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Synthesis and application of novel UV-curable hyperbranched methacrylates from renewable natural tannic acid

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ABSTRACT

With a view to developing high performance UV curable coatings with high renewable contents, acrylated epoxidized soybean oil (AESO) was combined with a novel kind of biorenewable tannic acid-based hyperbranched methacrylates (TAHAs). The TAHAs were synthesized by ring-opening reaction of glycidyl methacrylate (GMA), glycidyl ester of Versatic acid (CE10) and natural tannic acid (TA). The epoxy groups of GMA and CE10 were involved in the ring-opening reaction with the hydroxyl groups of TA while residual methacrylate groups can carry out photopolymerization. By controlling the ratio of GMA and CE10, TAHAs with varying degree of methacrylate groups have been prepared. The synthesized TAHAs were formulated into acrylated epoxidized soybean oil (AESO) based UV curable coatings to produce the biorenewable materials based UV curable coatings. The effects of TAHAs on AESO coated film properties of pendulum hardness, flexibility and adhesion were investigated. Mechanical properties, thermal properties and biodegradability of the cured films were also evaluated. With the incorporation of TAHAs, the hardness, adhesion, tensile strength of the cured coating films were remarkably improved, which were attributed to the unique structure of hyperbranched methacrylates. Meanwhile, the biorenewable content was not greatly decreased due to the biorenewable character of tannic acid in TAHAs. These results showed that TAHAs as efficient toughening agents could produce UV-curable coatings of balanced coating performance with reasonably high biorenewable content. Moreover, the environment degradability of AESO-based cured films was also enhanced after the addition of TAHAs.

1. Introduction

In an age of fast depleting petroleum reserve, ever-increasing oil prices, global warming and other environmental problems, as the coatings industry is pressured to a "greener" industry, UV curable coating technology have gained increasing interest due to their distinct advantages including low energy consumption, low space and capital requirement for curing equipment, less VOC emission, high curing speed and excellent properties of products [1,2]. UV curable coatings have been enjoying fast market growth since its introduction to the coatings industry. However, up to now, most UV-curable coating systems and the predominant sector of the UV-curable coating market are still based on petrochemical-derived acrylate oligomers and monomers, which has a foreseeable limit and an ever-increasing cost as petroleum production is facing exhaustion day by day. In recent years, utilization of biorenewable raw resources in UV curing coatings technology has attracted intensive interests among scientists and technologists throughout the world, which is considered to be a promising "green + green" solution to the challenges that the coatings industry is facing [3–6]. UV-curable coating materials with high biorenewable content, comparable coating performance to petrochemical-based formulations and lower cost are highly desirable.

Renewable resources such as plant derived fats and oils have traditionally been used in organic coatings both as resins by themselves and as raw material components for coating resins. The features of renewable resources, such as biodegradability, nontoxic and short regeneration, meet the demand of a sustainable chemical industry [7–15]. Soybean oil derived chemicals, such as acrylated epoxidized soybean oil (AESO), are important biorenewable materials for the development of coatings industry [16–24]. However, the cured coating films of AESO alone do not show properties of rigidity and strength required for structural applications as their petrochemical-based counterparts. The soft fatty acid triglyceride backbone, the lower reactivity for the mid-chain acrylates and the low crosslinking degree are the main reasons for the inferior coating properties [25–27].

In order to improve the coating performance, toughening agents petrochemicals additives which have rigid structure or

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custom-design the structure of the bio-based resins, had to be incorporated into AESO. One promising agent for this purpose is found in the growing field of hyperbranched polymers or oligomers [4,5]. With the advantages of high functionality, fast curing time, high solubility and low viscosity, hyperbranched polymers or oligomers are expected to produce UV-curable coatings with better crosslinking and thus greatly enhanced coating film properties. For example, hyperbranched acrylates (HBAs) have been shown to be effective low-viscosity toughening agents for acrylate-based UV-curable coatings. Chen et al. reported that the addition of HBAs as synthetic toughenners to UV-curable AESO-based biorenewable coating systems greatly improved the corresponding coating properties such as film hardness, adhesion, solvent resistance, tensile modulus and toughness [23]. However, since the HBAs they used are petrochemicals, the biorenewable content (%BRC) of soy-based UV curable coatings was decreased as a result, which means that the coating performance was improved at the sacrifice of %BRC. In order to get high %BRC bio-based UV curable coatings, it is a promising way to use bio-based hyperbranched methacrylates as alternatives of petroleum based HBAs.

Tannic acid (TA) belongs to water-soluble high molecular weight polyphenolic compounds, mostly extracted from plants and microorganisms, and contains a central carbohydrate (glucose) core, which is esterified by phenols (gallic acid). The chemical formula for commercial TA is often given as $C_{76}H_{52}O_{46}$, and it is an attractive molecule for incorporation in surface films because of its known biofunctional properties, such as antienzymatic, antibacterial, antimutagenic, and antioxidant activities [28–30]. TA in general, their precursors and/or derivatives have been used in the manufacture of coatings, adhesives, inks, lithographic plates, and so forth, because of their remarkable mechanical properties (elongation, flexibility and impact resistance) as well as optimal thermal behavior [29–32].

In the present study, a novel kind of UV-curable tannic acid-based hyperbranched methacrylates (TAHAs) were prepared and characterized by epoxy value, FTIR, ^{1}H NMR and GPC. The study also concerns formulating TAHAs into AESO based UV curable coatings to produce high biorenewable materials based UV curable coatings. The effects of TAHAs on the cure kinetics of formulations and the final UV cured films properties were investigated and discussed in this contribution.

2. Experimental

2.1. Raw materials

Tannic acid (TA) was purchased from Aladdin (Shanghai, China). Glycidyl methacrylate (GMA) and glycidyl ester of Versatic acid (Cardura E10) (CE10) were supplied by Hexion Specialty Chemical Management Co., Ltd. (Shanghai, China). Triphenylphosphine (TPP), hydroquinone monomethylether (MEHQ), ethyl acetate (EA) and butyl acetate (BA) were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). 2,4,6-(Trimethyl benzoyl)-diphenyl phosphine oxide (TPO) and Irgacure 500 were provided by Ciba Specialty Chemicals Co., Ltd. (Shanghai, China). Acrylated epoxidized soybean oil (AESO) was provided by Jiangsu San-Mu Group Co., Ltd. (Wuxi, China). Phosphate adhesion promoter (CD9051) was purchased from Sartomer Company Inc. (Guangzhou, China). All materials were used as received.

2.2. Synthesis of tannic acid-based hyperbranched methacrylates

A series of TAHAs were synthesized according to the same general procedure as described for $TAG_{80}E_{20}$ below. The reaction scheme for TAHAs is summarized in Fig. 1. TA (17.012 g, 0.01 mol), TPP (0.865 g, 1.5 wt.%) as catalyst, MEHQ (0.058 g, 0.1 wt.%) as inhibitor, 12 mL EA and 8 mL BA were mixed in a 250 mL four-neck round-bottom flask in oil bath which was equipped with a thermometer, a mechanical stirrer, a dropping funnel and a cold-water condenser. The reaction mixture was stirred at 95 °C while GMA (28.430 g, 0.20 mol) and CE10 (12.250 g, 0.05 mol) mixture was dropped into the flask for 2 h. Afterwards, the reactions were performed for 48 h at 95 °C. TAHAs were obtained as brown viscous liquids by evaporating the solvent.

2.3. Characterization of tannic acid-based hyperbranched methacrylates

The epoxy value of reaction system was determined by titration with hydrogen bromide (HBr) according to ASTM D1652; the end point of the titration was determined by a Mettler Toledo T50 potentiometric titrator. The molecular weights and molecular weight distribution of TAHAs were measured by GPC with a differential refractive index and a photodiode array detector, using

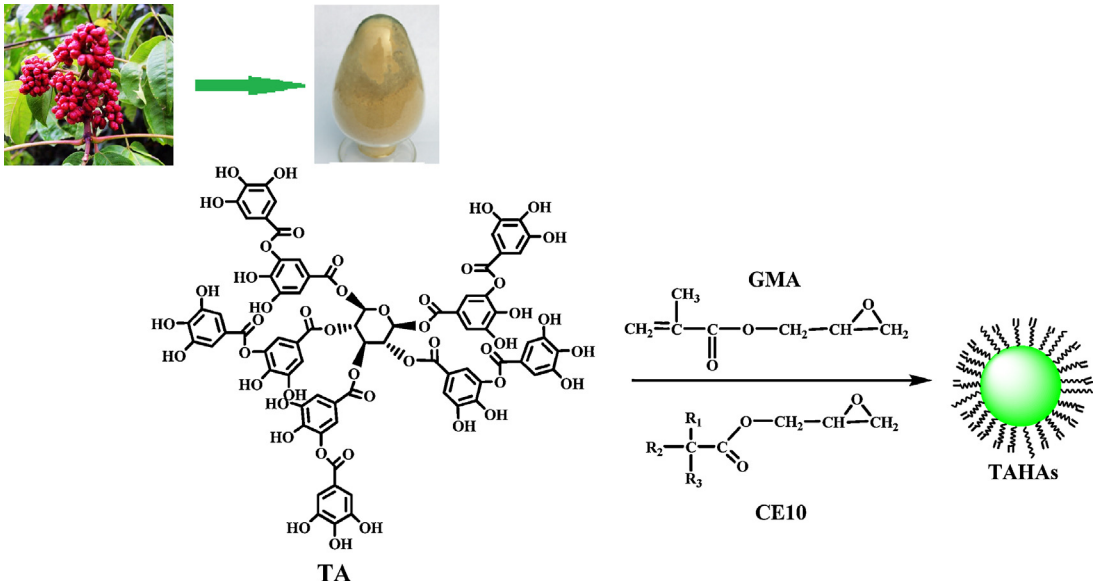

Fig. 1. Schematic illustration of synthetic route to TAHAs.