvom rezultiralo je najvećom vlačnom čvrstoćom i udarnom čvrstoćom (žilavost), te tvrdoćom. Sredstvo na bazi cijanoakrilata doprinijelo je boljom vlačnom čvrstoćom i udarnom čvrstoćom (žilavost), u odnosu na sredstvo na bazi poliuretana. Sredstvo na bazi poliuretana, s druge strane, doprinijelo je boljim svojstvima tvrdoće krajnjih otisaka. Proučavanje površine dokazalo je da uzorci završno obrađeni sredstvom na bazi poliuretana imaju slične površinske karakteristike kao i neobrađeni uzorci, dok su epoksi i cijanoakrilatni infiltranti doprinijeli jednoličnijim površinama. Utjecaj ovih dvaju infiltranata na promjenu u dimenziji, kao i na moguće blokiranje finih udubina i reljefnih detalja krajnjih otisaka mora biti uzet u obzir prilikom proučavanja.

Što se tiče reprodukcije u 3D ink-jet tisku, evaluirana je za nekoliko moguće utjecajnih postavki tiska i materijala na određenom broju primjera elemenata. Predstavljen je utjecaj različitih postavki tiska i smještaj tiskovnih površina u različite pozicije u komori za građenje na reprodukciju, te su raspravljene morfološke karakteristike testnih elemenata, kao što su analizirane opisanim rutinama. Slikovna analiza proučena je kao alat za objektivnu analizu reprodukcije površinskih elemenata. Istraživanje slikovne analize kao tehnike za analizu objektivne reprodukcije pokazalo je da može biti vrijedan alat, uzimajući u obzir specifične parametre prilikom aplikacije u evaluaciji reprodukcije u trodimenzijskom ink-jet tisku. Predstavljeni rezultati diskutiraju i daju perspektivu na istraživanje interakcije materijala te definiraju faktore koji utječu na reprodukciju u specifičnom području trodimenzijskog tiska. Oni su od važnosti stoga što pokazuju kako principi trodimenzijskog tiska, sa parametrima specifičnima za proces, kao što su orijentacija objekta i površina,

kontrola razlijevanja i razina zasićenja, utječu i u kojoj količini, na reprodukciju i izgled površinskih elemenata 3D otisaka.

Što se tiče reprodukcije boje u 3D ink-jet tisku, trenutni kapaciteti boje i područja aplikacije boje u RP-u, i specifičnije u 3D ink-jet tisku su opisana. Diskutirani su metodologija mjerenja boje, svojstva boje, parametri prilikom reprodukcije boje i kontrola. Zbog karakteristika boje i površinske topografije 3D otisaka, korišten je sferni spektrofotometar ( $d/8^\circ$  mjerna geometrija). Završna obrada 3D otisaka, ovisno o korištenom sredstvu za infiltraciju, doprinosi na način da smanjuje vrijednosti svjetline i povećava vrijednosti krome (zasićenja boje). Kut tona boje se značajno ne mijenja. Infiltracija sa sredstvom na bazi cijanoakrilata, u usporedbi sa epoksi sredstvom, pridonosi višim vrijednostima krome (zasićenja boje), dok se vrijednosti svjetline i tone značajno ne mijenjaju. Posljedično, gamut (što označuje prostor boja koji se može reproducirati) 3D otisaka završno obrađenih cijanoakrilatnim sredstvom veći je nego kod infiltriranih epoksijem, iako postoje dijelovi gamuta koji su reproducirani vrlo slično. Istraživanje je pokazalo da se razvijene, postojeće standardne metode za mjerenje boje, monitoring i kontrolu, korištene u grafičkoj tehnologiji, tisku i znanosti o boji mogu, do određene granice, koristiti za proučavanje parametara novog područja 3D ink-jet tiska u boji. Također je identificirano da je potrebno daljnje istraživanje, posebno u područjima kao što su kontrola procesa reprodukcije boje i stabilnost boje za različite aplikacije.

Što se tiče stabilnosti boje i postojanosti 3D ink-jet otisaka, istraživanje je provedeno putem procedure ubranog starenja na bazi ksenonskog svjetla i procedure prirodnog starenja. Istraživanje je bilo koncentrirano na dobivanje osnovnih komparativnih podataka o netretiranim 3D otiscima i 3D otiscima završno obrađenim s dva odabrana infiltranta. Bazirano na korištenoj metodologiji, analiza je pokazala promjene u izgledu boje različito završno obrađenih 3D otisaka, a koje su se većinom mogle pripisati varijacijama u kromi, ili zasićenju, i svjetlini. Slijedom toga, gamut (prostor boja koji se može reproducirati) netretiranih i završno obrađenih 3D otisaka, bazirano na odabranim bojama, će varirati. Analiza stabilnosti boje na uzorcima podvrgnutim ekspoziciji ksenonskom svjetlu tijekom 72 sata je pokazala da vrsta završne obrade ima primjetan utjecaj na dobivenu boju. Diskutirana je razlika boje  $\Delta E$  između netretiranih i različito završno obrađenih 3D otisaka, kao i promjene specifičnih parametara, svjetline, krome i tona, te spektralnih krivulja. Primjećeno je da stabilnost boje proučavanih uzoraka varira i ovisna je o boji, postotku pokrivenosti površine bojom i završnoj obradi. Kod prirodnog starenja 3D otisaka, evaluiran je utjecaj

svojstava procesa i materijala 3D otisaka i odabranih uvjeta okoliša na stabilnost boje. Rad je koristio metodologiju koja je adaptirana iz mjerenja standardnih ink-jet otisaka. Kod uzoraka izloženih u uvjetima izlaganja (vanjsko i unutarnje), najveće vrijednosti razlike u boji primjećene su kod uzoraka izloženim filtriranom dnevnom svjetlu, a najmanje promjene kod izloženosti miješanom svjetlu u izložbenom ormariću, nepokriveni uzorci. Kod razlika u boji kod uzoraka izloženih u uvjetima pohrane, veće vrijednosti promjene u boji primjećene su kod uzoraka izloženih otvoreno (jako slabo svjetlo/bez svjetla), dok su manje promjene primjećene kod zatvorenih uzoraka. Proučavani parametri materijala i procesa koji imaju potencijalni utjecaj na stabilnost boje i ponašanje 3D ink-jet otisaka su vrsta završne obrade, uvjeti izlaganja i okoliša. Pitanja boje i stabilnosti 3D ink-jet otisaka će potencijalno postati važna kako 3D tisak bude ulazio u nova područja aplikacija, u kojima će objekti morati zadržati svojstva određenu količinu vremena. Na bazi prezentiranog i raspravljenog, mogu se definirati otvorena pitanja u istraživanju stabilnosti boje i postojanosti 3D otisaka, a uključuju razvoj adekvatne standardizirane metodologije za proučavanje boje i postojanosti, uključujući prirodno i ubrzano starenje; prediktivne testove; s definiranom greškom u reciprocitetu; daljnja obješnjenja mehanizama starenja i karakterizaciju svojstava 3D otisaka.

Cilj istraživanja bio je karakterizirati strukturu i definirati postojanost i stabilnost materijala za 3D tisak i otisaka primjenom odabranih mikroskopskih, spektrofotometrijskih metoda, metoda slikovne analize, metoda za evaluaciju površine, metoda za mehaničko ispitivanje i ispitivanje postojanosti. Ovo je izvršeno koristeći postojeća znanja i ona novo stečena tijekom interdisciplinarnog istraživanja, te su raspravljena optimalna rješenja i metode.

Može se zaključiti da je glavna postavljena hipoteza, da je koristeći gore spomenute metode, poštujući njihove prednosti i ograničenja, moguće shvatiti promjene u strukturi, boji i postojanosti materijala za 3D tisak i otisaka, dokazana.

## ZNANSTVENI DOPRINOS

Znanstveni doprinos disertacije primarno se sastoji u sveobuhvatnom istraživanju svojstava materijala za 3D tisak i 3D otisaka odabranim metodama za analizu strukturnih, površinskih, kolorimetrijskih svojstava kao i postojanosti, primjenom standardnih i prilagođenih metoda iz područja grafičke tehnologije i znanosti o materijalima. Ovo je od važnosti zbog toga što do sada nije pronađeno da postoji sveobuhvatno istraživanje, koje pokriva ova specifična pitanja koja su se pokazala kao relevantna za postojeće i nove aplikacije 3D ink-jet otisaka.

Znanstveni doprinos disertacije očituje se specifično u slijedećem:

Odabrane metode karakterizacije dokazane su i verificirane kao pogodne za istraživanje svojstava materijala za 3D tisak i 3D otiske.

Metode i procedure, unutar grafičke tehnologije i srodnih grana, za istraživanje odabranih karakteristika, strukture, površinskih, kolorimetrijskih svojstava su istražene i definirane.

Metodologija i optimalne procedure vrednovanja postojanosti 3D otisaka s naglaskom na trajnost boje 3D otisaka prema svjetlu pod uvjetima prirodnog i ubrzanog starenja su postavljene i definirane.

Kvantitativni i kvalitativni podaci o odabranim svojstvima 3D otisaka, boje i mehanizama trajnosti boje, su sistematski prezentirani i analizirani.

Znanstveni doprinos je također i u doprinosu stvaranju standarada za procedure provjere površinskih svojstava i postojanosti 3D otisaka.

# **APPENDICES**

## CURRICULUM VITAE



### Europass Curriculum Vitae



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#### Work experience

Dates	March 2010 – till present
Occupation or position held	Scientific novice Researcher/Project manager
Main activities and responsibilities	(Inter)national projects work Project related research and literature review work Reports, presentations, workshop and meetings preparation and work Correspondence with target groups Supervision of students
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Type of business or sector	Higher education/Institute

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Main activities and responsibilities	EU funded projects –preparation of application proposals, technical advising, correspondence Participating in and organizing seminars about funding possibilities Outgoing/incoming exchange students Outgoing/incoming teaching staff Regular correspondence with other IROs and relevant institutions Preparation of proceedings, brochures
Name and address of employer	University of Zagreb, Faculty of Graphic Arts, Getaldiceva 2, 10000 Zagreb, CROATIA
Type of business or sector	Higher education
<b>Education and training</b>	
Dates	March 2006 – till present
Title of qualification awarded	PhD/Dr.sc. Candidate
Principal subjects/occupational skills covered	Graphical engineering Three dimensional ink-jet printing PhD thesis title “Structure, Surface and Permanence Properties of Three Dimensional Printing Materials”, expected completion in 2010 Material characterization of three dimensional inkjet printing – currently focused on colour related aspects of 3D prints, prints permanence and colour stability. Colour characterization of prints finished with different infiltrants – colour difference, gamut, colour shifts. Instrument-related aspect of colour measurements of 3D prints. The present research activities also include mechanical testing, accelerated aging of the material, analysis of surface topography with non-destructive methods etc.
Name and type of organisation providing education and training	Postgraduate doctoral study Graphical Engineering University of Zagreb, Faculty of Graphic Arts
Dates	2000 – 2006
Title of qualification awarded	Dipl. ing. graph. techn./mag. ing. techn. graph.
Principal subjects/occupational skills covered	Graphical technology Diploma thesis title “Quality Control of Offset Printing Process using Control Charts”
Name and type of organisation providing education and training	University of Zagreb, Faculty of Graphic Arts
<b>Personal skills and competences</b>	
Mother tongue(s)	<b>Croatian</b>

Other language(s)

Self-assessment

European level (\*)

**English**

**Italian**

Understanding		Speaking		Writing
Listening	Reading	Spoken interaction	Spoken production	
Proficient user	Proficient user	Proficient user	Proficient user	Proficient user
Basic user	Basic user	Basic user	Basic user	Basic user

Social skills and competences

Experience in communicating with people, working in team, intercultural skills

Organisational skills and competences

Experience in organising project meetings, seminars about international project funding possibilities, organisation of preparing applications for EU funded projects

Technical skills and competences

Experience in using colour measurement and analysis software, using and developing image analysis procedures, conducting laboratory material testing

Computer skills and competences

Competent with Microsoft Office, Internet applications, graphic prepress software, image analysis software

Driving licence

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## PUBLICATIONS

Levlin, Grossmann, Read, Ervasti, Hooimeijer, Lozo, Sain-Armand, Cochaux, Faul, Ringman, Stawicki, Bobu, Miranda, Blanco, Stanić: "The Future of Paper Recycling in Europe: Opportunities and Limitations", PITA, Bury, UK, 2010

Lozo, Stanić, Muck, Jamnicki, Mahović Poljaček: "Three-Dimensional Ink-jet Prints: Impact of Infiltrants", Journal of Imaging Science and Technology, 52/5, IS&T, USA, 2008

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Barbarić Mikočević, Jamnicki, Stanić, Muck, Lozo: "Recycling of Varnished Offset Printed Packaging Prints", Celulosa i hartia, Bulgaria, 2008

Stanić, Lozo: "Permanence and Color Stability in 3D Ink-Jet Printing", International Conference Digital Fabrication 2010 (collocated with Non-impact Printing 26 Conference), Austin, TX, USA, 2010

Stanić: "Printed 3D coloured objects: 3D ink-jet prints colour properties and colour stability", CREATE 2010 Conference, Gjøvik, Norway, 2010

Stanić, Lozo: "Image Analysis in 3D Printing Reproduction", 5th International Symposium on Novelties in Graphics (5. simpozija o novostih v grafiki), Faculty of Natural Sciences and Engineering, Ljubljana, Slovenia, 2010

Hooimeijer, Vos, Stanić: "Smart and Slim Supply-Chains, Integrated Intelligent and Communicative Technologies for More Efficient and Effective Supply-Chains", 5th International Symposium on Novelties in Graphics (5. simpozija o novostih v grafiki), Faculty of Natural Sciences and Engineering, Ljubljana, Slovenia, 2010

Starešinič, Muck, Stanić, Klanjšek Gunde: "The Use of Image Analysis for Evaluation of Organic Electronics Printability", 5th International Symposium on Novelties in Graphics (5. simpozija o novostih v grafiki), Faculty of Natural Sciences and Engineering, Ljubljana, Slovenia, 2010

Stanić, Lozo: "Colour and Permanence Issues in 3D Ink-jet Printing", 33rd International Convention MIPRO, GVS – Grid and visualisation systems, Opatija, Croatia, 2010

Stanić, Walters, Lozo: "Image Analysis of Surface Elements Reproduction Quality in 3D Ink-jet Printing", International Conference Digital Fabrication 2009 (collocated with Non-impact Printing 25 Conference), Louisville, KY, USA, 2009

Stanić, Lozo, Baučić: "3D Printing – Effect of Object Orientation on Print Elements Reproduction", Impact 6 Print Conference, Bristol, UK, 2009

Walters, Parraman, Huson, Stanić: "3D Printing in Colour: Technical Evaluation and Creative Applications", Impact 6 Print Conference, Bristol, UK, 2009

Muck, Hladnik, Stanić: "Analysis of Print Quality with ImageJ", 4th Symposium about Novelties in Graphics (4. simpozija o novostih v grafiki), Faculty of Natural Sciences and Engineering, Ljubljana, Slovenia, 2009

Muck, Starešinič, Stanić, Klanjšek-Gunde: "Evaluation of Organic Electronics Printability by Image Analysis", Large-area, Organic & Printed-Electronics Convention, LOPE-C 2009: The Future of Organic and Printed Electronics, Frankfurt, Germany, 2009

Stanić, Lozo, Lovrić: "Three-dimensional Printing and Graphic Technology: How Do They Fit In?", Management of Technology, Steps to Sustainable Production International Conference, Šibenik, Croatia, 2009

Stanić, Lozo, Muck, Jamnicki, Kulčar: "Color Measurements of Three-dimensional Ink-jet Prints", International Conference Non-impact Printing 24 Conference (collocated with Digital Fabrication 2008 Conference), Pittsburgh, PA, USA, 2008

Paulenka, Kulčar, Stanić: "Evaluation of Color Reproduction and Print Quality Elements of Ink-jet Prints on Uncoated Paper", 2nd International Student Conference Print and Media Technology: PrintingFutureDays 2007 (Iarigai), Chemnitz, Germany, 2007

Lozo, Stanić, Jamnicki, Muck: "3D Printing as a Function of 2D Printing", International Conference Digital Fabrication 2007 (collocated with Non-impact Printing 23 Conference), Anchorage, AK, USA, 2007

Jamnicki, Stanić, Barbarić Mikočević, Muck, Lozo: "Multi-stage Chemical Flotation of Food Packaging Prints", International Symposium Present and Future of Paper Recycling Technology and Science, Bilbao, Spain, 2007

Milčić, Zjakić, Stanić: "Some Possibilities in Analysis of Influential Characteristics of Print Quality", 10th International Conference on Printing, Design and Graphic Communications Blaž Baromić, Novi Vinodolski, Croatia, 2006

Hladnik, Stanić, Muck: "Analysis of the Paper Formation and Periodic Structures by FFT Processing", ImageJ User & Developer Conference, Centre de Recherche Public Henri Tudor, Luxembourg, Luxembourg, 2008

Stanić, Muck, Hladnik, Lozo: "Application of ImageJ in Printing Technology – Use of Macros for Automation of Analysis Procedures", ImageJ User & Developer Conference, Centre de Recherche Public Henri Tudor, Luxembourg, Luxembourg, 2008

Stanić, Jamnicki, Muck, Lozo: "The Interpretation of IGT Fluff Test by Image Analysis", International Meeting of Slovene Paper Industry 2007, Bled, Slovenia, 2007

Stanić: "3D Colour Printing", Forum of New Technologies, Zagreb, Croatia, 2009

Stanić: "Analysis of Selected Physical Properties of Linerboards in Food Contact Materials", COST E48 STSM Report, COST E48 Project Meeting, Iasi, Romania, 2008

Stanić: "Characterization of 3D Prints", 0.99 International Student Seminar, Zagreb, Croatia, 2008

Stanić, Kulčar: "3D Prints – Color Measurement Methodology", 0.99 International Student Seminar, Zagreb, Croatia, 2008

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Lozo, Stanić: "The Universal Value of the Museum Item: Postage Stamp Printing", Univerzalnost jednog muzejskog predmeta, Poštanski muzej, Zagreb, Croatia, 2007

Stanić: "Kodovi na kvadrat", Poslovni dnevnik, Zagreb, Croatia, 2010

## PARTICIPATION IN EU PROJECTS

COST E48 “The Limits of Paper Recycling”

CREATE “Colour Research for European Advanced Technology Employment”

Cornet AIP – Competence Platform, Active and Intelligent Packaging  
“Development of tools to communicate advanced technologies on active and intelligent packaging to meet the needs and trends in food processing and retailing and to improve the knowledge transfer especially for SMEs”

## RECEIVED SCHOLARSHIPS & TRAINING COURSES

COST Short-Term Scientific Mission “Analysis of Selected Physical Properties of Linerboards in Food Contact Materials”, granted by COST Action E48, August 2008, VTT, Otaniemi, Helsinki, Finland, COST-STSM-E48-03866

Training Course “New Ways to Use Print Technology...On Paper”, granted by CREATE, October 2008, School of Creative Arts, UWE, Bristol, UK

Training Course “New Ways to Use Print Technology...On Paper”, granted by CREATE, October 2008, University of Ulster, Belfast, UK

Training Course “Communicating Colour”, granted by CREATE, May 2009, Pannon University, Veszprem, Hungary

Training Course “Colour Heritage and Conservation”, granted by CREATE, October 2009, Università Degli Studi Di Milano, Italy

“CREATE 2010 conference”, granted by CREATE, June 2010, Gjøvik University College, Gjøvik, Norway

## LIST OF FIGURES

Figure 1. Scheme of 3D printing process, patented by MIT ©3DPTM Laboratory, MIT .....	19
Figure 2. Scheme of 3D printing process, side view (upper figure) and top view (bottom figure) of three-dimensional printing process, powder is distributed by the roller in the arrow 1 direction, while the binder is applied from the printheads in the return motion, arrow 2 direction. The printing starts in the striped arrow direction. ....	21
Figure 3. Example of a 3D colour print, model of a house, ©ZCorporation .....	22
Figure 4. 3D printed model of city of Zagreb, ©Ib-procadd.....	32
Figure 5. 3D printed model of Sečovlje Salina, ©Ib-procadd.....	32
Figure 6. 3D printed model of Šaleška Valley, displayed at the site near town of Gaberke, ©Ib-procadd .....	33
Figure 7. Flat view (z axis not shown) of the samples printed in x-y and y-x directions. The powder is distributed in a layer in the arrow 1 direction onto the print area. In the return direction, the binder is ink jetted onto the layer of powder. The ink jetting of the binder is in the arrow 2 direction. Bar A shows orientation of prints printed in y-x direction, bar B in the x-y direction. ....	39
Figure 8. Graphical representation of the samples set up for printing .....	39
Figure 9. Workflow of the material mechanical testing sample production .....	40
Figure 10. Samples set up in pre-print software, ZPrint .....	40
Figure 11. Printing, print carriage in motion, ZPrinter 510 .....	41
Figure 12. Printing, process in progress, ZPrinter 510.....	41
Figure 13. Printing, process in progress, top view, ZPrinter 510.....	41
Figure 14. Post-processing, gross de-powdering, ZPrinter 510 .....	42
Figure 15. Printed and de-powdered prints, prior to infiltration .....	42
Figure 16. Post-processing, example of finishing by dipping in infiltrant.....	42
Figure 17. Designed test plate with elements.....	46
Figure 18. Prepared test target file was applied as a texture on a test plate, visualization of the test plate in ZPrint software .....	47
Figure 19. Graphical representation of the second group of samples set up, different positions in the build bed, numbers correspond to the labels in Table XX .....	47
Figure 20. RGB profile of a sample microscope image of a 5 mm circle and its background, showing the difference in values of channels for the element and the background; the bottom image shows the line of the RGB profile .....	53
Figure 21. RGB histograms of element (a) and background (b) of the sample image of a 5 mm circle, showing differences in channels; R channel histogram top, G channel histogram middle, B channel histogram bottom .....	54
Figure 22. Close up of the samples images, border (outline) obtained by applying threshold overlaid on the original microscope image .....	54
Figure 23. Image analysis procedure, illustration; original microscope image (a), mask of analyzed element (b), outline of analyzed element overlaid on the original microscope image (c) .....	55
Figure 24. Designed test plate with elements.....	56
Figure 25. Image of the constructed test plate, with test elements on its surface .....	57
Figure 26. Graphical presentation of the test plates set up in the build bed.....	57
Figure 27. Example of printed and post-processed test plate.....	58
Figure 28. Effect of scanning resolution on the obtained outline of the analyzed elements; resolutions 200, 300, 600, 1200, 2400 dpi, from left to right .....	59
Figure 29. Image processing and analysis routine .....	61
Figure 30. 3D prints used for measurements, non-infiltrated sample presented.....	62
Figure 31. The ECI 2002 V test target, with Group 1 patches circled .....	63

Figure 32. Images from the ECI 2002 V test target which were fitted onto the sample plates .....	63
Figure 33. Image of the CMY+ target, with the before described patches .....	64
Figure 34. Coloreye XTH (© X-Rite).....	66
Figure 35. Test chart designed and used as a texture .....	69
Figure 36. Test plate designed for colour and stability measurements .....	70
Figure 37. SEM image of NF sample cross section (20X).....	77
Figure 38. SEM image of NF sample cross section (35X).....	77
Figure 39. SEM image of CY sample cross section (20X) .....	77
Figure 40. SEM image of CY sample cross section (35X) .....	78
Figure 41. SEM image of EX sample cross section (20X) .....	78
Figure 42. SEM image of EX sample cross section (35X) .....	78
Figure 43. SEM image of PU sample cross section (20X).....	79
Figure 44. SEM image of PU sample cross section (35X).....	79
Figure 45. Optical microscope image of NF sample surface cross section (25X), bar denotes 0.5 mm .....	80
Figure 46. Optical microscope image of CY sample surface cross section (25X), bar denotes 0.5 mm .....	80
Figure 47. Optical microscope image of CY BK sample surface cross section (25X), bar denotes 0.5 mm .....	80
Figure 48. Optical microscope image of EX sample surface cross section (25X), bar denotes 0.5 mm .....	81
Figure 49. Optical microscope image of PU sample surface cross section (25X), bar denotes 0.5 mm .....	81
Figure 50. Tensile strength plot .....	82
Figure 51. Impact strength plot .....	82
Figure 52. Brinell hardness plot.....	83
Figure 53. SEM image of NF sample surface (200X).....	84
Figure 54. SEM image of CY sample surface (200X) .....	84
Figure 55. SEM image of EX sample surface (200X) .....	85
Figure 56. SEM image of EX sample surface (200X), example of filled in surface.....	85
Figure 57. SEM image of PU sample surface (200X).....	85
Figure 58. (a) SEM images of samples NF, PU, CY, EX; from top to bottom image, respectively (30X); (b) surface plots of samples NF, PU, CY, EX; from top to bottom image, respectively .....	87
Figure 59. Surface plots of sample NF.....	88
Figure 60. Surface plots of sample CY .....	88
Figure 61. Surface plots of sample EX .....	89
Figure 62. Surface plots of sample PU.....	89
Figure 63. Scanner (left), SEM Stereo (right).....	90
Figure 64. SEM Stereo, height map (left), Laser profilometry (right).....	90
Figure 65. Surface plots from the same areas as measured on the SEM stereo images (left) and laser profilometry (right).....	91
Figure 66. Stereo SEM image of ZB1_01 .....	92
Figure 67. Stereo SEM image of ZB1_02.....	92
Figure 68. Stereo SEM image of ZB2_01 .....	92
Figure 69. Stereo SEM image of ZB2_02.....	93
Figure 70. Stereo SEM image of ZB3_01 .....	93
Figure 71. Stereo SEM image of ZB3_02.....	93
Figure 72. Stereo SEM image of ZB4_01.....	94
Figure 73. Stereo SEM image of ZB4_02.....	94
Figure 74. Stereo SEM image of ZB5_01.....	94
Figure 75. Stereo SEM image of ZB5_02.....	95

Figure 76. Stereo SEM image of ZB6_01.....	95
Figure 77. Stereo SEM image of ZB6_02.....	95
Figure 78. Stereo SEM image of ZB7_01.....	96
Figure 79. Stereo SEM image of ZB7_02.....	96
Figure 80. Stereo SEM image of ZB8_01.....	96
Figure 81. Stereo SEM image of ZB8_02.....	97
Figure 82. Stereo SEM image of BB1_01.....	97
Figure 83. Stereo SEM image of BB1_02.....	97
Figure 84. Stereo SEM image of BB2_01.....	98
Figure 85. Stereo SEM image of BB2_02.....	98
Figure 86. Stereo SEM image of BB3_01.....	98
Figure 87. Stereo SEM image of BB3_02.....	99
Figure 88. Stereo SEM image of BB4_01.....	99
Figure 89. Stereo SEM image of BB4_02.....	99
Figure 90. Stereo SEM image of BB5_01.....	100
Figure 91. Stereo SEM image of BB5_02.....	100
Figure 92. Stereo SEM image of BB6_01.....	100
Figure 93. Stereo SEM image of BB6_02.....	101
Figure 94. Stereo SEM image of BB7_01.....	101
Figure 95. Stereo SEM image of BB7_02.....	101
Figure 96. Stereo SEM image of BB8_01.....	102
Figure 97. Stereo SEM image of BB8_02.....	102
Figure 98. Images showing the sample element, 5 mm circle, captured by microscope (a) and the same area marked on the scanned image of the test plate surface (b).....	104
Figure 99. Reproduction of character “E”, from the first group of samples, printed in different relative xyz positions in the print bed, scanned images, sample num marked in the bottom right corner.....	105
Figure 100. Image showing close up of the outline of the thresholded element (right) overlaid on the original microscope image and the outline of an “ideal” circle with the diameter of 5 mm (left).....	106
Figure 101. Reproduction of characters “E”, 24 pt and 12p, downwards and upwards facing surfaces; C_D sample (a), C_U sample (b), scanned images, 1200 dpi.....	108
Figures 102. and 103. Original scan, binarized mask and outlines of the analyzed elements from test plates 1 and 2, left and right.....	109
Figures 104. and 105. Original scan, binarized mask and outlines of the analyzed elements from test plates 3 and 4, left and right.....	109
Figures 106. and 107. Original scan, binarized mask and outlines of the analyzed elements from test plates 5 and 6, left and right.....	110
Figure 108. Original scan, binarized mask and outlines of the analyzed elements from test plate 7.....	110
Figure 109. Total area (mm <sup>2</sup> ) of all elements on test plates, green columns; average circularity of all elements on test plates, purple columns.....	111
Figure 110. Diagram showing the direction of application of powder (green arrow) and binder (blue arrow) on test plates 3, 4, 5 and 6.....	112
Figure 111. Perimeter (mm) of all elements on test plates.....	112
Figure 112. Diagram showing the “staircase” effect in processes that used layers as basic element (slojevi = layers; efekt stepenica = staircase effect; teoretska površina objekta = theoretical area of object; z os = z axis).....	113
Figure 113. Gamut representation of 3D prints infiltrated with cyanoacrylate agent (Z-Bond).....	117
Figure 114. Gamut representation of 3D prints infiltrated with epoxy-based agent (Z-Max).....	117

Figure 115. Some similarly represented colours of both gamuts, Z-Bond gray, Z-Max pink .....	118
Figure 116. Differences in reproduction between samples finished with two infiltrants, patches with highest $\Delta E$ marked .....	119
Figure 117. Screen visualization of measured C colour from various CMY+ test plates....	120
Figure 118. Printed sample test plates from ECI 2002 V, Z-Max (left), non-infiltrated (centre), Z-Bond (right) respectively .....	121
Figure 119. Custom colour charts, infiltrated with cyanoacrylate (left), non-infiltrated (middle), infiltrated with epoxy resin (right) .....	121
Figure 120. Example of custom designed and printed test colour charts in the form of plates .....	122
Figure 121. ZCorp. Sample Color Chart, example tile, preview .....	123
Figure 122. ZCorp. Sample Color Chart, option with large tiles, preview .....	123
Figure 123. ZCorp. Sample Color Chart, option with small tiles, preview.....	123
Figure 124. Custom designed 3D colour test object, preview .....	124
Figure 125. Example of printed custom designed 3D colour test object, with the respective GretagMachbeth ColorChecker patches shown (Walters, XX) .....	124
Figure 126. Example of custom designed colour test object, 3D printed colour test blocks (Walters, XX).....	125
Figure 127. CIELab plot of NF, CY and EX samples coloured patches.....	127
Figure 128. L*C(ab) plot of NF, CY and EX samples coloured patches.....	128
Figure 129. L*a* plot of NF, CY and EX samples coloured patches .....	128
Figure 130. L*b* plot of NF, CY and EX samples coloured patches.....	129
Figure 131. $\Delta E_{2000}$ values compared to $\Delta E_{cmc}$ values plot of NF, CY and EX samples coloured patches.....	129
Figure 132. $\Delta E$ values of 100% ink coverage colour patches for NF, CY and EX samples	130
Figure 133. $\Delta E$ colour difference, NF sample, by the percentage of ink coverage.....	131
Figure 134. $\Delta E$ colour difference, CY sample, by the percentage of ink coverage .....	131
Figure 135. $\Delta E$ colour difference, EX sample, by the percentage of ink coverage .....	132
Figure 136. $\Delta L$ , $\Delta C$ and $\Delta H$ parameters, NF sample .....	133
Figure 137. $\Delta L$ , $\Delta C$ and $\Delta H$ parameters, CY sample .....	133
Figure 138. $\Delta L$ , $\Delta C$ and $\Delta H$ parameters, EX sample.....	133
Figure 139. 100% ink coverage colour patches, changes in chroma (increases from centre towards edge, as shown e.g. in the direction of the arrow) and hue (angles are changed along the sample circle, dotted line) .....	134
Figure 140. a*b* plot of initial and exposed colour patch, C 100% ink coverage, visualization of patch also shown, for NF, CY and EX samples .....	134
Figure 141. a*b* plot of initial and exposed colour patch, M 100% ink coverage, visualization of patch also shown, for NF, CY and EX samples .....	135
Figure 142. a*b* plot of initial and exposed colour patch, Y 100% ink coverage, visualization of patch also shown, for NF, CY and EX samples .....	135
Figure 143. Example of spectral reflectance curves, C, M and Y colour patches, NF sample; dotted line initial sample values, full line sample after exposure values .....	136
Figure 144. Example of spectral reflectance curves, C, M and Y colour patches, CY sample; dotted line initial sample values, full line sample after exposure values .....	137
Figure 145. Example of spectral reflectance curves, C, M and Y colour patches, EX sample; dotted line initial sample values, full line sample after exposure values .....	137
Figure 146. Spectral reflectance curves of W patch, NF, CY and EX samples; dotted line initial sample values, full line sample after exposure values .....	138
Figure 147. Display conditions, mixed natural/artificial lighting, under glass cabinet.....	139
Figure 148. Office/display conditions, mixed artificial/natural lighting, no coverage .....	139
Figure 149. Display conditions, sunlight behind window, no coverage, north facing .....	140
Figure 150. Display conditions, sunlight behind window, no coverage, south facing.....	140

Figure 151. Storage conditions, no coverage .....	141
Figure 152. Storage conditions, sealed .....	141



## LIST OF TABLES

Table 1. Table of Abbreviations.....	39
Table 2. Printing set up, same printing preferences, different xyz positions .....	48
Table 3. Printing set up, different printing preferences.....	48
Table 4. Set up of the test plates in the build bed.....	57
Table 5. List of Abbreviations .....	67
Table 6. Colour and percentage of area coverage of specific patches of test chart.....	69
Table 7. Exposure conditions for natural aging in display and storage set-up.....	73
Table 8. Results of image analysis, sample element characteristics, 5 mm circle, samples printed in different relative xyz positions .....	105
Table 9. Results of image analysis, sample element characteristics, circle with diameter of 5 mm, samples printed with different printing preferences .....	106
Table 10. a) to c) Measured and calculated 3D colour data.....	115
Table 11. a) to c) 3D prints colour differences .....	116