Biobased epoxy vitrimer for reprocessable composites

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Vitrimers are a class of plastics, which are thermosetting derived from polymers (thermosets), but can be reprocessed, or recycled via network topology rearrangement through exchange reaction of the dynamic covalent bonds under external stimulus such as heat, pH, and UV light. There are different types of dynamic bonds such as disulfide, imine, or urethanes [1-2].

Epoxy vitrimers are being widely analyzed for developing fiber reinforced composites, but most of the explored epoxy vitrimers were still prepared from non_renewable and toxic DGEBA. [3]

In this study, a biobased epoxy vitrimer with dynamic Schiff based groups (imine bond) has been synthesized by reacting epoxidized oils, with a dynamic hardener obtained by reacting biodegradable vanillin (VAN), with 4.4'diaminediphenylmethane (DAM). Two different biobased biodegradable epoxidized oils, soybean, and rapeseed oil, have been tested, to relate their chemical structure with the final properties of the vitrimers.

The synthesis of the dynamic hardener (VSB) has been carried out by dissolving the starting compounds VAN and DAM in methanol (MeOH) and heating the mixture at 65°C for 7h. After the time elapsed, the mixture was filtered and dried in the oven. The successful synthesis of the dynamic hardener has been checked by Proton nuclear magnetic resonance (NMR), Fourier transform infrared (FTIR), Differential calorimeter (DSC) scanning and thermogravimetry (TGA). For the preparation of the epoxy-amine system,

the VSB was mixed with the epoxidized oils. The curing process was carried out at 190°C 2h under 10MPa pressure. for The characterization of the vitrimers has been carried out by_DSC, TGA or Dynamic Mechanical Analysis (DMA). The soybean based vitrimer and the rapeseed oil based vitrimer presented a Tg around 50 and 90 degradation °C, respectively and а temperature higher than 350 °C in both cases. The reprocess ability and self-healing capacity of the vitrimers have been also tested in a hot plate press.

Obtained vitrimers presented good solvent stability and good reprocess ability until 20 cycles, making them very interesting compounds for composite preparation.

Once the vitrimer was synthesized, the preparation of the composite was carried out. Two different composites have been synthesized, one based on glass fibers and the other based on linen fibers.

The new vitrimer thermosets will allow not only reprocess the composites at high temperatures, but also, recycling the cured composites by a simple chemical treatment to separate fibers from vitrimer, thus allowing the recovery of fibers and resins of end-of-life composites.

References

- [1] Xiao-Li Zhao et al, ACS Sustainable Chemistry&Engineering, 2020
- [2] Xiaohong Liu et al. Polymer 210, 2020,123030
- [3] Hafeezulah Memon et al. Composites Science and Technology 199, 2020, 108314