

LOCAL UV-MEDIATED PHOTOACTIVATION OF VITRIMERIC POLYMERS

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Vitrimers are an advanced class of polymers capable of rearranging their covalently crosslinked network topology by dynamic associative exchange reactions. They generally behave like classic thermosetting polymers, however, when the topology freezing transition temperature (T_v), defined as the onset temperature of the covalent bond exchange reactions, is exceeded, they are able to flow like viscoelastic liquids [1]. Nevertheless, vitrimers are not able to replace classic thermosets in applications where elevated temperatures may occur, since up to now it has not been possible to prevent or induce the onset of exchange reactions, i.e. a viscoelastic flow, in a controlled manner when T_v is exceeded. We developed a concept by which this considerable application boundary can be overcome.

A high temperature stable photobase generator was incorporated into a three-dimensional covalently crosslinked network structure appropriate to undergo base-catalyzed transesterification. The controlled UV radiation-mediated release of the efficient transesterification catalyst, i.e. a strong guanidine base, was demonstrated by stress relaxation measurements. Even at temperatures considerably above T_v , only a controlled catalyst release, mediated by UV irradiation of the test specimen, enabled the immediate onset of dynamic covalent bond exchange reactions, i.e. base catalyzed transesterification reactions. During an ongoing measurement stress relaxation is significantly accelerable on demand by UV irradiation.

Moreover, the spatially resolved photoactivation of these vitrimeric properties was examined by means of a reshaping experiment. Only the UV-irradiated parts of a free-standing test specimen are permanently reshapable when T_v is exceeded.

In conclusion, this work provides a fundamental building block for the development of thermally stable, spatially resolved photoactivatable vitrimers, which enable a locally controlled malleability, weldability and repairability of defects.

[1] Montarnal, D., Capelot, M., Tournilhac, F., & Leibler, L. (2011). Silica-like malleable materials from permanent organic networks. *Science*, 334(6058), 965-968.