

PU Dispersions — Effect of Glycol in Polyol Moiety on the Properties of PU Coatings

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Polyurethane dispersions are binary colloidal systems having PUR particles dispersed in aqueous phase, which can be classified into anionic, cationic, and non-ionic systems. In this paper, PUR ionomers prepared by anionic dispersions process, using toluene di-isocyanate [TDI], polyester polyol, and trimelletic anhydride [TMA] as the potential ionic center with NMP as the co-solvent are discussed. A series of polyols based on various glycols have been prepared while keeping the composition of the reactants the same. It is found that the dispersion prepared by a polyol containing neopentyl glycol [NPG] gives better results of a coated film with respect to gloss, scratch resistance, flexibility, and abrasion resistance.

Keywords: Polyurethane dispersion, Diisocyanate, Coating, Glycol, Polyol moiety

Introduction

It has become essential to develop aqueous PUR dispersions mainly due to strict government legislations for low VOC and to discourage use of environmentally detrimental materials. Continuous increase in solvent prices, low raw material cost, and easy clean up of the reactor system made water borne PUR system more common. Aqueous PUR dispersions can be classified into anionic, cationic, and non-ionic systems¹⁻³. The dispersions can be obtained by processes like, acetone process, prepolymer mixing process, hot melt process, and ketamine/ketarine process^{3,4}. The basic principle involved in producing ionomers is to produce solubilising groups into the backbone of the polymer which render the polymer self-emulsifiable.

In a typical anionic PUR dispersion process, anionic groups (namely carboxylic or sulphonic) are introduced along the length of the polymer chain. The dispersions obtained possess the properties comparable to solvent borne PUR system. Higher values of mechanical properties without compromising in water and solvent resistance can be achieved⁵.

In this paper, PUR ionomers, based on TDI and polyols, are prepared by anionic dispersion process by incorporating carboxylic groups along the length of the polyol chain with the help of trimelletic anhydride (TMA) as the potential ionic centre, NMP is used as the co-solvent.

Materials

- (i) Glycol component viz., ethylene glycol/propylene glycol/neopentyl glycol of commercial grade are used in polyol synthesis.
- (ii) Acid components viz., adipic acid, commercial grade, TMA (extra pure), TDI (extra pure) are used in polyol preparation.
- (iii) NMP (M/s S D Fine Chem, India), extra pure grade was used as co-solvent.
- (iv) Triethyl amine (M/s Ranbaxy Laboratories, India), extra pure grade was used as neutralizing agent.
- (v) Ethylene diamine (M/s Ranbaxy Laboratories, India), extra pure grade was used as chain extender.

Characterization

(i) Acid Value

The polyols prepared by selecting various glycols with a definite composition, are reported in

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Table 1. The polyesterification reaction was monitored by determining acid value every half an hour. Acid Value is determined by dissolving 1gm of resin in 20 mL mixture of Methyl alcohol and chloroform (1:1), and titrated against dilute alcoholic KOH solution, using phenolphthalein as an indicator.

(ii) Hydroxyl Value

The proportion of addition of TMA was decided by determining hydroxyl value of the polyester polyol. The Hydroxyl value is determined by taking 0.3-0.5 gm resin reacting with excess of acetylating reagent (10 mL) and refluxing the mixture for 1 h. If the reaction mixture is colourless, even after refluxing, add little amount (known quantity) of acetylating reagent so that the colour of the mixture is yellow. The mixture is titrated with alcoholic KOH solution, after cooling and adding 50ml of Distilled water, using phenolphthalein as a indicator. The blank titration is carried out without the sample and repeating the above procedure exactly. The difference in the burette reading helped in calculating Hydroxyl value using standard formula.

(iii) Viscosity

Viscosity of the dispersion is measured by "Brookfield Viscometer" at a speed of 100 RPM using spindle no-3 at 25 °C. The spindle was allowed to deep in the dispersion up to the mark.

(iv) pH

The pH of dispersion is measured at 25 °C by using pen type pH meter (Hanna Checker, Mauritius)

(v) Total Solids Content of the Resin (NVC)

Take the weight of glass watch (W_1) and weigh approximately 1 g of resin on an analytical balance. Put the watch glass in an oven at 110 °C for 1 h. After cooling record the weight of watch glass with resin (W_2). By doing so, one can determine total solids content (TSC)/ non- volatile content (NVC) and

remaining will be the volatile content and can be expressed in per cent.

(vi) Colour

The colour of the polyester is measured by using Gardner scale.

Characterization of PU Coatings

(i) Thermal Stability

Thermal stability of PU coating is determined by putting the coated film in an oven at 55° C for 30 d.

(ii) Freeze Thaw Stability

Freeze Thaw Stability of PU coating is determined by putting the coated film at -20° C for 16 h, followed by 8 h between 25-30 °C.

(iii) Gloss

The gloss of the coated film is measured by "Digital Gloss Meter" Rajadhani make, Delhi at an angle of 45 °C.

(iv) Scratch Hardness

Scratch hardness of the coated film is measured by using "Scratch hardness tester". This measurement was carried out by putting weight on the pointer and pulling it on the surface of the coated film at a specified rate.

(v) Flexibility

Flexibility of the coated film is measured by using "Conical mandrel" instrument. The film coated on a tin substrate was bent to 90°. The bend was observed for any break or crack.

(vi) Acid Resistance

The acid resistance of the film was checked by immersing in 2 per cent H_2SO_4 for 24 h.

(vii) Alkali Resistance

The alkali resistance of the film was tested by immersing in 2 per cent Na_2CO_3 solution for 24 h.

Table 1— Properties of polyester polyol

Sl No.	Property	Glycol containing polyols		
		EG	PG	NPG
1	Appearance	Solid	Solid	Solid
2	Acid value (after TMA addition)	25	25	25
3	Hydroxyl value (mg KOH/gm)	525	650	600
4	Colour	Gardner <1	Gardner <1	Gardner <1
5	Viscosity	570 cps	570 cps	570 cps

(viii) Water Resistance

The water resistance of the films was tested by immersing in distilled water for 24 h.

(ix) Solvent Resistance

The solvent resistance of the film was tested by immersing in mineral turpentine oil for 24 h.

Experimental Procedure**(i) Preparation of Polyester Polyol**

Polyester polyols were prepared by reacting (1.1 mole) ethylene glycol (EG)/propylene glycol (PG)/neopentyl glycol (NPG) with (0.6 mole) adipic acid in a four-necked round bottom flask equipped with stirrer, thermowell, nitrogen gas inlet, and a reflux condenser with guard tube. The reaction was continued till the acid value reached below 4. A predetermined quantity of (0.4 mole) trimellitic anhydride was then added and reacted till the acid value reached to 25.

The properties of polyester polyol are given in Table 1.

(ii) Preparation of Polyurethane Dispersions

The respective polyester polyols and solvent (NMP) were charged in a 250 mL four-necked round bottom flask equipped with mechanical stirrer, thermowell, nitrogen gas inlet, condenser, guard tube,

and a dropping funnel. The contents of the flask were stirred below 70°C for 1 h after which TDI was added dropwise, below 70°C. After complete addition the reaction was continued at 70°C for half-an-hour. The contents were then neutralized with triethyl amine (TEA) and dispersed in water. Ethylene diamine was then added to obtain high molecular weight. The composition of PUR dispersion prepared using toluene diisocyanate (TDI) and properties of coated film using PU Dispersion are given in Table 2 and Table 3, respectively.

Results and Discussion

The performance of polyester polyols with respect to the glycol, used in its synthesis, was evaluated by preparing PU dispersion and coating on tin substrate. Three glycols viz., ethylene glycol,

Table 2 — PU dispersion composition

SI No.	Material	Weights
1	Polyester polyol (EGP/PGP/NPGP)	36.80
2	N-methyl-2-pyrrolidone (NMP)	3.40
3	Toluene di-isocyanate (TDI)	2.08
4	Triethyl amine (TEA)	1.80
5	Water	51.10
6	Ethylene diamine (ED)	0.871

Table 3 — Properties of coated film using PU dispersions

SI No.	Property	EGP	PGP	NPGP
1	Appearance	Milky	Milky	Milky
2	pH	7.5	7.3	7.9
3	Viscosity (cps)	68	125	200
4	Drying time, in h, at 25°C	14	14	14
5	Thermal stability (at 55°C for 30 d)	Passes	Passes	Passes
6	Gloss *	54°C	50°C	56°C
7	Freeze thaw stability **	Passes	Passes	Passes
8	Scratch hardness	150g	200g	600g
9	Flexibility	Passes	Passes	Passes
10	Acid resistance (after 24 h)	Passes	Passes	Passes
11	Alkali resistance (after 24 h)	Passes	Passes	Passes
12	Water resistance (after 24 h)	Passes	Passes	Passes
13	Solvent resistance (after 24 h)	Passes	Passes	Passes
14	Abrasion resistance	Passes	Passes	Passes

* Standard gloss value is 57°C, ** - 20°C for 16 h followed by 8 h at 25-30°C

propylene glycol, and neopentyl glycol were selected for preparing polyols. The polyols were prepared under the identical condition, using the same composition, so as to have comparable molecular weight by way of controlling acid and hydroxyl value. Coating properties such as, gloss, scratch, and flexibility were determined for the PU dispersion prepared using these polyols. The results are reported in Table 3. It was observed from the Table 3 that the polyurethane film based on neopentyl glycol containing polyol showed best performance against the other polyols. The scratch hardness, gloss, and flexibility of neopentyl glycol based polyester polyol showed higher values, while ethylene glycol containing polyester polyol based polyurethane showed lower values. The superior properties exhibited by NPG containing polyester polyol may be attributed to the higher number of methylene carbons (highly branched structure), and short chains present in the glycol. The order of performance decreased from NPG to PG to EG. The only change in these

polyols being the structural moiety imparted by each glycol.

Conclusion

Among three polyols used for PU dispersions in the study NPG containing polyester polyol based PU dispersion showed better coating performance.

References

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