

## 烷二胺基环氧 vitrimer 的制备及其性能研究

马慧茹<sup>1,2</sup>, 张海波<sup>1</sup>, 陈玉湘<sup>1\*</sup>, 赵振东<sup>1</sup>, 毕良武<sup>1</sup>

(1. 中国林业科学研究院林产化学工业研究所; 生物质化学利用国家工程实验室; 国家林业和草原局林产化学工程重点实验室; 江苏省生物质能源与材料重点实验室, 江苏 南京 210042; 2. 南京林业大学 江苏省林业资源高效加工利用协同创新中心, 江苏 南京 210037;)

**摘要:**【目的】热固性材料具有质量轻、力学性能强、耐腐蚀性好等优点, 广泛应用于航空航天、交通运输、医疗等领域, 但是, 以化石资源为原料制备的热固性环氧树脂具有永久三维交联结构, 一旦加工成型便难以降解、回收以及再加工, 造成了资源浪费及环境污染等问题。本研究利用松节油衍生物盖烷二胺为原料, 制备了生物基可回收环氧 vitrimer。【方法】以樟脑酸为原料制备了环氧化樟脑酸 (EDCA), 并与盖烷二胺 (MDA) 固化制备了具有无催化、自修复性能的 EDCA-MDA vitrimer 材料。通过傅里叶变换红外光谱、核磁共振仪、差示扫描量热仪、动态热机械分析仪、万能试验机、热重分析仪、光学显微镜及平板热压硫化仪等对材料的结构与性能进行了研究。【结果】由于刚性松节油萜环的引入, EDCA-MDA vitrimer 材料具有优异的机械性能 (61 MPa)、高储存模量 (2266 MPa) 和玻璃化转变温度 (141 °C)。EDCA-MDA vitrimer 材料交联密度高, 具有稳定的 3D vitrimer 网络, 材料失重 10% 的温度为 318 °C, 800 °C 的碳残留率为 4.4%。在不添加外部催化剂的情况下, EDCA-MDA vitrimer 材料在叔胺的催化下可实现快速的应力松弛, 活化能为 182.908 kJ/mol<sup>-1</sup>。EDCA-MDA vitrimer 材料涂层的自修复率为 91.03%, 表现出良好的自修复性能, 且 EDCA-MDA vitrimer 具有热压重塑性能。【结论】该研究结果对热固性树脂的回收问题提供了解决思路, 对松节油的综合利用具有重要的理论意义。

**关键词:** 环氧 vitrimer; 松节油; 生物基; 自修复; 回收

## Preparation of dianediamine-based self-catalyzed self-healing epoxy vitrimer

Huiru Ma<sup>1,2</sup> Yuxiang Chen<sup>1\*</sup>

(1. Chinese Academy of Forestry, Nanjing 210000)

**Abstract:**【Objective】Thermoset materials have the advantages of light weight, strong mechanical properties, good corrosion resistance, etc., and are widely used in aerospace, transportation, medical and other fields. However, thermoset epoxy resins prepared from fossil resources have a permanent three-dimensional cross-linking structure, and are difficult to be degraded, recycled, and reprocessed once they are processed and molded, which results in a waste of resources and environmental pollution. In this study, bio-based recyclable epoxy vitrimer was prepared using turpentine derivative dianediamine as raw material. 【Methods】Epoxidized camphoric acid (EDCA) was prepared from camphoric acid and cured with dianediamine (MDA) to prepare EDCA-MDA vitrimer materials with non-catalytic, self-healing properties. The structure and properties of the materials were investigated by Fourier Transform Infrared Spectroscopy, Nuclear Magnetic Resonance (NMR), Differential Scanning Calorimetry (DSC), Dynamic Thermo-Mechanical Analyzer (DTMA), Universal Testing Machine (UTM), Thermogravimetric Analyzer (TGA), Optical Microscope (OM), and Flat Plate Thermal Pressing and Vulcanizing (FPHPV). 【Results】Due to

the introduction of a rigid turpentine terpene ring, the EDCA-MDA vitrimer material has excellent mechanical properties (61 MPa), high storage modulus (2266 MPa) and glass transition temperature (141 °C). The EDCA-MDA vitrimer material has a high cross-linking density and a stable 3D vitrimer network, with a material weight loss of 10% at 318 °C and a carbon residual of 4.4% at 800 °C. Without the addition of an external catalyst, the EDCA-MDA vitrimer material achieves rapid stress relaxation catalyzed by tertiary amines with an activation energy of 182.908 kJ/mol<sup>-1</sup>. The self-repair rate of the EDCA-MDA vitrimer material coating was 91.03%, which showed good self-repair performance, and EDCA-MDA vitrimer has the performance of hot press remodeling. **【Conclusion】** The results of this study provide a solution to the problem of thermosetting resin recycling, which is of great theoretical significance for the comprehensive utilization of turpentine.

**Key words:** Epoxy vitrimer; Turpentine; Biobased; Self-healing; Recycling