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New bio-based materials obtained by thiol-ene/thiol-epoxy dual curing click procedures from eugenol derivates

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ABSTRACT

Novel bio-based and dual-curable thermosets were prepared from eugenol derivatives. The curing sequence combined two click reactions, a photoinduced radical thiol-ene reaction followed by a thermally activated thiol-epoxy reaction.

Eugenol was transformed into a triallyl (3A-EU) and a diallyl glycidyl derivative (2AG-EU) with high yields, and they were used as starting monomers in order to study the thiol-ene reaction and the dual-curing process, respectively. Three different thiol crosslinkers were tested, one commercially available tetrathiol derived from pentaerythritol (PETMP) and two other that were also synthesized: a trithiol derived from eugenol (3SH-EU) and a hexathiol derived from squalene (6SH-SQ).

FTIR and DSC were used to monitor both curing stages and analyze the obtained materials. The results evidenced the occurrence of side reactions that led to incomplete thiol-ene reaction. The dual-curable materials showed higher T_gs than the materials obtained by a simple thiol-ene process and presented higher mechanical and thermomechanical performance.

1. Introduction

Green chemistry is synonymous of health and environmental sustainability. Green chemistry explores new ways of preparing chemical substances or materials in more environment-friendly conditions from renewable resources. This concept includes the reduction or elimination of dangerous substances in the design, manufacture, and use of chemical products [1–3]. This is the reason behind the increasing demand for novel synthetic polymers made from components derived from renewable sources that has appeared in the recent years [4,5]. The use of natural components allows to reduce the dependence on fossil resources and implies a positive economic impact [6–10].

There are several biomass resources that have been proposed to prepare new biobased materials as rosin [11–15], fatty acids [16], gallic acid [17], tannins [18,19], itaconic acid [20], lignin [21,22], vanillin [23], cardanol [24], succinic acid [10] and furan derivatives [25,26]. Eugenol (4-allyl-2-methoxyphenol), obtained from the essential oil of clove tree, is highly attractive as feedstock for development of new materials, since it is a phenolic compound that can be further modified to reach the convenient functionality and a rigid structure [27,28]. This aromatic compound is used in the pharmaceutical industry and therapeutic medicine because it

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has properties of reduction on blood sugar, triglyceride and cholesterol levels [29]. In addition, it can act as antioxidant agent preventing typical processes of oxidation of lipids in the first stages of inflammatory processes working as captor agent of free radicals [30]. According to that, eugenol derivatives can be a good alternative to get monomeric compounds without toxicological issues.

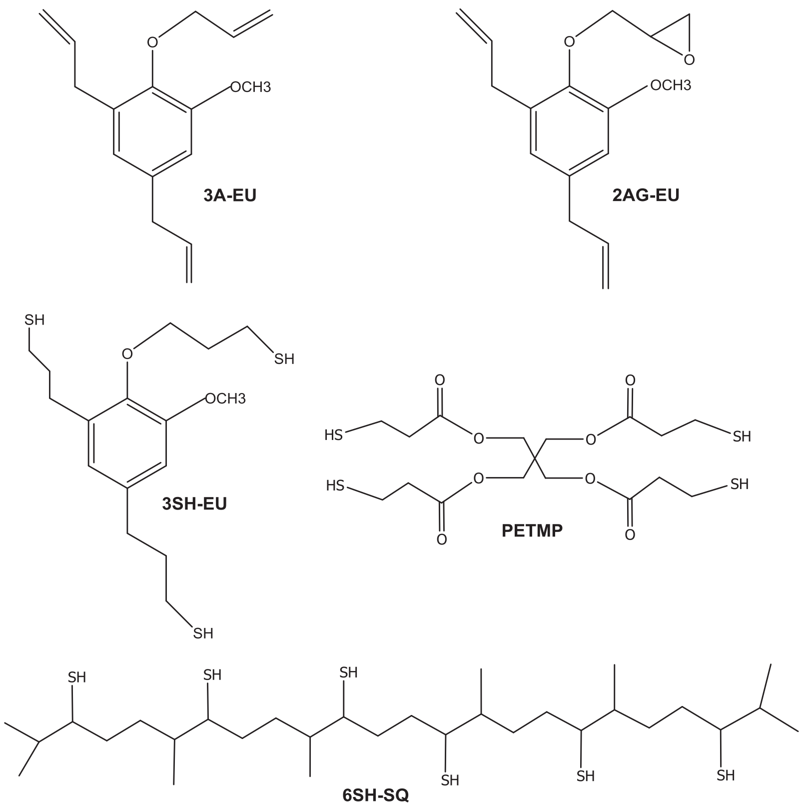
Recently, many researchers opted for the use of eugenol to prepare new biobased materials. Donovan et al. [31] prepared adhesives by thiol-ene reactions from an eugenol derivative as vinylic compound and pentaerythritol triallylether and PETMP as thiols. Increasing the concentration of eugenol derivative in the thiol-ene network resulted in improved adhesion on a variety of substrates, including glass, aluminium, steel and marble. In another study, Yoshimura et al. [32] prepared new materials by thiol-ene reactions from a triallyl derivative of eugenol. This compound was prepared by allylation of eugenol, followed by a Claisen reaction, and further allylation of the phenol formed. Three different thiols were used to crosslink but the materials obtained did not reach T_g values higher than 10 °C and therefore their applicability was quite limited.

Green engineering is another concept strongly related to green chemistry. It focuses on the optimization of processes and systems to maximize mass, energy, space, and time efficiency. Renewable rather than depleting material and energy inputs are other concepts included in the green engineering principles [33].

Dual curing procedures have been proposed for clean and efficient processing, which facilitates manufacturing and assembling, reducing the waste production. Dual curing methodologies consist in a first stage of curing leading to a stable intermediate material, which upon application of a second stimulus, undergoes further reaction and crosslinking to achieve the ultimate properties.

In a previous study, we developed a completely sequential dual curing procedure based in a first photochemically induced thiol-ene reaction followed by a thermal thiol-epoxy reaction, using commercially available diglycidyl ether of bisphenol A (DGEBA), triallylisocyanurate (TAIC) and pentaerythritol tetrakis(3-mercaptopropionate) (PETMP) [34]. This procedure allowed us to obtain materials with tailored intermediate and final properties by just changing the formulation composition, and to store them for a certain time in the intermediate state before the final application and completion of the curing process. Due to the toxicological issues of DGEBA and TAIC, the substitution of these monomers by other bio-based derived from a renewable feedstock such as eugenol could contribute to obtain safer thermosetting materials from more sustainable procedures.

Considering both green chemistry and engineering concepts, in the present study the preparation of new sustainable materials from eugenol by thiol-ene or the combination of thiol-ene and thiol-epoxy click reactions will be tackled. The strategy of using dual curing by combination of thiol-ene and thiol-epoxy is aimed at increasing the T_g of the final materials, whereas at the same time improvements in the processability could be reached. As starting monomers, we have prepared different compounds derived from eugenol with a functionality of three, being the functional groups allyl or epoxide. As thiol monomers, we selected three different compounds derived from renewable resources: commercially available PETMP, derived from pentaerythritol that can be obtained from biosynthetic procedures [35] and two thiols synthesized from squalene [36] and eugenol, by a clean methodology consisting in



Scheme 1. Chemical structures of the allyl and epoxy eugenol derivatives and the thiols selected as monomers.