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RHEOLOGICAL AND SOLID VISCOELASTIC BEHAVIOR OF A BIOBASED EPOXY RESIN CURED WITH ANHYDRIDE AND AMINE HARDENERS

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Abstract
This study aimed to evaluate the viscosity behavior and viscoelastic properties during curing with anhydride and amine hardeners. The rheological and viscoelastic behavior of epoxy resin based on epoxidized linseed oil (ELO), prepared with these hardeners were investigated through viscosity analysis (rheometry) and characterized using dynamic mechanical analysis (DMA). The ELO-AD, formulation with an anhydride-type curing agent showed a higher glass transition temperature (T_g), higher storage modulus (E'), and faster curing reaction, presenting higher viscosity at shorter times. Alternatively, the ELO-AM formulation, with an amine-type curing agent, exhibited a slower curing reaction, lower viscosity over longer times, as well as a lower storage modulus, T_g, resulting in a more flexible polymer.

Keywords: *epoxidized linseed oil; rheological behavior; viscosity; dynamic mechanical analysis, epoxy resin*

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Introduction

Vegetable oils are excellent candidates to replace petrochemical-based precursors in synthetic epoxy resins. This is due to the high degree of unsaturation in their molecules, which can be functionalized into oxirane groups through an epoxidation reaction. Among the vegetable oils used as bio-based epoxy resins, linseed oil stands out due to its characteristics and the high degree of unsaturation in its structure, as well as its easy accessibility and abundant availability [1]. The conversion of epoxidized linseed oil into a thermoset material occurs through a curing reaction with a chemical compound commonly referred to as a hardener and can be used in combination with catalysts or accelerators and are responsible for promoting the crosslinking reaction of the resin. Their chemical nature can vary, with the most commonly used types being anhydrides and amines [2].

During the curing process, the stages of gelation and vitrification occur, which are fundamental for the progress of the reaction, and the material changes from a liquid or viscous state to a solid and rigid state [3]. In these stages, chemical reactions form crosslinks between the polymer chains of the resin and the curing agent, resulting in a three-dimensional network structure. In this context, the final properties of the cured material also depend on the type of hardener used. The chemical composition of these agents plays a crucial role in determining the final structure of the polymer network, directly influencing characteristics such as viscosity, thermal stability, and flexibility [4-6].

Therefore, it is necessary to understand the effect of different types of curing agents on the curing process of bioepoxy resins in order to perform a more in-depth evaluation of the final properties of the cured material. Thus, this study aimed to evaluate the viscosity behavior and the viscoelastic properties during curing with anhydride and amine hardeners.

Experimental

Materials

Epoxidized linseed oil (ELO) with 5.5 epoxy groups per molecule: The ELO used in this study was synthesized and characterized according to the procedure previously reported [7]. Curing agents: an anhydride type, Listestone™ 2131H, composed of methyl tetrahydrophthalic anhydride, a cyclic anhydride that is liquid at room temperature, containing 1-4% benzyltriethylammonium chloride, a quaternary ammonium compound, as an accelerator, donated by Olin Corporation; and an amine type, Priamine™ 1071, a fully biobased diamine liquid at room temperature, with an active hydrogen equivalent weight (AHEW) of 140 g/eq, donated by Cargill BioIndustrial Inc. All reagents, were used as received without further purification.

Methods

Two resin formulations were prepared one with an anhydride curing agent, named ELO-AD, and another with an amine, named ELO-AM. The epoxy:hardener ratio was determined in previously studied [7]. Rheological analysis (Anton Paar MCR 101) of both formulations was carried out at 130 and 150 ºC, in shear rate of 1 s^{-1} with a 50 mm parallel plate geometry with a 1 mm gap. Dynamic-mechanical analysis (DMA Q850 TA Instruments) was performed using a single cantilever geometry. The experiments were carried out within the linear viscoelastic region, at an amplitude of 1%, from -80 to 150 °C at 2 °C.min^{-1}, at the frequency of 5 Hz. Prismatic specimens (dimensions: 35 mm × 10 mm × 3.2 mm) were used.

Results and Discussion

Fig. 1 shows the isothermal evolution of viscosity over time for two formulations at 130 and 150 °C. Both systems exhibited an exponential increase in viscosity as the polymer network formed, with this effect being more pronounced in the anhydride-based formulation. In this system, higher temperatures significantly accelerated the viscosity increase within less than 14 minutes, indicating a faster polymerization compared to the amine-based formulation, which required over 100 minutes. The observed behavior is explained by the curing mechanisms. In the anhydride system, a tertiary amine is generated *in situ* at the beginning of the reaction [8], reacting with both anhydride and epoxy groups to form active species that rapidly promote network growth [4,5]. Additionally, anhydride systems initiated by tertiary amines are highly temperature-sensitive, contributing to the faster viscosity increase at elevated temperatures [9].

In contrast, the amine-based formulation follows a slower mechanism involving the nucleophilic attack of the amine on the epoxy group and an amidation reaction with the ester groups in the triglycerides of fatty acids [4,6], which results in a more gradual polymerization and a longer time to form a well-structured polymer network.

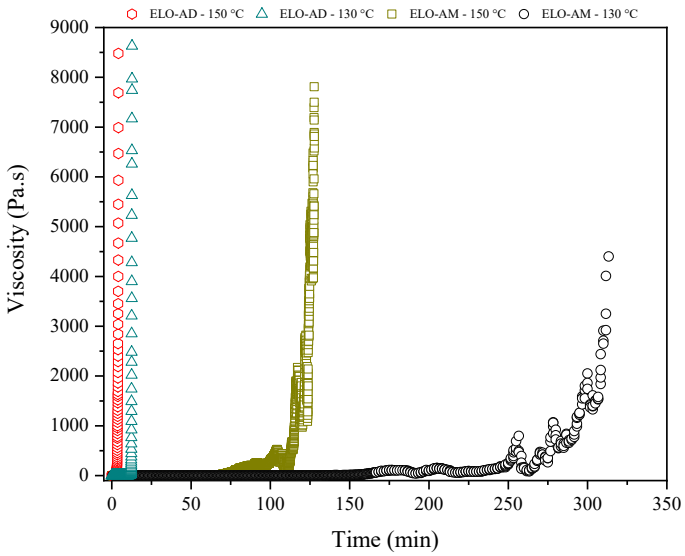

Figure 1. Viscosity as a function of temperature for ELO-AD and ELO-AM.

Fig. 2 shows the storage modulus (E′) and tan delta vs. temperature curves for the formulations. The ELO-AD formulation exhibited a higher T_g, determined by the storage modulus (E′), of 44 °C, and an E′ at 25 °C of 1198 MPa, indicating a rigid and vitreous material (Fig. 2a). This is attributed to the greater restriction of polymer chain mobility provided by the higher crosslink density [1,2]. On the other hand, the ELO-AM formulation showed a T_g (E′) of -13 °C, along with a significantly lower storage modulus at 25 °C (1.6 MPa) (Fig. 2b). This behavior is directly related to the chemical structure of the curing agent, which contains long aliphatic chains that promote greater polymer chain mobility. As a result, the material exhibits higher mechanical flexibility and reduced mechanical properties compared to the anhydride-based formulation [1,3]. Table 1 summarizes the results of DMA analysis for both formulations.

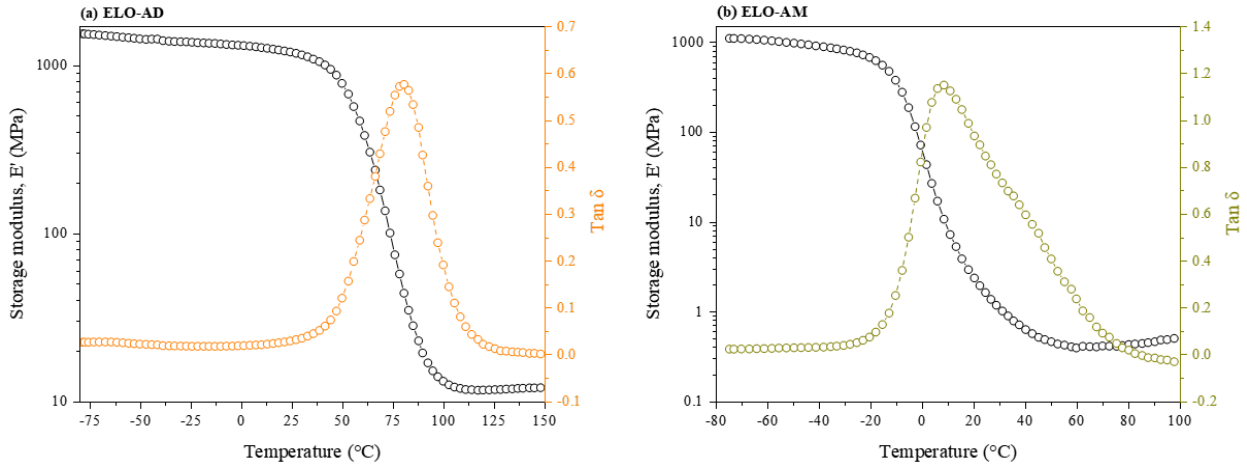

Figure 2. Storage modulus and Tan delta curves for (a) ELO-AD and (b) ELO-AM.

Table 1. Summarized DMA values for formulations ELO-AD and ELO-AM.

Property	ELO-AD	ELO-AM
T_g (from E') (°C)	44	-13
T_g (from Tan delta) (°C)	81	9
E' (25 °C) (MPa)	1198	1.6

Conclusions

The resin cured with methyl tetrahydrophthalic anhydride, initiated by a tertiary amine, exhibited a highly crosslinked structure compared to the amine-based formulation, resulting in high stiffness and mechanical strength. Moreover, this formulation showed a higher E', and higher T_g. In contrast, the resin cured with the bio-based diamine presented a less dense and more flexible network. This formulation exhibited lower values of E', and T_g. It was observed that, in the anhydride system, higher temperatures significantly accelerate the increase in viscosity over shorter time intervals, indicating a faster polymerization reaction compared to the amine-based formulation. On the other hand, the amine-based formulation requires a considerably longer time to reach exponential viscosity values, reflecting a slower curing mechanism.

Acknowledgments

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