UV-curable Polyurethane Coatings Derived from Cellulose

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A B S T R A C T

At the present time coating industry is devoting much research in the direction of low volatile organic compounds to make eco-friendly coating material. In this study, such materials are developed from cellulose derived from bagasse, a sugar industry waste. Cellulose is converted to cellulose glycoglycoside by acid hydrolysis of cellulose under heterogeneous condition. Cellulose glycoglycoside is treated with polyethylene glycol having different molecular weights to give glycoglycosides which in turn are reacted with various diisocyanates to obtain polyurethane having free NCO groups. These materials are then reacted with hydroxyethylmethacrylate (HEMA) to give polyurethane acrylates. The acrylates are characterized for specific gravity, viscosity, colour and molecular weight as well as by FTIR spectroscopy. The UV-curable coating composition was prepared by blending PU-acrylate, reactive diluents and photoinitiator. Coating compositions were cured under UV-light and characterized for adhesion, flexibility, impact resistance, solvent resistance and for dynamic mechanical analysis as well as by TGA for thermal stability. The cured films give thickness of 23-24 microns and cure time required is less than 1.5-2.0 min. There is no liberation of any volatiles during curing and films have good adhesion to mild steel substrate. The cured coatings give excellent dynamic, mechanical and chemical properties. The scratch resistance was found to be satisfactory. The application was made in unpigmented form but it is found that various pigments can be used to give coloured UV-curable coatings.

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INTRODUCTION

Cellulose is the most abundant carbohydrate in the world. The raw material is available in sufficient amounts. Its total annual world production is estimated to be between 25 and 45 million tons. To fulfil various demands for the functionality in different cellulosic products, industrially processed cellulose is modified enzymatically, physically or chemically. In most chemical modifications of cellulose, usually referred to as chemical derivatization, the granular form is maintained and the hydroxy groups are partially substituted, yielding cellulose ethers and esters. Other types of chemical derivatization are oxidation, cross-linking and grafting of cellulose. Cellulose esters have played important roles in solvent borne coatings for over

50 years. Typical cellulose esters that are commonly used in coating application include cellulose acetate, cellulose acetate propionate, cellulose acetate butyrate and nitro cellulose [1,2]. Granat et al. have successfully developed acrylated ethyl cellulose for UV-curing inks [3].

UV-Radiation curable coatings represent a class of coatings with no or little volatile organic compounds (VOCs). In addition, compared to thermally cured coatings, the use of UV-radiation curable coatings offers some advantages, such as instant drying, broad formulating range, reduced energy consumption, coating on heat sensitive substrate, low space and capital requirement for curing equipment [4]. Current UV-cure coatings are mostly based on acrylated oligomers due to their relatively higher reactivity and lower volatility. It is essential to replace volatile styrene with higher molecular weight and functional-ity reactive diluents to increase reactivity, line speed and mechanical properties [5]. Among the oligomers used for UV-curable coatings, polyurethane acrylate (PUA) oligomers have gained more and more atten-tion and speedy development due to a wide range of excellent application properties, such as high impact and tensile strength, abrasion resistance and tough-ness combined with excellent resistance to chemicals and solvents [6-9].

In the present study, bagasse was selected as source of cellulose, which was used to synthesize UV-curable urethane acrylate oligomer. Bagasse, a sugar cane waste, comprising 33% of cellulose, was extracted by nitric acid process and then purified. Cellulose glycoglycoside was prepared by acid hydrolysis of cellulose under heterogeneous condition. Cellulose glycoglycosides based polyether polyol were derived from cellulose and polyethylene glycol (of different molecular weights) and further these polyols were converted to urethanes prepoly-mer by reacting -NCO groups of hexamethylene diisocyanate (HMDI) and isophorone diisocyanate (IPDI) which results in chain consisting of alternating short sequences forming flexible (soft) and rigid (hard) segments. The soft segments originated from the polymer polyols impart elastomeric characteris-tics to the UV-cured film [10-13]. Further, these urethanes were converted to urethane acrylate oligomer by reacting -NCO end group of urethane with hydroxyethyl methacrylate (HEMA). UV-curable coating compositions were obtained by blending these oligomers with different reactive diluents (cross-linking monomer), photoinitiator and other additives. These compositions were cured under UV light at (200 Watt/inch) (280-360 nm) medium pressure mercury vapour lamp of UV-2KW-2-35 intensity. In this study, UV-curable polyurethane acrylate was synthesized from PEG with different molecular weights (M_n) of 200, 400 and 600; two types of diisocyanate: HMDI and IPDI; and HEMA. The effects of PEG (M_n), di-isocyanate type and the reactive diluents type were studied by FTIR, VPO, DMA and TGA. The physico-mechanical properties of the UV-cured were also studied by standard ASTM tests methods like colour, density, percentage solid, viscosity, adhesion, flexibility, impact, scratch hardness, chemical and solvent resistance were reported in the paper. The application performance and related work concerning evaluation of film properties of each of these UV-curable compositions are well elaborated in the paper.

EXPERIMENTAL

Materials

Cellulose was extracted and purified in our laborato-ry using well-known nitric acid process [14]. A physical property of the cellulose is its relative hygroscopicity and under normal atmospheric condition, it adsorbs 8-14% of water, and swells in water. It is however, insoluble in water or in dilute acids. Cellulose is non-melting, thermal decomposi-tion starts at 180ºC and density is 1.52-1.59 g/cm^3.

Ethylene glycol and barium hydroxides were procured from Chitichem Corporation, Baroda. Polyethylene glycol with different molecular weights: 200, 400, 600, and ethylmethyl ketone (Merck, USA) were used as received. Isophorone diisocyanate, hexamthylene diisocyanate and 2-hydroxy-ethylacry-late were supplied by Grand Polycoats, Padra, Vadodara, India. Photoinitiator (benzophenone) and reactive diluents like EGDMA (ethylene-glycol dimethacrylate), SA (stearyl methacrylate), PEA (2-phenoxy ethyl acrylate) and DBTDL (dibutyltin dilaurate) were obtained from Merck, USA.

Cellulose   Ethylene glycol

$$H_2SO_4$$

Cellulose glycoglycoside
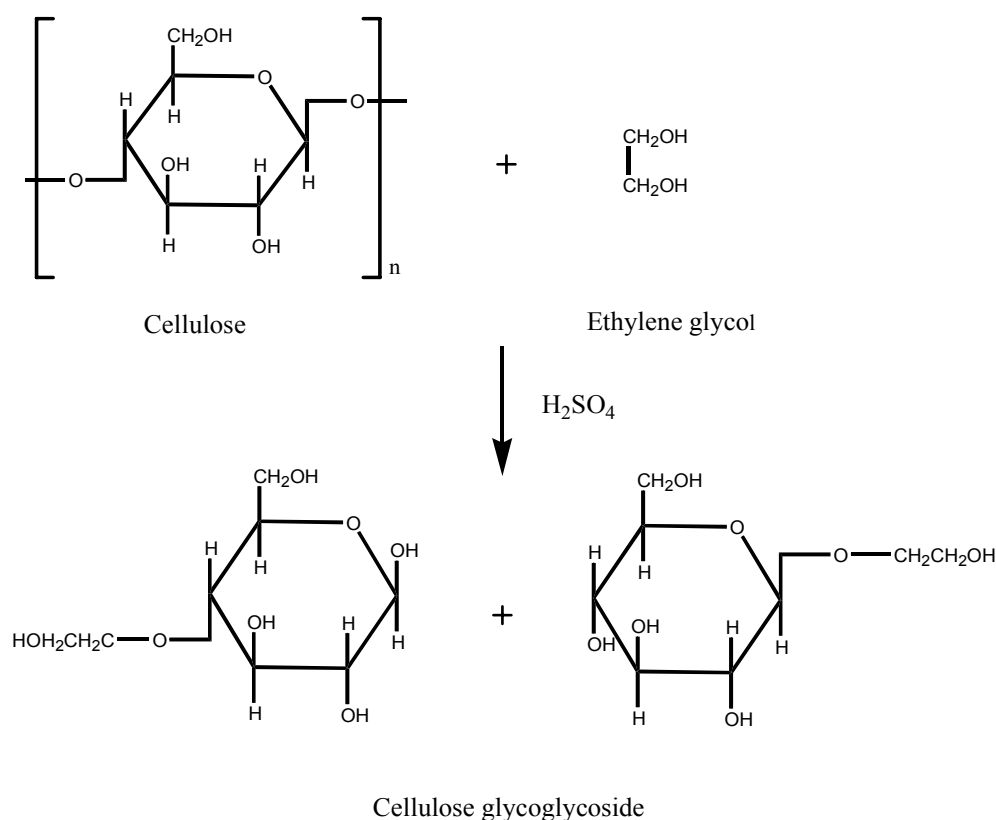
Scheme I. The reaction scheme of glycoglycoside via ethylene glycol.

Synthesis

Preparation of Cellulose Glycoglycoside by Acid Hydrolysis

Ethylene glycol (300 mL) and concentrated sulphuric acid (1.0 mL) were mixed in a three-necked flask (500 mL), equipped with a stirrer, thermowell, nitrogen inlet, and vacuum line. The mixture was heated with constant stirring to 80ºC under nitrogen atmosphere at 125 mmHg pressure to remove traces of water, and then cellulose (obtained from bagasse) (10 g) was added and the temperature raised to 110-120ºC. The materials were allowed to react at this temperature and pressure condition for 1 h. After this, the glycoglycosides formed were transferred to a beaker (500 mL) and barium hydroxide solution (2%)

added to neutralize the remaining sulphuric acid. The pale-yellow coloured viscous glycoglycoside was filtered to remove the barium sulphate formed during neutralization.

The unreacted ethylene glycol was distilled out at 150ºC under 125 mmHg pressure. The glycoglycoside prepared above was a mixture of α-D glycoglycoside and β-D glycoglycoside [15]. The reaction scheme of glycoglycoside via ethylene glycol is shown in Scheme I. Physical properties and FTIR spectra of cellulose glycoglycoside are shown in Table 1 and Figure 1, respectively.

Preparation of Urethane Acrylate Adduct

A dry, four-necked flask was placed in a water bath,

Table 1. Physical properties of cellulose glycoglycoside.

Sample	Viscosity Gardner Holdt tube designation	Colour Gardner scale	Clarity	Specific gravity (wt/L)	Hydroxyl value ASTM D (1957)
Cellulose glycoglycoside	A	2.0	Transparent	1.15	1048-1232
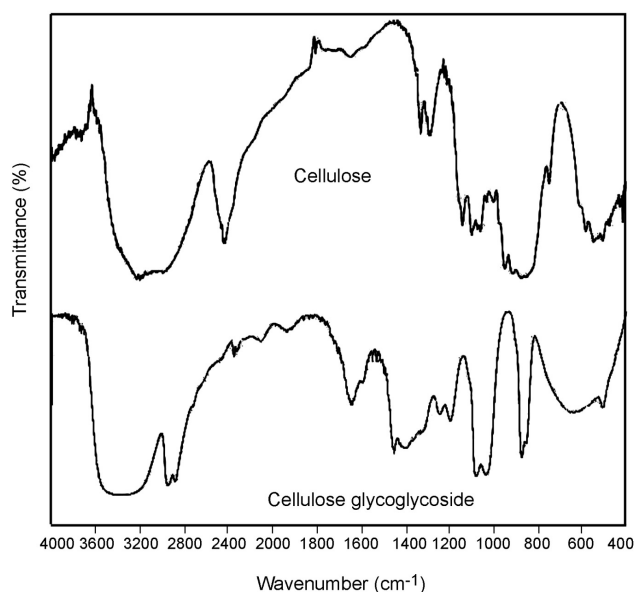
Figure 1. FTIR spectra of cellulose and cellulose glycoglycoside.

polyisocyanate (IPDI/HMDI) was added and temperature of the bath raised to 40-45ºC. Polyethylene glycol (MW 200, 400, 600) was added dropwise to the reaction flask through dropping funnel (within 2 h). Temperature of the bath was controlled within 50-55ºC and reaction allowed to continue until a desired percentage of -NCO was obtained. 2-Hydroxyethyl methacrylate (HEMA) was then added dropwise through dropping funnel at the same reaction condition and allowed to continue until desired percentage of -NCO acquired. Thus the prepared isocyanate terminated adduct was ready for the next steps [16]. The composition for each experimental set is given in Table 2 and the reaction scheme

is shown in Scheme II.

Preparation of Urethane Acrylate Oligomer
To the above isocyanate terminated urethane acrylate adduct (Step 1), stoichiometric proportion of cellulose glycoglycoside (5:1 molar ratio adduct: cellulose glycoglycoside) was added dropwise at 55ºC. One percent DBTDL (dibutyltin dilaurate) was charged in the reaction flask. The reaction progress was monitored by determining unreacted -NCO groups by dibutylamine back titration method [17]. The reaction was allowed to continue until the percentage of -NCO became zero. The resultant urethane acrylate oligomer was found a transparent viscous liquid. The reaction scheme is shown in Scheme III. The composition for each experimental set is given in Table 2. These prepared urethane acrylate oligomers were subsequently used for the preparation of UV-curable coating composition. The physical properties of urethane acrylate oligomer like specific gravity (wt/L), solid content, viscosity and colour are shown in Table 3. The FTIR spectra of urethane acrylate are shown in Figure 2.

Preparation of UV-curable Coating Composition
The urethane acrylate oligomer was taken in a beaker and after addition of stoichiometric amount of reactive diluent and photoinitiator the contents were stirred at room temperature [18]. The amount of each ingredient used in formulation is shown in Table 4.

Application and Curing of Coating Composition
Sample to be tested for UV-curing was coated onto a mild steel panel (15 cm × 5 cm) as follows: an excess

Table 2. Compositions of urethane acrylate oligomer.

PEG type	Designation	Adduct composition				PUA composition	
		PEG	PDI	HMDI	HEMA	Adduct	CEG
-	CPI-2	24.40	54.26	-	15.88	94.6	5.4
PEG-200	CPH-2	28.16	-	47.32	18.30	93.18	6.2
-	CPI-4	39.30	43.62	-	12.77	95.70	4.3
PEG-400	CPH-4	43.92	-	36.89	14.27	95.10	4.9
-	CPI-6	49.26	36.45	-	10.67	96.40	3.6
PEG-600	CPH-6	54.03	-	30.25	11.70	96.00	4.0

CPI: Cellulose glycoglycoside-PEG-IPDI based urethane acrylate, CPH: cellulose glycoglycoside-PEG-HMDI based urethane acrylate, 2,4,6: number indicates the molecular weight of polyethylene glycol, 200, 400 and 600, respectively.
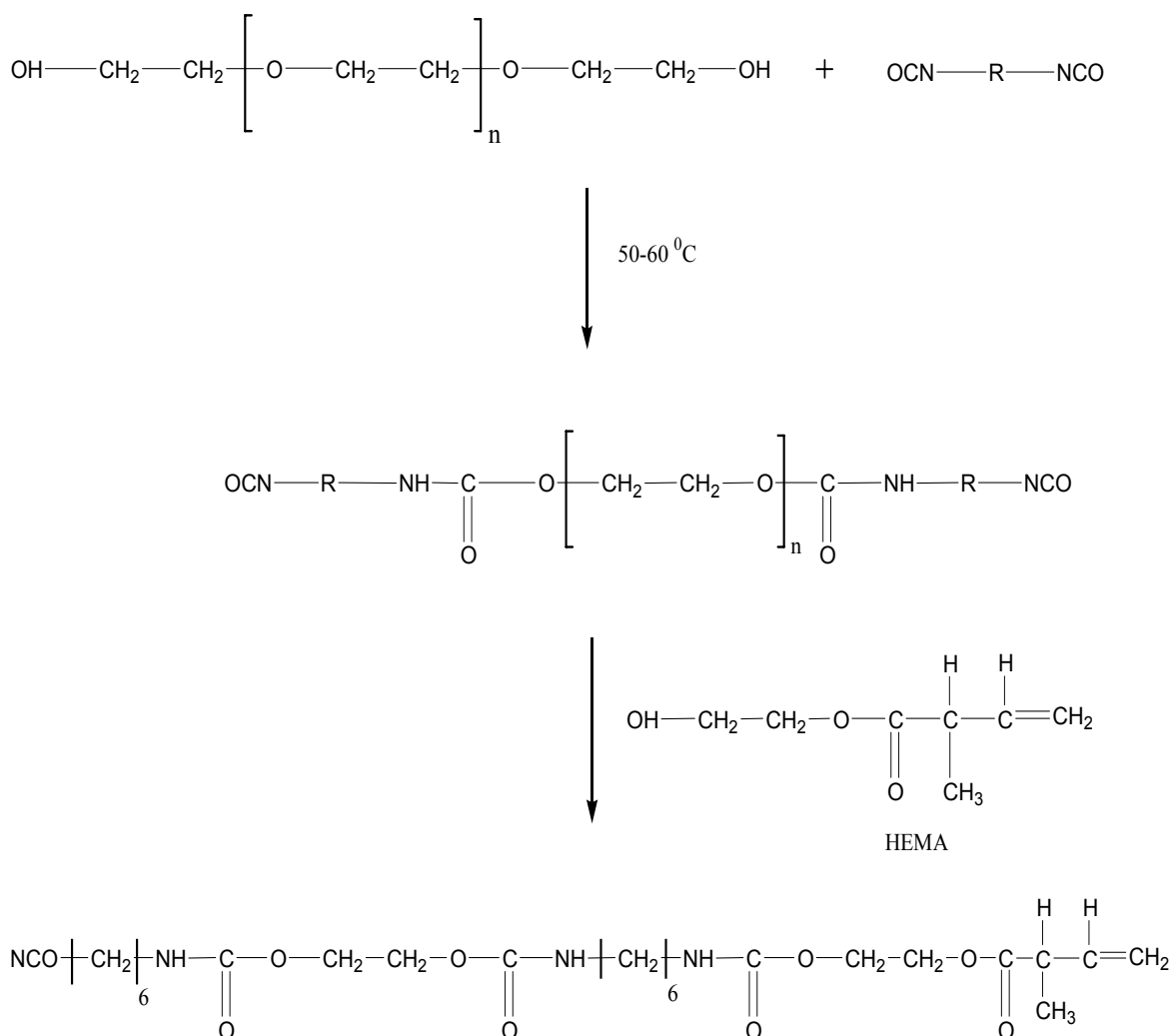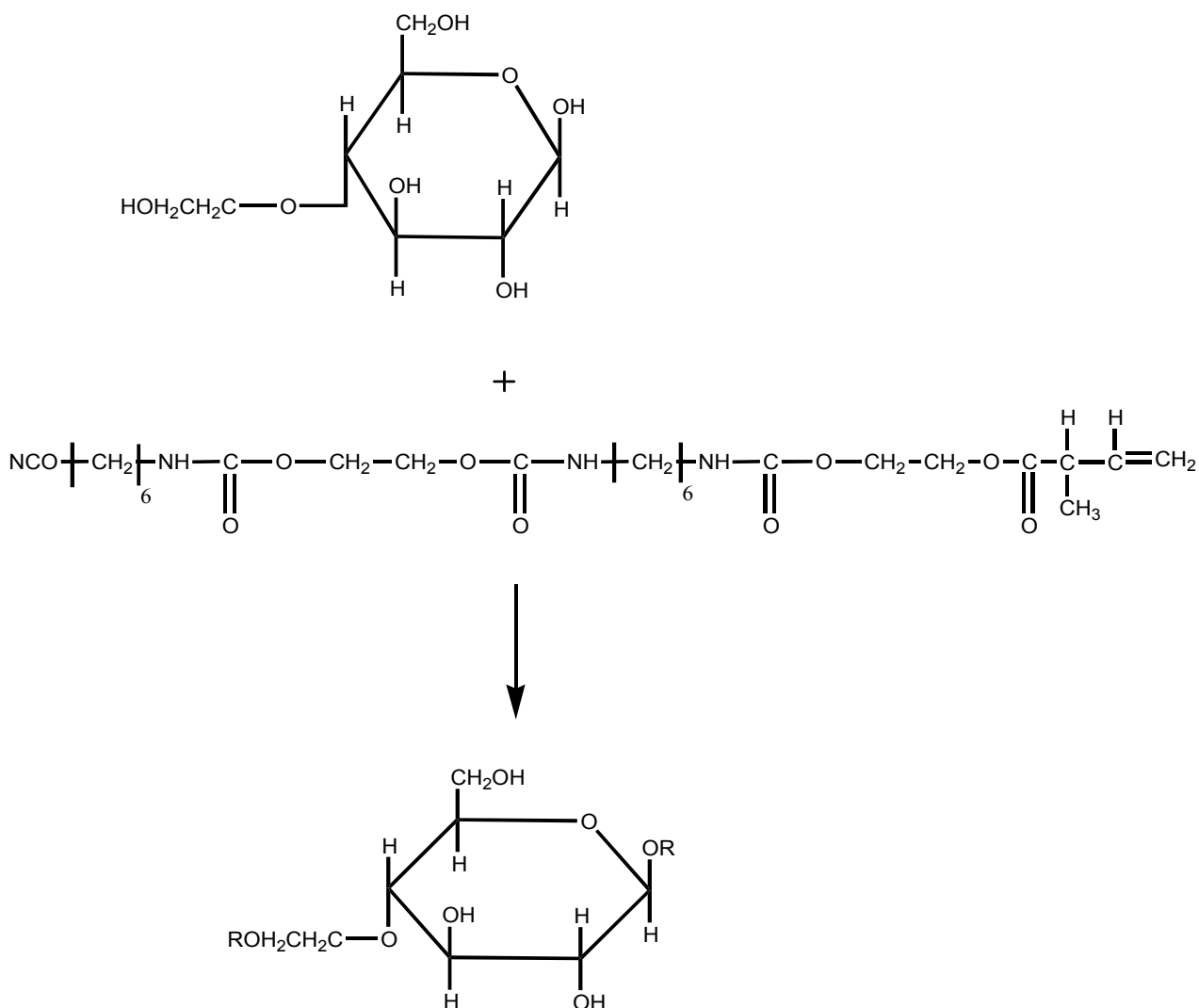
Scheme II. The reaction scheme of urethane acrylate adduct.

of the sample was placed at one end of the test panel and using a rod applicator (K-Bar No.5) drawn across the substrate evenly pressure pushing excess material off the edge [19]. The coated panel was exposed to a

(200 Watt/in) (280-360 nm) medium pressure mercury vapour lamp of UV-2KW-2-35 curing system for 1.5-2.0 min. This method produced coating with an average wet film thickness of 23-35 μm.

Table 3. Physical properties of urethane acrylate oligomers.

Code	Specific gravity (wt/L)	Solid (%)	Viscosity at 30ºC (cPs)	Colour	Molecular weight
CPI-2	1.18	98.01	1180	3	4478
CPH-2	1.17	97.00	1040	3	3446
CPI-4	1.19	97.80	1200	3	5037
CPH-4	1.19	98.46	1170	3	4365
CPI-6	1.21	97.80	1300	3	5953
CPH-6	1.20	98.75	1280	3	5457
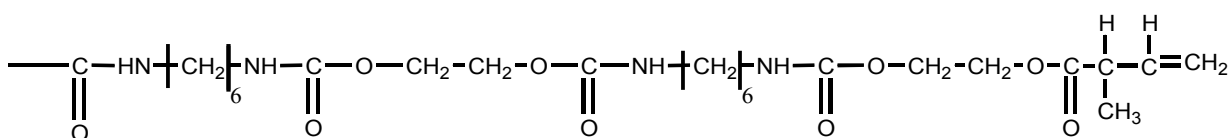
Scheme III. The reaction scheme of urethane acrylate oligomer.

**Characterization of Cellulose Glycoglycoside**
The cellulose glycoglycoside was characterized for viscosity, colour, clarity, density, hydroxyl value (OH), as per standard methods [20]. The physical properties of cellulose glycoglycoside are shown in Table 1.

Characterization of Urethane Acrylate Oligomer
The urethane acrylate oligomer prepared as above was a free flowing viscous liquid. Various characteristics of this oligomer were determined as per the standard methods. The physical properties like specific gravity, percentage solid, viscosity (Brookfield viscometer, RV-II (cPs), colour and molecular weight were determined [21,22]. The results are shown in Table 3.

This urethane acrylate was also characterized by instrumental methods like IR spectroscopy (Nicolet-FTIR spectrophotometer).
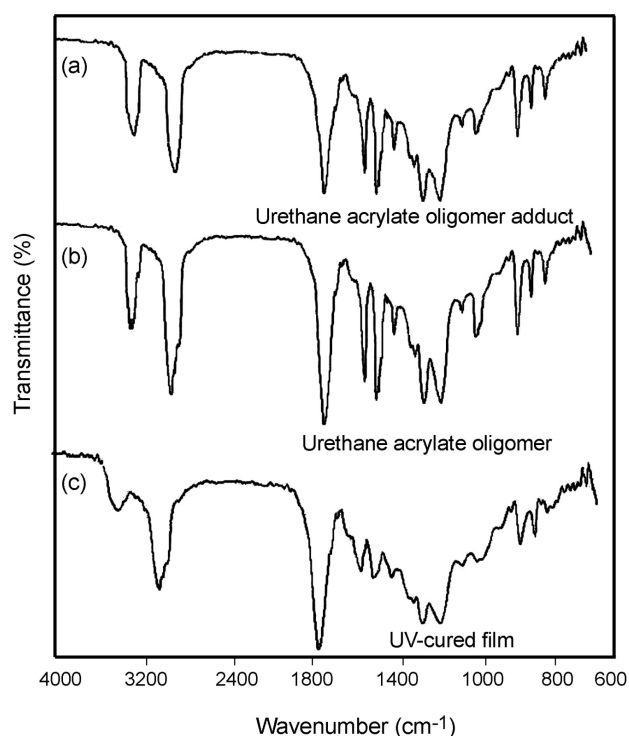
Figure 2. (a) FTIR spectra of: urethane acrylate oligomer adduct, (b) urethane acrylate oligomer, and (c) UV-cured film.

Table 4. UV-curable coating compositions.

Ingredient	wt%	Function
Urethane acrylate	65	Oligomer
EGDMA/SA/PEA	30	Reactive diluents
Benzophenone	3.5	Photoinitiator
DMEA	1.5	Activator/catalyst
Total	100	

EGDMA: ethyleneglycol dimethacrylate, SA: stearyl methacrylate, PEA: 2-phenoxy ethyl acrylate.

Evaluation of Coatings

The coatings were evaluated within one hour after irradiation. The coatings were examined for various mechanical properties like adhesion, flexibility, impact resistance and scratch hardness as per ASTM D 3359-97, ASTM D0522-93 and ASTM 2197, respectively. The impact resistance of the dried film was checked by tubular impact tester. Film thickness was measured by using a micro test magnetic coating thickness gauze. Each panel had an average of three measurements to determine the thickness of panels.

Table 5. Mechanical properties of UV-cured films based on cellulose glycoglycoside and polyethylene glycol.

Designation	DFT Micron	Adhesion cross-hatch	Flexibility 1/4" mandrel	Scratch hardness (g)	Impact resistance 2lb, 25" height Lb/Sq inch
CPI-2S	24	F	F	1700	F
CPI-2P	23	F	F	1800	F
CPI-2E	24	F	F	2000	F
CPH-2S	26	F	P	1500	F
CPH-2P	26	P	F	1600	F
CPH-2E	25	F	F	1900	F
CPI-4S	25	P	P	1900	F
CPI-4P	27	P	F	1800	F
CPI-4E	26	F	F	2000	F
CPH-4S	26	P	P	1700	P
CPH-4P	23	P	P	1900	P
CPH-4E	25	P	P	2100	P
CPI-6S	24	P	P	2100	P
CPI-6P	22	P	P	2300	P
CPI-6E	27	P	P	2600	P
CPH-6S	27	P	P	1900	P
CPH-6P	26	P	P	1900	P
CPH-6E	26	P	P	2100	P

E: ethyleneglycol dimethacrylate, S: stearyl methacrylate, P: 2-phenoxy ethyl acrylate.

Flexibility of the UV-cured film was estimated by using conical mandrel bending tester. Scratch hardness of the films was measured under specified load on a UV-cured film of coating by a mechanized apparatus. The films were also evaluated for their chemical, corrosion and solvent resistance as per methods of their characterization described in the literature [23]. The results of the film characterization are shown in Tables 5 and 6.

Dynamic Mechanical Analysis

The dynamic mechanical properties were obtained using DMA analyzer Triton Technology Ltd., UK Tritec 2000 model. The testing was carried out in a three-point flexural mode. The specimen was heated at a rate of 10ºC/min. The frequency used was 10 Hz. The storage modulus (E') and the loss tangent (tan δ) were obtained as a function of temperature. The glass transition temperature (T_g) of the resins was obtained from the peaks of the loss tangent (tan δ) curve.

RESULTS AND DISCUSSION

Characterization of Cellulose Glycoglycoside

IR Spectra of cellulose and cellulose glycoglycoside are represented in Figure 1. In the IR spectrum of cellulose glycoglycoside the bands due to C-O-C linkage are observed at 1090-1040 cm^{-1} for symmetrical stretching and at 1260-1200 cm^{-1} for asymmetrical stretching. The disappearance of strong band at 1100 cm^{-1}, a shoulder in cellulose glycoglycoside spectra, conform that the degradation of cellulose is through 1,4-β-glycosidic linkage as compared to cellulose IR spectra [24]. The broad band at 3300 cm^{-1} reveals the -OH stretching and confirms the presence of -OH group in glycoglycosides. The bands at 2900-2800 cm^{-1} are due to the -CH_2 stretching and 1450-1420 cm^{-1} are due to the -C-H bending. The band at 1650 cm^{-1} is argued for the presence of carboxylic group in cellulose [25].

Table 6. Chemical resistance, corrosion resistance, solvent resistance of UV-cured film based on cellulose glycoglycoside and polyethylene glycol.

Designation	H_2SO_4 (5%) 7 days	NaOH (5%) 7 days	NaCl (5%) 7 days	MEK double rub
CPI-2S	4	4	3	> 200
CPI-2P	4	4	4	> 200
CPI-2E	5	5	4	> 200
CPH-2S	4	1	2	> 200
CPH-2P	4	3	4	> 200
CPH-2E	3	5	3	> 200
CPI-4S	5	5	1	> 200
CPI-4P	5	5	5	> 200
CPI-4E	5	5	5	> 200
CPH-4S	5	5	5	> 200
CPH-4P	5	5	5	> 200
CPH-4E	5	5	5	> 200
CPI-6S	5	5	5	> 200
CPI-6P	5	5	5	> 200
CPI-6E	5	5	5	> 200
CPH-6S	5	5	5	> 200
CPH-6P	5	5	5	> 200
CPH-6E	5	5	5	> 200

1: complete lifting of films, 2: several blistering, 3: film softens - rust observed, 4: very slight blistering, 5: not affected.

Characterization of Urethane Acrylate Adduct and Oligomer

IR Spectra of urethane acrylate adduct and oligomers are shown in Figures 2a and 2b, respectively. The -N-H stretching and bending vibration of urethane linkage are observed at 3380-3300 cm^{-1} and 1550-1500 cm^{-1}, respectively, in both cases. In the spectrum bands at 2950-2850 cm^{-1} and 1470-1430 cm^{-1} are observed due to -C-H stretching and bending vibration of alkane group. The sharp bands at 1710-1730 cm^{-1} reveal the presence of ester group. The additional band at 770-815 cm^{-1} confirms the presence of double bonds (-C=C-). Figures 2a and 2b also reveal the formation of urethane acrylate adduct and urethane acrylate oligomers. In Figure 2c, the disappearance at 770-815 cm^{-1} band at this frequency region was monitored for the extent of curing.

Mechanical and Chemical Properties

Adhesion

Adhesion test of coated material was carried out by cross-hatch adhesion conducted according to ASTM D 3359-97 Method B to determine adhesion.

The high functionality of cellulose glycoglycoside is reflected as failure in adhesion of coating composition based on PEG 200 and few of PEG 400 (Table 5). This may be argued in terms of shrinkage [26].

The higher extent of adhesion observed (Table 5) in CPH-2S and CPH-2P can be argued in two ways. First, the aliphatic character of HMDI decreases somewhat the shrinkage and secondly, could be due the chemical nature of reactive diluents [27].

Flexibility

Higher functionality of urethane acrylate oligomer resulted in highly cross-linked polymeric network. The term 'cross-link density' here refers to the average number of cross-links per unit volume of cured film. This shows failure in flexibility of the cured film. The results of flexibility for coating composition CPI-2S, CPI-4S, CPI-6S, CPI-2E, CPI-4E and CPI6E (Table 5) clearly indicate that as the molecular weight of PEG increases the flexibility of film increases. Thus, the observed flexibility can be explained in two ways, first, due to increased aliphatic chain length and secondly, due to increase in number of ether linkages.

CPI-4E and CPH-4E, CPI-2S and CPH-2S indicate that HMDI-based composition shows good flexibility compared to IPDI.

Impact Resistance

The result of impact resistance of the cured films followed the same trend as that of adhesion and flexibility. For satisfactory impact resistance, UV-coated film must have sufficient flexibility.

Scratch Resistance

The coating compositions based on cellulose glycoglycoside and PEG give surprising result in the present work. The poor results of scratch hardness in PEG-200 based coating composition (Table 5) can be due to two reasons. First, due to the excessive cross-link density which causes brittleness and secondly, poor adhesion of the film.

Chemical Resistance

High acid and alkali resistance of the cured film for almost all coating compositions can be explained in terms of higher urethane linkage content in the film network, as, the urethane linkage is well known for their better stability against chemicals and at the same time higher cross-link density of the network in the film.

The high polarity of urethane acrylate oligomer imparts hydrogen bonding in the cross-linked network which, also decreases the ability of the polymer to dissolve or even swell in solvents. The solvent resistance of the film can also be argued on the same ground.

Dynamic Mechanical Properties

UV-cured polyurethane acrylate possesses a two-phase microstructure of diisocyanate and flexible long chain diol soft segments. The microstructure of UV-cured polyurethane acrylates was investigated through the measurements of dynamic mechanical properties. The effect of the structure of urethane acrylate for three different molecular weights of the PEG (200, 400, and 600) and different functionalities of the reactive diluents were investigated. The storage modulus (E'), loss modulus (E") and loss factor (tanδ) obtained at 10 Hz are shown in Figures 3-5.

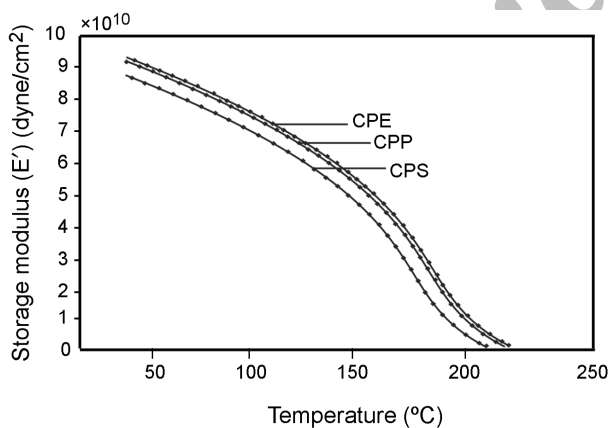The dynamic mechanical properties of the UV-cured
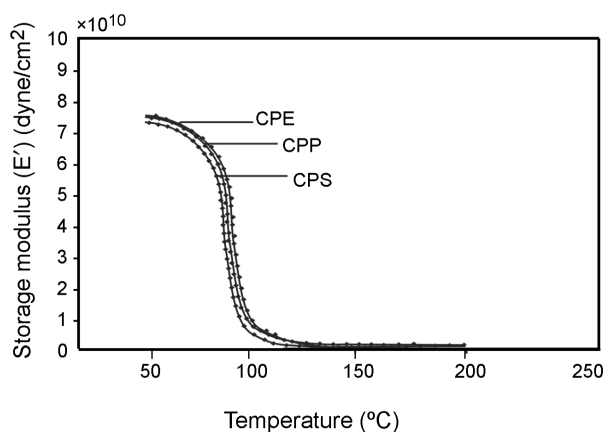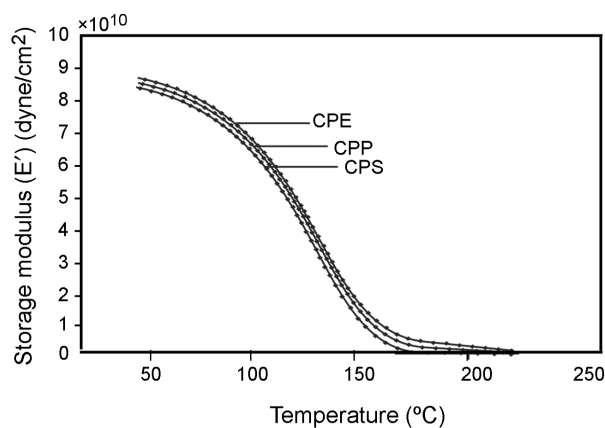
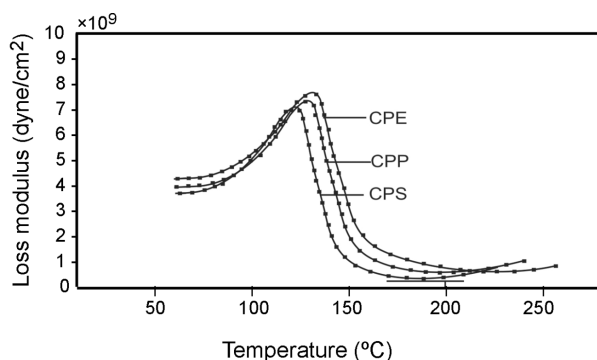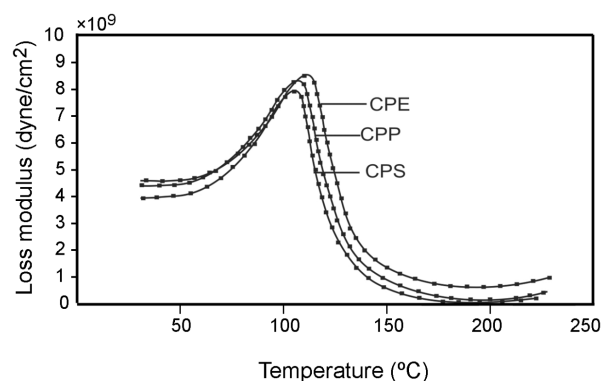**Figure 3.** Storage modulus vs temperature of the UV-cured films for PEG-200 (a), PEG-400 (b), and PEG-600 (c).

Figure 4. Loss modulus vs temperature of the UV-cured films for PEG-200 (a), PEG-400 (b), and PEG-600 (c).

cured films for samples (CPE200, CPP200, CPS200, CPE400, CPP400, CPS400 & CPE600, CPP600, CPS600) were determined as a function of temperature (as shown in Figures 3-5) over the temperature range of 0ºC to 250ºC.
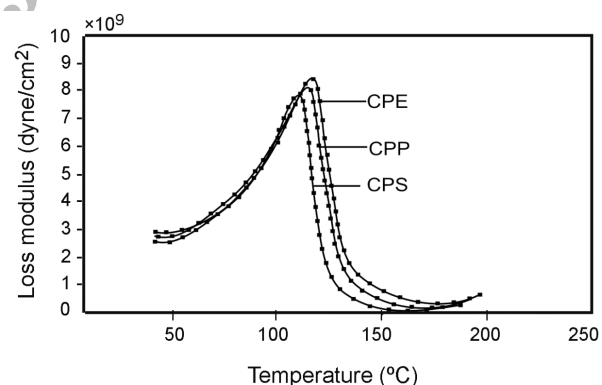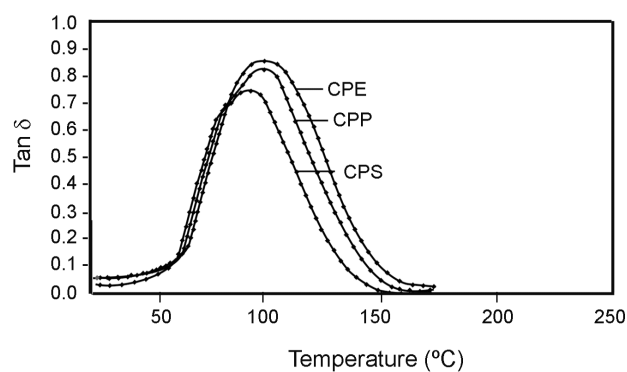
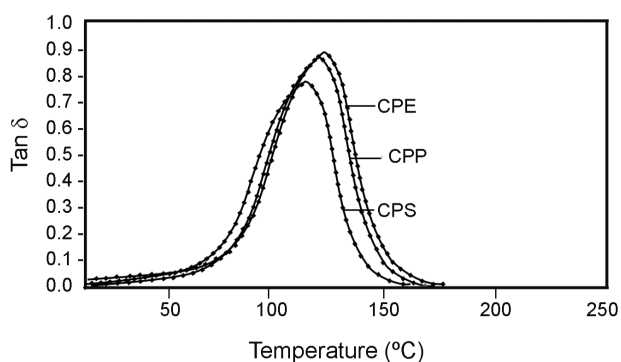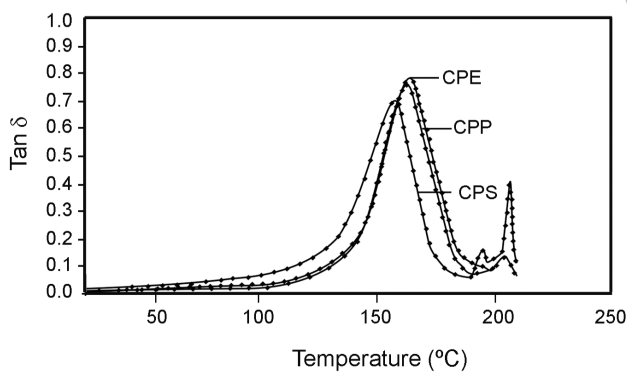Storage modulus vs temperature of the UV-cured films is shown in Figure 3. The molecular weight of PEG increases with increase in the value of storage modulus (E') as shown in the figure. The higher functionality of reactive diluents is also increased with the increased storage modulus (E') value. A sample of CPE-600 has the higher molecular weight of PEG-600 and higher functionality of the reactive diluents (EGDMA) has higher storage modulus in comparison with the other sets of thesample. This result may be due to the increase in the molecular weight of the

(a)

(b)

(c)

Figure 5. Loss factor (tan δ) vs temperature of the UV-cured films for PEG-200 (a), PEG-400 (b), and PEG-600 (c).

polyurethane acrylate and reactive diluents function-ality also affects the storage modulus (E').

Loss modulus (E") vs temperature of the UV-cured films is shown in Figure 4. The sets of CPE600, CPP600 and CPS600 have higher area of curve for loss modulus in comparison with the other sets of the sample like CPE200, CPP200, CPS200, CPE400 and CPP400. This result is due to the increase in the molecular weight of the polyurethane acrylate which affects the loss modulus (E").
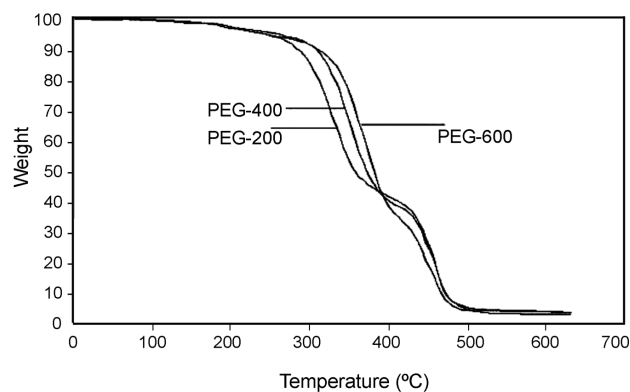
Figure 6. TGA thermograms of PEG-200, PEG-400, and PEG-600.

The functionality of reactive diluents (EGDMA, SA & PEA) does not seem to have affected the tempera-ture of loss modulus (E").

Loss factor (tan δ) vs temperature of the UV-cured films is shown in Figure 5. The sets of CPE600, CPP600 and CPS600 have higher values of the glass transition temperature in comparison with the other sets of the samples like CPE200, CPP200, CPS200, CPE400 and CPP400. The tan δ indicates that CPE600, CPP600 and CPS600 have the highest glass transition temperatures as well as the largest peak among the other set samples due to the increase in the molecular weight of the polyurethane acrylate cured film. The increased glass transition value and func-tionality of reactive diluents (EGDMA, SA & PEA) did not affect the loss factor (tan δ) value [28,13].

Thermal Stability by TGA Analysis

The TGA thermograms (Figure 6) clearly indicate good thermal stability of cured film up to 250ºC with only minimum amount of weight loss, which may be due to some unreacted components. The TGA thermograms clearly indicate that the degradation occurs in three steps. In the first step the degradation through urethane linkage may occur, leaving highly cross-linked products which degrade completely at slow rate.

CONCLUSION

Renewable resources based on coatings like cellulose are used to prepare UV-curable urethane acrylates.

The synthesized urethane acrylates were subsequently formulated using as photoinitiator and different reactive diluents. The clear coat was applied at 23-35 micron thickness using rod applicator and cured under (200 Watt/in) (280-360 nm) medium pressure mercury vapour lamp of UV-2KW-2-35. The overall curing rates less than 1.5-2.0 min were easily attained indicating economical viability of radiation curable system due to faster production schedules. These compounds during curing liberate no volatiles and so they are eco-friendly in nature. At the same time the cured coatings give excellent dynamic, mechanical and chemical properties. The scratch resistance and adhesion properties of UV-cure coats were found to be satisfactory.

ACKNOWLEDGEMENT

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