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Additive Manufacturing of Epoxy-Amine Vitrimers with Built-in Catalytic Functionality

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 Vitrimeric materials uniquely combine the advantageous properties of thermosets such as high mechanical strength and dimensional stability with those of thermoplastics, including repairability, reprocessability, and recyclability. This synergy is enabled by associative dynamic bond exchange mechanisms. As such, vitrimers offer a promising route to reducing resource consumption and waste, key priorities in the transition to a circular economy. In this study, we report the first development of epoxy-amine-based vitrimers that offer ease of processing, repairability, and recyclability without compromising thermomechanical performance. During crosslinking, in situ generated tertiary amines act as internal transesterification catalysts, eliminating the need for external catalysts, which can plasticize the network and potentially leach out over time. Network properties were optimized by varying the structure of the diamines (Fig. 1), resulting in materials with the following characteristics: T_{onset} up to 260°C, T_g up to 145°C, τ^* ~ 15-20 min at 180°C, E' up to 2GPa. The optimal formulation, based on phthalic acid diglycidyl ester and 4,4′-methylenebis(cyclohexylamine), was a liquid mixture that cured readily at room temperature. This composition was further evaluated as a potential candidate for material extrusion additive manufacturing (MEX). To tailor the formulation's viscosity for 3D printing process, the incorporation of two types of silica particles (fumed silica and PDMS-modified silica) was explored. Increasing the silica content from 5 to 15 wt% enhanced viscosity by three orders of magnitude and introduced desirable shear-thinning behavior for MEX processing. As a result, a variety of complex geometries (bars, honeycombs, dog bones, dice) were successfully 3D printed with high resolution, excellent dimensional accuracy (<2%), strong interlayer adhesion, and minimal shrinkage (<2%). This work was supported by the Luxembourg National Research Fund (FNR) under the SusPoCo (PRIDE21/16748260) project.

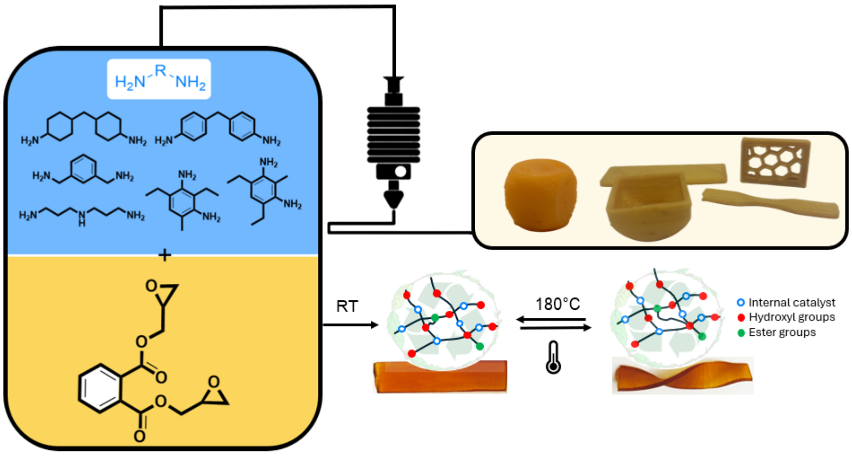

Figure 1: Formation of Epoxy-Amine Vitrimers via 3D Printing.

Reference:
[1] Daniel F. Schmidt, et al., WO2025/082849 A1, 2023.