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New insights on the mechanical recycling of vitrimers

Vincent Boulic [1,2]*, Mariapaola Staropoli [1], Pierre Verge [1], Frédéric Addiego [1]

[1] Luxembourg Institute of Science and Technology, 5 Avenue des Hauts-Fourneaux, L-4362 Esch-sur-Alzette, Luxembourg

[2] University of Luxembourg, 2 avenue de l'Université, L-4365 Esch-sur-Alzette, Luxembourg

Vincent.boulic@list.lu

Within the last decade, vitrimers have emerged as a sustainable alternative to thermosets. Thanks to their unique structure composed of a crosslinked backbone involving dynamic bonds, vitrimers gather the high resistance of thermosets and the recyclability of thermoplastics. Typically, they can be mechanically recycled by subsequently grinding and hot pressing them into a new shape. If the objective of recycling is to retain at maximum the properties of the non-recycled material, the vitrimer is exposed to degradative conditions involving high temperature and pressure, as well as the grinding process. It is often reported that reprocessed vitrimer properties tend to vary, but insights on the reconsolidation mechanisms are lacking and are critical to improve the formulation and reprocessability of these materials.

This study is focusing on the reprocess-to-properties correlation, in a multi-scale analysis, of a mechanically recycled polybenzoxazine vitrimer. Following a design of experiment method, the contribution of each reprocessing parameter on the porosity is investigated through micro-computed x-ray tomography. It has been found that grain size and temperature are the predominant factors, and at equivalent reprocessing conditions, the dynamic bond content strongly affects the reconsolidation. On a lower scale, investigations on the network re-arrangements are carried out through thermomechanical analysis. Stress relaxation and dynamic mechanical thermal analysis (DMTA) give hints on the network homogeneity and vitrimeric properties. It is shown that the first recycling does not affect the re-arrangement; however, further reprocessings increase the heterogeneity of the network due to thermal degradation. Finally, the influence of recycling is evaluated through the investigation of tensile behaviour. In this part, it is shown that a competition exists between network re-arrangement kinetics and thermal degradation.

This approach not only provides insights into the mechanisms of reconsolidation of a polybenzoxazine vitrimer, but also guidance for researchers to understand and set up optimized mechanical recycling protocols to maximize the properties recovery.