Studies on Novel UV-Curable Waterborne Polyurethane Coating

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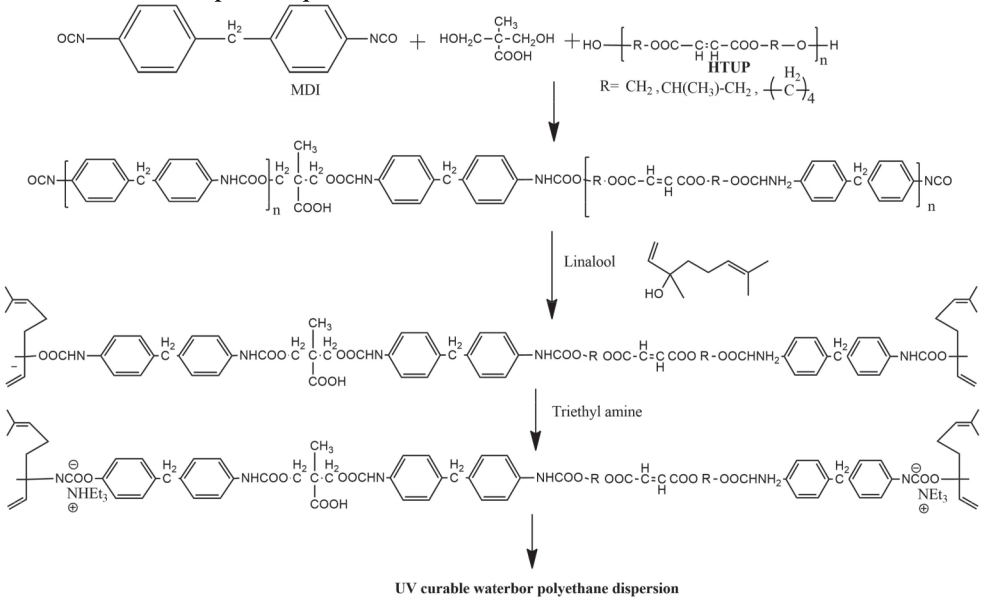
ABSTRACT
The novel ultraviolet(UV) curable waterborne polyurethane dispersion was formulated from 4,4'-methylenebis(phenyl isocyanate) (MDI),hydroxy terminated unsaturated polyesters (HTUP),2,2-dimethylol propionic acid(DMPA) and Linalool(LL) (a terpiniol).MDI has been selected for receiving more thermo resistant coating. LL has been selected for fast curing process. The resultant dispersion was coated as steel panel. The panels were irradiated by UV mercury lamp (15w) for 10-15 min. The resultant coatings were characterized by thermal and mechanical properties.

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

I INTRODUCTION

The research emphasises an ecofriendly 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 researches have been developed improved UV-curable waterborne coatings [8-11]. Recently the present author reported the novel waterborne polyurethanes (WBPU) based as hydroxy terminated unsaturated polyesters [12]. Such WBPU have unsaturation so called dispersion may have tendency to cure via UV radiation. Thus the present paper is extension of our earlier work [13] with introduction of more unsaturation by Addition of natural product i.e. a terpinoid-linalool. The present paper comprises the modified formulate as shown in scheme.



II EXPERIMENTAL DETAILS

(a) Materials- 4,4'-methylenebis(phenyl isocyanate) (MDI), 2,2-dimethylol propionic acid (DMPA), Triethyl amine (TEA) and all other chemicals were used of pure grade. The hydroxy terminated unsaturated polyesters (HTUP-1 to 3) were prepared as per our earlier communication [14].Their specification are shown below: (Table-1)

Table-1
Specification of HTUP

Resin	OH value mg/KOH	Mol.Wt.
HTUP-1	110	1020
HTUP-2	90	1250
HTUP-3	80	1400

(b) Aqueous polyurethane dispersion - The synthesis of dispersion was carried out in multinecked round bottomed flask set with stirrer, dropping funnel,N_2 gas inlet tube and HTUP(each of 1 to 3) (0.05 mole) were added. The dibutyltin dilaurate (as catalyst) was added into the flask with good stirring. The reaction was carried out at 85-90°C until yield –NCO terminated product obtained. Then DMPA (0.001 mole) was added and stirred the reaction mixture for 1hr. Again the –NCO terminated product obtained. The resultant product was added by required amount of linalool (as per –NCO group) and reaction was kept for 80°C for 2hrs. The dry acetone was added into the reaction product to receive desire viscosity of solution. It was cooled to room temperature and neutralized by Triethyl amine (TEA). Then the dispersion was obtained by distilled water adding under reduced pressure. The –NCO was determined during the reaction followed by method reported [13].

(c) Preparation of UV curved resin on steel panel - The prepared dispersion with Benzophenone as photoinitiator were mixed through stirring at room temperature and was employed on metal panels and UV radiation was expose to panels into UV lamp chamber.(GT Ultra cure 350w/cm) The cured coating panels were stored in a glass chamber at room temperature. The cured films were also obtained by similar method by using Teflon panels. The steel panels were studies for mechanical properties. While the films were studied for infrared, gel content, chemical resistance and thermogravimetry.

(d) Measurements

(i) The cured films: FT-IR spectera 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/min.

(ii) The coating on steel penals: The coating characteristics studies by chemical resistivity and mechanical properties 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

III RESULTS AND DISCUSSION

The waterborne polyurethane dispersion was performed by reacting varies HTUP with MDI 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 C≡N of NCO. So all NCO groups are almost repeated.

The IR spectra of all three UV cured coating film as a function of time was carried out. The data are shown in Table-3. It was found that all three formulation showed the absorption band at C=C at 1630 and 810 cm^{-1} decreased with increasing curing time. This is due to photo cross linking existing by HTUP linalool segments. The % age cross linking of C=C band was determined formula [14].

It was observed that the introduction of linalool may increase the cross linking by one of internal double bond. The end double bond may not be participating in cross linking due to allylic system. So % age conversions of curing and gel fraction are limits to 90%.

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

Where A_0 and A_t are relative absorption of C=C band at 810 and 1730 cm^{-1} before curing and curing at time t respectively. 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 HTUP 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 24hrs.The sample was dried and gel fraction was calculated from the wt. of total after drying versus original wt. The results (Table-2) show that gel fraction of three film increase rapidly by UV irradiation. The HTUP-1 has higher gel fraction.

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%age. While beyond 250°c all the film degrades rapidly and 90% loss at around 500c. 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 MDI.

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 good for produced coating material.

The X- hatch adhesion was determined by crosscul adhesion tester. It consistva die having 9 parallel blends of 1m long with 1/16" gap. The die was prepared into coated panel two dimensionally. A strip of self Adhesive was staked over the panel and stripped rapidly by pulling the tape bozol. The results are good and presented in Table-4 and Va. Results of flexibility test (by mandrel bend tester) are shown in Table. The results shows that the HTUP-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 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 are good for all three coating materials.

The chemical resistance of cured film was dipped into test chemicals (5% aq. acid, alkali and common organic solvents: methyl ethyl ketone, ethanol, n-hexane etc.) for 24 hrs. After removal of panels from chemicals the observed results were monitored with any change of in the appearance or deterioration of the film. The observation is shown in Table-5.

Table-1
Specification of HTUP[16]

coating	OH value mg/KOH	Mol.Wt.
HTUP-1	110	1020
HTUP-2	90	1250
HTUP-3	80	1400

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,sec.) (% conversion)				Gel fraction (%age) of UV coating (as a function of time,sec.)			
	5	10	15	20	5	10	15	20
HTUP-1	50	56	70	80	70	80	90	92
HTUP-2	46	50	66	75	60	75	88	90
HTUP-3	43	48	64	74	48	75	85	85

Table-3
TGA data of all HTUP films

Coating	% age Ion at Temperature °C			
	200°C	300°C	400°C	500°C
HTUP-1	0.95	5	50	95
HTUP-2	1.2	7	56	95
HTUP-3	1.3	7.5	58	95

Table - 4
Mechanical properties of UV cured HTUPs

Coating	Scratch hardness (gms)	Impact hardness	Pencil hardnes	Flexibility 1/8" mandrel	cross hatch adhesion
HTUP-1	3500	P	4H	P	Ex
HTUP-2	3450	P	4H	P	Ex
HTUP-3	3000	P	4H	P	VG

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

Table 5
Chemical resistivity of UV-cured HTUP

Coating	Acid 5%	Alkali 55	Corrosion 5% NaCl	Solvents acetone/ ethanol/n-hexane
HTUP-1	5	5	5	5
HTUP-2	5	5	5	5
HTUP-3	4	4	4	5

5: Film practically unffeeted
4: slight loss on gloss of film

IV 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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