



High biocontent natural plant oil based UV-curable branched oligomers



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ABSTRACT

A new, green approach to improve the performance and biorenewable content of natural plant oil based UV-curable materials is presented. A novel kind of soy-based UV-curable branched oligomer (ACSO) was synthesized by chemically introducing cashew nutshell liquid (CNL) onto the epoxidized soybean oil (ESBO) backbone, followed by epoxidization and acrylation. The synthesized ACSO were used to produce UV-curable films and coatings. The UV-curing behavior of ACSO was investigated using real-time IR. The properties of UV cured films were studied using differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), tensile testing, and nanoindentation technique. Compared to coating from acrylated epoxidized soybean oil (AESO), ACSO based coating exhibited higher impact resistance, better crosshatch adhesion, and enhanced thermal and mechanical properties. Meanwhile, high biorenewable content was maintained due to the biorenewable character of CNL in ACSO. The improved coating properties can be attributed to the incorporated aromatic ring from CNL and multi-branched structure of ACSO. This approach provided a new direction to the future development of advanced bio-based UV-curable oligomers with reasonably high biorenewable content.

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1. Introduction

UV cure technology is a green coating technology featured by its high productivity, low energy consumption and extremely low VOC emission [1]. It is one of the most promising materials fabrication technologies which are enjoying fast-pace market expansion. The rising petroleum raw material cost and stricter environmental regulations call for the development of advanced UV curable materials from renewable resources, in order for sustainability and reduced carbon foot-prints. The use of renewable materials in UV cure coatings is a promising “green + green” solution to the challenges that the coating industry is facing [2].

As one of the most important renewable resources, natural plant oils have been used to prepare bio-based UV curable materials via various chemical approaches. Acrylated and epoxidized plant oils are generally produced via fatty unsaturation peroxide oxidation and acrylic acid ring open epoxy process, and used for free radical and cationic UV curable systems [3–7]. Acrylated sunflower oil has recently been prepared by a new route, which is involved with

an “ene” reaction with singlet oxygen [8]. Plant oil based multi-functional thiols and enes can be produced by a thiol ring opening epoxidized soybean oil and used for thiol-ene UV curable materials [9–12]. However, plant oil based UV curable materials possess the inherent “softness” owing to the presence of the long fatty chains, which results in lower materials T_g that subsequently limits the plant oil-based materials' applications as durable materials.

Further development of these bio-based UV curable materials aims at increasing their T_g s and performance. Increasing the crosslink density and incorporation of more rigid structures onto the plant oil backbone are considered as two effective approaches. For example, AESO was reacted with maleic acid to increase the reactive carbon-carbon double bonds content, resulting in increased crosslinking density of the biopolymers; A series of UV-curable oligomers based on allyl, acrylate or vinyl ether functionalized vegetable oil were synthesized by isocyanate prepolymer process, and each biobased oligomer exhibited excellent thin film performance when blended with multifunctional thiols as thiol-ene UV curable formulation [13]; Stiff cyclic rings were incorporated into the backbone of AESO by reacting with cyclohexane dicarboxylic acid, which subsequently increased the T_g of the UV cured biopolymers [14]; Chen et al. [15] synthesized a norbornyl epoxidized linseed oil via Diels-Alder reaction of cyclopentadiene with linseed oil, which showed higher UV-curing rate and overall

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epoxide conversion than epoxidized linseed oil due to the higher ring strain of the incorporated norbornyl groups.

However, in all the reported examples, usually petroleum-based ingredients are introduced which leads to lower biorenewable contents. It is still a challenge to obtain coating materials with higher biorenewable content and good properties at the same time. It is believed that the approach to advanced bio-based UV curable materials should be focused on the careful molecular design and synthesis to incorporate biorenewable building blocks. Among a few reports along this direction, Chen et al. synthesized acrylated sucrose monomers which were formulated into acrylated soybean oil based UV curable coatings with commercial hyperbranched acrylates [16]. It was reported that the incorporation of the acrylated sucrose monomers increased the toughness of the UV cured coatings. A gallic acid based tetrafunctional crosslink agent (GACA) was synthesized by Ma et al. which showed more functional groups and better co-photopolymerization with AESO. GACA crosslinked AESO networks showed higher crosslink density, better mechanical performance as well as much better coating properties than TAIC crosslinked AESO networks [17]. Jang et al. prepared a novel bio-based UV photocrosslinked polymer network from vegetable oil using 2,5-furan diacrylate as a difunctional stiffener [18]. The addition of 2,5-furan diacrylate increased the tensile strengths of the polymer films by up to 1.4–4.2 times. Our group synthesized a novel kind of biorenewable tannic acid-based hyperbranched methacrylates (TAHAs) which were formulated into acrylated epoxidized soybean oil (AESO) based UV curable coatings [19]. With the incorporation of TAHAs, the mechanical properties of the cured coating films were remarkably improved, which were attributed to the unique structure of the hyperbranched methacrylates.

In this paper, we report a novel green approach to improve the performance and renewable content of natural plant oil-based UV-curable materials by introducing cashew nutshell liquid (CNL) into the plant oil backbone. A commercial epoxidized soybean oil (ESBO) was used to illustrate this approach, but almost any vegetable oil with fatty unsaturations can be modified using this route. CNL is contained in the soft honeycomb structure of the cashew nut, which is a non-edible by-product of the cashew industry. The generic structures of the soybean oil and CNL are shown in Fig. 1 [20,21]. Compared to soybean oil, CNL has a rigid benzene ring, higher fatty unsaturation content and shorter fatty chain [22,23]. A novel soy-based UV-curable branched oligomer (ACSO) was synthesized by a chemical modification of epoxidized soybean oil (ESBO) with CNL. The characterization of the UV cured materials suggested that ACSO had higher T_g and biorenewable content, better mechanical properties and thermal stability than AESO, due to the incorporation of the rigid benzene ring from CNL and the multi-functional architecture.

2. Experiment

2.1. Materials

Epoxidized soybean oil (ESBO) was obtained from Cargill Industrial Oil & Lubricants Company. Cashew nuts liquid (CNL) was provided by Cardolite Co. Ltd. Triphenylphosphine (TPP), acetic acid, hydrogen peroxide, hydroquinone, acrylic acid, AMBERLYST® 120H ion-exchange resin (A120), were purchased from Aldrich. Irgacure 2022 (PI) was kindly supplied by Ciba Specialty Chemicals. Cyacure™ UVR 6110 difunctional cycloaliphatic epoxide and UVI 6974 photoinitiator (PI) were obtained from Dow Chemical Company. All materials were used as received. Acrylated epoxidized soybean oil (AESO) was synthesized in our lab using the same acrylation process to produce ACSO.

2.2. Synthesis of soy-based UV-curable branched oligomer (ACSO)

2.2.1. Synthesis of CSO

Into a one-necked 250 mL round bottom flask fitted with a magnetic stirrer, 60 g (0.06 mol) of ESBO, 79.2 g (0.264 mol) of CNL and 2.78 g of TPP were added. The reaction mixture was stirred in nitrogen atmosphere at 120 °C for 72 h to obtain the CNL modified ESBO (CNL-g-ESBO, which is designated as CSO). GPC: $M_w = 5063$, $M_w/M_n = 1.45$.

2.2.2. Epoxidation of CSO

CSO was heated at 65 °C, then 15 g (0.25 mol) of acetic acid, 20 g of toluene and 28 g of A120 catalyst were added. 68 g of 50% hydrogen peroxide (1.0 mol) was slowly added to the mixture maintained at 65 °C in a water bath. After stirring for 5 h, the A120 catalyst was filtered out, and the reactants was washed twice with saturated sodium carbonate solution at 50 °C and washed three times with water at 50 °C. Finally, water and toluene were removed using a rotary vacuum evaporator to obtain the epoxidized CSO (ECSO).

2.2.3. Acrylation of ECSO with acrylic acid

0.05 g of hydroquinone and 0.58 g of TPP were mixed with 32 g of ECSO. The mixture was heated to 95 °C. Then, 6.58 g (0.09 mol) of acrylic acid was slowly added. After 10 h' reaction, the soy-based UV-curable branched oligomer (ACSO) was obtained. GPC: $M_w = 6672$, $M_w/M_n = 1.85$. The synthesis of ECSO and ACSO is illustrated in Scheme 1.

2.3. UV curing

After adding free radical photoinitiator (PI) into the synthesized oligomers, the liquid materials were drawdown on aluminum substrates and the corresponding cured films were obtained by UV curing with a Fusion LC6 B Benchtop Conveyor with an F300 UVA lamp in air. The total UV irradiation energy was 7257 mJ/cm² as measured by UV Power Puck® II from EIT Inc.

2.4. Characterization

The molecular weight information of the synthesized products was obtained by using a Waters GPC with a refractive index detector, and the samples were diluted to 3 mg/mL in tetrahydrofuran (THF) for GPC runs. THF was used as the eluent at a flow rate of 2.0 mL/min. NMR spectra were obtained in deuterated chloroform using a JEOL 400 MHz ECA400 spectrometer, equipped with a 24 position autosampler. Hardness testing was performed with a BYK Gardner pendulum hardness tester in König mode. Cross-hatch adhesion testing was performed on aluminum Q-panels using a Gardco cross-hatch cutter which creates a 5 × 5 pattern of squares. An adhesive tape was then applied onto the pattern and pulled off, followed by a visual examination of the coating loss. Real Time FTIR (RTIR) experiments were performed using a Nicolet Magna-IR 850 spectrometer Series II with detector type DTGS KBr. The light source was a LESCO Super Spot MK II 100W DC mercury vapor short-arc lamp, and scans were taken over a 180 s period at 2 scans per second. The UV source was adjusted to 3.6 mW cm⁻² and the experiments were performed in air. The C=C conversion was monitored at 810 cm⁻¹. DSC experiments were performed utilizing a TA Instruments Q2000 DSC with a heat-cool-heat cycle. Thermogravimetric analysis (TGA) was performed using a TA Instruments TGA Q500 under nitrogen purging from 25 to 650 °C at a ramping rate of 10 °C/min. Tensile tests were performed using an Instron 5542 testing system (Instron Corp., Norwood, MA). ASTM D412-D dumbbell specimens were used, the strain rate was 0.2% s⁻¹, and at least three replicates of each sample were conducted. Nanoindentation and nanoDMA tests were carried out on a Hysitron TriboIndenter® with

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