

LATENT CATALYSTS IN DYNAMIC PHOTOPOLYMER NETWORKS

David Reisinger¹, Elisabeth Rossegger¹, Sandra Schlögl¹

¹Polymer Competence Center Leoben GmbH, Austria

Latent catalysts are a versatile approach to temporally and locally control the rate of bond exchange reactions and the related material flow in dynamic polymer networks. In particular, we explored novel families of photolabile transesterification catalysts to equip dynamic covalent networks with creep resistance as well as high bond exchange rate (once activated). The applicability of various (commercially available) photolabile acids was demonstrated by exploiting the orthogonality between the curing (410 nm) of a thiol-acrylate photopolymer and the activation reaction of the catalyst (365 nm).[1, 2] Recently, we applied photochemically (UV light) generated acids to catalyze a deprotection reaction of a tert-butoxycarbonyl group, which was employed to mask the hydroxy groups of a vinyl monomer.[3] At the same time, the released acid served as a catalyst for thermo-activated transesterifications between the deprotected hydroxyl and ester moieties in an orthogonally-cured (450 nm) thiol-click photopolymer. We further incorporated thermally stable photolabile bases (e.g. quaternary ammonium salts [4] and *N*-substituted derivatives of the amidine base 1,5-diazabicyclo[4.3.0]non-5-ene [5]) in thiol-click networks and realized a local and temporal change in material reflow due to the light-mediated release of strong Brønsted bases. In a follow-up study, we reported on the application of a photolabile transesterification catalyst, which releases a strong guanidine base upon irradiation with 405 nm LED light.[6] Incorporated in a visible-light-cured (450 nm) thiol-ene polymer, spatially resolved catalyst activation enabled a selective rearrangement of the network topology via thermo-activated transesterification. As the liberated catalyst (tetramethylguanidine) is volatile, the network was reverted back to a permanent one by a simple heat treatment at 210 °C for 10 min. We further studied thermolabile catalysts, whose activation is not limited by sample geometry and optical transparency of the materials. As proof of principle, the selective activation of dynamic transesterification was shown in fiber-reinforced and highly filled magneto-active thiol-ene polymer composites giving rise to the wide range of potential future applications offered by this concept.[7]

References

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