Synthesis and Properties of UV-Curable Polyfunctional Polyurethane Acrylate Resins from Cardanol

Yun Hu,† Qianqian Shang,† Caijing Bo,† Puyou Jia,*,† Guodong Feng,† Fei Zhang,‡ Chengguo Liu,*,† and Yonghong Zhou*‡

†Institute of Chemical Industry of Forest Products; Key Laboratory of Biomass Energy and Material, Jiangsu Province; Co-Innovation Center of Efficient Processing and Utilization of Forest Resources, Jiangsu Province; Key Laboratory of Chemical Engineering of Forest Products, National Forestry and Grassland Administration; National Engineering Laboratory for Biomass Chemical Utilization, Chinese Academy of Forestry, Nanjing 210042, P. R. China
‡Jiangsu Police Institute, Nanjing 210031, P. R. China

ABSTRACT: A novel UV-curable polyurethane acrylate (PUA) oligomer was synthesized by modifying cardanol with a polyfunctional acrylate precursor obtained through reacting pentaerythritol triacrylate with isophoronedisocyanate. Chemical structures of the obtained cardanol-based PUA (C-PUA) oligomer were confirmed by Fourier transform infrared and 1H NMR. Subsequently, viscosity and gel content of the C-PUA resins containing different quantities of hydroxymethyl methacrylate (HEMA) were characterized. The C-PUA oligomer possessed a viscosity of 8360 mPa s, which reduced to 115 mPa s when 40% of the HEMA diluent was added. Furthermore, thermal, mechanical, coating, and swelling properties of the resulting UV-cured C-PUA/HEMA materials were investigated. The ultimate biomaterials showed excellent performance, including a glass transition temperature (Tc) of 74–123 °C, maximum thermal degradation temperature of 437–441 °C, tensile strength of 12.4–32.0 MPa, tensile modulus of 107.2–782.7 MPa, and coating adhesion of 1–2. In conclusion, the developed C-PUA resins show great potential to be applied in UV-curable materials like coatings.

INTRODUCTION

UV-curing technology has attracted much attention because of its various advantages such as high efficiency, mild curing conditions, low capital spending, low energy consumption, and low volatile organic chemical.1 Therefore, UV-curing materials are considered “clean and green” and have been widely used in modern industry like coatings, adhesives, drug delivery systems, etc.2 In recent years, due to the scarcity of fossil feedstock and concern on environmental pollution, there is a growing interest in developing polymeric materials from renewable resources, such as carbohydrates, proteins, and plant oils.3,4 The incorporation of UV-curing technology into biobased polymeric materials may provide a “greener” strategy for the polymer industry.

Cardanol is an agricultural byproduct obtained from cashew nut shell liquid (CNSL).5–7 Although the total production of CNSL is only around 1 million tons annually in the world, it is one of the few major sources of naturally occurring phenols.8 Cardanol contains an aromatic ring with an unsaturated long C15 chain at the meta-position and a polar hydroxyl group, which may endow the resulting products with many desirable properties like flexibility, hydrophobicity, thermal resistance, acid/alkali resistance, etc. As a result, cardanol and its derivatives have been widely used in industrial fields9,10 such as coatings,11–15 polybenzoxazine,16 plasticizers,17 antioxidants,18 surfactants,19 and polymeric materials.20–22 Cardanol has also been involved in the preparation of UV-curable materials. Rekha et al.23 reported the synthesis of a telechelic urethane–methacrylate cross-linkers based on cardanol, and their curing process and double-bond conversion upon UV irradiation was studied. Chen et al.24 investigated the cationic photopolymerization, thermal, and mechanical properties of thin-film materials containing epoxidized cardanol. It was found that epoxidized cardanol imparted balanced physicochemical properties to the cationic UV-curable materials, thus demonstrating a great potential to be utilized as a reactive ingredient in cationic UV-curable systems. Li et al.25 reported the synthesis of a cardanol-based UV-curable vinyl ester monomer and its copolymerization with maleic anhydride modified dimer fatty acids polymerized glycyl methacrylate to form rigid biobased materials. The resulting materials showed good mechanical and thermal properties, all them to be used as eco-friendly materials in coatings. In our group, we developed several new cardanol-based diluents, including cardanyl acrylate, epoxidized cardanyl acrylate, and epoxidized cardanol glycidy ether.26–28 When these diluents were...
employed to modify a castor oil-based polyfunctional polyurethane (PUA) oligomer, they demonstrated good ability in reducing viscosity and volumetric shrinkage as well as improving the biobased content of the obtained bioresins. Compared with the many cases related to cardanol-based diluents or modifiers for UV-curable resins, examples of cardanol-based oligomers as main ingredients are few. Liu and his coauthors reported the synthesis of a series of novel hyperbranched UV-curable oligomers from cardanol.\(^7\)\(^{13–15}\) The resultant oligomers contained rigid carbon rings as "hard cores" and high acrylic C=C functionality, thus leading to enhanced thermal, mechanical, and coating properties, as well as reasonably high biorenewable contents for the UV-cured biomaterials. However, the synthesis of these oligomers generally involved four steps, which may clearly increase the cost of products. Besides, high viscosities (>12 000 mPa s) were observed for the oligomers,\(^12,14\) which could also be attributed to the long route of synthesis. All these disadvantages may greatly limit their real application in the industry of UV-curable materials.

In this paper, we developed a cardanol-based polyurethane acrylate (C-PUA) resin via a two-step procedure. To improve the active C=C functionality of the C-PUA product, cardanol was capped with a polyfunctional acrylate precursor obtained by reacting pentaerythritol triacrylate (PETA) with isophoronedisocyanate (IPDI). The structure of C-PUA was characterized by Fourier transform infrared (FT-IR) and \(^1\)H NMR. Moreover, UV-curable resins were formulated using hydroxyethyl methacrylate (HEMA) as diluent and ultimate modifiers for UV-curable resins, examples of which were observed at 1635, 808, and 1726 cm\(^{-1}\). These peaks are new compared to the spectrum of cardanol. Moreover, the peak at 2267 cm\(^{-1}\) representing the −NCO group almost diminished. All these results indicated that the target compound of C-PUA was synthesized successfully.

\(^1\)H NMR spectra of cardanol, IPDI−PETA, and C-PUA are shown in Figure 2. In the spectrum of cardanol, the peaks at 6.8−7.3 ppm can be attributed to the protons on the benzene ring and the peaks at 5.1−5.7 ppm were ascribed to the protons on the C=C groups of the aliphatic segment.\(^7\) The peaks at 5.9 ppm were assigned to the hydroxyl group. The absorption at 2925 and 2854 cm\(^{-1}\) were assigned to the C−H stretching on methylene and methyl groups.\(^7\) The peaks at 1594, 1490, and 1457 cm\(^{-1}\) corresponded to the vibration absorption of benzene ring.\(^7\) In the spectrum of IPDI−PETA, the characteristic absorption peaks at 3359 and 2267 cm\(^{-1}\) represented the groups of −NH and −NCO, respectively. Moreover, the characteristic absorption of the C=C groups and ester carbonyl from PETA are observed at 1635, 808, and 1726 cm\(^{-1}\), respectively. In the spectrum of C-PUA, several characteristic peaks were shown: −NH group (3359 cm\(^{-1}\)), ester carbonyl (1726 cm\(^{-1}\)), and C=C groups (1635 and 808 cm\(^{-1}\)).\(^3,9,30\) These peaks are new compared to the spectrum of cardanol. Moreover, the peak at 2267 cm\(^{-1}\) representing the −NCO group almost diminished. All these results indicated that the target compound of C-PUA was synthesized successfully.

\(\text{Figure 2. } \text{\(^1\)H NMR spectra of (a) cardanol, (b) IPDI−PETA, and (c) C-PUA.}\)
C-PUA resin with the content of the HEMA diluent. It can be seen that the pure C-PUA resin showed a viscosity value of 8360 mPa s at 25 °C. Notably, the viscosity of the C-PUA/HEMA resin dropped from 8360 to 115 mPa s with the increase of HEMA concentration from 0 to 40%. To provide an efficient flow to facilitate good processability, the favored viscosity for liquid resins is controlled commonly in the range of 200−1000 mPa s at ambient temperature. Therefore, the viscosity of the C-PUA/HEMA systems can be adjusted to meet the requirements of the UV-curable techniques.

**Photopolymerization Kinetics of the C-PUA/HEMA Resins.** Photopolymerization kinetics of the C-PUA/HEMA resins was studied by real-time infrared (RT-IR) technique. The C=C conversion curves of the resins are depicted in Figure 4, and the values of final C=C conversion are listed in Table 1. The initial C=C conversion of the resins generally increased when the content of HEMA rose from 0 to 40%. The reason for this change may lie in the fact that the addition of more HEMA diluent decreases the viscosity of resin, which promotes the motion of radical groups during the UV-curing process. The final C=C conversion of the bioresins dropped from 52.0 to 46.0% as the HEMA content increased to 10% and then grew gradually to 70.5% as the content of HEMA increased from 10 to 40%. The reason was that as the content of HEMA increased, the C=C concentration of C-PUA/HEMA system was increased. At the same time, the viscosity of the system was lowered and the diffusion ability of the free radicals increased, and the final C=C conversion of the C-PUA/HEMA system showed an increasing trend.

**Gel Content.** The C_{gel} of the cured C-PUA/HEMA resins were determined by Soxhlet extraction, and the corresponding results are shown in Figure 3. First, all of the cured C-PUA/HEMA presented high gel contents, with values ranging from 93.3 to 97.9%, suggesting that the C-PUA resins were well cross-linked. As the content of HEMA increased, the C_{gel} of the cured C-PUA biomaterial increased gradually, indicating that the employment of HEMA diluent can improve the cross-link extent of the C-PUA resin.

**Properties of the UV-Cured C-PUA Resins. Dynamic Mechanical Analysis.** Figure 5 presents changes of the storage modulus (E') and the loss factor (tan δ) with temperature for the cured C-PUA resins, and the related data are shown in Table 1. The glass transition temperature (T_g) was determined from the peak temperatures of the tan δ curves. First, the pure C-PUA material demonstrated a E' at 25 °C (E'_{25}) of 708.6 MPa and T_g of 74 °C, both of which were much higher than those of the pure cardanol-based multiarmed oligomers. Furthermore, as the HEMA content grew from 0 to 40%, E' at 25 °C (E'_{25}) increased from 708.6 to 1578.8 MPa. Meanwhile, the T_g value increased apparently from 74 to 123 °C as the content of HEMA increased. These results indicated that the incorporation of the HEMA dilute could improve the thermomechanical properties of the resulting UV-cured bioresins. The thermomechanical properties of the thermosets usually have close correlation with the structural factors, such as cross-link density (ν_e). According to the kinetic theory of rubber elasticity, the ν_e of the cured copolymers could be determined with the following formula

\[ ν_e = \frac{E'}{3RT} \]

where E' is the storage modulus of the cross-linked copolymers in the rubbery plateau region, R is the universal gas constant, and T is the absolute temperature. In this study, the rubber modulus at the temperature of T_g + 60 °C was employed for the calculation of ν_e. The calculated ν_e data are presented in Table 1. The ν_e value increased with the growth of HEMA, which was one of the possible reasons for the increase of both E'_{25} and T_g. Besides, the incorporation of HEMA could bring

**Figure 3.** Effect of HEMA on viscosity and gel content of the C-PUA/HEMA resins.

**Figure 4.** (a) Double-bond conversions and (b) conversion rate of the C-PUA/HEMA resins measured by FT-IR.
steric hindrance into the cross-linked structures, which is another possible reason for the growth of $E'_{25}$ and $T_g$.

Thermogravimetric Analysis (TGA). TGA thermograms and their derivative curves of the UV-cured C-PUA/HEMA resins are shown in Figure 6. The relevant results are summarized in Table 1. The degradation process of UV-cured C-PUA/HEMA can be divided into four stages. The first stage (<240 °C) was slowest, which is due to the removal of residual low-molecular-weight ingredients. The second stage at 240−380 °C can be assigned to the decomposition of hard segment in the urethane structures connecting with cardanol or PETA. The third stage at 380−510 °C was quickest and can be ascribed to the degradation of the cross-linked bonds and char formation, while the last stage (>510 °C) corresponded to the gradual degradation of char residue. Furthermore, when the content of HEMA increased from 0 to 40%, the 5% weight-loss temperature ($T_{5\%}$) increased from 247 to 263 °C, while the maximum thermal degradation temperature ($T_p$) and char yield ($w_{\text{char}}$) slightly decreased, indicating that the incorporation of the HEMA diluent did not influence the thermal stability of the new bioresins too much.

Mechanical Properties. The typical tensile stress−strain curves of the UV-cured C-PUA/HEMA resins are shown in Figure 7, and the corresponding data are listed in Table 2. It can be seen that all the biobased materials fractured without reaching a yield point, indicating the rigid characteristic of the materials. When the content of HEMA grew from 0 to 40%, the tensile strength increased significantly from 12.4 to 31.9 MPa, and Young’s modulus increased from 107.2 to 782.7 MPa. The large increase may also be attributed to the growing cross-link density of the obtained materials and the incorporation of the HEMA diluent with steric hindrance.

Coating Properties. The coating properties of the UV-cured C-PUA/HEMA materials including adhesion, pencil hardness, and flexibility were investigated, and the data are listed in Table 2. Obviously, as the HEMA concentration grew from 0 to 40%, the adhesion grew from 2 to 1, the pencil hardness changed gradually from B to HB, while the flexibility was maintained at the minimum value of 2 mm. The improvement of adhesion is probably attributed to the increase of the hydroxyl concentration provided by HEMA, while the growth
of hardness can be ascribed to both the growth of νe and the incorporation of steric structure too.38,39

**Swelling Properties.** The solvent resistance of the cured C-PUA/HEMA resins was examined, and the results are listed in Table 3. In general, all the cured materials exhibited better resistance to water than to organic solvents. As the concentration of HEMA rose from 0 to 40%, the uptake of water increased basically from 0.2 to 1.5%, which is possibly because of the growing content of hydroxyl groups from HEMA. Meanwhile, the uptake of ethanol and toluene dropped gradually from 3.8 to 2.7% and from 9.3 to 2.9%, respectively, while the absorbed amounts of acetone grew from 5.4 to 8.9% and then dropped to 6.6%. The improvement of resistance to ethanol and toluene may be attributed to the growing cross-link density of the cured materials when the HEMA content increased.33,40

### CONCLUSIONS

In this work a novel cardanol-based polyfunctional PUA oligomer was successfully synthesized by a simple two-step procedure. The viscosity of oligomer was obviously lower than those of the hyperbranched cardanol-based oligomers shown in previous works. Moreover, the resulting UV-cured biomaterials containing the HEMA diluent demonstrated excellent ultimate properties such as storage modulus, Tg, maximum thermal degradation temperature, tensile strength and modulus, and adhesion and flexibility of coatings, mainly due to the high C= C functionality of oligomer and the special structures (e.g., benzene ring) involved in cardanol. Therefore, the developed cardanol-based PUA resins show promise to be used in UV-curable materials like coatings.

### EXPERIMENTAL SECTION

**Materials.** Cardanol (MD5036) was purchased from Shanghai Meidong Biological Materials Co., Ltd. (China). Isophoronedisocyanate (IPDI, 99%) was supplied by Nine Ding Chemistry Co., Ltd. (China). Dibutyltin dilaurate (DBTDL) was obtained from Shanghai Titan Scientific Co., Ltd. (China). 2-Hydroxy-2-methoxypropophene (Darocur 1173, 98%), pentaerythritol triacrylate (PETA, 96%), and 4-methoxyphenol (98%) were bought from Sahn Chemical Co., Ltd. (China). HEMA (97%) was purchased from Adamas Reagent Co., Ltd. (China). methoxyphenol, 30 mL of hexane, and 0.25 g of catalyst DBTDL were placed together into a four-neck round-bottom flask equipped with a mechanical stirrer, refluxing condenser, dropping funnel, and an inlet for nitrogen (N2) gas. Under the atmosphere of N2, the reaction mixture was agitated and heated to 45 °C and then 29.8 g (0.10 mol) of PETA was slowly added. After that the mixture was heated to 60 °C and agitated at this temperature for 6 h. Subsequently, 27.45 g (0.09 mol) of cardanol was used to react with the remaining isocyanate at 60 °C. The reaction did not stop until the concentration of free isocyanate (determined by the method of n-butyl amine reverse titration41) dropped to ~0%. Finally, the hexane solvent was evaporated via rotary evaporation and the C-PUA product as a light yellow transparent viscous liquid was obtained.

**Curing of the C-PUA Resins.** The UV-curable samples were formulated by mixing the obtained oligomer, HEMA diluent, and Darocur 1173 (3% of the total weight of C-PUA and HEMA) for 20 min, followed by centrifuged to remove air bubbles. After that the mixture was poured into homemade poly(tetrafluoroethylene) molds or spread on tinplates, which

### Experimental Details

**Synthesis of Cardanol-Based Polyurethane Acrylate.** The synthetic route for the C-PUA product is outlined in Scheme 1. IPDI (19.98 g, 0.09 mol), 0.30 g of 4-methoxyphenol, 30 mL of hexane, and 0.25 g of catalyst DBTDL were placed together into a four-neck round-bottom flask equipped with a mechanical stirrer, refluxing condenser, dropping funnel, and an inlet for nitrogen (N2) gas. Under the atmosphere of N2, the reaction mixture was agitated and heated to 45 °C and then 29.8 g (0.10 mol) of PETA was slowly added. After that the mixture was heated to 60 °C and agitated at this temperature for 6 h. Subsequently, 27.45 g (0.09 mol) of cardanol was used to react with the remaining isocyanate at 60 °C. The reaction did not stop until the concentration of free isocyanate (determined by the method of n-butyl amine reverse titration41) dropped to ~0%. Finally, the hexane solvent was evaporated via rotary evaporation and the C-PUA product as a light yellow transparent viscous liquid was obtained.
were polished and cleaned with acetone. At last, all of the samples were cured by an Intelli-Ray 400 W UV light-curing microprocessor (Uvitron International Corporation) with an UV light intensity of 100 mW cm$^{-2}$ for 4 min. The cured samples were stored in a glass desiccator for 7 days before further evaluation.

**CHARACTERIZATION**

FT-IR spectra of the samples were recorded on a Nicolet iS10 IR spectrometer (Thermo-Fisher) with a scanning range from 4000 to 500 cm$^{-1}$. $^1$H NMR spectra of the samples were performed on a DRX-300 spectrometer (Bruker, Germany) with deuterated chloroform as the solvent.

Viscosity ($\eta$) of the UV-curable resins was tested by a DVS + digital-display viscometer (Brookfield Corporation) with a microprocessor (Uvitron International Corporation) with an oscillating frequency of 1 Hz in double cantilever mode.

Dynamic mechanical analysis of the UV-cured samples was carried out on a Q800 solids analyzer (TA Corporation) with an oscillating frequency of 1 Hz in double cantilever mode. The cured samples with a size of $40 \times 6 \times 1$ mm$^3$ were measured from $-80$ to 200 °C at a heating rate of 3 °C min$^{-1}$.

Thermogravimetric analysis (TGA) of the UV-cured samples was performed on an STA 409PC thermogravimetry instrument (Netzsch Corporation, Germany) with a Nicolet FT-IR, with a microprocessor (Uvitron International Corporation) with an oscillating frequency of 1 Hz in double cantilever mode. The cured samples with a size of $40 \times 6 \times 1$ mm$^3$ were measured from $-80$ to 200 °C at a heating rate of 3 °C min$^{-1}$.

Mechanical properties of the UV-cured samples were carried out on a SANS7 CMT-4304 Universal tester (Shenzhen Xinsansi Jiliang Instrument Corporation, China) with a cross-head speed of 5 mm min$^{-1}$. Dumbbell specimens with a size of $62 \times 10 \times 3$ mm$^3$ were measured. The tensile properties for each sample were determined from an average value of five specimens.

Coating properties of the UV-cured samples including adhesion, pencil hardness, and flexibility were evaluated according to GB 1720-79(89), GB/T 6739-2006, and GB/T 6739-1996, respectively. Detailed procedures are reported in our previous works. $^{27,30}$

Swelling properties of the UV-cured samples were determined using water, ethanol, acetone, and toluene as solvents. Specimens were weighed and immersed in different solvents for 48 h at ambient temperatures, then dried, and weighed again. The swelling properties with various solvents were calculated by the following formula

$$S = \frac{W_f - W_i}{W_i} \times 100\%$$

where $W_0$ and $W_i$ are the masses of the cured sample before and after immersion in the solvent, respectively.

UV-curing behaviors of the biobased resins were studied by a modified Nicolet 5700 spectrometer from Thermo-Nicolet Instrument. The conversion of double bond ($C=\text{C}$) was determined by monitoring the change of absorption at about 810 cm$^{-1}$.

**AUTHOR INFORMATION**

**Corresponding Authors**

*E-mail: liuchengguo@icifp.cn. Tel/Fax: +86-25-85482520 (C.L.).

*E-mail: zyh@icifp.cn. Tel/Fax: +86-25-854825777 (Y.Z.).

**ORCID**

Puyou Jia: 0000-0002-3372-9135

Chengguo Liu: 0000-0001-5768-5184

Yonghong Zhou: 0000-0001-5385-5414

**Notes**

The authors declare no competing financial interest.

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