EFFECT OF MIXED OXIDES AS ACID CATALYSTS IN PHOSPHINE OXIDE EPOXY-BASED COVALENT ADAPTABLE NETWORKS

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Main message: Epoxy resins (ERs) are highly flammable, and their recycling is full of hurdles. To overcome this issue, recyclable and inherently flame retardant (FR) epoxy-based covalent adaptable networks (CANs) represent a promising solution. Epoxy polyester vitrimers were developed by curing epoxy with a diphenyl phosphine oxide derivative (DPPOIPA), citric acid, and sol-gel binary (Nb_2O-SiO_2, NbSi; P_2O_5-SiO_2, SiP) and ternary (Nb_2O_5-P_2O_5-SiO_2, SiNbP) acid solids. These latter enable dynamic bond exchange and a strong condensed phase action.

Keywords: Covalent adaptable network, epoxy vitrimer, dynamic bond exchange, solid acid catalyst, flame retardancy.

Introduction
ERs are widely employed in daily life. FR additives are required to pass specific industrial requirements. ERs can not be thermally reshaped and thus their recycling is very challenging. The development of more recyclable and sustainable FR ERs is an urgent task [1]. Among CANs, phosphonate ester-based epoxy vitrimers made of non-hydrolysable P-C bonds and containing transition metal oxides as catalysts for transesterification reactions may offer a new perspective for future functional systems.

Experimental
Inherently recyclable and FR epoxy vitrimers were obtained by modifying bisphenol A diglycidyl ether (DGEBA)-based thermoset with DPPOIPA and incorporating three acid solids as heterogeneous catalysts for the transesterification reaction. The solid acid materials (SiNbP, SiP and NbSi oxides) were synthesized by sol-gel chemistry and the nature and distribution of their acid sites was determined by FTIR in situ spectroscopy of adsorbed probe molecules [2, 3]. The thermomechanical recyclability of the epoxy vitrimers was tested to prove the role exerted by DPPOIPA and solid acids [4]. The UL 94 vertical burning test attested the no-dripping V-0 rating for the prepared materials of the DPPOIPA containing vitrimers, even with a low P content (2 wt.%), solely in the presence of the solid catalysts. Finally, the FR mechanisms in the gas and condensed phases were explored by cone calorimetry tests and DIP-MS analysis.

Results and Discussion
Acid solids in an epoxy polyester matrix with phosphine oxide moieties serve as both flame retardant synergists and catalysts for the transesterification reaction. Their use lowers the curing activation energy and permits the thermomechanical recycling of the polyester epoxy vitrimers containing citric acid and DPPOIPA. Solid catalysts, especially SiP oxide, are exploited to produce uniform reprocessable samples with unvaried Tg, in comparison to the original materials. According to FTIR spectroscopy, the recycling features of vitrimers is attributed to the considerable surface acidity of the catalysts, which is mostly given by the presence of Brønsted acid sites.

Even with a very low P content (about 2 wt.%), the epoxy polyester vitrimers show good thermomechanical recycling and no-dripping self-extinguishing capability. In particular, among the

prepared catalysts, SiNbP allows for the production of a significant amount of protective char and permits a low peak of the heat release rate. Besides, SiNbP increases the release of phosphorous radicals because of the proper distribution of acid sites, resulting in a significant gas phase inhibition effect. Acidic mixed oxides can boost the flame retardancy of polyester vitrimers, also acting as solid catalysts for recycling.

Additionally, all the vitrimers containing solid acid and DPPOIPA exhibit a no-dripping V-0 grade in the UL 94 vertical burning test. They also greatly improve the vitrimers' fire behavior. The use of SiNbP in the P-modified epoxy system enables a low peak of the heat release rate and a notable residual mass (29 wt.%), according to the cone calorimetry tests. The efficiency of SiNbP in enhancing the flame retardancy of the vitrimers can be attributed to a ceramic and continuous char that works as an oxygen and heat barrier at the condensed phase during the combustion, as confirmed by cone calorimetry tests and SEM-EDX measurements of the char residues. However, as shown by DIP-MS analysis and in agreement with the increased CO/CO_2 values, all the formulations that comprise an acid catalyst and DPPOIPA reveal a condensed phase action in concert with an inhibitory effect imposed by phosphorus radicals in the gas phase.

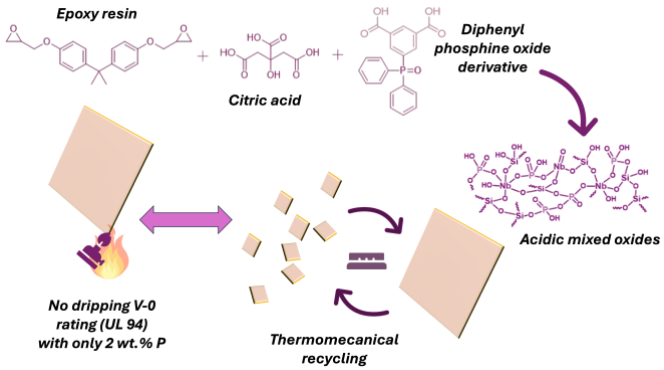

FIGURE 1. Main details concerning the manufacturing process and features of reprocessable flame retardant polyester vitrimers.

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