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Synthesis and Characterization of UV Oligomer based on Cardanol

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Abstract: In the present research, cardanol based di-acrylic UV oligomer was synthesized by thiol-ene coupling followed by ring opening reaction with glycidyl methacrylate. The intermediate as well as final diacrylate materials were analyzed by chemical as well as spectroscopic analysis. Further, ultraviolet (UV) radiation curable formulations were prepared by replacing commercial epoxy acrylate with synthesized UV oligomer in 10-50 wt% and applied on wood panels. The coated films were then evaluated for their optical, mechanical, chemical and thermal properties. Studies showed that up to 30 wt% amount of UV oligomer the coatings exhibited at par mechanical and chemical properties. The stain resistance of all the coatings was observed to be excellent.

Keywords: Cardanol; UV oligomer; renewable; radiation curable; sustainable

1 Introduction

It is well known that the conventional solvent based coatings will cause environmental pollution during their thermal curing processes by emitting a large amount of volatile organic compounds (VOC) and other hazardous air pollutants. The radiation curing process has been found to be an effective alternative to solvent borne technology in the coating industry [1-4].

UV radiation curing is a fast-growing field in coatings industry due to its diverse advantages over a conventional thermal curing. It has distinct advantages like high speed process, operates at room temperature which results in low energy consumption, solvent free process and ecofriendly operations. It is an effective method to form a highly crosslinked polymer network within a short period of time as compared to conventional curing method. UV cured coatings provide both economical and ecological benefits compared to other kinds of coatings due to which it can be also called as green process [5, 6]. The most commonly used UV-curable formulations involve unsaturated acrylic oligomers, including epoxy acrylates, polyester acrylates, polyether acrylates, urethane acrylates and silicone acrylates. Among the oligomers used for UV-curable coatings epoxy acrylate offer a wide range of properties such as high tensile strength, hardness, chemical resistance and stain resistance. As a result, epoxy coatings have found a large number of applications on various substrates such as wood, plastics, metal, glass and ceramics [7-10]. Growing environmental concerns regarding the use of petroleum-based products forced researchers to find sustainable solution. Use of biobased materials could be the possible alternative to reduce the consumption of the petroleum-based products. In modern polymer and coating industry various bio-based materials have been used in the past including cashew nutshell liquid, vegetable oils

[11-15], lignin derivatives [16] etc. Utilization of biobased materials in combination of radiation curable technology could be considered as a step towards more sustainable solutions.

Owing to its multiple functionalities, cardanol can be modified through variety of chemistries to make it suitable for various applications including composites [17-19] adhesives [20] plasticizers [21], coatings [22, 23] UV oligomers and reactive diluents etc. Considering the advantages of radiation curable coatings, Hu et al. synthesized cardanyl acrylate (CA) and utilized for crosslinking castor oil-based polyurethane acrylate oligomer. Results revealed that coating adhesion, hardness, thermal stability and hydrophobicity improved with addition of CA [24-26]. Similarly, Asha et al. [27] prepared UV curable urethane–methacrylatecross linkers from cardanol by one pot synthesis. The methodology involved an endcapping of isophorone diisocyanate with one equivalent of hydroxyethyl methacrylate followed by condensation with cardanol. The structures of the resins were characterized by FTIR, ^{1}H-NMR, ^{13}C-NMR, Matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) spectroscopies and size exclusion chromatography (SEC). Further, the synthesized acrylate oligomer was formulated for UV curable coatings. The experimental results revealed that the hydrogen bonded cross linkers based on cardanol and its derivatives had higher double bond conversion when compared to a non-hydrogen bonding standard such as hexane diol diacrylate (HDDA) under identical conditions. The temperature effects on the hydrogen bonding and thereof on the curing process were also investigated. In another work, cashew nutshell liquid was chemically introduced onto epoxidized soybean oil (ESBO) followed by epoxidization and acrylation. Resultant UV coatings exhibited excellent mechanical and thermal properties and retained high biorenewable content [28]. Chen et al. studied the mechanical and film properties of epoxidized cardanol based materials cured via cationic photo polymerization [29]. In another work, cardanol based benzophenone initiator was synthesized via etherification reaction. The initiator was utilised in the homo polymerization of methacrylate to obtain cardanol end-PMMA which when mixed with tertiary amine functional cardanol (co-photo initiator) a UV cured adduct was obtained. The final polymer exhibited excellent chemical resistance and hardness that increased with increase in irradiation time [30]. Li et al., synthesized cardanol based vinyl ester monomer and mixed with varying proportions of maleic anhydride modified dimer acid polymerized glycidyl methacrylate to obtain hard and rigid UV cured polymer network [31]. In addition to that various authors prepared multi-armed cardanol based oligomers for UV curable coatings [2, 22].

Present work discloses the preparation of cardanol based UV oligomer (GMA-CDS) and its subsequent confirmation by chemical as well as spectroscopic analysis. Synthesis involved the thiol-ene coupling of cardanol with thioglycolic acid followed by ring opening reaction with glycidyl methacrylate. The synthesized di-acrylic oligomer was replaced to commercial epoxy acrylate from 10% to 50% (on weight basis) and coatings were characterized for performance properties. Results revealed that beyond 30% of the addition of synthesized oligomer, mechanical and chemical properties got inferior. However, all the coatings showed excellent stain resistance irrespective of the amount of GMA-CDS.

2 Materials

Cardanol (NC-700) was kindly provided by Cardolite Specialty Chemicals Ltd., Mangalore, India. All the reagent grade chemicals including glycidyl methacrylate, thioglycolic acid, 1,8-Diazabicycloundec-7-ene (DBU), Irgacure-184, sodium carbonate, triethylamine, hydroquinone, sodium hydroxide, butanol, tetrahydrofuran, ethyl acetate was purchased from SD Fine Chemicals, Mumbai, India. Epoxy acrylate resin (see Fig. 1.) Desmolux VPLS2266 was received from Covestro, Mumbai. Reactive diluent trimethylolpropane triacrylate (TMPTA) was obtained from Pidilite Industries Ltd., Mumbai. All reagent grade chemicals were used as received without further purification.

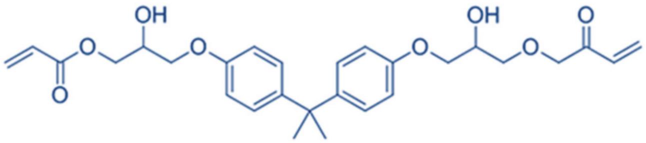


Figure 1: Representative structure of bisphenol- A based epoxy diacrylate

3 Experimental

In a 100 ml round bottom flask, cardanol and thioglycolic acid in a molar ratio 1:3 was poured along with 0.5 wt% Irgacure 184 and 0.5 wt% DBU catalyst was added. The entire mixture was magnetically stirred at 80°C under exposure of UV light for 20 hrs. The resultant mixture was purified by washing it with 5% aq. NaOH followed by 5% aq. Na_2CO_3 solution and finally with lukewarm water to remove unreacted chemicals. The resultant product "CDS" was confirmed with chemical and spectroscopic analyses. In the second step, CDS and GMA in a molar ratio 1:2 was taken in a single necked round bottom flask. To which, 1 wt% (of total solids) triethylamine and 0.02 wt% (of GMA) hydroquinone was added and mixture is allowed to stir for 4 hrs at 80°C. After completion of the reaction, the mixture was diluted in ethyl acetate and purified by washing it with 5% aq. NaOH followed by 5% aq. Na_2CO_3 solution and finally with lukewarm water to remove unreacted species. The resultant product was abbreviated as GMA-CDS (see Fig. 2.) and also confirmed by chemical and spectroscopic analyses. The viscosity of GMA-CDS was found to be 3200 cps at 28°C.

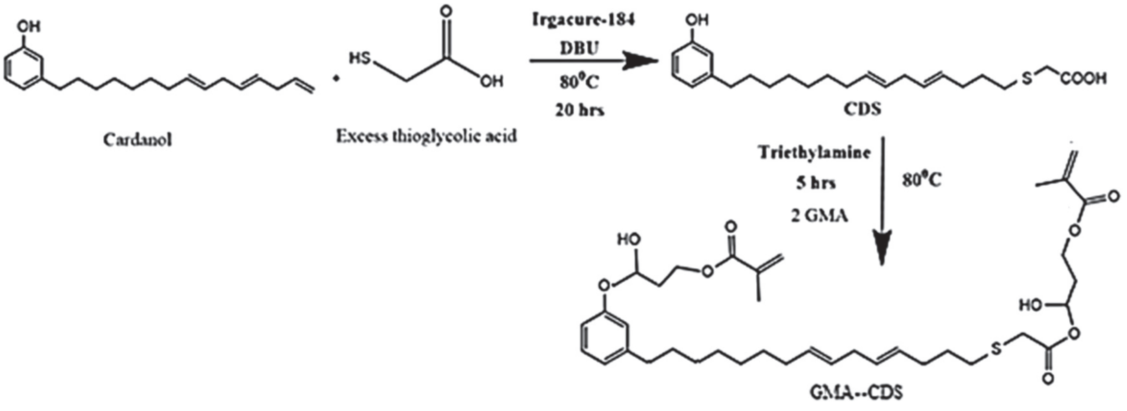


Figure 2: Schematic representation of synthesis of GMA-CDS

The coatings were formulated by replacing GMA-CDS to commercial epoxy acrylate from 10 wt% to 50 wt%. Trimethylolpropane triacrylate (TMPTA) was used as reactive diluent and its concentration was kept 15 wt% in all formulations. Irgacure-184 was used as photo initiator in 3 wt% concentration. Concentration of crosslinker and photo initiator was kept constant in all the formulations so that the variation in performance properties can be directly related to the concentration of GMA-CDS in the formulation. These UV formulations (as shown in Tab. 1) were applied on wood panels (10 × 7 cm^2) using a bar coater to obtain uniform dry film thickness of around 50-55 micron. Along with this, thin films were also casted onto the Teflon moulds. To effect curing, the panels and moulds were exposed to UV irradiation in medium pressure mercury lamp (3000 W) built into a UV machine. The belt speed was adjusted to 20 m/min which gives around 6-7 seconds of exposure time.

Table 1: Formulation of coatings based on GMA-CDS

Formulation	Epoxy acrylate (wt%)	GMA-CDS (wt%)	TMPTA (wt%)	Photo initiator (wt%)
EA-100	82	–	15	3
GMA-CDS-10	72	10	15	3
GMA-CDS–20	62	20	15	3
GMA-CDS-30	52	30	15	3
GMA-CDS-40	42	40	15	3
GMA-CDS-50	32	50	15	3

4 Characterization and Instrumentation

Acid value and Iodine value of products were evaluated according to ASTM D 1980 and ASTM D 1959 respectively. Brookfield viscosity was recorded at room temperature (28°C) on Brookfield viscometer (DV-II +Pro, Model No. LVDV-II+P). A Rhopoint Novoglass glossmeter was used to test the light reflection properties of the specimens according to ASTM D 523. Applied coatings were tested for adhesion properties by crosscut adhesion technique according to ASTM D 3359. Pencil hardness of the coating was measured on hardness tester according to ASTM D 3363. The solvent resistance was measured by rub test using MEK and xylene as per ASTM D 4752-10. The gel content of the cured films was determined by extraction method using THF solvent for 24 hrs. The insoluble gel fraction was dried in an air circulating oven for 24 hrs at 80°C and weighed to determine extent of curing. Stain test of coatings was performed according to ASTM D 3023-98. Different stains were applied on coatings and covered with a filter paper for 24 hrs and subsequently washed with water and then ethanol. Water absorption of cross-linked coating film was determined as per ASTM D-573. The coating sample of known weight was dipped in water at room temperature for 24 hrs. Afterwards the wet sample was dried with tissue paper and weighed. The water absorption was then calculated from the difference in the weights of the sample before and after soaking in water according to Eq. (1)

$$\text{Water absorption}(\%) = \frac{W_1 - W_0}{W_0} * 100 \tag{1}$$

W_1 = Weight of the sample after dipping in water

W_0 = Weight of the sample before dipping in water

The FTIR spectra were evaluated on Perkin-Elmer Spectrum100 Instrument (Eco-ATR (Bruker, Germany). Spectra were obtained from KBR pellets at 40 scans and 2 cm^{-1} of resolution in the region of hydroxyl stretching (4000–3000 and 1000–400 cm^{-1}), carbonyl symmetric stretching (1800–1600 cm^{-1}), carbonyl asymmetric and alcohol linkages (1400–1000 cm^{-1}) with the purpose of evaluating the chemical structure of the end-products. NMR spectra were recorded on Mercury Plus ^{1}H NMR spectrometer (400 MHz, Varian, USA). The spectra were recorded using CDCl3 as a solvent. The chemical shifts in the discussion are reported in parts per million. The number average molecular weight (Mn) and molecular weight distribution was determined by gel permeation chromatography (GPC) (Agilent 1100 series). The sample was dissolved in tetrahydrofuran (THF) and placed in Agilent 1100 series instrument, consisting of a refractive index (RI) detector and Agilent PL gel 10 μm column.

5 Results and Discussion

The products synthesized in both the steps were analysed with acid value and iodine value and tabulated in Tab. 2. It was observed that acid value of CDS was increased to 138.2 mg of KOH/g after addition of thiol

Table 2: Chemical analysis of products

Product	Hydroxyl value		Iodine value		Acid value	
	Theoretical	Practical	Theoretical	Practical	Theoretical	Practical
Cardanol	180-210	189	251.3	235.2	–	8.2
CDS	142.0	131.5	109.2	105.7	142	138.2
GMA-CDS	165.4	140.2	138.0	141.1	–	–

compound. Similarly, iodine and hydroxyl value of GMA-CDS also confirmed the formation of product as practical values were observed to be closer to theoretical values.

5.1 FTIR Spectroscopy

FTIR spectra of cardanol, CDS and GMA-CDS are shown in Fig. 3. Thiol-ene addition of thioglycolic acid to cardanol can be confirmed by FTIR spectra. As can be seen in the FTIR spectrum of CDS, peak at 1712 cm^{-1} indicated the presence of carbonyl group (–C=O) and there is no peak in the region 2500-2600 cm^{-1} associated with –SH group confirming the formation of desired product.

Further, in case of GMA-CDS, the peak at 3434 cm^{-1} could be attributed to secondary hydroxyl(–OH) group. Moreover, Peak at 1710 cm^{-1} suggested the presence of carbonyl (–C=O) group in the GMA-CDS structure and peaks at 1598, 966 and 868 cm^{-1} confirmed the presence of unsaturation in GMA-CDS.

5.2 ^{1}H-NMR Spectroscopy

Evaluation of chemical structure of CDS and GMA-CDS was done by ^{1}H-NMR spectroscopy and is shown in Figs. 4A-4C. ^{1}H-NMR spectrum of cardanol revealed the presence of protons from aromatic ring at chemical shifts 6.25, 6.66 and 7.28 ppm. Chemical shift at 3.71 ppm can be associated to the proton from phenolic –OH group attached to aromatic ring [32]. –CH=CH– linkages present in the long aliphatic chain can be attributed to chemical shifts at 5.28 ppm and 5.71 ppm. Further, when cardanol is reacted with thioglycolic acid, chemical shift at 11.11 ppm appeared due to the proton of carboxyl group confirming the addition of thioglycolic acid to one of the unsaturations of cardanol. After ring opening reaction of CDS with GMA, protons associated with acrylic linkage –CH_2=CH– can be observed at Moreover, chemical shift at 4.35 ppm showed the presence of proton from hydroxyl group generated during the ring opening reaction. Other common shifts related to the protons in benzene ring could be observed at 7.06, 6.65 ppm. Protons in long aliphatic chain of cardanol could be observed at 1.52-1.91 ppm.

5.3 Gel Permeation Chromatography

GPC technique was performed to evaluate molecular weight of oligomer and is represented in Fig. 5. Chromatograph revealed that practical molecular weight was much closer to the theoretical molecular weight of GMA-CDS with polydispersity index of 1.8, suggesting that desired oligomeric product was synthesized.

5.4 Coating Properties

GMA-CDS contains one aromatic ring, one C15 long aliphatic chain and two unsaturations at terminal positions. Upon partial incorporation of GMA-CDS in epoxy acrylate entire coating properties will vary accordingly. So, we analysed variation in coating properties due to change in oligomer ratio and structure property relationship was established.

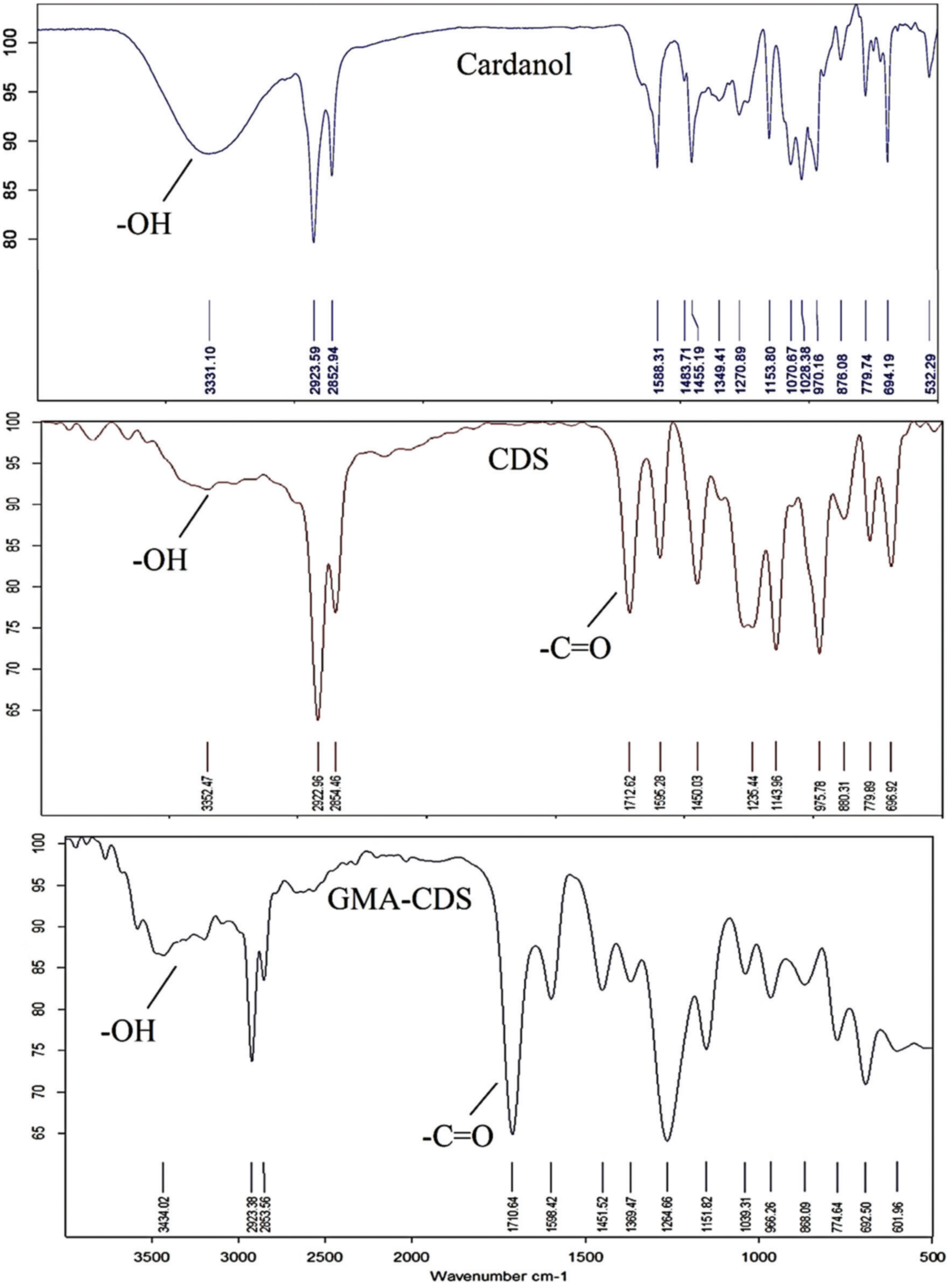
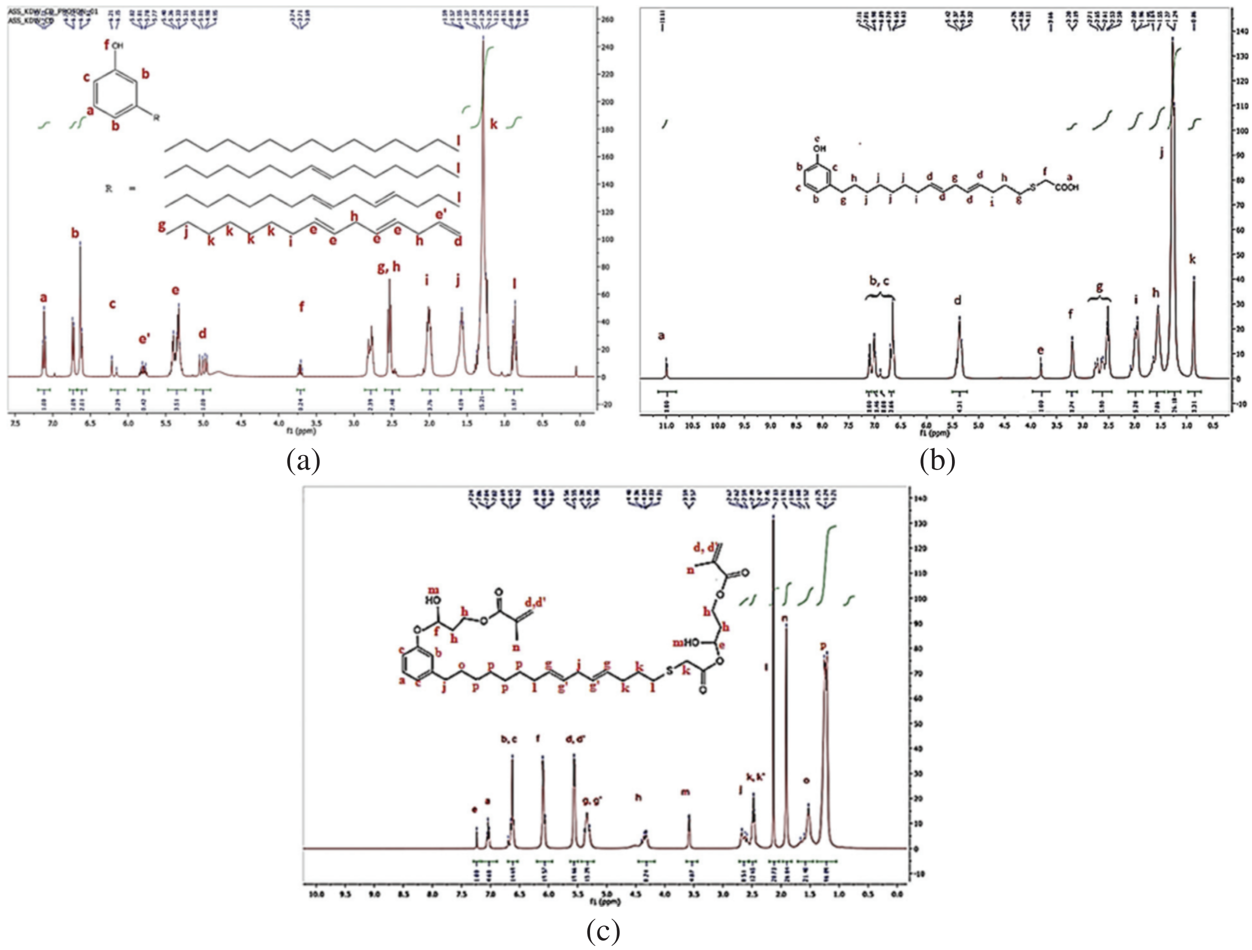


Figure 3: FTIR spectra of cardanol, CDS and GMA-CDS



(a) (b)

(c)

Figure 4: A: ^{1}H-NMR spectrum of Cardanol. B: ^{1}H-NMR spectrum of CDS. C:^{1}H-NMR spectrum of GMA-CDS

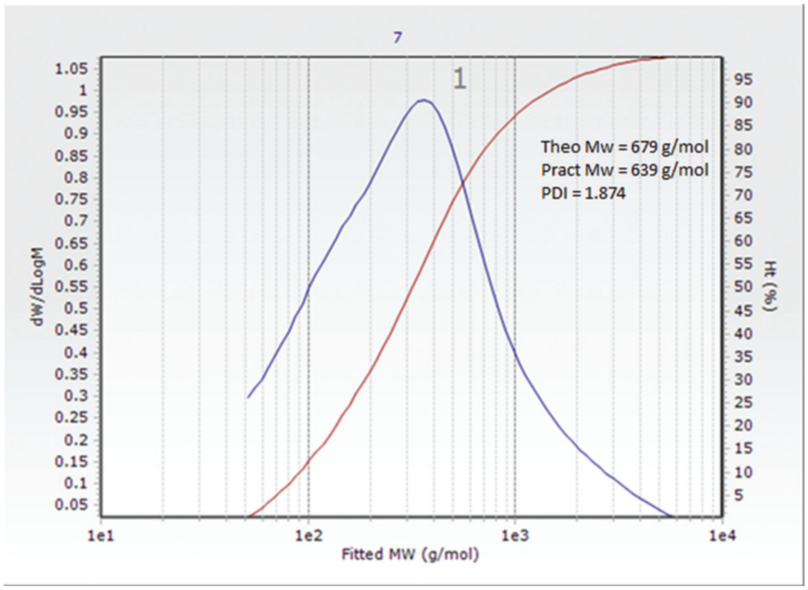


Figure 5: GPC curve of GMA-CDS

5.4.1 Mechanical and Chemical Properties

It was observed that adhesion of coatings reduced as concentration of GMA-CDS was increased. (as can be seen from Tab. 3) The additional hydroxyl group should have improved the adhesion of coatings however increase in concentration of GMA-CDS also reduced effective crosslinking of coating film which resulted in etching out of coating film. In a similar way, gloss values also reduced with increase in concentration of GMA-CDS however reduction in values was not significant. Commercial epoxy acrylate is based on bisphenol-A which has two aromatic rings in its structure and when it was replaced with GMA-CDS, compactness and rigidity of coatings reduced thereby reducing the gloss values. The changes in crosslinking and polymer backbone structure also had an effect on hardness of coatings which was observed to be lowered from 6H to 3H with increase in concentration of GMA-CDS. On the other hand, solvent resistance of coatings was excellent irrespective of concentration of GMA-CDS. It was observed that, coatings remain unaffected even after 150 rubs each of ethanol, methylethyl ketone and xylene.

Table 3: Mechanical and Chemical properties of coatings based on GMA-CDS

Formulation	Adhesion	Gloss@60°	Pencil Hardness	Solvent resistance		
				Ethanol	MEK	Xylene
EA-100	5B	120 +/- 5	6H	> 200	> 200	> 200
GMA-CDS-10	5B	120 +/- 5	6H	> 200	> 200	> 200
GMA-CDS-20	4B	115 +/- 5	5H	> 200	> 200	> 200
GMA-CDS-30	4B	115 +/- 5	5H	> 200	> 200	> 200
GMA-CDS-40	3B	110 +/- 5	4H	> 175	> 175	> 150
GMA-CDS-50	3B	110 +/- 5	3H	> 150	> 150	> 125

5.4.2 Gel Content

Extent of crosslinking was determined using % gel content values. Coating films were kept in THF solvent and evaluated for its weight loss after 24 hrs. As we know, gel content depends on functionality, polymer backbone structure of oligomer, concentration of cross linker and time of exposure. Fig. 6 shows

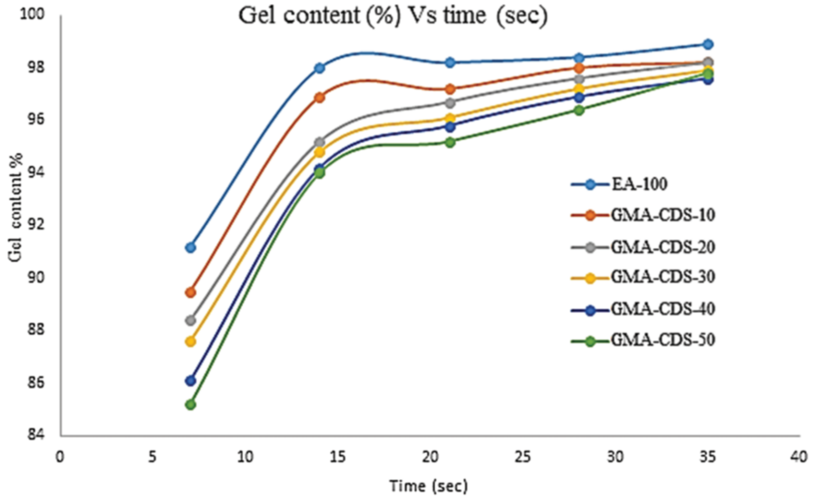


Figure 6: % Gel content of coatings based on GMA-CDS

the graph of gel content vs time of exposure. It can be seen that as expected gel content value increased with time of exposure. When coatings are exposed to UV light, photo initiator initiates crosslinking reaction and crosslinking increases with increase in time of exposure.

Further, gel content values increased linearly with time of exposure and more than 92% of crosslinking achieved in just 14 seconds. It was observed that with addition of GMA-CDS, coatings required more time for crosslinking. This is due to the structure of oligomer which consists of aliphatic long chain which does not impart as much crosslinking as that of commercial epoxy acrylate.

5.4.3 Water Absorption

Absorbed water causes detrimental effects in wood and deteriorates its properties and integrity. Therefore, water absorption of coating is crucial and should be as low as possible. Fig. 7 shows the bar graph of water absorption of coatings. As can be seen from the plots, there is an increase in water absorption with increase in concentration of GMA-CDS. The presence of two hydroxyl groups in GMA-CDS could be responsible for increasing the water affinity of coatings. Further, GMA-CDShas a long aliphatic chain which could be responsible for increase in the inter-chain space in cross-linked structure as compared to that of epoxy acrylate system resulting in micro-porous structure. This created cavities in the network structure wherein the porosity would allow water migration into the film [33-34].

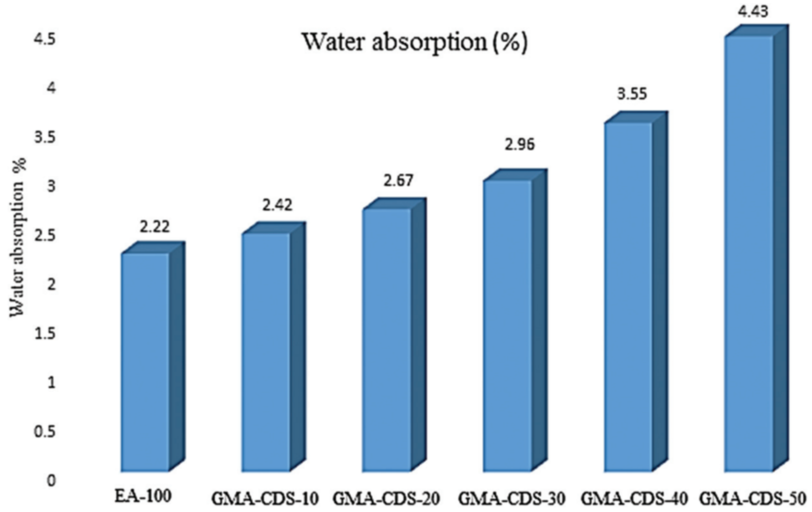


Figure 7: % Water absorption of coatings based on GMA-CDS

5.4.4 Stain Resistance

Stain resistance of coatings is very important, indicating the capability of protection of wood against liquid spills and stains. Stain resistance was examined using permanent marker, ink, nail polish, wax etc. It was observed that irrespective of concentration of GMA-CDS, stain resistance of all coatings was observed to be excellent (as shown in Fig. 8 and Tab. 4). Coatings showed no significant film defects even after 24 hrs of test.

Figure 8: Stain resistance of coated panels

Table 4: Stain resistance of coatings based on GMA-CDS

Formulation	Permanent Marker	Ink	Nail polish	Wax	Coconut oil	Sauce	Shoe polish
EA-100	5	5	5	5	5	5	5
GMA-CDS-10	5	5	5	5	5	5	5
GMA-CDS-20	5	5	5	5	5	5	5
GMA-CDS-30	5	5	5	5	5	5	4
GMA-CDS-40	5	5	5	5	5	4	3
GMA-CDS-50	4	5	5	5	4	4	3

Note- 1- Poor, 5- Excellent.

6 Conclusion

Cardanol based UV oligomer was successfully synthesized and confirmed with chemical as well as spectroscopic analysis. The synthesized oligomer was replaced from 10 wt% to 50 wt% in commercial epoxy acrylate resin. The coatings formulated were applied on wood panels and analysed for mechanical and chemical properties. It was observed that, adhesion of the coatings reduced as the concentration of cardanol based UV oligomer was increased. Moreover, longer period was required to achieve sufficient degree of crosslinking as concentration of synthesized UV oligomer was increased. Further, addition of UV oligomer resulted in reduction in pencil hardness and gloss values. Such trend in properties could be explained by comparing the chemical structure of commercial epoxy acrylate and GMA-CDS. When hard and rigid structure of bisphenol-A based epoxy acrylate was replaced with less compact GMA-CDS, it resulted in increase in time of curing and water absorption while simultaneously reducing pencil hardness, gloss and adhesion values. Nevertheless, it could be concluded that coatings formulated by replacing 30 wt% of commercial epoxy acrylate exhibited at par mechanical and chemical properties.

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Conflicts of Interest: The authors declare that they have no conflicts of interest to report regarding the present study.

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