Optimization of Biodegradable Resins for Additive Manufacturing

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The purpose of this study is to evaluate the properties of custom resins to optimize them for use in a FormLab Form 2© Stereolithography (SLA) printer. The resins used various ratios of poly (ethylene glycol) diacrylate (PEGDA, Mn 700) and poly (ethylene glycol) (PEG, Mn 300). PEG is a biocompatible polymer used in biomedical applications, and PEGDA is a form of PEG that is used in many drug delivery applications. The ratios under investigation were 3.5:6.5, 6.5:3.6, and 9:1 where PEGDA: PEG. Diphenyl (2,4,6-trimethylbenzoyl) phosphine oxide was used as the photoinitiator added at 1 g/L. These custom blends were then used in the Form 2 to print test shapes; however, the resulting prints were not fully polymerized and did not maintain shape. By comparing the custom resins to resins produced by FormLab, it was hypothesized that there were differences in particular properties.

The two properties that were selected for testing were the energy released during polymerization and viscosity.[1] The three custom ratios (3.5:6.5, 6.5:3.5, 9:1) were tested against the white and clear resins supplied by FormLab. In addition, the concentration of photoinitiator in the custom resins was varied during the differential scanning calorimeter (DSC) testing (photoinitiator concentrations: 10%, 25%, 50%, 75%, 100%). No photoinitiator was used in the resins that underwent viscosity testing because of light sensitivity concerns. Viscosity is hypothesized to be critical because of the way the printer operates. Since the printer wipes the resin off the window before lowering the stage again, the viscosity could impact the amount of resin that flows into the printing area. The viscosity was measured using a Rheometer with 60 mm steel concentric plates at 1° with a gap distance of 27μm. These results are presented in Figure 1.

Heat flow of the resin was tested using a DSC (Texas Instruments DSC Q100©). The samples were polymerized using a Novacure 2100 Q Series PCA©. The two sets of data obtained are presented in Figures 2 and 3. Roughly 25g of resin was polymerized in hermetic aluminum pans. The DSC was programmed to maintain 30°C for these runs. The printer operates at about 31°C. The DSC would equilibrate at 30°C and then remain isothermal for 15 seconds before turning on the light source.

Each sample was run twice on the DSC. Note that the isothermal step resulted in the zero slope lines (Figure 2). Peak heat flow occurred at the same time for both the 100% and 50% photoinitiator concentrations. These times were much quicker than those for the standard resins (0.437 min for clear and 0.463 min for white). The other ratios exhibited similar reaction times to the 100% and 50% concentrations.

It was observed that viscosity and heat flow of the custom resins did in fact vary significantly in most cases. More trials are needed to confirm observed trends and identify any outliers. Future testing will explore the effects of higher molecular weight as a solution to the differences in viscosity.

Statement of Research Advisor

Steven's work focused on identifying the window of fundamental resin properties that enable printing on commercial SLA printers. His findings laid the groundwork required to engineer SLA printable biodegradable resins for a range of biomedical applications.
-Edward Davis, Mechanical Engineering

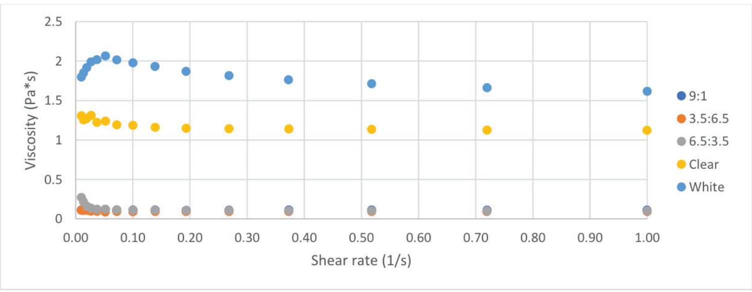

Figure 1: Viscosity vs shear rate of resins; custom resins contain no photoinitiator.

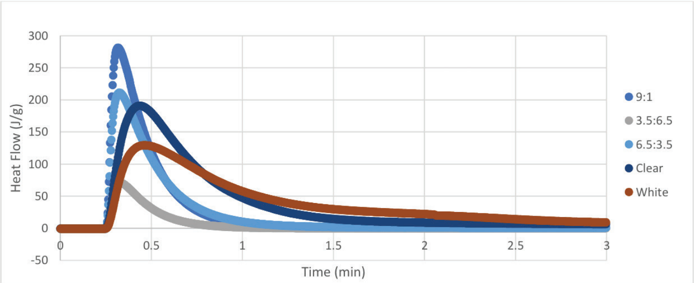

Figure 2: Heat flow vs time of resins with 100% photoinitiator concentrations.

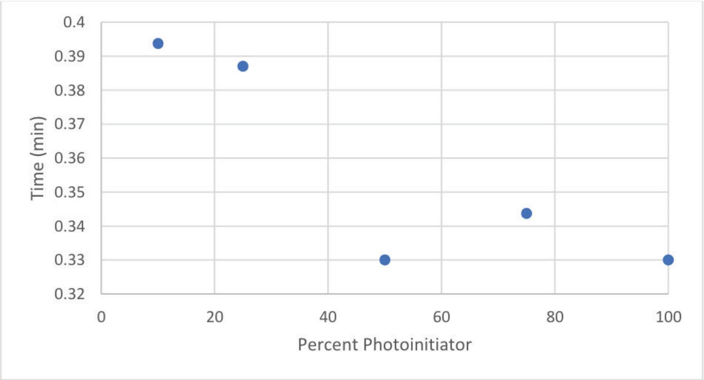

Figure 3. Time at max heat flow for various photoinitiator concentrations of the 3.5: 6.5 blend.

References

[1] Dickens, S. H., et al. "Photopolymerization Kinetics of Methacrylate Dental Resins." *Macromolecules*, vol. 36, no. 16, 16 July 2003, pp. 6043–6053., doi:10.1021/ma021675k.