

Polyurethane–Urea Anionomer Dispersions. I

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SYNOPSIS

Polyurethane–urea anionomer dispersions with different stoichiometric DMPA/polyol and NCO/OH ratios were prepared from poly(oxypropylene)glycol, toluene diisocyanate (TDI), dimethylolpropionic acid (DMPA), and ethylenediamine (EDA). The dispersion-cast films were prepared and characterized by mechanical properties, dynamic mechanical analysis (DMA), and differential scanning calorimetry (DSC). Increasing the hard-segment content by either increasing the DMPA/polyol or the NCO/OH ratios affects the glass transition temperature (T_g) of the soft segments. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The introduction of small amounts of pendant ionic groups on the polymer chains has found increasing applications in the modification of the properties of polymers. Polyurethane ionomers are polyurethanes containing pendant acid groups (anionomer) or tertiary amine groups (cationomer). These groups are neutralized to form internal salt groups prior to the application. Polyurethane ionomers are one of the most rapidly developing and active branches of polyurethane chemistry due to their ability to form water dispersions. The increasing applications in the coating and adhesive industries are due mainly to their unique properties and the advantage of the VOC-free systems. Among polyurethane ionomers, anionic polyurethane dispersions have been most frequently used in the coating and adhesive industries. Anionic polyurethanes are usually prepared by introducing a pendant acid group, such as dimethylolpropionic acid (DMPA), into the backbone of the polyurethane prepolymer. The pendant carboxylic acid groups are neutralized with base to form internal salt group-containing prepolymers that can easily be dispersed in water. Diamines are generally used as chain extenders after dispersion to produce high molecular weight anionic polyurethane–urea dispersions.

The microphase separation between the incompatible soft- and hard-segment sequences contribute to the unique properties of polyurethane ionomers.¹ The hard-segment microdomains act as thermally labile physical cross-link sites as well as fillers for the rubbery soft-segment matrix. The driving force for the microdomain formation includes hydrogen bonding in urethane and urea groups, the electrostatic interaction (Coulombic forces) between the ionic groups, as well as crystallization of both hard and soft segments. The morphology and properties of polyurethane–urea dispersions are dependent upon the chemical structure and compositional variation, the block length, as well as the ionic and urea group content. In the last 40 years, more than 800 patents for the preparation and application of aqueous polyurethane dispersions have appeared.^{2–5} Systematic data on structure–properties relationships are found infrequently in the literature for aromatic polyisocyanate-based aqueous polyurethanes.^{6,7} In this article, we report on the synthesis and properties of toluene diisocyanate (TDI)-based aqueous polyurethane–urea dispersions. The effect of hard-segment and salt-group content on the morphology and properties have been studied.

EXPERIMENTAL

Materials

Toluene diisocyanate (TDI) (Miles Chemical Co.) and dimethylolpropionic acid (DMPA) (Trimet

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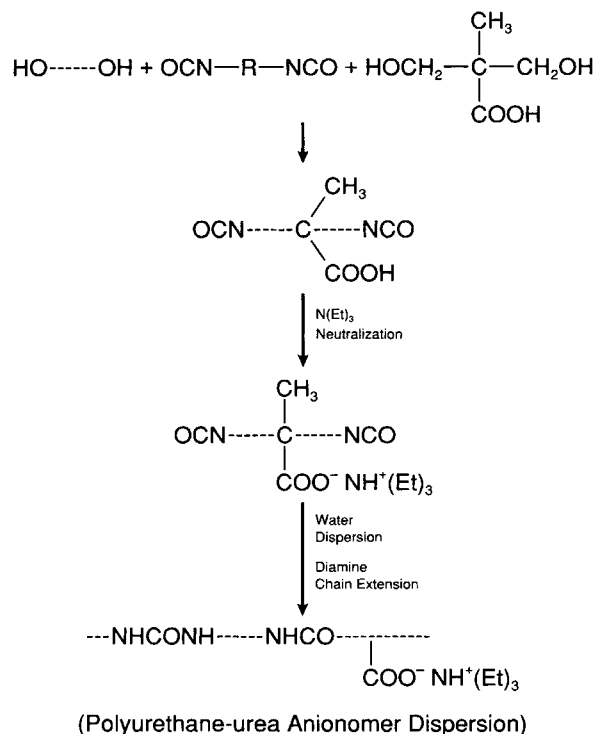
Tech. Products) were used as received. 1,2-Ethylenediamine (EDA), triethylamine (TEA), and *N*-methyl-2-pyrrolidone (NMP) were dried over 4 Å molecular sieves before use. Poly(oxypropylene)-glycol (PPG2000, MW = 2000) from Dow Chemical Co. was degassed at 70°C under vacuum overnight before use.

Preparation of Polyurethane-Urea Anionomer Dispersions

A series of polyurethane-urea anionomer dispersions were prepared. Their formulations are presented in Table I. A typical synthesis procedure is as follows: DMPA was dissolved in NMP (50/50 w/w) in a reaction kettle equipped with a thermometer, stirrer, inlet and outlet of dry nitrogen, and a heating jacket. PPG-2000 and TDI were then placed in the kettle with stirring. The reaction was carried out at 70–75°C under dry nitrogen until the NCO group content reached a given value that is calculated based on that all the hydroxy groups were consumed by NCO groups, as determined by the di-*n*-butylamine titration method. The product was then neutralized by adding TEA at 50°C. The reaction mixture was then cooled, and the dispersion and subsequent chain extension were carried out immediately at 5–10°C in order to avoid the reaction between the NCO groups and water. Two series of dispersions were prepared: In series A, the molar ratio of NCO/OH was held constant, while the DMPA content was raised, providing higher hard-segment and salt-group content (Table I). In series B, the ratio between DMPA and polyol was fixed, but the NCO/OH ratio was increased (Table I). This resulted in a slight decrease of salt-group content with an increase in both the urea-group and hard-segment

Table I Compositional Data on Polyurethane-Urea Anionomer Dispersions

Designation	NCO/OH Ratio	DMPA/PPG2000 Ratio	Hard Segments (%)	COOH Content (%)
A1	1.5	0.6	21.5	1.06
A2	1.5	0.8	24.0	1.37
A3	1.5	1.0	26.4	1.66
A4	1.5	1.2	28.6	1.92
B1	1.2	1.0	22.3	1.74
B2	1.5	1.0	26.4	1.66
B3	1.7	1.0	28.8	1.60
B4	2.0	1.0	32.2	1.53



Scheme I Preparation of polyurethane-urea anionomer dispersion.

content. The preparation of polyurethane-urea anionomer dispersion is described in Scheme I.

Polyurethane-urea films were made by casting the aqueous dispersions in a silicone-coated mold. They were dried at room temperature for 72 h and at 110°C for 4 h. The mechanical properties were measured on an Instron tensile tester at 5 in. min crosshead speed. The viscosity was measured with a Brookfield viscometer at room temperature. Differential scanning calorimetry (DSC) measurements were carried out at a heating rate of 20°C/min on a DuPont 910 differential scanning calorimeter with a DuPont 9900 thermal analyzer system. Indium was used to calibrate the instrument. Dynamic mechanical studies were carried out on a DuPont 983 dynamic mechanical analyzer (DMA) at a frequency of 1 Hz and a heating rate of 5°C/min. The particle sizes of various dispersions were measured by a Brookhaven B1-90 particle sizer.

RESULTS AND DISCUSSION

The polyurethane-urea dispersions were characterized using pH values, viscosities, solids content, and particle size. The results are listed in Table II. All measurements were based on 25% solids content.

Table II Some Physical Properties of Polyurethane-Urea Anionomer Dispersions

Designation	Viscosity (cps)	pH	Solids Content (%)	Particle Size (nm)
A1	15	8.9	25	430
A2	20	9.1	25	266
A3	15	9.1	25	141
A4	15	9.0	25	83
B1	15	9.0	25	120
B2	20	9.1	25	141
B3	15	9.0	25	152
B4	15	8.9	25	301

The pH of the dispersions indicated weak basicity, presumably due to the carboxylate salt of DMPA. The viscosity of the dispersions of both series A and B remained essentially unchanged, as shown in Table II. In both series A and B, the average particle size decreased with increasing internal salt-group content. This is due to an increase in the hydrophilic structure by introducing more salt groups.

The storage modulus E' and the loss modulus E'' are plotted as a function of temperature for polyurethane-urea with different DMPA/polyol ratios in Figure 1 (a) and (b). The relaxation peaks correspond to the glass transition temperatures (T_g 's) of the soft segments (Table III). The T_g 's of the soft segments for these samples are about -40°C , which are much higher than that of pure poly (oxypropylene) glycol, which has been reported as -69°C .⁸ The increase in the T_g of the soft segment indicates the presence of hard segments dispersed in soft-segment microdomains. From the morphological model by Wilkes et al.,^{9,10} it is suggested that polyurethanes contain two phases: the "nearly pure" hard microdomains and the soft microdomains that contain soft segments in a partially extended conformation together with some trapped hard segments with a shorter chain length. The chain mobility of the soft segments is restricted by the trapped hard segments, resulting in an elevated T_g of the soft microdomain. The extent of mixing of hard and soft segments in polyurethanes is reflected, at least qualitatively, by the T_g of the soft segments,¹¹ even though there is a lack of data regarding the T_g of the hard-segment domains. It can be seen from Table III and Figure 1 that the T_g of the soft segment for samples of series A shifts to higher temperatures and the height of the loss modulus (E'') peak decreases as the DMPA/polyol ratio increases, indicating a higher extent of phase mixing.

It is known that the factors that affect the extent of phase separation include copolymer composition, block length, and inter- or intramolecular interactions. In this series, increasing the DMPA/polyol ratio increases both the hard-segment content and the salt-group content. The enhancement of the hard-segment content effectively increases the extent of phase mixing as indicated by the higher T_g 's of the soft segment as reported by Cooper et al.^{12,13} In this study, similar results were obtained as the samples with higher DMPA/polyol ratios exhibited higher T_g 's for the soft segment. Furthermore, the increased hard-segment (TDI-DMPA segment) content tends to promote irregularity in packing of the hard segments, resulting in domains of lower density and crystallinity because of the increase in the concentration of the pendant salt groups. These hard segments are likely to mix with polyether segments. It should also be noted that the formation of the ionic multiplets or clusters is also a driving force for the microphase separation.¹⁴ In this case, the salt-group content increases with increasing DMPA/polyol ratio. However, only 1–2 wt % of $-\text{COOH}$ groups are incorporated to render the anionomer water-dispersible; hence, the effect of the variation in Coulombic interaction on T_g is not likely to be significant.

DSC curves, as shown in Figure 2, of the series A samples show the T_g 's of soft segments at about the same temperature as those obtained from DMA. In Figure 2, all samples exhibited an endothermic peak in the temperature range of $160\text{--}180^\circ\text{C}$. It is suggested that these endotherms reflect the melting behavior that is associated with the disappearance of the long-range order in the hard-segment microdomains.¹⁵ The glass transition temperatures from DSC, the melting points (T_m), as well as the en-

Table III Transition Temperatures of Polyurethane-Urea Anionomer Dispersions

Designation	T_g ($^\circ\text{C}$) ^a	T_m ($^\circ\text{C}$)	ΔH_m (J/g)
A1	-49 (-46)	159	17.7
A2	-46 (-47)	167	15.5
A3	-45 (-46)	169	13.6
A4	-39 (-44)	182	10.2
B1	-41 (-46)	163	11.6
B2	-46 (-46)	169	13.6
B3	-47 (-46)	202	14.9
B4	-48 (-45)	215	16.8

^a From DMA measurement. Values in the parentheses indicate the T_g from DSC.

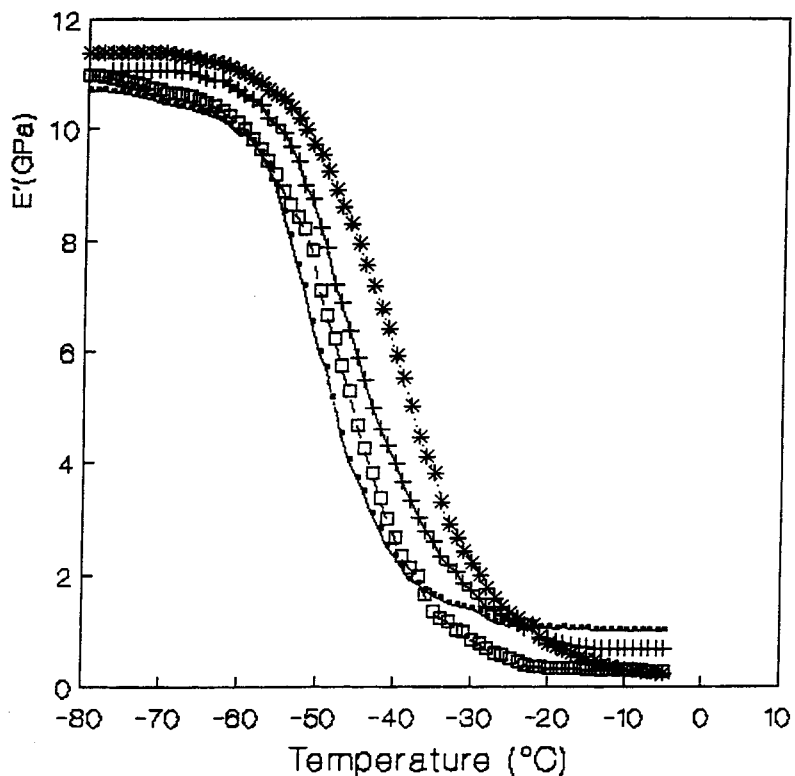


Figure 1(a) Storage modulus vs. temperature of polyurethane-urea anionomers at various DMPA/polyol ratios. (— \square) A1 (DMPA/polyol = 0.6); (— \square) A2 (DMPA/polyol = 0.8); (— $+$) A3 (DMPA/polyol = 1.0); (— $\ast\ast\ast$) A4 (DMPA/polyol = 1.2).

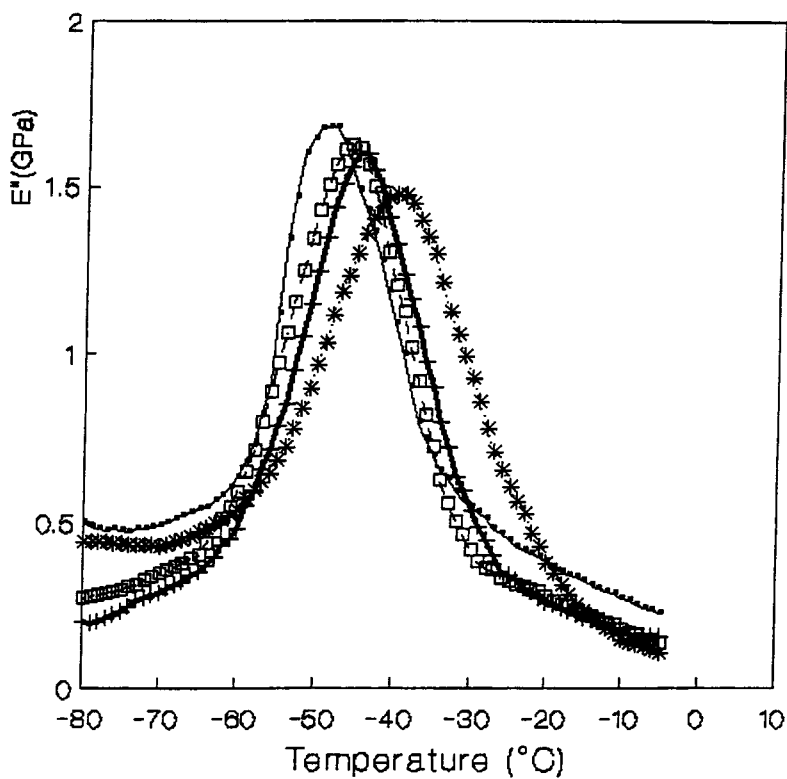


Figure 1(b) Loss modulus vs. temperature of polyurethane-urea anionomers at various DMPA/polyol ratios. (— \square) A1 (DMPA/polyol = 0.6); (— \square) A2 (DMPA/polyol = 0.8); (— $+$) A3 (DMPA/polyol = 1.0); (— $\ast\ast\ast$) A4 (DMPA/polyol = 1.2).

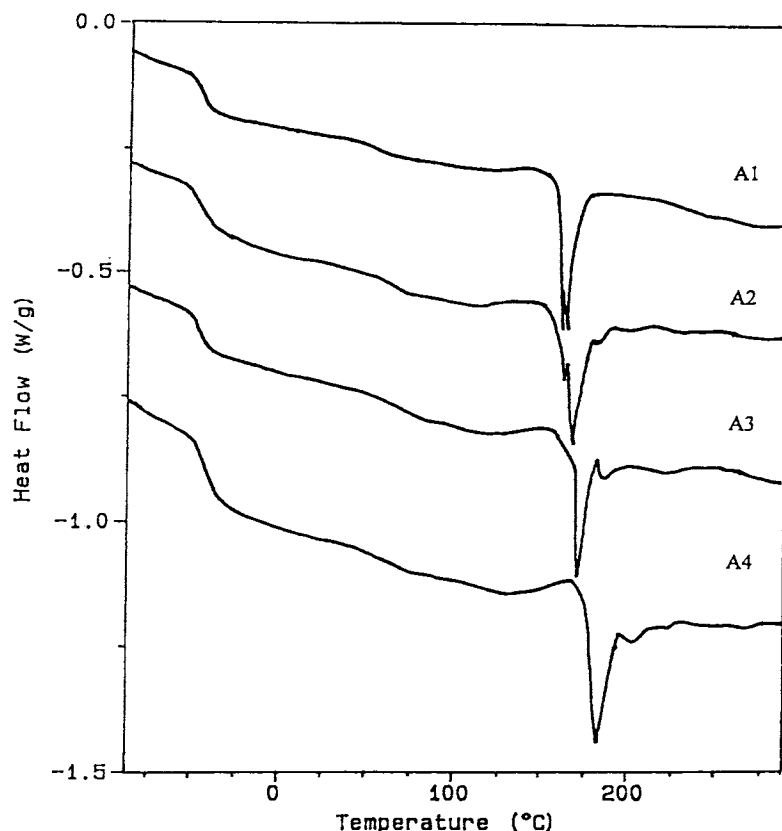


Figure 2 DSC analysis of polyurethane-urea anionomers based on different DMPA/polyol ratios. A1 (DMPA/polyol = 0.6); A2 (DMPA/polyol = 0.8); A3 (DMPA/polyol = 1.0); and A4 (DMPA/polyol = 1.2).

thalpies for the long-range order are also listed in Table III. The T_m of the films shifts to higher temperatures as the hard-segment content increases. This might be a consequence of the increase in the average hard-segment sequence length. Similar results have been reported by Clough and Schneider.¹⁶ The enthalpies of the dissociation of long-range order in the hard-segment microdomain decrease with increasing DMPA/polyol ratio, implying more mixing of hard segments in the soft microdomains. This is consistent with the results from the T_g measurements of soft segments by DMA.

The mechanical properties are shown in Table IV. The stress-strain curves of these films indicate the behavior of typical elastomers, implying soft microdomains as the continuous phase. In polyurethane ionomers, the mechanical strength is governed mainly by the hard segments, and the flexibility by the soft segments. It is known that the type and concentration of hard and soft segments and of ionic groups strongly affect the final properties. As shown in Table IV, the tensile strength and modulus increased, whereas the elongation decreased with in-

creasing DMPA content. The increase of tensile strength and modulus is due to the increased amount of urethane linkages and the interchain ionic interaction. The decreased flexibility can be explained by the increased chain rigidity and intermolecular interaction with decrease of the soft-segment fraction by increasing the DMPA content.

Table IV Mechanical Properties of Polyurethane-Urea Dispersions

Designation	Tensile Strength (MPa)	Modulus at 100% (MPa)	Elongation (%)
A1	1.79	1.03	960
A2	5.59	1.72	900
A3	7.45	1.72	800
A4	9.93	1.72	700
B1	2.76	1.45	600
B2	7.45	1.72	800
B3	11.86	3.86	700
B4	16.20	6.41	600

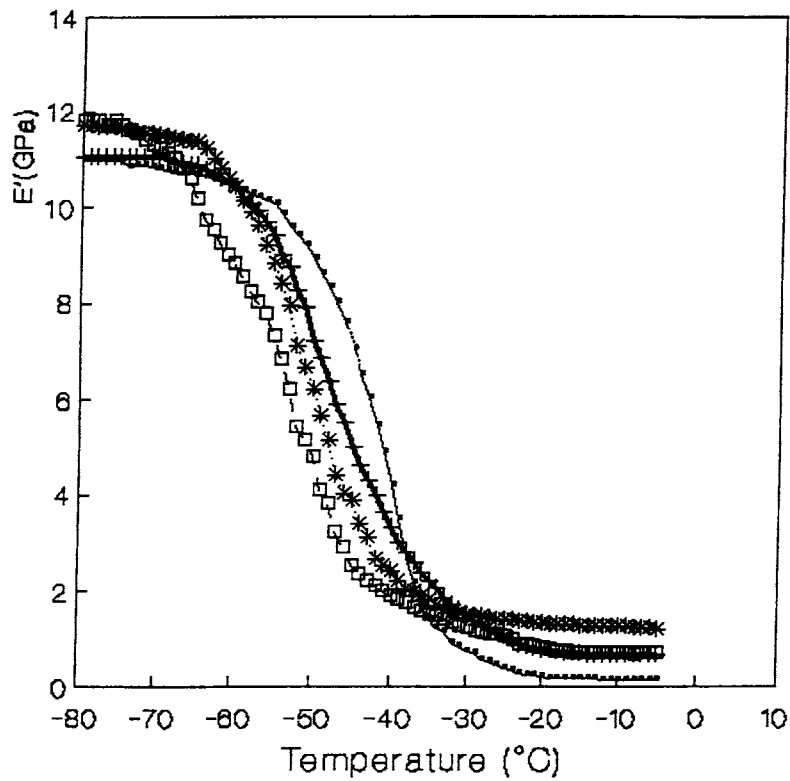


Figure 3(a) Storage modulus vs. temperature of polyurethane-urea anionomers at various NCO/OH ratios. (—□—) B1 (NCO/OH = 1.2); (—+—) B2 (NCO/OH = 1.5); (·····) B3 (NCO/OH = 1.7); and (—□—) B4 (NCO/OH = 2.0).

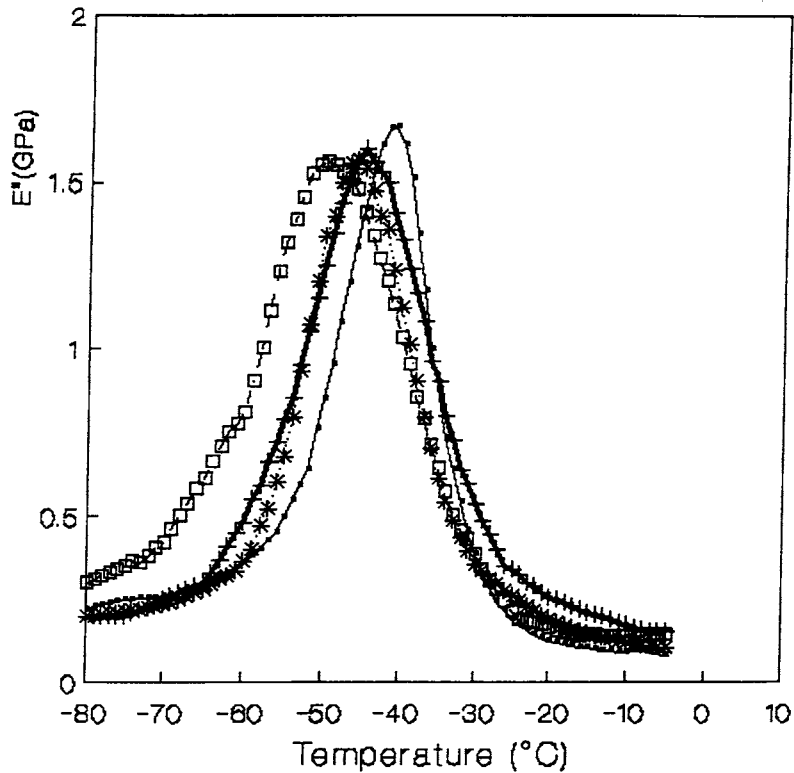


Figure 3(b) Loss modulus vs. temperature of polyurethane-urea anionomers at various NCO/OH ratios. (—□—) B1 (NCO/OH = 1.2); (—+—) B2 (NCO/OH = 1.5); (·····) B3 (NCO/OH = 1.7); and (—□—) B4 (NCO/OH = 2.0).

The dynamic mechanical spectra of samples with different NCO/OH ratios are shown in Figure 3. In these samples, as the salt-group content decreased slightly, the hard-segment contents increased due to the increased urea content. The incorporation of urea linkage in polyurethane hard segments is expected to have a profound effect on the microphase separation and the morphology of polyurethane-ureas. This is due to the high polarity difference between the hard and soft segments and the likely development of a higher degree of the hydrogen-bonding network.¹⁷ As shown in Figure 3, the T_g 's of soft segments shift to lower temperature with increasing NCO/OH ratios (from -41°C for sample B1 to -48°C for sample B4, Table III). This indicates an increase in phase separation between hard and soft segments, presumably due to the increased urea-group content. Moreover, a slight decreasing ionic-group content and increasing the chain length of the hard segment may contribute to higher packing ability of the hard segments, which could result in a higher-ordered structure. This, at least in part,

should favor an increase in the hard-soft phase separation.

The results of DSC measurements of the B series samples are shown in Figure 4 and Table III. The T_g 's from DSC were found almost unchanged with variation of the hard-segment content. Similar results were also observed for the A series. For both series of samples, the DMA measurements seemed to be more sensitive to morphological changes. As shown in Figure 4, the endotherms in the temperature range of $160\text{--}220^\circ\text{C}$ are attributed to the disappearance of long-range order or the microcrystal in the hard-segment microdomain. The degree of crystallinity increases with increase of the hard-segment content due to the longer hard-segment sequences.

The mechanical properties of the B series are given in Table IV. The stress-strain curves show the typical behavior of elastomers. With increasing hard-segment content, the tensile strength and modulus increased, while the elongation decreased. By comparing samples B2 with A2, as well as B4

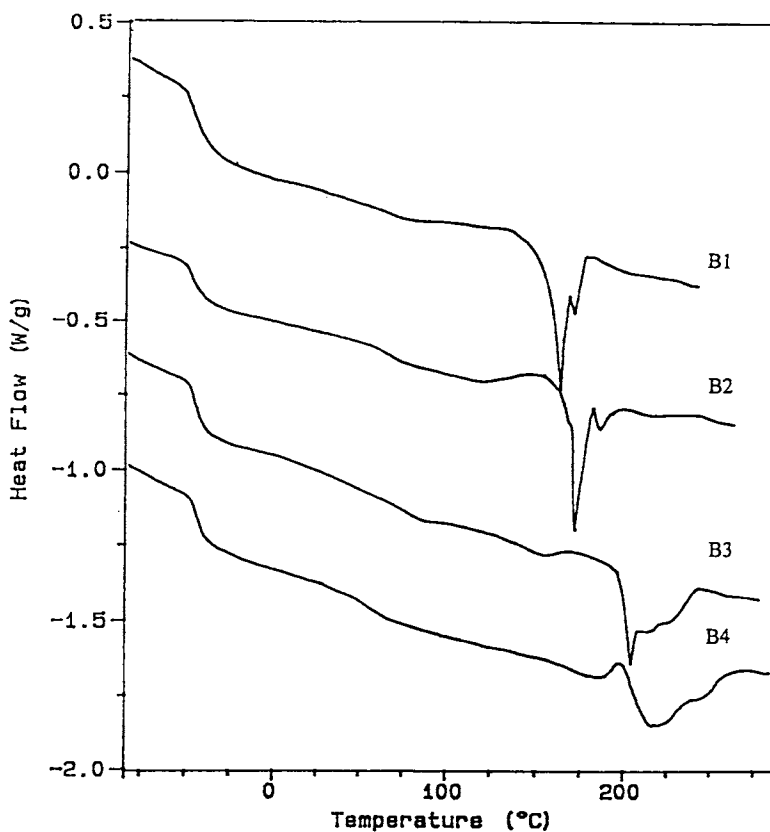


Figure 4 DSC analysis of polyurethane-urea anionomers based on different NCO/OH ratios. B1 (NCO/OH = 1.2); B2 (NCO/OH = 1.5); B3 (NCO/OH = 1.7); and B4 (NCO/OH = 2.0).

with A4, it was found that the samples in the B series had higher tensile strength and modulus compared with the samples in the A series, even though the hard-segment content was similar. This might be due to the higher urea content in the B series samples.

CONCLUSIONS

The synthesis and structure-properties relationship of polyurethane-urea dispersions with different DMPA/polyol and NCO/OH ratios have been described. Increasing the DMPA/polyol ratio increased the T_g of the soft segment, indicating an increase in hard-soft segment mixing. The T_g of the soft segment shifted to lower temperature with an increase of the NCO/OH ratio, resulting in an increase in phase separation between hard and soft segments, presumably due to the increase in the urea-group content. By increasing either the DMPA/polyol or the NCO/OH ratios, both the tensile strength and modulus increased while the elongation decreased in the polyurethane-urea dispersion-cast films.

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