



A one step route synthesis of polyurethane network from epoxidized rapeseed oil



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ABSTRACT

Biobased polyurethane networks were prepared by a one step curing epoxidized rapeseed oil (ERO) with isophorone diisocyanate (IPDI) as a hardener at 130 °C. The in-situ monitoring of the curing process by FTIR has confirmed the progressive consumption of the oxirane ring and the isocyanate function along with the emergence of the urethane groups. Investigation of model systems using phenyl isocyanate confirmed the ring opening of oxirane during the reaction between ERO and the isocyanate. Based on the spectroscopic investigation, it was hypothesised that the reaction started by the condensation between hydroxyl groups of ERO and isocyanate. Then, the oxirane was ring-opened by the urethane group and the hydroxyl group further reacted with isocyanate. The glass transition of the polyurethane network as well as the stiffness and strength were shown to be strongly dependent on the ratio between ERO and IPDI. Polyurethane film from ERO/IPDI in a ratio 80/20 results in a transparent elastic film with a T_g around -20 °C and a tensile modulus and strength of 1.5 and 9.4 MPa, respectively.

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1. Introduction

Over the last decade, there has been a growing interest for biobased polymers derived from renewable biomass due to the increasing awareness of environmental issues, depleting of petroleum resources in the near future and the need for sustainable resource without compromising food security. In this context, vegetable oils are highly suitable starting materials for polymers due to their ready availability, inherent biodegradability and low toxicity [1,2]. Vegetable oils have been used in paints and coatings for centuries, because the unsaturated oils can be crosslinked via oxy-polymerization when exposed to the oxygen in air [3]. The wide possibility to generate a large panels of polymerizable functionalities, including epoxy, aldehydes or carboxylic acids through the chemistry of the double bond, is another driving force to the increasing interest in vegetable oils. Oil can be also used as a precursor to create large oligomeric macromonomers, or through controlled cross-linking, and even to prepare polymers through olefin cross-metathesis [4].

Epoxidized oils, especially epoxidized soybean oils, are the most readily available chemically modified oils in the world [5]

at a relatively low price. The epoxidation is typically carried out using peroxy (performic or peracetic) acid generated in-situ from carboxylic acid and hydrogen peroxide [6]. Epoxidized oils are commercially available at a reasonable cost and are a promising intermediate for chemical modification because of reactive epoxy groups. Epoxidized vegetable oils and epoxidized fatty acids are largely used as thermal stabilizer plasticizers and antioxidants for PVC [7] as they offer ease of processing and improve flexibility. ESO can be used as lubricants because of high index viscosity, good thermal stability, low volatility, and good lubricity. EO can be used in manufacturing intermediate chemicals and monomers using a wide possible chemical pathway, including hydrolysis, acrylation, ethoxylation, propoxylation, hydroxylation, hydrogenation, and carbonation. The resulting monomers possessing desirable functionalities can be used in polymers thermoset, adhesive or coating. Epoxidized plant oils can be cured in similar ways as petroleum-based epoxy counterparts by reaction with polyamine [8], anhydride [9], mercaptans [10], imidazoles, and acids [11].

Polyurethane (PU) is one of the most widely investigated classes of synthetic polymers, exhibiting versatile properties suitable for use in practically all fields of polymer applications foams, elastomers, thermoplastics, adhesives, coatings, sealants, fibers, and so on. PUs are obtained by the reaction of an oligomeric polyol (low molecular weight polymer with terminal hydroxyl groups) and a diisocyanate (or polyisocyanate). The use of biobased polyol from

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vegetable oils [12,13] in the formulation of polyurethane material and commercially available polyol are proposed by several companies including Cargill, BASF, and Hobum Oleochemicals.

Epoxidized polyols (polyols derived from epoxidation and subsequent oxirane ring-opening) have long been used for the preparation of many PU products such as resins, foams, elastomers and coatings [14]. By controlling factors such as vegetable oil composition, ring-opening agent, and degree of epoxidation, polyols and PUs with varying properties have been produced [15]. However, this is a two steps approach involving firstly the conversion of epoxydized oils into polyols via alcoholysis or hydrolysis, and the subsequent reaction of the ensuing polyol with isocyanate. The direct reaction of isocyanate with epoxydized oil has not been reported in the literature.

Although premature epoxy ring opening is considered to be an undesirable side reaction leading to the formation of hydroxyl groups, epoxy polyols can be crosslinked via reaction with a curing agent capable to react with hydroxyl and oxirane but with different kinetics. This made possible the production of latent thermoset or elastomer with no activity under normal conditions, but activates the crosslinking reaction only when the temperature exceeded a critical threshold.

In this study, a new approach of crosslinking epoxidized rapeseed-oil bearing a low content of hydroxyl groups, to produce cross-linkable elastomers by reaction with a diisocyanate. The process involved the reaction of free hydroxyl groups of ESO with isocyanate followed by crosslinking through ring-opening reaction between urethane and oxirane at higher temperature. This approach is different than the well known two steps route involving firstly the alcoholysis or hydrolysis of epoxidized oils into polyols followed by a second step where the polyol is reacted with isocyanate to produce a biobased polyurethane [16].

2. Experimental section

2.1. Material

Isophorone diisocyanate (IPDI) and phenyl socyanate (PI) were obtained from Sigma- Aldrich. Refined rapeseed oil purchased from the local producer was used as received.

Anhydrous magnesium sulfate, glacial acetic acid, Hydrogen peroxide solution in water (30 wt%) were purchased from Fisher Scientific. Refined rapeseed oil purchased from the local producer was used as received.

Epoxidized soybean oil (ESO) was obtained from Traquisa S.L. (Barcelona Spain), with an epoxy oxygen content of 7.1%, corresponding to around 4 epoxy rings per triglyceride.

All materials were used as received without further purification.

2.2. Epoxidation of oils

Rapeseed oil (100 g), glacial acetic acid (24.5 mL) and concentrated sulfuric acid (4.5 g) as catalyst were charged into 500 mL round bottom flask, equipped with a condenser, dropping funnel and mechanical stirrer. The mixture was heated at 40 °C under vigorous stirring. Then, hydrogen peroxide (30 wt%, H₂O₂) solution (101.4 mL) was added to the mixture dropwise. After the peroxide addition was completed, the temperature was increased to 60 °C. After 6 h, organic phase was separated, neutralized with sodium hydroxide (10% NaOH) and washed with distilled water repeatedly until a pH of 7.0 was obtained. The remaining water was removed with anhydrous sodium sulfate. The degree of double bond conversion and epoxy content was calculated on the basis of the determined values of iodine and epoxy number according to ASTM D 5554 and ASTM D 1652-04 methods, respectively.

2.3. Curing of ERO with IPDI

RSO and IPDI were mixed under nitrogen flushing and then poured into a Teflon mold and cured at constant temperature for 15 h. Finally, the polyurethane films were removed from the mold and cut into specific dimensions for characterization.

2.4. Characterization

The epoxy content was determined according to the standard method of ASTM D 1652-04. Hydroxyl numbers were determined according to ASTM D 1957-86.

¹H NMR spectra were recorded by using a Bruker AV400 NMR spectrometer at a frequency of 400 MHz with CDCl₃ as solvent.

FTIR spectra of the samples were recorded on a Perkin-Elmer Fourier transform infrared spectrophotometer. The in-situ kinetic measurement of the curing of ERO with IPDI was performed on a 50 μm path cell placed on a temperature-controlled sample holder ± 0.1 °C.

Dynamic mechanical analysis (DMA) measurements were carried out on a dynamic mechanical analyzer in tension mode using a PYRIS Diamond DMA (Perkin- Elmer, USA). The specimens were about 20 mm length, 5 mm width and about 1 mm thickness. The temperature dependence of the loss factor tan δ was measured in the range –60 to 100 °C at a frequency of 1 Hz and an amplitude of 10 μm and a heating rate of 2 °C/min.

Thermogravimetric analysis (TGA) of the films was carried out on a Perkin-Elmer Instrument. The samples were heated to 700 °C at a heating rate of 10 °C min⁻¹ in air.

The non-linear mechanical behavior of the films was analysed using an Instron testing machine in tensile mode, with a load cell of 500 N working at a strain rate of 10 mm min⁻¹ at 25 °C. The specimens were obtained using a cutting device. Average values were taken of at least three replicates of each sample.

2.5. Swelling test and gel content

Gel content of cured film was determined after Soxhlet extraction. Specimens of 10 mm length and about 1 mm thickness were cut and extracted with 200 mL of refluxing toluene via Soxhlet extraction for 24 h. The extracted materials were then dried at 80 °C and the gel content was calculated from the difference in weight of the dry samples before and after extraction.

Approximately 0.2 g of the cured resins with a cubic shape (8 mm × 8 mm × 3 mm) were placed in toluene for 48 h to reach absorption equilibrium. The swollen samples were removed from the solvents, blotted with dry paper, and weighed. The equilibrium swelling ratio of the polyurethane (PU) film was calculated from the difference in weight of the dry samples before and after swelling.

3. Results and discussion

3.1. Characterization of the ERO

The epoxidized rapeseed oil (ERO) was prepared by the reaction of rapeseed oil with glacial acetic acid and hydrogen peroxide as a catalyst in toluene at 60 °C for 7 h. The obtained ERO is a low-viscosity yellowish liquid. The structure of ERO was confirmed by their FTIR, ¹H NMR and ¹³C NMR spectra. The formation of epoxide rings after epoxidation was evident from the peaks shown at 2.8–3.2 ppm in the ¹H NMR spectrum and between 53 and 57 ppm in the ¹³C spectra of the epoxidized soybean oil. No chemical shifts at 5.3 ppm (in ¹H NMR) and 130 ppm (in ¹³C NMR) were witnessed after the reaction, indicating the total disappearance of double bonds. However, in addition to the epoxy ring, a low amount of hydroxyl groups were detected at 3.4 ppm and 74.5 ppm in the ¹H

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