



Synthesis of elastomeric networks from maleated soybean-oil glycerides by thiol-ene coupling

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ABSTRACT

Maleated soybean-oil glycerides were photopolymerized with multifunctional thiols to give elastomeric networks. Polymers were characterized by Raman, DSC, TGA and DMTA analyses. Materials exhibited properties that resemble those of elastomers with glass transition temperatures below room temperature. Influence of thiol functionality over polymer properties was analyzed. Model reactions of monoethyl maleate and methyl oleate with monofunctional thiol were studied by ¹H NMR to control the curing process.

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1. Introduction

In the last decades, and due to concerns about the environment and the depletion of non renewable resources, the use of raw materials derived of plants, animals, microorganisms and waste has been increasing in polymer applications [1]. The use of natural oils and derivatives as polymer building blocks has several advantages such as renewability, availability and versatility [1]. Triglycerides themselves contain polymerizable functional groups such as unsaturations and ester groups. Likewise, several exotic oils such as lesquerella, vernonia and cashew offer further interesting functional groups like epoxide, hydroxyl and phenol [2,3].

Direct radical polymerization of triglycerides is possible through unsaturations, such as in the case of drying oils used in varnishes. On the other hand, direct cationic copolymerization of soybean oil with styrene, divinylbenzene

and dicyclopentadiene has been extensively investigated by Lu et al. [4]. Because triglycerides contain long fatty acid chains, they act as plasticizers reducing modulus and affording rubbers, therefore copolymerization with other olefinic monomers is necessary to obtain tougher plastics [4]. An interesting approach to obtain thermosets from vegetable oils consists of the attachment of readily polymerizable functional groups on the triglyceride structure forming vegetable oil macromonomers (VOMMs) [5]. Attachment of these functionalities can be done through unsaturations, allylic carbons, ester groups, hydroxyl groups and α -carbons to carbonyl groups [1,6]. Specifically, in order to obtain fatty vinyl monomers different routes such as epoxidation–acrylation, glycerolysis–maleinization and hydroxylation–maleinization have been used [7].

Alcoholysis reactions, followed by maleinization, is one of the most used strategies to obtain fatty vinyl monomers from vegetable oils [8–11]. Pentaerythritol, glycerol and bisphenol A propoxylate have been used as polyols for the alcoholysis reactions [8,9]. Copolymerization of soybean and castor oil maleates with styrene afforded rigid

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materials. Resins exhibit viscosities that are suitable for use in liquid molding processes. Castor oil based polymers presented comparable properties to those based on unsaturated polyester resins derived from petroleum. Castor oil based polymers exhibited higher modulus, strength and T_g than polymers based on soybean oil [9].

It has been shown that the carbon–carbon double bond of a fatty acid chain can react with thiols via thiol-ene coupling [12,13]. The reaction between a thiol and unsaturations is well-documented. In the last decade, a renewed interest in thiol-ene coupling for polymer synthesis has emerged due to its number of advantages: tolerance to many different reaction conditions/solvents, clearly defined reaction pathways/products, and facile synthetic strategies from a range of easily obtained starting materials [14]. Thiol-ene chemistry allows obtaining well-defined materials with few structural limitations and synthetic requirements [15]. The thiol-ene coupling makes use of the high nucleophilicity of the sulfhydryl moiety and proceeds under mild conditions. The formed thioether linkage is very stable under physiological conditions and resists a strong basic or acidic environment and is also stable toward reducing agents; however, it is susceptible toward oxidizing agents [15]. Recently, the thiol-ene addition of multifunctional thiols to soybean oil to produce low molecular weight oligomers has been described [16]. Also, chemical modification of triglycerides to produce polyols by thiol-ene has been described [17].

Thiol-ene reaction can be initiated by heat or light. However, the use of light allows better control of the reaction both temporally and spatially. In addition, less secondary reactions, such as chain transfer, occur during photopolymerization [18,19]. Many works focusing on UV-curable systems based on monomers derived from vegetable oils have been reported [5,20–22], but UV-curable systems based on maleates, fumarates and acrylates has not been widely studied. In one of these works, Esen et al. [20] reported the photolytic polymerization of mono-methyl maleate esters of epoxidized soybean oil (MESO). Photopolymerization of a mixture of MESO and styrene (35 wt/total weight) for 40 min afforded an infusible film. Also, Black and Rawlins [5] reported the synthesis of thiol-ene UV-curable coatings based on allyl, acrylate, and vinyl ether derivatives of castor oil together with a multifunctional thiol. The films exhibited high solvent resistance and hardness as well as excellent adhesion and flexibility.

To the best knowledge of the authors, thiol-ene photo-initiated polymerization of VOMMs containing both maleic and olefinic double bonds and without any other reactive diluents (such as styrene) has not been reported before. Suppression (or reduction) of reactive diluents in the reaction is highly recommended due to environmental issues. This work is focused on the photoinitiated crosslinking of maleated soybean oil glycerides (MASOG) with tri- and tetra-functional thiols. The glycerides modification conditions were established on the basis of model reactions of monoethyl maleate (MEM), methyl oleate (MO) and MASOG with a mono-functional thiol. The properties of the resulting networks were analyzed in order to establish their potential applicability.

2. Experimental

2.1. Materials

Refined soybean oil (SO) was purchased in a local market (acid value 0.17 mg KOH/g). Glycerol ($\geq 99\%$), sodium hydroxide ($\geq 97\%$), maleic anhydride ($\geq 98\%$), ethanol (99.5%), trimethylolpropane tris(3-mercaptopropionate) (TMP-3MP, $\geq 95.0\%$), pentaerythritol tetrakis(3-mercaptopropionate) (Penta-3MP4, $\geq 96.0\%$), 2,2-dimethoxy-2-phenylacetophenone (DMPA, 99%), 3-mercaptopropionic acid (3-MP, $\geq 99\%$) and acetonitrile (99.8%) were purchased from Sigma-Aldrich. 2-Methyl imidazole ($\geq 97\%$) was purchased from Alfa Chemicals. Methyl oleate (MO, 90% Mallinckrodt, St. Louis) was synthesized from oleic acid and methanol following a standard method.

Structures of the multifunctional thiols used are represented in the Fig. 1.

2.2. Synthesis of soybean oil glycerides (SOG) (Scheme 1)

Fifty gram (0.058 mol) of SO was added to a 150-mL round-bottom flask equipped with nitrogen inlet and mechanical stirring. Glycerol (15.8 g) (0.170 mol) was mixed with 0.1 g (1.2 mmol) of sodium hydroxide and stirred until total homogenization of the catalyst. Then, the glycerol–catalyst mixture was added to the oil. The reaction was carried out at 200 °C [23]. Once the reaction was completed (20 min), 0.3 mL of H_2SO_4 solution in water (50% w/w) was added to neutralize the catalyst. The mixture was allowed to cool to 120 °C and then it was centrifuged at 6000 rpm for 10 min to separate the remaining glycerol from monoglycerides and diglycerides. The product was obtained as viscous oil, with 85% yield. 1H NMR [$CDCl_3$, δ (ppm), TMS]: 5.35 (m, $-CH=CH-$ from oleic moieties), 5.08 (m, $-CHO(C=O)-$), 4.25–4.05 (m, $-CH_2O(C=O)-$), 3.93 (m, $-CH-OH$), 3.73–3.55 (m, CH_2OH), 2.78 (m, $CH=CH-CH_2-CH=CH-$ from linoleic moieties), 2.29 (t, $-CH_2(C=O)O-$), 2.01 (m, $-CH_2-CH=CH-$), 1.58 (t, $-CH_2-CH_2-(C=O)O-$), 1.41–1.14 (m, nCH_2-), 0.85 (t, CH_3-).

2.3. Synthesis of maleated soybean-oil glycerides (MASOG) (Scheme 1)

10.0 g (0.023 mol) of SOG, obtained as described above, were mixed with 6.7 g (0.068 mol) of maleic anhydride and 0.1 g of 2-methyl imidazole in a 25-mL round-bottom flask equipped with a condenser according to the procedure of Can et al. [10]. The system was introduced in a silicone bath heated at 80 °C. The reaction was carried out for 3 h under vigorous stirring (600 rpm). The product was washed three times with hot water–NaCl solution to remove the excess of maleic anhydride. Then, the product was dissolved in ethyl ether, dried over anhydrous magnesium sulfate and filtered. The solvent was evaporated under reduced pressure. The product was obtained as viscous oil, with 91% yield. 1H NMR [$CDCl_3$, δ (ppm), TMS]: 6.89 (m, $-OCOCH=CH-COOH$, *trans*), 6.32 (m, $-OCOCH=CH-COOH$, *cis*), 5.35 (m, $-CH=CH-$ from oleic

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