

ASSESSING THE CURING PROCESS OF LIMONENE DIOXIDE USING DSC ANALYSIS

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Abstract – In this study, we present the findings of a brief investigation into the curing process of limonene dioxide (LDO) using three different hardeners: phthalic anhydride (PA), 4,4'-methylenediamine (MDA), and tetramethylenetriamine (TETA). The cured systems were characterized by measuring their glass transition temperatures (T_g) through differential scanning calorimetry (DSC). The observed T_g values ranged from -2 to 81 °C, indicating a significant variation in thermal properties among the cured systems. Furthermore, we preliminary optimized the epoxidation process for limonene using Oxone® and acetone.

Keywords: Epoxy resin, Bio-based epoxy, Limonene, Epoxidation, DSC

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Introduction

The development of bio-based epoxy resins with mechanical and thermal properties comparable to commercial bisphenol A-based epoxies is a challenging goal pursued by researchers in academic and industrial fields [1]. The global need for advanced materials derived from renewable sources is necessary to sustain the production and advancement of such products. While bio-based epoxy resins are available in the market, they are predominantly used for applications that do not require high thermal resistance, typically up to around 100 °C. A substantial body of research publications and patents describe various bio-based epoxy resins. The terpene *R*-limonene has promising features, particularly its availability, low toxicity, and ease of handling [2]. Moreover, current methods for epoxidizing limonene are relatively inexpensive and mild [2]. However, limonene presents challenges when applied to epoxy resins, such as its hindered chemical structure and the fully saturated nature of the molecule after epoxidation, making it challenging to achieve resins with high glass transition temperatures (T_g) [3]. One of the few examples of limonene being used for bio-based resin involves solvents and a complex iron catalyst [4].

In this study, our objective was to determine the T_g of a bio-based epoxy resin called limonene dioxide (LDO), cured with three different hardeners that have not been previously reported for LDO curing. Additionally, we aimed to investigate potentially more cost-effective conditions for synthesizing LDO using Oxone® and acetone in a Shi-type epoxidation reaction.

Experimental

Materials

All reagents were used directly without further purification. Their structure and supplier are presented in Table 1.

Table 1: Materials suppliers

Material	Purity (%)	Supplier
<i>R</i> -Limonene	97	Local supplier
Acetone	98	Synth
Oxone®	98	Sigma-Aldrich
NaHCO ₃	98	Sigma-Aldrich
PA	98	Sigma-Aldrich
MDA	97	Sigma-Aldrich
TETA	96	Sigma-Aldrich

Synthesis of limonene dioxide

The procedure used for the epoxidation of *R*-limonene was based on previously described methods [2]. In a 250 mL round bottom flask containing NaHCO₃ (51 mmol, 4,3 g), *R*-limonene with 97% purity (10 mmol, 0,14 g) in acetone (20 mL) was added and mechanical stirring (400 rpm) was applied while the temperature was kept at 25 °C. Then, a potassium monopersulphate (Oxone®) solution in water is added to the system at 1 mL/min. After 4 h, agitation ceased, and ethyl acetate (40 mL) and water (20 mL) were added to the system. Liquid-liquid extraction was performed by washing the aqueous phase three times with ethyl acetate. The solvent was removed by evaporation under reduced pressure. LDO structure was confirmed by ¹H NMR analysis comparing with reported spectra [2]. The conversion of *R*-limonene to LDO was above 99%. This is in accord with the base reference.

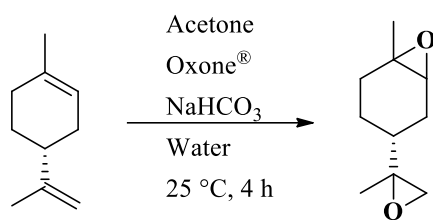
Differential scanning calorimetry

The glass transition temperature (*T*_g) of the LDO-Hardener systems was using a TA Instruments Q2000 calorimeter. Samples (~10 mg) were placed inside hermetically-sealed aluminum crucibles and subjected to the following thermal cycle under nitrogen atmosphere (50 mL min⁻¹): heating from -80 °C to 210 °C at 20 °C/min.

Results and Discussion

Initially, a set of variations on the quantities of reagents used in the base epoxidation protocol was employed to evaluate if lower amounts of reagents could lead to a similar conversion of limonene to LDO. Maximum amounts were chosen as the ones already reported, while the minimum amount of Oxone® and NaHCO₃ was determined based on the reaction stoichiometry. It was observed that in every set of conditions in which the amount of NaHCO₃ was the minimum, epoxide ring opening took place as observed by ¹H Nuclear Magnetic Resonance (¹H NMR) of signals of ROH hydrogens at ~4,7 ppm and of aldehyde at 9.6 ppm, and almost no LDO remained after the reaction time. A plausible explanation for this result is that epoxide ring opening quickly occurs under pH > 7.

Regarding cases with the maximum amount of base, lower conversion rates were observed when the amounts of Oxone® and acetone were minimized. The average conversion to LDO was 88% under these conditions. However, when acetone was minimized while the other two reagents were maximized, the conversion rate matched when all reagents were maximized, resulting in a 99% conversion. This modification led to a 50% reduction in the amount of acetone used in the protocol (Table 2, entry 4). Additionally, we conducted a final experiment using an intermediate amount of base, which yielded an 82% conversion to LDO. Scaling up the conditions from entry four did not alter the conversion to LDO.

Table 2: Optimization of conditions for LDO synthesis.

	<i>R</i> -limonene			LDO
Entry	Acetone (mL)	Oxone® (mmol)	NaHCO ₃ (mmol)	Conversion to LDO (%) ^[a]
1 ^[b]	2	2.2	2.2	>01
2	2	2.2	5.1	88
3 ^[b]	2	2.8	2.2	>01
4	2	2.8	5.1	99
5 ^[b]	4	2.2	2.2	>01
6	4	2.2	5.1	99
7 ^[b]	4	2.8	2.2	>01
8	4	2.8	5.1	99
9	2	2.4	3.8	82

^[a]Conversion determined by integrating limonene vinylic hydrogens and LDO epoxide ring hydrogens in ¹H NMR. Each condition was performed in duplicate. ^[b]Epoxide ring opening subproducts observed in ¹H NMR.

The subsequent stage involved investigating the curing of LDO using hardeners that have not been previously reported in the literature. The results revealed that a combination of LDO with phthalic anhydride (PA) yielded a polymer with a T_g of 82°C. When 4,4'-methylenediamine (MDA) was employed as the hardener, the observed T_g was 61°C. Notably, the same sample was subjected to a temperature of 110°C for 7 days, and the T_g remained relatively high at 81°C. However, when the molar ratio of MDA was doubled, the T_g dropped to 23°C, indicating that the NH₂ groups only reacted once with the oxirane groups present in LDO. In the case of tetramethylenetriamine (TETA), the resulting polymer displayed a T_g of -2°C (Table 3).

Table 3. Curing protocols and T_g

Hardener	LDO: Hardener molar ratio	T_g (°C)
PA	1:1	82
MDA	1:1	61 (81) ^[a]
MDA	2:1	23
TETA	1:1	-2

^[a]After DSC analysis, the sample was placed in a kiln at 110 °C for 7 days, and then the T_g was measured again by DSC.

These findings offer valuable insights into the impact of various hardeners on LDO's glass transition temperature (T_g), contributing to the development of bio-based epoxy resins. Furthermore, by exploring different hardeners, we better understand how they influence the thermal properties of the cured LDO polymer. This knowledge is crucial for advancing the field of bio-based materials and facilitating the design of epoxy resins with desirable characteristics.

Conclusions

A slight improvement to the epoxidation of limonene using Oxone® and acetone was developed, which can be helpful in processes for synthesizing LDO on an industrial scale. As for the T_g , we observed that using PA or MDA as hardeners were compatible with applications such as

adhesive, vacuum infusion, and coatings. Nonetheless, further investigations and characterizations are being conducted to obtain more complete data regarding LDO as a bio-based epoxy resin. These efforts deepen our understanding and provide a more comprehensive assessment of LDO's properties and potential applications.

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