



Use of cardanol-based acrylate as reactive diluent in UV-curable castor oil-based polyurethane acrylate resins

Yun Hu^{a,b,c,d}, Qianqian Shang^{a,b,c,d}, Jijun Tang^e, Cuina Wang^f, Fei Zhang^g, Puyou Jia^{a,b,c,d}, Guodong Feng^{a,b,c,d}, Qiong Wu^f, Chengguo Liu^{a,b,c,d,*}, Lihong Hu^{a,b,c,d}, Wen Lei^f, Yonghong Zhou^{a,b,c,d,*}

^a Institute of Chemical Industry of Forest Products, Chinese Academy of Forestry, Nanjing 210042, PR China

^b Jiangsu Key Laboratory for Biomass Energy and Material, Jiangsu Province, Nanjing 210042, PR China

^c National Engineering Lab for Biomass Chemical Utilization, Nanjing 210042, PR China

^d Key Lab on Forest Chemical Engineering, State Forestry Administration, Nanjing 210042, PR China

^e Department of Corrosion Prevention and Polymer Materials, College of Materials Science and Engineering, Jiangsu University of Science and Technology, Zhenjiang 212003, PR China

^f College of Science, Nanjing Forestry University, Nanjing 210037, PR China

^g Jiangsu Police Institute, Nanjing 210031, PR China

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ABSTRACT

A biobased diluent, cardanyl acrylate (CA), was synthesized from cardanol and used to modify a castor oil-based polyfunctional polyurethane acrylate (PUA) resin. Firstly, chemical structure of CA was characterized by FT-IR, ¹H NMR, and ¹³C NMR. Subsequently, the effect of CA's content on the biobased content, viscosity, and volumetric shrinkage of the obtained bioresins were studied and compared with the petroleum-based hydroxyethyl acrylate (HEA) diluent. Moreover, ultimate properties of the UV-cured biomaterials such as thermal, mechanical, coating, swelling, and hydrophobic properties were investigated. Finally, UV-curing kinetics of the resulting bioresins were determined by real-time IR. By the addition of CA, the biobased content of the resulting bioresins were improved and the viscosity and volumetric shrinkage were reduced. For example, the obtained bioresin containing 30% of CA possessed a biobased content of 62.8% and volumetric shrinkage of 9.51%, which were clearly better than those of the bioresin with 30% of HEA (50.8% and 21.94%), respectively. Furthermore, many other properties of the UV-cured biomaterials, such as thermal stability, coating's hardness and adhesion, and hydrophobic properties, were improved by the incorporation of CA. The final C=C conversions of the resulting bioresins were also enhanced by the addition of CA. Hence, the cardanol-based diluent showed good potential in the development of UV-curable coatings.

1. Introduction

UV-curable coatings have received considerable attention due to their low energy consumption, low volatile organic chemical (VOC) emission, low capital investment, and very rapid curing rate even at ambient temperature (Liu et al., 2015a). However, due to dramatic price fluctuation of fossil feedstocks and stricter environmental regulations, there has been a growing interest in development of UV-curable coatings from renewable resources such as plant oils (Xia and Larock, 2010; Wang et al., 2017), starch (Teixeira et al., 2011), and cellulose (Gao et al., 2012). The use of biorenewable resources in UV-curable coatings can provide a “green + green” solution to the current coating industry.

Among all the biomass-derived feedstocks, plant oils are the most frequently-used one for the preparation of UV-curable coatings because of their high availability, low toxicity, triglyceride structures feasibly converted into coating's constituents, and biodegradability (Fertier et al., 2013; Ma et al., 2016; Ma and Webster, 2015; Li et al., 2016). Plant oil-based polyurethane acrylate is an important type of UV-curable prepolymers, which has the advantages of facile synthesis, high solid content, narrow polydispersity, etc. A series of castor oil (CO)-based PUAs (COPUA) have been prepared by us and other researchers, which showed excellent thermal, mechanical, and coating properties when used solely or with other diluents (Li et al., 2015; Chen et al., 2015; Hu et al., 2017). However, some disadvantages were shown during the study of such PUAs. First, the PUAs usually possess relatively

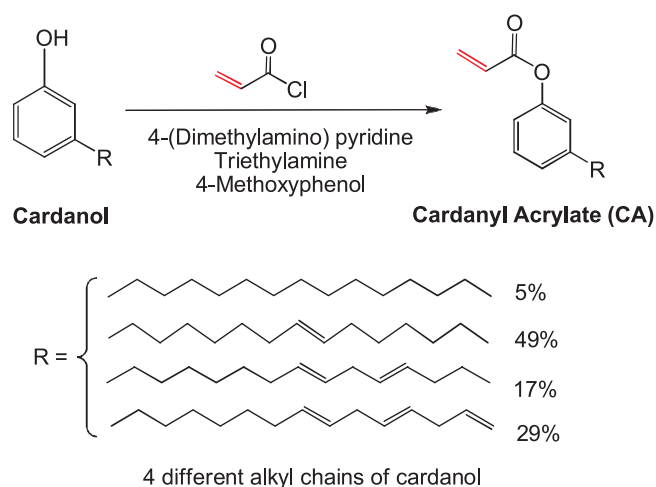
* Corresponding authors at: Institute of Chemical Industry of Forest Products, Chinese Academy of Forestry, Nanjing 210042, PR China.

E-mail addresses: liuchengguo@icifp.cn (C. Liu), zyh@icifp.cn (Y. Zhou).

high molecular weight, which easily leads to high viscosity. Second, serious volumetric shrinkage was observed for the cured PUA resins, especially for those highly functional PUA prepolymers. Vinyl diluents can be utilized to reduce the viscosity of prepolymers and adjust other physicochemical properties of the resultant materials (Srivastava et al., 2008; Wang and Soucek, 2013; Kunwong et al., 2011; Vani et al., 1993). Recently, biobased diluents have attracted increasing attention due to their effect on improving biobased content of UV-curable coatings and reducing VOC emissions (Dai et al., 2016). Despite several biobased diluents have been reported, accounts on new biobased diluents for UV-curable coatings are still limited, and the study on the shrinkage of UV-curable acrylate resins is barely seen.

Cardanol, extracted from cashew nut shell liquid, is a kind of common agricultural by products. With the reactive functional benzene ring, phenolic hydroxyl group, and long unsaturated C₁₅ alkyl chain, cardanol is regarded as a versatile platform for chemical modification (Rao and Palanisamy, 2013; Voirin et al., 2013). Cardanol and its derivatives are widely used in the fields of composites (Rao and Palanisamy, 2011; Bo et al., 2016; Barreto et al., 2011; Bloise et al., 2014), plasticizers (Mohapatra and Nando, 2014; Chen et al., 2015; Greco et al., 2010), coatings (Kathalewar and Sabnis, 2014; Darroman et al., 2015; Darroman et al., 2016; Liu et al., 2016a), epoxy curing agents (Huang et al., 2012; Sultania et al., 2012), antioxidant (Liu et al., 2016b), etc. Cardanyl acrylate (CA), which can be obtained by the modification of cardanol with acryloyl chloride (Scheme 1), has been shown as active acrylate in the synthesis of copolymers (Nguyen et al., 2002; Sitaramam and Chatterjee, 1989; John et al., 1994). The unique structure of cardanol endowed the resulting copolymers with many desirable properties, including flexibility, hydrophobicity, thermal resistance, and acid/alkali resistance. These results are in favor of employing it as reactive diluent in UV-curable systems.

Therefore, in this paper, CA monomer was synthesized and utilized as reactive diluent in an effort to develop UV-curable coatings with high biorenewable content and overcome the shortcomings of PUA mentioned above. The structure of CA was confirmed by FT-IR, ¹H NMR, and ¹³C NMR. The effect of CA's addition on important parameters such as biobased content, viscosity, and volumetric shrinkage of the resultant UV-curable resins was evaluated and compared to a petroleum-based diluent, hydroxyethyl acrylate (HEA). Herein HEA was chosen for comparison because it has an almost equivalent functionality of active unsaturated carbon-carbon double bond (C=C) as CA. Furthermore, thermal, mechanical, coating, swelling, and hydrophobic properties of the resulting UV-cured biomaterials were carefully studied. Finally, UV-curing behaviors of the bioresins were investigated using real-time IR (RT-IR).



Scheme 1. Synthetic route of cardanyl acrylate from cardanol.

2. Experimental

2.1. Materials

The polyfunctional COPUA was synthesized according to our previous work (Hu et al., 2017), which had a viscosity of 13540 cP at 25 °C. Cardanol (MD5036) was kindly supplied by Shanghai Meidong biological materials Co., Ltd. (China). Darocur 1173 (98%), 4-methoxyphenol (98%), and acryloyl chloride (98%) were supplied by Sahn chemical technology Co., Ltd. (China). 4-(Dimethylamino) pyridine (99%) was provided from Nine-Dinn Chemistry Co., Ltd. (China). Triethylamine ($\geq 99.0\%$) and tetrahydrofuran ($\geq 99.0\%$) were provided by Titan Scientific Co., Ltd. (China). Ethyl ether ($\geq 99.5\%$) was obtained from Nanjing Chemical Co., Ltd. (China). Anhydrous magnesium sulfate ($\geq 98.0\%$) was supplied by West Long Chemical Co., Ltd. (China). Sodium bicarbonate ($\geq 99.5\%$) was obtained from Shanghai Exhibition Cloud Chemical Co., Ltd. (China).

2.2. Synthesis of CA diluent

The CA diluent was synthesized by a single-step procedure, as indicated in Scheme 1. 30.4 g of cardanol, 0.62 g of 4-(dimethylamino) pyridine as catalyst, 10.1 g of triethylamine as acid absorber, 0.15 g of 4-methoxyphenol as inhibitor, and about 20 mL of tetrahydrofuran were added to a four-necked flask equipped with a mechanical stirrer, a thermometer, and a refluxing condenser. The mixture was cooled to about 0 °C and stirred. Then acryloyl chloride (9.05 g, 0.1 mol) was added dropwise into the flask. After that the reaction mixture was heated to 40 °C and agitated at the temperature for 8 h. During the work-up procedures, the mixture was filtered, dissolved with diethyl ether, and then transferred into a separating funnel. Subsequently, the product was washed by saturated sodium bicarbonate solution for three times and by distilled water until neutral. Afterwards the upper layer was obtained and dried by anhydrous magnesium sulfate for overnight. At last, the solution was filtered and diethyl ether was removed by rotary evaporation. The obtained product was a yellowish and transparent liquid.

2.3. Preparation of crosslinked polymers

The UV-curable samples were prepared by mixing COPUA with a certain amount of diluent and the Darocur1173 photoinitiator (3% of the total weight of COPUA and the dilute) at room temperature for about 20 min. All the mixtures were centrifuged to remove air bubbles, and then poured into homemade polytetrafluoroethylene (PTFE) molds or coated on polished tinplate sheets. Finally, the resins were cured by an Intelli-Ray 400W UV light-curing microprocessor (Uvitron International Corporation, USA) with an exposure intensity of 100 mw/cm² at 25.0 °C. The curing time is 20 min for samples in PTFE and 5 min for samples on tinplate. All the cured samples were kept in a glass desiccators at room temperature for a week before tests.

2.4. Characterization

FT-IR tests were performed on a Nicolet iS10 spectrometer (Thermo-Fisher Corporation, USA) equipped with Smart ARK accessory for liquid samples. The scanning range was from 4000 to 500 cm⁻¹ with a spectral resolution of 4 cm⁻¹. NMR tests were conducted on a DRX-300 Advance NMR spectrometer (Bruker Corporation, Germany) with the samples dissolved in deuterated chloroform (CDCl₃).

Viscosity (V_s) measurements of the liquid resin samples were conducted on a DVS+ digital-display viscometer coupled with a small sample adapter (Brookfield Corporation, USA). Measurements of volumetric shrinkage (ΔV) were carried out on a ZMD-2 electronic automatic density meter (Shanghai Fangrui Instrument Corporation, China). By determining the densities of the liquid systems before and after

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