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Synthesis and copolymerization of thermosetting resins obtained from vegetable oils and biodiesel-derived crude glycerol

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ABSTRACT

Alkaline crude glycerol from biodiesel production was used in the synthesis of soybean oil and castor oil-based polyols through glycerolysis reaction. These polyols were further converted into highly active unsaturated resins through maleinization reactions. The resins were copolymerized with styrene (10–50 wt%) using cobalt octoate and methyl ethyl ketone peroxide (MEKP) at 40 °C, affording rigid materials. Materials were characterized by FTIR spectroscopy, Soxhlet extraction, TGA, DMTA, and mechanical tests. T_g values of 72–152 °C and elastic modulus of 465–2945 MPa were obtained, depending on the type of resin and styrene concentration.

The materials presented flexural modulus and flexural strengths in the range of 246–1716 MPa and 24–89 MPa respectively. T_g values and elastic modulus at 25 °C were higher for materials obtained from castor oil glycerides. Materials obtained from both resins were stable under 200 °C. Higher thermal stabilities were obtained for castor oil based materials. These properties were related to a higher crosslinking density obtained for polymers derived from castor oil. In addition, radical homopolymerization of both resins at 100 °C during 24 h afforded viscous liquids with M_n values between 1358 and 3775.

1. Introduction

According to the US Department of Energy (DOE), vegetable oils are a potential feedstock for polymers because their fatty acid molecules can be modified to serve as polymer building blocks [1]. Unsaturated natural oils such as linseed and tung oil can be polymerized directly through radical mechanisms [2]. Main applications of these oils are found in paints and varnishes formulations. On the other hand, less unsaturated oils such as soybean oil have been cationic copolymerized with styrene, 1,4-divinlybenzene and dicyclopentadiene as reported by Larock et al. [3–6]. Properties of these materials range from soft rubbers to hard thermosets. Fatty acid chains present in the triglyceride oils act as plasticizers, reducing the stiffness of the materials. In addition, the C=C from the fatty acid chains are not enough reactive in radical polymerization, which is more commonly used than cationic polymerization. For this reason, and in order to obtain rigid materials, several polymerizable functional groups must be introduced in the triglyceride structure. These functionalities can be attached through unsaturations, allylic carbons, ester groups, hydroxyl groups and α carbons to double bonds [2].

In the last decade several works have been devoted to the modification of triglycerides to obtain monomers through different routes such as epoxidation-acrylation, alcoholysis-maleinization, and hydroxylation-maleinization [7–11]. These monomers have been copolymerized mostly with styrene. Properties of the resulting polymers were

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dependent on the structure of the alcohol used and the type and content of comonomer [4]. In addition to glycerol, pentaerythritol, and bisphenol-A propoxylate have been used as polyols for the alcoholysis reaction [11]. However, the use of glycerol is more convenient due to its low price. Price of glycerol has diminished due to the glut of crude glycerol from biodiesel production [12]. Crude glycerol contains, in addition to glycerol, several impurities such as methanol, the transesterification alkaline catalyst, soaps, glycerides, and water. Most of the applications of crude glycerol require, at least, the removal of the alkaline catalyst and the separation of methanol [13]. Recently it was reported by our group the synthesis of monoglycerides and diglycerides from crude glycerol without previous purification [14]. Monoglycerides and diglycerides can be used as raw materials of alkyds resins or can be modified affording thermosetting resins, as shown in this manuscript.

In this work vegetable oils (soybean oil or castor oil) and crude glycerol from biodiesel production were used as starting raw materials to obtain unsaturated resins. Soybean oil is mainly composed of triglycerides bearing unsaturated fatty acids (oleic, linoleic and linolenic) and saturated fatty acids (stearic), while castor oil is mainly composed of triglycerides of ricinoleic acid (an unsaturated fatty acid chain with hydroxyl functionalities). Crude glycerol was used without purification process (i.e. alkaline crude glycerol was used). To the best knowledge of the authors this application of crude glycerol has not been reported before in the literature. In addition, a method was developed specifically for the purification of maleated glycerides. Although thermosets based on maleated glycerides and styrene have been synthesized previously, certain properties have not been evaluated so far [11]. For instance, analyses of insoluble/soluble fractions as well as thermogravimetric assays have not been reported for these polymers. Moreover, DMTA analyses have not been reported for thermosets based on maleated soybean oil glycerides and styrene. In this work, such properties were evaluated at different resin/styrene ratios, comparing thermosets obtained from castor oil and soybean oil glycerides. Homopolymers derived from maleated glycerides were also synthesized and characterized in order to gain insights about reactivity of both resins without styrene. These type of homopolymers have not been studied previously.

2. Experimental

2.1. Materials

Refined soybean oil was purchased in a local market (acid value 0.17 mg KOH/g). Technical grade castor oil (acid value 1.96 mg KOH/g) was purchased from a local distributor. Sodium hydroxide ($\geqslant$97%), maleic anhydride ($\geqslant$98%), and styrene ($\geqslant$99%) were purchased from Sigma–Aldrich. MEKP (Butanox-M50) and cobalt octoate (NL51P) were purchased from AKZONobel.

2.2. Synthesis of soybean oil glycerides (SOG) (see Fig. 1)

Crude glycerol was obtained from a typical transesterification experiment of soybean oil with methanol using 0.37% of NaOH respect to the oil, according to the procedure of Echeverri et al. [15]. Methanol was removed from crude glycerol by evaporation under reduced pressure. No further purification was accomplished.

Soybean oil glycerolysis was conducted in a 250-mL round-bottom flask, equipped with mechanical stirring, nitrogen inlet, and heated with a heating mantle according to procedure of Echeverri et al. [15]. 150 g of soybean oil (0.17 mol) was heated to the reaction temperature (200 °C) and crude glycerol (45.01 g) was added under 2.5/1 M ratio of glycerol to oil, according to the purity obtained by gas chromatography (88.1%). Once the reaction was finished (20 min.), 2.2 mL of H_2SO_4 solution in water (50% w/w) was added to neutralize the alkaline catalyst. The mixture was allowed to cool to 110 °C to separate the neutralized catalyst and the most of the excess glycerol in the bottom of the flask.

^1H NMR spectra of the product showed the following signals:

^1H NMR [$CDCl_3$, δ (ppm)]: 5.35 (m) $-C\underline{H}=C\underline{H}-$ from oleic moieties; 5.08 (m) $-C\underline{H}O(C=O)-$; 4.25–4.05 (m) $-CH_2O(C=O)-$; 3.93 (m) $-C\underline{H}-OH$; 3.73–3.55 (m) $C\underline{H_2}OH$; 2.78 (m) $-CH=CH-C\underline{H_2}-CH=CH-$ from linoleic moieties; 2.29 (t) $-CH_2(C=O)O-$; 2.01 (m) $-C\underline{H_2}-CH=CH-$; 1.58 (t) $-C\underline{H_2}-CH_2-(C=O)O-$; 1.41–1.14 (m) $nC\underline{H_2}-$;0.85 (t) CH_3-.

^{13}C NMR [$CDCl_3$; δ (ppm)]: 179.5 $-(C=O)OH$; 174.0 $-(C=O)O-$; 130.3–128.0 $-\underline{C}H=\underline{C}H-$; 70.5–68.2 CHOH; 62.0 CH_2OH; 34.1–20.5 $-CH_2-$; 14.0 CH_3.

2.3. Synthesis of castor oil glycerides (COG)

Same above procedure was followed for the glycerolysis of castor oil. The weights of reactants were: castor oil, 150 g (0.16 mol), crude glycerol, 42.35 g. 2.0 mL of H_2SO_4 solution in water (50% w/w) were added to neutralize the catalyst.

^1H NMR spectra of the product showed the following signals:

^1H NMR [$CDCl_3$, δ (ppm)]: 5.54 (m) $-CH=C\underline{H}-CH_2-CH(OH)-$; 5.37 (m) $-C\underline{H}=CH-CH_2-CH(OH)-$; 5.08 (m) $-C\underline{H}O(C=O)-$; 4.25–4.05 (m) $-C\underline{H_2}O(C=O)-$; 3.98–3.84 (m) $-C\underline{H}-OH$; 3.76–3.52 (m) $C\underline{H_2}OH$; 2.34 (t) $-C\underline{H_2}(C=O)O-$; 2.20 (m) $CH-C\underline{H_2}-CH(OH)-$; 2.02 (m) $-C\underline{H_2}-CH=CH-$; 1.62 (t) $-C\underline{H_2}-CH_2-(C=O)O-$; 1.45 (m) $-CH_2-C\underline{H_2}-CH(OH)-$; 1.42–1.14 (m) nCH_2-; 0.85 (t) CH_3-.

^{13}C NMR [$CDCl_3$; δ (ppm)]: 179.5 $-(C=O)OH$; 174.0 $-(C=O)O-$; 133.2 $\underline{C}H=CH-CH_2-CH(OH)-$; 125.3 $CH=\underline{C}H-CH_2-CH(OH)-$; 71.5 $-CH_2-\underline{C}H(OH)-$; 70.5–68.2 CHOH; 62.0 CH_2OH; 35.3 $-\underline{C}H_2-CH(OH)-$; 34.1–20.5 $-CH_2-$; 14.0 $-CH_3$.

2.4. Synthesis of maleated soybean-oil glycerides (MASOG) (see Fig. 1)

Maleinization was carried out in 25 mL round bottom flask equipped with a condenser according to the