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Preparation of new biobased coatings from a triglycidyl eugenol derivative through thiol-epoxy click reaction

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ABSTRACT

A new triglycidyl eugenol derivative (3EPO-EU) was synthesized and characterized by spectroscopic techniques, and used as starting monomer in the preparation of novel bio-based thiol-epoxy thermosets. As thiols, commercially available tetrathiol derived from pentaerythritol (PETMP), a trithiol derived from eugenol (3SH-EU) and the hexathiol derived from squalene (6SH-SQ) were used in the presence of 4-(*N*,*N*-dimethylamino)pyridine as the basic catalyst. A flexible diglycidyl ether derived from hexanediol (2EPO-HEX) was also introduced in order to enhance conversion in formulations containing 6SH-SQ. The evolution of the curing was monitored by differential scanning calorimetry. The materials obtained are rigid at room temperature and showed T_gs up to 103 °C. The thermal stability, thermomechanical and mechanical properties were evaluated and discussed in terms of the structural characteristics of the resulting materials.

1. Introduction

Epoxy thermosets have been extensively used due to their great number of advantages ranging from excellent thermal resistance, mechanical performance and chemical and environmental stability, among others [1,2].

The most popular starting compound in the production of industrial epoxy resins is bisphenol A which is used in the preparation of coatings, adhesives, encapsulants, etc. [3,4]. However, excessive exposure to this compound causes serious damage to health and a lot of research is currently done to find out more convenient alternatives [5,6].

Nowadays, there is a great demand for products from renewable sources with the aim of reducing dependence on petrochemical compounds and finding safer alternatives to existing ones. In the last years, many investigations have been focused in the development of greener materials prepared from sustainable, friendly resources with safe behaviour from the point of view of health and environment [7–10]. In this respect, many studies have been performed in the preparation of epoxy thermosets from renewable sources with different structure [11–14] but many of them from vegetable oils [15–18].

Vegetable oils, although produced in huge quantities, cheap and easy to be transformed into pure epoxydated starting materials, have the drawback of their long aliphatic chains that leads to an excessive flexibility and too low T_g of the crosslinked materials, which limits their technological application [18,19]. For this reason, more rigid structures such as phenols approaching the bisphenol A molecule could be interesting as a green alternative to prepare epoxy thermosets with improved characteristics [20].

Eugenol (4-allyl-2-methoxyphenol) is a simple and aromatic compound, which is the main component (80–90%) of clove oil, the essential oil extracted of the clove plant (*Eugenia caryophyllata*). It has two functional groups, OH and allyl that can be further modified to form epoxy compounds with the adequate functionality and for this reason, it seems very attractive as starting material for the preparation of epoxy thermosets. This phenolic compound is a yellowish liquid-oil with its most important application in the medical field because it has great properties as analgesic, antibiotic, antiseptic, anti-oxidant, etc. [21–24]. It has also been used in perfumery and in manufacturing stabilizers and antioxidants for the plastics industry. As a better advantage, it should be noted that it can be used in foods at low concentrations and therefore is safe as starting material for the preparation of green thermosets [25].

Several authors reported on the preparation of epoxy thermosets starting from eugenol based structures. Wang et al. [26] prepared a new epoxy material with a bio-based content of 70.2%wt from an eugenol derivative cured by 4,4′-diamino diphenyl methane. The new material

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had a T_g of 114 °C, 40 °C lower than the DGEBA based material. Nevertheless, the new epoxy-eugenol material had higher Young modulus and hardness than DGEBA thermoset.

In another study [27], eugenol was transformed into a diepoxide and cured with methyl tetrahydrophthalic anhydride or with an anhydride derived from rosine (MPA) in the presence of an imidazole as the catalyst. The use of MPA as anhydride allowed to reach T_gs of 155 °C and the cured materials exhibited comparable performance to their petrochemical counterparts.

A highly stiff epoxy thermoset derived from eugenol with a triazine core structure and three epoxy groups per molecule was described in the literature [28]. This eugenol derivative was cured by using 3,3′-diamino diphenylsulfone. Compared with DGEBA materials cured under the same conditions, the new eugenol-based material led to improved thermomechanical properties (33 °C higher in T_g, 39% higher in Young's modulus and 55% improvement in hardness).

In previous papers, the amine catalyzed thiol-epoxy curing process was reported [29–31]. This reaction follows a *click* pattern with high yield, good regioselectivity in the attack to the epoxide and leads to a polycondensation type polymerization with the formation of a homogeneous network and transparent material appearance. Mechanistic and kinetic studies have been performed to determine the role of the amine added as nucleophile or as a base. Depending on the nature of the amine it can act as a base extracting the thiol proton forming the corresponding thiolate which is the true nucleophile that attacks to the oxirane. If the amine has better nucleophilic than basic characteristics then the amine can attack to the epoxide forming an alkoxide, which acts as the base that extract the thiol proton forming the thiolate [32,33].

In a previous study of our group we put into evidence that thiol-epoxy reaction is highly advantageous in front of thiol-ene processes to obtain crosslinked materials from eugenol derivatives [34]. Yoshimura et al. proposed the preparation of networks from triallyl eugenol by thiol-ene processes but the maximum T_gs reached for the materials were not higher than 9.1 °C [7]. On substituting an allyl by a glycidyl group we increased the T_g in more than 25 °C by the higher efficiency of the thiol-epoxy process compared to the thiol-ene in eugenol substrates.

The present study proposes the preparation of a new eugenol epoxy compound with three glycidyl groups with a compact structure (3EPO-EU), which will later be cured by means of a thiol-epoxy click reaction. According to our experience in thiol-epoxy curing systems a high functionality and rigid structures are needed to reach good thermomechanical characteristics [35]. As the thiol curing agent, we synthesized an eugenol derivative (3SH-EU) and we also prepared the hexathiol derived from squalene (6SH-SQ) previously reported [36]. We also selected as thiol the commercially available tetrathiol derived from renewable pentaerythritol (PETMP) [20]. Scheme 1 represents the structure of the starting monomers used in this study.

Through thiol-epoxy curing process, fully bio-based epoxy thermosets with different characteristics have been obtained. It should be mentioned that, depending on the basic catalyst used, the latent character of thiol-epoxy curing allows the formulations to be stored at room temperature for a certain period [37]. This fact, together with the easy control of the polymerization reaction, enhances the green character of this type of materials, accordingly to the reduction of the amount of waste material produced.

For the epoxidation of the compound derived from eugenol we followed the concept of green chemistry [38,39] and the epoxy compound was synthesized using the oxone methodology [40–42] instead of epoxidation by peracid (MCPBA) [43], because the former offers many advantages. Oxone is cheaper than MCPBA and the separation and purification processes are much easier and employs non-toxic organic compounds. MCPBA is non-stoichiometric and acts preferentially in chlorinated solvents. In addition, the thiols were also synthesized by a clean methodology, consisting in the photoinitiated thiol-ene click addition of thioacetic acid to olefins in the absence of any solvent and further saponification by base [31].

The study of the thermal curing of different thiol-epoxy formulations was performed by calorimetry and the materials prepared were characterized by thermogravimetry, thermomechanical analysis and mechanical tests. To improve the curing of some formulations and reach their complete curing, the addition of a linear renewable diglycidyl compound derived from 1,6-hexanediol (2EPO-HEX) was tested. This compound acts as flexible chain extender when the compactness of the monomers derived from eugenol and squalene limits the complete reaction that is caused by topological restrictions.

2. Experimental part

2.1. Materials

Eugenol (EU), allyl bromide, thioacetic acid (TAA), 2,2-dimethoxy-2-phenylacetophenone (DMPA), 4-(N,N-dimethylamino)pyridine (DMAP), pentaerytritol tetrakis (3-mercaptopropionate) (PETMP), squalene (SQ) and oxone (potassium peroxomonosulphate) were purchased from Sigma-Aldrich and were used without further purification. 1,6-hexanediol diglycidylether (2EPO-HEX from EPOTEC RD 107 Aditya Birla Chemicals, Thailand. EE 147 g/eq) was used as received. Benzyl triethyl ammonium chloride (TEBAC) was purchased from Alfa Aesar. Inorganic salts and bases were purchased from Scharlab. Methanol from Carlo Erba was used as received. Acetone, ethyl acetate and N,N-dimethylformamide (DMF) from VWR were purified by standard procedures.

2.2. Preparation of starting compounds

2.2.1. Synthesis of the diallyl and triallyl derivatives from eugenol (2A-EU, r2A-EU and 3A-EU)

Diallyl and triallyl eugenol were prepared following a previously reported procedure [7]. The synthesis includes the allylation of eugenol in basic medium to obtain O-allyl eugenol (2A-EU) and then a Claisen rearrangement on heating to obtain 6-allyleugenol (r2A-UE). This product was allylated and the triallyl eugenol (3A-EU) was obtained (see Scheme 2). The ^{1}H NMR spectra of these compounds were coincident with those reported [7].

2.2.2. Synthesis of triepoxy derivative from eugenol (3EPO-EU)

In a 1000 mL three-necked flask equipped with magnetic stirrer, thermometer and addition funnel, 1 g (4.1 mmol) of 3A-EU was dissolved into 120 mL of acetone and 100 mL of ethyl acetate. To this mixture, 0.2 g (0.8 mmol) of TEBAC, 43.0 g (511.8 mmol) of $NaHCO_3$ and 60 mL of water were added. The flask was cooled at 5 °C and then 56.7 g of oxone (equivalent to 93.0 mmol of $KHSO_5$) dissolved in 190 mL of H_2O were added dropwise over 3 h at 5 °C under vigorous stirring. The mixture was kept at room temperature for 48 h. The organic layer was separated and washed with a solution of 20%wt NaCl in water. After drying with Mg_2SO_4, the solvent was eliminated at vacuum and the residue purified by silica gel chromatography (*n*-hexane/ethyl acetate (4:6), as eluent). The product 3EPO-EU was a viscous yellow liquid, 50% yield. ^{1}H NMR ($CDCl_3$, δ in ppm), 6.72 m (Ar, 2H), 4.24 and 3.90 m (−CH_2−O−, 2H), 3.84 s (CH_3−O−, 3H), 3.34 m (CH of glycidyl ether, 1H), 3.18 and 3.4 m (CH of glycidyl groups attached to phenyl, 2H), 2.93–2.77 m (-CH_2- of oxirane rings, 6H) and 2.76, 2.68, 2.58 and 2.56 four dd (−CH_2− of glycidyl groups directly attached to Ph, 4H) (see Fig. 1).

^{13}C NMR ($CDCl_3$, δ in ppm): 32.6 (−CH_2−), 38.2 (−CH_2−), 44.1 (−CH_2−oxirane), 46.5 (−CH_2− oxirane), 46.8 (−CH_2− oxirane), 50.3 (−CH− oxirane), 51.6 (−CH− oxirane), 52.1 (−CH− oxirane), 55.4 (−OCH_3), 73.5 (−CH_2−O−), 111.4 (C-3), 122.4 (C-5), 130.6 (C-6), 133.0 (C-4), 144.2 (C-1) and 152.0 (C-2) (see Fig. 2).

FT-IR (ATR): 3050, 2996, 2918, 2847, 1589, 1489, 1464, 1430, 1403, 1336, 1290, 1010, 968, 908, 831, 804, 754 cm^{-1}.