

Synthesis and properties of UV-curable polyurethane surface coating using (Rosinified phenolic resin-coconut alkyd resin) blends

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Abstract

UV-curable coatings are a boon to the paint industry, as they not only reduce VOCs but also speed up production processes and provide protective, durable and attractive finishes. UV-curable polyurethane acrylates have been synthesized from polyester polyol (hydroxy terminated alkyd resin and rosinified phenolic resin), toluene diisocyanate and reactive diluents i.e., Hydroxyethylmethacrylate (HEMA). In this paper several formulations of UV-curable polyurethane acrylate resins were used to study the effect of reactive diluents on performance properties. It was observed from the results that UV-cured polyurethane acrylate resin films on metal surfaces exhibit excellent gloss (60°), mechanical, and chemical properties.

Keywords: UV-curable coatings, CAR-RMPR blends, rosinified phenolic, resin-coconut, alkyd resin

1. Introduction

Polymerization of multifunctional monomers is one of the most efficient methods to rapidly synthesize highly crosslinked polymer networks. A liquid resin can be transformed within seconds into a solid polymer totally insoluble in organic solvents and very resistant to heat, chemical and mechanical treatments [1, 2]. This technique has been applied commercially in printing, thin film coatings and adhesives [3, 4].

UV-curable formulations usually consist of multifunctional monomers, reactive diluents, oligomers and photoinitiators, which generate reactive species on UV exposure [5, 6]. Typically it is a segment of polyurethane oligomer tipped with acrylic functionality such as 2-hydroxyethylacrylate (HEA) or 2-hydroxyethylmethacrylate (HEMA). 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 [7]. More over alkyd resins are excellent film formers and possess outstanding elasticity, adhesion, gloss and durability in outdoor exposure. The reactive diluents are acrylic monomers that are added to modify properties and to reduce viscosity of the precursor liquid.

The acrylated urethanes ideally combine the abrasion resistance, toughness, tear strength and good low-temperature properties of PU with the superior optical properties and weatherability of polyacrylates [8-10]. The reactive diluent phase is more compatible with the hard segments of polyurethane rather than the soft segments, due to similar polarity and hydrogen bonding formation between the urethane NH and acrylate carbonyls [11].

This paper considers the preparation and properties of UV-curable polyurethane acrylates. The NCO-terminated polyurethane prepolymers were synthesized from toluene diisocyanate (TDI) and (RMPR-CAR) Blends followed by tipping with 2-hydroxyethylmethacrylate (HEMA). In addition, reactive diluents having difunctionality were used in different concentrations. A series of coating compositions having PU

acrylate and reactive diluents were prepared, and their mechanical and chemical properties studied.

2. Materials and Methods

2.1 Reagents

Hydroxy terminated alkyd resin (-OH value 130 mg KOH/gm) as polyol was purchased from Reliable Paints, Makarpura G.I.D.C., Vadodara. Rosinified Phenolic Resin (RPR) was purchased from local market. Dibutyltin dilaurate (DBTDL) used as a catalyst which was purchased from himedia. Toluene diisocyanate (TDI) and Isophorone diisocyanate (IPDI) were purchased from bayer co., (Berlin, Germany). Xylene used as a solvent was purchased from the S.d.fine chemical limited, (Mumbai). Hydroxyethyl methacrylate (2-HEMA) was purchased from Aldrich Chemical Co. Benzophenone was used as a photoinitiator was purchased from Alfa-Asser Co., Trimethylolpropanetriacrylate (TMPTA) was used as a reactive diluent was purchased from Hi-media Co. All the reagents were used as received without further purifications.

2.1.1 Preparation of CAR-RMPR blends

The blending process carried out an earlier publication [12, 13]. The physical properties of resultant different percentage composition blends (CAR-RPR) are given in Table -1.

Table 1: Physical Properties of RPR and CAR blends

Sr. No.	Composition CAR+RPR	OH Value in mg of KOH/gm	Moisture content, %
C1	40:60	105	0.042
C2	50:50	87.5	0.031
C3	60:40	70	0.052

2.1.2 Urethane Acrylate Synthesis

The UV curable poly(urethane acrylate)s oligomer was synthesised as follows, (CAR-RMPR)blends and IPDI (1:1 and 1:1.2 mol/mol) with hydroquinone (50 ppm) 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) oligomers with different compositions were synthesised by the same method and are summarized in Table-2.

Table 2: Composition of Urethane acrylates oligomers (Weight of Diisocyanates/10gm of polyol)

Sr. No.	Sample Code	TDI (g)	IPDI (g)	NCO/OH ratio	HEMA (g)
1	PUAC1-I1	-	4.360	1	0.20
2	PUAC2-I2	-	5.400	1	0.26
3	PUAC3-I3	-	6.660	1	0.35
4	PUAC1-I1	-	5.232	1.2	0.53
5	PUAC2-I2	-	6.480	1.2	0.60
6	PUAC3-I3	-	7.992	1.2	0.71
7	PUAC1-T1	3.900	-	1	0.23
8	PUAC2-T2	4.900	-	1	0.30
9	PUAC3-T3	5.940	-	1	0.36
10	PUAC1-T1	4.680	-	1.2	0.57
11	PUAC2-T2	5.880	-	1.2	0.63
12	PUAC3-T3	7.128	-	1.2	0.72

3. Evaluation and Characterization:

An FTIR spectrum of polyurethane acrylate resin was recorded using a NaCl cell on a Perkin-Elmer 1750 FT-IR spectrophotometer.

3.1 Coating Sample Preparation

Coating samples were prepared by using resin, Trimethylolpropanetriacrylate (TMPTA, 25% by wt.) and reactive diluents in different ratios. The sample designations are given in Table 3.

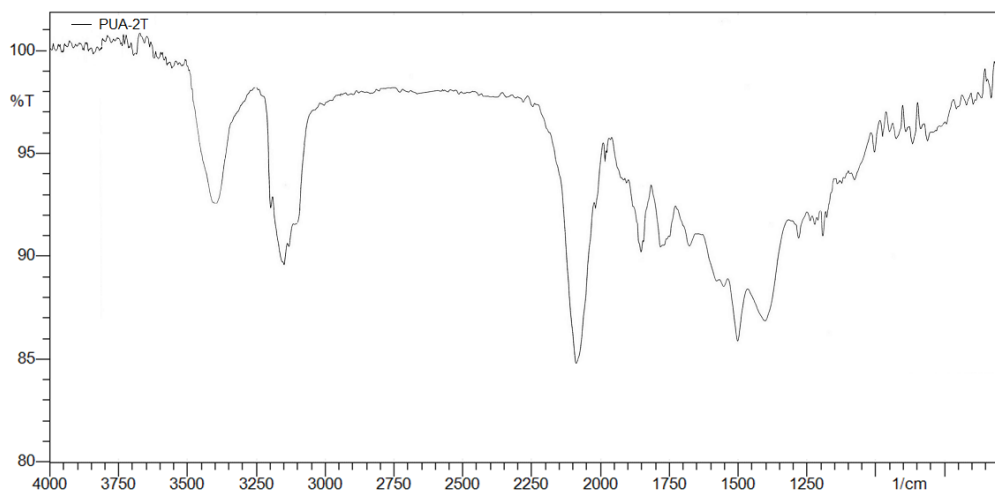


Fig 1: FT-IR spectra of poly (urethane acrylate)s oligomer

4.2 Characterization of Coating Films

Various coating formulation panels were cured in the UV chamber and tested for different mechanical and chemical resistance properties, as per the following test methods: gloss

at 60° (ASTM D 523-99); scratch hardness (ASTM D 5178); pencil hardness (ASTM D 3363-00); chemical resistance (EN: 438-2:1991).

Table 3: Coating sample preparation

Sr. No.	Ingredients	Wt. %
1	PUA oligomer	70
2	Reactive Diluent	28
3	Photoinitiator (Benzophenone)	2
	Total	100

3.2 Curing

The UV-cured PU-acrylate films were prepared by applying the various coating formulations on mild steel panels using a bar applicator. The dry film thickness was maintained at ~12 microns with the help of a film applicator for the evaluation of various mechanical and chemical resistance properties. The panels were then exposed to a UV lamp chamber (GT Ultra Cure, 120 w/cm) maintained as follows.

- UV dryer type : GT Ultra Cure 250
- Curing width: 250 mm
- Bulb type: UV (medium pressure)-GT 250 pure
- Transparent: 120 watt/cm
- Silica Quartz
- Air cooling: 100 mm
- Operating voltage: 440 volts 3 phase A.C.
- Speed: 50 cycles
- Power consumption: 120 w/cm for UV

4. Results and Discussion

4.1 Infrared Analysis

Figure 4 shows the IR spectrum of the PU-acrylate resin. A weak band 1180 cm⁻¹ is attributed to C-N stretching. A band at 1651 cm⁻¹ confirms the formation of the urethane group. A band at 1534 cm⁻¹ is attributed to N-H deformation. A strong band at 1735 is from the acrylate ester carbonyl group present in PU-acrylate resin. A strong band at 2963 cm⁻¹ is believed to be due to C-H stretching and a strong band at 3345 cm⁻¹ is thought to be arising from -OH stretching, due to residual hydroxyl group present in the resin. Moreover, the absence of any band at 2270 cm⁻¹ in the spectrum confirms that unreacted NCO groups are not present.

4.2.1 Scratch hardness

Scratch hardness is one of the important mechanical properties required for a coating to fulfill its protective role. The damage caused by a scratch on a cured surface may lead to a change in the gloss properties of the coating or it may be severe enough to cause deformation and finally induce cracking in the coating. Scratch hardness was determined using an automatic scratch hardness tester having a hardened steel hemispherical point of 1 mm diameter as a scratching needle. Results are shown in Table 4. It is clear from the data that films having a higher concentration of HEMA, i.e., sample having high scratch hardness due to maximum extent of crosslinking of the monomer.

4.2.2 Cross-hatch hardness

Cross-hatch was measured by using a cross-cut adhesion tester. The tester consists of a die made up of 9 parallel blades, 1/16 inches apart and 1 mm in length. The die is pressed into the panel in two directions at right angles to each other. A strip of self-adhesive was staked over the pattern, left in contact for 10 seconds and stripped rapidly by pulling the tape back on itself at an angle of ~120°. The test was rated good if 5% of

the squares were removed. All the coating samples had good cross-hatch hardness properties (Table 4).

4.2.3 Pencil Hardness

In the test, a strip is drawn under a pencil until a hardness grade is reached that will scratch the surface. The coating film is then assigned a hardness value such as H, 2H, 3H, etc., signifying the hardness grade. Coating films of HEMA showed maximum hardness due to higher functionality that led to a maximum degree of crosslinking (Table 4).

4.2.4 Gloss

Gloss was measured using a Triglossometer (Sheen). After watching the films from a 60° angle, it was observed that all the coating films had good gloss. Coating films of HEMA showed maximum gloss (Table 4).

4.2.5 Flexibility

Flexibility testing was carried out on a ¼-inch Mandrel bend tester. Films of all coatings compositions were flexible enough to pass through the Mandrel (Table 4).

Table 4: Physico-Mechanical property of UV cured coatings

Sample Code	Scratch Hardness	Cross-Hatch Hardness	Pencil Hardness	Gloss	Flexibility
PUAC1-I1	2150	Ex	4H	71	P
PUAC2-I2	2465	Ex	4H	73	P
PUAC3-I3	2854	Ex	5H	74	P
PUAC1-I1	2475	VG	4H	74	P
PUAC2-I2	2810	VG	4H	77	P
PUAC3-I3	3225	G	5H	82	P
PUAC1-T1	2410	VG	4H	75	P
PUAC2-T2	2630	VG	5H	78	P
PUAC3-T3	2995	VG	5H	82	F
PUAC1-T1	2870	G	4H	79	P
PUAC2-T2	3015	VG	5H	83	F
PUAC3-T3	3270	G	5H	86	F

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

4.3 Chemical Properties

The coatings samples were tested for their chemical resistance properties. The results of the tests are shown in Table 5.

4.3.1 Distilled water resistance

Coating films exhibit good resistance when exposed to distilled water. Samples, which have a high percentage of HEMA, showed better resistance (Table 5).

4.3.2 Acid resistance

Films of polyurethane acrylate coating showed excellent resistance against acid solution due to difunctionality of HEMA as well as NCO/OH molar ratio. (Table 5).

4.3.3 Alkali resistance

To examine alkali resistance, coating films were exposed to 0.1 N NaOH solutions. Films of HEMA showed better resistance due to high functionality of the monomer that leads to maximum crosslinking (Table 5).

Table 5: Chemical property of UV cured coatings

Sample Code	Distilled Water Resistance	Acid Resistance	Alkali Resistance 0.1 N NaOH
PUAC1-I1	3	3	3
PUAC2-I2	4	4	4
PUAC3-I3	4	4	4
PUAC1-I1	4	3	3
PUAC2-I2	4	4	4
PUAC3-I3	4	4	4
PUAC1-T1	5	5	5
PUAC2-T2	4	4	4
PUAC3-T3	4	5	5
PUAC1-T1	5	4	5
PUAC2-T2	4	5	4
PUAC3-T3	5	5	5

0	Film completely removed	3	Loss in gloss
1	Film removed and particularly cracked	4	Slight loss in gloss
2	Film partially cracked	5	Film largely unaffected

5. Conclusion

UV radiation was effectively used to cure PU-acrylate resins in the presence of reactive diluents to obtain coatings for metal surfaces having excellent mechanical and chemical properties. UV-cured metal surfaces also exhibit excellent mechanical and chemical properties. Coating properties were greatly affected when the reactive diluents were incorporated in the resin. At higher concentration of reactive diluents, gloss and scratch hardness increases. Therefore these coatings can be used as protective coatings for metals and can also reduce VOC and hazardous air pollutants.

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