



Polymeric networks based on tung oil: Reaction and modification with green oil monomers



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ABSTRACT

A highly unsaturated vegetable oil (tung oil) was cationically copolymerized with a vegetable oil derived monomer, that replaces the more frequently used styrene. The synthesized comonomer was methyl ester of tung oil, obtained by transesterification of the plant oil with methanol. Alternatively, the incorporation of a green modifier, a commercial acrylated epoxidized soybean oil, was also considered. The use of any of these modifiers allowed preparing materials with an elevated content of bio-derived components.

All the materials obtained presented good mechanical damping capacity, as well as dynamic mechanical properties comparable to analogous materials obtained by copolymerization with styrene. Incorporation of low concentrations of divinylbenzene in the formulations allowed increasing rigidity and glass transition temperatures (T_g) of the materials. One of the formulations prepared by copolymerization with the tung oil methyl ester presented shape memory behavior.

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1. Introduction

The interest in using renewable resources to develop new materials has been growing during the last years. In particular, the use of natural oils has received much attention because they offer the advantages of wide availability and a basic structure with varied chemical functionalities (depending on the plant origin) that allows synthesizing different products for a large number of applications [1–4].

Vegetable oils are considered one of the most important sources of renewable raw materials for the production of bio based polymers because of the large number of reactive sites in their structures capable of being chemically modified or, in some cases, capable of directly reacting to form polymeric materials [1,5,6]. In particular, tung oil (TO) is extracted from the tung tree seeds and is composed mainly

of α -elaeostearic acid (77–82%) containing three conjugated double bounds, oleic acid (3.5–12.7%) with one double bond and linolenic acid (8–10%) with three non-conjugated double bonds [7–10]. This feature is responsible for the excellent drying properties, which are widely exploited in the industry of paints and varnishes [9,11–13], and it is also responsible for the capability of this oil to cationically polymerize with monomers such as styrene, giving rise to materials with a variety of properties from elastomers to rigid polymers, depending upon the monomer and the used stoichiometry [6,7,14]. In particular, the use of tung oil is appealing because the conjugated $C=C$ of the α -elaeostearic acid make unnecessary any modification of the oil.

In recent years, different groups have published scientific contributions focused on resins or polymer precursors obtained from vegetable oils and fatty acids (Wool et al. [15–18]; Larock et al. [5,19–27]; Petrovic et al. [26,28,29]; Mosiewicki et al. [30]). On the other hand, other authors have devoted their efforts to find/synthesize

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environmentally friendly monomers based on vegetable oils that could replace petroleum-based monomers such as styrene and divinylbenzene (Khot et al. [31]; Hu et al. [32]; La Scala et al. [33]; Can et al. [17]; Quirino et al. [34]). For example, La Scala et al. [33] synthesized unsaturated monomers starting from fatty acid and glycidyl methacrylate, which were free radically polymerized with a vinyl ester resin.

Following the international pressure of the general public, governments and organizations for replacing petroleum based chemicals, commercial bio-based products have already been introduced in the market. According to international regulations a material that has more than 20% of bio-based content, can show a “bio” label indicating such a percentage.

Fatty esters obtained from the transesterification of tung oil with methanol, can be considered as polymeric precursors with conjugated unsaturations that are reactive in cationic polymerizations. In general, the transesterification reaction of a vegetable oil is one in which a triglyceride is reacted with an alcohol in the presence of a strong acid or a base to produce a mixture of esters of fatty acids and glycerol [35,36].

Vegetable oil have been extensively modified by reaction of the original unsaturations to produce chemicals of different functionalities from those originally present in vegetable oils, such as acrylate groups that can participate in radical polymerization reactions. The synthesis of this type of precursor is possible by the epoxidation of the unsaturations followed by reaction with acrylic acids that incorporates terminal unsaturations [37]. Although, acrylate groups do not participate in cationic reactions [38], the acrylated epoxidized soybean oil can be used as a highly compatible green modifier in oil based reactive mixtures.

Thus, in the present work, petroleum based comonomers, which were used in the past [5–7] in the cationic copolymerization of vegetable oils, were replaced by a bio-based comonomer, methyl ester of tung oil. This type of formulation allows increasing even more the percentage of bio-based content in the final materials and avoids the use of an aggressive chemical reactant such as styrene. Also a bio-based modifier, acrylated epoxidized soybean oil, was considered in the formulation of modified tung oil networks.

The properties of the obtained polymers were compared with those measured previously for tung oil/styrene copolymers.

2. Experimental

2.1. Materials

Tung oil (TO) composed of α -elaeostearic acid (main component, 84 wt.%) was supplied by Cooperativa Agrícola Limitada de Picada Libertad, Argentina. For the transesterification reaction, methanol (99.98% pure, Biopack, Argentina), sodium hydroxide (97% pure, Anedra, Argentina) and sulfuric acid (98.5% pure, Anedra, Argentina) were used. Acrylated epoxidized soybean oil (AESO) was purchased by Sigma–Aldrich. The following materials were purchased

from Cicarelli Laboratory, Argentina: divinylbenzene 80% pure (DVB), styrene 99.5% pure (St) and tetrahydrofuran 99% pure, (THF). Boron trifluoride diethyl etherate ($\text{BF}_3\cdot\text{OEt}_2$) with 46–51% BF_3 , obtained from Sigma–Aldrich was the initiator of the cationic reaction.

2.2. Methods and techniques

2.2.1. Methyl ester (ME) synthesis from tung oil (TO)

For the synthesis, 300 mL of TO were mixed with 90 mL of methanol and 1.8 g of sodium hydroxide in a glass reactor with mechanical stirring for 45 min at 50 °C. Two phases were obtained (ME and glycerol) which were separated in a separating funnel. The ME was purified by washing with a 0.015 N sulfuric acid solution, and subsequent washings with distilled water to neutral pH. Finally, the ME was dried using a rotary evaporator under vacuum for 2 h at 50 °C.

2.2.2. Preparation of green polymeric materials

A selected quantity of ME, AESO or St (and minimum amounts of DVB depending on the formulation) were incorporated to the tung oil (TO) and the mixture was stirred. This step was followed by the addition of the modified initiator prepared by mixing tetrahydrofuran, THF (5 wt.% with respect to the reactive mixture) with boron trifluoride diethyl etherate (3 wt.% with respect to the reactive mixture). As it was reported in previous works, due to the poor miscibility of the catalyst in the oils, it must be solvent-modified to obtain a homogeneous initial solution [12,39,40]. The mixture was vigorously stirred and finally poured into glass plates of 13 mm \times 18 mm separated by a rubber cord of 1 mm of thickness and kept closed with metal clamps. The reactants were heated first at 25 °C for 12 h, then at 60 °C for 12 h and finally at 100 °C for 24 h. The weight ratio of TO/ME was selected as 70/30 and the percentage of DVB (0, 5 and 10 wt.%) was calculated relative to that of the total mix of TO/ME. The chosen nomenclature was 70TO/30ME, [70TO/30ME]/5DVB and [70TO/30ME]/10DVB. For the polymers modified with AESO, the weight ratio of TO/AESO was 90/10 with aggregates of 5 and 10 wt.% of DVB calculated relative to that of the total mix of TO/AESO. Besides, polymers TO/AESO with weight ratios of 70/30, 80/20 and 90/10 were also prepared. The chosen nomenclature is indicative of the weight ratios utilized in the synthesis as shown: 70TO/30AESO, 80TO/20AESO, 90TO/10AESO, [90TO/10AESO]/5DVB and [90TO/10AESO]/10DVB.

2.2.3. Chemical characterization of the materials (FT-IR)

FT-IR spectra of the ME, AESO and derived modified polymers were recorded by using the attenuated total reflection method (ATR) with a Thermo Scientific Nicolet 6700 FT-IR spectrometer. The spectra were obtained over the range of 500–4000 cm^{-1} with a resolution of 2 cm^{-1} and averaged over 32 scans.

2.2.4. Nuclear magnetic resonance spectroscopy (^1H NMR)

^1H NMR spectra of the samples were recorded on a Bruker AM500 spectrometer (500 MHz) using CDCl_3 as solvent.

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