

Effect of Dicarboxylic Acids on the Performance Properties of Polyurethane Dispersions

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ABSTRACT: A series of low molecular weight linear polyester polyols were synthesized by using various diacids, neopentyl glycol, as a diol, and a trimethylol propane, as a branching monomer. Polyurethane dispersions were prepared primarily from isophorone diisocyanate, polyester polyol, and dimethylol propionic acid, as potential ionic center for water dispersibility, and were subsequently chain extended with ethylene diamine. The effect of polyester polyols based on variable diacids, on the physico-chemical and thermal properties of polyurethane dispersions were evaluated by hardness, flexibility, impact resistance, solvent resistance, thermogravimetric analysis, and differential

scanning calorimetry. Particle size was evaluated by particle size analyzer. It was observed that the number of alkylene groups present in the polyester polyol soft segment in addition to its molecular weight had a pronounced effect on the particle size, physico-chemical, and thermal properties. With a proper selection of the soft segment, it is possible to fine-tune properties of aqueous polyurethane dispersion coatings with respect to the final application. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 572–580, 2010

Key words: coatings; colloidal stability; polyurethane dispersions; polyester polyol

INTRODUCTION

In the last decade, aqueous dispersions of polyurethane urea (commonly known as polyurethane dispersions) have become one of the most popular binders because of their unrivalled overall properties and scope for applications in functional coatings. Though much more expensive than acrylic dispersions, polyurethane dispersions (PUDs) have several advantages: exceptionally good abrasion resistance, hardness, flexibility, impact resistance, gloss, general chemical resistance, and weatherability coupled with zero to low volatile organic compound (VOC) emission.¹ A further great advantage of PUDs is their ability to form films at quite low temperatures. Aqueous polyurethane dispersions are considered as two-phase colloidal system in which polyurethane particles are dispersed in water as a continuous phase.² They consist of PU backbones with minority of pendant acid or tertiary nitrogen groups, which are completely or partially neutralized by or quaternized, respectively, to form salt.³ There are many parameters such as choice of isocyanate, different ionomers, and types of polyols, which influence the performance of waterborne PUD coatings. Their relative merits and demerits are of great research inter-

est and have been discussed by many authors.^{4–6} Linear saturated polyesters of low molecular weight, find commercial applications mainly as plasticizer in poly(vinyl chloride) where minimal plasticizer losses are required.⁷ However, hydroxyl terminated saturated polyesters are used as a polyol soft segment (SA) for the syntheses of PUDs to obtain a good balance between the hardness and flexibility owing to their plasticizing efficiency.

To date polyurethane industry uses various polymeric polyols mainly polyesters, polyethers, polycarbonates etc. Each has its own advantages and drawbacks, and therefore, rarely, they can fulfill specific application requirements.⁸ However, polyester polyols have gained more importance among them because of their broad spectrum of desirable properties.⁹ Considerable academic and industrial efforts are focused on elucidating the structure–property relationships in segmented polyurethanes, as a result of their versatility in a broad range of applications. The possibility of altering the number of alkylene groups present in a repeat unit of polyol to fine-tune the surface and bulk mechanical properties of polyurethanes though may not be new, remained relatively unexplored in polyurethane dispersion chemistry. Consequently, we have decided to investigate effect of number of alkylene groups and its chain length on the overall performance of PUDs. The present article tries to throw light on this aspect of designing, rather tailoring the coating binder as per the end use requirements.

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TABLE I
Designing Parameters for Polyester Polyols

Polyester Polyol	Diacid/Diol/Triol mole ratio	Parameters			Average functionality fav = e_0/m_0
		Alkyd constant $K = m_0/e_A$	Excess hydroxyl content ratio $R = e_B/e_A$	OH excess%	
POLY I ^a	0.5 : 0.5 : 0.08	1.082	1.250	25%	2.001
POLY II ^b	0.5 : 0.5 : 0.08	1.083	1.250	25%	2.000
POLY III ^c	0.5 : 0.5 : 0.08	1.083	1.250	25%	1.980

^a AA + NPG + TMP.

^b AZA + NPG + TMP.

^c SA + NPG + TMP.

m_0 , total moles; e_0 , total equivalents; e_A , equivalents of acids; e_B , equivalents of glycols.

EXPERIMENTAL

Materials

Sebacic acid (SA) LR (98%), azelaic acid (AZA) LR (99%), adipic acid (AA) LR (98%), triethyl amine (TEA) LR (99%), trimethylol propane (TMP, 98%), and neopentyl glycol (NPG), (99%) were procured from s.d. fine-chem, (Mumbai, India). Dimethylol propionic acid (DMPA) LR (99%) and isophoron diisocyanate (IPDI) were purchased from Aldrich (St. Louis, MO). TMP was dried under vacuum at 1 mmHg and 85°C for 5 h before use. TEA and *N*-methyl-2-pyrrolidinone (NMP) (s. d. fine-chem, India) were dried over 3 Å molecular sieves for 7 days. Ethylene diamine (EDA) was purchased from, Fluka, Switzerland and was used as such without any further purification. Catalyst Fascat 4100 (Butyl stannic acid with 56.85% Sn) was kindly provided by "Tarapur Coatings & Adhesives," Boisar, India. Solvents used in the titration were procured from s. d. fine-chem, (Mumbai, India), and dried over 3 Å molecular sieves before use. The emulsifying agent, defoamer, and biocides were supplied by KTECH, India.

Synthesis of polyester Polyol

In a four-necked round bottom flask, equipped with mechanical stirrer, Dean Stark assembly, thermometer, and nitrogen gas inlet, a predetermined quantity of glycols and diacids were charged as per the formulations given in Table I. The temperature was initially raised to 120°C and thereafter increased with small increments of 20°C per hour, until it finally settled at 180°C, where the reactions were continued (~8 h) till the desired acid value¹⁰ and hydroxyl value¹¹ were obtained (Table II). Polyesterification was carried out in presence of catalyst, Fascat 4100 (0.05 wt % based on total weight of monomers), under a slow stream of N₂ to avoid oxidation because of atmospheric oxygen. The progress of reaction was solely monitored from acid value and the quantity of water of esterification accumulated during the course of reaction. Finally, the polyester polyols thus produced were discharged into glass stoppered bottle and were placed in vacuum desiccator before the on set of further reactions. The reaction scheme for the synthesis of polyester polyol is given in Figure 1. Table II displays the characteristics of newly synthesized polyester polyols.

TABLE II
Characteristics of Synthesized Polyester Polyols

Property	POLY I	POLY II	POLY III
Physical properties			
Molecular weight	950	1000	1050
Nominal functionality	2	2	2
Physical state	Light viscous liquid	Yellow viscous liquid	Clear viscous liquid
Colour (visual observation)	Pale cream	Pale yellow	Off white
Solids (Wt %)	100	100	100
Chemical properties			
Hydroxyl number (mg KOH/g)	118.10	112.2	104.85
Acid number (mg KOH/g)	<5	<5	<5
Polyester type	Aliphatic	Aliphatic	Aliphatic

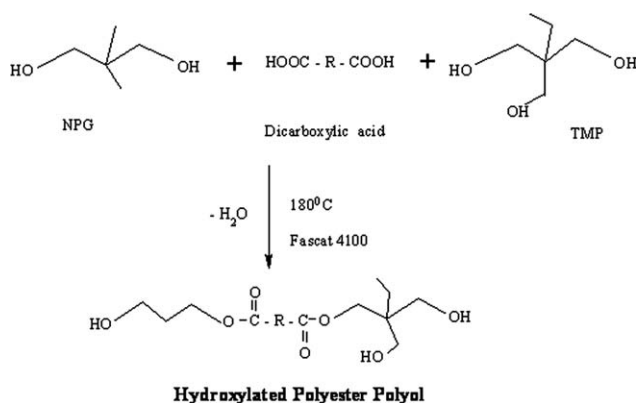


Figure 1 Scheme for the synthesis of polyester polyol.

Synthesis of polyurethane dispersions

Anionic PUDs were prepared by “prepolymer mixing” method¹ in two steps viz. synthesis of NCO-terminated prepolymers and preparation of dispersions by introducing anionic centers to aid dispersions (Fig. 2). Basic formulation and characteristics of PUDs are given in Tables III and IV, respectively. Isocyanate terminated prepolymer was prepared by reacting POLY I from previous step with hydrophilic monomer DMPA in cosolvent NMP (5 wt % based on the total reaction mass) in a 500 mL four necked round bottom flask fitted with mechanical stirrer, thermometer, nitrogen gas inlet, and reflux condenser. The mixture was heated on heating mantle at 80°C under nitrogen atmosphere for about 30 min. The mixture was homogenized by mechanical stirring. After complete mixing, the IPDI and catalyst DBTDL (0.03 wt % based on total solids) were slowly added to the flask to maintain the reaction temperature at 85°C. The reaction proceeded until the amount of residual isocyanate groups reached a theoretical end point, and calculated on the basis that all hydroxyl groups had reacted with isocyanate groups. The NCO content of the prepolymer was determined by dibutylamine back titration method.¹² Upon obtaining the theoretical NCO value, the prepolymer was cooled to 60°C, and the stoichiometric amount of TEA dissolved in NMP was added to it and stirred for 1 h to ensure complete neutralization of carboxylic groups of prepolymer. The resultant polyurethane anionomer was then dispersed in water at stirring rate of 4000 rpm and desired molecular weight was achieved by add-

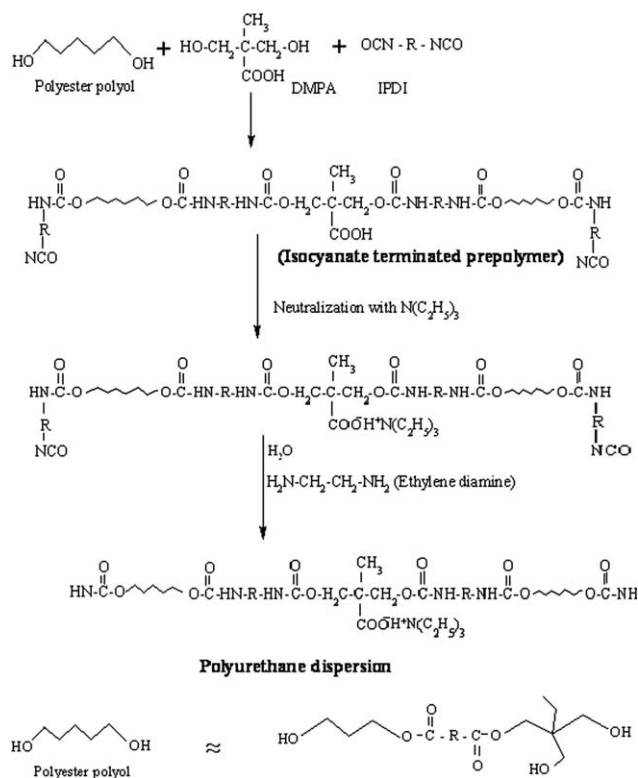


Figure 2 Scheme for the synthesis of anionic polyurethane dispersions.

ing EDA as a chain extender. For stabilization of dispersion, the emulsifying agent USOL K-98 (0.9% of total mass), defoamer, and biocides (0.1% of total mass) (KTECH, India) were added to aqueous dispersions. PU dispersion thus obtained had the solid contents of 30% by weight.

Preparation of films

Films were prepared by casting the newly synthesized samples onto a Teflon plate at room temperature, followed by drying at 40°C (24 h), at 60°C (24 h), and at 70°C (24 h). This trend of drying is essentially to ensure slow drying. It is also possible to evaporate the solvent at a fixed temperature either room or elevated temperature. After demolding, the films were stored in a desiccator at room temperature for further studies.

TABLE III
Basic Composition (g) of Polyurethane Dispersions with Variable Dicarboxylic Acid

Sample	Polyester backbone	Polyester polyol (g)	DMPA (g)	IPDI (g)	TEA (g)	EDA (g)
PUD I	POLY I	25.00	3.460	8.520	0.620	0.929
PUD II	POLY II	25.00	4.160	10.55	0.478	1.000
PUD III	POLY III	25.00	3.400	9.190	0.468	0.980

TABLE IV
Characteristics of Polyurethane Dispersions

Property	PUD I	PUD II	PUD III
Polyester backbone	POLY I	POLY II	POLY III
Charge	Anionic	Anionic	Anionic
Isocyanate type	IPDI	IPDI	IPDI
Chain extender	Ethylene diamine	Ethylene diamine	Ethylene diamine
NH ₂ /NCO equivalent ratio	1.05	1.05	1.05
Appearance	Transparent	Transparent	Milky white
Particle size (nm)	72.8	34.4	27.8
PH	8.2	8.1	8
Viscosity @ 30°C (cps)	35	46	59
Colloidal stability	>6 Months	>6 Months	>6 Months
Solids (wt %)	~ 30	~ 30	~ 30

Fourier transform infrared spectroscopy

The infrared spectra of polyurethane dispersions were obtained on a Perkin Elmer FT-IR spectrophotometer. Being in the form of thick syrup, a thin film of resin was cast over NaCl block.

Particle size analysis

Particle size is the important parameter in deciding the end use industrial applications of aqueous polyurethane dispersions. Particle size was measured using Malvern Instrument India, Malvern Instrument, Type Zetasizer 1000 HS.

Colloidal stability

The colloidal stability of waterborne dispersions is a very vital characteristic, which determines their safe storage period. These measurements were carried out in a sealed container on storage of the newly synthesized PUDs at room temperature (30–36°C) and were observed for any kind of phase separation.

Thermo gravimetric analysis

The decomposition profile of samples was thermogravimetrically analyzed using 'Diamond' Perkin Elmer analyzer. Film samples ranging from 4 to 6 mg were placed in a platinum sample pan and heated from 30 to 800°C, under N₂ atmosphere at a heating rate of 10°C/min. The weight loss and temperature difference were recorded as a function of temperature.

Glass transition temperatures

The glass transition temperatures (T_g s) were determined on a NETZSCH DSC200 PC using aluminium crimped pans and a N₂ flow at 20 mL min⁻¹. To erase the thermal history effects from the samples, the temperature was equilibrated at 150°C for 3 min

at the beginning of each experiment. The measurements were carried out between -100°C and +150°C at a heating rate of 10°C min⁻¹.

Mechanical properties

The samples were applied onto previously degreased mild steel and glass panels using "RDS USA make" bar coater (50 μ film thickness). Coated panels were then allowed to air dry at room temperature in fully ventilated atmosphere and were subjected to testing only after 7 days to ensure the full maturation of coated films.

Shore A hardness

The hardness was measured by Shore A Hardness Tester as per ASTM D 2240-75. The hardness value is determined by the penetration of the Durometer indenter foot into the sample. The final value of the hardness depends on the depth of the indenter. Hardness values range from 0 (for full penetration) to 100 (for no penetration).

Pencil hardness

The PUD samples were coated onto mild steel panels using bar coater ("RSD" USA make) of 50 μm and were allowed to dry at room temperature for a week before testing. A relative measurement of hardness was achieved by rating the hardness of lead pencils of the same brand ranging in hardness from (softest) 6B, 5B, 4B.4H, 5H, 6H (hardest) as per ASTM D3363-92a.

Scratch hardness

The scratch hardness was measured using scratch hardness tester having a hardened steel hemispherical point of 1 mm diameter as a needle according to ASTM D 5178. The panels were loaded with

different weights, until a clear scratch showing the bare metal was seen.

Adhesion

The samples coated onto mild steel were cut into squares of 1mm × 1mm using cross hatch tester ("Sheen" make) as per ASTM D-3359-95a. Adhesive tape was applied to the cross-cut section and then stripped off. The number of squares intact gives a measure of adhesion of the sample. The percent adhesion was calculated as follows:

$$\% \text{Adhesion} = \frac{\text{Number of intact squares in the tapa application area}}{\text{Number of total squares in the tapa application area}} \times 100 \quad (1)$$

Flexibility

This property is related to elongation of the film, and it can be measured by using conical mandrel (1/4") as per ASTM D 522-939. Tin plates were coated with the sample to check for flexibility. These plates were allowed to dry for a week before checking the flexibility on conical mandrel (1/4").

Impact resistance

Impact resistance was measured using a falling weight type impact tester (Komal Scientific, Mumbai, India) as per ASTM D2794A. In this method, a hemispherical indenter of known weight is dropped down onto a coated (50 μ film thickness) panel, which is fixed at the base of the instrument. An opening opposite to the indenter in the base support on which the panel rests permits deformation of the panel. The indenter is dropped from increasing heights until the film cracks (the maximum height of the instrument is 48 inches and weight of the indenter is 6.25 lbs). If the coated side is up so the indenter directly hits the film, the test is called a direct impact test. If the back of the coated panel is up, the test is called a reverse impact test.

Chemical resistance

Chemical resistance was checked according to the ASTM D 1647-89. Glass panels coated with samples of WPU and emulsion hybrids were allowed to dry for 3 days. The periphery of the glass panels was coated with wax to restrain the migration of water under the film from open ends. The panels were then dipped into 3% (w/w) sulphuric acid solution

and 3% (w/w) NaOH solution, and the change in the appearance was monitored after 3 days.

Solvent resistance

The solvent resistance was carried out as per the "Double Rubs" method using a piece of white cotton cloth. (ASTM D 5402 - 93). The solvents used were methyl ethyl ketone and toluene. The result reported was the minimum number of double rubs at which the films were observed to fail or else 100, which was the maximum number of double rubs carried out.

RESULTS AND DISCUSSION

Infrared spectroscopy

The Infrared spectroscopy (IR) spectra of all the waterborne PUD films (Fig. 3) showed characteristic absorption bands at 3361–3382 cm⁻¹ and 2928–2961 cm⁻¹, indicating N–H stretching vibrations and –CH₂ asymmetric stretching, respectively. The band at 1728 cm⁻¹ to 1738 cm⁻¹ corresponds to C=O stretching from ester and urethane groups. Absence of characteristic NCO band at 2270 cm⁻¹ confirmed the formation of urethane linkage because of complete reaction of NCO with active hydrogen of a chain extender. The band between 1535 and 1560 cm⁻¹ (ν C–N and δ N–H), was attributed to amide II stretching modes of polyurethane and polyurea, and band at 1167–1169 cm⁻¹ is because of asymmetric ν C–O–C.

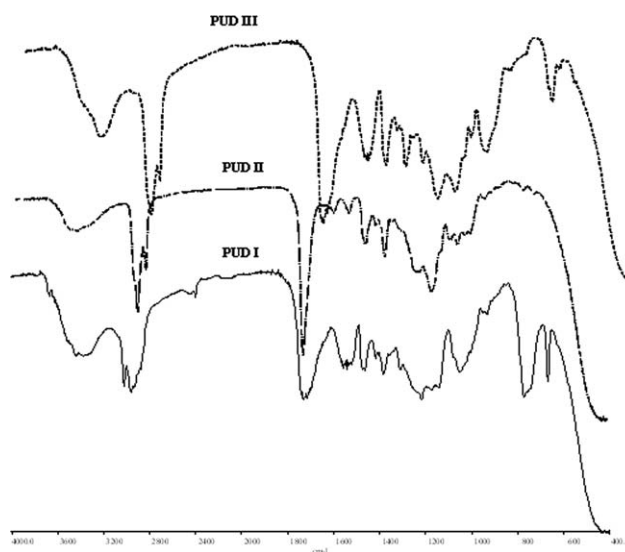


Figure 3 IR spectrum of polyurethane dispersion with variable dicarboxylic acids.

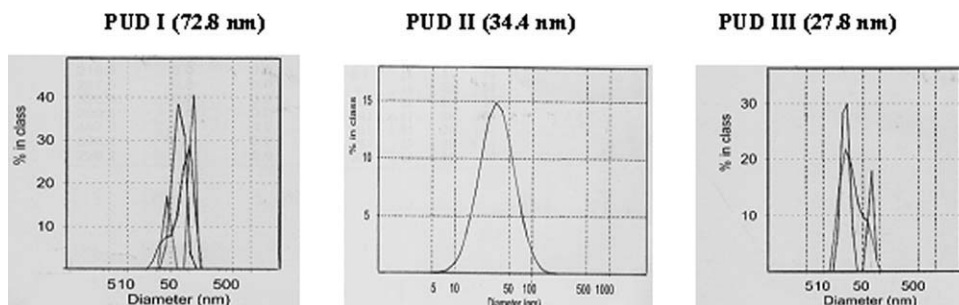


Figure 4 Mean intensity particle size distribution of polyurethane dispersions based on variable diacids.

Particle size

A representative mean intensity particle size distribution was given in Figure 4. All the samples exhibited particle size in the range of 27–72.8 nm, which was in nanometer scale. It is interesting to note that, as molecular weight of the SA in PUD sample increased, the particle size decreased and viscosity increased. Chain flexibility plays a pivotal role in particle size distribution. With increase in number of alkylene groups present in the polymer SA, chain flexibility of PUD increases, which in turn reduces particle size of dispersion. This can be explained as flexible particles are more deformable in shear field, and thus, at the disperse stage, the dispersed phase can be more easily broken into smaller ones.^{13,14} It is widely accepted that the ionic groups are located predominantly on the surfaces of particles, and the ionomer dispersions are stabilized by the formation of electrical double layers. As the flexibility of PU chain increases with increasing number of alkylene groups, the formation of micelle structure in water having ionic sites on the surface will be more plausible. This augments the thickness of electrical double

layers because of the effective structuring of the micelles, leading to an increase in effective volume of the dispersed phase of the emulsion. The rate of water swelling also increases as the particle size decreases because of the increased total surface area of the particles.¹⁵ Thus, dispersion viscosity increased because of the hydrodynamic volume of the finer particle size and swelling of droplets. Particle size has a strong influence on stability of PUDs. Finer particles prevent coagulation during the dispersion process and result in more stable form of dispersion. The broadness in distribution of particle size of PUDs could be the result of synthetic procedure involving step-growth polymerization followed by dispersion in water. The order of particle size is as follows

$$\text{PUD I} > \text{PUD II} > \text{PUD III}$$

The variation of average particle size and PH are shown in Table IV.

Colloidal stability

The results reported in Table IV reveal that all the three PUDs were stable for more than 6 months. It was proposed that ionomer dispersion can be stabilized because of the formation of electrical double layers between the ionic constituents, which were chemically bound to PU and their counterions, which migrate into water phase around the particles. The interference of electrical double layers of

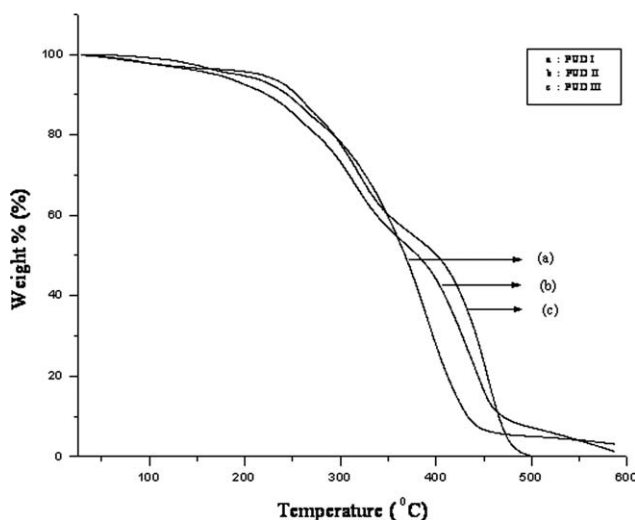


Figure 5 Thermogravimetric curves of different polyurethane dispersions.

TABLE V
Characteristics of Polyurethane Dispersions

PUD	Glass transition temperature from DSC	TGA weight loss	
		T_{10}	T_{50}
PUD I	-37.7°C	244°C	367°C
PUD II	-39.1°C	230°C	385°C
PUD III	-45.4°C	255°C	406°C

T_{10} , temperature corresponding to 10% weight loss; T_{50} , temperature corresponding to 50% weight loss.

different particles resulted in particle repulsion, leading to the stabilization mechanism of dispersions.¹⁶

Thermogravimetric analysis

TGA curves of various PUDs were shown in Figure 5, and thermal decomposition data were given in the form of IDT (initial degradation temperature) and thermal indexes T_{10} and T_{50} (i.e., the temperatures corresponding to a 10% and to 50%) of weight loss in Table V. An investigation of thermograms reveals that in all the three cases, there is hardly any weight loss before 198°C. The TGA curves show two distinct steps of degradation. The first stage of decomposition is because of degradation of hard segment and starts above 200°C and ends at ~ 360–380°C, while the second step of degradation is because of degradation of SA and ends above 480°C with a less carbonaceous mass. In the initial stage of degradation, the order of stability had the trend PUD III > PUD I > PUD II, whereas in the second degradation stage, the thermal stability of PUD II falls intermediate between PUD III and PUD I. This trend of degradation shows that there is a linear relationship between thermal stability of PUDs and the molecular weight of their SAs. Thus, the higher stability of PUD III can be attributed to higher molecular weight of its SA, whereas lowest stability of PUD I can be ascribed to the least molecular weight of its polyester backbone (AA). While synthesizing polyurethane dispersions, we have used same type of IPDI, hydrophilic monomer DMPA and maintained the same isocyanate index, NCO/OH and NCO/NH₂ equivalent ratio. Therefore, the difference in the thermograms could be attributed only because of the difference in polyol structure resulting from the variation in number of alkylene groups on the main polyester backbone of PUD. Thus, it can be inferred from earlier analyses that type of dicarboxylic acids have pronounced effect on the degradation behaviour of PUDs.

DSC analysis

The effect of nature of backbone on the thermal behaviour of polyurethane dispersion was shown in Figure 6. The T_g s obtained from DSC measurement are listed in Table V.

There was a slight variation in glass transition temperature of three PUD samples, which was found in the temperature range of -45.4°C to -37.7°C.

PUD I exhibits two glass transition zones at temperatures -37.7°C and 44°C. The lower glass transition temperature (T_g) is attributed to the SA, whereas higher T_g is attributed to hard segment phase. Thus,

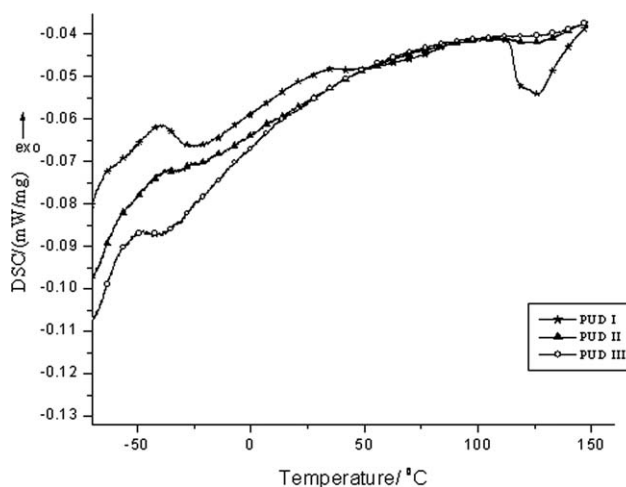


Figure 6 DSC analysis of polyurethane dispersions based on different diacids.

the occurrence of two separate T_g s in case of PUD I is indicative of phase separated morphology,¹⁷ which facilitates the crystallization and regular arrangement of hard domains in case of PUD I.

PUD II and III exhibit single T_g , indicative of higher miscibility of hard and SAs. However, in this study, we have focused mainly on T_g of SA. PUD I has the highest T_g (-37.7°C), whereas PUD III shows the lowest T_g value (-45.4°C). PUD II falls intermediary with the T_g value -39.1°C. Thus, we can say that T_g increased linearly with decrease in chain length of polyester backbone. This may be because of the presence of less number of alkylene moieties on shorter chain of polyester polyol backbone, which would increase the crosslinking density and thereby offered more resistance to rotatable bonds.¹ In case of PUD I, the endotherm is observed around 100–150°C. It is suggested that this endotherm reflects the melting behaviour that is associated with the disappearance of the long range order in the hard segment microdomains of urethanes.¹⁸ Thus, an obvious relationship can be observed between T_g of PUDs and number of alkylene groups present on their polyester backbone.

HARDNESS

Shore A

Shore A hardness observations (Table VI) confirmed the slow and steady increase in the hardness of the films, as the molecular weight of the SA decreased. The shorter SA implies the closer molecular packing and higher film hardness. The PUD I has the higher hardness when compared to other two PUDs, which may be because of higher cohesive forces in its shorter polyol backbone leading to relatively denser crosslinking.

TABLE VI
Coating Properties of Polyurethane Dispersions

Property	PUD I based on POLY I	PUD II based on POLY II	PUD III based on POLY III
Mechanical properties			
Hardness (shore A)	81	69	60
Pencil hardness	H	5B	2B
Scratch resistance	1400	1200	1150
Adhesion (cross hatch)	100%	100%	100%
Flexibility (conical mandrel 1/4")	Passes	Passes	passes
Impact Resistance (inch – pound)			
Direct	160	160	160
Reverse	100	120	120
Performance properties			
Acid alkali resistance^a			
H ₂ SO ₄ , 3%	Unaffected	Unaffected	Unaffected
NaOH, 3%	Blushed	Haziness	Haziness
Solvent resistance^b			
MEK	40	28	70
Acetone	32	40	60
Toluene	40	28	65

^a 3 days immersion test.

^b Number of double rubs that the coating sustained without any damage.

Pencil hardness

It can be seen from Table VI that PUD I showed highest hardness value followed by PUD II and PUD III, which satisfy universal accepted rule of hardness.

Scratch hardness

The data in Table VI reveal that the PUD based on a adipic acid (PUD I) offered comparatively better hardness among the three samples. It could bear the weight of 1400 g. The PUD coatings based on AZA and SA (PUD II and III respectively) had the hardness of 1200 and 1150 g, respectively. These results are in good agreement with shore A and pencil hardness results.

Adhesion

Adhesion or adherence is the phenomenon in which interfacial forces hold surfaces together. No change in the adhesion was observed with a variation of diacids in case of all the polyurethane dispersions. All the coatings showed a 100% adhesion. (Table VI).

Flexibility

All the PUDs showed excellent flexibility on conical mandrel bend test. (Table VI) The principal linkage of polyurethanes, $-\text{NH}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-$ itself was responsible for the high degree of flexibility of polyurethane dispersions, where the presence of extra oxygen other than the carbonyl group oxygen imparted flexibility to the chains. However, in such linear PUDs, long chain of polyester SA could be the primary reason for flexibility of PUDs.

Impact resistance

It can be seen from Table VI that all the samples show full scale direct impact; however, their reverse impact was limited to a maximum value 100 for PUD I and 120 for PUD II and III, respectively.

Chemical resistance

The resistance of PUD films to acid and alkali is shown in Table VI. The data showed that all the PUD film samples offered a good resistance to sulphuric acid (3%); however, PUD I showed a kind of blistering and blushing effect after 24 h, when immersed in 3% NaOH. In case of PUD II and III, there was slight loss in gloss (visual observation) after 24 h and slight swelling was observed only after 3 days. It was apparent that increase in chain length and there by number of alkylene moieties on the polyester polyol backbone would increase the chemical resistance of PUDs and, thus, shows the following trend:



Solvent resistance

The solvent double rub test revealed that the number of double rubs that the coating sustained without any damage was more in case of PUD III; however, coatings of other PUDs (PUD I, and II) were seen to have comparatively poor solvent resistance.

CONCLUSIONS

Waterborne polyurethane dispersions offer a great promise in VOC compliant coatings because of their versatility and broad array of thermal and mechanical properties. From the present study, it can be concluded that, in case of PUDs based on the aliphatic polyester polyols, number of alkylene groups present in the SA played a significant role in deciding the final thermo-chemical and mechanical properties of the coatings. Particle size of polyurethane dispersions was found to have strong correlation with colloidal stability, chain flexibility, and viscosity of dispersion. Thus, the results indicate that the length of polyester chain and number of alkylene groups present in the backbone of PUD have pronounced effect on their ultimate performance properties. The chemical modifications of these polyurethane dispersions through C=C double bond unsaturation are under investigations in our laboratory.

References

1. Athawale, V. D.; Peshane, S. N. *Eur Coat J* 2002, 1, 45.
2. Hourston, D. J.; Williams, G.; Satguru, R.; Padget, J. D.; Pears, D. *J Appl Polym Sci* 1998, 67, 1437.
3. Zhang, S.; Miao, W.; Zhou, Y. *J Appl Polym Sci* 2004, 92, 161.
4. Krol, P.; Krol, B.; Pikus, S.; Kozak, M. *Colloid Polym Sci* 2006, 285, 169.
5. Krol, P.; Krol, B.; Holler, P.; Telitsyna, N. *Colloid Polym Sci* 2006, 284, 1107.
6. Chen, Y.; Chen, Y. L. *J Appl Polym Sci* 1992, 46, 435.
7. Subramani, S.; Park, Y. J.; Lee, Y. S.; Kim, J. H. *Prog Org Coat* 2003, 48, 71.
8. Yeganeh, H.; Shamekhi, M. A. *Polym Int* 2005, 54, 754.
9. Kim, B. S.; Kim, B. K. *J Appl Polym Sci* 2005, 97, 1961.
10. ASTM D 16392-90. Standard Test Method for Acid Value of Organic Coating Materials, Annual Book of ASTM standards; ASTM: Philadelphia, 1997; Vol. 06.03, p 325.
11. ASTM D 1957-286. Standard Method for Hydroxyl Value of Fatty Oils and Acids, Annual book of ASTM standards; ASTM: Philadelphia, 1997; Vol. 06.03, p 403.
12. David, D. J.; Staley, H. B. *Analytical Chemistry of Polyurethanes*, High Polymer Science Series; Wiley-interscience: New York, 1969.
13. Han, C. D. *Multiphase Flow in Polymer Processing*; Academic Press: New York, 1981.
14. Utraki, L. A. *Polymer Alloys and Blends*; Hans Publishers: New York, 1989.
15. Li, Q.-A.; Sun, D.-C. *J Appl Polym Sci* 2007, 105, 2516.
16. Satguru, R.; McMahon, J.; Padget, J. C.; Coogan, R. G. *J Coat Technol* 1994, 66, 45.
17. Lee, Y. M.; Lee, J. C.; Kim, B. K. *Polymer* 1994, 35, 1095.
18. Xiao, H.; Kiao, H. X.; Frisch, K. C.; Malwitz, N. *J Appl Polym Sci* 1994, 54, 1643.