

LOCAL CONTROL OF DYNAMIC EXCHANGE REACTIONS IN 3D PRINTED THIOL-ACRYLATE VITRIMERS

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Traditional photosensitive resins for DLP (=digital light processing) 3D-printing techniques are characterized by fast curing rates, low viscosity, high resolution and tunable mechanical properties. Once processed, they behave like classic thermosets and neither reprocessing, re-cycling or malleability is feasible. By introducing dynamic covalent bonds into photopolymers, topology rearrangements upon an external stimulus are enabled, even after manufacturing. These so-called covalent adaptable networks (=CANs) are based on bond exchange reactions above the topological freezing temperature (T_v) of the network. One prominent example are thermo-activated and catalysed transesterification reactions between carboxylic ester linkages and free hydroxyl groups.

Advancing from classic initiators for thermally triggered bond exchange reactions, photolabile transesterification catalysts can be applied to spatially control topology rearrangements. The usage of photoacid generators as latent transesterification catalysts leads to the local formation of Brønsted acids upon UV exposure, which can efficiently catalyze thermo-activated transesterification reactions. Owing to the orthogonality between the curing reaction of the network (visible light) and the photo-activation of the catalyst (UV-light), bond exchange reactions can be selectively switched on. By utilizing a dual-wavelength digital light processing 3D printer (operating at 405 and 365 nm) the fabrication of soft active devices, which undergo locally controlled topology rearrangements above the networks' T_v is feasible.

