



Development of biobased unsaturated polyester resin containing highly functionalized castor oil



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ARTICLE INFO

Article history:

Received 11 August 2013

Received in revised form 2 November 2013

Accepted 5 November 2013

Keywords:

Functionalized castor oil
Unsaturated polyester resin
Biomodifier
High functionality
Structural plastic

ABSTRACT

A highly functionalized castor oil product mainly composed of castor oil pentaerythritol glyceride maleates (COPERMA) was employed to fabricate a partial biobased unsaturated polyester resin (UPR) through blending it with petroleum-based UPR. The COPERMA product synthesized was characterized by FT-IR, ¹H NMR, and ESI-MS to determine its possible structure and its functionality. The ¹H NMR results showed that the maleate C=C functionality of the COPERMA product was high (2.62). This highly functionalized product was then mixed with 35 wt% styrene before blending this mix with petroleum-derived UPR to prepare a new partial biobased UPR. Physical, thermal, and mechanical properties of the UPR/COPERMA resins were carefully studied. Physical properties data indicate that the resultant biobased resins are suitable for liquid molding process and had a less shrinkage than the neat UPR. Compared to the neat UPR, the cured UPR/COPERMA resins demonstrated comparable or even better thermal and mechanical properties when the content of COPERMA resin was up to 10 wt%. When the content of COPERMA resin increased to 20 wt%, the tensile strength and storage modulus at 35 °C decreased gradually, but not as much as reported in other oil/UPR systems, while other properties, such as crosslink density, glass transition temperature, tensile and flexural moduli, and impact strength, were still improved.

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1. Introduction

Petroleum-derived unsaturated polyester resin (UPR) is currently the most widely used thermosetting polymer due to its low cost, ease of handling, and good balance of mechanical, electrical, and chemical properties. The fiber reinforced UPR composites have been broadly employed in aerospace, automotive, marine, infrastructure, military, sports, and industrial fields (Mighani, 2012). However, due to the uncertainties concerning petroleum supply and prices in the future as well as their environmental pollution problems, substitutes of UPR from natural resources, such as natural oils, lignin, and proteins have been explored (Wool and Sun, 2005; Raquez et al., 2010). The advantages of using natural biobased sources as starting materials are their low cost, the

unique chemistry that their molecular structures provide, and their biodegradability.

In the past decade, there is a growing trend to incorporate natural oils and/or their derivatives into UPR in order to fabricate novel structural bioplastics. For example, Mehta et al. (2004) used methyl ester of soybean oil and epoxidized methyl linseedate (EML) to modify UPR, and prepared biocomposites containing the modified UPR and hemp fiber mat. The notched Izod impact strength of these resulting biocomposites was enhanced by 90% compared to that of the pure UPR composites. Miyagawa et al. (2006, 2007) partially replaced UPRs with epoxidized methyl soyate (EMS) or EML to prepare novel biobased resins. These novel bioplastics showed relatively high elastic modulus values and notched Izod impact strength. Haq et al. (2009, 2011) prepared biobased resins by a partial substitution of UPR with EMS or EML, and then fabricated new hybrid composites from the resins, natural fibers, layered silicates, and nanoclays. Toughness of the biobased resins was greatly improved by the addition of EMS or EML. Ghorui et al. (2011) utilized maleated castor oil (COMA) as biomodifier in UPR/fly ash composites. By the incorporation of 5 wt% COMA, impact strength of the obtained matrix increased by 52% as compared to that of the neat UPR/fly ash matrix. Das et al. (2011) prepared novel biomaterials through blending UPR with tung oil. Improved impact

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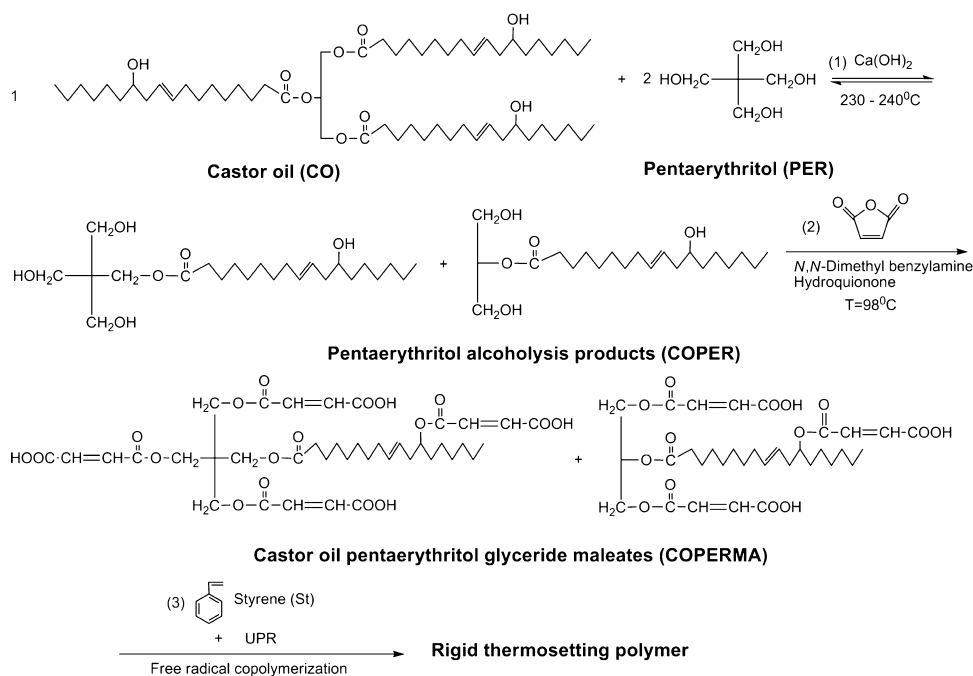


Fig. 1. Ideal reaction scheme for the synthesis of COPERMA from castor oil triglyceride and its copolymerization with UPR and styrene.

strength at a very low content of tung oil was observed. In our group, we also reported that UPR terminated with dicyclopentadiene (DCPD-UPR) was modified by tung oil triglyceride via intermolecular Diels–Alder reaction occurring at the later stage of melt polycondensation (Liu et al., 2013b). Compared to the neat DCPD-UPR matrix, the obtained bioplastic with a tung oil content of about 14.8 wt% has a maximum increase of 373% in impact strength. However, most of the present oil-based modifiers can hardly participate in the free radical copolymerization with UPR and styrene. They were usually employed as a toughening agent because of the formation of a second phase by them (Mehta et al., 2004). When the addition content of them is up to a not-so-high value (about 15–20 wt%), a large loss of stiffness (represented by storage modulus 30°C) in the obtained biobased UPRs was observed (Miyagawa et al., 2006, 2007). Although some of them (e.g. COMA) could copolymerize with UPR and styrene, the cured UPR/COMA/fly ash matrix with a COMA content of about 15 wt% still had a much lower stiffness (represented by elastic modulus) than the pure UPR/fly ash matrix (Ghorui et al., 2011).

For these oil-based UPRs, the loss of stiffness mainly resulted from a decrease in crosslink density (Can et al., 2006a; Miyagawa et al., 2006, 2007; Liu et al., 2013a,b). Thus, to develop high-performance oil-based UPRs, it is important to incorporate an oil-based additive that will not cause too much decrease of crosslink density. The present literature in this field suggests to us that incorporating highly functionalized oils into UPR may solve the problem. Thus, a highly functionalized castor-oil-based product, which was mainly constituted by castor oil pentaerythritol glyceride maleates (COPERMA), was employed to modify UPR in this study. As shown in Fig. 1, the COPERMA product was obtained by functionalizing castor oil triglyceride in two basic steps: alcoholysis to produce a castor oil pentaerythritol alcoholysis product (COPER), and then reaction of this product with maleic anhydride (MA) to produce COPERMA (Can et al., 2006b). Because there is an extra hydroxyl group on each fatty acid chain of castor oil, this product was expected to have a maleate C=C functionality of 3–4. It could copolymerize with styrene to give rigid plastics with high performance, and its polymer matrix possessed a crosslink density high to 4400 mol/m^3 (Can

et al., 2006a), which was comparable to that of petroleum-derived UPRs (Miyagawa et al., 2006, 2007).

Our goal is to study how the incorporation of this model highly functionalized castor oil will affect the resultant biobased UPRs in ultimate properties. Therefore, the physical, thermal, and mechanical properties of the prepared UPR/COPERMA resins were assessed. The surface morphologies at the impact failure of the cured resins were also investigated by scanning electron microscopy (SEM) after completion of the impact testing to correlate failure features with the obtained impact strength values.

2. Materials and methods

2.1. Materials

Commercial petroleum-derived UPR, which contains 35 wt% styrene, was kindly supplied by Nanjing Feilong Composites Co., Ltd. (China). Castor oil (chemically pure) was obtained from Nanjing Chemical Reagent Co., Ltd. (China). Pentaerythritol and MA in a solid state were obtained from Shanghai Lingfeng Chemical Reagent Co., Ltd. (China). Calcium hydroxide [$\text{Ca}(\text{OH})_2$] and *N,N*-dimethyl benzyl amine were obtained from Institute of Tianjing Chemical Reagent (China). The radical inhibitor hydroquinone and the reactive comonomer styrene were obtained from Chengdu Kelong Chemical Reagent Co., Ltd. (China). The initiators benzoyl peroxide and tert-butyl peroxy benzoate as well as the promoter *N,N*-dimethylaniline were obtained from Shanghai Aladdin Chemistry Co., Ltd. (China). Castor oil and styrene were dried using molecular sieves for at least one week before use. All the other reagents were used as received.

2.2. Synthesis of COPERMA (Can et al., 2006b)

About 120 g (0.13 mol) of castor oil, 35.3 g (0.26 mol) of pentaerythritol, and 0.778 g of $\text{Ca}(\text{OH})_2$ were placed together in a 500 mL four-neck round-bottom flask equipped with a mechanical stirrer, a thermometer, a nitrogen (N_2) gas inlet, and a refluxing condenser with a calcium drier. The flask was placed in a

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