

Synthesis and Characterization of Polyurethane Anionomers

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ABSTRACT: Un-ionized polyurethane was obtained by the reaction of an isocyanate-terminated urethane prepolymer, which was synthesized from 4,4'-diphenylmethane diisocyanate and poly(oxytetramethylene)- α,ω -glycol, with 2,2-bis(hydroxymethyl)propionic acid. A carboxylate-based polyurethane anionomer was then derived from the polyurethane by the use of the sodium, potassium, or magnesium salt of acetic acid as a neutralizer. The ionomerization resulted in the following changes in the characteristics of the polyurethane: (1) an increase in the tensile strength, (2) a

decrease in the glass-transition temperature, (3) an increase in the wettability and hygroscopicity with respect to water, and (4) susceptibility to thermal decomposition. A sulfonate-based polyurethane was also synthesized for comparison with the carboxylate-based polyurethane. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 2144–2148, 2005

Key words: mechanical properties; polyurethanes; thermal properties

INTRODUCTION

Ionomers are polymers possessing ionic groups at the main chains, side chains, or chain ends. They have characteristic functions based on the electrostatic interaction of the ionic groups and constitute a type of functional polymers. Ionomers having a cation as the ionic group are called *cationomers*, whereas those having an anion as the ionic group are called *anionomers*. Ionomers have ideal physical properties as polymer materials: not only do they form crosslinked ionic bonds because of the ionic groups that partially exist between polymer chains, but they also exhibit fluidity at high temperatures because of the dissociation of the crosslinked ionic bonds. In addition, the partial introduction of ionic groups into polymer materials makes it possible to improve the dynamic and optical characteristics as well as the adhesion properties of the host polymer while other characteristics are retained.^{1–4} Research has been carried out on polyurethane-based ionomers belonging to substances known as thermoplastic elastomers for the purpose of preventing the diffusion of environmental pollutants from coated films and achieving solubilization and/or dispersion in water.^{5–12} We report herein the syntheses of carboxylate-based polyurethane anionomers

(PUACs) and sulfonate-based polyurethane anionomers (PUASs), as well as the results of a study of their mechanical characteristics, thermal properties, wetting characteristics, and hygroscopicity.

EXPERIMENTAL

Reagents

4,4'-Diphenylmethane diisocyanate (MDI; purity = 99.9%; Nippon Polyurethane Industry Co., Ltd., Japan) was used as received as the diisocyanate. Poly(oxytetramethylene)- α,ω -glycol [PTMG; number-average molecular weight (M_n) = 1000; Hodogaya Chemical Co., Ltd., Japan] was used as the polyol, the chains of which composed the soft segment of the thermoplastic elastomer, after drying under reduced pressure for 6 h at 80°C in a nitrogen atmosphere. 2,2-Bis(hydroxymethyl)propionic acid (DMPA; Tokyo Kasei Kogyo Co., Ltd., Japan) was used for PUAC synthesis as a chain extender, which formed the hard segment of the thermoplastic elastomer by the reaction with diisocyanate, after drying at atmospheric pressure at 110°C. In the PUAS synthesis, sodium *N,N*-bis(2-hydroxyethyl)-2-aminoethane sulfonate (PUAS-ENa) and sodium *N,N*-bis(2-hydroxyethyl)-2-aminobutane sulfonate (PUAS-BNa; Asahi Kasei Finechem Co., Ltd.) were used as both chain extenders and ionic group introducers after drying under reduced pressure over diphosphorus pentoxide. *N,N*-Dimethylacetamide (DMAc; dehydrated; Kanto Kagaku Co., Ltd.,

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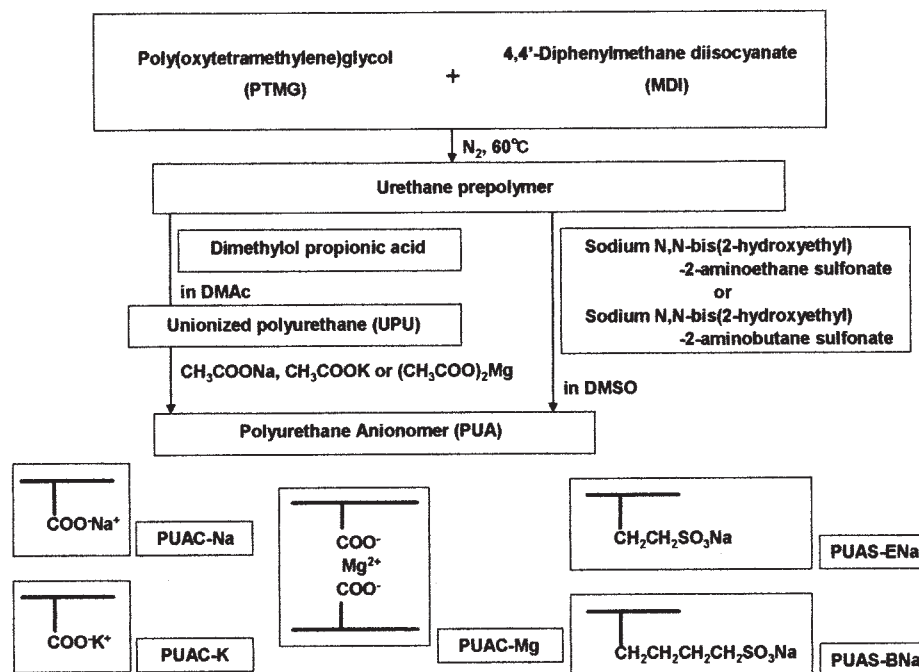


Figure 1 Synthetic approach to the polyurethane anionomers.

Japan) and dimethyl sulfoxide (DMSO; dehydrated; Kanto Kagaku) were reagent-grade and were used without further purification. The other reagents were used as received.

Synthesis

MDI and PTMG were added to a four-necked separator flask and allowed to react with stirring at 60°C in a dry nitrogen atmosphere to produce an isocyanate-terminated urethane prepolymer (ITUP). DMAc as a solvent was used to dilute the concentration of ITUP to 30 wt % (calculated to be the solid content). A 30 wt % DMPA (chain extender) solution in DMAc (molar ratio of NCO groups to OH groups = 1.0) was added dropwise to this solution during rapid stirring at 40°C. The reaction was allowed to proceed until the IR absorption band of the NCO group of ITUP that appeared in the vicinity of 2270 cm⁻¹ disappeared, and this indicated the completion of the reaction to obtain un-ionized polyurethane (UPU; see the PTMG/MDI/DMPA molar ratio shown later in Table II). A stoichiometric amount of sodium acetate, potassium acetate, or magnesium acetate was added as a neutralizer, and this was followed by stirring to synthesize PUAC (PUAC-Na, PUAC-K, or PUAC-Mg). Partially ionized PUAC (PUAC-Na₅₀ and PUAC-Na₇₅) were prepared by neutralization with 50 and 75% of a stoichiometric amount of sodium acetate. In the synthesis of PUAS (PUAS-ENa and PUAS-BNa), 30 wt % PUAS-ENa or PUAS-BNa in DMSO was added dropwise to a 30 wt % DMSO solution of ITUP with rapid stirring at 40°C.

The completion of the reaction was confirmed by the disappearance of the NCO absorption band in the IR spectrum. The scheme for the aforementioned syntheses is shown in Figure 1. The abbreviations of the ionomers are also shown in the figure. A polyurethane elastomer in which 1,4-butanediol was used as the chain extender (PUBD) was also synthesized for comparison with the ionomers of PUAC and PUAS.

The absence of urea bonds in the synthesized ionomers was confirmed by Fourier transform infrared and ¹H-NMR measurements. The *M_n* values of UPU, PUAS-ENa, PUAS-BNa, and PUBD were measured by size exclusion chromatography with polystyrene as the standard (the solvent was *N,N*-dimethylformamide for both polyurethane and polystyrene).

Thermoplastic polyurethane elastomers are block copolymers composed of soft segments originating from polyol chains and hard segments produced by reactions between diisocyanates and chain extenders.

Preparation of the film

An ionomer solution was cast into a Teflon-coated vat and degassed at room temperature. The solvent was removed over the course of 1 week by drying at 60°C under reduced pressure to obtain an ionomer film.

Measurement of the glass-transition temperature (*T_g*)

T_g was measured with a model DSC220 differential scanning calorimeter (Seiko Instruments, Inc., Japan)

TABLE I
Characterization of UPU and PUACs with Different Degrees of Ionization

Sample	Degree of ionization (%)	T_b (MPa)	E_b (%)	T_{gs} ($^{\circ}$ C)	θ_w ($^{\circ}$)	γ_s (mJ/m 2)
UPU	0	6.5	450	-40.9	92	29.7
PUAC-Na $_{50}$	50	8.5	270	-46.3	83	39.4
PUAC-Na $_{75}$	75	17.6	170	-50.8	75	39.4
PUAC-Na	100	21.7	160	-51.8	69	42.0

T_b , tensile strength at break point; E_b , ultimate elongation at break point; T_{gs} , glass-transition temperature of the soft segment; θ_w , contact angle of water; γ_s , surface free energy of the film.

with a sealed aluminum cell at a nitrogen flow rate of 50 mL/min and a heating rate of 5 $^{\circ}$ C/min over a temperature range of -130 to 220 $^{\circ}$ C.

Tensile testing

The stress-strain curve was measured at a pulling speed of 500 mm/min with a test piece molded into the shape of a dumbbell with a model 5566-P5123 tensile tester (Instron Japan Co., Ltd., Japan).

Thermal stability testing

The thermal stability was measured with a model TG/DTA220 simultaneous thermogravimetric differential thermal analyzer (Seiko Instruments) with an aluminum cell at a nitrogen flow rate of 200 mL/min and a heating rate of 10 $^{\circ}$ C/min over a temperature range of 25-600 $^{\circ}$ C.

Measurement of the contact angle

Two types of contact angles (water and diiodomethane) were measured at 25 $^{\circ}$ C with a model CA-D contact-angle gauge (Kyowa Interface Science Co., Ltd., Japan). The free energy of the film surface was calculated with eqs. (1)-(3).¹³

$$(1 + \cos\theta)\gamma_L = 2\sqrt{\gamma_s^d\gamma_L^d} + 2\sqrt{\gamma_s^p\gamma_L^p} \quad (1)$$

$$\gamma_s = \gamma_s^d + \gamma_s^p \quad (2)$$

$$\gamma_L = \gamma_L^d + \gamma_L^p \quad (3)$$

where γ_L is the surface tension of the liquid (mJ/m 2), γ_s is the surface free energy of the solid (mJ/m 2), γ_s^d and γ_L^d are the dispersion force components of the surface free energy (mJ/m 2), and γ_s^p and γ_L^p are the polarizing force components of the surface free energy (mJ/m 2).

Hygroscopic properties

The change in weight was measured by the suspension of a sample contained in a commercially available tea bag (5 cm \times 4 cm) in a chamber (model 1H40, Yamato Scientific Co., Ltd., Japan) under controlled temperature and humidity conditions of 30 $^{\circ}$ C and 100%, respectively, and this was followed by the determination of the moisture absorption rate at equilibrium (in other words, the equilibrium moisture absorption rate). Equilibrium was reached within 48 h for all samples.

The experimental error for all measurements in this study was within $\pm 5\%$.

RESULTS AND DISCUSSION

For UPU and PUACs having various degrees of ionization of the carboxyl group by sodium acetate, the tensile strength and elongation at break, the T_g value of the soft segment, the contact angle of water, and the surface free energy are shown in Table I. When the degree of ionization is high, namely, when the concentration of sodium carboxylate is increased, the tensile strength is increased, and the elongation percentage is decreased. This indicates that clusters of sodium carboxylate are produced, and they result in the formation of a pseudonetwork structure.

As shown in Figure 2, the yield point can be clearly observed in samples with high sodium carboxylate concentrations. This suggests that soft segments are easy to disperse in the matrix of hard segments with an increasing sodium carboxylate concentration. As for T_g , it is lowered as the sodium carboxylate concentration is increased. This means that the degree of phase separation of hard and soft segments is increased because of the introduction of ionic groups.

The contact angle of water is reduced, whereas the surface free energy is increased, as the concentration of sodium carboxylate is increased. The introduction of hydrophilic ionic groups imparts higher wettability to the polyurethane.

The effect of the ionic group type on T_g and the effect of the molar ratios of MDI, PTMG, and DMPA

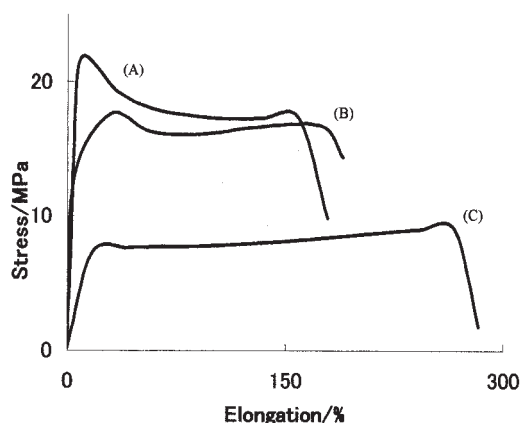


Figure 2 Stress-strain curves for PUAC-Na samples with different degrees of ionization: (A) PUAC-Na, (B) PUAC-Na₇₅, and (C) PUAC-Na₅₀.

on the T_g , thermal stability, wetting characteristics, and hygroscopicity of the ionomers are shown in Table II.

When the molar ratios of the raw materials are changed, the soft-segment concentration (SSC) is changed, and T_g of the soft segment is shifted accordingly. The T_g values of 4/1/3 UPU (SSC = 40.5%) and 4/2/2 UPU (SSC = 59.4%) are -40.9 and -23.9°C , respectively. Although the T_g value of the soft segment is generally shifted to a higher temperature as SCC becomes lower, namely, as the hard-segment concentration becomes higher,¹⁴ the experimental results do not agree with this trend. For 4/1/3 UPU with a high carboxyl group concentration, the T_g value is low because the structure of 4/1/3 UPU is such that the crosslinking density and the degree of phase separation are increased, depending on the number of hydrogen bonds of the carboxyl groups. With respect to the T_g value of PUAC, T_g is in the vicinity of -50°C for

both molar ratios (4/1/3 and 4/2/2), regardless of the type of ionic group. This suggests that phase-separation structures in which the ionic groups within PUAC form rigid clusters govern the T_g values. A comparison of the T_g values of carboxylate-type PUACs with those of sulfonate-type PUASs reveals that the latter are markedly higher. When the molar ratios 4/1/3 and 4/2/2 are compared, higher T_g values are found for the former. Altogether, the results confirm that the use of sulfonate as an ionic group leads to the production of an ionomer having an extremely high degree of phase separation.

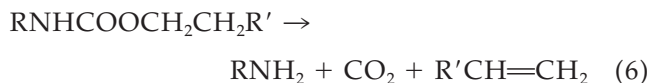
The initial thermal decomposition temperature of the ionomers (T_i ; the temperature at which the weight loss reaches 5%) is 200°C or lower for both PUAC-Na and PUAC-K, regardless of the ratio of the raw materials charged. The T_i value of PUBD exceeds 300°C and is considerably higher than those of the other ionomers. Such basic salts as sodium carboxylate and potassium carboxylate have a marked effect on the thermal decomposition of the ionomers and possess the so-called self-catalyzing action. In general, the initiation of the thermal decomposition of polyurethane involves the dissociation of urethane bonds [eq. (4)] and thermal decomposition [eqs. (5) and (6)]. When a urethane compound undergoes thermal decomposition, carbon dioxide is generated, and the thermal decomposition reaction is known to be accelerated under basic conditions.^{15,16} Thus, the susceptibility of PUAC-Na and PUAC-K to thermal decomposition is presumed to be caused by the promotion of the release of carbon dioxide from urethane bonds, which is accelerated by sodium carboxylate or potassium carboxylate:



TABLE II
Characterization of PUACs and PUASs

MDI/PTMG/DMPA (mol/mol/mol)	Sample	M_n	SSC (%)	T_{gs} ($^\circ\text{C}$)	T_i ($^\circ\text{C}$)	T_{50} ($^\circ\text{C}$)	θ_w ($^\circ$)	γ_s (mJ/m^2)	W_e (%)
4/1/3	PUBD	30,300	42.6	-48.0	317	372	101	26	0.5
	PUAC-UPU	45,900	40.5	-40.9	197	405	92	30	7.1
	PUAC-Na		39.1	-51.8	175	386	69	42	55.0
	PUAC-K		38.7	-55.9	165	377	72	41	45.2
	PUAC-Mg		40.0	-48.4	221	390	74	39	23.4
	PUAS-ENa	11,200	35.7	-68.6	201	369	75	34	36.7
4/2/2	PUAS-BNa	14,000	34.6	-64.7	181	385	76	32	32.9
	PUAC-UPU	46,600	59.4	-23.9	224	407	101	24	3.3
	PUAC-Na		58.3	-49.2	198	396	72	40	36.1
	PUAC-K		58.1	-51.0	184	387	76	38	24.5
	PUAC-Mg		59.0	-45.5	248	420	78	36	12.4
	PUAS-ENa	21,800	55.7	-57.7	203	389	73	36	19.2
	PUAS-BNa	24,000	54.8	-55.9	201	400	75	34	17.6

T_{gs} , glass-transition temperature of the soft segment; θ_w , contact angle of water; γ_s , surface free energy of the film; W_e , percentage moisture absorption at equilibrium.



When the molar ratios of the raw materials are changed, the behavior of UPU and carboxylate-based ionomers during thermal decomposition is changed markedly, as shown in Table II. Regardless of the sample, as the molar ratio of DMPA is increased, T_i is lowered, and the temperature at 50% decomposition (T_{50}) follows a similar trend. The results suggest that the behavior of UPU and ionomers during thermal decomposition is dependent on the concentrations of carboxylic acid and carboxylate salts based on DMPA. On the other hand, although the T_i values of ionomers containing the neutral salt, sodium sulfonate, are slightly higher than those of ionomers containing sodium carboxylate, they are hardly affected by the molar ratios of the raw materials.

The contact angles of water for PUAC and PUAS are smaller than those for PUBD and UPU, whereas the surface free energies are large, and they are easily wet. This suggests that hydrophilic ionic groups are oriented on the film surface. PUAC and PUAS exhibit higher equilibrium moisture absorption rates than PUBD and UPU, which correspond to higher wettability. A comparison of the molar ratios 4/1/3 and 4/2/2 reveals that the former demonstrates higher equilibrium moisture absorption rates for all ionomers than the latter, and the rate is dependent on the ionic group concentration.

CONCLUSIONS

The following findings have been obtained as a result of ionizing carboxylate-based polyurethane by neutralization with metal acetates:

1. The tensile strength is increased.
2. T_g is decreased.
3. Wettability with respect to water is increased, and hygroscopicity is likewise increased.
4. The resulting polyurethane is increasingly susceptible to thermal decomposition.

Sulfonate-based polyurethane exhibits a higher degree of phase separation than carboxylate-based polyurethane.

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