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Three-Dimensional Ink Jet Prints—Impact of Infiltrants

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Abstract. *Among various rapid prototyping methods, some are based on a conventional ink jet printing process. The three-dimensional (3D) printing process discussed uses powder material as a substrate and liquid binder as an ink. Three-dimensional prints are usually finished by an infiltrant agent prior to the final use. Epoxy resin, cyanoacrylate, and a polyurethane-based agent are regularly used. The impact of infiltrant type on the selected mechanical properties and surface appearance of 3D ink jet prints was the focus of the study. The type of infiltrant agent used greatly contributes to the discussed final properties of the prints. As a case study, the application of 3D printing in conventional printing technology was studied. The 3D prints can be used as a negative matrix for conventional photopolymer flexographic printing plate production. It is important that the applied infiltrant does not influence the 3D print dimensions, as well as provide the optimum combination of mechanical and surface properties. © 2008 Society for Imaging Science and Technology.*
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INTRODUCTION

A three-dimensional (3D) printing process is a novel and propulsive way of digital fabrication. 3DP™ core technology has been developed and patented by the Massachusetts Institute of Technology (MIT) in the 1990s[1] and licensed to various companies in diverse fields of use. 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[2] 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.

This case study was based on the 3D printing of the matrix/mold for the production of a conventional printing plate for flexographic printing, in relation to finding the optimum combination of mechanical and surface properties of 3D prints used.

3D PRINTING PROCESS

The 3D printing technique is a type of rapid prototyping (RP) process. It is classified as an additive RP process. The process technology itself is based on ink jet printing; it employs a similar method of jetting a binder material in a form of droplets with controlled volume in order to join powder particles together. In a 3D color printer, the colorants are a part of the binder solution. The 3D printing process functions by building parts in layers, which have been sliced by computer algorithms from the CAD model of the desired object. For the production of each layer, the powder particles are evenly distributed over the printing surface and selectively joined by the image-wise deposited 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. It is then raised out of the unbound powder and usually finished with the appropriate agent.[3]

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.[4] Nowadays, 3D printing is used in various fields and areas, such as architecture, engineering, medicine, product development, concept modeling, direct casting, fine art, etc. Three-dimensional printing is considered one of the emerging application fields of standard ink jet printing,[5] and in consideration of the technological progress both in printing technology and materials research, it is one of the most dynamic RP processes.

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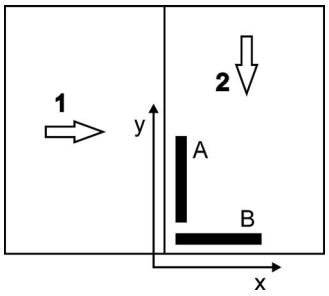

Figure 1. Flat view (*z* axis not shown) of the samples printed in *x-y* and *y-x* directions. The powder is distributed in a layer in the arrow 1 direction onto the print area. In the return direction, the binder is ink jetted onto the layer of powder. The ink jetting of the binder is in the arrow 2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

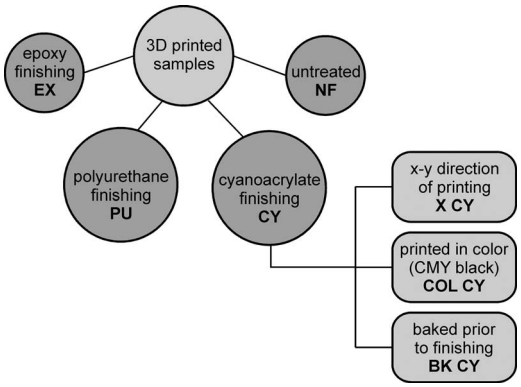

Figure 2. Workflow of the material mechanical testing sample production.

EXPERIMENTAL

Materials and Methods

Mechanical Properties

Characteristics addressed in the 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/Contex Spectrum Z510/Cx printer. The prints were made with the Zp130 high performance composite material[6] and Zb58 binder,[7] 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 1), one printed in additive synthesis black color (Table of Abbreviations), and one baked at approximately 60°C for 30 min. All three subgroups were later finished with the cyanoacrylate infiltrant and tested (Figure 2). A summary of the samples and the abbreviations used to designate them is given in Table I.

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,[8] 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.[9] Hardness of materials was tested by the ball indentation method (Brinell), in accordance with ISO 2039-1:2001 (E) standard.[10] 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.

Table I. Table of Abbreviations.

NF	Not finished, green
CY	Cyanoacrylate finishing
EX	Epoxy finishing
PU	Polyurethane-based finishing
CY COL	Color (R 0 G 0 B 0)
CY X	*x*–*y* direction of printing
CY BK	Baked prior to finishing, for 30 min at 140° F

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

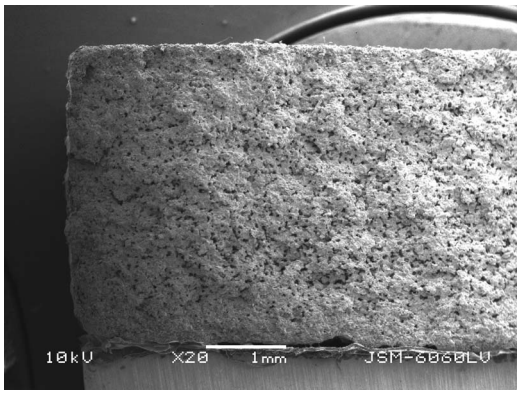

Figure 3. SEM image of EX sample cross section (20X).

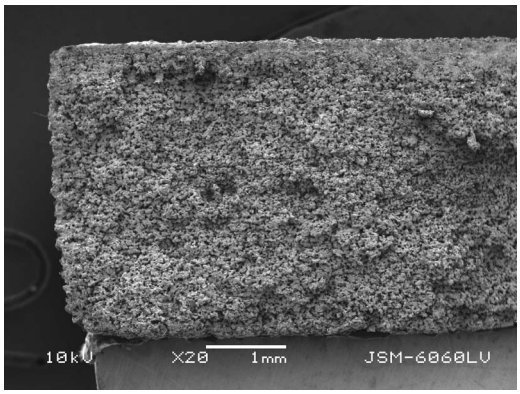

Figure 4. SEM image of PU sample cross section (20X).

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[11] 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.

RESULTS AND DISCUSSION

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. As an example, SEM images of EX and PU samples can be seen in

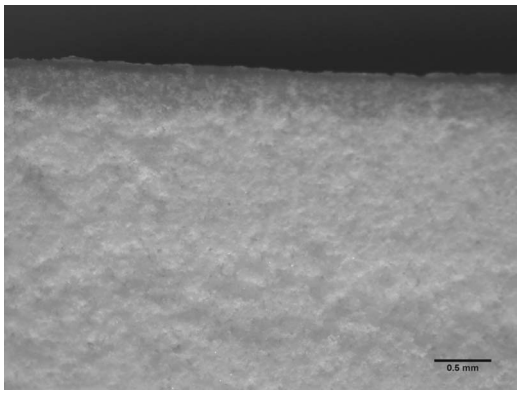

Figure 5. Optical microscope image of CY sample surface cross section (25X).

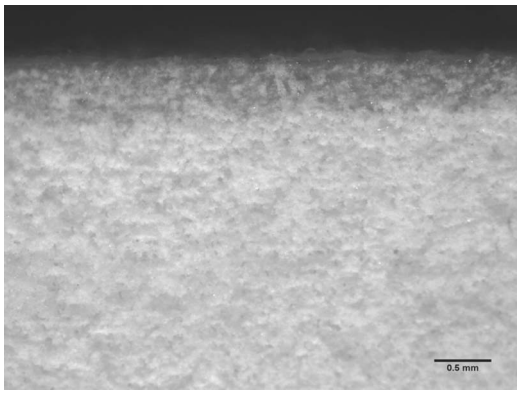

Figure 6. Optical microscope image of CY BK sample surface cross section (25X).

Figures 3 and 4, 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,[12] 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 Figures 5 and 6, 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.

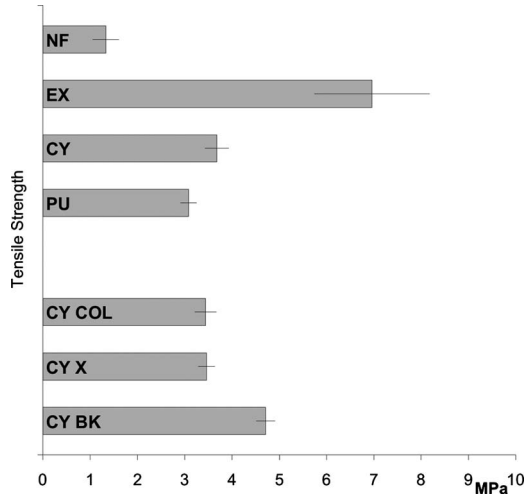

Figure 7. Tensile strength plot.

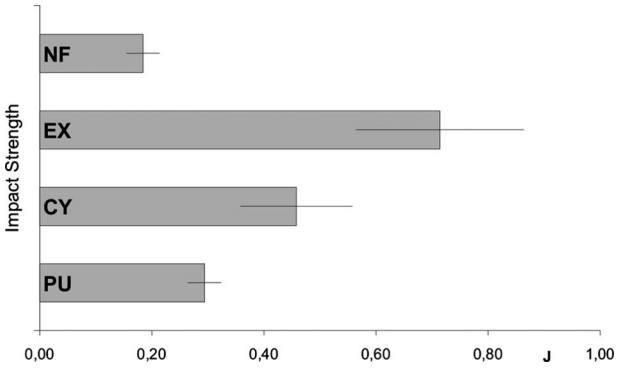

Figure 8. Impact strength plot.

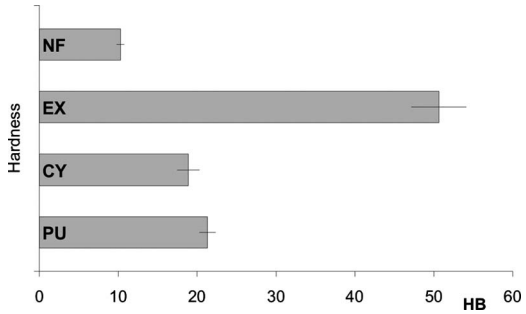

Figure 9. Brinell hardness plot.

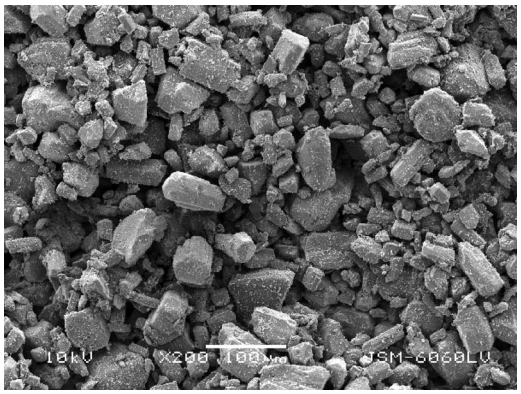

Figure 10. SEM image of NF sample surface (200X).

Figure 7 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 color 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.[13] 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 color.

The plot of the results for impact properties of samples is shown in Figure 8. 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 9 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.

Surface Properties

Surface of prints was evaluated visually, with the optical microscope and with the SEM. As an example, SEM images of the surfaces of NF and PU samples can be seen in Figures 10 and 11, respectively. Lower magnification SEM images of all the samples [Figure 12(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

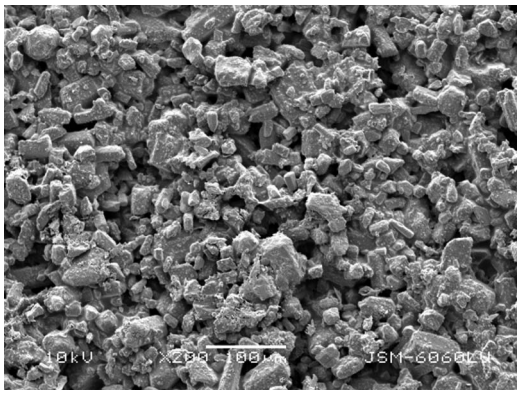

Figure 11. SEM image of PU sample surface (200X).

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 (Figs. 10 and 11).

The SEM images of NF, EX, CY, and PU samples surface [Fig. 12(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 Fig. 12(b). They represent the SEM images from Fig. 12(a), with the z-axis of the graph corresponding to the gray value of a pixel.

CASE STUDY—USE OF 3D PRINTS IN PRODUCTION OF A FLEXOGRAPHIC PRINTING PLATE

The application of 3D printing in conventional printing technology was studied. Considering existing research and patents that deal with more complicated methods of producing a standard printing plate with the ink jet process technology,[14,15] we investigated the possible use of 3D prints in production of a printing plate for a conventional flexography. Both methods of utilizing the 3D prints in printing plate production for flexography, one being direct printing and other being negative matrix printing, were considered. For a negative matrix printing method, the more widely used combination of plaster-based powder and water-based binder with the addition of an appropriate infiltrant, was considered. After evaluation of both methods, it was decided to continue with the attempt to produce the printing plate via 3D printing of the negative matrix, into which a conventional UV curable photopolymer would be poured, cured and later removed (Figure 13).

Conventional Flexography Printing Plate

Flexography is a direct printing process that derives from the conventional letterpress printing technique. It employs a flexible and resilient printing plate, whose thickness is in the range of millimeters. Currently, printing plates for flexography are made from rubber or polymer material. Printing plates are made by molding a matrix, by photographic/chemical process, or by laser engraving (CTP process). Rubber printing plates are mostly made by molding an embossed casting mold with natural rubber or by direct ablation of the printing plate by laser etching of the nonprinting areas. Photopolymer printing plates are the most commonly used flexography printing plates and are currently produced by photographic/chemical process or by one of the laser-based computer to plate processes. Unlike in other conventional printing processes, printing plates for flexography vary in hardness and thickness, and are chosen in accordance with the specific process characteristics. Their thickness varies from about 0.015 in. up to as much as 0.250 in., with the relief depth from about 0.008 to 0.120 in.. Having in mind various substrates and final uses of flexography prints, a wide variety of inks are used. It is important that the printing plate material must be inert when in contact with the ink, e.g., it must not swell in contact with ink or be etched by the ink.[16]

Employing a 3D Print as a Mold for Platemaking

The 3D file of the matrix was constructed in SolidWorks 3D modeling software. The design of digital test form consisted of various graphical and typography elements in various line widths and sizes (Figure 14).

The 3D plate matrix was printed on the Z510/Cx printer, from the ZP130 powder and ZB58 binder, with the layer thickness set to 0.0035 in. The relief depth of flexography printing form obtained by 3D printed matrix was 0.0394 in. and overall thickness was 0.0787 in. The printed matrix was finished with the chosen infiltrant, as explained below. The matrix was filled with the liquid photopolymer material (photosensitive polyurethane elastomeric material, VE 108 *W* 55) regularly used in the laboratory for production of rubber stamps and flexographic printing plates. The photopolymer was poured into the matrix and

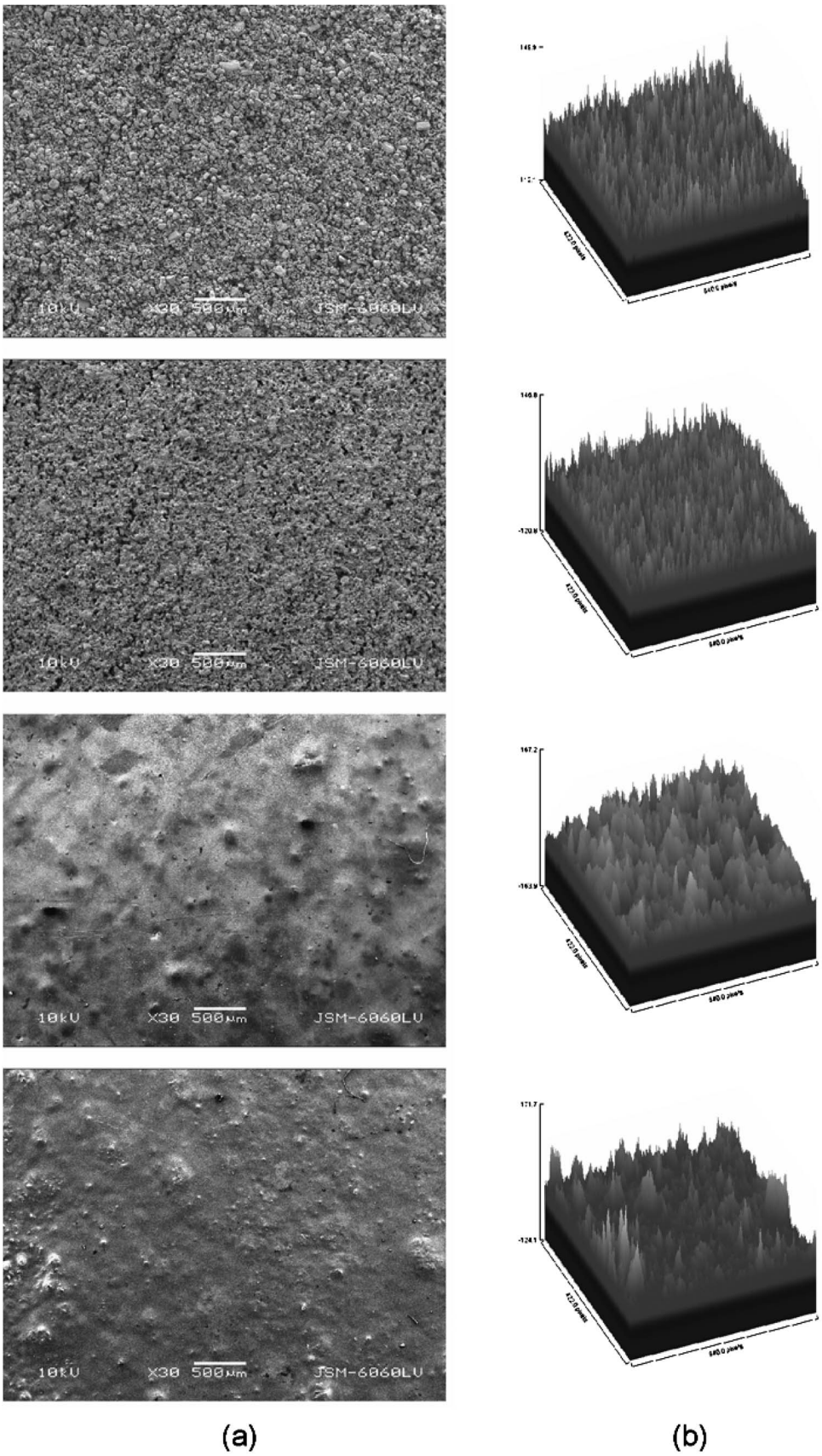

Figure 12. (a) SEM images of samples NF, PU, CY, EX; from top to bottom image, respectively (30X); (b) surface plots of samples NF, PU, CY, EX; from top to bottom image, respectively.

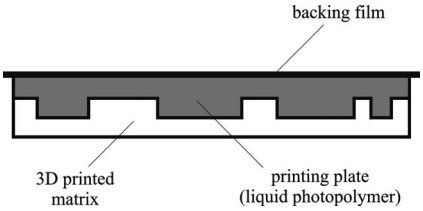

Figure 13. Scheme of utilizing 3D print as a negative matrix in photopolymer printing plate production.

Figure 14. Digital test form design elements.

the thin polyester foil was placed on the top, in order to serve as a backing film for the support and easy handling of the finished printing plate. The matrix was then placed into the platemaker apparatus (AZ 1500 N3), which employs an UV-A light emitting source in order to cure the photopolymer material. The matrix with the photopolymer filling was cured for 250 sec in main exposure (back exposure) and 600 sec in postexposure. The printing plate was than peeled out of the matrix.

The results of the mechanical properties testing combined with surface inspection, serve as decisive elements for the choice of the infiltrant to be used in production of the matrix for the printing plate. It was established that the appropriate infiltrant agent cannot change the dimensions of the 3D prints, must offer a smooth surface finish, and should not block fine details by filling the small cavities; it must also secure easy handling of the finished matrix (good mechanical properties).

For finishing of the printed matrix, all three infiltrant agents tested above were considered. The epoxy agent, although having the best mechanical characteristics, was discarded as it was established that a certain amount of it can sometimes stay on the surface of the prints and, thereby, change the surface dimensions and uniformity. The polyurethane finished samples have a somewhat rougher surface than the samples finished with the cyanoacrylate agent. On the other hand, on some occasions, some traces of leftover cyanoacrylate agent were noticed on the surface of the 3D prints, although the amount was nearly negligible. Polyurethane infiltrated samples have slightly lowered tensile and impact strength, and their hardness measurement results were only slightly better than for the cyanoacrylate finished samples. Considering these not very distinct differences, both cyanoacrylate and polyurethane agents could conceivably be used as infiltrants in this application. Photopolymer printing plates obtained from the polyurethane finished matrix and from the cyanoacrylate finished matrix were produced with all the elements of the original design conserved. The printing plate produced from the cyanoacrylate finished matrix displayed more uniform surface elements, but the

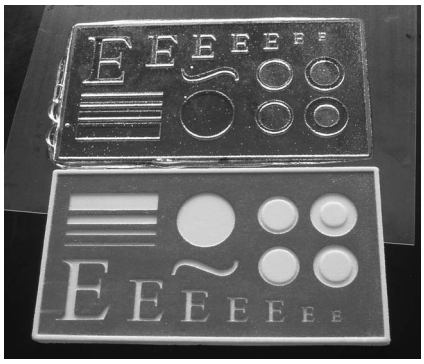

Figure 15. Three-dimensional printed matrix (bottom) and photopolymer printing plate made via mold method (top).

printing plate produced from the polyurethane finished matrix showed more precise and detailed reproduction. An illustration of the 3D printed matrix and obtained photopolymer printing plate is shown in the Figure 15.

New materials for rapid prototyping processes, including 3D printing, have been extensively researched. This is of great importance for the second suggested method for utilizing 3D printing in conventional printing technology, the direct printing of the printing plate. This method of producing the printing plate for flexography would have to use rubber or elastomeric materials of specific properties in order to achieve the criteria needed for practical usage of printing plates produced in this manner. When discussing the parameters of new materials for 3D printing that could be used for direct printing of flexography printing plates, the materials will have to fulfill a number of criteria important to printing plates when used on a press such as abrasion resistance, durometer hardness, resilience, and solvent resistance (reaction of the plate material with the ink components).[17] The method discussed in this work, the 3D printing of mold/matrix, can also benefit from new materials being researched, since the aim is to produce a material that will have the desired mechanical properties without the need for finishing and, at the same time, would produce objects with excellent dimensional accuracy (resolution) and smooth surface, which will not require posttreatment. Pfister et al. recently presented a material with these characteristics, which was used on a 3D printer.[18]

CONCLUSIONS

Type of infiltrant agent used for postprocessing of the ink jet-based 3D prints greatly contributes to the investigated mechanical and surface properties of the final prints. Finishing with an epoxy agent resulted in the highest tensile and impact strength and hardness. A cyanoacrylate agent ensureed 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.

The attempt to produce a 3D print as a printing plate matrix to serve as a mold for the UV curable photopolymer showed that the available materials and processes serve as a good starting point for this method of producing printing plates. Having in mind the results of the tested mechanical properties, as well as the requirements for 3D printed flexography printing plate matrix production, we concluded that the choice of infiltrant agent for the finishing of 3D printed matrix needs to focus on finding the optimum combination of the mechanical properties and surface roughness of the material.

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