

Studies of the thermal and mechanical properties of novel UV curable waterborne Polyurethane dispersion (WPUD)

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ABSTRACT

The novel ultraviolet (UV) curable waterborne polyurethane dispersion was formulated from 2,4-Tolylene diisocyanate (TDI), hydroxy terminated unsaturated polyesters (HTUP), 2,2-dimethylol propionic acid (DMPA) and Linalool (LL) (a terpeneol). TDI has been selected for receiving more thermo resistant coating. LL has been selected for fast curing process. The resultant dispersions were coated on steel panel. The panels were irradiated by UV mercury lamp (15w) for 10-15 minute. The resultant coatings were characterized by thermal and mechanical properties. The results showed that the thermal stability of coatings and mechanical properties is good due to high cross-link density. This might be responsible due to presence of unsaturated polyester segment.

Key words: UV-radiation, curing, waterborne polyurethane, diisocyanate, unsaturated polyester, coating, thermal and mechanical properties.

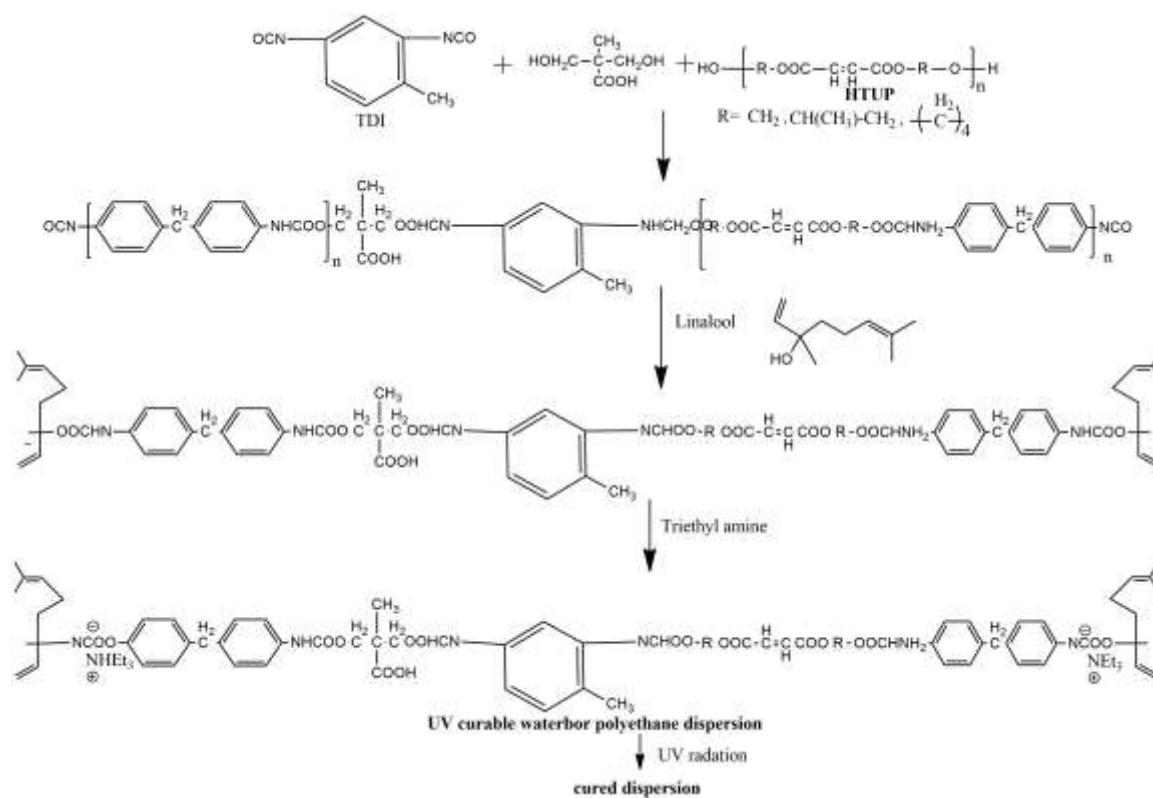
INTRODUCTION

Now the research emphasis an eco-friendly surface coating materials [1]. Thus, waterborne coatings are environmentally safe and thus attention received as substitute to solvent free coating [2]. Though waterborne coating are inferior to coating in terms of chemical and mechanical properties [3]. But the UV curable coatings overcome such drawbacks with affording excellent all over properties [4-7]. Several researchers had developed UV-curable waterborne coatings with improved properties [8-11].

In such waterborne coating formulation [8-11] mostly aromatic dicyanates, oligodiols and end capped acrylated derivatives are used. No report has been found in which unsaturated diol or oligodiol used in UV curable waterborn polyurethane in spite of the curing properties of unsaturated diol segments. Recently present authors [12] reported traditional water born polyurethans based on hydroxy terminated unsaturated polyesters (i.e. unsaturated diols).

Such unsaturated diols and their waterborn polyurethane dispersions may have tendency for further curing by thermal or photolytic. Thus it was thought to study the novel polyurethane dispersion with unsaturated diol segments as well as unsaturated molecule as an end capped.

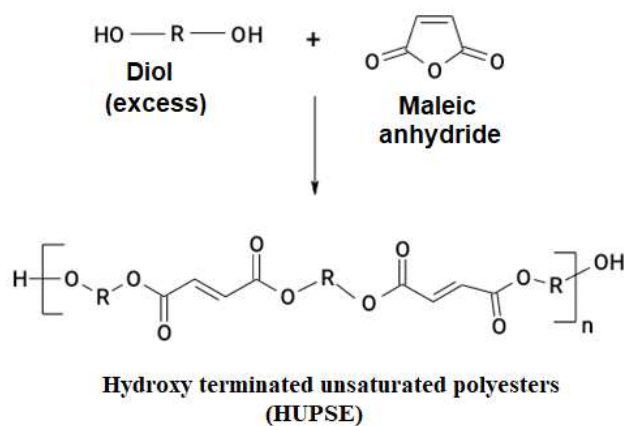
Thus, the present work is extension of our previous research work [12] with introduction of more unsaturation into product i.e. a terpinoid-linalool as end capped. The synthesised polyurethane dispersion was studied by UV curing. The research scheme is as follow.



EXPERIMENTAL

Materials

2,4-Toluene diisocyanate (TDI), 2,2-dimethylol propionic acid (DMPA), Triethyl amine (TEA), Linalool and all other chemicals were used of pure grade. The hydroxy terminated unsaturated polyesters (HUPSE-1 to 3) were prepared as reported in our previous communications [12]. Their structure and specification are also mention in Table-1.



Where, R = $-\text{CH}_2-\text{CH}_2-$, $-\text{CH}_2-\text{CH}-$, $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-$
 $\quad \quad \quad |$
 $\quad \quad \quad \text{CH}_3$

Table-1 Specification of hydroxy terminated unsaturated polyesters (HUPSE)

Polyester	Appearance	Hydroxy value mg KOH/ 1g	Mol.wt. g/mole
HUPSE-1	White turbid Viscous liquid	110	1020
HUPSE-2	White turbid Viscous liquid	90	1250
HUPSE-3	White turbid Viscous liquid	80	1400

Synthesis of UV curable waterborne polyurethane dispersion(UWPU)

The polymerization formation was carried out in two steps. 500ml mulls necked glass Kettle attached by mechanical stirrer, N₂ gas inlet tube, thermometer and condenser were fixed in a constant temperature oil bath.

First, HUPSE(0.1 mol)(1,2 or 3), 0.1% Dibutyl tin dilaurate (DBTDL) as catalyst and 2,4-Tolylene diisocyanate (TDI) (0.125 mol) were charged into kettle and the reaction was carried out 90-100° C for 6hr. Then DMPA was added and the reaction mixture was continued until constant value of diisocyanate (-NCO) group. The -NCO content was determined by volumetrically using dibutyl amine (DBA) (ASTMD2572-97 method).

In next step, the required amount of 'Linalool' (a terpinol) was added and reaction was proceeding until the complete reaction of -NCO group (Back titration with DBA). The whole mixture was than cooled to 50° C and viscosity was reduced by tetrahydrofuran (THF) solvent. The polymer product was neutralised by adding Triethyl amine (TEA). At room temperature the distilled water was added (about 150-200ml) until homogenous dispersion. Finally THF was removed under vacuum. The obtained UWPU would be about 30% solid content. The three UWPU were prepared and designated as HUPSE-1 to 3.

Preparation of UV on steel panel

To the UWPU sample, Benzophenone as photo initiator was mixed through stirring at room temperature, then it was employed on steel panels of 15cm x 5cm. The process is as follow:

An excess of UWPU sample was placed at one end of steel panel and by employing red applicator (K-Br No.5) drawn through the whole surface of panel with equal presence by putting excess HTUP sample off other end of steel panel.

Then UV radiation was exposed to panels into UV lamp chamber (GT Ultra cure 350w/cm). The cured coating panels were stored in a glass chamber at room temperature. This produced coating average wet film thickness of 25-35µm. The cured films were also obtained by similar method by using Teflon panels. The steel panels were studies for their mechanical properties. The prepared films were studied for infrared spectroscopy, gel content, chemical resistance and thermogravimetry.

INSTRUMENTATION

FT-IR spectra of uncured dispersion and cured films were scanned by in KBr pellets on a Nicolet 400D spectrometer.

Chemical resistance of cured film was determined by ASTM-D-1308 and D-5402 methods.

Thermogravimetric analysis of cured films was carried out by DuPont 950 TGA analyzer at a heating rate of 10 K/minute.

The coating characteristics studies by chemical resistivity and mechanical properties coating or film were determines by methods mentioned below:

Test	Method
Scratch hardness	ISO 1518
X-hatch	ISO-2409
Flexibility	ISO-1303
Impact hardness	ISO-101
Pencil hardness	ISP-15184
Chemical/ solvent resistance	ASTM-D-1308,D-5402

Table-2 UV curing progress as a function of time by FT-IR spectroscopy and fraction of UV-coating as a function of time.

Coating	UV-curing progress by FT-IR spectroscopy (As a function of time in sec.) (% conversion)				Gel fraction (percentage) of UV coating (As a function of Time in sec.)			
	5	10	15	20	5	10	15	20
HUPSE-1	54	60	75	85	78	82	92	94
HUPSE-2	50	58	70	80	90	80	87	90
HUPSE-3	50	55	70	80	60	73	85	95

Table-3 TGA data of all HUPSE films.

Coating	% age Ion at Temperature °C			
	200°C	300°C	400°C	500°C
HUPSE-1	0.9	5	48	95
HUPSE-2	1.0	5.5	52	86
HUPSE-3	1.2	6	53	90

4. RESULTS AND DISCUSSION

The unsaturated polyester diols were in these novel UV-curable coatings.

The waterborne polyurethane dispersion was performed by reacting varies HUPSE with TDI to produced polyurethane. The IR spectra (not shown) of all polyurethane dispersion show the absorption bands at 3300, 1732 (-NHCOO- Urethane) and 1635 and 810 cm^{-1} (double band). The band in this region of 2200-2300 cm^{-1} is absent for $\text{C}\equiv\text{N}$ of NCO. So, all NCO groups are almost reacted.

The IR spectra of all three UV cured coating films as a function of time was carried out. The data are shown in Table-2. It was found that all three formulation showed the intensity of absorption band at $\text{C}=\text{C}$ at 1630 and 810 cm^{-1} decreased with increasing curing time. This is due to photo cross linking existing by HUPSE - linalool segments. The percentage cross linking of $\text{C}=\text{C}$ band was determined by formula reported [14].

$$\% \text{ Cross-linking} : \frac{A_0 - A_t}{A_0} \times 100$$

Where A_0 and A_t are relative absorption of $\text{C}=\text{C}$ band at 810 and 1730 cm^{-1} before curing and curing at time t respectively.(Fig.1)

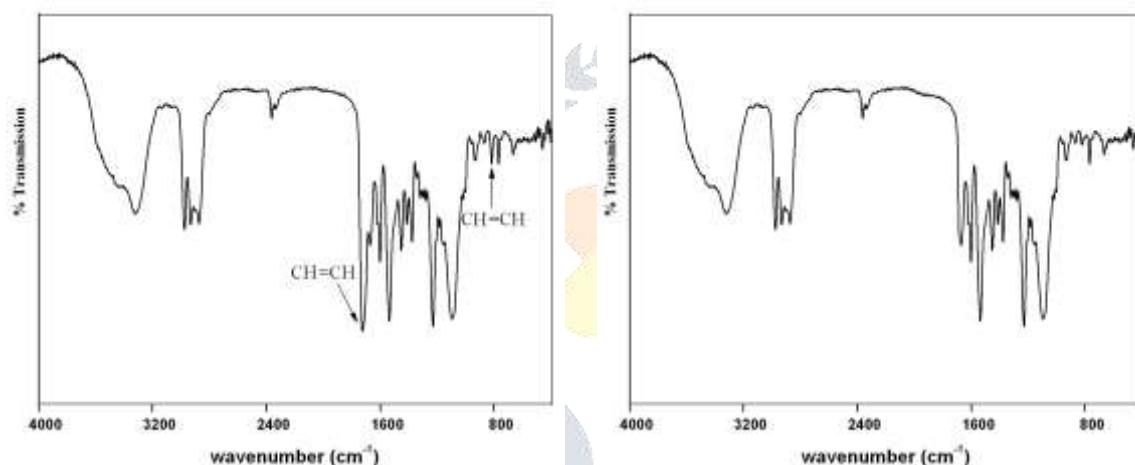


Figure 1 IR spectra and UV cured IR spectra of HUPSE-2(for 20s time)

The data are shown in Table-2. The data indicate that curing is increased by increasing the UV curing time. This is due to unsaturation present in HUSPEs and linalool segments.

The curing was confirmed by finding the gel fraction. The gel fraction was determined by method reported by Park and his coworker. [15] The cured film (100 mg) was dipped in to hexane at 50°C for 24 hours. The sample was dried and gel fraction was calculated from the weight of total after drying versus original weight.

$$\% \text{ Gel fraction} : \frac{W_0 - W_d}{W_0} \times 100$$

Where W_0 = original weight and W_d = Weight after hexane treated films

The results (Table-2) show that gel fraction of three film increase rapidly by UV irradiation. The HUPSE-1 has higher gel fraction.

Table-4 Mechanical properties of UV cured HUPSEs

Coating	DFT (μ)	Scratch hardness (gms)	Impact hardness	Pencil hardness	Flexibility 1/8" mandrel	cross hatch adhesion
HUPSE-1	23	3400	P	4H	P	Ex
HUPSE-2	24	3200	P	4H	P	Ex
HUPSE-3	26	2800	P	4H	P	VG

P: Pass, Ex: Excellent, VG: Very Good

Pencil Hardness: 6H>5H>4H>3H>2H>H>HB>B>2B>3B>4B>5B>6B

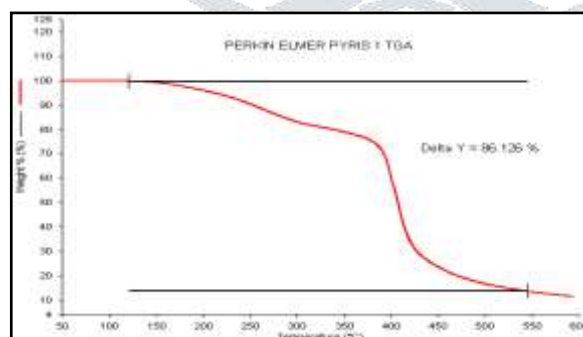
Table-5 Chemical resistivity of UV-cured HUPSE

Coating	Acid	Alkali	Corrosion	Solvents
	5%	5%	5% NaCl	acetone/ ethanol/ n-hexane
HUPSE-1	4	5	5	5
HUPSE-2	4	5	5	5
HUPSE-3	5	4	4	5

4 : slight loss on gloss of film

5 : Film practically unaffected

The TGA data of all the three cured film are shown in Table-3. The examination of the results reveals that all the film starts their degradation around 200°C. The initial wt. loss is about 1.5 percentage. While beyond 250°C all the film degrades rapidly and 90% loss at around 500°C. The rapid losses mainly due to decarboxylation of urethane linkage. The stability upto serviceable temperature (~200°C) of film may be due to presence of aromatic segment of TDI.(Fig.2)

**Figure 2 TGA thermogram of HUPSE-2**

The results of scratch resistance of all coated panels are shown in Table-4. It is mechanical property to fulfill coating role. The damage created by scratch on panel surface change in gloss or deformation by cracking. The results are excellent for produced coating material. This may be due to high cross-linking density exhibit from HUSPEs and Linalool segments.

The X-hatch adhesion was determined by crosscut adhesion tester. It consists a die having 9 parallel blades of 1m long with 1/16" gap. The die was prepared into coated panel two dimensionally. A strip of self-adhesive was stuck over the panel and stripped rapidly by pulling the tape back. The results are excellent and presented in Table-4. It indicates that 'No Peeling' exhibit in coating during testing.

Results of flexibility test (by mandrel bend tester) are shown in Table-4. The results show that the HUPSE-3 have better than other two. This may mainly due to higher aliphatic segment.

Impact hardness of coating is effect at sudden impacts. By using standard method the impact area was observed for crack in coating and accordingly presented as passed or failed. The results are shown in Table-4 and indicate that the coating is good (i.e. passed) against impact.

For the pencil hardness a strip was drawn and H-grade pencil till which scratch the coated surface. The results are shown in Table-4. The results show that the 4H pencil cannot strip the surface. So, all three coating materials are good.

For the measurement of the chemical resistance of cured film, the film panels were dipped into test chemicals (5% aq. acid, alkali and common organic solvents: methyl ethyl ketone, ethanol, n-hexane etc.) at room temperature for 24 hrs. After removal of film or panel from chemicals the observed results were monitored with any change of in the appearance or deterioration of the film. The observations are shown in Table-5. The overall chemical resistance for all coating is good.

CONCLUSION:

The hydroxy terminating unsaturated polyesters were formulated UV curable waterborne polyurethane dispersion. Three samples have been prepared by using three diols viz; 1,2-ethane diol, 1,2-propanediol and 1,4-butanediol. The UV-curing of all three samples was carried out as steel panels. Then UV-curing conversion, mechanical and chemical properties were evaluated. The results of all three coats are excellent.

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