Plant oil-based epoxy resins from fatty diamines and epoxidized vegetable oil

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ABSTRACT

Herein, the synthesis of vegetable oil-derived diamines by thiol-ene coupling (TEC) using cysteamine hydrochloride is reported. Despite the amine group in cysteamine that is unfavorable to TEC, fatty allylamide (FAl-A) provides an aminated fatty amide (AFA). Due to other diamides, the influence of the fatty structure on the TEC reactivity was demonstrated. The structures were characterized using FTIR and ^{1}H NMR spectroscopies, and the crosslinking of epoxidized linseed oil (ELO) with AFA was investigated using differential scanning calorimetry (DSC) and dynamic rheometry. The thermomechanical behavior of the plant oil-based thermoset was also characterized and compared to a commercial diamine based on a fatty dimer structure and a branched polyamine prepared from grapeseed oil. Finally, the beneficial effect of oxidation of the epoxy resin on the thermomechanical properties is highlighted.

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1. Introduction

Based on the current petroleum issues (i.e., increase in the price and depletion of fossil reserves), biomass has attracted much attention as a feedstock for material applications. Various bio-based compounds (i.e., polysaccharides, rubbers or vegetable oils) could be used or modified to elaborate attractive polymers [1,2]. The major advantages of vegetable oils include their relative abundance, low price and non-toxicity. Therefore, lipids have been widely exploited for the polymerization of bio-based thermoplastic materials [3–5], such as polyamide 11 [6], and thermoset materials, such as polyurethanes [7–9] and epoxy resins [10]. Plant oil-based epoxy resins have attracted industrial interest due to the lack of bisphenol A or aromatic amine precursors that are carcinogenic or toxic. These resins are typically produced by catalytic homopolymerization of epoxidized oil [1,11,12] or polyaddition using polyol [13,14], polyacid, anhydride in the presence of catalyst [15,16] or a polyamine hardener [17,18]. Our study focuses on epoxy-amine thermosets with lipidic structures.

Few natural amines, aliphatic diamines (i.e., 1,4-butanediamine, 1,5-pentanediamine, 1,12-dodecanediamine or 1,18-octadecanediamine) and triamine (spermidine), and bioderived amines, such as aminated isosorbide, have been reported [19]. Biermann et al. reviewed different methods for functionalizing unsaturated fatty acids with amine groups [20]. The addition of sodium azide followed by the catalyzed reduction of the azide group into an amine was explored. Recently, Zhao et al. prepared secondary amines in a five steps process starting from epoxidized triglyceride [21]. The oxirane groups were successively transformed into diols, bromines, and azide groups and finally reduced to amines. Some attempts at

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enzymatic biotransformation have been successfully employed for the production of polyamines through the synthesis of an azadicarboxylate diethyl ester derivative of soybean oil [22,23]. Under basic conditions, the derivative was converted to a substituted hydrazine. The same authors discovered another method for the production of an oleate-aniline using catalytic amounts of an ionic liquid [24]. The use of a nitrile compound as an amine precursor after catalytic reduction has also been investigated with fatty acids [25]. Finally, the addition of an excess amount of diamine to epoxidized vegetable oil can lead to an aminated fatty ester [26].

Our group focused on the synthesis of fatty polyamines by thiol-ene coupling (TEC) to extend the bio-based amine series. In the literature, the TEC reaction is widely employed in polyol synthesis. However, only a few examples have described the synthesis of polyamine due to the formation of thiolate in the presence of an amine group, which affects the radical addition on the unsaturation. In a previous study, we reported the synthesis of an aminated oil bearing four amine groups per triglyceride using the thiol-ene reaction with cysteamine hydrochloride, and this oil was cured with commercial epoxidized linseed oil (ELO) [27]. Using the same synthetic strategy, Meier et al. modified fatty esters and used them for the preparation of polyamides and copolyamides [28].

In this study, we extend the thiol-ene coupling (TEC) methodology using cysteamine chloride with various fatty amides and diamides and demonstrate the influence of the fatty structure on the reaction efficiency. The curing process of the aminated fatty amide (AFA) and ELO was also studied at different temperatures, and the crosslinking kinetics were investigated using calorimetric and rheological analyses. Finally, the thermomechanical properties of the lipidic thermosets were characterized.

2. Materials and methods

2.1. Materials

Absolute ethanol (EtOH, Carlo Erba), *n*-hexane (Carlo Erba), toluene (Sigma Aldrich), ethyl acetate (AcOEt, Carlo Erba), tetrahydrofuran (THF, Carlo Erba), isopropanol (iPrOH, Carlo Erba), dioxane, dichloromethane, hydrochloric acid (HCl, Carlo Erba), potassium hydroxide (KOH, Aldrich), sodium hydroxide (NaOH, Aldrich), $MgSO_4$ (VWR), silica gel (Aldrich), hexylenediamine (HDA, Aldrich), ethylenediamine (EDA, Aldrich), p-xylenediamine (p-XDA, Aldrich), diethylenetriamine (DETA, Aldrich), allylamine (Aldrich), DCC (N,N-dicyclohexyl carbodiimide), DMAP (4(dimethylamino) pyridine), cysteamine hydrochloride (CAHC, Aldrich), 2,2-dimethoxy-2-phenylace-tophenone (DMPA, 99% Aldrich) and Priamine 1075 (Priamine, Croda) were used as received. Deuterated chloroform ($CDCl_3$) was purchased from SDS and used without purification. Epoxidized linseed oil (ELO) was generously provided by ONIDOL, and the grapeseed oil was produced by SICA RAISINOR FRANCE. The grapeseed oil contained linoleic acid (65.9% C18:2), palmitoleic acid (0.1% C16:1), oleic acid (22.7% C18:1), linolenic acid (0.5%

C18:3) and palmitic and stearic acids (6.9% C16:0) and (3.9% C18:0). In addition, the grapeseed oil has 4.75 double bonds per triglyceride. The linseed oil contained linolenic acid (47.4% C18:3), unsaturated oleic (19.0% C18:1), linoleic (24.1% C18:2) and palmitic and stearic (6.0% C16:0) and (2.5% C18:0) and others (1.0). In addition, the linseed oil contains six carbon double bonds per triglyceride.

2.2. Analytical techniques

^{1}H and ^{13}C NMR spectra were recorded using a Bruker AVANCE spectrometer (^{1}H at 300 MHz, ^{13}C at 75.47 MHz). ^{1}H NMR spectra (δ, ppm) were recorded on an NMR Bruker Avance I 300 MHz sonde QNP (^{1}H/^{13}C/^{19}F/^{31}P) or on a Bruker Avance III 600 MHz sonde QXI (^{1}H/^{13}C/^{31}P/^{15}N) with $CDCl_3$ as a solvent. The chemical shifts ^{1}H NMR spectra were referenced to the peak of residual $CHCl_3$ at 7.26 ppm. The chemical shifts in the ^{13}C NMR spectra were referenced to $CDCl_3$ at 77 ppm. Calorimetric analyses were carried out using a Star1 differential scanning calorimeter (DSC) from Mettler Toledo® to determine the temperature zone characteristics of the crosslinking reaction. 10 mg of the non-cured mixture was poured into an aluminum pan that was consecutively placed in the measurement-heating cell. An empty pan was used as a reference. These calorimetric experiments were achieved under inert atmosphere with a heating rate maintained at 5 °C min⁻¹. Fourier Transform infrared (FTIR) spectra were recorded with a Perkin–Elmer Spectrum 100 spectrometer equipped with an attenuated total reflectance (ATR) crystal (ZnSe). The thermo-oxidative stability of the reactive formulation was examined using a Q50 thermogravimetric analyzer (TGA) from TA Instruments®. The experiments consisted of registering the weight loss of the sample under an air flow (25 mL min⁻¹) as a function of temperature from ambient temperature to 550 °C. Different experiments were performed with heating rates of 1–10 °C min⁻¹. All of the rheological experiments were performed using a stress-controlled rheometer (AR2000Ex from TA Instruments®) in dynamic mode. The viscoelastic experiments consisted of studying the kinetics of the crosslinking reaction using a cup-plate geometry as a sample container. The inner diameter of the cup was 40 mm, and the inner diameter of the upper plate was much smaller (5 mm) to prevent parasitic side effects. The same rheometer was employed to investigate the evolution of the dynamic mechanical behavior of the cured sample as a function of the temperature. Because the cured samples were solid materials, the experiments were performed using a rectangular torsion geometry. Typical dimensions of the sample were 45 mm × 10 mm × 1 mm. The thermomechanical tests were carried out at a heating rate of 3 °C min⁻¹ from −150 up to 200 °C and a fixed oscillating angular frequency, which ranged from 1 to 100 rad s⁻¹.

2.3. Synthesis

2.3.1. Synthesis of fatty acid (FA)

Grapeseed oil was dissolved in a solution of KOH (10 equiv.) in ethanol (1.7 mol L⁻¹), and the mixture was stirred for 3 h under reflux conditions. After cooling, the