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Preparation of New Vitrimeric Materials Based on Glycidyl Vanillin-imines

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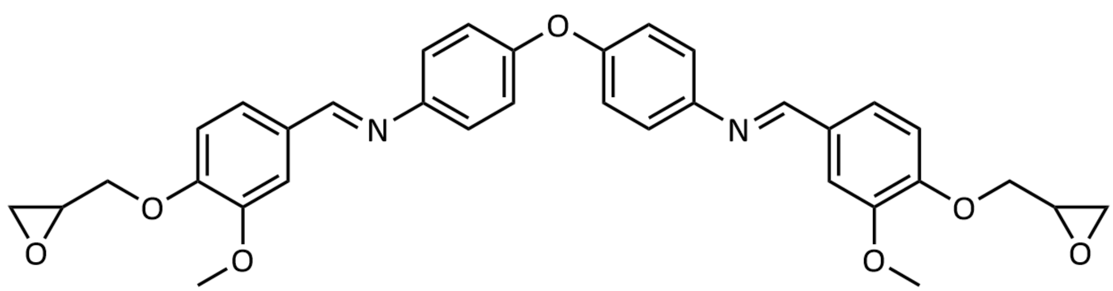
Abstract

The current exponential growth of the human population is associated with a degradation of the environment. In terms of lack of degradability and persistence in the environment, increasing attention is being paid to polymers. Among them, thermosets, that become hardened in the curing, lead to infusible networks with high strength and solvent resistance and superior mechanical and thermal properties. On the downside, their use raises a severe environmental concern because the covalent linkages in the network are irreversible, preventing recycling. An alternative that overcomes this issue is the use of dynamic covalent chemistry, which relies on chemical processes causing reversible formation and breaking of covalent bonding in response to stimuli and allows obtaining easily recyclable thermosets while retaining the overall polymer structure. Incorporating reversible groups like imines in the network structure can allow the reprocessing and recycling of these materials, maintaining their mechanical performance. The associative mechanism of the imine interchange leads to these materials being included in the group of vitrimers.

In our work, the inclusion of the imine groups in the network is based on the use of a diglycidyl diimine obtained from vanillin. This renewable product is condensed with 4,4'-oxydianiline to form the bisphenol-diimine, and then it is reacted with epichlorohydrin to obtain the epoxy-imine monomer with the following structure.



The diglycidyl-diimine and trimethylolpropane triglycidyl ether (TMPTE) mixture was cured with different Jeffamines (D-230, D-400, and T-403). These amine curing agents have poly(ethylene oxide) moieties with different chain lengths and functionalities. TMPTE has been added to help prepare the formulation and improve the mechanical characteristics of the materials.

The materials obtained were characterized by TGA to know the temperature regions where the reforming and recycling processes can be safely performed. DMTA allowed us to determine the tan d peak temperatures, higher than 70 °C, and the moduli in the rubbery and glassy state. The most important characteristic of these materials, their relaxation behavior, was also determined by DMTA. These tests proved that between 150 and 180 °C the materials reached the 37% relaxation of initial stress in less than 70 s and the complete relaxation in less than 1 hour, without appreciable changes in their properties. Their recycling ability was also been determined by grinding and hot-pressing in an aluminum mold. The recycled samples were subjected to several thermal and mechanical tests to prove the similarity to the virgin material.