



Acrylated betulin as a comonomer for bio-based coatings. Part II: Mechanical and optical properties



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ABSTRACT

Acrylated epoxidized soybean oil (AESO) is an interesting bio-based starting material for the development of biomaterials. Betulin, another bio-based product, can be extracted in large amounts from birch trees. Acrylated betulin (AB) was synthesized and added as a comonomer to the AESO at different loading levels (5 wt% and 10 wt%). AESO and AESO-AB mixture were cured photochemically to form films. The properties of the newly formulated coating systems were evaluated. The mechanical properties of cured AESO were affected by addition of AB comonomer. Modulus of elasticity (MOE) and tensile strength, hardness and abrasion resistance of the cured film increased, while strain at break was reduced. AB comonomer addition increased the glass transition temperature (T_g) of the cured AESO polymer while it yellowed AESO formulations and reduced optical clarity (transparency) of the cured film coating.

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1. Introduction

The last decade triggered extensive research efforts on new coating systems based on renewable resources. These include waterborne coatings, organic–inorganic hybrid and nanocomposite coatings. The non-renewability of crude oil, its environmental pollution and its price fluctuations have forced the coating industry to look for other resources as “green” raw materials. Vegetable oils are prominent candidates to replace crude oil as a source of raw materials in the coating industry. Vegetable oils have been the primary constituent in paints and coatings for centuries.

Vegetable oils have unique chemical structure with unsaturation sites, hydroxyls, esters and other functional groups along with inherent fluidity characteristics. Such a unique structure enables vegetable oils to undergo various chemical transformations producing low molecular weight polymeric materials with versatile applications, particularly as main ingredients in paints and coatings. Vegetable oils represent a promising source of renewable chemicals and polymers due to their ready availability, inherent biodegradability and low toxicity. Vegetable oils have been used

in paints and coatings as the unsaturated oils (Van De Mark and Sandefur, 2005).

Among the vegetable oils, soybean oil (*Glycine max*) is one of the most abundant. Industrial uses consumed 15% of all soybean oil from 2001 to 2005 (Belgacem and Gandini, 2008). Low reactivity of the double bonds within the soybean oil molecule and the flexibility of the triglyceride fatty acid structure necessitate the modification of soybean oil for industrial applications. The modification can be done by introducing more reactive functional groups. The carbon–carbon double bonds in the fatty acid chains of the vegetable oils can undergo various reactions to introduce into the molecules different polymerizable functionalities, such as acrylates, to increase the reactivity of the vegetable oils. Use of acrylated epoxidized soybean oil (AESO), an important starting material for the development of soybean oil-based materials such as coatings, adhesives, plasticizers, and lubricants, has been reported in many papers (Adhvaryu and Erhan, 2002; Gu et al., 2002; Bajpai et al., 2004; Liu et al., 2005; Lee et al., 2006). Bajpai et al. (2004) synthesized AESO and used it for UV curable coatings. 100% solids UV curable coatings have many advantages, including fast curing, low amount or absence of VOC and good mechanical properties. A 100% solids UV curable coating systems using a renewable material (like soybean oil) can replace conventional coating systems. Although using AESO in a coating has both economic and environmental prospects, its overall performance including poor mechanical properties restricts its applications in coating systems. In order to find

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further applications in coating systems the performance of AESO should be improved.

The white birch tree (*Betula papyrifera*) is widespread in the northern latitudes of the world; it represents an abundant and currently under-utilized natural resource, especially in regards to its bark. Bark is mostly used as a low value fuel source in wood products industries. Betulin is present in large amounts, as high as 30 wt%, in free form in the outer bark of white birch (Jeromenok et al., 2011), hence, its use is not in conflict with food production, unlike soy. Betulin is easily extractable from bark with ethanol. The latest interest toward betulin and its derivatives in medicine is due to its biological activity. It has been shown that betulin derivatives exhibit antiseptic, anti-inflammatory, anticancer, and antioxidant properties (Alakurtti et al., 2006; Pohjala et al., 2009). Apart from pharmaceutical uses of birch bark extract, there have been a few attempts to synthesize polyesters and polyurethanes based on betulin back in the 1980s (Erä et al., 1980; Erä and Jääskeläinen, 1981; Vasnev et al., 1987; Nemilov et al., 2005). Betulin was used as a rigid monomer to synthesize polyester and polyurethane networks with intrinsic microporosity (Jeromenok et al., 2011, 2013). The stiff structure of betulin prevents close packing of the polymer chains. Betulin can also serve as a monomer for linear polymers which can be cast into self-supporting membranes. The obtained materials showed promising results for CO₂ over N₂ selectivity and might be useful as gas separation membranes (Jeromenok et al., 2011). Betulin is the main material in the snow-white bark of the white birch, very resistant to UV light. It is not clear whether this whiteness is due to inherent properties of betulin, or due to scattering of light due to the structure of the bark.

In this study an attempt was made to develop a completely bio-based coating system by using AESO as a matrix polymer. Betulin was first functionalized by acryloyl chloride. The objective of this research was to develop an eco-friendly coating system by using AESO as a matrix polymer and acrylated betulin (AB) as a comonomer. Such as an entirely bio-based coating system with improved properties will enable the coating industry to decrease its dependency on petroleum-based polymers. The results of this study can be used to open up further research on development of vegetable oil based coatings with superior properties. Also it will be evaluated whether the light absorbing properties of betulin, as a white birch component, will appear in the copolymer.

The main objective of this research was to develop coating systems having all aspects of green coating systems. Such a completely bio-based green 100% solids UV coating systems emits little VOC, has low energy consumption and sustainable features with high performance. The mechanical and physical properties of the AESO based coating and its combinations with AB are reported in this paper, which is a follow-up of previous work (Auclair et al., 2015).

2. Material and methods

2.1. Materials

Acrylated epoxidized soybean oil (AESO) and acryloyl chloride were purchased from Sigma–Aldrich, USA. AESO underwent epoxidation before being acrylated. The AESO contains a minimal amount of 4-methoxyphenol, in the order of 4000 ppm, as an oxidation inhibitor and was used in this research without any further modification. For the polymerization, Darocur 1173 (2-hydroxy-2-methyl-phenyl-propanone) was supplied by BASF, USA, and was used as a free-radical photoinitiator. Betulin with 98% purity was purchased from Skyherb, China. Betulin and acryloyl chloride were used as received without any further purification. THF and pyridine were obtained from Fisher Scientific, Canada.

2.2. Modification of betulin

The modification was conducted under nitrogen atmosphere in a flask at a room temperature. During the reaction, the mixture was stirred by a magnetic bar. First, betulin (2 g, 4.5 mmol) was dissolved in a solvent, THF (20 mL), followed by pyridine addition (1.6 mL, 19.8 mmol) as a catalyst. Then, first batch of acryloyl chloride (1.2 mL, 14.8 mmol) was added very slowly (drop by drop) over a 15 min period. After one hour, the second batch of acryloyl chloride (0.2 mL, 2.46 mmol) was added to the reaction mixture. The reaction continued for another 30 min before being stopped by addition of a small amount of water (6 mL). The added water dissolved the salt formed during the reaction. The organic phase was then washed by dilute hydrochloric acid (HCl, 4 M) followed by an aqueous solution of sodium bicarbonate (saturated NaHCO₃) and finally with brine (saturated NaCl in water). The final product was obtained after evaporation of the solvents using a rotary evaporator. The final product, acrylated betulin (AB), obtained after synthesis was solid with a slightly brownish color. This AB is a blend of mono and diacrylated betulin (about 1:3 ratio, respectively). Scheme 1 illustrates this reaction.

The characterizations of AESO and AB combinations were explained in another publication (Auclair et al., 2015), where it was shown that the properties of cured AESO were improved by combining it with AB, like its thermal stability which was tested by TGA. Betulin was modified using the method explained in this section. Spectroscopic techniques were used to study the chemical structure of modified and unmodified betulin: FTIR and NMR analyses confirmed the synthesis of a mixture of acrylated, mono-substituted and disubstituted, betulin. GCMS analysis showed that diacrylated betulin was the more abundant compound after the reaction. Photo-DSC analysis of the formulations was also carried out, showing that both AESO and AB polymerized to form a film.

2.3. Preparation of UV-curable formulations

In order to study the effects of AB as a comonomer on AESO, different coating formulations were prepared (Table 1). 4% free-radical photoinitiator (Darocur 1173) by total weight of components was added to the formulations of AESO. To ensure good distribution of the photoinitiator, the mixture was prepared using a high speed mixer. The mixing was performed initially at 1000 rpm, increased to 5000 rpm over a 20 min period. The mixing was then continued for another 10 min. For the formulations containing 5% and 10% of AB, the AB was added to mixture at the initial step of mixing (1000 rpm). At the end of the mixing time, some AB particles had not completely dissolved in the formulations. To help AB particles to solubilize in the mixture, small amounts of chloroform (2 mL) were added to the mixture. As the last step of mixing, the formulations were further mixed by sonication using an ultrasonic bath for 5 min. Finally, the chloroform was evaporated in vacuum using a rotary evaporator to obtain solvent-free formulations.

Depending on the tests, different substrates were used. For tensile tests, optical clarity and glass transition temperature (T_g) measurements, formulations were applied on Teflon sheets. The Teflon sheets allowed us to obtain free standing films. For hardness and for abrasion resistance tests, formulations were applied on glass substrates and steel plates, respectively. Formulations were applied manually on the substrates by using a 4-sided film applicator (BYK-Gardner, stainless steel with 50, 100, 150, 200 μm gap clearances and 80 mm width). Depending on the tests, different gap clearances i.e., thickness, were used. For tensile tests, optical clarity, color measurement and measuring glass transition temperature (T_g) a gap clearance of 100 μm were used. For hardness and abrasion resistance tests, a gap clearance of 200 μm was used. The application of coating was followed immediately by the curing pro-

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