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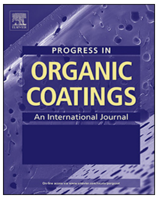

Influence of modified cellulose nanocrystals (CNC) on performance of bionanocomposite coatings

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ABSTRACT

In this study, a renewable reinforcement, namely cellulose nanocrystals (CNC), was used to develop a bio-based nanocomposite UV-cured coating system with improved performance. CNC was modified in order to be compatible with the nonpolar polymer matrix (acrylated epoxidized soybean oil (AESO)). The CNC was modified by two methods, with acryloyl chloride or a cationic surfactant (HDTMA). The mechanical properties and structure of bionanocomposites were evaluated. The addition of CNC increased modulus of elasticity (MOE) and tensile strength of the cured film coatings. Use of CNC modified by HDTMA and acrylated CNC led to a higher increase in tensile strength and MOE, relative to un-modified CNC. Best performance enhancement was in hardness and reduced elastic modulus (Er), measured by the nanoindentation technique, which were improved several fold by CNC addition. Hardness, Er, MOE and tensile strength increased with CNC loading level in the matrix. Hardness measurements of cured film coating by pencil hardness test methods confirmed that CNC improved the hardness of the films. Studying the morphology of the nanocomposites revealed that surface modification method of CNC affected nanocomposite film structure and thus the mechanical properties.

1. Introduction

Coating industry depends on petroleum-based products as sources of raw materials. Because of increasing demand for petroleum-based products and the resulting negative impact on the environment, there has been a growing interest for the utilization of renewable resources as an alternative to petroleum-based polymers in the coating industry. The replacement of petroleum-based raw materials with renewable resources constitutes a major contemporary challenge in terms of both economic and environmental aspects. Vegetable oil-based biopolymers are of great interest to the coating industry. Soybean oil is a vegetable oil dominating today's food oil market. About 80% of the soybean oil produced each year is used for human food; another 6% is used for animal feed, while the remainder (14%) serves nonfood uses (soaps, fatty acids, lubricants, coatings, etc.) [1].

The use of vegetable oils and fatty acids for polymer applications has a long tradition. Vegetable oils are used as polymer additives (e.g., epoxidized soybean oil as plasticizer), as building blocks for thermoplastic polymers (e.g., dicarboxylic acids such as azelaic, sebacic, and dimer acid for polyesters or polyamides), and as components for thermosets formulations. Soybean oil must be chemically modified (i.e., grafted with reactive functional groups) to be useful for applications in industrial products. The double bonds present on the fatty acid chains can undergo cationic or radical polymerization processes. In the last decade, a broad range of chemical routes has been developed for using natural or modified vegetable oils as a basis for polymers, adhesives, coatings and composites with specific properties and applications [2].

The modification of the double bonds can incorporate functionalities like maleates [5], hydroxyl [3–5] or epoxide groups [2,6,7], making possible a further reaction via ring opening or polycondensation polymerization. After this reaction step, the product can be used without further modification in crosslinking reactions or it can be further modified through other chemical steps broadening the variety of functional molecules to be obtained. For instance, epoxidized triglycerides may be bonded to vinyl functionalities. Acrylates have been incorporated by reaction of the epoxide groups with acrylic acid, and as an example, acrylated epoxidized soybean oil (AESO) has been frequently reported in the preparation of bio-based polymers and

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composites [8].

The coating industry has a long story in using vegetable oil-based polymers in its products. Introduction of nanotechnology in recent years has opened up opportunities for the industry to develop a new generation of materials with improved properties. Nanotechnology has been used in coating industry extensively and there have been success stories on using nanoparticles with various coating systems [9–14]. Also, in some nanocomposite formulations, different nanocelluloses have been added [15–18].

Little attempt has been made to develop bio-based polymers as a matrix in developing nanocomposite coatings. AESO has already been used as a matrix polymer to develop nanocomposites [19,21]. Composites with good mechanical properties have been prepared from acrylate–modified soybean oil and natural fibers [19]. Organic-inorganic hybrid coatings have been developed using plant oils and metal (Ti and Zr) oxides [20], while carbon nanotubes have been also used as reinforcements for AESO [21].

In the production of biopolymers-based nanocomposites, one can use nanoreinforcements of biological origin that ensure biodegradability of final products. Nanocelluloses have been incorporated into a number of different polymeric matrices, for example, cellulose acetate butyrate [22], poly(hydroxyalkanoates) [23], poly(lactic acid) [24], poly(oxyethylene) [25], poly(vinyl chloride) [26] and starch [27,28]. In this study, such a bionanocomposite coating was developed. Cellulose nanocrystals (CNC) were combined with the AESO matrix. Such a nanocomposite coating should display improved properties in comparison to those of pure AESO matrix.

AESO is a hydrophobic matrix, while CNC is hydrophilic in its natural form. Based on previous experience, such an incompatibility calls for surface modification of CNC. Therefore, before mixing CNC with AESO matrix, surface modification of CNC was conducted with two different methods. The main objective of this research was to develop a bionanocomposite coating system with improved properties. In addition, the effects of different methods of CNC surface modification on the performance of the bionanocomposites were assessed. Results on mechanical properties measurements and structure of such bionanocomposites are presented in this paper.

2. Materials and methods

2.1. Materials

Acrylated epoxidized soybean oil (AESO), the cationic surfactant (hexadecyltrimethylammonium (HDTMA), acryloyl chloride, 1,4-dioxane and methylimidazole (99.99% purity) were purchased from Sigma-Aldrich, USA. AESO went through epoxidation before being acrylated. The AESO contains about 4000 ppm of 4-methoxyphenol 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), supplied by BASF, USA, was used as a UV free-radical photoinitiator. A defoaming agent (Byk-1798 from BYK) was used to reduce the bubbles /foam produced during mixing process. Cellulose nanocrystals (CNC), kindly provided by Forest Products Laboratory in Madison, WI USA, was used as the reinforcing material (5.5 wt% suspension in deionized water). CNC properties and preparation method are presented in other publications [29–31]. Concentrations of CNC added to AESO formulation was limited to 2% since, in precedent work [16,17,32], it was shown to give optimal results, with higher concentrations being less performant due to aggregation phenomena.

2.2. Methods

2.2.1. CNC surface modification with hydrophobic cationic surfactants

Before planning the experimental design, pre-tests were conducted to test the compatibility of the matrix with unmodified CNC and CNC modified by various methods and conditions. Pre-tests were visual inspection tests where the incompatibility was observed when particles did not stay in suspension and fell directly to the bottom of the blend in about a minute. The results of pre-tests showed that unmodified CNC and modified CNC at low concentration (0.35 mmol/g) of added HDTMA had no compatibility with the matrix. Inversely, CNC modified by two methods, namely; 1.4 mmol/g of HDTMA (ionic bonding with anionic sites on CNC) and acryloyl chloride (covalent bonding of an acrylic hydrophobic moiety on −OH groups) demonstrated good compatibility with the matrix [17]. As a result, the study was focused on the effects of adding CNC modified by the two methods. The CNC surface modification procedure with 1.4 mmol/g of HDTMA was mentioned in details in other publications [17,32]. CNC surface modification procedure by acryloyl chloride is described in the following section.

2.2.2. Acrylation of CNC

The reaction was based on catalyzed esterification of CNC as described by Connors and Pandit [33]. The surface modification involves use of an alcohol or −OH group, and an acryloyl. The reaction was catalyzed by 1-methylimidazole. The grafting reaction should add acryloyl groups which replaced the −OH groups in unmodified CNC. The reaction was carried out on 4 g CNC with 110.5 mmol of acryloyl chloride and 6.1 mmol of catalyst (1-methylimidazole) in 80 mL of 1,4-dioxane. The mixture of CNC, acryloyl chloride, dioxane and the catalyst was allowed to stir over night at 50 °C under a nitrogen atmosphere. The modified CNC was obtained after concentration of resulting mixture by centrifugation. The suspensions were centrifuged for 5 separate 15-minute periods at 15,000 rpm to remove any excess of the unreacted chemicals. At the end of each round of centrifugation, the supernatant was removed, and then suspensions of CNC were filtered and washed with warm deionized water.

The CNC samples were kept in a freezer at -80 °C, before being freeze-dried at −91 °C for at least four days. Results of such modified CNC characterizations were reported in another publication [17].

2.2.3. Preparation of UV-curable formulations

Formulation designs used in this study are presented in Table 1. CNC modified by the two methods was added to AESO matrix at two loading levels (1 and 2%). First, AESO was mixed with a high speed mixer (Dispermat LC30, VMA-Getzmann GmbH) at 2000 rpm for 1 min, then the speed rotation was raised to 5000 rpm, at which point the defoaming agent and the modified CNC (if needed) was added. Then, the speed was increased up to 8000 rpm. After 5 min of mixing, the speed was lowered to 5000 rpm for another 30 min. At the end, the photoinitiator was added and the mixing was done for 5 more min.

To make sure that the CNC was well dispersed in the matrix, the formulations were mixed and homogenized by ultrasonication. The ultrasonication was conducted by an ultrasonic processor (CPX 750 from Cole-Parmer) equipped with a high intensity ultrasonic probe (diameter of 13 mm, tuned to resonate at 20 kHz). The temperature of the solution was kept below 80 °C to ensure that the formulations did not overheat. To maintain the temperature of the mixture below 80 °C, the vessel with the mixture was cooled by an ice bath. Ultrasonication

Table 1
Composition of the formulations.

Formulation	AESO wt%	Photoinitiator wt%	Defoaming Agent[a] %	Modified CNC wt%
AESO	96	4	0.4	0
1% Acrylated CNC	95	4	0.4	1
2% Acrylated CNC	94	4	0.4	2
1% HDTMA-CNC	95	4	0.4	1
2% HDTMA-CNC	94	4	0.4	2

[a] Not recorded for the wt% calculation.