UV-Curable Coatings from Multiarmed Cardanol-Based Acrylate Oligomers

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S *Supporting Information*

Cardanol derivatives + Biobased polyols → UV-curable acrylate oligomers → High performance coatings
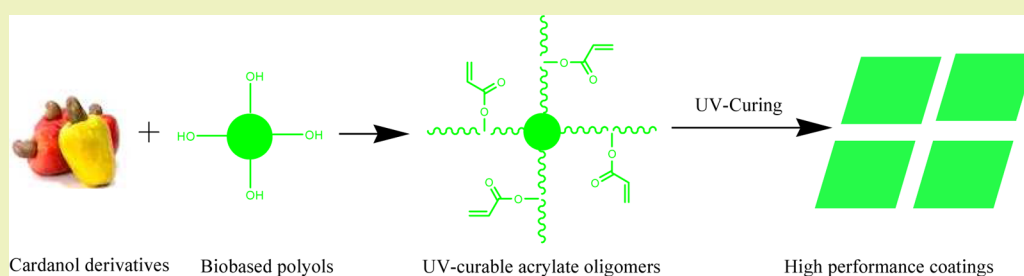
ABSTRACT: Multiarmed, cardanol-based acrylate oligomers were prepared via the ring-opening reaction between cardanyl glycidyl ether (CGE) and polyacids, followed by epoxidization of the unsaturation in alkyl side chains of cardanol segments, and acrylation of the resulting epoxy groups. Biobased coatings were produced from UV-radiation-initiated curing of these acrylates; the coating properties were then characterized in detail. The acrylate oligomers were fully characterized using gel permeation chromatography (GPC), Fourier transform infrared spectroscopy (FTIR), and proton nuclear magnetic resonance (^{1}H NMR). The UV-curing behavior of these acrylates was determined using real-time IR. The results indicated that the conversion of acrylate unsaturation increased with increasing oligomer functionality. These oligomers were formulated into UV-curable coatings, and the coating properties were evaluated to determine hardness, adhesion, chemical resistance, gloss, and surface properties. The properties of cured thermosets were also studied using tensile testing, dynamic mechanical thermal analysis (DMTA), and thermogravimetric analysis (TGA). Compared to coating from benchmark biobased UV-curable oligomer, acrylated epoxidized soybean oil (ASBO), cardanol-based coatings showed higher hardness, excellent adhesion, and enhanced thermal and mechanical properties while maintaining reasonably high biorenewable contents. These improvements in coating performances can be contributed to their unique oligomer architectures that combined the structural features of rigid benzene ring, long flexible alkyl chains, and polar hydroxyl groups.

KEYWORDS: *Multiarmed acrylate oligomers, Cardanyl glycidyl ether, UV-curable coatings, Biobased*

INTRODUCTION

Polymeric coatings are widely used in modern industry for different purposes, such as decoration, protection, and some specific functions. Conventionally, volatile organic chemicals (VOCs) are included in most coating formulations to make the viscosity low enough for applications. The reduction of VOC emission has been a main driving force for the development of environmental-friendly coating technologies.[1] Among the green coating technologies, UV-curable coatings have been receiving increased attention due to their advantages such as low energy consumption, low VOC emission, low capital investment, and very rapid curing even at ambient temperature. However, the petroleum-based acrylates are still predominant in UV-curable coating system.[2]

Due to the foreseeable limit of fossil feedstock and the increasing environmental concerns, the coating industry is suffering from soaring cost and stricter environmental regulations.[3−6] The utilization of biorenewable resources in UV-curable coatings provides a "green + green" solution to current coating industry. A variety of biorenewable raw materials (such as vegetable oils, polysaccharides, natural rubbers, and their derivatives) have been used for producing UV-curable coatings. Among these biobased chemicals, vegetable oils are the most widely used due to their high annual production, high availability, low toxicity, relatively low cost, and biodegradability.[7] Some unmodified vegetable oils, such as linseed oil, can be cured upon UV exposure via photo-oxidation mechanism, but the drying time is relatively long.[8] Because the double bonds in most vegetable oils are not sufficiently reactive for UV-radiation curing, more reactive vinyl

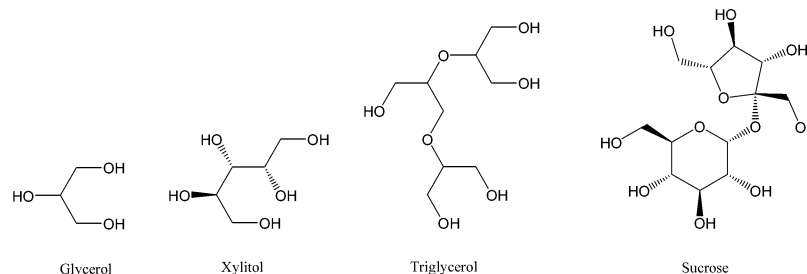**Scheme 1. Representative Synthetic Route to Multi-Armed Cardanol-Based Acrylate Oligomers**
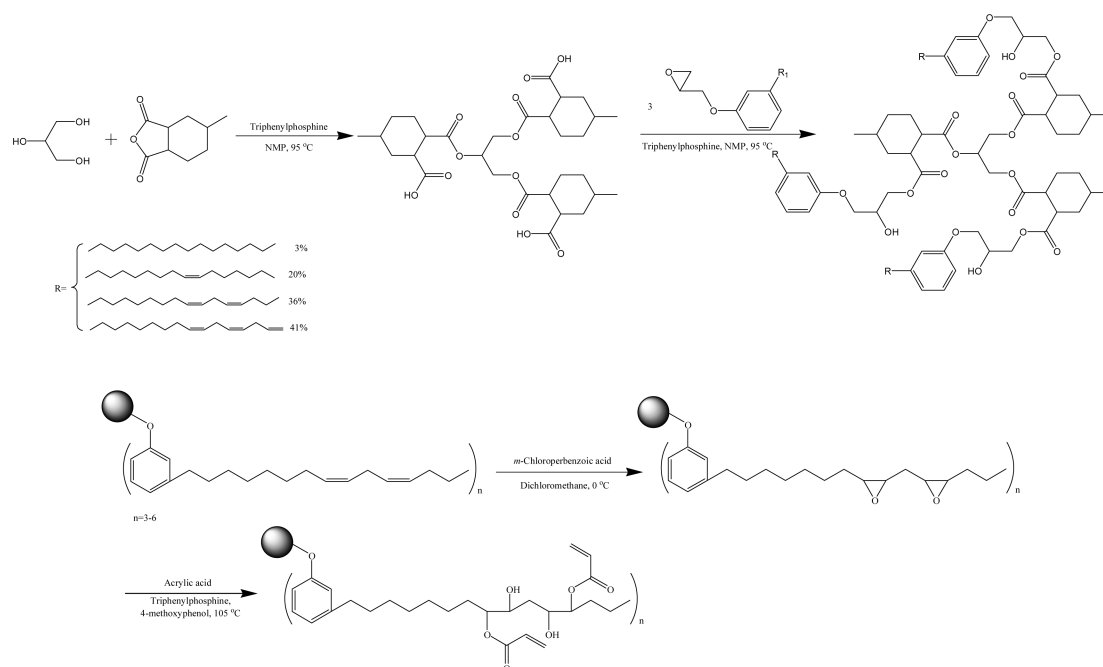
Scheme 2. Structures of Biobased Polyol Raw Materials in This Work

Glycerol   Xylitol   Triglycerol   Sucrose

groups, including acrylate, methacrylate, and allyl groups, have been introduced into vegetable oils by the chemical modifications.[9−15] Acrylated epoxidized soybean oil (ASBO) is a very important renewable oilgomer for UV curable coatings, and has been successfully commercialized by UCB Chemicals Company under the brand name of Ebecryl 860. UV-curable coatings based on pure ASBO showed inferior thermal and mechanical properties to their petroleum-based counterparts, due to the softness of fatty acid chain. Therefore, petroleum-based acrylates were usually combined with ASBO to produce coatings with satisfying properties. However, the biorenewable contents were sacrificed in this approach. It is still a challenging task to develop UV-curable coatings with both high performance and high biorenewable content.[16−18]

Cardanol is an agricultural byproduct obtained from cashew nut shell liquid (CNSL). Cardanol possesses a reactive phenolic hydroxyl group and an unsaturated C_{15} alkyl chain, which makes it a good platform for chemical modification. Therefore, cardanol and its derivatives have been widely utilized for applications in forms of coatings, paints, Novolac resins, brake linings, nanocarriers, and polymer productions.[5,19−23] Most chemical modifications of cardanol were related to the reactive phenolic hydroxyl group and the ortho- and para-hydrogen atoms. Epoxide and alcoholic hydroxyl groups can be attached to the phenolic hydroxyl group of cardanol, and these compounds have been commercialized as reactive or unreactive

diluents for coatings applications by Cardolite Corporation.[24−26] Phenalkamines, synthesized with the Mannich reaction of formaldehyde, cardanol, and amines, were widely utilized as curatives for epoxy resins.[27−29] Polyols were also prepared from cardanol via the epoxidization and ring-opening reactions, taking advantage of the unsaturation of the side chain in cardanol. Rigid polyurethane foams were produced from these polyols and petroleum-based isocyanates.[30−32] Due to its unique structure, polymers derived from cardanol showed many desirable properties, including flexibility, hydrophobicity, weatherability, and acid and alkali resistance.

As mentioned above, cardanol and its derivatives have been widely used in polymer and coating industries. However, to the best of our knowledge, there was no report dealing with the synthesis and coating formulations of multiarmed, cardanol-based acrylates. In this work, we present the synthesis of a series of multiarmed cardanol-based acrylates via a four-step route using cardanyl glycidyl ether and biobased polyols, including glycerol, xylitol, triglycerol, and sucrose, as raw materials. These acrylate oligomers were then formulated into UV-curable coatings, and their coating properties were also investigated in detail.

■ EXPERIMENTAL SECTION

Materials. 4-Methyl hexahydrophthalic anhydride (MHHPA) was purchased from Puyang Huicheng Chemical Co., Ltd. (Puyang,

China). Cardanyl glycidyl ether was kindly supplied by Cardolite Corporation (Zhuhai, China). m-Chloroperbenzoic acid was purchase from Changzhou Baokang Pharmaceutical & Chemical Co., Ltd. (Changzhou, China). 2, 4, 6-Trimethylbenzoyl diphenyl phosphine oxide and 1-hydroxycyclohexyl phenyl ketone (Irgacure 184) were provided by Ciba Specialty Chemicals Co., Ltd. (Shanghai, China). Epoxidized soybean oil (ESBO) was purchased from BASF SE (Shanghai, China). All the other chemicals were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All chemicals were used as received unless specified. Acrylated epoxidized soybean oil (ASBO) was synthesized according to a procedure in the literature,[13] with an acid equivalent of 0.7.

Synthesis of Multiarmed Cardanol-Based Acrylate Oligomers. As shown in Scheme 1, multiarmed cardanol-based acrylates were prepared via a four-step procedure: the reaction between biobased polyols and 4-methyl hexahydrophthalic anhydride, the ring-opening reaction between cardanyl glycidyl ether and polyacids, the epoxidization of the unsaturation in the side chain of cardanol, and the acrylation of the resulting epoxide groups using acrylic acid. A representative procedure for the oligomers synthesis is shown below (see Schemes 1 and 2 for representative structures).

Synthesis of Three-Armed Polyacid Based on Glycerol and 4-Methyl Hexahydrophthalic Anhydride. Glycerol (2.763 g, 0.03 mol) and triphenylphosphine (0.268 g, 1.5 wt % of total weight) were placed into a three-necked, round-bottomed flask equipped with a mechanical stirrer, a pressure-equilibrated dropping funnel, and a condenser. The mixture was heated to 95 °C with stirring. 4-Methyl hexahydrophthalic anhydride (15.120 g, 0.09 mol) was added dropwise into the flask over 60 min. The mixture was kept at 95 °C with stirring until the acid value became constant. After cooling to room temperature, three-armed polyacid was obtained as a yellow solid (yield: 99%).

Synthesis of Three-Armed Unsaturated Oligomer Based on Glycerol and Cardanyl Glycidyl Ether (U-Gly-3). Cardanyl glycidyl ether (32.040 g, 0.09 mol) was added dropwise over 60 min into a flask containing three-armed polyacid (17.901 g, 0.03 mol) at 95 °C. The reaction mixture was then heated to 100 °C, stirred until the acid value was lower than 5, and cooled to room temperature to afford three-armed cardanol-based unsaturated oligomer as a brown liquid (yield: 98%).

Epoxidization of the Unsaturation of the Side Chain in Cardanol Segment (E-Gly-3). Three-armed unsaturated oligomer derived from glycerol and glycidyl cardanyl ether (49.924 g, 0.03 mol), m-chloroperbenzoic acid (36.550 g, 0.18 mol), and dichloromethane (200 mL) were placed into a round-bottomed flask equipped with a mechanical stirrer. The mixture was cooled to 0 °C by ice bath and stirred for 3 h. The byproduct, m-chlorobenzoic acid was removed by filtration, and the resulting filtrate was washed with 10% sodium carbonate solution (100 mL × 3), deionized water (100 mL × 3), and dried thoroughly over magnesium sulfate. Dichloromethane was then removed by rotary evaporation to afford epoxidized three-armed oligomer based on glycerol and cardanyl glycidyl ether as a viscous liquid (yield: 95%).

Acrylation of Three-Armed Cardanol-Based Epoxide Oligomer (A-Gly-3). Epoxidized three-armed cardanol-based oligomer (35.200 g, 0.02 mol), triphenylphosphine (0.657 g, 1.5 wt %), and 4-methoxyphenol (0.044 g, 0.1 wt %) were placed into a three-necked, round-bottomed flask equipped with a mechanical stirrer, dropping funnel, and condenser. The reaction mixture was heated to 105 °C, and then acrylic acid (8.650 g, 0.12 mol) was added dropwise over a period of half an hour. The mixture was heated until the acid value was below five, and cooled to room temperature to afford three-armed acrylate oligomer as a transparent, yellowish, and viscous liquid (yield: 96%).

Coating Formulation. A mixture of 1-hydroxycyclohexyl phenyl ketone (Irgacure 184) and 2, 4, 6-trimethylbenzoyl diphenyl phosphine oxide (2.5:0.5 w/w) was utilized as the photoinitiator with 3 wt % of the total resin weight. The UV-curable resins and photoinitiator were thoroughly mixed and cast on aluminum panels (7.6 cm × 15 cm, Q-Lab Corporation) and glass panels with a

drawdown bar to form a thin film. The mixture was UV-cured using an F300 UVA lamp (UVA, intensity: 1600 mJ cm^{-2}, measured with a UV-Integrator 140 power meter) coupled with a Fusion LC6B Benchtop conveyor belt in air. The curing protocol was two passes through the lamp with a belt speed of 5.0 in. min^{-1}. Samples on aluminum panels were used for regular coating characterization, and the films on glass panels were peeled off for thermal and mechanical tests. All the samples were conditioned for 24 h at room temperature before measurements. The film thickness was measured using a Qnix 1500 thickness gauge. Three measurements were repeated, and the averages were reported. Coatings with a thickness of about 30 μm were used for regular coating characterizations, and coatings with a thickness of around 110 μm were used for thermal and mechanical tests.

Characterization. Epoxy equivalent weights (EEW) were determined by epoxy titration using a Mettler Toledo T50 potentiometric titrator, according to ASTM D 1652. A solution of 0.1 N hydrobromic acid in glacial acetic acid was used as the titrant. Acid number titration was carried out according to ASTM D664. Iodine values were determined according to ASTM 5768-02. The relative molecular weights of UV-curable oligomers were measured using a PL-GPC 120 gel permeation chromatography (Polytech Instruments) equipped with a refractive index detector and a GPC/SEC column sets (Varian Inc.). Tetrahydrofuran was used as the eluent at a flow rate of 1.0 mL min^{-1}, and relative molecular weights were determined using polystyrene standards. Fourier-transform Infrared Spectroscopy (FTIR) was performed with a Thermo Scientific Nicolet 5700 FTIR spectrometer. ^{1}H NMR was conducted with an AVANCE III 400 MHz Digital NMR spectrometer at 25 °C, using DMSO-d_6 as the solvent. The viscosity of the oligomers was measured at 60 °C using a DHR-2 Rheometer (TA Instruments) operating from 0.001 rad/s to 400 rad/s with an optimal strain of 1%.

The photopolymerization behavior of cardanol-based acrylate oligomers was determined by real-time infrared (RTIR) spectroscopy. The experiments were performed using a Thermo Scientific Nicolet 5700 FTIR spectrometer equipped with an EfosLite fiber optic UV light. The samples were exposed to UV light for 10 min with an irradiance of 50.0 mW cm^{-2}. The acrylate conversion was calculated by the absorption decrease of the peaks at around 800−820 cm^{-1}, which corresponded to the acrylate functionality.

König hardness test was performed according to ASTM D 4366 using a BYK Gardener pendulum hardness tester, and the values were reported in seconds. Pencil hardness was measured according to ASTM D 3363. Crosshatch adhesion test was performed according to ASTM D 3359. The chemical resistance of the coatings was assessed by MEK double rubs. The numbers of double rubs needed to remove the coating to expose the substrate were reported. T bend test was also used to assess the flexibility of the coatings according to GB12754. Gloss was determined by a Gloss Checker JKG gloss meter (Tianjin Jingke Materials Testing Co., China) according to ASTM D523. Contact angles were measured by a DATA physics OCA40 contact angle goniometer equipped with an environmental chamber. Gel contents of the coatings were measured by Soxhlet extraction using dichloromethane. Tensile measurements were performed on a WDT-10 electronic universal testing machine (Shijiazhuang Zhongshi Testing Machine Co., Ltd., Hebei, China). Rectangular specimens (40 cm × 0.5 cm × 110 ± 10 μm) were used with a crosshead speed of 5 mm min^{-1}. Five samples were tested for each coating, and the averages were reported. Thermogravimetric analysis (TGA) was determined on a Mettler-Toledo STAR thermogravimetric analyzer with a heating rate of 15 °C min^{-1} from 25 to 650 °C under a continuous nitrogen flow. Dynamic mechanical thermal analysis (DMTA) was obtained on a Q800 DMTA (TA Instruments) operating at 1 Hz and a heating rate of 3 °C min^{-1} from −50 to 150 °C (tensile mode). The dimension of the samples for DMTA tests was 40 cm × 0.5 cm × 110 ± 10 μm. Biodegradability of the coatings was evaluated by comparing the weights of the coatings before and after they were buried in soil for 30 days at 23 °C.

■ RESULTS AND DISCUSSION

Synthesis of Multiarmed Cardanol-Based Acrylate Oligomers. Four multiarmed cardanol-based acrylates were synthesized via a four-step route using biobased polyols, cardanyl glycidyl ether, and 4-methyl hexahydrophthalic anhydride (MHHPA) as starting materials. A representative procedure is depicted in Scheme 1. Polyacids were first prepared by reacting biobased polyols with MHHPA at 95 °C. The molar ratios of MHHPA to hydroxyl group were 1:1 (for glycerol), 3:4 (for xylitol), 1:1 (for triglycerol), and 3:4 (for sucrose). Lower molar ratios of MHHPA to hydroxyl group were applied for xylitol and sucrose, considering the fact that their secondary hydroxyl groups were relatively less reactive. The resulting polyacids were characterized via acid number titration. The measured acid number values agreed generally with the calculated ones (Table S1), which demonstrated the success of the synthesis. Multiarmed oligomers were then synthesized via the ring-opening reaction between polyacids and the epoxy group in cardanyl glycidyl ether. The epoxy ring-opening reaction was confirmed by ^{1}H NMR, FTIR, and epoxy value and acid number titrations. As shown in Figure 1, peaks
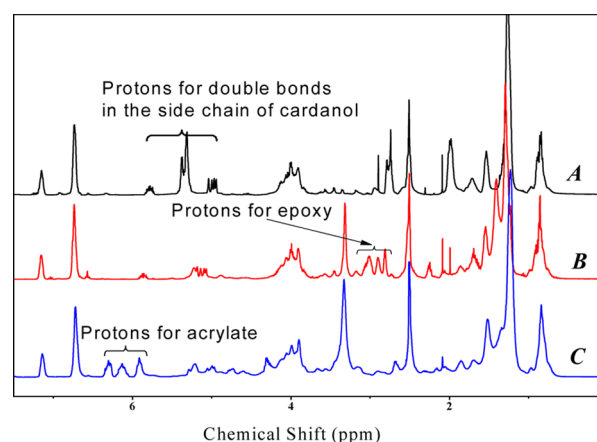

Figure 2. FT-IR spectra for A-Gly-3 and its intermediates (A: three-armed cardanol-based unsaturated oligomer (U-Gly-3), B: epoxidized three-armed cardanol-based oligomer (E-Gly-3), C: acrylated epoxidized three-armed cardanol-based oligomer (A-Gly-3)).

Figure 1. ^{1}HNMR spectra for A-Gly-3 and its intermediates (A: three-armed cardanol-based unsaturated oligomer (U-Gly-3), B: epoxidized three-armed cardanol-based oligomer (E-Gly-3), C: acrylated epoxidized three-armed cardanol-based oligomer (A-Gly-3)).

located at 3.2 and 2.6−2.8 ppm, which are attributed to the protons in epoxy group, disappeared in ^{1}H NMR spectra of three-armed unsaturated oligomer. Furthermore, the epoxy value and acid number of the unsaturated oligomer were 0.02 and 2.3, respectively, which confirmed the completion of epoxy-acid reaction. Then the double bonds in unsaturated oligomers were epoxidized with *m*-chloroperbenzoic acid according to a traditional method for the epoxidization of vegetable oils. In ^{1}H NMR spectra, peaks around 5.2−5.3 ppm, related to the protons in double bonds, almost disappeared after epoxidization. Meanwhile, new peaks showed up at about 2.8−3.2 ppm, which corresponded to epoxy functionality. As illustrated in Figure 2, the success of epoxidation was confirmed by the complete disappearance of the FT-IR peak at around 3008 cm^{-1} (assigned to C=C−H function), as well as the new absorption bands at around 826 cm^{-1} (assigned to epoxy groups). The conversion from double bond to epoxy was also evidenced by the measurements of epoxy equivalent weight (EEW) and iodine value. Epoxidization conversion spanned a range of 72−77% according to EEW values. UV-curable
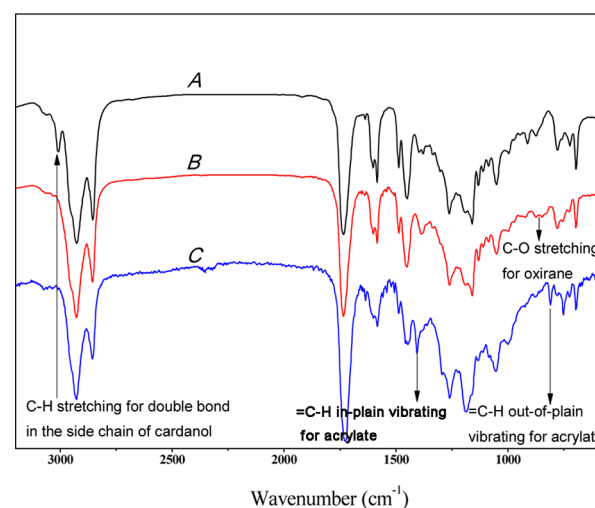
functionality was incorporated into these oligomers via the reaction between acrylic acid and epoxy, using triphenylphosphine as the catalyst. The molar ratio of acid to epoxy was 0.8. The successful conversion from epoxy to acrylate was evidenced by ^{1}H NMR and FTIR. Peaks at around 2.8−3.2 ppm, which were assigned to protons in epoxy group, became invisible in ^{1}H NMR spectra of acrylate oligomer. Furthermore, new peaks at 6.43, 6.10, and 5.91 ppm, which presented the protons in the vinyl group of acrylate, appeared in ^{1}H NMR spectra of the final products. In FT-IR spectra, the absorption band around 826 cm^{-1} for epoxy groups disappeared, and acrylate absorption bands at 1410 and 810 cm^{-1} appeared. The epoxy value and acid number of A-Gly-3 were 0.031 and 5.0, respectively, which further revealed the success of acrylation. It was found that further increase in acid equivalents could give rise to a large fraction of unreacted acrylic acid, according to acid number titration. The acrylate functionality of these oligomers ranged from 3.6 to 7.3, as calculated from the conversion of epoxidization and acrylation.

The relative molecular weights of the multiarmed cardanol-based acrylates were determined by GPC with polystyrene as the standard. As listed in Table 1 and Figure S1, the measured number-average molecular weights were slightly higher than the calculated ones, and polydispersity index (PDI) were in the range of 1.4−1.7. These results were the consequence of epoxy homopolymerization and epoxy-hydroxyl reaction during acrylation, which led to higher molecular weights and higher PDI. The viscosity values of cardanol-based acrylates were in the range of 12.4−23.4 Pa s at 60 °C, while that of ASBO was 0.85 Pa s at the same temperature. The higher viscosity of cardanol-based oligomers can be attributed to extra hydroxyl groups from the ring-opening reaction between cardanyl glycidyl ether and polyacids.

The biobased content was defined as the percent of biobased carbons in the total organic carbons. In case of the acrylate oligomers in this study, cardanol and polyols were considered as biobased chemicals, whereas 4-methyl hexahydrophthalic anhydride and acrylic acid were petroleum-based ones. The biobased content of these oligomers was calculated according to a method in the literature,[33] and the results are listed in

Table 1. Properties of Multi-Armed, Cardanol-Based Acrylate Oligomers

oligomer[a]	epoxidization conversion (%)[b]	biobased content (%)[c]	acrylate functionality	acrylate equivalent (g/eq)	viscosity (Pa s)[d]	PDI[e]	Mn (g/mol)	
							calcd	measured[f]
A-Gly-3	75	58.5	3.6	554	12.4	1.4	1895	2330
A-Xyl-4	73	58.8	4.7	560	16.2	1.4	2690	3250
A-Tgly-5	72	59.4	5.9	569	17.3	1.5	3412	3790
A-Suc-6	77	59.6	7.3	576	23.4	1.7	4148	4490
ASBO	-	86.0	3.1	394	0.75	1.2	1222	1720

[a]The oligomers were named after their core and number of arms, e.g., A-Gly-3 was three-armed acrylate oligomer with a glycerol core. [b]Determined by epoxy equivalent titration. [c]Calculated according to a method in the literature.[31] [d]Measured by rheometer at 60 °C, and the viscosity was taken at a frequency of 60 Hz. [e]Polydispersity index, measured by GPC. [f]Measured by GPC.

Table 1. The biobased content of these oligomers was around 60%, which are reasonably high as biorenewable products. Because biobased acrylic acid is being developed from renewable raw materials (such as lactic acid), the biobased content of multiarmed cardanol-based acrylates could be further increased by using acrylic acid derived from lactic acid.

Photopolymerization Kinetics of Multiarmed Cardanol-Based Acrylate Oligomers. The double bond conversion profiles for the photopolymerization of biobased acrylate oligomers and ASBO were characterized by monitoring the peak densities at around 800−820 cm^{-1} in real-time infrared (RTIR) spectroscopy, and the results are illustrated in Figure 3. All the oligomers were rapidly cured upon exposure to
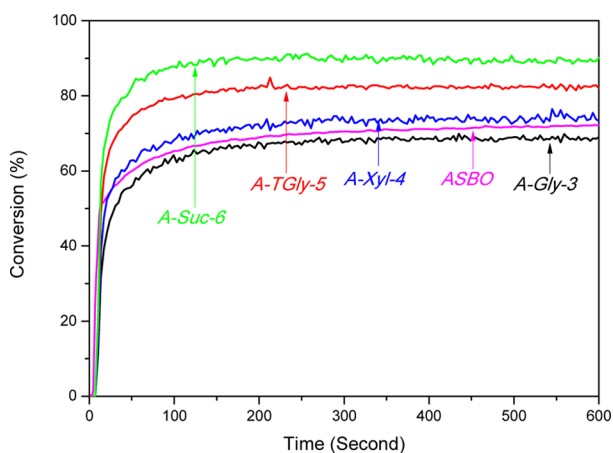

Figure 3. Conversion of acrylate functionality for multiarmed cardanol-based oligomers determined by RTIR (800−820 cm^{-1}).

UV radiation, and the final conversion was reached in approximately 200 s. The induction time for these oligomers was around 7 s. The final conversion of acrylate functionality spanned the range of 68−89%, which was greatly impacted by acrylate functionality of the oligomers. In general, higher acrylate functionality led to higher final conversion. As listed in Table 1, the viscosity values of the cardanol-based acrylates increased with the increasing acrylate functionality. The termination reactions of photopolymerization were suppressed for resins with high viscosity, which accounted for the higher acrylate conversion of resins with higher functionality (see Figure 3).

Coating Properties. The glass transition temperatures (T_g) of the coatings were characterized via DMTA, and the temperature dependence of storage modulus and tan δ are shown in Figure 5. The tan δ curves were very broad for all the coatings, which was associated with the multiple relaxations

stemmed from the heterogeneous structures of cardanol-based polymers. All the cardanol-based coatings showed higher T_g values than that based on ASBO, which can be attributed to the rigid benzene ring in cardanol-based coatings. The T_g values of these coatings followed the trend of A-Suc-6 > A-TGly-5 > A-Xyl-4 > A-Gly-3, ranging from 26 to 39 °C. Oligomers with higher functionality can produce coatings with higher cross-linking density, which led to higher T_g values. Coatings derived from cardanyl glycidyl ether and sucrose showed the highest T_g value due to its highest cross-linking density, as well as the extra rigidity of sucrose ring (see Figures 4−6
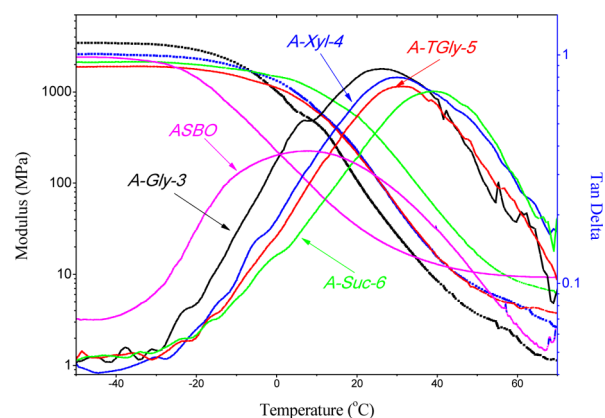

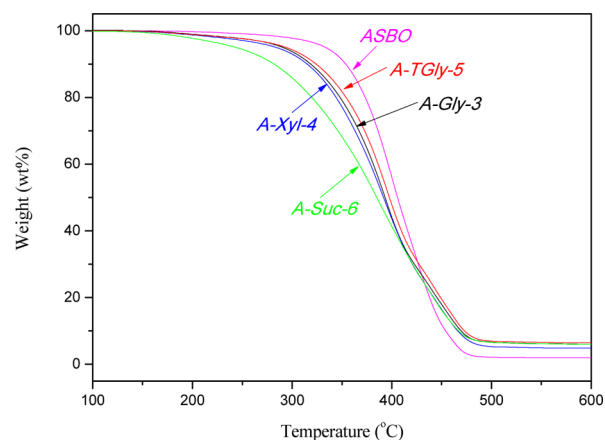**Figure 4.** DMTA curves of UV-curable coatings derived from multiarmed cardanol-based acrylate oligomers.

Figure 5. TGA traces of UV-curable coatings derived from multiarmed cardanol-based acrylate oligomers.
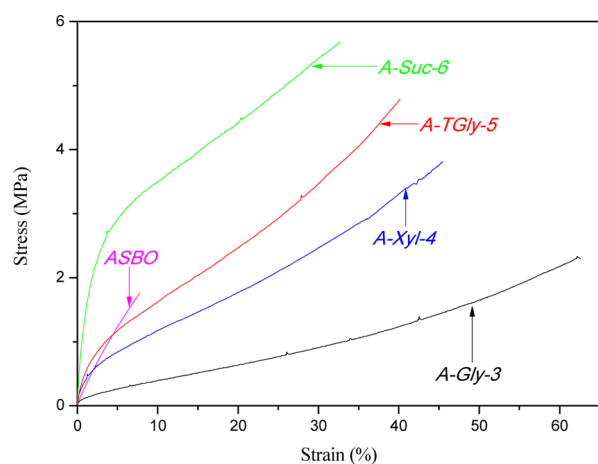
Figure 6. Stress−strain curves of UV-curable coatings derived from multiarmed cardanol-based acrylate oligomers.

The thermal stability of these coatings was assessed by thermogravimetric analysis, and the results are illustrated in Figure 5. These coatings exhibited a 5% weight loss temperature ($T_{5\%}$) of 243−333 °C. In general, coatings derived from higher functional oligomers decomposed at a relatively higher temperature. Coating-based A-Suc-6 showed relatively lower thermal stability considering its highest functionality. The partially substituted sucrose segment accounted for the relatively low thermal stability of the resulting coating.

The mechanical properties of these coatings were examined by tensile testing. All the cardanol-based coatings possessed higher tensile strength and elongation at break compared to ASBO-based one, which is the consequence of the aromatic nature of cardanol segment. The tensile strength values for these coatings increased upon the increase of oligomer functionality, whereas the elongation values decreased with the increase of cross-linking densities. Coating from A-Suc-6 showed the highest tensile strength and lowest elongation values due to its highest oligomer functionality and the existence of rigid sucrose core.

The chemical resistance of the coatings was characterized using MEK double rubs. The MEK double rub values ranged from 64 to 220, increasing with the increase of oligomer functionality. The hardness of the coatings showed a strong correlation with their glass transition temperatures (T_g). Higher T_g led to higher hardness values. All the coatings showed higher hardness compared to ASBO-based coating, which can be explained in terms of their rigid benzene segments. Crosshatch adhesion test was performed according to ASTM D 3359. All the coatings showed excellent adhesion (100%) to aluminum substrates. The polarity of aromatic rings and hydroxyl groups in cardanol-based oligomers accounted for the adhesion improvement. Furthermore, these coatings also possessed good flexibility indicated by T bend test results. The biodegradability of these coatings was evaluated by soil burying. The degradation rate was defined as the percentage of weight loss after soil burying. As listed in Table 2, the degradation rates were all higher more than 5% after 30 days' degradation in soil at 23 °C.

◼ CONCLUSIONS

In this work, a series of multiarmed cardanol-based acrylate oligomers were prepared via a four-step procedure using cardanyl glycidyl ether and biobased polyols as raw materials. The overall conversion from double bond to acrylate was around 60%, and the structures of the acrylate oligomers were confirmed by FTIR, ¹H NMR, and GPC. Real-time IR analysis indicated that these oligomers could be rapidly cured upon UV radiation, and the final acrylate conversions for these oligomers increased with the increasing oligomer functionality. These oligomers were then formulated into UV-curable coatings. Compared to their counterpart based on ASBO, cardanol-based coatings showed an excellent combination of reasonably high biorenewable contents and glass transition temperatures (T_g), good mechanical properties, high hardness, and excellent adhesion to aluminum substrates. The unique oligomer architectures, which combined the structural features of rigid benzene rings, flexible aliphatic chains, and polar hydroxyl groups, accounted for the excellent coating performances. These oligomers showed great potential in the application of UV-curable coatings due to their good overall coating performances and biorenewable characteristics. This study provided our community a new insight on how to design and

Table 2. Properties of UV-Curable Coatings Derived from Multi-Armed Cardanol-Based Acrylate Oligomers

coatings derived from	ASBO	A-Gly-3	A-Xyl-4	A-TGly-5	A-Suc-6
$T_{5\%}$ (°C)[a]	333	290	284	294	243
T_g (°C)[b]	20	26	30	31	39
storage modulus at 23 °C (MPa)[b]	27.4	65.9	138.6	147.8	413.5
pendulum hardness (s)	31	104	107	109	111
pencil hardness	HB	2H	2H	3H	3H
MEK double rubs	210	64	83	205	220
cross-hatch adhesion (%)	0	100	100	100	100
T-bend	0T	0T	0T	0T	0T
60° Gloss	119	114	115	120	123
tensile stress (MPa)	1.6 ± 0.4	2.4 ± 0.3	3.7 ± 0.4	4.6 ± 0.2	5.5 ± 0.5
modulus (MPa)	29.5 ± 2.3	11.9 ± 1.6	42.0 ± 3.6	57.3 ± 5.7	117.2 ± 6.2
elongation at break (%)	7.5 ± 1.4	62 ± 5.0	45 ± 2.5	40 ± 4.3	32 ± 5.9
water contact angle (deg)	98	88	87	85	88
gel content (%)	82	76	78	81	79
biodegradation rate (%)[c]	-	6.30	7.94	7.65	7.19

[a]The 5% weight loss temperature by TGA in nitrogen with a heating rate of 15 °C min⁻¹. [b]Obtained from DMTA at a heating rate of 3 °C min⁻¹ at 1 Hz in air. [c]The percentage of the weight loss of the coatings after buried in soil for 30 days.

prepare high-performance UV-curable oligomers and coatings without sacrificing biorenewable contents.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Acid numbers, epoxy equivalent weights, and iodine values of multiarmed cardanol-based acrylate oligomers and their intermediates (Table S1). Characteristic chemical shifts of protons for representative cardanol-based acrylate and its intermediates (Table S2). GPC traces for A-Gly-3 and its intermediates (Figure S1). Images of cardanol-based acrylates and acrylated epoxidized soybean oil (ASBO) (Figure S2). The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.5b00029.

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Notes

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