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Biorenewable thermosetting copolymer based on soybean oil and eugenol

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ABSTRACT

A novel biorenewable thermoset based on acrylated epoxidized soybean oil (AESO) and methacrylated eugenol (ME) was prepared via free radical polymerization. The chemical compositions of the monomers were investigated using proton nuclear magnetic resonance (^{1}H NMR) technique. The properties of this resin system were investigated using small amplitude oscillatory shear flow rheology, dynamic mechanical analysis (DMA), thermogravimetric analysis (TGA), and compression testing. Soxhlet extraction was also performed on the cured thermoset to determine the percentage of monomers that are incorporated into the crosslink network. In addition, the gelation time of this resin at different curing temperature was also monitored using a rheometer. The Soxhlet extraction data indicated that more than 95% of the monomers were incorporated into the crosslink network. Gelation time study showed that this resin system can become a solid within 10 min. This resin system possesses high strength and modulus, and it is thermally stable up to 300 °C. This high biorenewable content resin system possesses good mechanical properties, high thermal stability, and fast curing speed, making it a suitable matrix resin for the pultrusion process and other composite manufacturing processes.

1. Introduction

In recent years, polymeric materials derived from biorenewable resources have attracted a lot of attention due to the shortage and high price of petroleum and the increase in environmental concerns. Currently, almost all commercially available polymers are derived from non-sustainable petroleum resources. About 7% of oil and gas are used to produce plastic [1]. A wide range of biorenewable polymeric materials have been developed that utilize biorenewable resources such as sugars, polysaccharides, lignins, plant oils, pine resin derivatives, and furans [2].

Vegetable oils are one of the most abundant biorenewable materials. Their inherent biodegradability and low toxicity make them a promising starting material for polymer synthesis. Vegetable oils are composed of triglyceride molecules. Triglycerides consist of three fatty acid chains combined with glycerol through ester linkage. The length of fatty acid ranges from 8 to 22 carbon, and some of them have chemical functionalities such as hydroxyl groups, epoxide groups, and unsaturation (carbon–carbon double bond) [3]. Recently, there are many research activities focusing on using vegetable oil as partial replacement of petroleum components in plastic. Vegetable oils such as soybean oil [4–6], linseed oil [7–9], corn oil [10],

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and tung oil [11–13] contain unsaturation sites (carbon–carbon double bonds) and have been copolymerized with petroleum-based chemicals, such as styrene (ST), divinylbenzene (DVB), dicyclopentadiene (DCPD), and acrylonitrile using cationic, free radical or thermal polymerization. The properties of the resulting thermosetting polymers range from rigid plastics to soft and flexible rubbers. However, soybean oil, corn oil, and linseed oil do not contain conjugated double bonds in their triglyceride chains, making them difficult to be incorporated into the crosslinked thermoset network. Conjugation of vegetable oils can be accomplished using catalysts containing rhodium or ruthenium [14]. On the other hand, epoxidation can be performed on vegetable oil to turn the carbon–carbon double bonds into oxirane rings [15,16]. The epoxidized vegetable oils (EVO) can be blended into commercially available epoxy systems to yield a new class of epoxy. Epoxidized vegetable oils have been blended with commercially available epoxy systems such as bisphenol A diglycidyl ether (DGEBA) and di-glycidyl ether of bisphenol F (DGEBF) [17,18]. It was found that the storage modulus at room temperature, the glass transition temperature, and the crosslink density of the epoxy blend decreased with increasing content of EVO, while fracture toughness and flexural modulus were increased with increasing amount of EVO [17–19]. The epoxide rings of EVO can be ring-opened by alcohols [20] or acids [21,22] to introduce other functionalities. After the epoxide rings had been opened, hydroxyl groups were introduced, and polyurethanes with a wide range of properties can be produced by the reactions between hydroxyl groups and diisocyanates [23]. EVO can also be ring-opened to produce molecules with acrylates to increase the reactivity of vegetable oils.

Acrylated epoxidized soybean oil (AESO) is produced by reacting epoxidized soybean oil with acrylic acid [24], and the steps of synthesizing AESO is shown in Fig. 1. AESO is commercially available under the trade name Ebecryl 860, and it can be polymerized using free radical initiators [25,26]. Due to the high viscosity of AESO, it has been copolymerized with styrene to increase its processiblity [26,27]. AESO has also been combined with hemp fibers [25], cellulose fibers [28], pyrolyzed chicken feather [29], and montmorillonite clay [30] to produce composites with high renewable content. In addition, it has been proposed that AESO-based resins can be used in electronics [31,32] and coating applications [33].

Eugenol is an aromatic compound found in plants such as clove, cinnamon, basil, and nutmeg. It is considered a safe additive to food and has been used as a flavoring agent in cosmetic and food products [34]. The combination of eugenol and zinc oxide has been widely used in the dental industry as a cement material [35]. Eugenol also has antibacterial property, and it has been incorporated into polypropylene to produce antibacterial plastics [36]. Qin et al. has attached epoxy groups onto eugenol to produce a biorenewable epoxy system [37]. Polyacetylene based on eugenol and propargyl chloride has also been synthesized, with molecular weight above M_n = 30,000 g/mol [38]. High-performance bismaleimide resin has also been synthesized utilizing eugenol and succinic acid [39]. On the other hand, even though nowadays eugenol is extracted from clove, studies have shown that eugenol can potentially be obtained from pyrolysis [40,41] or depolymerization [42] of lignin. Because of the low cost and abundance of lignin, the price of eugenol can be dramatically decreased if an economical pathway of obtaining eugenol from lignin is developed.

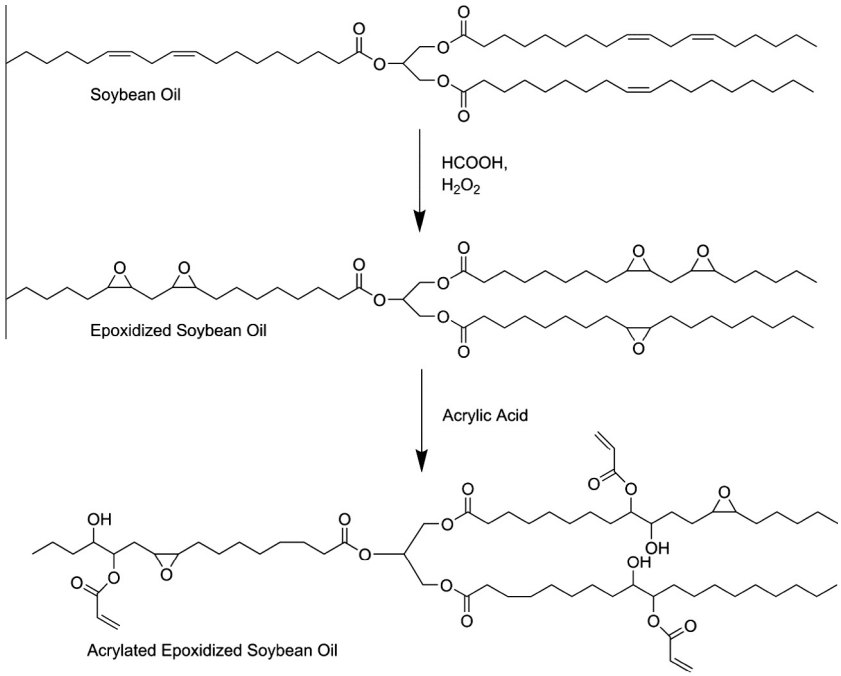

Fig. 1. Synthesis of acrylated epoxidized soybean oil (AESO).