



Hybrid UV–curable poly(urethane acrylate)s surface coatings using coconut oil based alkyd resin

Premal C. Panchal and Hasmukh S. Patel*

Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar, Gujarat, India

ABSTRACT

A various environmental friendly ultraviolet (UV) curable poly(urethane acrylate)s coatings from renewable resources were synthesised for various industrial applications. In this contest, polyurethane prepolymers were synthesised from coconut oil based alkyd resin as polyol with aromatic and aliphatic diisocyanates by varying NCO/OH mole ratio, these polyurethane prepolymers were coupled with hydroxyl functional methacrylate (2-HEMA). These poly (urethane acrylate)s oligomers, reactive diluents and benzophenone as photoinitiator were cross linked using UV radiations in form of solid coating films. The effect of NCO/OH mole ratio on the structure and properties of these poly(urethane acrylate)s were characterized by IR spectroscopy and also on the physico-mechanical and chemical resistance properties of the coated panels.

Keywords: hydroxy terminated alkyd, polyurethane, polyurethane acrylate, UV coating

INTRODUCTION

An important aim of 21st century is to support the environmental friendly and sustainable use of renewable natural resources. Vegetable oils and fats make up the greatest proportion of the current consumption of renewable raw materials in the chemical industries because they offer a large number of possibilities for applications to the chemistry which can be rarely met by petroleum products [1, 2]. Polyurethanes (PUs) are one of the growing segments of surface coatings and have been extensively used in coating industries, because of their excellent abrasion and chemical resistance, and good mechanical and physical properties. Two-pack PU coatings system are more preferred over one pack system because of flexibility in formulations. The two-pack PU coatings are typically used for plastics, wood, aircraft topcoats, and automotive topcoats. A major component of PU is polyol which provides flexible segment, cross-linking sites and also provide the thermosetting potential to the resulting polymers [3-5]. Thus in this study, we have used coconut oil modified alkyd resin as polyol. Alkyd resins are extremely versatile and they can be synthesized from a variety of natural raw materials [6]. More over alkyd resins are excellent film formers and possess outstanding elasticity, adhesion, gloss and durability in outdoor exposure.

Growing concerns about environmental protection have motivated toward the use of UV curing and has become a possible alternative to the conventional solvent containing polymer formulations [7-9]. UV curable is one such a advantage to surface coating which not only reduced the VOC (volatile organic compound) but also increases the productivity [10] and added benefits such as fast curing speed, energy preservation, cost efficient, and have led to their increased used in various applications such as paints, thin-film coatings, adhesives, packaging overcoat films, and inks.

UV-curable coatings are formulated with three basic components including prepolymers, diluents, and photoinitiators [11-13]. In the presence of UV-radiation, the photoinitiator could be decomposed into a radical or cation active debris, which would initiate the active monomers or oligomers in the reaction system. Thus the liquid

coating system would convert into a solid coating instantly [14]. The most commonly used UV-curable formulations contain unsaturated acrylates due to their greater reactivity and large choice of monomers. Poly (urethane acrylate)s are widely used as oligomers for UV coatings because they provide excellent physical and mechanical properties, good adhesion, high flexibility, and excellent impact strength [15]. However, few studies have been performed to prepare highly crosslinked urethane acrylates for the practical applications of UV-curing systems.

In this work, highly cross-linked poly(urethane acrylate)s were prepared through the reaction of coconut oil based hydroxyl terminated alkyd resin as polyol (-OH value 130 mgKOH/gm) with aromatic and aliphatic diisocyanates having different NCO/OH mole ratio. Isocyanate terminated polyurethane prepolymer were linked through joint reaction of a hydroxyl functional acrylate 2-HEMA, and both were linked among themselves. They were characterized with Fourier transform infrared (FTIR) spectroscopy, and also on the physico-mechanical and chemical resistance properties of the coated panels.

MATERIALS AND METHODS

Materials

Hydroxy terminated alkyd resin (-OH value 130 mg KOH/gm) as polyol was purchased from Reliable Paints., Makarpura G.I.D.C., Vadodara. IPDI, HMDI, MDI and TDI as diisocyanates were purchased from Bayer Co. (Berlin, Germany). Hydroxyethyl methacrylate (2-HEMA) was purchased from Aldrich Chemical Co. Dibutyltindilurate (DBTDL) was used as catalyst was purchased from Hi-media Co. Benzophenone was used as a photoinitiator was purchased from Alfa-Aesar Co., and Trimethylolpropanetriacrylate (TMPTA) was used as a reactive diluent was purchased from Hi-media Co. All the reagents were used as received without further purifications.

Synthesis of the urethane-acrylate oligomers

The highly cross-linked UV curable poly(urethane acrylate)s oligomer PUA-II was synthesised as follows, HTAR (hydroxyl terminated alkyd resin) and IPDI (1:1.25 mol/mol) were charged into a 250ml four neck flask with a reflux condenser in a waterbath and equipped with mechanical stirrer, a thermometer, a dropping funnel, under nitrogen atmosphere and were mixed perfectly. 0.05% (w/v) DBTDL was added in the reaction mixture and then the urethane-forming reaction proceeded at 65°C for over 90 minutes. The reaction mixture as cool down to 45°C then HEMA and 0.05% (w/v) DBTDL were added dropwise with continuous stirring for 60 minutes. Other poly(urethane acrylate)s oligomers with different compositions were synthesised by the same method and are summarized in **Table-1**.

Table -1: Composition of Urethane acrylates oligomers

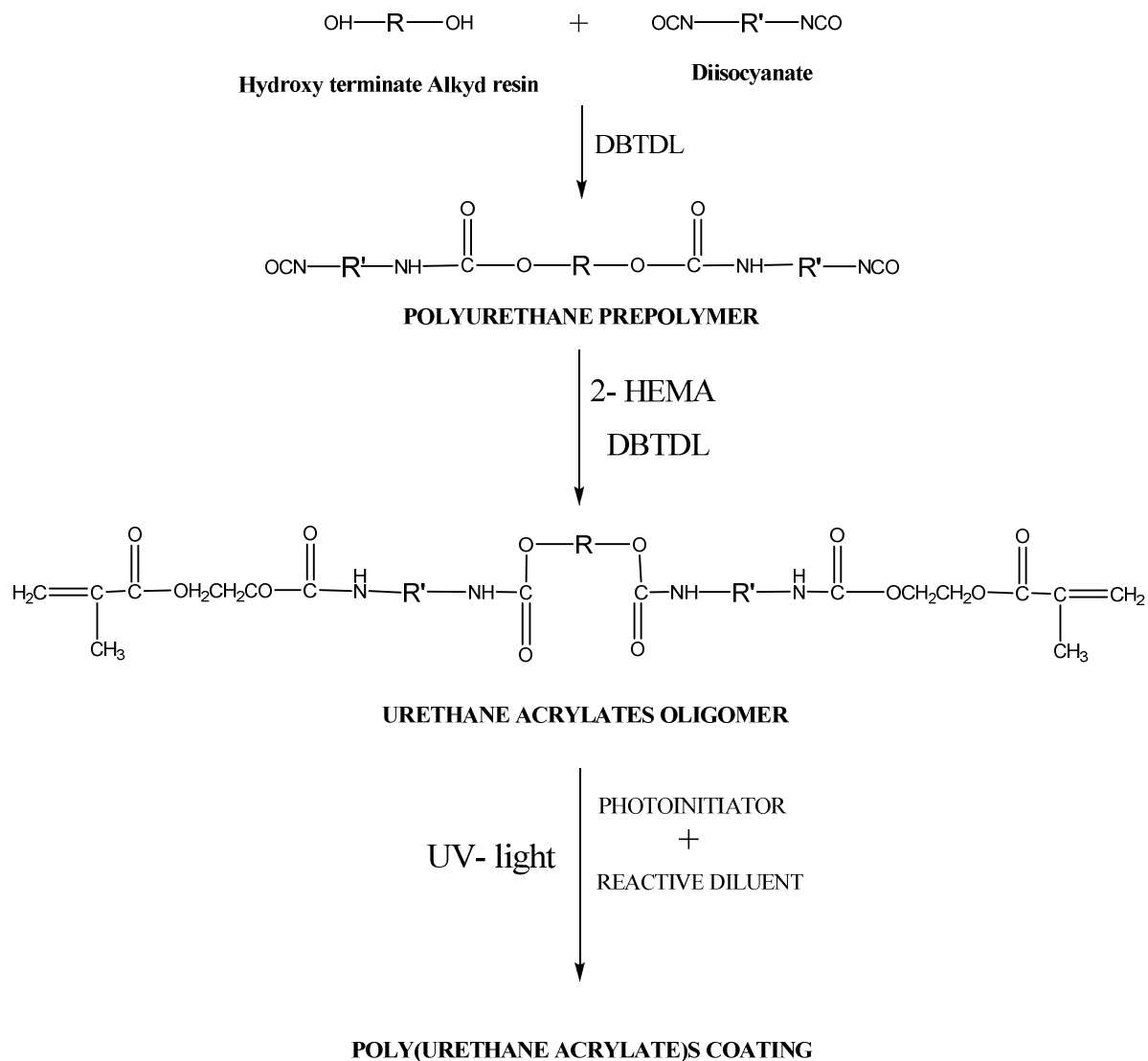
Sr. No.	Sample code	HTAR (g)	IPDI (g)	TDI (g)	MDI (g)	HMDI (g)	NCO/OH ratio	HEMA (g)
1	PUA-1I	7.15	2.3	-	-	-	1.25	0.53
2	PUA-2I	6.5	2.51	-	-	-	1.5	0.98
3	PUA-3I	5.96	2.68	-	-	-	1.75	1.34
4	PUA-4I	5.5	2.83	-	-	-	2	1.65
5	PUA-1T	7.53	-	1.9	-	-	1.25	0.56
6	PUA-2T	6.88	-	2.08	-	-	1.5	1.03
7	PUA-3T	6.33	-	2.23	-	-	1.75	1.43
8	PUA-4T	5.86	-	2.36	-	-	2	1.76
9	PUA-1M	6.95	-	-	2.51	-	1.25	0.52
10	PUA-2M	6.3	-	-	2.74	-	1.5	0.95
11	PUA-3M	5.77	-	-	2.92	-	1.75	1.3
12	PUA-4M	5.31	-	-	3.08	-	2	1.6
13	PUA-1H	7.58	-	-	-	1.84	1.25	0.57
14	PUA-2H	6.93	-	-	-	2.02	1.5	1.04
15	PUA-3H	6.38	-	-	-	2.17	1.75	1.44
16	PUA-4H	5.91	-	-	-	2.3	2	1.78

Sample preparation

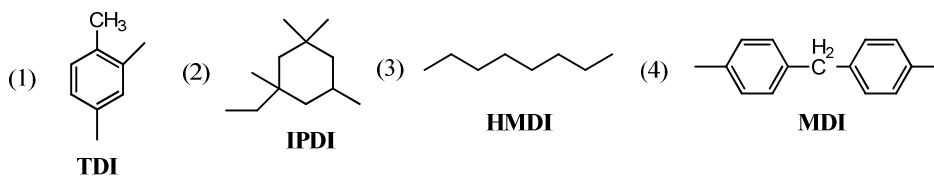
A mixture of poly(urethane acrylates) with a Benzophenone as photoinitiator, and TMPTA as reactive diluents were mixed perfectly through stirring at 45°C for 25 minutes and these was applied on metal panels and UV curing was carried out through the exposure of the panels to UV lamp chamber (GT Ultra Cure, 350 w/cm). The cured films were stored at room temperature for further studies.

Sr. No.	Ingredients	Wt%
1.	PUA oligomer	70%
2.	Reactive Diluent	27%
3.	Photoinitiator (Benzophenone)	3%
4.	Total	100%

Figure 1: Synthesis of poly(urethane acrylates) coating



Where R' =

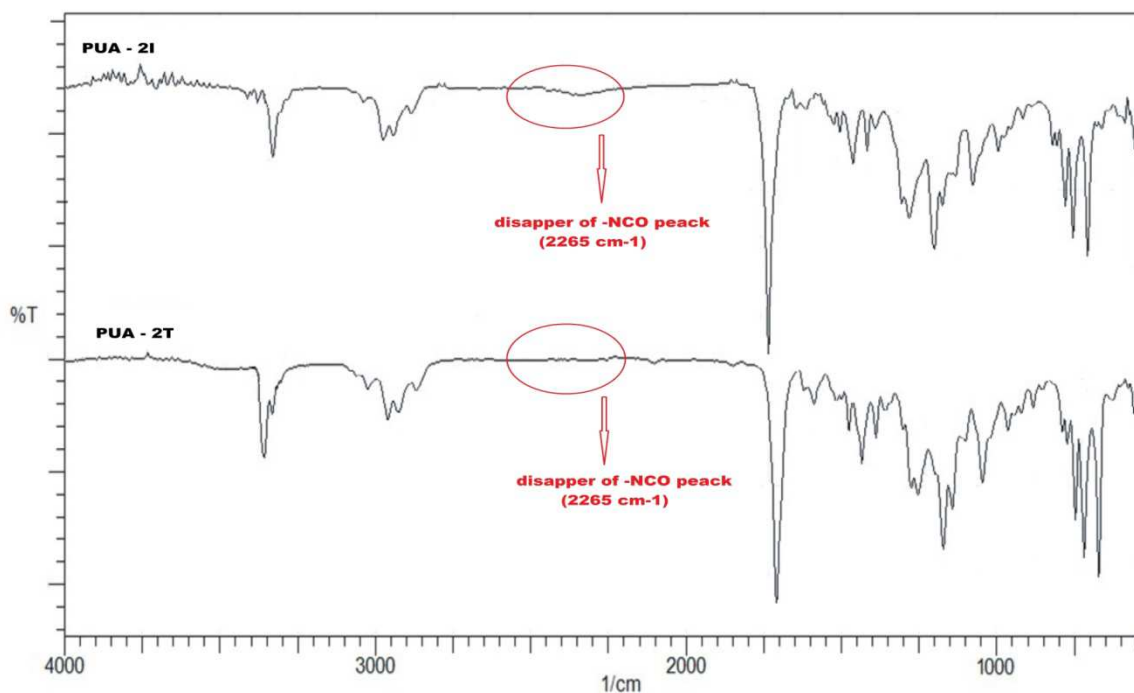


RESULTS AND DISCUSSION

FT-IR Analysis

Typical FT-IR spectra of two different urethane acrylate oligomers are depicted in Figure 2. The spectral analysis was mainly used to check the completion of the polymerization reaction in terms of the disappearance of the NCO band at 2265 cm^{-1} and the appearance of the N-H band at 3000-3400 cm^{-1} , which could be ascribed to the hydrogen bonding between N-H and carbonyl groups. As shown in Figure 2, the spectra of the two urethane acrylate oligomers did not show any detectable band at 2265 cm^{-1} but did show strong absorption bands at 1724 cm^{-1} (amide I, stretching of the ester C=O bond). Absorption at 1068 and 1192 cm^{-1} showed stretching frequencies for C-O group of acrylic compound. IR spectra of polyurethane acrylate oligomers showed additional absorption bands at 1740 and 3390 cm^{-1} corresponding to the presence of urethane carbonyl (-C=O) and amide (-NH) stretching respectively. The band at 1281 cm^{-1} is because of stretching of C-N in urethane. The characteristic stretching band of -N=C=O at 2265 cm^{-1} is absent that indicates all -NCO have reacted.

Figure 2: IR- spectra of poly(urethane acrylate)s oligomer



Scratch resistance

It is one of the most important mechanical properties required for a coating to fulfil its protective role. The damage caused by scratch on a cured surface of the panels may be causing change in the gloss or it may be caused deformation and finally induce cracking in the coating, scratch resistance was determined using an automatic scratch hardness tester having a hardened steel hemispherical point of 1mm diameter as a scratching needle (Morgans). Respective results were shown in Table 2. Which are shows that the aromatic diisocyanates using films shows better results than the aliphatic diisocyanates and also as NCO/OH mole ratio increases the scratch resistance property also increases.

X- hatch adhesion

It was measured using crosscut adhesion tester. The tester consisted of die made up of 9 parallel blades, 1/16 inch apart and 1mm long. The die was pressed into the panel in two directions right angles to each other. A strip of self adhesive was staked over the pattern, and stripped rapidly by pulling the tape back. The test was rated good if not more than 5% of squares were removed. Respective results were shown in Table 2. Which are shows that the all coated panels has satisfactory cross hatch adhesion property.

Pencil hardness

In the pencil hardness, a strip was drawn under a pencil until a hardness grade was reached which would scratch the surface. Respective results were shown in Table 2 and that are shows that aromatic diisocyanates using films has more hardness than the others and as NCO/OH mole ratio increases the pencil hardness also increases.

Flexibility

Flexibility test was carried out through 1/8 inch. mandrel bend tester (IS: 1303-1983). Respective results were shown in Table 2. Which are shows that the aliphatic diisocyanates using films shows better results than the aromatics diisocyanates using film.

Impact hardness

It is the resistance of coatings to the effects of rapid impacts (Wicks, 1992.). The impact hardness of different cured films in the present study was evaluated as per standard method using a heavy duty tubular impact tester with 2 lbs mass and 25 inch height with round nose punch according to IS-101-1989 method. The impact area was observed for cracks in the coating and accordingly reported as passed or failed. Respective results were shown in Table 2. Which are shows that all the coated panels has good impact hardness but in the case of higher NCO/OH mole ratio the coated panels shows poor results. That is mainly due to the higher cross linking density.

Table-2: Physico-Mechanical property of UV cured coatings

Description Code	Scratch Hardness (gms)	Impact Hardness	Pencil Hardness	Flexibility 1/8" mandrel	Cross Hatch Adhesion
PUA-1I	1730	P	2H	P	Ex
PUA-2I	2250	P	3H	P	Ex
PUA-3I	2600	P	3H	P	VG
PUA-4I	2950	P	4H	P	VG
PUA-1T	2250	P	3H	P	VG
PUA-2T	2700	P	4H	P	VG
PUA-3T	3100	P	4H	F	VG
PUA-4T	3450	P	5H	F	G
PUA-1M	1800	P	3H	P	VG
PUA-2M	2400	P	4H	P	VG
PUA-3M	2650	F	4H	F	G
PUA-4M	3000	F	5H	F	G
PUA-1H	1760	F	2H	P	Ex
PUA-2H	1980	P	3H	P	Ex
PUA-3H	2400	P	3H	P	VG
PUA-4H	2830	P	3H	P	G

P-Pass, F-Fail, Ex-Excellent, VG-Very Good, G-Good

6H>5H>4H>3H>2H>1H>H>HB>1HB>2HB>3HB>4HB>5HB>6HB

Chemical Resistance ASTM D 1308 (Patel, 2005.)

The chemical resistance of the cured films is measured by the immersion of the coated panel in 5 % of the acid as well as alkali solution. After immersion the test, panels were observed from time to time for any deterioration of the film. The results for all cured films are given in Table 3.

Table-3: Chemical property of UV cured coatings

Description Code	Acid Resistance 5%HCl	Alkali Resistance 5%NaOH	Corrosion Resistance 5%NaCl	MEK Double rub
PUA-1I	4	3	3	73
PUA-2I	4	3	4	80
PUA-3I	4	4	4	86
PUA-4I	5	4	5	92
PUA-1T	4	4	4	82
PUA-2T	4	4	4	87
PUA-3T	5	4	5	91
PUA-4T	5	5	5	93
PUA-1M	4	3	4	79
PUA-2M	4	3	4	81
PUA-3M	4	4	4	87
PUA-4M	5	4	5	90
PUA-1H	3	3	3	72
PUA-2H	4	3	3	78
PUA-3H	4	3	4	83
PUA-4H	4	4	4	88

0	Film completely removed	3	Loss of gloss
1	Film cracked and partially removed	4	Slight loss of gloss
2	Film partially cracked	5	Film Practically affected

Solvent Resistance ASTM D 5402 (Patel, 2005.)

The solvent resistance of the cured film is measured by the solvent rub test. The coated panels were rubbed with ethyl methyl ketone soaked cotton pad. Any changes in the appearance or deterioration of the film are observed. The results are reported in Table 3.

CONCLUSION

From this study it may be concluded that the oils could be successfully utilized for the synthesis of UV curable poly(urethane acrylates)s surface coatings and also the UV radiations were effectively used to cure poly(urethane acrylates)s resins in the presence of reactive diluents on metal surface. The PUA-2T and PUA-2M shows good scratch resistance and pencil hardness due to tri-functional TMPTA and higher NCO/OH mole ratio which increase the cross linking density, and also presence of aromatic rings of aromatic diisocyanates in the polymeric chain. All the samples shows excellent results of X-hatch adhesion due to incorporation of TMPTA as well as shows good flexibility and impact hardness due to using of alkyd resin as polyol. In addition, all the samples show good acid resistance properties than the alkali resistance. This indicates that these PUA films can be good candidates for the UV-curable coating of metal substrate.

Acknowledgment

Authors would like to thank the Head, Department of Chemistry, Sardar Patel University for providing infrastructural and other facilities for this type of research.

REFERENCES

- [1] Lligadas G, Ronda JC, Galia M, Biermann U, and Metzger JO, *J. Polym. Sci.: Part A*, **2006**, 44, 634-645.
- [2] Gite VV, Mahulikar PP, and Hundiwale DG, *Prog. Org. Coat.*, **2010**, 68, 307-312.
- [3] Patel BK, Patel HS, Desai SN, *Der Chemica Sinica*, **2012**, 3(5), 1052-1057.
- [4] Jongchul S, Jang ES, Song JH, Choi S, Khan SB, and Han H, *J. Appl. Polym. Sci.*, **2010**, 118, 2454-2460.
- [5] Srivastava A, Agarwal D, Mistry S, *Pig. Res. Technol.*, **2008**, 37(4), 217-223.
- [6] Park MN, Oh SW, Ahn BH, Moon MJ, Kang YS, *Mol. Cryst. Liq. Cryst.*, **2008**, 492, 56[420]-63[427].
- [7] Xiao X, and Hao C, *Colloids Surf.- A*, **2010**, 359, 82-87.
- [8] Yang Z, Wicks DAD, Yuan J, Pu H, and Liu Y, *Polymer*, **2010**, 51, 1572-1577.
- [9] Patel DS, Nimavat KS, Vyas KB, *Der Chemica Sinica*, **2011**, 2, 118.
- [10] Sharmina E, Akrama D, Zafara F, Ashrafa SM, Ahmada S, *Progress in Organic Coatings*, **2012**, 73, 118– 122.
- [11] Sangermano M, Gasparia E, Vescovia L, Messorib M, *Progress in Organic Coatings*, **2011**, 72, 287– 291.
- [12] Milinaviciute A, Jankauskaite V, Narmontas P, *Materials Science (Medziagotyra)*, **2011**, 17(4), 1392–1320.
- [13] Patil RN, Sharma BV, Mahnwar PA, *Der Chemica Sinica*, **2012**, 3, 458.
- [14] Jindal K, Bhattacharya D, Francis LF, McCormicka AV, Germinariob LT, Williams C, *Progress in Organic Coatings*, **2010**, 67, 296–301.
- [15] Takami K, Matsuno R, Ishihara K, *Polymer*, **2011**, 52, 5445-5451.