Fibers and Polymers 2002, Vol.3, No.3, 97-102

Preparation and Properties of Waterborne Poly(urethane-urea) Ionomers -Effect of the Type of Neutralizing Agent-

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(Received May 29, 2002; Revised September 9, 2002; Accepted September 16, 2002)

Abstract: A series of waterborne poly(urethane-urea) anionomers were prepared from isophorone diisocyanate (IPDI), polycaprolactone diol (PCL), dimethylol propionic acid (DMPA), ethylene diamine (EDA), and triethylamine (TEA), NaOH, or $Cu(COOCH_3)_2$ as neutralizing agent. This study was performed to decide the effect of neutralizing agent type on the particle size, viscosity, hydrogen bonding index, adhesive strength, antistaticity, antibacterial and mechanical properties. The particle size of the dispersions decreased in the following order: TEA based samples (T-sample), NaOH based samples (N-sample), and $Cu(COOCH_3)_2$ based sample (C-sample). The viscosity of the dispersions increased in the order of C-sample, N-sample, and T-sample. Metal salt based film samples (N and C-sample) had much higher antistaticity than TEA based sample. By infrared spectroscopy, it was found that the hydrogen bonding index (or fraction) of samples decreased in the order of T-sample, N-sample, and C-sample. The adhesive strength and tensile modulus/strength decreased in the order of T-sample, N-sample, and C-sample. The C-sample had strong antibacterial halo, however, T- and N-samples did not.

Keywords: Waterborne, Poly(urethane-urea), Ionomer, Neutralizing agent, Hydrogen bonding, Antibacterial

Introduction

Poly(urethane-urea) ionomers contain a minor component carrying pendent acid or tertiary nitrogen groups (<10 mol%) that are completely or partially neutralized or quarternized, respectively[1,2]. PU ionomers are interesting polymers which contain associated ionic centers in the polymer backbone at different chain intervals. The presence of the coulombic forces in the urethane-urea ionomers obviously changes the properties of polyurethane-urea.

PU ionomers are of considerable scientific as well as of commercial interest because of their unique structure and properties which find industrial applications. Three types of hydrophilic groups for PU ionomers: cations, anions, and zwitterions, known as "ionogenic groups", are generally employed and form, according to the ionic charges on the polymeric main chain: cationomers[3,4], anionomers[1,5-7], and zwitterionomers[8], respectively. Both cationomers and anionomers are quaternized or neutralized by neutralization agent, in order to form opposite charge groups (or salt groups) resulting in coulombic forces.

In particular, PU anionomers are usually prepared by reaction of a NCO-terminated PU prepolymer with DMPA or dimethylol butanoic acid containing pendant carboxylic acid groups, followed by neutralization with base[5-7]. Ionic moieties have a strong effect on properties of PU anionomers [5,6,9,10].

Countercations strongly affect the physical properties of PU anionomers containing carboxylate anions[7]. The interactions between ions and their counterions are responsible for these effects[6,11,12]. Chen and Chen[10] investigated the effects of neutralizing agents (ammonia, trimethylamine, triethylamine, LiOH, NaOH, and KOH) on the properties of polyurethane anionomer dispersions. Hourston *et al.*[13] discovered that the degree of neutrization, the type of ionic component, and the counterion contribute significantly to the properties of waterborne polyurethane ionomer. However, the reserch on the influence of countercation Cu^{++} on the properties of waterborne polyurethane anionomer is hardly found.

In this study, we report on the preparation and properties of polyurethane anionomers from isophorone diisocyanate (IPDI), polycaprolactone (PCL), dimethylol propionic acid (DMPA), ethylene diamine (EDA), and triethylamine (TEA), NaOH, or $Cu(COOCH_3)_2$ as neutralizing agent. Studies have been made on the effects of the type of neutralizing agents on properties such as the particle size, viscosity, antistaticity, antibacterial property, adhesive strength, and mechanical property.

Experimental

Materials

Dimethylol propionic acid (DMPA, Aldrich Chemical Inc.) and polycaprolactone diol (PCL M_n=1250, Aldrich) were dried in a vacuum oven (100 °C) for at least 5 hours. Isophorone diisocyanate (IPDI, Merck Co.), triethylamine (TEA, Aldrich), and ethylene diamine (EDA, Aldrich) were used after dehydration with 4 Å molecular sieves for one day. Dibutyl tin dilaurate (DBTDL, Aldrich) and stannous octotate,

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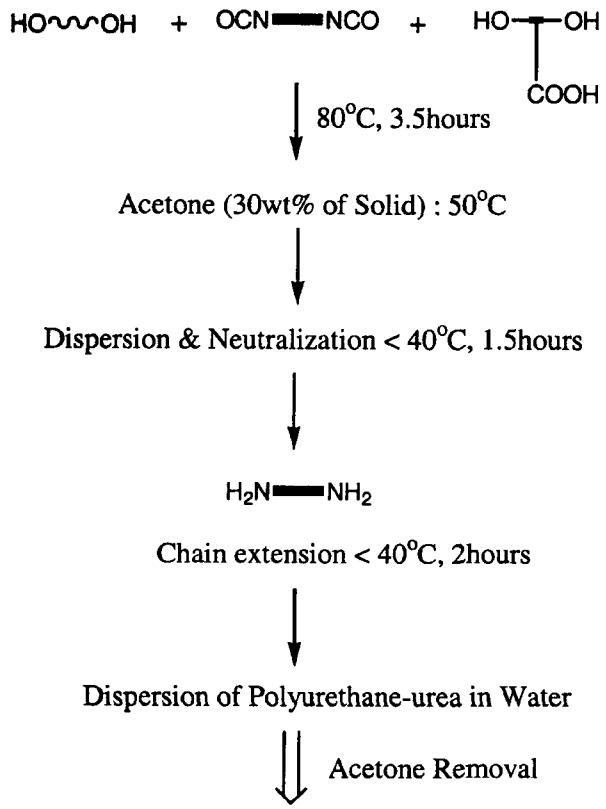
cupric acetate ($Cu(COOCH_3)_2$, Aldrich), sodium hydroxide (NaOH, Aldrich), and N-methyl-2-pyrrolidone (NMP, Aldrich) were used without further purification.

Preparation of Waterborne Polyurethane Anionomers

A series of waterborne polyurethane anionomers were prepared as following. DMPA was dissolved in NMP (50/50, w/w) in a four neck round-bottom flask equipped with a thermometer, a stirrer, an inlet of dry nitrogen, a condenser and a heat jacket. PCL was placed in the flask and degassed under vacuum at 60 °C for 1 hour. IPDI/acetone and DBTDL were then added slowly under gentle stirring, and the mixture was allowed to react at 80 °C until the theoretical NCO content was reached. It took about 3.5 hours to reach the theoretical value. Acetone (30 wt% of solid)was added to the NCO-terminated polyurethane prepolymer mixture to adjust suitable viscosity of solution. The dispersion and neutralization were carried out simultaneously by adding distilled water/neutralizing agent (TEA) at 40 °C for 1.5 hours with vigorous stirring. The neutralized prepolymer was chain-extended by dropping EDA at 40 °C for 2 hours. The reaction continued until NCO absorption peak (2270 cm^{-1}) in IR spectra had completely disappeared. All the aqueous dispersions of 40 wt% solid were obtained after removal of acetone by evaporating. The preparation process of waterborne polyurethane-urea anionomers is outlined in Scheme 1. Films were prepared for test by pouring the dispersions into a Teflon disk at ambient conditions. The films (typically about 0.5 mm thick) were dried in vacuum at 50 °C for 2 days.



Scheme 1. The preparation process of waterborne poly(urethane-urea) anionomers.

The sample designation and composition of waterborne polyurethane anionomers prepared in this study are listed in Table 1.

Characterization

Particle size analysis was done using a laser-scattering equipment (Autosizer, Malvern IIC). A few drops of the dispersion were diluted in non-ionized water before the measurement. The viscosity of waterborne polyurethane dispersions was measured at 25 °C using the Brookfield digital viscometer (Model LVDV-II+). IR spectra were acquired by using a Fourier Transform Infrared Spectrometer (Nicolet Impact 400D). For each sample, 32 scans at 4 cm^{-1} resolution were collected in the absorption mode. The NCO stretching band near 2270 cm^{-1} was used to monitor the extent of the reaction between isocyanate and the hydroxyl group. The electrostatic properties of films were measured using Honestmeter (Type H-0110) at 60 % RH and room temperature. The half life time was obtained from the electrostatic meter. The antistaticity (1/sec) of polyurethane anionomer films was taken as the 1/electrostatic half life time of films. Tensile properties were measured at room temperature using United Data System Tensionmeter (Instron, SSTM-1) according to the ASTM D-638. A crosshead speed of 20 mm/min was used throughout these investigations to determine the ultimate tensile strength and elongation at break for all the samples. The values quoted are the average of five tests. The peel strength of adhesives was measured using United Data System Tensionmeter (Instron, SSTM-1) according to KS M 3725 using T type test sample. The dimension of substrate (rubber) was 0.5/20/70 mm of D/W/L.

Table 1. Sample designation and composition (mole ratio) of waterborne poly(urethane-urea) anionomers

Sample designation	IPDI	PCL M_n=1250	DMPA	EDA	Neutralization agent		
					TEA	NaOH	$(CH_3COO)_2Cu$
T	2.7	1	0.65	1	0.65	-	-
N	2.7	1	0.65	1	-	0.65	-
C	2.7	1	0.65	1	-	-	0.65

Halo test was used to determine the antibacterial properties of samples using Pseudomonas as a bacterium. The films prepared in this study were put on the petri dish containing the cultured bacterium on agar culture medium and then were cultured again for 2 days. The antibacterial property was determined by observing the halo (clear zone) after the period.

Results and Discussion

A series of polyurethane-urea anionomers were prepared from IPDI, PCL, DMPA, EDA, and TEA, NaOH, or $Cu(COOCH_3)_2$. The neutralizing agents TEA, NaOH, or $Cu(COOCH_3)_2$ were used to produce the counterions $(C_2H_5)_3NH^+$, Na^+ or Cu^{++}, to the waterborne polyurethane-urea anionomers. The influence of the type of neutralizing agents on the extent of hydrogen bonding, particle size, viscosity, adhesive strength, antistaticity, antibacterial and mechanical properties was studied. The origin of our paper is on the comparison of the effect of three different counterions including Cu^{++} ion, which was seldom found in many studies.

The nature of hydrogen bonding of the hard segments causes a strong mutual attraction leading to domain formation. Infrared spectroscopy has been employed extensively to study the hydrogen bonding and is a useful tool in characterizing of hydrogen bonding in domains[14,15]. Interface adhesion between polyurethane-urea ionomers and the adhered substrates is also increased due to the presence of coulombic forces and enhanced hydrogen bonding.

Figure 1 shows the IR spectrum of a typical T film sample. The IR spectra were analyzed using the curve resolving technique based on the linear least-squares analysis to fit the combination of the Lorentzion and Gaussian curve shapes. Some studies[16,17] reported that the band centered at around 1725 cm^{-1} was attributed to the stretching of free carbonyl groups, whereas the carbonyl stretching at about 1710 cm^{-1} was due to hydrogen bond in disordered regions. The urethane carbonyl stretching at about 1710 cm^{-1} was found to attribute to the carbonyl groups participating in urethane linkage of interfacial regions or being dissolved in the soft phase. The stretching of the stronger hydrogen bonds in ordered or crystalline regions occurs at a lower frequency at about 1695 cm^{-1}. The infrared bands at 3440 and 3320 cm^{-1} are assigned to the N-H stretching modes of the free and hydrogen bonding N-H groups of PU, respectively.

Decomposition of the C=O and N-H stretching bands for the typical sample T are shown in Figure 2. The extent of hydrogen bonding index (HBI) and the fraction of hydrogen bonding (X_B) for three samples prepared in this study is shown in Table 2. A reasonable estimate of the fraction of free - and hydrogen bonding - carbonyl groups can be obtained from curve fitting and by adjusting the areas to account for the difference in absorptivity coefficient ratio. Hydrogen bonding index is defined as the relative absorbances ratio of hydrogen bonding C=O (or N-H) peak to free C=O (or N-H) peak[18]. The hydrogen bonding fraction(X_B) is expressed as $X_B=C_B/C_T$, where C_T is the total peak area of C=O or N-H groups and C_B is the peak area of hydrogen bonding C=O or N-H groups. HBI and X_B are in the order of T-sample > N-sample > C-sample. HBI and X_B of T-sample have higher

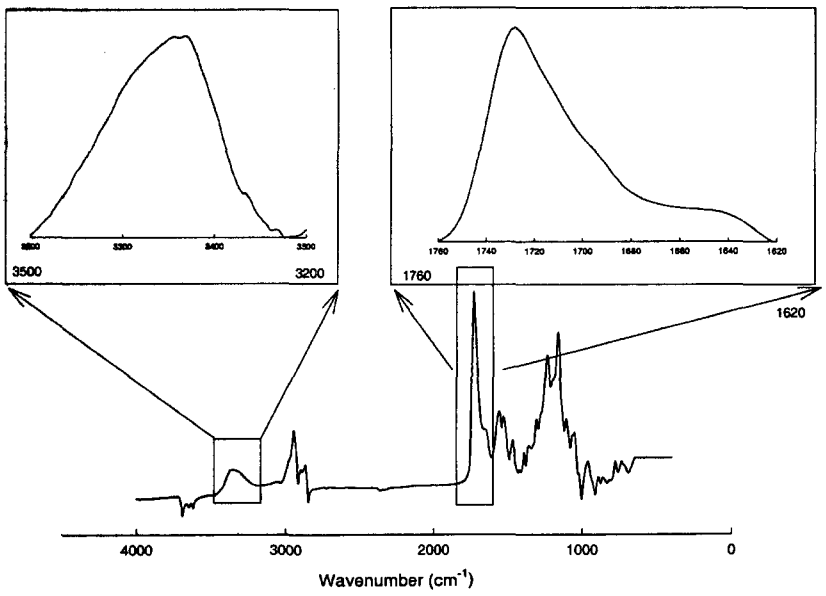


Figure 1. Infrared spectrum of typical T film sample.

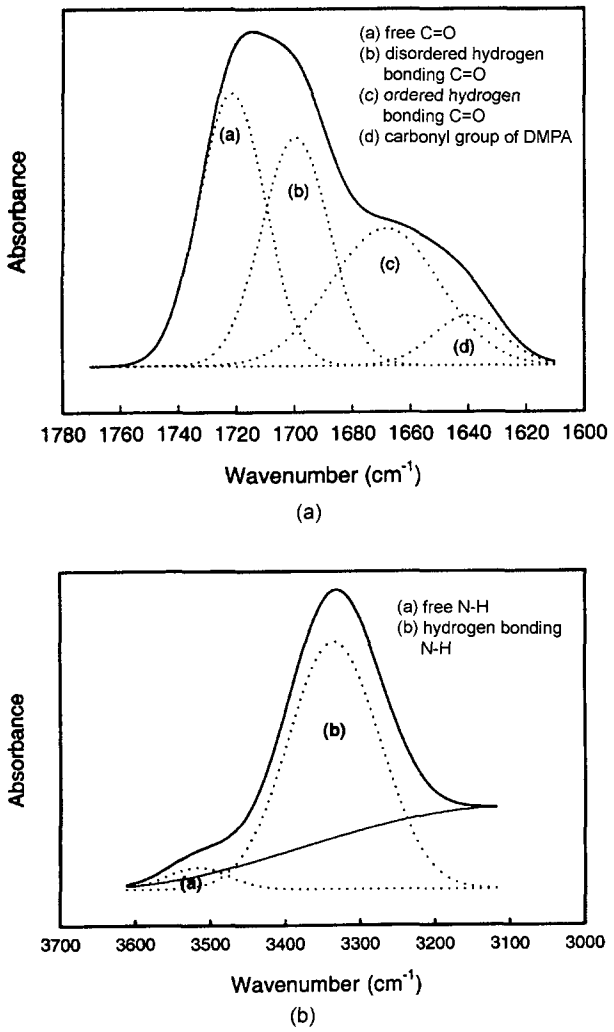


Figure 2. Decomposition of the C=O and N-H stretching for Sample T.

Table 2. Decomposition results of the C=O and N-H stretching band

Sample designation	C=O stretching		N-H stretching	
	HBI[a)]	X_B[b)]	HBI[c)]	X_B[d)]
T	1.984	0.815	2.350	0.834
N	1.494	0.740	2.012	0.806
C	1.419	0.735	2.077	0.805

[a)]HBI=Hydrogen bonding C=O peak intensity/free C=O peak intensity.
[b)]$X_B=C_B/C_T$ [C_B: hydrogen bonding C=O peak area (b+c), C_T: total peak area (a + b + c)].
[c)]HBI=Hydrogen bonding N-H peak intensity/free N-H peak intensity.
[d)]$X_B=C_B/C_T$ [C_B: hydrogen bonding N-H peak area (b), C_T: total peak area (a+b)].

Table 3. Colloidal properties of poly(urethane-urea) and antistaticity of film samples

Sample designation	Particle size (nm)	Polydispersity	Viscosity (cps)	Antibacterial performance[a)]
T	211.1	0.304	750	X
N	248.9	0.300	681	X
C	280.0	0.305	653	O

[a)]The existence of antibacterial function: O, Non-existence: X.

values than those of N- and C-samples. This higher values of TEA based sample (T-sample) may be the reason of its excellent mechanical properties compared with N- and C-samples.

Particle sizes and viscosity of polyurethane-urea dispersions prepared in this study are shown in Table 3. The particle size of PU dispersions are in the range of 210-280 nm. The particle size of dispersions decreased in order of C-sample, N-sample, and T-sample (see Table 3). The C-sample containing Cu^{++} has a bigger particle size compared with T- and N-samples having $(Et)_3NH^+$ and Na^+. This may be due to the bridging function of divalent Cu^{++}. The viscosity of dispersions decreased in order of T-sample, N-sample, and C-sample (see Table 3). Generally, the polymer dispersion of lower particle size has higher viscosity than that of higher particle size. Therefore, the higher viscosity of T-sample is caused by relatively their lower particle size.

The effect of the type of counterion on the antistaticity (1/sec, reciprocal of electrostatic half life time (sec)) of film samples are shown in Figure 3. The antistaticity decreased in the order of C-sample, N-sample, and T-sample. Metal counterion-based film samples (N- and C-samples) have much higher antistaticity compared with organic counterion-based T-sample. This might be related to the higher conductivity of metal ions acting as counterions.

Figure 4 shows the strength of adhesive of polyurethane-

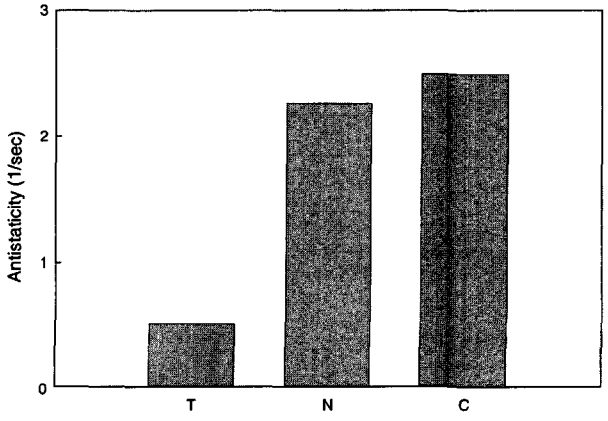


Figure 3. Effect of the counterion on the antistaticity.

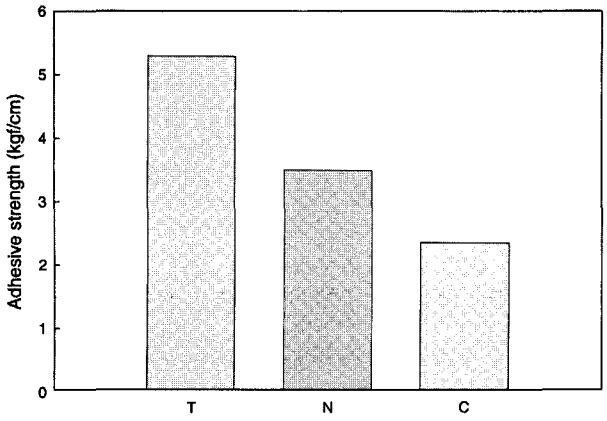


Figure 4. Effect of the counterion on the adhesive strength.

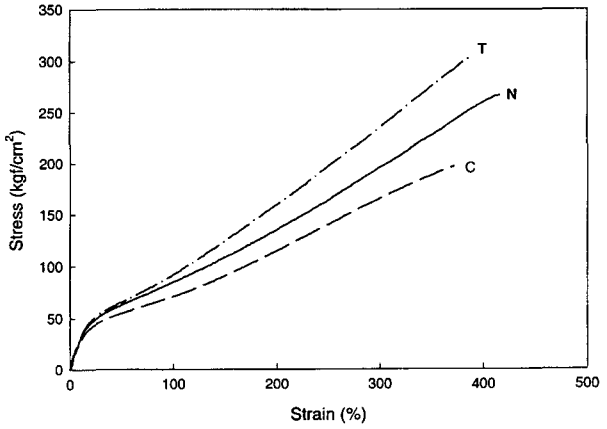


Figure 5. Effect of the counterion on the tensile properties.

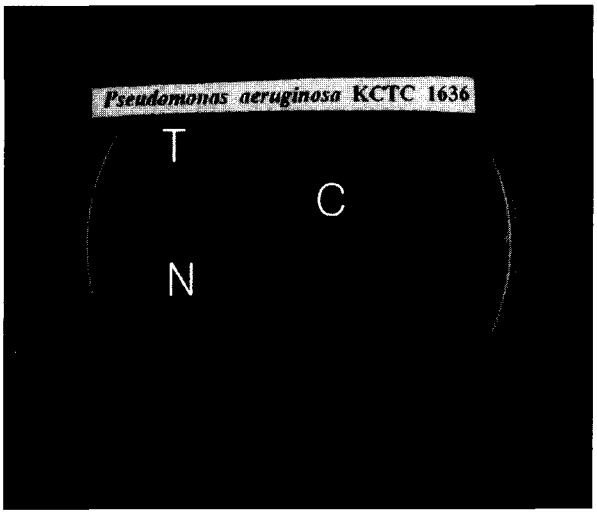


Figure 6. The photomicrograph of antibacterial halo.

urea dispersions prepared. The adhesive test was done using T type test sample with CR-rubber/CR-rubber as a substrate (D/W/L: 0.5/20/70 mm). The adhesive strength decreased in the order of T-sample, N-sample, and C-sample. The higher strength of T-sample may be attributed to the higher coulombic forces of ionic groups.

Figure 5 shows the stress-strain curve of film samples. Tensile modulus and strength decreased in the order of T-sample, N-sample, and C-sample. The higher modulus and strength of samples may be due to their higher coulombic force and hydrogen bonding compared with others.

Halo test was used to determine the antibacterial property of samples using pseudomonas as a bacterium. C-sample containing countercation Cu^{++} had strong antibacterial halo, however, T- and N- film samples did not (see Figure 6). This may be attributed to the antibacterial power of Cu^{++} countercation in itself.

Conclusions

Waterborne polyurethane anionomers were prepared from isophorone diisocyanate (IPDI), polycaprolactone (PCL), dimethylol propionic acid (DMPA), ethylene diamine (EDA), and TEA, NaOH, or $Cu(COOCH_3)_2$ as neutralization agent. The effect of counterion type on the properties of the dispersions and films was investigated. By infrared spectroscopy, it was found that the extent of hydrogen bonding C=O and N-H stretching was decreased in the order of TEA based sample (T-sample), NaOH based sample (N-sample), and $Cu(COOCH_3)_2$ based sample (C-sample). The particle size of the dispersions decreased in the order C-sample, N-sample, and T-sample. However, the viscosity of the dispersions increased in the order of C-sample, N-sample, and T-sample. Metal salt-based film samples (N- and C-samples) had much higher antistaticity than T-sample. The C-sample had strong antibacterial property, however, T- and N-samples did not. The adhesive strengthand tensile modulus/strength decreased in the order of T-sample, N-sample, and C-sample.

Acknowledgement

This work was supported by Pusan National University Research Grant.

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