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POLYURETHANE–UREA ANIONOMER DISPERSIONS. II

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ABSTRACT

Polyurethane–urea anionomer dispersions containing about 50% hard segments were prepared from poly(oxypropylene) glycols, toluene diisocyanate (TDI), or a mixture of TDI and polymeric MDI (PMDI), dimethylolpropionic acid (DMPA), 1,4-butanediol (BD), and different diamines as chain extenders. The structure–properties relationships of these polyurethane–urea anionomers were studied. The effects of compositional ratio, type of chain extender, and isocyanate structure on the morphology and properties of the dispersion-cast films were investigated by means of differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and determination of mechanical properties.

INTRODUCTION

Anionic polyurethanes are copolymers containing a urethane backbone and pendant salt groups which result from the neutralization of acid groups. They are of increasing interest for coating and adhesive applications due to their pollution-free status, high performance properties, and the ease of tailoring the materials to meet the specific end use requirements. Polyurethane anionomer dispersions have been studied by many investigators [1–6]. However, relatively little systematic work

has been reported in detail on aromatic polyisocyanate-based anionomer systems [5, 6]. In continuation of the previous work concerning polyurethane-urea anionomer dispersions [7], the present work deals with the synthesis and characterization of polyurethane-urea anionomer dispersions based on toluene diisocyanate (TDI) and the mixtures of TDI with polymeric MDI (PMDI). The effects of isocyanate structure, chain extenders, and compositional ratio on the morphology and properties of these dispersions were determined.

EXPERIMENTAL

Materials

The materials used are listed in Table 1. TDI, Mondur CD, Isonate 143L, PAPI 2094, and dimethylolpropionic acid (DMPA) were used as received. 1,6-Hexamethylenediamine (HMDA), 1,2-ethylenediamine (EDA), hydrazine (HZ), triethylamine (TEA), *N*-methyl-2-pyrrolidone (NMP), and 1,4-butanediol (BD) were dried over 4 Å molecular sieves before use. Poly(oxypropylene) glycols (PPGs) were degassed overnight at 70°C under vacuum before use.

Preparation of Polyurethane-Urea Anionomer Dispersion

A series of polyurethane-urea anionomer dispersions were prepared and their formulations are presented in Table 2. A typical synthesis procedure is as follows: DMPA was dissolved in NMP (50/50 w/w) in a reaction kettle equipped with a thermometer, a stirrer, inlet and outlet for dry nitrogen, and a heating jacket. PPG, 1,4-BD, and isocyanate were placed in the kettle with stirring. When the mixture of isocyanates was used, polymeric MDI (Mondur CD, Isonate 143L, or PAPI 2094) was added first and TDI was added after 1 hour. The reaction was carried out at 70–75°C under dry nitrogen until the theoretical NCO value was reached, as determined by the di-*n*-butylamine titration method. The product was then neutralized by adding TEA at 50°C. Acetone (10% of total solids content) was added to decrease the viscosity of the reaction mixture. The reaction mixture was then cooled. The dispersion in water and chain extension with diamine were carried out immediately at 5–10°C in order to avoid the reaction between free NCO groups and water.

Characterization

The sample films were cast by placing the polyurethane-urea anionomer dispersions in a silicone-coated mold, dried at room temperature for 72 hours, and at 110°C for 4 hours. The mechanical properties were measured on an Instron tensile testing machine at 5 in./min of 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 Du Pont 910 differential scanning calorimeter attached to a Du Pont 9900 thermal analyzer system. Indium was used to calibrate the instrument. Dynamic mechanical studies were carried out on a Du Pont 983 dynamic mechanical analyzer at a frequency of 1 Hz and a heating rate of 5°C/min.

TABLE I. Raw Materials

Name	Chemical description	Supplier
TDI	Toluene diisocyanate	Miles Chemical Co.
Mondur CD	Modified MDI (PMDI) (Eq. wt = 134, $f = 2.0$)	Miles Chemical Co.
Isonate 143L	Modified MDI (PMDI) (Eq. wt = 143, $f = 2.1$)	Dow Chemical Co.
PAPI 2094	Crude MDI (PMDI) (Eq. wt = 132, $f = 2.3$)	Dow Chemical Co.
PPG1000	Poly(oxypropylene) glycol (MW = 1000, $f = 2.0$)	Dow Chemical Co.
PPG1200	Poly(oxypropylene) glycol (MW = 1200, $f = 2.0$)	Dow Chemical Co.
DMPA	Dimethylolpropionic acid	Alcolac Inc.
BD	1,4-Butanediol	E. I. du Pont de Nemours & Co.
HMDA	Hexamethylenediamine	E. I. du Pont de Nemours & Co.
EDA	Ethylenediamine	E. I. du Pont de Nemours & Co.
HZ	Hydrazine	E. I. du Pont de Nemours & Co.
TEA	Triethylamine	E. I. du Pont de Nemours & Co.
NMP	<i>N</i> -Methylpyrrolidone	BASF

TABLE 2. Composition of Polyurethane-Urea Anionomer Dispersions

Designation	Composition	Equivalent ratio	Hard segments	COOH content
A1	TDI/PPG1000/DMPA/EDA	9/2/3/4	55.7	2.99
A2	TDI/PPG1000/DMPA/BD/EDA	9/2/2/1/4	54.2	2.06
C1	TDI/Mondur CD/PPG1000/DMPA/EDA	7/2/2/3/4	57.4	2.87
C2	TDI/143L/PPG1000/DMPA/EDA	7/2/2/3/4	57.8	2.85
C3	TDI/PAPI2094/PPG1000/DMPA/EDA	7/2/2/3/4	57.4	2.88
B1	TDI/PPG1200/DMPA/BD/HMDA	9/2/2.5/0.5/4	52.6	2.22
B2	TDI/PPG1200/DMPA/BD/EDA	9/2/2.5/0.5/4	50.4	2.33
B3	TDI/PPG1200/DMPA/BD/HZ	9/2/2.5/0.5/4	49.2	2.38

RESULTS AND DISCUSSION

The aqueous dispersions of polyurethane-urea anionomers were characterized by pH value, viscosity, and solids content. The pHs of these dispersions were 8.8–9.1, indicating weak basicity, presumably due to the carboxylate salt of DMPA. The viscosities of these dispersions containing 25% of solids content were 15–100 cP.

The stress-strain properties of the dispersion cast films are plotted in Fig. 1. The behavior is typical of reinforced rubbers. The tensile strength at break, modulus

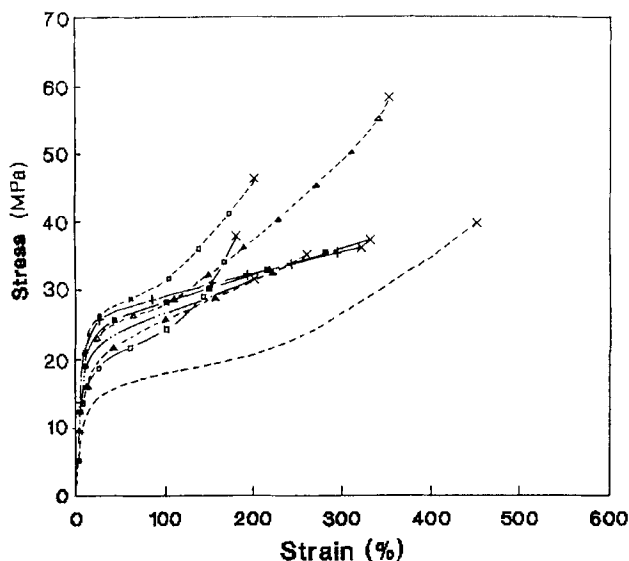


FIG. 1. Stress-strain curves of polyurethane-urea anionomers: A1 (---), A2 (-+-), C1 (-□-), C2 (-·-·-), C3 (- - - -), B1 (- -△-), B2 (-■-), B3(-▲-).

at 100% elongation, and elongation at break for all samples are given in Table 3. The tensile behavior of a polyurethane-urea anionomer generally depends upon the structure and concentration of the hard segments, intermolecular interaction within the hard segments, as well as the type of concentration of ionic groups. In all these samples, the hard segment content was almost the same, but the structure of the hard segment was varied to study its effect on the mechanical properties. As shown in Table 3, by comparing Sample A1 with Sample A2 it was found that the modulus increased while the elongation decreased as part of the DMPA was replaced by BD. On the other hand, the tensile strengths did not show a significant difference. This is probably due to higher crystallinity of the BD-based hard segments than that of the DMPA-based segments. The polyurethane-urea anionomers containing a mixture of TDI with PMDI (Samples C1-C3) exhibited increased modulus and decreased elongation as compared to the sample without PMDI (Sample A1). This could be caused by the more rigid chain structure of the PMDI-based hard segments. The tensile strength and modulus were relatively high for Sample C3, which may have a higher crosslinking density due to the high functionality of PAPI 2094 ($f = 2.3$). The choice of diamine chain extender also had a significant effect on the mechanical properties. Samples with different chain extenders (HMDA, EDA, and HZ) showed improved mechanical properties with increasing chain length of the chain extenders. This is presumably due to the increased crystallinity in the hard segments.

The DSC curves for these samples are shown in Figs. 2 and 3. The glass transition temperatures of soft segments and the melting points of hard segments as well as the enthalpies are given in Table 4. The T_g s of the soft segments for these samples are higher than the reported value (-69°C) [8] for the poly(oxypropylene) glycol. A quantitative analysis of the compatibility was not possible due to the difficulty of determining the T_g of the hard segments, similar to the other polyurethane systems [9]. However, the variation in the position of the soft segment T_g provided at least qualitative information for the degree of microphase separation between the hard and soft segments. The increase in the T_g of the soft segments implied the presence of "dissolved" hard segments in the soft segment microdomains, indicating partial microphase mixing between the hard and soft segments.

TABLE 3. Mechanical Properties of Polyurethane-Urea Anionomer Dispersions

Designation	Tensile strength, MPa (psi)	Modulus at 100% elongation, MPa (psi)	Elongation at break, %
A1	39.81 (5780)	17.84 (2590)	450
A2	36.16 (5250)	29.21 (4240)	320
C1	37.88 (5500)	25.78 (3742)	180
C2	31.55 (4581)	26.93 (3910)	200
C3	46.38 (6734)	31.44 (4550)	200
B1	58.27 (8460)	27.97 (4060)	350
B2	37.20 (5400)	28.24 (4100)	330
B3	35.13 (5100)	26.17 (3800)	260

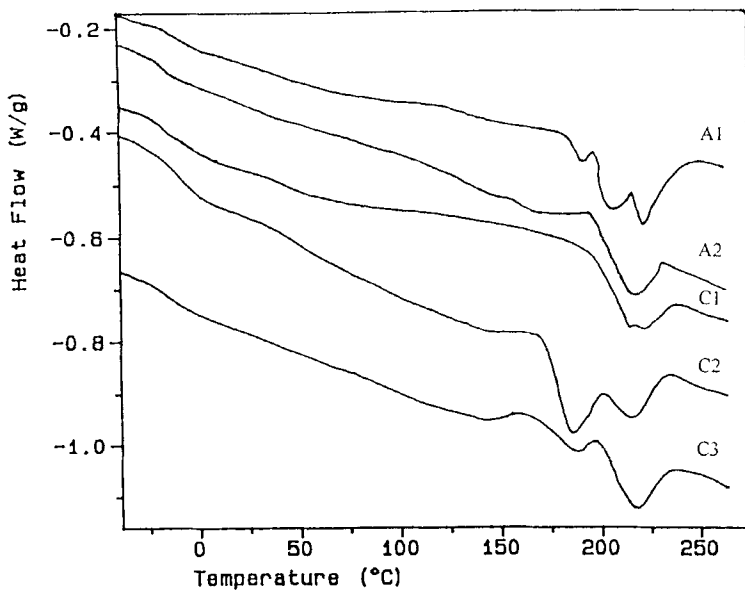


FIG. 2. DSC curves of polyurethane-urea anionomers based on different compositions.

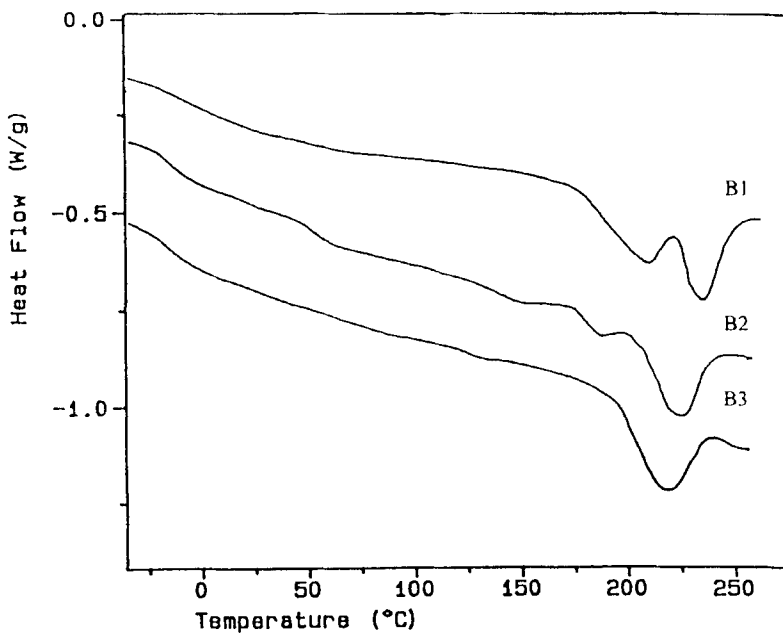


FIG. 3. DSC curves of polyurethane-ureas based on different chain extenders: B1 (HMDA), B2 (EDA), B3 (HZ).

TABLE 4. Transition Temperatures of Polyurethane-Urea Anionomer Dispersions

Designation	Soft segment T_g , °C, from		T_m , °C	ΔH_m , J/g
	DSC	DMA		
A1	-20	-16	214	15.1
A2	-18	-14	222	19.4
C1	-17	-13	213	20.1
C2	-17	-13	187, 216	18.9
C3	-16	-15	183, 219	11.3
B1	-23	-19	233	18.0
B2	-24	-19	220	13.6
B3	-23	-19	211	12.9

Figure 2 shows that the T_g s of the soft segments for Samples A1 and A2 are observed as 18 and 20°C, respectively. Frisch et al. reported that the T_g of the soft segments decreased when the DMPA/BD ratio decreased [10]. For the samples of this series, only a small amount of DMPA was incorporated for rendering a stable aqueous dispersion. The replacement of part of DMPA with BD did not cause significant compositional variation between Samples A1 and A2 so that its effect on T_g was not likely to be obvious. However, as indicated in Table 4, the melting enthalpy increased as the BD content was increased, indicating the higher crystallinity of the hard segments. This might be attributed to the higher regularity of TDI-BD-based hard segments.

The results of the DSC analysis for the samples containing mixtures of TDI with PMDI are also indicated in Fig. 2. Samples made from a mixture of TDI/Mondur CD (C1), TDI/Isonate 143L (C2), TDI/PAPI 2094 (C3), and pure TDI (A1) exhibited almost the same T_g for the soft segments. A similar result was reported by Cooper et al. [11], who found that polyurethanes based on MDI and TDI had identical soft segment T_g s. The melting enthalpy decreased with increasing functionality of PMDI. It seemed that crosslinking in the hard segments decreased the crystallinity of the hard segments.

Figure 3 contains DSC spectra of the samples with different chain extenders. The T_g s of the soft segments did not show any significant change when the different chain extenders were used. The enthalpy increased in the order of HMDA > EDA > HZ. The degree of crystallinity in the hard segments increased with increasing chain length of the chain extenders.

DMA measurements were also used to characterize the morphology. The temperature dependence of the storage modulus, E' , and the loss modulus, E'' , are shown in Figs. 4a and 4b, respectively for Samples A1-A2 and C1-C3. The T_g s of the soft segments were determined from the peak positions in the loss modulus (E'') curves, as shown in Table 4. The glass transition temperatures obtained by DMA were slightly higher than the T_g s determined by DSC, due to the difference in the experiment time scale [12]. In accordance with DSC data, the T_g s of the soft

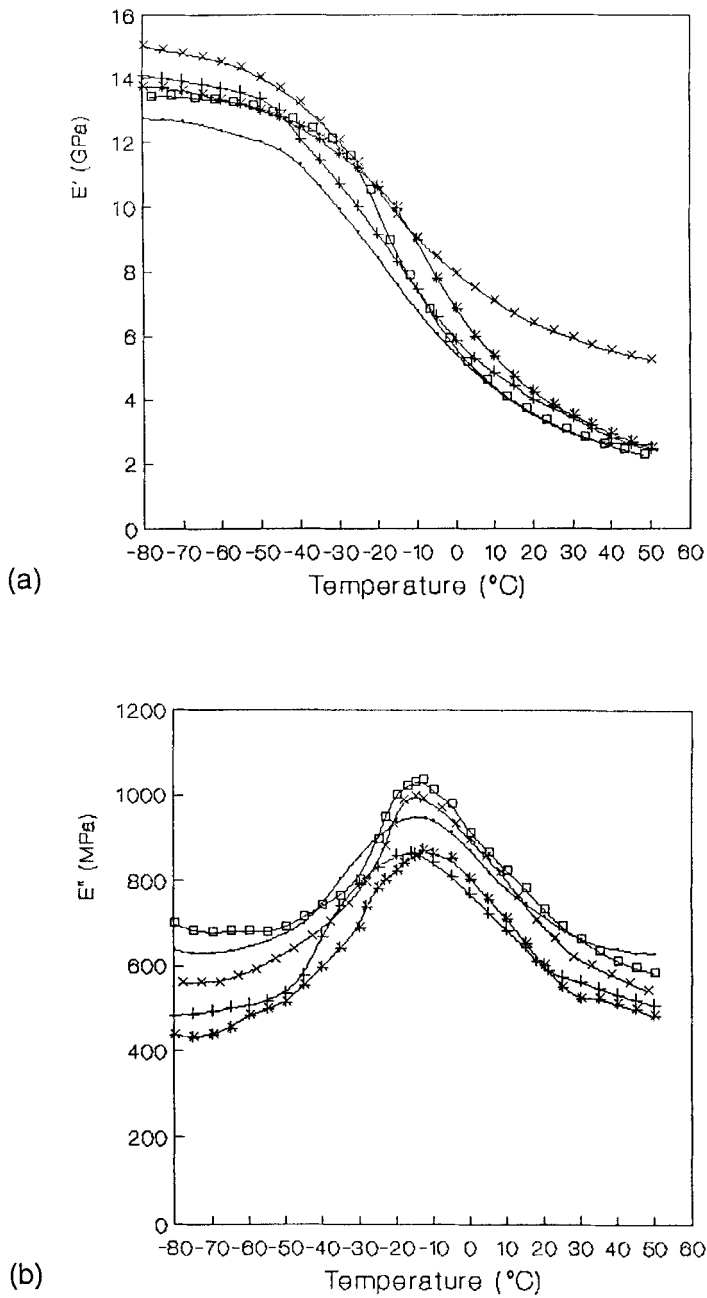


FIG. 4. (a) Storage modulus (E') vs temperature curves of polyurethane-urea anionomers: A1 (\cdot), A2 (+), C1 (*), C2 (\square), C3 (\times). (b) Loss modulus (E'') vs temperature curves of polyurethane-urea anionomers: A1 (\cdot), A2 (+), C1 (*), C2 (\square), C3 (\times).

segments appeared at approximately the same temperature for these samples. The DMA results for Samples B1-B3 (not shown) with different chain extenders were similar. The storage modulus above the soft segment glass transition for Sample C3 was higher than that of the other samples. The higher level of crosslinking density in the hard segment domains, caused by the higher functionality of PAPI 2094, may lead to a higher modulus.

CONCLUSIONS

The synthesis and structure-properties relationships of polyurethane-urea anionomer dispersions were studied. The mechanical properties were found to depend on the hard segment structures. The replacement of part of the DMPA by BD and part of the TDI by polymeric MDI as well as the type of chain extenders showed significant effects on the physical properties. The materials investigated in this study exhibited partial phase mixing between the hard and soft segments. The glass transitions of the soft segments were not sensitive to the variation of the hard segment structures.

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