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Acrylated betulin as a comonomer for bio-based coatings. Part I: Characterization, photo-polymerization behavior and thermal stability

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ABSTRACT

The coating industry is under increasing pressure to find and use renewable resources as a source of raw materials. Substituting products from crude oil by value-added wood products can have both positive environmental and economic aspects. Betulin, mainly found in the bark of white birch, is often left over following wood processing. Betulin has a very interesting molecular structure for the synthesis of polymers. Soybean oil is increasingly used to develop new coatings because of its unique properties. In this study, the properties of acrylated epoxidized soybean oil (AESO) were improved by combining it with a modified betulin sample. Betulin was modified using acryloyl chloride. Spectroscopic techniques were used to study the chemical structure of modified and unmodified betulin. FTIR and NMR analyses revealed that there were chemical reactions between betulin and acryloyl chloride. GCMS analysis showed that diacrylated betulin was the more abundant compound after the reaction. Photo-DSC analysis showed that the speed of polymerization of coatings was slowed down by adding modified betulin to AESO. Thermal stability studies showed that modified betulin developed a cross-linked and rigid structure with AESO. The results of this study confirmed that modification of betulin is possible and the resulting products can be used as a comonomer with AESO for coating formulation.

1. Introduction

In search of sustainable development, the chemical industry is moving towards lowering their impact on the environment, as a majority of raw materials come from crude oil or natural gas. These fossil resources are limited and have an important negative impact on the environment (air pollution, non-biodegradable waste, recent large oil spills etc.). Thus, the industry needs to investigate alternative solutions. Biomass is a renewable material from which various products can be derived from (Hatti-Kaul et al., 2007). The products that can be obtained from biomass cover a wide variety of domains, including; biofuels (Tyagi et al., 2010; Jang et al., 2012; Limayem and Ricke, 2012), drugs (Cilurzo et al., 2013) and even structural or functional materials like bio-composites and bio-polymers (Zini and Scandola, 2011; Espigule et al., 2013). Biomass can also supply the organic chemistry industry with sustainable resources of raw materials.

During the past years, several polymeric materials have been developed from biomass for different applications. For instance, polymeric materials have been developed for textiles (Zhang et al., 2013), adhesives (O'Dell et al., 2013; Xing et al., 2013) and coatings (Alam and Chisholm, 2011; Chen et al., 2011). Vegetable oils are an excellent source of polymer synthesis raw materials (Meier et al., 2007). Some of the polymers coming from vegetable oils are very popular in the coating industry because of their capacity to crosslink by the action of oxygen of the air (Rheineck and Austin, 1968). The properties of oil based coatings are often modified by functional groups containing thiols (Chen et al., 2010), styrenes (Güner et al., 2000), or even urethanes (Guo et al., 2002).

Soybean oil is one of the easiest sources of raw material to obtain for coatings (Smith, 2006). Soybean oil has a fair amount of unsaturated fatty acid moieties on its aliphatic chains. This oil is categorized as semi-drying oil. Despite being considered a semi-drying oil, its polymerization is not rapid enough and does not necessarily have desirable properties in its original form (Behera and Banthia, 2008). Several studies were performed to improve the properties

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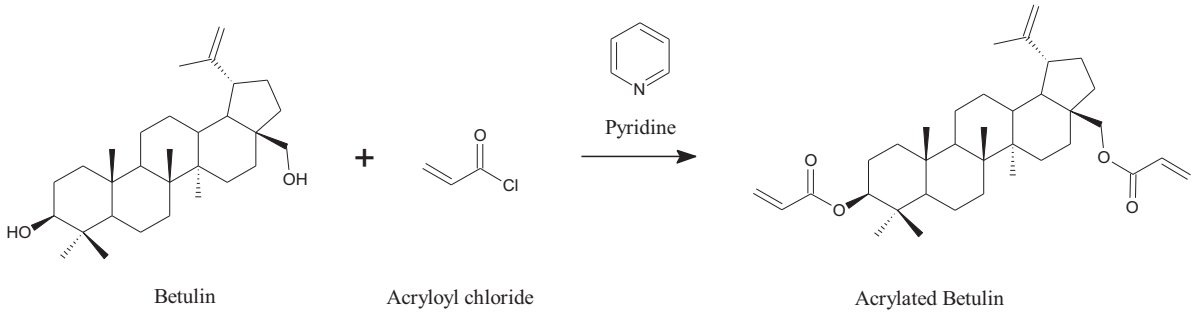

Scheme 1. Synthesis of acrylated betulin.

of soybean oil. For instance, epoxide groups were grafted on soybean oil (Cai et al., 2008). It is also possible to add acrylate functions to the epoxidized oil (Pelletier and Gandini, 2006; Rengasamy and Mannari, 2013). This acrylated soybean oil (AESO) can be used in coating formulations. Comonomers can be added to the AESO in order to improve further the properties of the oil (Saithai et al., 2011).

Other products of biomass can also be used as a polymer source. The capacity of the forest as a natural inventory of the biomass is not fully used by the industry. A large volume of biomass remains unused or not effectively used following forest products harvesting. After such harvesting, wood, leaves, branches, bark and roots are left over in the forest or burned, although they do contain valuable components such as lignin and extractives. The forest industry has faced a crisis during the past several years and is in the process of developing value added products from these underutilized materials. This can bring new opportunities to this industry, such as evolving pulp and paper plants into biorefineries. Wood extractives, like terpenes and terpenoids, often have interesting structure and features for chemical synthesis of polymers (Singh and Kamal, 2012; Shibata and Asano, 2013; Zhao and Schlaad, 2013).

Betulin is a triterpenoid which is found in large quantities in the bark of white birch (*Betula papyrifera*) (Zhao et al., 2007), a very common tree, although somewhat underutilized, in northern forests. Betulin has an interesting structure (Fig. 3) with three potential reactive sites that can be used for any modification. The hypothesis of this research is that the performance of AESO as a coating can be improved by adding modified betulin as comonomer to AESO. The main objective of the present research was to develop an acrylated betulin monomer and to use it as a comonomer for AESO.

In this specific study, betulin was esterified by acryloyl chloride. The chemical structure of the products was verified by chromatographic and spectroscopic techniques. The modified betulin was added to the AESO as a comonomer. The effects of using the modified betulin as a comonomer with AESO on curing behavior and thermal properties of resulting polymers were evaluated.

2. Materials 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 the order of 4000 ppm, of 4-methoxyphenol as an oxidation inhibitor and was used in this research as such without any further modification. For the coating cure/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, from white birch bark, was purchased from Sky-herb, China. Betulin and acryloyl chloride were used as received without any further purification. THF and pyridine were obtained from Fisher Scientific, Canada.

Table 1
Composition of the formulations.

Formulation	Amount of AESO (g)	Quantity of Darocur 1173 (g)	Amount of AB (g)
AESO (0%)	7.68	0.32	0.00
AESO + AB (5%)	7.28	0.32	0.40
AESO + AB (10%)	6.88	0.32	0.80

2.2. Modification of betulin

The modification was conducted under a nitrogen atmosphere in a flask at 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, the 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 resulting salt. The organic phase was then washed by dilute hydrochloric acid (HCl, 4 M) followed by an aqueous solution of sodium bicarbonate (saturated $NaHCO_3$) 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 a solid with a slightly brownish color. Scheme 1 illustrates this reaction.

2.3. Preparation of UV-curable formulations

In order to study the effects of AB as a coating comonomer with AESO, different formulations of coatings were prepared (Table 1). To prepare the formulations, first 4% by weight of the free-radical photoinitiator (Darocur 1173) was added to each formulation consisting of AESO. To ensure a 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 modified betulin, the modified betulin was added to mixture at the initial step of mixing (1000 RPM). At the end of the mixing time, some AB particles did not completely dissolve in the formulations. To help AB particles to dissolve in the mixture, small amount of chloroform (2 ml) was added to the mixture. As a last step of mixing, the formulations were further agitated 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.