

Synthesis and Properties of Anionic Aqueous Polyurethane Dispersions

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ABSTRACT: A series of aqueous polyurethane dispersions containing pendant carboxylate anion as the hydrophilic were synthesized, and the particle size and the mechanical properties of the dispersions were measured. The effects of the molar ratio of NCO/OH groups or the other functional groups on the chemical structure and the properties were discussed. The particle size mainly depended on the molar ratio of the functional groups. The -NH groups in urethane and urea linkage formed hydrogen bonding with the carbonyl group (C=O) of other urethane group in the hard segments or ether group (C-O-C) in the soft segments. Fourier transform infrared (FTIR) analysis showed

that the higher molar ratio of NCO/OH concentrated the -NH group, leading to the hydrogen bonding, which resulted in the increasing mechanical strength of the polyurethane. The tensile testing and dynamic mechanical analysis measurement revealed that the pendant carboxylate anion made the modulus and the stiffness of the polyurethane increase. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 3461–3465, 2002

Key words: water-dispersible polyurethane; anionic type; NCO/OH ratio; DMA; tensile property

INTRODUCTION

For over 40 years, waterborne or water-based polyurethanes have been studied and their performance properties improved continuously in hundreds of papers and patents in the field of water-based polyurethane.^{1–3} There are at least three important reasons why aqueous polyurethane has been become commercially important in the last few years. The first reason is environmental concerns regarding volatile organic compounds (VOCs) as solvents being issued into the atmosphere and causing ozone depletion, acid rain, and possibly an imbalance of the earth's ecosphere. The second reason is the economical aspect; that is, aqueous polyurethanes do not contain the expensive solvents. The third, and perhaps most important, reason is related to the fact that the modified aqueous polyurethanes are comparable to or better than the conventional solvent-based polyurethanes for many applications.

It has been well known that the segregation of the ionic groups into microdomains, forming physical cross links, gives rise to many of the unique properties of ionomers.⁴ Extensive attention has been devoted to understanding the factors controlling the ionic association. The compatibility of the backbone and the ionic

groups, the placement of ionic groups, the degree of ionization, the length of spacer groups between the polymer backbone and ionic groups, and the choice of neutralizing cation have all been shown to have important effects on the morphology and properties of the ionomers.⁵

A waterborne polyurethane dispersion can be defined as a binary colloidal system in which polyurethane particles are dispersed in a continuous aqueous medium. Self-emulsified anionic polyurethane dispersions can be prepared from NCO-terminated prepolymers containing a pendant carboxylate anion.⁶ These urethane prepolymers can also be made from a reaction of diisocyanates such as isophorone diisocyanate (IPDI), macrodiols such as polyether diols and polyester diols, and dimethylolpropanic acid (DMPA). The carboxylic ion of DMPA in the prepolymers is a hydrophilic group and serves as an internal emulsifier for polyurethane dispersions.

In the first phase of production, a medium-molecular weight prepolymer is synthesized at an elevated temperature, leaving terminated isocyanate groups. For this type of polyurethane to have high-performance properties, for example, flexibility, hardness, acid, and solvent and other chemical resistance, it must be chain-extended in water, usually by reacting the prepolymer with amine. Two important problems must be dealt with during the course of reaction: the control or stabilization of the extremely fast urea formation reaction and the control or minimizing the

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ensuring viscosity build-up resulting from increasing the molecular weight. Because of these problems, the solid content of the water-based aliphatic polyurethane dispersions is limited to 40% or lower.

This article describes the synthesis and characterization including Fourier transform infrared spectroscopy (FTIR), dynamic mechanical analysis (DMA), and stress-strain measurements. The influence of carboxylate anion content and chemical composition on the physical properties of polyurethane ionomers is described.

EXPERIMENTAL

Materials

Polytetramethylene glycol (PTMG, $M_n = 2000$, BASF Inc.) was dried under vacuum before use. DMPA (Aldrich) was dried at 90°C. Triethylamine (TEA) was dried over 4-Å molecular sieves before use. IPDI (BASF Inc.) and tin octanoate (T-9, Air Products Co.) and the chain extender ethylene diamine (EDA) were used as received.

Preparation of anionic aqueous-based polyurethane dispersions⁷

A reaction vessel equipped with a stirrer, condenser, nitrogen inlet, and thermometer was charged with PTMG, DMPA, and IPDI. The amount of catalyst used was 0.02%, based on the monomers weight. The reaction was carried out at 75°C with stirring until the desired extent of reaction was reached. The change of the NCO content during reaction was determined using a standard dibutylamine back-titration method (ASTM D1638). Then, the prepolymers were cooled to about 60°C, TEA was added, and the solution was stirred for another 30 min. The polyurethane dispersions resulted from a high shear rate mixing of these prepolymers with a 400-mL aqueous solution of EDA. The final amino-terminated polyurethane dispersions had about 35% solids contents and were pH 8.0 to 9.0.

Analysis and tests

The average particle size of the aqueous polyurethane dispersions were measured by a laser light scattering instrument (DLS, Ostuka Electronics Co., LPA-300 310). FTIR analysis for the polyurethane films was carried out by a MOMEM MB Series FTIR spectrometer.

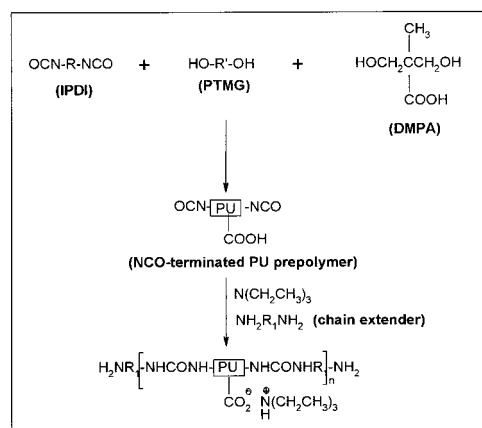
Dynamic mechanical analysis was performed in a tension mode using Universal V2.6D TA Instruments over the temperature range from -150° to 150°C at a frequency of 10 Hz and a heating rate of 5°C /min. The size of the bar type specimens was 20 × 5 × 1 mm³. Tensile testing was carried out with an Instron

Model STM-10E Universal Testing machine. A 1-kN load cell was used, and the crosshead speed was 50 mm/min. The results reported here are the average values for 10 replicates.

RESULTS AND DISCUSSION

The physical properties of the polyurethane films depend on the molecular structure. They also depend on the content of functional groups and on the molar ratio of NCO/OH. The isocyanate used in this work was IPDI, which has good thermal stability, low vapor pressure, low toxicity, and relatively high stability. DMPA, a carboxylic group containing diol, was used to form a water-dispersible urethane prepolymer without any significant reaction between the carboxylic group and isocyanate group because the hydroxyl group is much more reactive relative to the aliphatic isocyanate component. The reaction scheme for the prepolymer preparation and the processes of dispersion and chain extension are shown in Figure 1. Samples were prepared by changing the NCO/OH ratio and carboxylic group content, as shown in Table I.

The infrared analysis on polyurethane has been focused on two main vibrational regions: the N-H stretching vibration (3200–3500 cm⁻¹) and the C=O stretching vibration (1700–1730 cm⁻¹). In Figure 2, a typical infrared spectrum of the aqueous polyurethane film showed a carbonyl stretching of the carboxylic group at 1722 cm⁻¹, an amide I band (urethane and



Where,

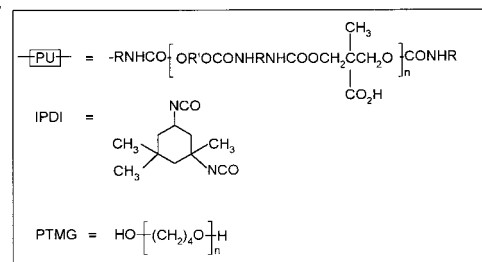


Figure 1 Preparation of water-based polyurethane dispersions.

TABLE I
Chemical Composition and Particle Size of Aqueous Polyurethanes

Sample	Molar ratio of NCO/OH	DMPA (wt %)	Hard segment content in polyurethane (wt %)	\bar{d}_p (nm)
APU36	1.3	6	30.4	33.7
APU38	1.3	8	36.1	27.8
APU52	1.5	2	21.7	88
APU54	1.5	4	27.9	22.3
APU56	1.5	6	34.2	55.5
APU58	1.5	8	40.5	49.1
APU82	1.8	2	25.4	46.9
APU84	1.8	4	32.5	47.1
APU86	1.8	6	39.6	31.7
APU88	1.8	8	46.7	22.8

urea carbonyl stretching vibrations) at 1695 cm^{-1} , and an amide II band (N–H bending vibrations) at 1553 cm^{-1} . The N–H stretching vibration is shown at 3320 cm^{-1} . The effect of the two functional groups on the hydrogen bonding and DMA results will be discussed in Figure 4.

It is known that aqueous polyurethane dispersions are two-phase systems, with water being the continuous phase. The dispersed phase is a solid polymer, although the aqueous polyurethane dispersions obtained are seemingly clean solutions. The particle size of the polymer ionomer dispersions depends on a variety of parameters, the most important of which is the number of ionic groups in the polymers. It is well known that particle size has a direct effect on the polyurethane dispersion stability and that the larger average particle size ($>1000\text{ nm}$) is generally unstable with respect to sedimentation. Small particle size ($<200\text{ nm}$) is sought after as these dispersions are storage stable and possess a high surface energy.⁸ As

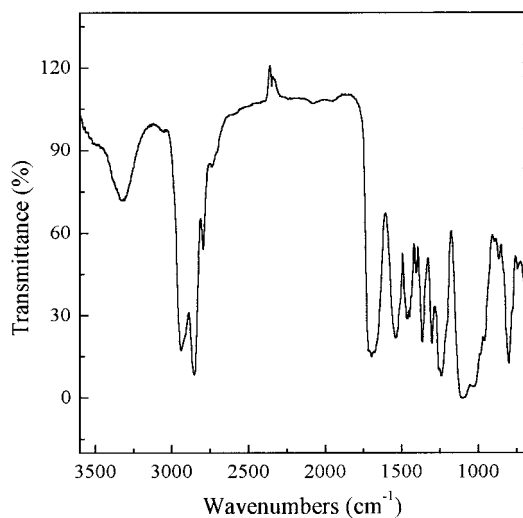


Figure 2 Typical infrared spectra of aqueous polyurethane dispersion.

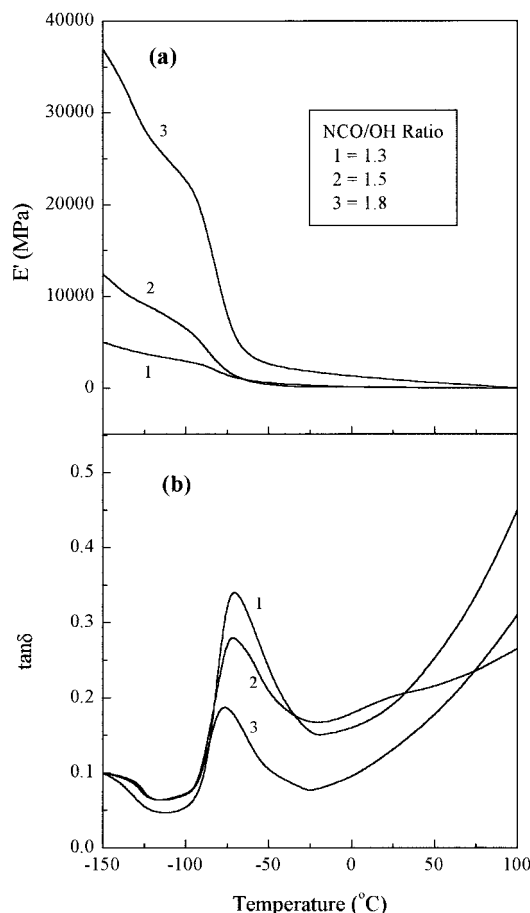


Figure 3 Dynamic mechanical analysis plots of APUs of 6 wt %–dimethylolpropanoic acid with different NCO/OH ratios.

shown in Table I, the particle sizes of aqueous polyurethane dispersions were indeed affected either by the molar ratio of NCO/OH or by the carboxylic ion proportion. For the same NCO/OH ratio, the particle size of dispersions decreasing with increasing ionic groups in polymer chain proved that ionic centers in polyurethane ionomers are located on the surface of dispersed particles, whereas hydrophobic chain segments form the interior of the particle. A similar result has also been reported by other researchers.⁹ It is difficult to obtain a stable dispersion if NCO/OH

TABLE II
The Glass Transition Temperature of APUs from DMA

Sample	T _g (°C)	
	From tanδ peak vs. temperature plot	From E'' vs. temperature plot
APU36	-79.5	-79.4
APU54	-67.7	-79.6
APU56	-70.4	-80.3
APU58	-72.7	-80.5
APU86	-77.3	-83.4

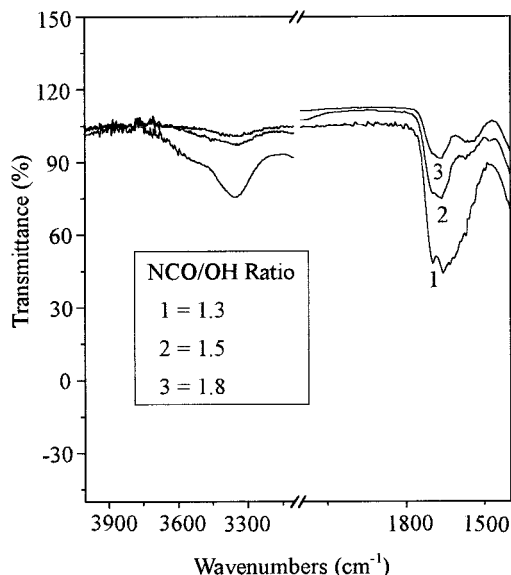


Figure 4 Fourier transform infrared spectra of APUs of 6 wt% dimethylolpropanoic acid with different NCO/OH ratios.

≤ 1.3 when the DMPA content is 2%. For the same proportion of DMPA, the particle size of dispersions with a different NCO/OH ratio slightly increased at a low NCO/OH ratio and then rapidly decreased with an increasing NCO/OH ratio in the NCO/OH ratio of 1.3~1.8. Therefore, we believe that there exists an optimum NCO/OH ratio to obtain aqueous polyurethane dispersions with small particle sizes.

Figure 3 presents DMA data, where the temperature versus storage modulus (E') plot is shown in (a) and the temperature versus $\tan\delta$ plot is shown in (b). The energy requirement for the storage measurement was related to the stiffness of the specimens. All samples showed a typical elastic behavior without a marked glass-state plateau region. As expected, the modulus of samples below glass transition temperature (T_g) was slightly increased with increasing carboxylic groups from 4% to 8% because it acted hard segments. However, the modulus increased markedly as the NCO/OH ratio increased from 3% to 8%, as shown in Figure 3(a). This behavior must be associated with the hydrogen bond concentration in the polymer chains. As is well known, the $-NH$ groups in urethane and urea linkage form a hydrogen bond with the carbonyl

group ($C=O$) of the hard segment or with an ether group ($C-O-C$) of the soft segment.¹⁰ As the ratio of NCO/OH increases, the urethane and urea linkage increases, which makes the hydrogen bonds form more effectively. Therefore, the modulus increased and it was found that the NCO/OH ratio also affected the modulus of the samples below T_g .

The T_g of APUs were given in Table II. Although the storage modulus of samples decreased continuously with temperature, only one peak was observed on the $\tan\delta$ versus T plots or loss modulus (E'') versus T plots. The $\tan\delta$ variation with temperature is shown in Figure 3(b). A similar result was also found for the samples with the same NCO/OH ratio. The T_g are assigned to the relaxation of soft segments. They are lower than the T_g value (-84°C) of polyoxytetramethylene, indicating that the soft and hard segments are partly compatible. The values from the loss modulus versus temperature plots, which are a little lower than those obtained from $\tan\delta$ peak temperature, are associated with the soft/hard segment interfaces.¹¹ Although the NCO/OH ratio and carboxylic group content can increase the storage modulus, they decrease T_g because of phase separation. It has been reported that more complete phase separation in polyurethane elastomers results in an increase in modulus and mechanical strength and a decrease in soft domain T_g .^{12,13}

As mentioned above, the modulus of the samples increased rapidly as the NCO/OH ratio increased as a consequence of the hydrogen bonding formation in polymers. FTIR is the most useful method for investigating the hydrogen bonding structure of polyurethanes; there have been a significant number of previously published studies about that using FTIR.¹⁴⁻⁶ Several spectral regions are involved in the hydrogen bonding: N-H stretching, $C=O$ stretching, and $C-O-C$ stretching vibration. It is generally agreed that the $C=O$ stretching region is favorable for analyzing hydrogen bonding in polymers. Both the FTIR spectra displaying the amide I stretching vibration and N-H stretching vibration regions of samples with different NCO/OH ratios were shown in Figure 4. As can be observed, the absorption band at 3340 cm^{-1} associated with the free NH group was very small in APU56 and APU86. That result indicates that most of NH groups in the two samples are hydrogen bonded. It is also

TABLE III
Mechanical Properties of APUs

Sample	Fail stress (MPa)	Fail strain (%)	Stress at 100% elongation (Mpa)	Stress at 300% elongation (Mpa)	Young's modulus (Mpa)
APU36	4.6	820	2.2	2.5	14
APU54	1.7	1080	1.3	1.5	3.2
APU56	6.9	770	2.1	2.6	6.5
APU58	6.7	720	2.8	2.9	9.8
APU86	27	390	6.6	16	23

noted that the carbonyl peaks of APU56 and APU86 split into two peaks: the one at about 1690 cm^{-1} resulting from self-association of N–H with C=O in the interior of hard domains, the other, at about 1730 cm^{-1} , is related to the free carbonyl group. This observation was in good agreement with the result from DMA analysis.

The mechanical properties of APUs are shown in Table III. APU54, the softest material, showed the lowest ultimate tensile strength and Young's modulus, but the largest elongation at break. APU86 showed the largest tensile strength because it contains the highest hydrogen bonding density, as described above, but the smallest elongation at break. It is clear that the Young's modulus increased and the strain at breakpoint decreased with the pendant carboxylic group contents for the same NCO/OH ratio. Compared with APU56 and APU58, APU36 has a lower ultimate tensile strength but a larger strain at breakpoint and modulus. The stress-strain curves of samples are shown in Figures 5 and 6.

CONCLUSION

Aqueous anionic polyurethane dispersions were synthesized and their particle sizes mainly influenced by the functional group contents. The –NH groups in urethane and urea linkage form hydrogen bonding with the carbonyl group (C=O) of hard segments or the ether group (C–O–C) of soft segments. FTIR analysis showed that increasing the NCO/OH ratio effectively enhances the hydrogen bonding by increasing –NH group concentration and that, as a consequence, the mechanical strength of polyurethanes increased. In DMA analysis, all samples showed typical elastic behavior without a marked glass-state plateau region, and the

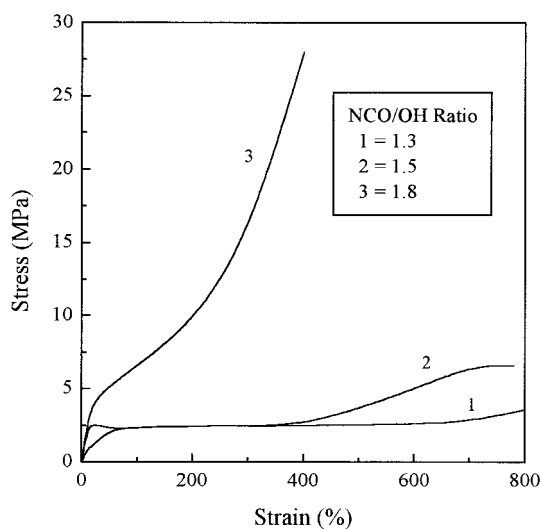


Figure 5 Stress-strain curves of APUs of 6 wt % dimethylolpropanic acid with different NCO/OH ratios.

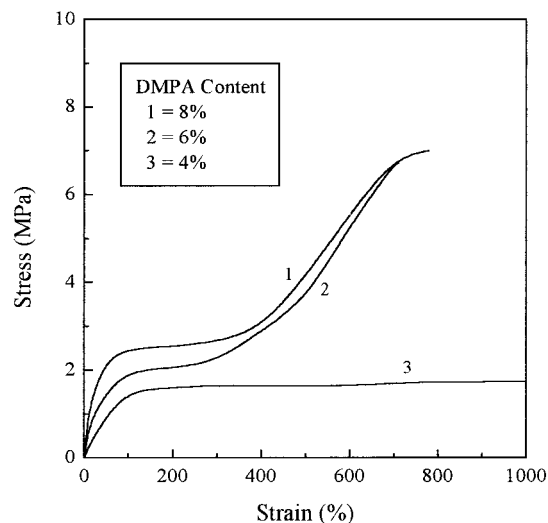


Figure 6 Stress-strain curves of APUs of a 1.5-NCO/OH ratio with different dimethylolpropanic acid content.

modulus of the samples below T_g slightly increased with an increasing carboxylic group from 4% to 8%. However, it increased abruptly as the NCO/OH ratio increased from 3% to 8%. These behaviors were associated with the hydrogen bonding concentration in the polymer chains between the –NH groups or urea linkage and the carbonyl group (C=O) of hard segment. Tensile testing revealed that the pendant carboxylic group made the modulus or stiffness increase.

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