Influence of exposure time on mechanical properties and photocuring conversion ratios for photosensitive materials used in Additive Manufacturing

J. Bonada\textsuperscript{a,b,*}, A. Muguruza\textsuperscript{a}, X. Fernández-Francos\textsuperscript{c}, X. Ramis\textsuperscript{c}

\textsuperscript{a} Universitat Politècnica de Catalunya, Centre CIM, c/Llorens i Artigas, Barcelona 08028, Spain.
\textsuperscript{b} Universitat Politècnica de Catalunya, Strength of materials and Structural Engineering, Av. Diagonal 647, Barcelona 08028, Spain
\textsuperscript{c} Universitat Politècnica de Catalunya, Thermodynamics Laboratory, Av. Diagonal 647, Barcelona 08028, Spain

Abstract

The influence of UV post-curing process on mechanical properties as well as photocuring conversion ratios is presented. An analytical model to determine the conversion ratio for frontal polymerization is used to define 3D printing parameters in order to obtain a conversion profile as homogenous as possible. The mechanical properties of 3D printed coupons with and without UV post-curing process were obtained through experimental tensile and bending tests. Furthermore, the experimental conversion ratios of printed samples were obtained by means of FTIR spectrometry analysis. It was observed that conversion ratios and some mechanical properties increase because of UV post-curing treatment, enabling the chance to optimize the whole manufacturing process in function of the 3D printed part requirements.

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1. Introduction

Additive Manufacturing (AM) processes can build-up 3D parts adding material layer by layer. Therefore, it is

* Corresponding author. Tel.: (+34)934017171 E-mail address: jbonada@fundaciocim.org
possible to manufacture complex geometries without using specific tools or fixtures. One of the main additive manufacturing processes uses a light-based technology and photosensitive materials. Consequently, each layer of the 3D part is obtained through a photopolymerization reaction of the material after a controlled light emission. Light-based technologies can be mainly classified as stereolithography (SLA) and mask-image-projection (MIP) or digital light processing (DLP). SLA uses a UV laser and a scanning process to obtain each layer, whereas DLP uses a Digital Micromirror Device (DMD) to project the whole layer geometry simultaneously.

Previous research has been done in order to analyse the material photopolymerization and its cure depth [1, 2] according to the energy exposure. On the other hand, the conversion ratio, as well as, cure depth, can be determined by the frontal photopolymerization (FPP) model presented in [3]. The photocuring conversion ratio depends on exposure dose and it has a significant influence on material properties, such as density, shrinkage or elastic modulus [4, 5]. Therefore, right calibration of these parameters is a key factor to obtain a successful 3D printing process and to avoid a non-homogeneity photocuring conversion profile that could cause several non-desired consequences.

The main goal of this paper is to analyse mechanical properties of photosensitive materials in function of their photocuring conversion ratio after a UV post-curing process. This could allow a printing process optimization in function of the 3D part mechanical requirements and understanding its mechanical behavior for a printed part with a non-uniform conversion ratio profile.

2. Photopolymerization model

2.1. Analytical Model

Frontal photopolymerization (FPP) is a solidification process in which a small stripe of photosensitive material (front or photopolymerization zone) is formed and spread into photosensitive resin, as a consequence of an external light source. It is a directional process and can be initiated, controlled and stopped through light exposure dose.

When the manufacturing process starts, the photocurable resin is irradiated and the photopolymerization process takes places. The FPP model presented and developed in [3-5] describes the spatio-temporal conversion ratio ($\chi$) of a photosensitive material. The extent of photopolymerization ($\Phi(z, t)$) is the main parameter of the FPP model (Eq 1). It is a dimensionless parameter ($\Phi=\chi/\chi_{\text{max}}$) used to describe the monomer-to-polymer conversion:

$$\Phi(z, t) = 1 - \exp(-K l_0 \exp(-\mu z) t)$$  \hspace{1cm} (1)

where $z$ is the direction of the manufacturing process (normal to the irradiated surface), $t$ is exposure time, $K$ is the material effective reaction conversion rate, $l_0$ is the light intensity at the irradiated surface and $\mu$ is the attenuation coefficient. The FPP model is assumed to be photoinvariant; therefore the attenuation coefficient is constant and is not dependent of the conversion ratio. Furthermore, the gel point of the photosensitive material corresponds to a threshold conversion ratio value ($\Phi_*$). If the conversion ratio is higher than $\Phi_*$ a network is formed, the material results insoluble and a solidified stripe is obtained. For a single exposure layer, the solidified thickness could be obtained through Eq 2.

$$Z_t = \frac{\ln(\frac{1}{\mu})}{\mu}$$

$$\tau = \frac{\ln(\frac{1}{1-\Phi_*})}{K l_0}$$  \hspace{1cm} (2)

Other research has been done to take into account mass and thermal effects [6] as well as oxygen inhibition effect [7] in analytical models. However they are not considered in this paper.
2.2. Experimental determination of FPP model parameters

Several experimental tests have been done in order to determine the material parameters of FPP model. For these tests, the same light source of the DLP printer has been used to irradiate a small area with different exposure doses to obtain several samples with different thickness (Fig. 1). Fig. 2 show the solidified thickness obtained in function of exposure dose and logarithmic dose. The experimental attenuation coefficient is obtained as the inverse of this logarithmic slope (Fig. 2(b)).

![Experimental solidified samples](image1)

Fig. 1. Experimental solidified samples obtained after different exposure doses (a) 780 mJ/cm²; b) 624 mJ/cm²; c) 468 mJ/cm²).

![Sample solidified thickness in function of exposure dose](image2)

![Experimental determination of resin attenuation coefficient](image3)

Fig. 2. (a) Sample solidified thickness in function of exposure dose; (b) Experimental determination of resin attenuation coefficient.

The threshold value of conversion ratio ($\Phi_c=0.248$) has been obtained by means of FTIR spectrometry analysis of the last solidified surface of the experimental samples. Finally, the material effective reaction conversion rate ($K$) is adjusted to fit numerical and experimental measurements (slope of Fig. 3).
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![Fig. 3. Experimental determination of reaction conversion ratio (K).](image3)

3. Additive manufacturing process

Two main configurations are commonly used as DLP printer equipment: Top-Down and Bottom-Up. The principal difference between both configurations is the position of the light emission source and the direction of the manufacturing axis (Fig. 4). All 3D printed samples have been obtained through 3D DLP Bottom-Up AM system in order to avoid oxygen inhibitory effect during the photopolymerization process.

![Fig. 4. (a) Bottom-up; (b) Top-down DLP schematics.](image4)

A layer thickness of 50 microns and an exposure dose of 158.3 mJ/cm² were defined as manufacturing parameters for all printed samples. FPP model presented in Section 2 (Eq. 1) has been used to determine this exposure dose (158.3 mJ/cm²) in order to obtain a conversion ratio higher than \( \Phi_c \) along all layer thickness to ensure a successful bond among layers. Figure 5 (b) shows the conversion ratio obtained for one single layer. It can be observed that \( \Phi > \Phi_c \) for \( Z < 210 \) microns; thus all layers should be completely bonded (\( \mu = 0.6761 \text{ mm}^{-1} \)).

During the manufacturing process all layers could receive a different accumulated dose. The first layers could receive more accumulated dose than the last ones. This effect is shown in Fig. 6. After the first layer is completely done, the second layer receives the exposure dose \( (d_0) \) whereas the first layer also receives an additional non-desire dose \( (\Delta d_0) \), which can be calculated through Eq 3. Moreover, the influence of attenuation factor is presented in Fig 5 and 7. The more the attenuation factor (\( \mu \)) increases the less \( \Delta d_0 \) is obtained (Fig. 5(a)). Consequently, the conversion ratio profile along manufacturing direction could be different between layers as well as along the layer thickness.

\[
\Delta d = d_0 \exp(-\mu \Delta z)
\]
In addition, the exposure dose has also been chosen to obtain a conversion profile as homogenous as possible in the construction direction in order to minimize non-uniform mechanical properties along manufacturing direction of printed samples. It can be observed (Fig. 7(b)) that mainly the last ten layers have a non-homogenous conversion ratio. The previous printed layers show a practically unitary conversion ratio; thus the maximum conversion for visible light has been reached. However, after a UV post-curing process, the monomer-to-polymer conversion could be increased because $\chi_{\text{max}}$ UV light $\geq \chi_{\text{max}}$ visible light.

![Fig. 5. (a) Dose received along Z direction; (b) Conversion ratio for a single layer obtained with FPP model.](image)

![Fig. 6. (a) In the first step layer 1 only has received the initial exposure dose; (b) During the second step the accumulated dose of layer 1 increase because light is not completely attenuated.](image)

![Fig. 7. (a) Accumulated conversion rate during AM process obtained with FPP model; (b) The last layers show a typical stepped conversion profile.](image)
4. Results and Discussion

4.1. Photocuring conversion ratios

The photocuring conversion ratios have been determined by means of FTIR spectrometry bands (Fig. 8) of acrylate groups through the decrease of the normalized peak area of the absorption band of 810 cm$^{-1}$ and using the band at 1730 cm$^{-1}$ as a reference (Eq. 4).

$$
\chi = 1 - \frac{A_t^{810}}{A_0^{1730}} \frac{A_0^{1730}}{A_t^{1730}}
$$

(4)

Where $A_t$ and $A_0$ indicates the peak areas of the absorption band after the post-curing process and for the resin before receiving any energy dose, respectively.

Fig. 8. (a) Results obtained from FTIR spectrometry; (b) Detail of the absorption band (810 cm$^{-1}$) where the photoconversion ratio is calculated.

The samples for FTIR analysis have been cut off from the middle layer of tensile test coupons to avoid possible oxygen inhibitory effects at top or bottom surfaces. The experimental conversion ratios can be observed in Table 1. The results show that the maximum conversion ratio for the DLP light source used (visible light) is around 77%. On the other hand, after a UV post-curing process almost 89% monomer-to-polymer conversion is achieved. Moreover, it does not appear significant differences in conversion ratios among 20 and 40 min UV post-curing samples;
therefore, similar mechanical properties are expected.

Glass transition temperatures ($T_g$) of all samples were determined using dynamic-mechanical analysis (DMA) in a cantilever bending mode at a frequency of 1 Hz. The temperature profile involved heating the sample from -30 to 130 °C at 3°C/min. It is well known that several differences on $T_g$ could appear if different conversion ratios are achieved during the UV post-curing process. It can be observed in Fig 9 that $T_g$ increases (maximum of curves) with the UV post-curing time; thus the conversion ratio should be different among samples. Small difference also appears between 20 and 40 min UV post-curing samples.

![Graph showing $T_g$ measurement](image)

**Fig. 9.** $T_g$ is measured by the peak position of DMA results.

### 4.2. Mechanical properties

The material stress-strain behavior has been obtained for printed tensile test coupons after and before a post-curing process in a UV oven in order to evaluate its influence (Table 1). Several tensile coupons have been tested with the same exposure dose and different post-curing process in a UV oven (2 or 3 coupons for each case). The mechanical properties increases as a result of a UV post-curing process. Although tensile strength for both UV post-cured samples are practically the same, some differences appear on the elastic modulus and elongation due to the increase of post-curing time. Consequently, this treatment could be optimized to reduce post curing time. Furthermore, it could be adapted to obtain specific mechanical properties inside the material range possibilities.

<table>
<thead>
<tr>
<th>UV post-curing time(min)</th>
<th>Elastic Modulus (MPa)</th>
<th>Tensile Strength (MPa)</th>
<th>Elongation (%)</th>
<th>Conversion Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>501</td>
<td>14.60</td>
<td>9.35</td>
<td>0.77</td>
</tr>
<tr>
<td>20</td>
<td>882</td>
<td>21.09</td>
<td>6.63</td>
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<td>40</td>
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Three-point bending tests have been done in order to evaluate the mechanical properties under flexural load (Table 2). The results show a relevant difference between tensile and flexural strength whereas the difference between elastic and flexural modulus are significantly lower.
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Table 1. Tensile test results.

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<tr>
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<td>791</td>
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<td>6.63</td>
<td>0.89</td>
</tr>
<tr>
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Three-point bending tests have been done in order to evaluate the mechanical properties under flexural load (Table 2). The results show a relevant difference between tensile and flexural strength whereas the difference between elastic and flexural modulus are significantly lower.

Table 2. Flexural test results.

<table>
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<th>Flexural Modulus (MPa)</th>
<th>Flexural Strength (MPa)</th>
<th>Conversion Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>492</td>
<td>28.87</td>
<td>0.77</td>
</tr>
<tr>
<td>20</td>
<td>791</td>
<td>41.72</td>
<td>0.89</td>
</tr>
<tr>
<td>40</td>
<td>817</td>
<td>40.36</td>
<td>0.89</td>
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5. Conclusions

A FPP analytical model is presented to determinate the monomer-to-polymer conversion profile according to the exposure dose. It can be used to define and optimize the manufacturing parameters in order to obtain homogeneous conversion ratio as much as possible. Therefore, the non-desire effects of a non-homogeneous conversion profile could be avoided, such as variable mechanical properties along printing direction. Moreover, the influence of attenuation factor is also presented. Although a lower attenuation factor allows obtaining a more homogeneous conversion profile it could cause a hard dimensional control along the manufacturing process, especially in a Top-Down configuration due to high values of non-desired accumulated doses.

The influence of conversion ratio and UV post-curing process on mechanical properties has been analysed. First of all, the maximum conversion ratio using a visible light source is smaller than using a UV light source. Thus, the maximum mechanical properties could only be achieved after UV post-curing process. The first results obtained show that a UV post-curing process increases the elastic modulus and tensile strength of the material and reduces the maximum elongation. Therefore, the post-curing time could be optimized in function of which mechanical properties would be enhanced. Finally, the results show a relevant difference between tensile and flexural strength whereas flexural modulus are similar.

In following steps, more UV post-curing times will be analysed in order to obtain a completely evolution of mechanical properties in function of conversion ratios. Furthermore, the chance to analyse conversion ratios in different layers in the same sample will be considered in order to obtain more accurate results, evaluate inhibitory oxygen effects and as well as to analyse the stepped conversion profile in a sample without UV post-curing process. Moreover, the material anisotropy will be evaluated.

Acknowledgements

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