Investigation of UV processing & post-cure conditions on the mechanical properties of 3D DLP printed polymer resins

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Introduction

The aim of this project is to determine the mechanical properties of a 3D printed polymer as a result of changing its post cure conditions such as heat to determine the most effective and stable cure conditions.

In photopolymer resins, polymerisation occurs upon light irradiation. This polymerisation in the resin results in the solidification of the material into the 3D printed object. As most of the (meth)acrylate-based photocurable resins contain diacrylates, such as the hexamethylene diacrylate used, which experience auto acceleration in the early phase of the free radical polymerization since termination reactions are mobility restricted as acrylates forms unstable secondary radicals on the propagating group. This produces a high kinetic chain length which would result in the formation of networks with low uniformity and high brittleness, with an increase of shrinkage stress with each newly formed bond. This is less efficient in dissipating stress, and therefore, cracks might propagate more readily in the final material.

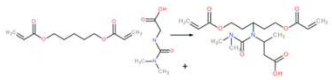

Fig 1.Reaction scheme of the co-polymer formation between hexamethylene diacrylate and N-(Dimethylcarboyl)glycine

One method of preventing the production of a weak material is the use of a co-polymer as shown above, however this yielded little
Due to this it is difficult to determine when the reaction should be ended to ensure sufficient curing of the polymer without compromising strength and stability.

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Mechanical Test 1: Tensile Test

Mechanical Test 2: Three-point bend test

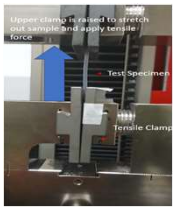

Fig.2 Set up of the tensile test

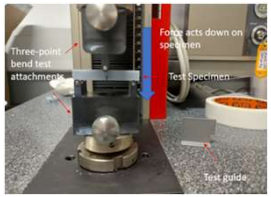

Fig. 3 Set up of the three-point bend test

After the mechanical tests were completed, FTIR and SEM were done to determine the level of cure in the samples

Preparation of Samples

A set of fracture and tensile samples were printed from four photopolymer resins by Elegoo: ABS-like, Plant Based, Water Washable and a Standard Photopolymer, all commercial resins intended for novel use.
The samples were made from the following designs:

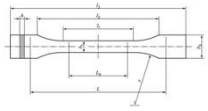

Fig. 4 Design of Tensile specimen[1]

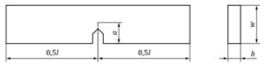

Fig 5. Design of Fracture Specimen[2]

For the thermal cure samples were placed on a tray at 30°C or 60°C for 2 hours or 24 hours. The same was done with the water immersion samples, where samples were submerged in a jar of deionised water.

3D printing of Test Specimen → 5-minute UV cure → Thermal Cure and/or water immersion → Tensile Test / Three-point bend test

Results and Discussion

The initial test involved determining the best UV cure time for the sample, between 0–10-minute post UV cure. However, FTIR showed that there was a minimal difference in the UV cured samples and a tensile strength difference of 5N. The UV cure was insufficient due to the 45° angle of the LED in the cure station to the samples, resulting in a surface-level cure.
Thus, a thermal cure was determined to be necessary to complete the polymerisation process.

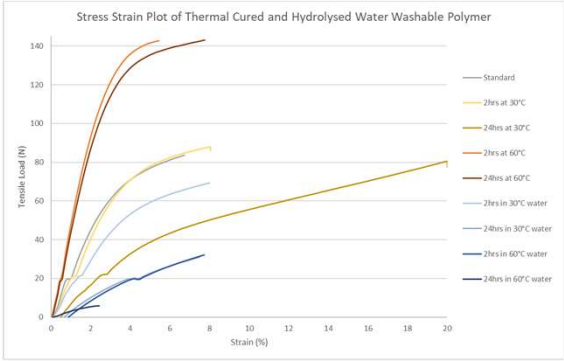

Fig. 6 Stress-Strain Plot of Thermal Cured and Hydrolysed Water Washable Polymer

The thermal cure completed the termination step. After 24hrs at 60°C, samples had a 75% increase in strength. After two hours, minimal decrease in strain occurs, with any excess cure time beginning to result in degradation[3]. The 30°C sample after 24 hours appears to be an exception, with high flexibility making it suitable for tubes.
Next the stability of the thermal cure was tested with water immersion. Using the water washable resin, as once its cured it should be resistant to water degradation.

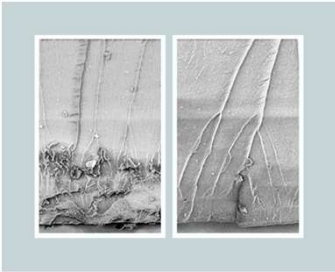

Fig. 7 SEM at x1000 magnification of water washable resin after a 24hr thermal cure at 60 °C with no immersion (left) and water immersion (right)

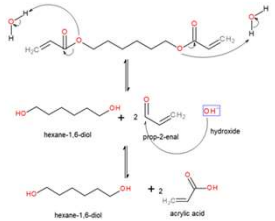

Fig. 8 Hydrolysis Reaction Mechanism of hexamethylene diacrylate

The photopolymer hexamethylene diacrylate upon hydrolysis produces the monomer acrylic acid upon cleavage of the ester group, which can only form dimers. This dimer results in weaker material due to shorter chain length and minimal cross-linking capability.
The thermal cured sample on the left of fig 7. shows brittle fracture with larger oligomer groups observed as rougher texture resisting applied force. The smooth ductile fractures of the hydrolysed resin on the right, imply the lack of oligomer groups and suggest a less polymerised weaker surface. The higher resistance of the thermal cured samples is attributed to the presence of a rigid crystalline structure where water cannot easily penetrate. [4]

Conclusion

The tensile strength of a photopolymer resin is proportional to the temperature of its thermal cure. While this is the case, lower cure temperatures provide more flexible yet strong and stable material, slightly less resistant to hydrolysis. The termination step occurs within 2 hours of thermal cure.
Hydrolytic degradation of the Elegoo resins results in the production of acrylic acid, a reversible process where the starting material can be regenerated. This could be used to improve recycling of resins for sustainability goals.

References

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