

Effect of Ionic Content, Solid Content, Degree of Neutralization, and Chain Extension on Aqueous Polyurethane Dispersions Prepared by Prepolymer Method

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ABSTRACT: There are many variables in the preparation of aqueous polyurethane (PU) dispersions. Carboxylic acid content, solid content, degree of pre/postneutralization of the carboxylic acids, and chain extension all impact dispersion particle size, viscosity, pH, molecular weights, and glass transition temperature. This study evaluated the impact of these variables on a given PU dispersion formulation prepared from isophorone diisocyanate, an aliphatic polyester polyol, dimethylol propionic acid, and hexamethylene diamine with triethyl amine as the neutralizing base and *N*-methyl pyrrolidone as the cosolvent. Changes in carboxylic acid content, degree of preneutralization, and chain extension were found to have the expected impacts on dispersions properties. Increased ionic content in the dispersion

step led to lower particle size and higher viscosity, increased chain extension with its concurrent increase in molecular improved subsequent film properties. Surprising results were obtained by varying the amount of postneutralization and from increased solids content at the time of dispersion. Unexpectedly, both of these variations led to much higher dispersion viscosities and particle size in solution. To have these changes take place, it is theorized that there is a major change in solution morphology caused by these modifications. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 2514–2520, 2005

Key words: polyurethane dispersion; prepolymer method; compositional variations

INTRODUCTION

Owing to the stronger calls for low-pollution chemical industry, aqueous polyurethanes have been forcing their way into the marketplace. Furthermore, waterborne polyurethanes possess their unique price advantage, for the costly organic solvents could be replaced by the aqueous medium. In the past 60 years, much literature and thousands of patents were issued, which kept steady improvement of the production technology and the quality of waterborne polyurethanes. The work of Dr. Dieterich and his colleagues at Bayer A. G. should be noted,^{1,2} which pioneered the field and inspired much of the work in this area. Today, waterborne polyurethanes have begun to find their application in areas previously serviced only by their solventborne analogs, especially as coating for various fibers, adhesives for alternative substrates, primers for metals, caulking materials for sewer sealants, emulsion polymerization media for different monomers, paint additives, defoamers, associate thickeners, pigment pastes, and textile dyes.^{3–15}

Polyurethanes (PU) are segmented polymers comprising of alternating sequences of soft segments and hard segments, which constitute a unique microphase separation structure.¹⁶ Since ions are introduced into either hard or soft segments, and imparting many properties to the polyurethane matrix, attention being drawn to these polyurethane ionomers.^{16,17} There has been a wide range of work done in the field of synthesis and characterization of various kinds of polyurethanes and polyurethane ionomers.^{18–20} Ionomer type PU dispersion is made by the dispersion of amphiphilic prepolymers prepared by the addition of diisocyanates, polyols, and dimethylolpropanic acid (DMPA) and subsequent chain extension.^{21–22} As in the case of conventional segmented PU, polyurethane ionomers contain low-polarity flexible segments and urethane groups, which are polar and capable of interaction *via* hydrogen bonds. Ionic groups in polyurethane tend to interact with each other and aggregate but are attached to the "alien" hydrophobic neighborhood.

To understand the complexities of these new aqueous polymer systems and to improve and tailor-make them for various innovative end-uses is a scientific and technological challenge. It has been discovered that the degree of preneutralization,^{23–28} the type of ionic component,²⁹ and the counterion³⁰ used all con-

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tribute significantly to the properties of PU ionomers. Our recent investigation on the effect of ionic content and preneutralization on the properties of PU dispersion is very much in agreement with the results reported earlier by other researchers.^{23–30} However, detail studies with regard to the effect of postneutralization, solid content, and chain extension on the properties of PU dispersions is scarcely reported in the literature.²⁶

This article considers the preparation and properties of ionomer-type waterborne PU dispersions. The effect of ionic content, solid content, pre and postneutralization, chain extension on the particle size, viscosity, pH, molecular weights, glass transition temperature, and degradation temperature of PU dispersion are discussed.

EXPERIMENTAL

Materials

Polyester polyol (Desmophen 1019–55) and isophorone diisocyanate (Desmodur-I) were supplied by Bayer MaterialScience, Pittsburgh, PA. Dimethylol propionic acid (DMPA), dibutyltin dilaurate (DBTDL), 1-methyl pyrrolidinone (NMP), triethyl amine (TEA), hexamethylene diamine (HMDA), diethyl amine (DEA), and tetrahydrofuran (THF) were received from Aldrich Chemical Co. Ethoxylated nonylphenol ammonium sulfate (Abex EP-110, Rhodia Chemicals, Cranbury, NJ) was used as an external surfactant to increase the storage stability. Defoamer (Foamstar-111) was received from Cognis Co., Cincinnati, OH. All the materials were used as received.

Prepolymer synthesis. A 250-mL round-bottomed, four-necked flask with a mechanical stirrer, thermometer, condenser with nitrogen in/out let, and a pipette outlet was used as a reactor. The polymerization was maintained using a constant temperature oil bath. Desmophen 1019–55 and DMPA were charged into the dried flask at 70°C. While stirring, NMP (12 wt % based on total feed) was added, and stirring was continued until homogenized mixture was obtained. Desmodur-I and DBTL were added drop wise, and stirring was continued for 30 min at this temperature. The mixture was heated to 80°C for about 3 h to afford NCO-terminated prepolymers. The change of the NCO content during the reaction was determined using a standard dibutylamine back titration method. On reaching the theoretical NCO value, the reactions were cooled to 60°C, and the neutralizing solution TEA (DMPA equiv.) dissolved in NMP (2 wt %) was added, and stirred for 30 min while maintaining the temperature at 60°C.

Dispersion and chain extension. Dispersion of PU was accomplished by adding the neutralized prepolymer to the mixture of water and surfactant (4 wt % based

on total solid). Agitation was maintained at 750 rpm. After 20 min, 20 wt % solution of HMDA in water was added for a period of 30 min, and chain extension was carried out for the next 1 h. At the end, defoamer (Foamstar-I) was added, and stirring continued for 5 min at a speed of 250 rpm. For experiments requiring control of the polymer molecular weight, diethyl amine was included in the chain extension step. In the preparation of all polymers, the ratio of isocyanate groups to amine groups (from chain extension/termination) was 1.1:1. The rest of the isocyanate groups (10%) reacted with water.

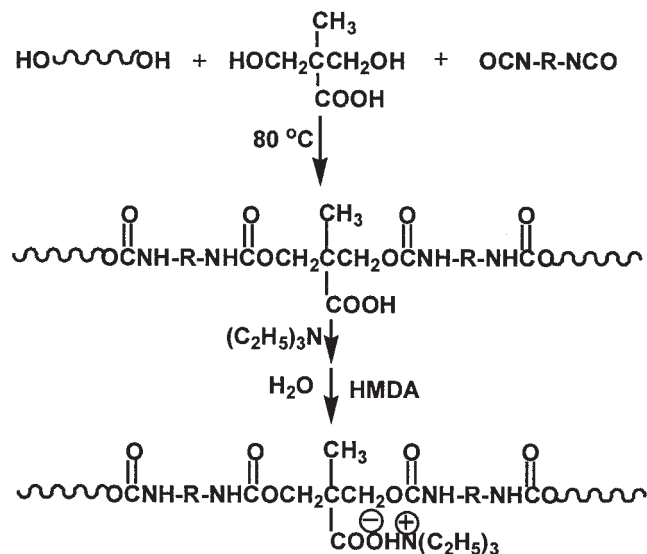
Solid polymer isolation. Films were prepared by casting onto a polypropylene plate and drying in a vacuum oven at 120°C for 3 days. The films were used for gel permeation chromatography (GPC), differential scanning calorimetry (DSC), and thermogravimetric analyses (TGA).

Measurements. Particle sizes (PS) were determined using a Microtrac UPA 250 light-scattering ultrafine particle analyzer. The sample was diluted to the required concentration with distilled water before measurement. Viscosity measurements of the dispersions were performed using Brookfield DV-I viscometer, at a shear rate of 100/s at 25°C. GPC measurements were carried out using a Polymer Laboratories model PL-ELS 1000 equipped with an ELSD detector, PL gel 5 μm mixed C, $300 \times 7.5 \text{ m}^2$ column and Waters 590 HPLC pump using THF as a solvent at a flow rate of 1 mL/min. The GPC was calibrated with PMMA standards. DSC was performed using a TA Instruments DSC 2920 module (TA 2100 controller) at a heating rate of 10°C/min in a nitrogen atmosphere. TGA was conducted on a TA instruments SDT 2960 module (TA 2100 controller) at a heating rate of 20°C/min under nitrogen. The viscoelastic measurements of PU films were carried out using an advanced Rheometrics Expansion System (ARES), equipped with two 25 or 40 mm diameter parallel plates.

RESULTS AND DISCUSSION

The synthesis of PU dispersion is presented in Scheme 1. The ionic groups play a major role for making a stable dispersion in water.

Effect of DMPA content. The effect DMPA content (wt % on solids) on particle size and viscosity (η) of the PU dispersions is shown in Figure 1. For all samples, the other parameters were kept constant for this portion of the study with 32 wt % solids, with neutralization and chain extended to 90%. The particle size decreased markedly from 140 to 50 nm with an increase in DMPA content from 4 to 5 wt %, and then decreased slowly or remained constant at higher level. The η showed a corresponding increase with DMPA content, and remained constant after 6 wt %. With increase in DMPA content and a stoichiometric



Scheme 1 Elementary steps for the synthesis of PU dispersion.

amount of $N(C_2H_5)_3$, the number of $-COO^-HN^+(C_2H_5)_3$ ionic groups in PU dispersion increased. Each particle in the dispersion is absorbed by a thin layer of water due to the presence of hydrophilic $-COO^-HN^+(C_2H_5)_3$ groups on the surface of the particle. With a decrease of the size of polymer dispersion particles, the relative size of the water layer to total particle size is increased. Concurrent with the particle size decrease, there is an increase in the number of particles.^{26,31,32} Hence, the effective volume of the dispersed phase increases resulting in an increase in viscosity. The pH of the PU dispersions decreased slightly from 8.3 to 7.7 with increase in DMPA content from 4 to 7 wt %.

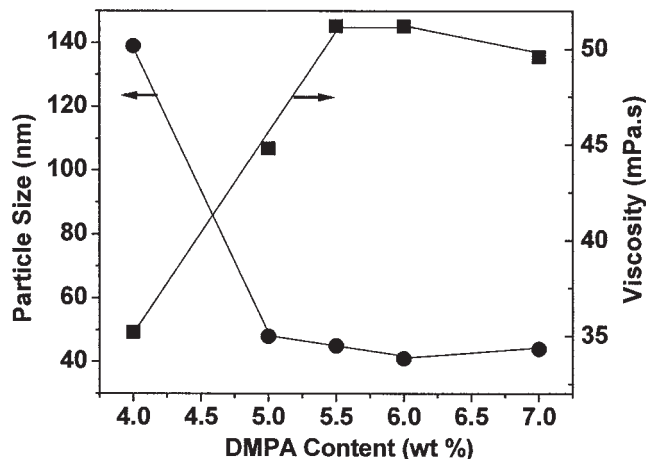


Figure 1 Effect of DMPA content on particle size and η of PU dispersions. Chain extension = 90%, Preneutralization = 100%.

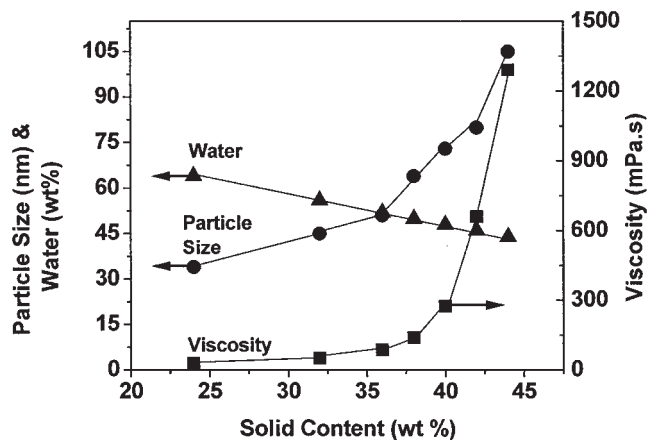


Figure 2 Effect of solid content on particle size and η of PU dispersions. Chain extension = 90%, Preneutralization = 100%.

Impact of solid content. The impact of the solid content on particle size and viscosity of PU dispersion is presented in Figure 2. All of the samples for this portion of the study were prepared at 5.5 wt % DMPA, 100% neutralization, and chain extended to 90%. Both the particle size and viscosity found to increase with higher solid content. The increase in particle size at a fixed ionic content as a function of solids during the dispersion step is surprising. This may be a result of either (1) the NMP partitioning differently at higher solids (it is fixed at 12% of total system) or (2) a high NMP content in the continuous phase may decrease dispersant efficiency. The water content (wt %) in the dispersion decreases (Fig. 2) with an increase in solid content, because NMP content (12 wt %) was kept constant for all the experiments. Hence, as would be expected there is an increase in viscosity, which is attributed to the increased dispersed volume fraction. At 46 wt %, the dispersion step failed as the dispersed volume exceeded that of the continuous phase. When water content is equal or more than the solid content, the particle was dispersed in water. Hence, the maximum solid content for PU dispersion is 44 wt %, where the water content is same as solid content (Fig. 2).

Effect of degree of neutralization. The results for changing the degree of neutralization on particle size and viscosity of the PU dispersion is presented in Figure 3. All of the samples for the study of the neutralization effects were prepared at 32 wt % solids, with 5.5 wt % DMPA and chain extended to 90%. With simple preneutralization, the particle size decreased from 252 to 45 nm with increase in the $N(C_2H_5)_3$ equivalents from 60 to 100% based on DMPA. The decrease in particle size with increase in the degree of preneutralization was attributed to the increase in the ionic content due to the transformation of hydrophobic $-COOH$ groups to hydrophilic $-COO^-HN^+(C_2H_5)_3$ ions. With increase in the ionic content, the particle size

	Equiv. % of TEA vs DMPA					
	40	50	60	70	80	100
Particle Size(nm)						45
Viscosity(mPa.s)						51
Particle Size(nm)					84	90
Viscosity(mPa.s)					38	57
Particle Size(nm)				140	140	148
Viscosity(mPa.s)				36	36	153
Particle Size(nm)			252	252	252	290
Viscosity(mPa.s)			34	34	34	2568
Particle Size(nm)		bimodal				298
Viscosity(mPa.s)		30				4692
Particle Size(nm)	bimodal					300
Viscosity(mPa.s)	28					5504

Figure 3 Effect of degree of pre and postneutralization of PU dispersion.

decreased with a concurrent increase in the number of particles.^{31,32} Again, as discussed for the DMPA study, increase in ionic content increases the effective dispersed volume. Hence, viscosity increases with an increasing degree of preneutralization.

The particle sizes were bimodal for the PU dispersion made with 40 and 50% preneutralization. This was due to the lack of ionic groups present to stabilize the dispersion. The pH of PU dispersions increased from 7.3 to 8.2 with increase in the degree of preneutralization from 40 to 100%.

To study the effect of the degree of postneutralization, additional TEA was added to the PU dispersions made with different levels of preneutralization. It was assumed that the postneutralization did not change the number of particles. For all the dispersions, the particle size and the viscosity increased following the postneutralization to a 1:1 ratio of TEA to COOH (100%). Postneutralizing the PU dispersion made with 60% preneutralization changes resulted in changes in particle size and viscosity of 252 to 290 nm, and from 35 to 2568 mPa s, respectively. As prepared, the 60% preneutralized PU dispersion contains a maximum of 60% $\text{—COO}^-\text{HN}^+(\text{C}_2\text{H}_5)_3$ ions as of the acids. The remaining —COOH groups are hydrophobic, and trapped inside the core of the particle, and the ionic groups are hydrophilic, and remain on the surface of the particle. The residual —COOH groups are to some extent converted to $\text{—COO}^-\text{HN}^+(\text{C}_2\text{H}_5)_3$ ions by the addition of 40% TEA in the postneutralization stage. However, as the surface is already fully stabilized in the predispersion process, the newly formed ions are

trapped inside the particle and pull some water molecules inside the particle. As a result of this, the size of the particle increased while the number of particles remained constant (Fig. 4). Hence, the effective volume of the polymer changes, and a rapid increase in the η was observed (Fig. 3). Similar phenomenon was observed by the postneutralization of the dispersion made by 40, 50, 70, and 80% preneutralization (Table I). *Effect of degree of chain extension on particle size and viscosity.* The effect of the degree of chain extension on the particle size, viscosity, and pH on PU dispersion is presented in Figure 5. The chain extension and termination was carried out by adding HMDA and DEA to the dispersion. All of the samples for this portion of the study were prepared at 32 wt % solids, with 5.5 wt % DMPA and neutralized to 100% with TEA. The particle size increased slightly from 38 to 45 nm with increase in chain extension from 0 to 90%. There is a slight change in viscosity due to negligible change in particle size with the chain extension. The pH decreased slightly with increase in the degree of chain extension (Fig. 5).

The chain extender was added to the reaction flask after making the dispersion. PU particles have NCO group at the chain end of the prepolymer, which are present inside the core of the particle. With the addition of chain extender, the prepolymer reacted with each other and formed PU chain with higher molecular weight (Table I). The chain extension reaction takes place inside the core of the PU particle. Hence, the particle size did not change much with the chain ex-

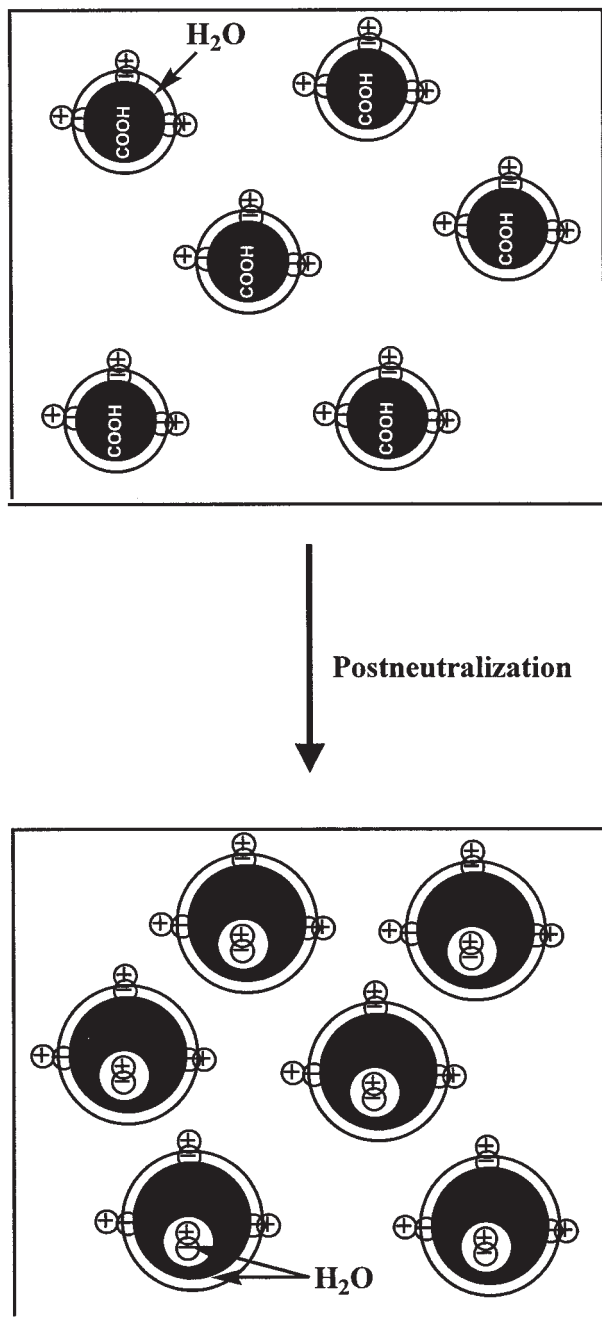


Figure 4 Effect of particle size by postneutralization.

tension. As a result of this, viscosity increased slightly with chain extension.

Effect of the degree of chain extension on molecular weight. The effect of degree of chain extension on molecular weight is presented in Table I. The weight average molecular weights (M_w) and number average molecular weights (M_n) were determined using GPC with respect to PMMA standards. The PU films were able to be dissolved in hot THF. The M_n values increased with increase in the degree of the chain extension (Table I). The M_n values measured by GPC are lowered compared with the theoretical M_n values (Table

TABLE I
Effect of Degree of Chain Extension on Molecular Weights of PU Dispersion

Chain extension (%)	M_n (g/mol) (calculated)	M_n (g/mol) (GPC)	M_w (g/mol) (GPC)
0	2200	2900	8200
50	4500	4000	13,000
70	7900	5000	16,000
90	29,000	14,000	32,000

I). This is most likely due to different hydrodynamic volume of PU compared with PMMA standard, or perhaps the insolubility of high molecular weight fractions.

Effect of degree of chain extension on complex viscosity of PU film. As seen in Figure 5, there is negligible effect of the degree of chain extension on particle size and viscosity of PU dispersion although molecular weights increased with increase in the degree of chain extension (Table I). To observe the effect of viscosity on PU film, the complex viscosity of PU films were determined rheometrically. Figure 6 demonstrates the effect of chain extension on the dynamic viscosity of PU in the melt at 120°C at different shear frequencies. Obviously, the dynamic viscosity increased up to three orders of magnitude at $\omega = 1$ rad/s with increasing the chain extension from 0 to 90%. This increase in the dynamic viscosity is attributed to the increase in the molecular weight of PU with increasing the chain extension, which leads to the increase in the number of entanglement points per unit. It is also clear that the dynamic viscosities of both 50 and 90% chain extension are shear frequency dependent (non-Newtonian Behavior), and the viscosity of 0% chain extension is frequency independent (Newtonian behavior).

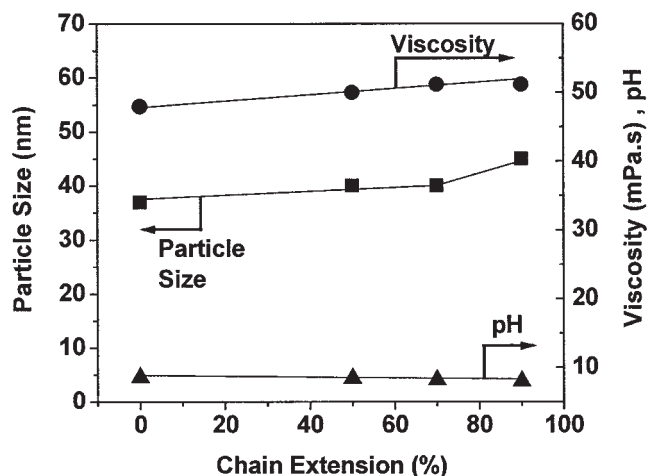


Figure 5 Effect of degree of chain extension on particle size, η , and pH of PU dispersion. Preneutralization = 100%; DMPA = 5.5 wt %.

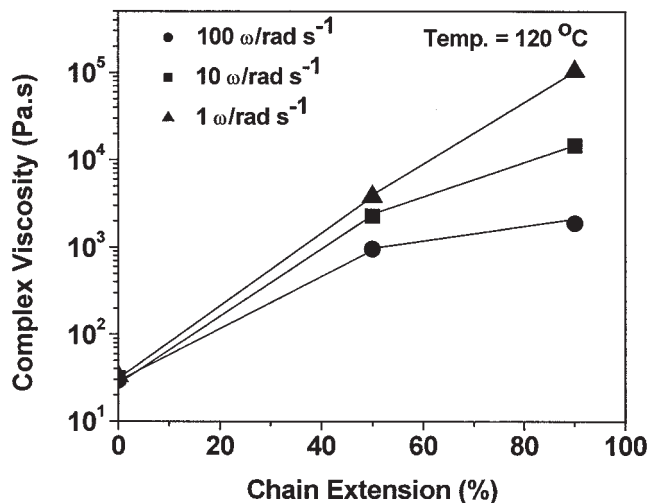


Figure 6 Effect of complex viscosity on chain extension of PU films.

DSC studies. DSC analyses of polyurethane films of 0, 50, and 90% chain extension are presented in Figure 7. The glass transition temperatures at -41 , -40 , and -38°C for 0, 50, and 90% chain extensions, respectively, are corresponded to the presence of soft segment (ester linkage) of PU chains. The hard segment T_g are 10, 11, and 12°C for 0, 50, and 90% chain extension, respectively. The T_g of the PU films increases slightly with increase in the degree of chain extension.

TGA studies. TGA studies of PU film showed the degradation of PU film starts at 260°C . The degradation at 480°C corresponds to char formed from the film (Fig. 8).

CONCLUSIONS

The current study highlights the effect of the degree of DMPA content, solid content, pre/postneutralization

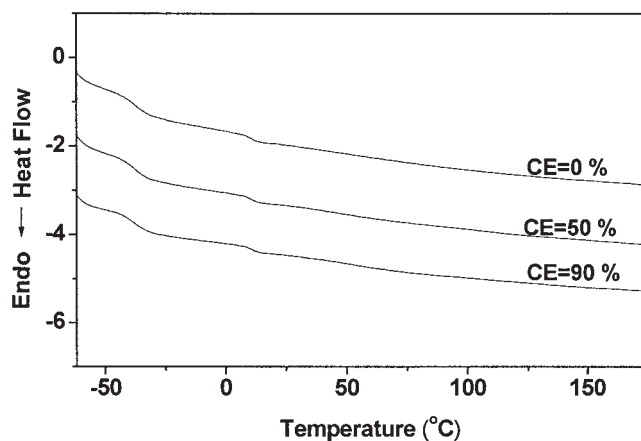


Figure 7 DSC traces of PU films.

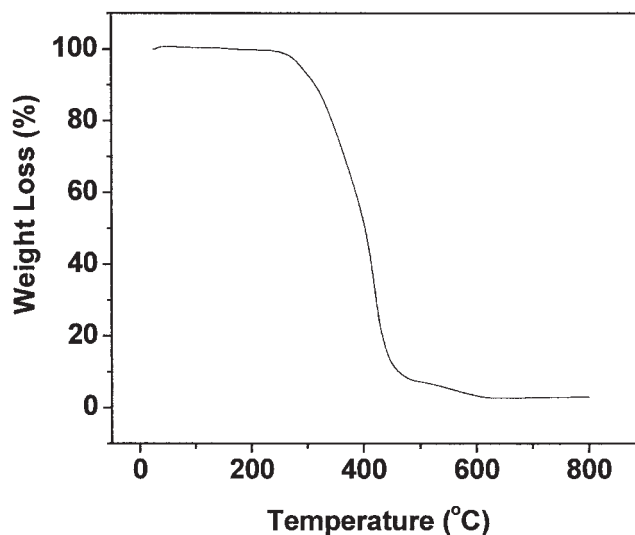


Figure 8 TGA trace of PU film.

and degree of chain extension on particle size, viscosity, pH, molecular weights, glass transition temperature, and degradation temperature of a given formulation prepared by prepolymer method. The DMPA content of 5 wt % gave particle size of 50 nm, and the effect of DMPA was less effective afterwards. Both the particle size and viscosity increased with increase in the solid content. Maximum solid content for this PU dispersion was found to be 44 wt %, and thereafter the PU dispersion had a solid like structure.³³ The order of neutralizing amine addition was found to be critical. Lower particle size was obtained with increase in the degree preneutralization of the PU prepolymer; however, a significant increase in the particle size and viscosity of PU dispersion was seen by the postneutralization. The PU films showed the presence of two T_g at lower and higher temperatures corresponded to soft and hard segments, respectively. TGA studies showed the degradation of PU films at 260°C .

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