

Vitrimers based on epoxidized cardanol resin and cystamine for 3D printing applications

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To address the need for greener epoxies for 3D printing applications, a vitrimer formed by a bio-based epoxy resin (Cardolite[®] Lite 514HP) and cystamine was studied. Cystamine is an aliphatic diamine containing a disulfide bond derived from an amino acid. When combined with epoxy resins, it enables the formation of covalent adaptable networks that can be reshaped and reprocessed above the glass transition temperature through an associative mechanism based on disulfide exchange. The cross-linking process of epoxy-cystamine samples was studied by differential scanning calorimetry (DSC), and stress-relaxation measurements were performed to assess bond exchange within the cured vitrimers. The optimized formulation was applied to a 3D printing process based on Liquid Deposition Modeling (LDM), that involves printing a paste followed by cross-linking in the oven. Micro- and nanocellulose were used as fillers and rheology modifiers to formulate bio-based printable pastes, with rheological analysis used to evaluate printability. The ability of cystamine to initiate the cross-linking reaction with epoxy resins at relatively low temperatures (above 30 °C) helped preserving the shape of the 3D printed pieces during curing, while avoiding premature curing during printing. The post-printing curing procedure was optimized: after gelation temperature (T_{gel}) is reached to set the shape, the temperature can be increased to complete the cross-linking of the polymer. The printed composite vitrimers demonstrated successful mechanical recyclability (1.5 h, 160 °C, 3 metric tons), with no observed changes in activation energy or relaxation time upon cellulose addition. Finally, a preliminary Life Cycle Assessment (LCA) was performed to evaluate the environmental impact of the chemicals used and the recycling process.