MALEIMIDE-STYRENE-BUTADIENE TERPOLYMERS AS TOUGH PHOTOPOLYMERS FOR ADDITIVE MANUFACTURING

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With the transition of additive manufacturing of photopolymers through techniques such as digital light processing (DLP) from research to industry, material properties of the printed parts have moved into focus. [1] Photopolymers are traditionally brittle materials due to their inhomogeneous polymer architecture and high crosslinking density. For DLP printing, however, tough and thermoplast-like materials are desirable. One particularly successful toughening strategy is rubber addition to polymers [2], which is also utilized in ABS, a phase separated thermoplastic terpolymer with highly regarded mechanical properties. However, photopolymerization of this system is impossible due to volatility of the monomers, the quenching of the exited state of the photoinitiators by styrene, and the opacity of the final polymer.

Therefore, we have developed an analogous monomer system for photopolymerization consisting of maleimide and styrene with varying substituents, and 0, 10, or 20 wt% poly(butadiene). Reactivity and mechanical properties could be tuned through substituent choices for maleimide and styrene and through poly(butadiene) content. Furthermore, we were able to show phase separation for these systems despite their transparency. This is a result of the phase separation between rubber and maleimide styrene copolymer, which is counteracted by the covalent incorporation of poly(butadiene) into the network. As a result, the domain sizes are below 40 nm and the material appears transparent. While mechanical properties close to ABS could be achieved for the best material, its volatility was still too high for 3D printing. A sufficiently non-volatile formulation with larger substituents still exhibited tough behavior upon curing and was utilized for DLP printing as a proof of concept.

[1] Fiedor, P. and J. Ortyl, A New Approach to Micromachining: High-Precision and Innovative Additive Manufacturing Solutions Based on Photopolymerization Technology. Materials, 2020. 13: p. 2951.

[2] Ligon-Auer, S.C., et al., Toughening of photo-curable polymer networks: a review. Polym. Chem., 2016. 7(2): p. 257-286.