

Preparation and Properties of UV-Curable Polyurethane Acrylate Ionomers

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ABSTRACT: Ultraviolet (UV)-curable polyurethane acrylate ionomer (PUAI) prepolymers were synthesized from isophorone diisocyanate (IPDI), poly(methylene ether) glycol (PTMG), 2,2-bis(hydroxymethyl) propionic acid (DMPA), triethylamine (TEA), 2-hydroxy ethyl acrylate (HEA), and dibutyl tin dilaurate (DBT) as a catalyst. UV-curable polyurethane acrylate ionomer aqueous dispersion was formulated from the prepolymers, water (30 wt %), and 1-hydroxycyclohexylphenyl ketone (Irgacure 184) as a photoinitiator. The films of UV-cured polyurethane acrylate ionomer were formed by curing the dispersion using a medium-pressure mercury lamp (80 W/cm; $\lambda_{\text{max}} = 365 \text{ nm}$). Gel content decreased with increasing water content in the aqueous dispersion. Effects of DMPA content and molecular weight of PTMG and the degree of neutralization on the physical properties were investigated. It was found that the storage modulus increased with increasing DMPA content. Tensile modulus and strength decreased with increasing the molecular weight of PTMG from 650 to 2000. The glass transition temperature shifted to a higher temperature as the content of DMPA increased. As the degree of neutralization increased, the tensile strength and modulus decreased. However, the elongation at break increased. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* 67: 2153–2162, 1998

Key words: UV-curable; polyurethane acrylate; ionomer

INTRODUCTION

A polyurethane ionomer can be defined as a copolymer consisting of a polyurethane backbone with a minority of the repeat units carrying pendant acid or tertiary nitrogen groups, which are completely or partially neutralized or quaternized, respectively, to form salts.¹ The presence of ionic species in ionomers has a considerable effect on many of their physical properties.² Ion-containing polyurethanes have received considerable attention due to their usefulness in coatings and adhesives. Ionic centers in the hard segment generally favor segregation and cohesion within the hard

segment domains due to their strong electrostatic forces and thermodynamic incompatibility with the polymer matrix.

Due to the environmental advantage, waterborne polyurethane has been widely applied in coatings and adhesives to textile, leather, and many of the polymeric materials.³ Conventionally, polyurethane is insoluble in aqueous media and forms phase separations into large domains. For polyurethane to be dispersible in water, ionic and/or nonionic hydrophilic segments should be incorporated into polyurethane structure.

In the meantime, ultraviolet (UV) curing saves energy and reduces or eliminates solvent emission compared to solvent-based system since most formulations are 100% reactive oligomers and diluents.⁴ This technique has been applied commercially in coatings, printing, and adhesives.^{5,6} Recently, UV

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Table I Effect of DMPA Content on Physical Properties

System	DMPA (wt %)	IPDI (mol)	PTMG(650) (mol)	DMPA (mol)	HEA (mol)	TEA (mol)	Elongation at Break (%)	Stress at Break (MPa)	E' at 20°C by DMA	T_g (°C) by DMTA
A-1	3.89	1	0.325	0.175	1	0.175	51.78	15.3	646.39	70.4
A-2	5.44	1	0.270	0.230	1	0.230	43.74	17.8	654.60	79.3
A-3	6.68	1	0.226	0.274	1	0.274	29.84	18.5	815.00	83.7
A-4	7.73	1	0.191	0.309	1	0.309	10.90	19.5	869.10	92.2

Note: M_n of PTMG = 650; water content based on prepolymer = 30 wt %.

curing has also been used in photolithography.⁷ The UV-curable system is typically composed of reactive polyurethane oligomer, reactive diluents, and photoinitiator. The reactive polyurethane oligomer is the most important component in determining the ultimate physical properties of UV cured coatings. Typically it is a segmented copolymer, which consists of soft and hard segment units, tipped with acrylic functionality, such as 2-hydroxyethyl acrylate (HEA) and 2-hydroxyethyl methacrylate (HEMA). The soft segment generally consists of polyether or polyester polyol, whereas the hard segments are usually formed by the extension of diisocyanate with a chain extender of a low molecular polyol or amine. The microphase separation of the urethane segments, which is governed mainly by the soft segment length and type, is a key parameter to control the dynamic mechanical properties of the polyurethane acrylates.⁸⁻¹⁴ Recently, UV-curable polyurethane acrylates have been investigated in this laboratory.¹²⁻¹⁴

A liquid volatile reactive diluent miscible with the oligomer should be used to decrease the viscosity of the viscous oligomer in this system.¹² However, this system is not perfectly safe from fire during a UV-curing process due to the inflammability of the reactive diluent. A method to be free from dangerous volatile diluent is to use water

instead of the flammable diluent. However, almost all of the polyurethane acrylate oligomers do not have miscibility with water. Therefore, the oligomer should contain hydrophilic groups to be compatible with water.

In this study, to obtain polyurethane acrylate oligomer compatible with water, —NCO-terminated polyurethane oligomers containing carboxylic groups were synthesized from the reaction of isophorone diisocyanate (IPDI) and poly(methylene ether) glycol-2,2-bis(hydroxymethyl) propionic acid (PTMG-DMPA) by using dibutyltin dilaurate as a catalyst, then the carboxylic groups were neutralized by triethylamine. The polyurethane acrylate ionomer (PUAI) prepolymers were obtained by capping the —NCO groups with HEA until all the —NCO groups were reacted completely as confirmed by the disappearance of infrared (IR) absorption at 2270 cm^{-1} . UV-curable aqueous dispersions of polyurethane acrylate ionomer were formulated from prepolymer, water, and Irgacure 184. UV-cured films of the formulated material were obtained using a medium-pressure mercury UV lamp. The effects of DMPA content, molecular weight of PTMG, and degree of neutralization on the physical properties were investigated.

Table II Effect of Soft-Segment Molecular Weight on Physical Properties

System	PTMG (M_n)	IPDI (mol)	PTMG (mol)	DMPA (mol)	HEA (mol)	TEA (mol)	Elongation at Break (%)	Stress at Break (MPa)	E' at 20°C by DMA	T_g (°C) by DMTA
B-1	650	1	0.270	0.230	1	0.230	43.74	19.52	654.6	79.3
B-2	850	1	0.236	0.264	1	0.264	58.68	17.45	516.0	72.6
B-3	1,000	1	0.216	0.284	1	0.284	64.48	16.75	449.5	79.1
B-4	2,000	1	0.138	0.362	1	0.362	69.20	11.90	408.6	86.8

Note: DMPA = 5.44 wt %; water content based on prepolymer = 30 wt %.

Table III Effect of Degree of Neutralization on Physical Properties

System	Degree of Neutralization (%)	IPDI (mol)	PTMG(850) (mol)	DMPA (mol)	HEA (mol)	TEA (mol)	Elongation at Break (%)	Stress at Break (MPa)	E' at 20°C by DMA	T_g (°C) by DMTA
C-1	25	1	0.236	0.264	1	0.065	57.76	19.65	654.4	81.3
C-2	50	1	0.236	0.264	1	0.132	63.32	19.35	583.3	79.0
C-3	75	1	0.236	0.264	1	0.197	66.64	17.88	554.2	77.4
C-4	100	1	0.236	0.264	1	0.264	69.96	17.66	515.9	74.2

Note: DMPA = 5.44 wt %; \overline{M}_n of PTMG = 850; water content based on prepolymer = 30 wt %.

EXPERIMENTAL

Materials

PTMG (M_n = 650, 850, 1000, and 2000) was dried and degassed at 80°C and 1–2 mm Hg until no bubbling was observed. DMPA (Aldrich Chemical) was dried overnight at 80°C under a vacuum of 3–5 mm Hg. Isophorone diisocyanate (IPDI) (Aldrich Chemical), HEA (Aldrich Chemical), and triethylamine (TEA) (Junsei Chemical) were dried over 4 Å molecular sieve before use. Dibutyltin dilaurate (DBT) (Fluka Chemical) and 1-hydroxy cyclohexyl phenyl ketone (Irgacure 184) (Aldrich Chemical) were used without further purification.

Preparation of PUA1

A 500-mL round-bottomed, four-necked flask equipped with a mechanical stirrer, nitrogen inlet, condenser with drying tube, and thermometer was charged with PTMG and DMPA. While stirring, the mixture was heated to 80°C for about 30 min, followed by adding IPDI containing 0.03 wt % DBT based on the prepolymer. The reaction was conducted at 80°C until the theoretical isocyanate value was reached. A standard di-*n*-butylamine back-titration method was used to determine the NCO content of the prepolymer. The prepolymer were then cooled to 60°C, and a neutralizing agent, TEA, was added and stirred for 1 h. The reaction mixture was cooled down to 45°C, and HEA was added dropwise. Capping of NCO-terminated prepolymer with HEA was continued until the NCO-content reached zero as evidenced by the disappearance of the IR peak of NCO.

Formulation of UV-Curable Aqueous Dispersions of PUA1

The UV-curable emulsions (aqueous dispersions) of PUA1 were formulated from the viscous PUA1

prepolymer and water (0–60 wt %) and 2 wt % photoinitiator Irgacure 184 based on prepolymer at 60°C.

Preparation of UV-Cured Film

The UV-cured urethane acrylate films were formed by casting the above-formulated aqueous dispersion onto a glass plate at room temperature and then by curing the dispersion using a medium pressure mercury lamp (80 W/cm). Radiation curing has been carried out with the UV light of 365 nm of the main wavelength.

Fourier Transform Infrared Spectra

Thin films for IR spectroscopy studies were prepared by casting the PUA1 onto KBr pellets. IR spectra were obtained by using a computerized Nicolet Impact 400D Fourier transform infrared (FTIR) spectrometer. For each sample, 32 scans at 2 cm⁻¹ resolution were collected in the transmittance mode. FTIR spectra of prepolymer before and after UV curing were taken to measure the extent of curing. With the aid of computer analysis, curve-fitting of the N—H stretching band was performed. The spectra were analyzed employing a curve-resolving technique based on a linear least-squares analysis to fit a combination of the Lorentzian and Gaussian curve shapes.

Gel Content

The gel content of the cured film samples was determined by the Soxhlet extraction method using toluene for 24 h. The insoluble materials were dried under vacuum for about 2 days and weighed to determine the gel contents. The gel contents of the cured film samples were determined from the difference in weight before and after the extrac-

tion experiment as follows: gel content (%) = $w/w_0 \times 100$, where w_0 and w are sample weights before and after extraction, respectively. Several runs were made for each sample, and average values were taken.

Dynamic Mechanical Measurement

The dynamic mechanical properties of UV-cured films were obtained at 5 Hz using DMTA Mk III (Rheometrics Scientific) with a heating rate of 2°C/min over a temperature range of -50 to 200°C.

Tensile Measurement

The tensile properties of UV-cured films were measured using a tensile tester (Tinius Olsen 1000) at a cross-head speed of 5 mm/min and an average of at least five measurements was taken to report.

Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) model 200C (Seiko) was used to examine the thermal properties of PUA1 at temperatures ranging from -50 to 100°C and 20°C/min of heating rate.

RESULTS AND DISCUSSION

Identification of Reactions

The reactions of capping and curing were identified by IR spectroscopy. IR spectra of PUA1 with reaction time of capping (reaction of NCO-terminated prepolymer and HEA) were taken to confirm the completion of capping (see Fig. 1). The N=C=O stretching band near 2270 cm^{-1} completely disappeared after 6 h, indicating the completion of reaction. To certify the curing of acrylates, generally, the absorbance bands of acrylate at 1635, 1410, and 810 cm^{-1} are used. The characteristic C=C absorption of urethane acrylate at 1635 cm^{-1} was used to determine the extent of photopolymerization in this study. Figure 2 shows IR spectra taken prior to and after 1 min of UV irradiation. The urethane acrylate has a sharp C=C absorption band at 1635 cm^{-1} prior to UV irradiation, but the band completely disappeared after irradiation.

The gel content was also measured by Soxhlet

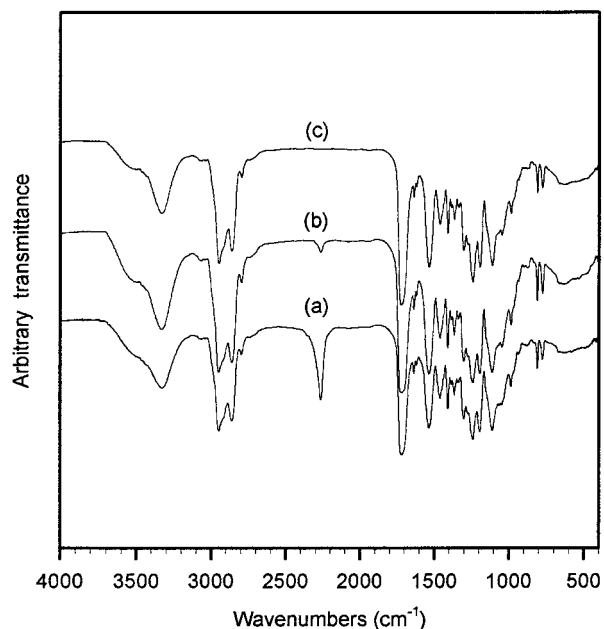


Figure 1 IR spectra of a prepolymer with reaction time of capping: (a) 2, (b) 4, and (c) 6 h.

extraction to estimate the extent of curing. Figure 3 shows the change in gel content as a function of curing time for the PUA ionomers consisting of different water contents. The gel content increased with decreasing water content. When the water content is below 30 wt %, there are dra-

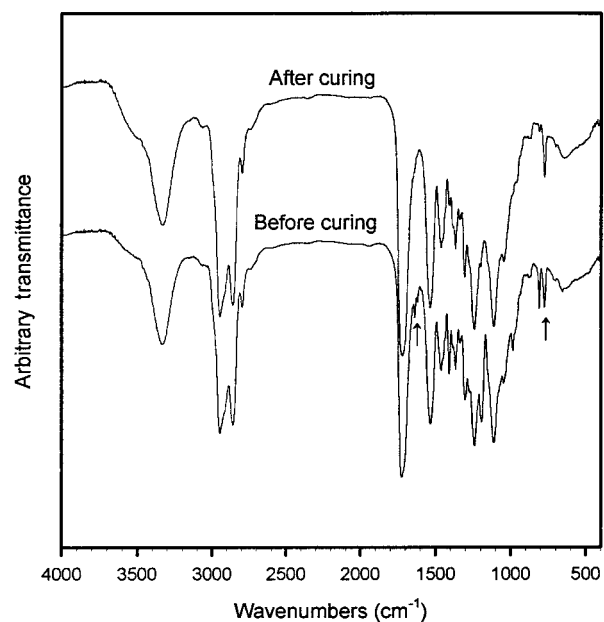


Figure 2 IR spectra of PUA1.

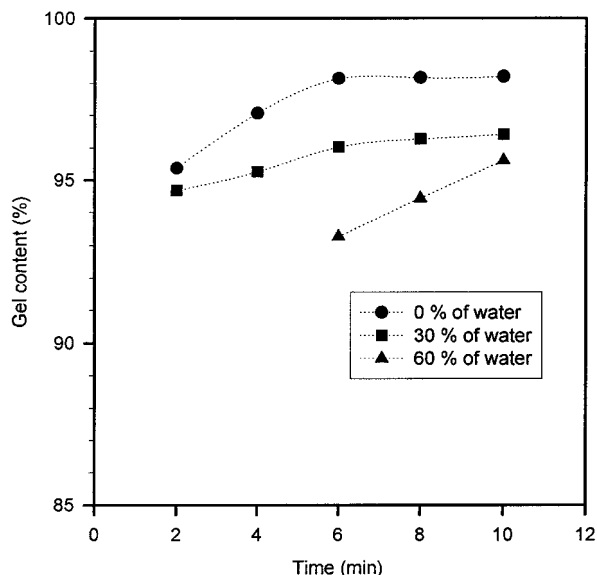


Figure 3 Reaction between gel content and curing time for sample A-1 consisting of different water content.

matic increases in gel content up to about 95% within 5 min; but, thereafter, there are very small gains in gel contents with further increasing time. Gelation did not occur within 5 min for the sample having 60 wt % water; however, thereafter, it increased with an increasing curing time.

The viscosity of the PUAI prepolymer without water is above 1000 cps. The phenomenon of

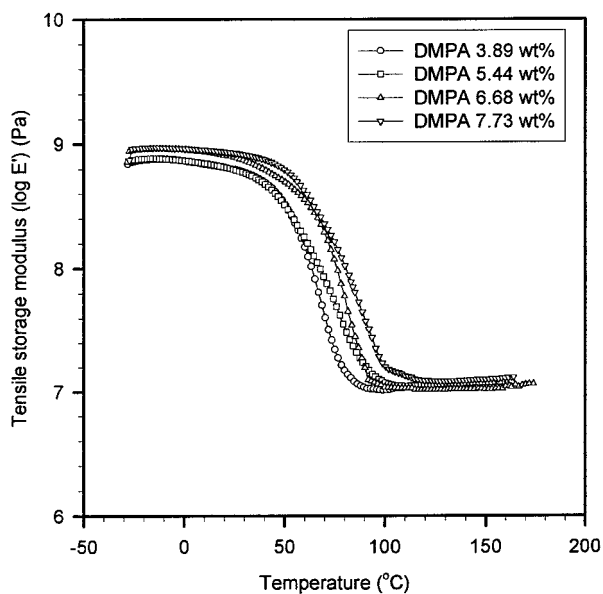


Figure 4 Effect of DMPA content on storage modulus.

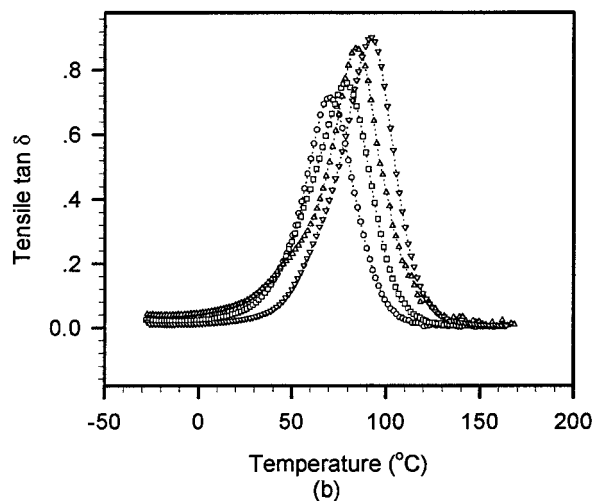
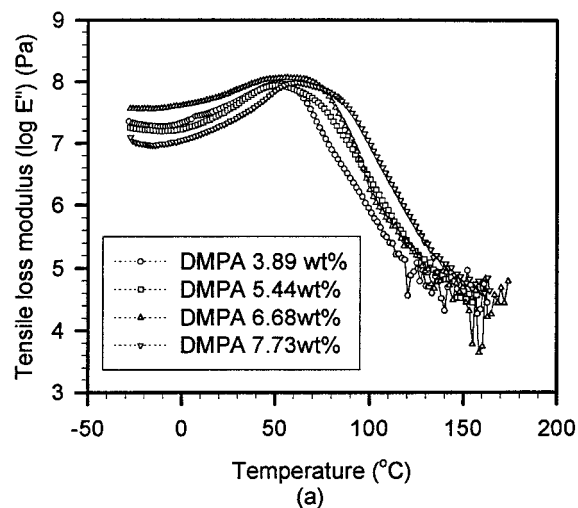


Figure 5 Effect of DMPA content on (a) E'' and (b) $\tan \delta$.

phase inversion and viscosity and conductivity changes that occur during the emulsification process of polyurethane ionomers have been well documented by Dieterich¹⁵ and Kim et al.^{16–19} The use of diluent water in PUAI is essential for easy coating. The most stable aqueous dispersion was obtained when the water content was about 30 wt %. By considering the conditions of curing, processing, and stability of dispersion, it was found that the optimum water content of PUAI dispersion is about 30 wt % in this system. Therefore, all the samples shown in Tables I–III contained 30 wt % water.

Effect of DMPA Content

In this series of experiments, the content of DMPA varied from 3.84 to 7.73 wt % based on the pre-

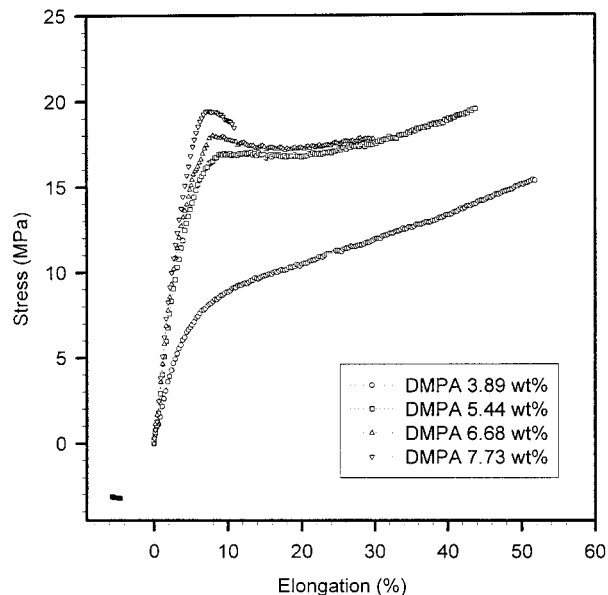


Figure 6 Effect of DMPA content on tensile properties.

polymer (Table I). The dynamic mechanical properties of the UV cured films for sample A-1, A-2, A-3, and A-4 are shown as a function of temperature in Figures 4 and 5. Over the temperature range examined, the higher content of DMPA, the higher the value of E' (Table I and Fig. 4). With increasing DMPA content, the main relaxation peak assigned to the glass transition temperature shifted to a higher temperature, as shown in Figure 5. The tensile properties of cast film are shown in Figure 6. As the DMPA content increased, tensile strength and modulus increased; however, the elongation at break decreased. The increases of glass transition temperature, modulus, and strength of UV-cured PUAI film may be attributed to the higher hard segment fraction from incorporating a higher content of DMPA inducing higher interchain interaction through Coulombic forces and hydrogen bonding.

Effect of Soft Segment Molecular Weight

In this series of experiments, PTMGs of different molecular weight ($M_n = 650, 850, 1000, \text{ and } 2000$) were used to prepare PUAI at a fixed DMPA content (Table II). Figures 7 and 8 show the dynamic mechanical properties of samples B (Table II systems) as a function of temperature.

Figure 7 shows the changes of loss modulus (E'') and $\tan \delta$. The peak position temperature of E'' and $\tan \delta$ are related to glass transition

temperature. The glass transition temperature obtained from the maximum peak of $\tan \delta$ is given as 79.3, 72.6, 79.1, and 86.8°C for samples B-1 (PTMG 650), B-2 (PTMG 850), B-3 (PTMG 1000), and B-4 (PTMG 2000), respectively. The peak (glass transition) temperatures were found to decrease in the order of B-4 (PTMG 2000), B-1 (PTMG 650), B-3 (PTMG 1000), and B-2 (PTMG 850). That is, the peak temperature decreases as molecular weight of PTMG increases from 650 to 850 and increases with further increase of molecular weight. As the molecular weight of PTMG increased from 650 to 2000, hard segment length decreased; however, the soft segment length increased. Generally, the increasing of hard and soft-segment length provides more complete

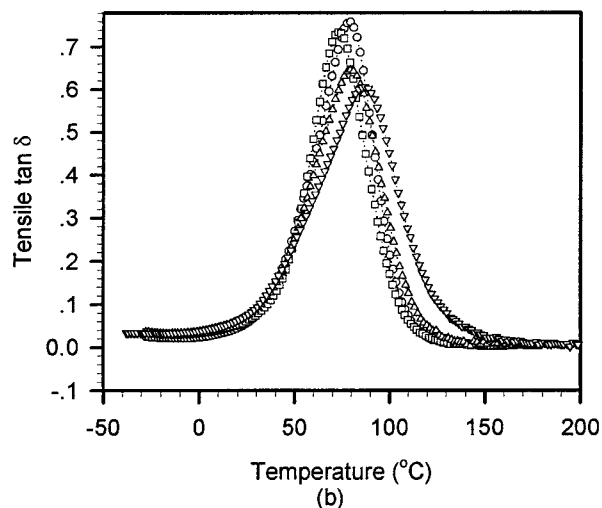
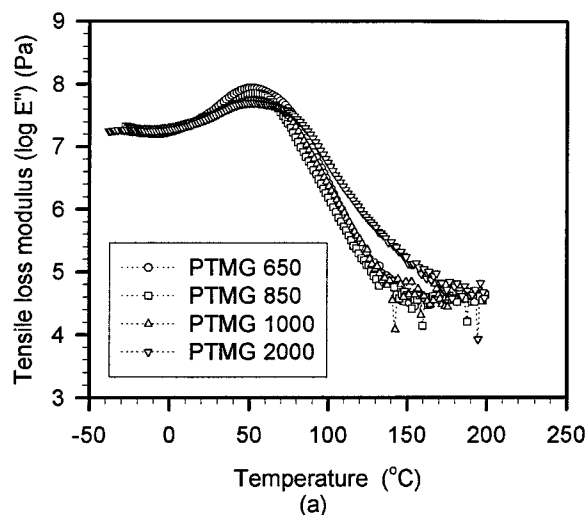


Figure 7 Effect of PTMG molecular weight on (a) E'' and (b) $\tan \delta$.

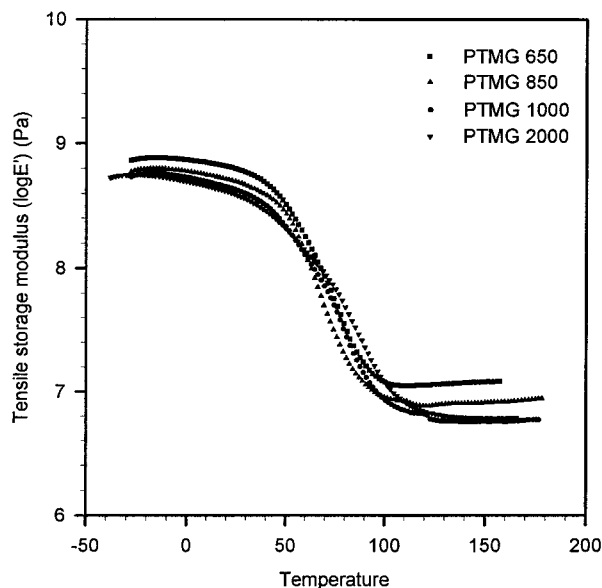


Figure 8 Effect of PTMG molecular weight on storage modulus.

phase separation. The decrease may be due to the decreased rigid fraction of virtually phase-mixed PUAI, and the increase may be related to the phase separation of soft segment and rigid segments region.

Figure 8 is the storage modulus (E') as a function of temperature for the samples B1-4. The storage modulus increased with decreasing molecular weight of PTMG in the temperature range of 30 to about 70°C. However, the order is changed in the higher temperature range of 70 to 100°C. The storage modulus increased in the same order as the glass transition temperature.

Figure 9 shows the stress-strain curves for the UV-cured films of samples B. The tensile strength and modulus increased with decreasing molecular weight of PTMG.

Generally, physical properties of PU ionomers depend largely on the length and contents of soft and hard segments. If the soft segment length is too short, phase separation is not found, and the materials are believed to be relatively homogeneous. If the soft segments are long enough, phase separation, as well as soft-segment crystallization, are expected. The strength should mainly be governed by the hard fraction; that is, with shorter polyol, more urethane linkages are formed to enlarge hard fraction, together with an increased chance of hydrogen bonding formation. Therefore, the increases of storage modulus and

tensile strength may be attributed to the higher homogeneous rigid segment region by decreasing the molecular weight of PTMG in PUAI.

Effect of Degree of Neutralization

Generally, ionic sites in the hard segment will increase the incompatibility between the hard and soft segment in PU ionomer, thus enhancing segregation as well as cohesion within the hard segment domains. However, the effect of ionic sites is not just additional to an already present strong interaction between urethane groups within a hard segment domain. Due to the energetically preferred bond between ionic and urethane groups, the ionic site may at least partially destroy the highly ordered hard segment, thus decreasing segregation. An increase in the number of ionic sites may then cause a new order.²⁰

To confirm this behavior, FTIR spectra of C-samples were investigated. The spectra were analyzed employing a curve-resolving technique based on linear least-squares analysis to fit a combination of the Lorentzian and Gaussian curve shapes. Curve fitting of N—H stretching region was performed for all C-samples. Figure 10 shows the results of the curve-fitting procedure for samples with various degrees of neutralization. The ratio of hydrogen bonded N—H stretching band-free N—H stretching band (K) decreased with

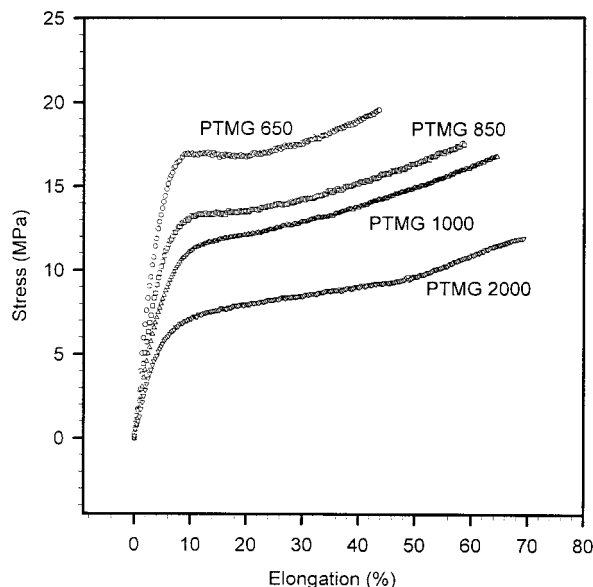


Figure 9 Effect of PTMG molecular weight on tensile properties.

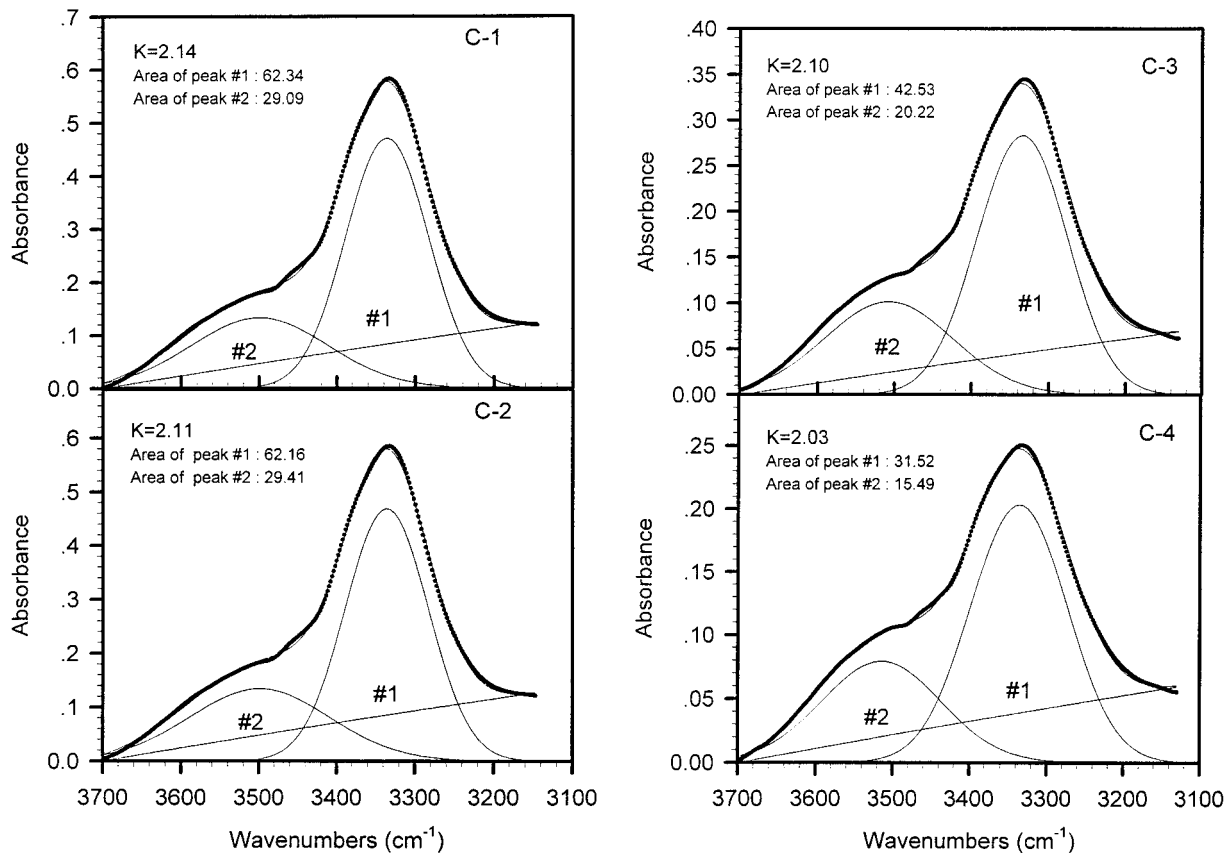


Figure 10 Curve-fitting analysis in the N—H stretching region of samples C-1, C-2, C-3, and C-4. ($K = \#1_{\text{H-bon}}/\#2_{\text{free}}$)

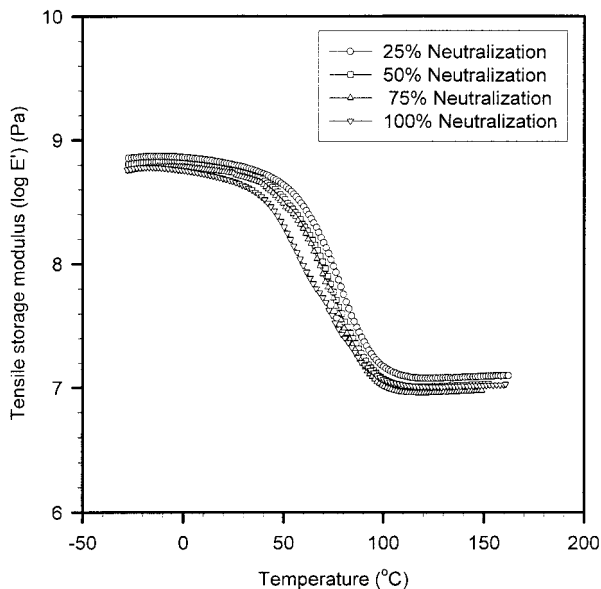


Figure 11 Effect of degree of neutralization on storage modulus.

increasing the degree of neutralization. This means that some of C=O groups previously bonded to the N—H of the urethane groups may be switched to bond with $^+\text{NR}_3\text{H}$. This reduction of hydrogen bonds will influence mechanical properties.

The degree of neutralization was varied from 25 to 100% for samples C (Table III). The storage moduli E' of the sample C-series are shown in Figure 11. The storage modulus decreased with increasing degree of neutralization.

Figure 12 shows the loss modulus and $\tan \delta$ peaks. The α -glass transition (α -relaxation) temperature determined from maximum $\tan \delta$ peak are 81.3, 79.0, 77.4, and 74.2°C, respectively. The temperature of loss modulus and $\tan \delta$ peaks shift slightly to lower temperature as the degree of neutralization is increased. These results indicate that the neutralization can lead to a decrease in the order of rigid hard segment regions and give phase mixing. The tensile properties of C-samples are shown in Figure 13. As the degree of neutral-

ization increased, the tensile strength and modulus also decreased; however, the elongation at break increased. From these results, it is concluded that properties may be related to the decreased structural order resulting from phase mixing because of the reduction of hydrogen bonds by neutralizing.

CONCLUSIONS

UV-curable PUIAI prepolymers were prepared from IPDI, DMPA, PTMG, HEA, TEA, and DBT as a catalyst. UV-curable aqueous dispersions of the PUIAI were formulated from prepolymer, water, and Irgacure 184. UV-cured films of the formulated material were obtained using a medium-pressure mercury UV lamp. The Effect of DMPA content, molecular weight of PTMG, and degree of neutralization on the physical properties were investigated. Results obtained are as follows.

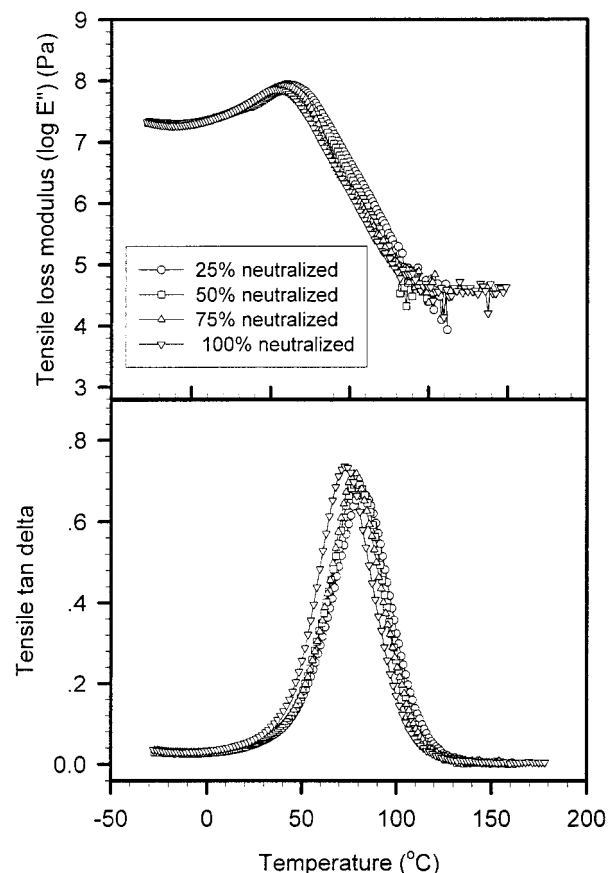


Figure 12 Effect of degree of neutralization on E'' and $\tan \delta$.

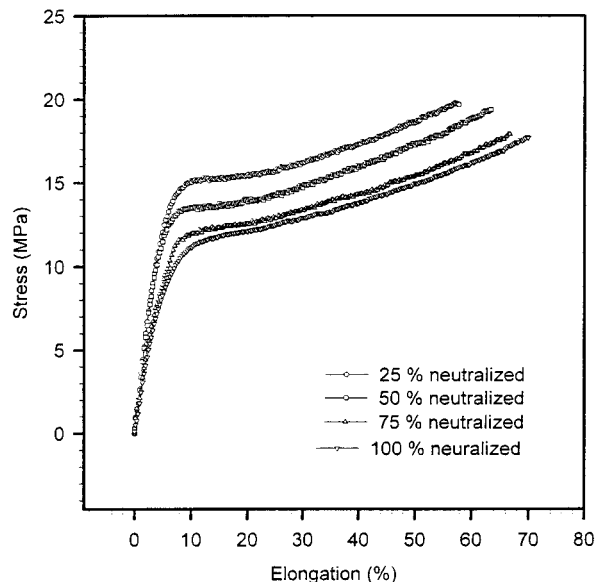


Figure 13 Effect of degree of neutralization on tensile properties.

1. Gel content decreased with increasing water content. When water content is below 30 wt %, there are dramatic increases in gel content up to about 95% within 5 min; but, thereafter, there are very small gains with further increase in time. Gelation did not occur within 5 min for the sample mix with 60 wt % water.
2. With increasing DMPA content, the glass transition temperature shifted to higher temperature, and the storage modulus and tensile strength increased, but the elongation at break decreased.
3. The glass transition temperature was found to decrease in the order of B-4 (PTMG 2000), B-1 (PTMG 650), B-3 (PTMG 1000), and B-3 (PTMG 850). The storage modulus increased with decreasing molecular weight of PTMG in the temperature range of 30 to about 70°C; however, the modulus was in the same order as the glass transition temperature in the higher temperature range of 70 and 100°C.
4. The tensile modulus and dynamic storage modulus and hydrogen-bonded NH groups decreased with increasing degree of neutralization, presumably since the neutralization led to a slight increase in phase mixing.

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