DUAL-CURABLE VITRIMERS FOR 3D-PRINTING

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3D-printed objects can greatly benefit from the introduction of molecular structure undergoing dynamic bond exchange [1] or the use dual-curing processing [2], leading to a significant enhancement of mechanical properties and extended capabilities such as adhesion, reshaping, healing and recycling.

We have developed a family of dual-curing 3D-printable materials based on acrylate homopolymerization for the printing stage and epoxy-acid reaction for the second thermal curing stage, with the purpose 1) having a stable intermediate material with desired reshaping and adhesion capabilities and 2) obtaining a network structure capable of undergoing dynamic work rearrangement promoted by transesterification between ester and available hydroxyl groups. A latent amine catalyst has been added in order to accelerate both the thermal curing stage and transesterification.

We have analyzed the curing kinetics, the storage stability of the printable formulations, the thermal and mechanical properties of the printed materials and their stress relaxation capabilities. In order to assess their performance in engineering applications, we have tested their adhesion capabilities in order to produce large assembled components with seamless bonding interphase, having controlled and predictable mechanical properties. We have exploited the existence of reactive groups and therefore intrinsic adhesion capabilities of the intermediate printed material in order to produce a strong bond between parts during the second thermal stage reaction. In addition, we have analyzed the effect of having an additional thermal post-treatment in order to further strengthen the bonding between parts, by enabling dynamic network rearrangement.

[1] Zhang B., Kowsari K., Serjouei A., Dunn M.L., Ge Q., “Reprocessable thermosets for sustainable three-dimensional printing”, *Nature Communications* **9**, 1831 (2018).

[2] Fernández-Francos X., Konuray O., Ramis X., Serra À., De la Flor S., “Enhancement of 3D-printable materials by dual-curing procedures”, 2021.