Department of Materials Science and Engineering,

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Toughening of Isosorbide-Methacrylate Thermoset Network via Molecular Chain Extension by Aza-Michael Addition with Piperazine

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Abstract:

In recent years, biobased polymers have gained increased interest in becoming an appropriate substitute for petroleum-based plastics. One promising biobased compound is isosorbide which is synthesized via esterification to fabricate Isosorbide-Methacrylate (IM). IM is a low viscosity (157 cP) vinyl-ester (VE) resin which forms a thermoset network via free radical polymerization. On its own, IM has a T_g of approximately 220^0 C and a degradation temperature of 400^0 C, making it a suitable candidate for a matrix material in high temperature environments. However, due to its high crosslinking density, IM is a relatively brittle material with a K_{1c} value of roughly 0.32 MPa/√m. In order to toughen IM, molecular chain extension by Aza-Michael addition was carried out using a difunctional compound known as Piperazine. By increasing the molecular spacing between IMs crosslinking junctions with Piperazine, the

crosslinking density is reduced; thus, causing an increase in toughness. However, molecular modifications cause macroscopic changes in material properties. In this research, we aimed to maintain a viscosity of around 500 cP to allow for the resin to be processed via vat photopolymerization using digital light processing (DLP) 3D-printing. We also aimed to identify to what extent toughness can be increased without a significant reduction in IM's T_g.

It was found that the addition of low concentrations of Piperazine (5 wt%) resulted in a relatively high T_g (160^0 C – 180^0 C). Although this is about a 60^0 C reduction, typical petroleum-based vinyl-ester resins have a T_g ranging from 110^0 C to 150^0 C.[4] Therefore, resins with low concentrations of Piperazine would qualify as an adequate substitute. On the other hand, viscosity increased by nearly 13 times with the addition of 5 wt% Piperazine and increased almost 130 times with the addition of 10 wt%. Despite this, we found that 5 wt% Piperazine printed adequately while further dilution methods using