Mechanical and Thermal Properties of 3D-Printed Thermosets by Stereolithography

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Mechanical and thermal properties of stereolithography 3D-printed thermoset polymers have been investigated with an emphasis on understanding how the layer-by-layer printed morphology affects their physical properties. Due to the finite UV penetration depth into the photocurable resins in the stereolithography, the 3D-printed polymers resulted in periodic surface undulation. The length scale of the surface undulation periodicity is determined by the 3D printing processing parameter of slice thickness (Δt) and has a strong effects on the mechanical and thermal properties of the 3D-printed thermoset polymers. Upon decreasing the Δt from 200 μm to 50 μm, the 3D printing produces more frequent UV curing of crosslinked layers along the printing direction to result in the increase of Young’s modulus and the more pronounced high glass transition peak in dynamic mechanical analysis. However, when the Δt is further decreased to 25 μm, its Young’s modulus is lower than the 50 μm printed samples. This decrease is attributed to the weaker inter-layer crosslinking, when there are not enough less-cured monomers to promote the crosslinking between densely crosslinked layers during the successive layer-by-layer photopolymers in stereolithography. 

Keywords: Stereolithography, Slice Thickness, Inter-layer crosslinking

1. Introduction

Photo-initiated polymerization is repeated layer-by-layer in a confined geometry with controlled thickness in stereolithography (SLA) for 3D printing polymers with network structures [1-4]. Recent advances in SLA include the enhancement of printing speed by eliminating resin mixing steps after the photocuring of each layer [5-7]. To take the advantage of additive manufacturing and versatility of designing and preparing 3D-printed polymer parts, the SLA relies on the crosslinking of multifunctional liquid monomers into thermoset polymers. Typically, acrylic or epoxy monomers are used as monomers and the UV LED light sources are irradiated to the photo resins by either moving laser beam or digitized light pixels using digital light processing (DLP) [8-11]. In this study, we are using the scanning laser-based SLA 3D printer to study how the physical properties of the SLA polymers depend on the photo-curing conditions.

The study of mechanical and thermos-physical properties of 3D printed polymers is closely related to the end use of the 3D printed parts [12-15]. The mechanical and thermal properties of the SLA 3D-printed polymers are greatly influenced not only by the monomer materials and formulation, but also by the SLA 3D printing parameters, such as printing orientation [16,17] and layer thickness [18,19]. Since the photo resins are not fully crosslinked after the 3D printing, the post UV-cure can be used to further change the mechanical properties of specimens [20-22]. To take the advantages of unique capability of 3D printing to produce polymer samples with complex geometry and shape, recent studies include the 3D printing of complex architected interpenetrating material structures having triply periodic minimal surfaces, such as diamond, gyroid and Fecher Koch, for the study of structure-property-relationships in polymer materials [23].

In this study, we used the laser-based SLA 3D printing of photocurable resins and investigated the effect of 3D printing process conditions on the mechanical properties and glass transition
temperatures of polymers with network structures. Specifically, we used Formlabs™ clear resin and Formlabs Form 1+ 3D printer to prepare tensile specimens for evaluation of mechanical properties at different printing layer thickness, Δt, which is also known as “slice thickness.” Mass and UV-vis spectrometry was performed to analyze the photo curable resin. Real time FTIR was used to study the photocuring kinetics upon the continuous irradiation of UV light. For the analysis of surface structure, optical and electron microscopy technique was used to reveal the layer-like surface morphology. Finally, the glass transition temperatures of the 3D printed specimens with different slice thickness were investigated using dynamic mechanics analysis.

2. Stereolithography (SLA) 3D printing resins and tensile specimen

The SLA 3D printing of specimen starts with slicing of Computer Aided Design (CAD) model upon selected layer thickness setup. The photo-crosslinking is repeated to layer-by-layer of specimen with defined shape while support plate is elevating from resin bath, as described in Fig. 1. The properties of printed specimen are affected by slice thickness and direction of printing.

To study the mechanical and thermal properties of 3D printed-crosslinked thermosets by SLA method, commercial clear resin (GPCL04, Formlabs) was investigated as model material. The chemical formula of resin was analyzed by MALDI-TOF mass spectrometry (UltraFlex III – Daltonics

Fig. 1. Schematic diagram of inverted laser SLA 3D printing to represent the layer-by-layer printing of specimens.

Autoflex, Bruker). The trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile and sodium trifluoroacetate were used as matrix and cationization salt, respectively. As shown in Fig. 2, differences of m/z, Δ(m/z), between successive distinct peaks were observed at a value of 114 g/mol, which indicate the resin contains ethyl methacrylate-based oligomers. The inset shows UV-vis absorption spectra (Lambda 750S, PerkinElmer) of a resin in methanol with 1 wt% of concentration, where background absorption from methanol was subtracted. Three different peaks were observed in UV-vis spectra at wavelength (λ) = 360, 380, and 402 nm, that correspond to absorption wavelength
of photo-initiators/photosensitizers in the photocuring resin for crosslinking reaction in SLA. From these results, it is expected that the photo-absorption of the Formlabs clear resin will be effective enough to trigger the photo-curing in the SLA 3D printer using 405 nm UV LED.

Real-time FTIR studies using Nicolet-iS-50 FTIR spectrometer, ThermoFisher Scientific with an attenuated total reflection (ATR) sample stage (PIKE Technologies, Inc.) were conducted to monitor the crosslinking kinetics and monomer conversions during photo-initiated polymerization of the clear resin. IR spectra were collected every 0.5 seconds over 60 seconds, with 0.482 cm\(^{-1}\) interval and optical velocity of 0.4747 cm/s using liquid nitrogen cooled mercury cadmium telluride (MCT-A) detector. Resin was prepared onto the ATR diamond crystal, then covered with a quartz plate. Thickness of resin was controlled using 100 μm-thick polyimide film spacer that placed between the ATR diamond crystal and the quartz plate. To simulate actual 3D printing of Form 1 printer, UV LED source (LX500, OmniCure) with 385 nm wavelength LED UV head was used. The intensity of UV irradiation was measured as 50 mW/cm\(^2\) by a LED calibration radiometer (LX500 OmniCure). As shown in Fig. 3, absorbance of characteristic peaks of -CH=CH\(_2\) stretching and twisting at 1640 and 810 cm\(^{-1}\) were decreased with increasing time at the early stage of UV irradiation. This spectra change indicates fast consumption of double bonds for crosslinking in methacrylate base resin. About 35% of monomer conversion was attained after 1 min UV irradiation using the following equation:

\[
\text{Conversion (％)} = (1 - \frac{A_{10}}{A_{0}^{10}}) \times 100 \quad (1)
\]

where \(A_{10}\) and \(A_{0}^{10}\) denote the absorbance and initial absorbance at 810 cm\(^{-1}\), respectively. The remained double bond from incomplete conversion can be utilized for further crosslinking by post UV-treatment.

Fig. 3. Real time FTIR using ATR stage for Formlab clear resin when UV LED (wavelength = 385 nm, intensity = 50 mW/cm\(^2\)) is continuously irradiated on the resin for a time span of 1 min.

Fig. 4. (a) Schematic diagram to represent the orientation of 3D printing layer planes that are perpendicular and parallel to the tensile elongation direction. (b) Perpendicular and parallel Young’s modulus as a function of printing layer thickness, \(\Delta t\).
3. Slice thickness effects on mechanical and thermo-physical properties

For the study of mechanical properties of SLA printed polymers, ASTM D638 tensile test method with type IV dimensions of specimen was selected. An inverted SLA printer (Form 1+, Formlabs) was used for printing of all the tensile specimens, using 405 nm wavelength UV LED laser. The resin was poured directly into the print bath and stirred well, prior to printing.

Perpendicular and parallel orientation of 3D printing layer planes to the tensile elongation direction were applied while printing of dumbbell-shaped object, as described in Fig. 4(a). Printed objects were tested by Universal Testing Machine (Instron 5969) with an elongation rate of 2 mm/s. Figure 4(b) shows Young’s modulus results as a function of printing layer thickness (slice thickness), Δt. The Δt is the physical gap between optical window and elevated support, where the photocurable liquid resins are confined and cured for the crosslinking of each layer that are repeated for the construction of 3D printed objects. It is controlled by the discrete elevation height increment of the sample support stage for the layer-by-layer 3D printing in SLA. More frequent UV curing process upon decreasing Δt from 200 μm to 50 μm induced higher crosslinking density along the printing direction and increased Young’s modulus. This is due to the formation of more densely spaced crosslinked layers at smaller Δt printing conditions.

However, when sample was printed with the shortest Δt of 25 μm, an expected decreased Young’s modulus was observed. It is attributed to the insufficient inter-layer crosslinking, when there are not enough monomers available between each crosslinked layers. When Δt = 25 μm, less-cured monomers are not sufficient enough to interlock the printed domains to result in less efficient stress transfer along the sample for lowering modulus. It is also interesting to notice that similar Young’s modulus values were observed for 3D printed samples with different printing layer orientation (i.e. $E_\perp \sim E_\parallel$). This is due to a pronounced stochasticity and heterogeneity of crosslinking density within each printed layer. Such a non-uniform uniform crosslinking with each layer induces many defects cannot serve as an effective rigid plane when being stretched parallel to the layer planes. Furthermore, compared to DLP 3D-printed object, there is no voxel effect from square pixels in SLA 3D-printed object. Therefore, similar modulus can be obtained during tensile test for laser-SLA printed specimens with different printing orientations.

Figure 5 shows thermos-physical property of 3D SLA-printed specimens with different slice thickness that characterized by Dynamic Mechanical Analysis (DMA 850, TA Instruments). The specimens were prepared with dimension of 35 mm × 12 mm × 3 mm and all the data was measured under nitrogen atmosphere on single cantilever mode. Temperature ramp was performed at a rate of 1.5 °C/min between 35 °C and 200 °C. Oscillation amplitude was 30 μm and frequency was set to 1.0 Hz. Bimodal glass transition temperatures were observed for all the samples, except when Δt = 200 μm. The lower and higher glass transition temperatures relate to the less and more crosslinked regions of the samples. This is due to the finite UV curing depth causing less curing of monomers located farther away from the optical window, when the photocuring is repeated at a physical gap of Δt during SLA 3D printing. Since there exists more dense spacing of photocured layers at lower Δt, more pronounced DMA signal is observed at higher glass transition temperature. This relates to that the overall degree of crosslinking is higher at lower Δt. It remains unclear why there is only a single $T_g$ suggesting lower crosslinking density for the sample prepared with Δt = 200 μm, and further studies on the photocuring conditions of laser power and scanning speed and spacing are needed.

4. Surface morphology of SLA 3D-printed specimens

The inter-layer of specimens depending on Δt was characterized by surface morphology analysis.
Figure 6 shows optical microscopy images of 3D-printed specimens with different $\Delta t$. Distinct lamellar-like surface morphology was observed from the repeated formation of densely crosslinked printing layer when the samples are being printed at $\Delta t$ from 200 $\mu$m to 50 $\mu$m. However, the distinct boundary between layers was not observed from the optical microscopy for specimens, when $\Delta t$ was at 25 $\mu$m. This is probably due to the insufficient amount of less cured monomer regions to produce the surface undulation structures for the sample with $\Delta t = 25 \mu$m. The scanning electron microscopy (SEM, Versa, FEI) was performed at an accelerating voltage of 5.0 kV to complement optical microscopy images. Specimens were coated with 0.5 nm of gold and palladium (60% and 40%, respectively) using plasma sputter (Hummer, Technics). Again, less distinct layer boundary was observed for specimen prepared at $\Delta t = 25 \mu$m (Fig. 7). SEM further revealed that the surface texture of flow lines that matches well along printing direction for all the samples. These surface morphology analysis supports the hypothesis on lower Young’s modulus for specimen having 25 $\mu$m of $\Delta t$. This is due to the weakened inter-layer crosslinking to lower the efficient stress transfer between cured printed layers.

5. Conclusion
The 3D printing layer orientation and slice thickness effects on tensile mechanical properties of the SLA 3D-printed Formlabs clear resin were investigated. When the printing layers are oriented parallel and perpendicular to the tensile elongation directions, there is no significant difference in Young’s modulus. This is because the laser scanning within each slice thickness produced stochastic and non-uniform layer of crosslinked domains that cannot exhibit stiffness under tensile deformation, particularly when being elongated parallel to the layer plane direction. Distinct lamellar-like surface morphology with undulating surface topography was observed. The length scale of surface undulation matched well with the 3D printing slice thickness. The lack of distinct surface undulation for samples with $\Delta t = 25 \mu$m suggested the weak interlayer crosslinking, because there are insufficient monomers to further crosslink and form bridge networks between the densely crosslinked printing layers. Such insufficient interlayer crosslinking resulted in lowering Young’s modulus for its weakened ability to transfer stress under elongation. DMA of the SLA samples typically showed two distinct glass transition temperatures to consistently support the formation of alternating regions of crosslinked chain networks with more and less dense crosslinking.

Acknowledgement
This work was supported by Korea Evaluation Institute of Industrial Technology Through Development of Core Industrial Technology Program (Project No. 20000965), funded by Ministry of Trade, Industry & Energy of Korea.
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