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Highly functional methacrylated bio-based resins for UV-curable coatings

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ABSTRACT

A series of highly functional methacrylated bio-based resins were synthesized and used in the formulation of UV curable coatings systems. Methacrylated epoxidized sucrose soyate (MESS) and dimethacrylated epoxidized sucrose soyate (DMESS) were synthesized from epoxidized sucrose soyate (ESS). The resins were combined with multifunctional reactive diluents and a photoinitiator and cured under UV light. A commercially available bisphenol A glycerolate dimethacrylate (BisGMA) resin was used as the control. The curing kinetics was studied using real-time infrared spectroscopy equipped with a UV light. Shrinkage of the coatings was measured by the volume change before and after the curing process. The extent of cure was determined using Attenuated Total Reflectance-Fourier transform infrared spectroscopy (ATR-FTIR). Thermal and mechanical properties were evaluated using thermogravimetric analysis (TGA), thermomechanical analysis (TMA), and atomic force microscopy (AFM). Performance of the coatings was also assessed by measuring the moisture uptake and abrasion resistance. Coatings made from these formulations displayed good solvent resistance and hardness due to the high crosslink density achieved due to the high number of functional groups on the bio-based resin system.

1. Introduction

The popularity of plant oils as alternative sources to petroleum-based materials has been due to the predicted rapidly rising costs of petrochemicals and its limited sources. In addition, plant oils are readily available, highly abundant, low cost, and biodegradable [1–6]. They are generally made up of triglycerides containing various amounts of unsaturated functional groups, depending on the type of plant. The unsaturation sites on the fatty acids can be chemically modified to produce useful functional polymers. Procter and Gamble (P&G) Chemicals previously commercialized an alkyd diluent SEFOSE (sucrose soyate) [7–9]. It is a structurally interesting molecule due to its rigid sucrose core and flexible fatty acid chains. Webster et al. further developed this molecule by transforming it into a more reactive molecule, epoxidized sucrose soyate (ESS), via the Prilezhaev epoxidation (Scheme 1) [10–12]. ESS has proven itself to be versatile in terms of crosslinking technologies and bio-based coatings applications [13–21]. It has also shown promise in composites applications as a bio-based polymer matrix [22–27]. Thus, this novel highly functional bio-based epoxy resin is slowly gaining ground as a potential alternative to petrochemical systems.

Bisphenol A (BPA) (Fig. 1) is a widely used petrochemical that has earned its place in the world of plastics through the years due to its unique sets of properties and its easily modified structure. The phenolic hydroxyls are typically converted into other functional groups that provide unique sets of material properties. A more advanced derivative of BPA is bisphenol A glycerolate dimethacrylate (BisGMA) (Fig. 1 right). BisGMA is an example of a conventional epoxy methacrylate that is commonly used as a monomer due to its unique sets of properties. The phenyl ring provides chemical resistance, the ether linkage allows flexibility (toughness), the hydroxyl gives good adhesion, and the methacrylate is the reactive site for crosslinking. However, much research shows that BPA has adverse effects on humans [28–30]. Consequently, the replacement of BPA remains an actively sought area of research.

Webster et al. [31,32] has developed bio-based methacrylated resins (methacrylated epoxidized sucrose soyate MESS and dimethacrylated epoxidized sucrose soyate DMESS, Fig. 2) that have exhibited good thermomechanical properties and have been used as the polymer matrix in fiber reinforced polymer (FRP) composite applications. In these applications, the materials were crosslinked via thermally-initiated free-radical polymerization. These systems could likewise be crosslinked via photoinitiated free-radical polymerization. Acrylated counterparts of these molecules have been previously studied in UV-curable coatings [15]. In that study, the degree of acrylation was varied and different reactive diluents were used to lower resin viscosities. The coatings produced were hard and had good chemical and abrasion resistance. Itaconic acid [33,34] and gallic acid [35] have also been used to produce soybean oil-based UV-cured thermosets and showed good coating properties. Soybean oil-based UV-curable coatings have also been formulated with hyperbranched acyrlates [36] and thiols [37] to produce good coatings.

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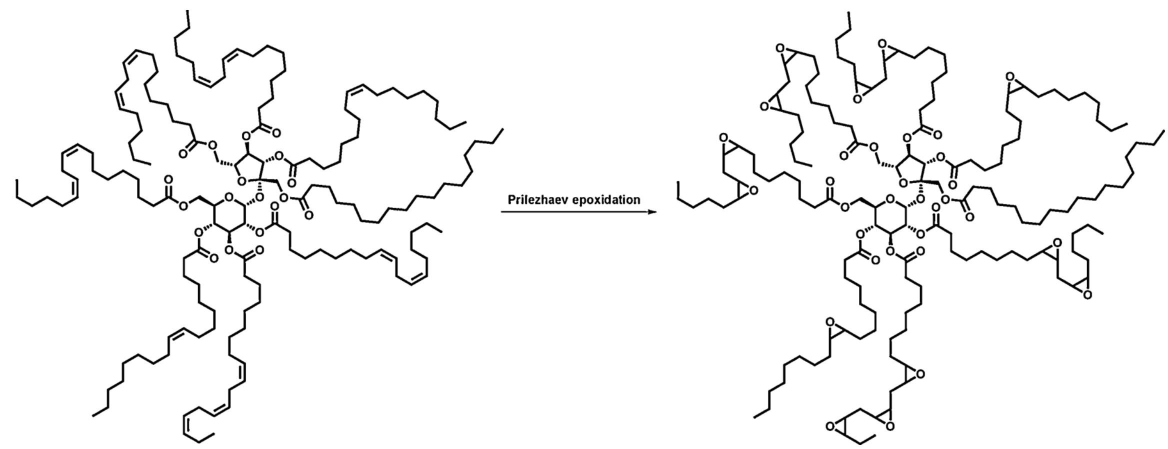

Scheme 1. Synthetic route of SEFOSE to ESS.

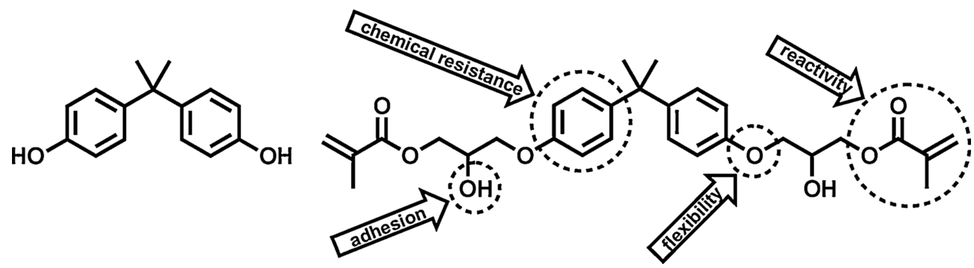

Fig. 1. Structures of bisphenol A (BPA, left) and bisphenol A glycerolate dimethacrylate (BisGMA, right).

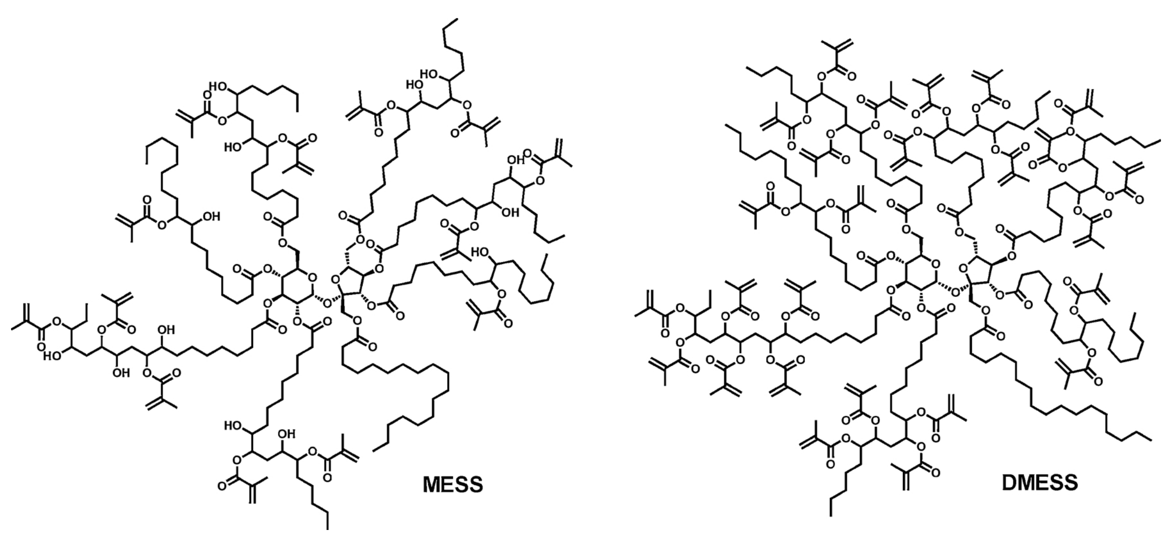

Fig. 2. Structures of the bio-based methacrylated resins: MESS and DMESS.

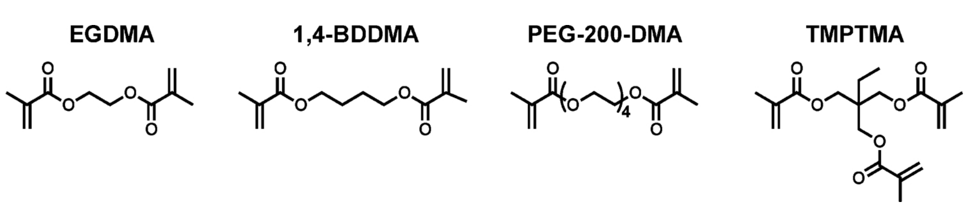

Fig. 3. Structures of the reactive diluents (left to right): EGDMA, 1,4-BDDMA, PEG-200-DMA, and TMPTMA.

In this study, the aim was to investigate the highly functional methacrylated bio-based resins as a replacement for BPA-based resins in photopolymer applications. The reactivity of these methacrylated resins was exploited and its potential use in coating applications was explored. The resins were mixed with several methacrylated reactive diluents and applied onto substrates as coatings. The high functionality of the bio-based methacrylated resins would produce highly crosslinked coatings compared with the linear BisGMA. The degree of functionality of the bio-based resins can be controlled during its synthesis. This dictates the amount of hydroxyl groups present in the molecule, which controls the strength of the adhesion onto substrates. The formulations were cured by irradiation of ultraviolet (UV) light. The coatings properties were