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Camelina oil derivatives and adhesion properties

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ABSTRACT

Camelina (*Cannabis sativa*) is an emerging low-input and stress-tolerant non-food oilseed feedstock in the USA. The seed contains 36–47% oil with 90% unsaturated fatty acids, which means it may be suitable for making oleochemicals and biopolymers. This paper describes the synthesis of several oleo derivatives from camelina oil (CO) and the development of polymers through UV polymerization for pressure-sensitive adhesive (PSA) applications. CO was converted into epoxidized camelina oil, then to partially acrylated epoxidized camelina oil, and finally to di-hydroxyl acrylated epoxidized camelina oil, an acrylic polyol with 1 acrylate functionality and a hydroxyl value of 293 mg KOH/g. These oil derivatives were characterized using Fourier transform infrared spectroscopy, ^{1}H nuclear magnetic resonance, rheometry, and differential scanning calorimetry. The acrylic polyol was copolymerized with 2-ethylhexyl acrylate (2-EHA) to form tacky viscoelastic polymers. Glass transition temperature of the polymers increased as increasing ratio of acrylic polyol to 2-EHA. A bio-based PSA with a good balance of peel strength (3.86 N/in), tack (5.2 N/in), and shear resistance (>30,000 min) was achieved with equal amounts of acrylic polyol and 2-EHA and a moderate amount of rosin ester added as a tackifier. Frequency sweeps indicated positive correlations between the adhesion performances and viscoelastic responses of PSAs.

1. Introduction

Camelina (*Cannabis sativa*, false flax, or gold of pleasure) is an ancient crop that has been cultivated in Europe as an oilseed for centuries (Kagale et al., 2014; Zubr, 1997). Camelina has several agronomic advantages compared with some other traditional commodity oilseed crops (e.g., rapeseed, canola, soybean, sunflower), including low water and fertilizer requirements, adaptability to adverse environmental conditions (e.g., cold weather, semiarid climate), capacity to grow in marginal lands, and resistance to common pests and pathogens of cruciferous vegetables (Francis and Warwick, 2009; McCann et al., 2014; Razeq et al., 2014). Camelina seed contains 36–47% oil in dry matter, which is twice of that of soybean (18–22%) (Moser, 2012). The content of unsaturated fatty acids in camelina oil (CO) is about 90%, with an average of 5.8 double bonds per triglyceride (Kim et al., 2015). Both the unsaturated fatty acid content and the degree of unsaturation of CO are higher than that of soybean oil (84% and 4.6, respectively), which makes CO more attractive for producing oil derivatives with higher functionality for high-performance biopolymers. Moreover, camelina is a non-food oilseed crop that does not compete with food production; therefore, it has been cultivated extensively in the USA as a low-input biofuel crop during the past decade (Gesch, 2014; Gesch and Cermak, 2011; Keske et al., 2013; McCann et al., 2014; Moser, 2010). Tests of jet fuel derived from CO by a commercial airline indicated that this renewable product not only met stringent engine fuel and performance specifications but also reduced environmental emissions (Han et al., 2013; Shonnard et al., 2010). A major challenge of using camelina for bioindustries, however, is the relatively high cost associated with processing camelina feedstock, partly because of the lack of effective technologies to convert camelina meals and oils into high-value bio-based products. A few recent studies have isolated protein fractions (Li et al., 2014) and developed biodegradable plastics and composites from camelina meal (Kim and Netravali, 2012; Reddy et al., 2012), but little has been done to derive high-value chemicals and polymers from oils (Balanuca et al., 2014; Kasetaite et al., 2014; Kim et al., 2015).

Pressure-sensitive adhesives (PSAs) are able to form adhesion joints solely based on the physical interaction between adhesive and adherent. The primary bonding mechanism of PSAs is polar attraction to the substrate surface (e.g., van der Waals interaction, electrostatic forces, and hydrogen bonding) (Tse and Jacob, 1996). PSAs have been widely used for many applications, including tapes, labels, graphics, and medical supplies, and the demand is

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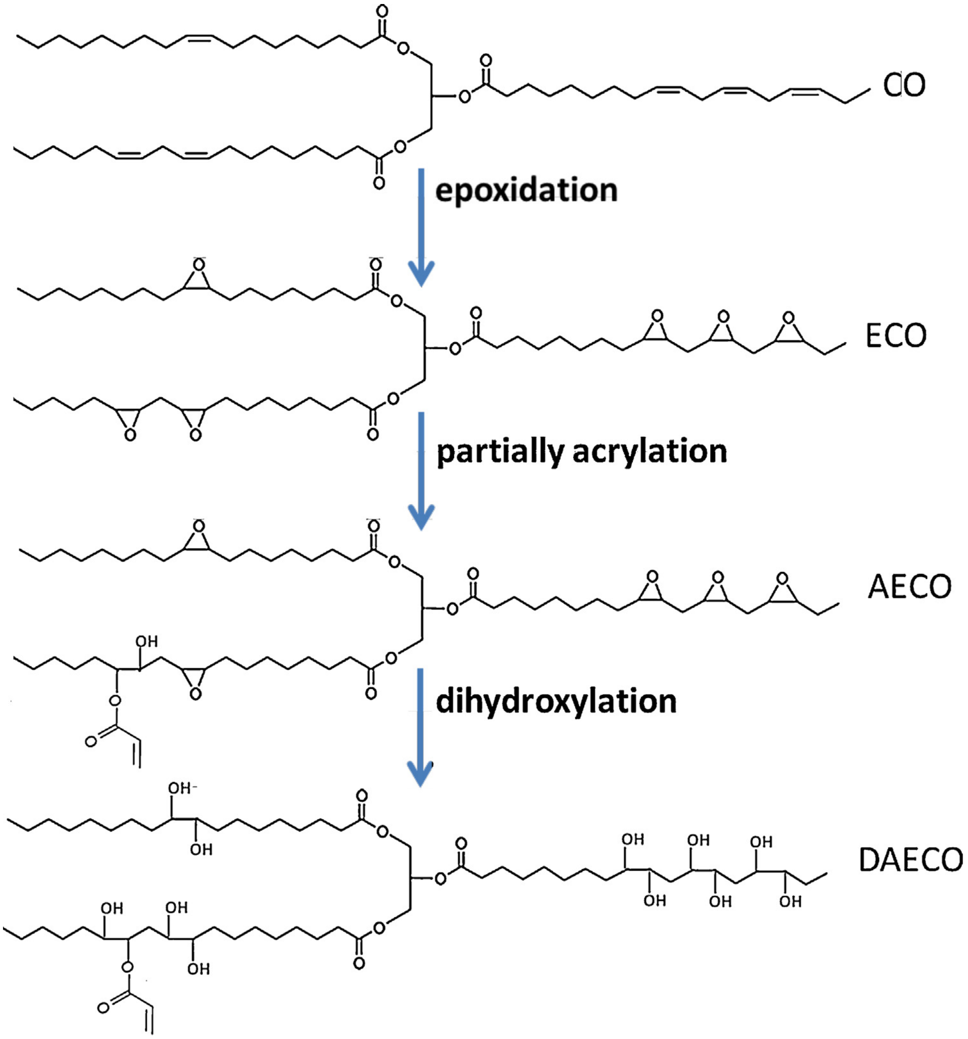

Fig. 1. Synthesis pathway of acrylic polyol (DAECO) from camelina oil.

increasing (Satas, 1999). The majority of PSAs currently are made from petroleum-based acrylate monomers, such as 2-ethylhexyl acrylate (2-EHA), butyl acrylate, and isooctyl acrylate (Czech, 2007; Satas, 1999). Some studies have been carried out to develop PSAs from plant oils (Ahn et al., 2011; Bunker et al., 2003; Koch, 2010; Koch et al., 2012; Li and Li, 2014; Li and Sun, 2014; Li et al., 2015b), but those work has focused mainly on soybean oils. Therefore, in this study, we are interested in converting camelina oil into oleochemicals and biopolymers for adhesive applications.

Acrylic polyol contains both a vinyl group and multi-hydroxyl functionalities. It can be synthesized from CO through several reaction steps: complete expoxidation, partial acrylation, and dihydroxylation of remaining epoxy groups (Fig. 1). Various oil intermediates, including epoxidized camelina oil (ECO), acrylated epoxidized camelina oil (AECO), and di-hydroxyl acrylated epoxidized camelina oil (DAECO, an acrylic polyol) are obtained. The degree of functionality of these derivatives can be modulated for different biopolymer applications. Because the hydroxyl group is more polar than the epoxy group and the double bond of fatty acid, DAECO with maximal hydroxyl functionality work better for PSAs. The hydroxyl groups of DAECO remain available after free-radical polymerization of the vinyl group. The strong polar nature of such polymers is expected to offer good polar attraction to substrates when used as PSAs. The hydroxyl groups are expected to form a polar adhesion site that improves wetting of the substrate and accelerates the rate of bond establishment and development via the formation of hydrogen bonding and other noncovalent interactions for PSA. Therefore, the objectives of this study were to: (1) synthesize various oleo derivatives (ECO, AECO, acrylic polyol) from CO and investigate their structure and physical properties; and (2) develop polymers from acrylic polyol and evaluate their thermal, mechanical, and viscoelastic characteristics for PSA applications.

2. Materials and methods

2.1. Materials

Camelina oil was provided by Montana Gluten Free Processors (Belgrade, MT). AMC-2 (a solution of 40–60% chromium(III) 2-ethylhexanoate in a mixture of di(heptyl, nonyl, undecy) phthalates) was supplied by Ampac Fine Chemicals (Rancho Cordova, CA). Rosin ester was obtained from Arizona Chemical (Jacksonville, FL). Darocur 1173 (2-hydroxy-2-methyl-1-phenyl-propan-1-one) was provided by BASF (Florham Park, NJ). Formic acid (88 wt%), hydrogen peroxide (30 wt%), perchloric acid (70 wt% solution in water), tetrahydrofuran, diethyl ether, sodium bicarbonate, sodium chloride, ethyl acetate, anhydrous magnesium sulfate, Celite 545, hydroquinone, acrylic acid (99%), 2-ethylhexyl acrylate (2-EHA, 98%), butyl acrylate (>99%), and methyl acrylate (99%) were purchased from Sigma–Aldrich (St. Louis, MO) and Fisher Scientific (Waltham, MA) and used as received.