Hybridization of Aqueous-Based Polyurethane with Glycidyl Methacrylate Copolymer

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ABSTRACT: The carboxyl group containing aqueous-based polyurethane (PU) dispersions were prepared from isophorone diisocyanate, poly(propylene glycol)-1000, and 2,2-dimethylol propanic acid via a PU prepolymer process. The amino content of this amino-terminated aqueous-based PU system was determined by a styrene oxide titration method. Glycidyl methacrylate (GMA) copolymer emulsions were prepared by an emulsion polymerization of GMA and other alkyl acrylates. The curing behavior of the GMA copolymer was demonstrated by a model reaction of the GMA copolymer with ethylenediamine. In the same token, the reaction took place between the PU amino groups and the GMA copolymer epoxides at ambient temperature and resulted in the formation of a hybridized homogeneous copolymer. This hybridized copolymer also consisted of carboxylic acid on the PU fraction after drying. Carboxylic acids of the copolymer were exchanged with calcium ion and this ionic coordination resulted in a calcium ion-crosslinked copolymer. The physical and mechanical properties and the thermal behaviors of the hybridized copolymers were evaluated. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 903–913, 1999

Key words: hybridized copolymer; aqueous-based PU; GMA copolymer; ionic crosslinking

INTRODUCTION

The conventional solvent-based polyurethanes (PUs) are being removed from the market because of environmental regulations, economical concerns, and safety considerations. Although aqueous-based PU as a replacement is becoming increasingly important,¹ its physical and mechanical properties have negative points due to its low molecular weight with a less extensive polymeric network.

Carboxyl groups containing aqueous-based PU dispersions were prepared by a polyaddition of isophorone diisocyanate, poly(propylene glycol)-

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1000, and 2,2-dimethylolpropanic acid, with a neutralization and a chain extension on the water dispersion. The final PU dispersion is a self-emulsified and carboxylic group containing an aqueous-based PU.² These carboxyl pendants are hydrophilic with some electronegative charges on the PU particle surface; they play the major role of stabilizing aqueous-based PU dispersion.

The aqueous-based PU prepared this way is an amino-terminated polymer. The amino groups are generated by a partial ethylenediamine (EDA) chain extension and a hydrolysis of NCO-terminated PU prepolymer on the dispersion process. Determination of the PU amino equivalent was carried out by a styrene oxide titration method.³

Both the pendent carboxyl and the terminal amino groups of PU are, respectively, reactive to such individual curing agents as aziridinyl²- and epoxide-containing compounds,³⁻⁵ for the post-

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curing reactions. A GMA copolymer emulsion was prepared by an emulsion copolymerization of glycidyl methacrylate (GMA) and other alkyl acrylate monomers. A model reaction of the epoxidecontaining GMA copolymer with EDA takes place at ambient temperature. This model reaction demonstrates the curing reaction between amino and epoxide groups containing polymers and can be used to formulate a hybridized copolymer. The available carboxyl groups on PU or the hybridized copolymer can also be treated further with calcium ion for an ionic crosslinked polymer.^{6–9} The physical, mechanical, and thermal properties of the resulting polymers were evaluated in this article.

EXPERIMENTAL

Materials

Triethylamine (TEA), EDA, and 2,2-dimethylol propanic acid (DMPA) were supplied by the Aldrich Chemical Co. Acetone, methanol, and the other solvents were dried and distilled over anhydrous calcium chloride before use. Isophorone diisocyanate (IPDI) was supplied by the Olin Chemical Co. Poly(propylene glycol)-1000 (PPG-1000) was supplied by the Arco Chemical Co. The GMA copolymer emulsions were prepared by the Tai-Chung Resins Co. All the materials were used as received without further purification.

Instruments

The dynamic mechanical behavior of the polymer films were investigated by a dynamic mechanical thermal analyzer, a Polymer Laboratories MK-2. Thermogravimetric data were measured by a Setaram TG-DTA 92–16. Infrared spectra were measured with a Nicolet Magna-IR Spectrometer 550. Stress and strain curves of the PU films were taken with a Shimadzu Autograph S-100-C. The contact angles of pure water droplets on a dried polymer film were measured with a FACE contact angle meter, Model CA-A, made by Kyowa Kaimenkagaku Co., Ltd.

Preparations of Anionic Aqueous-based PU Dispersions

PPG-1000 (0.1 mol) and DMPA (0.1 mol) were dried at 110°C overnight before being mixed with IPDI (0.3 mol) in a 500-mL four-necked resin flask. The resin flask was equipped with a me-

chanical stirrer, a thermometer, a nitrogen inlet, and a condenser with a $CaCl_2$ drying tube. The reaction mixture was kept at 110°C for about 4 h, until the NCO% dropped below 3.0 (ASTM D1638 NCO determination method) and remained constant for another 0.5 h.Then, freshly dried acetone (230 mL) was added into the reaction flask (when it was cooled to below 50°C) in order to adjust the viscosity of these PU prepolymers. The PU dispersions obtained from a high shear rate mixing of these PU prepolymers with a 450-mL aqueous solution of EDA (0.08 mol) and TEA (0.10 mol). The final PU dispersions had 30% solid contents with a pH value at 8.5 after acetone was removed under a vacuum.

Curing Reaction of GMA Copolymer Emulsions with EDA

GMA copolymer emulsions had 50% solid contents and 4.2×10^{-2} equivalent epoxide groups per 100 g of emulsion. A water solution (50 mL) of 0.5 g EDA (1.0 phr for the GMA copolymer) was added into 100 g of the GMA copolymer emulsions. The reaction mixture was kept agitated for an additional hour after its addition was completed. The final mixture was sampled for film casting.

Polymer Blend of Aqueous-based PU with GMA Copolymer Emulsions

Various dosages (phr) of the GMA copolymer emulsions were added into aqueous-based PU dispersions. The mixture was stirred at ambient temperature for an additional hour before the film casting.

Calcium Ion-Coordinated Aqueous-based PU

Each aqueous-based PU film was immersed into an aqueous $CaCl_2$ (20% w/w) solution overnight. The calcium ion-exchanged film was rinsed three times with distilled water before drying. The final films were sampled for the measurements of infrared spectra and other properties.

Properties of Aqueous-based PU/GMA Copolymer Hybrids

Tensile Strength and Elongation

Films were cast and air-dried from the blending of PU dispersions/GMA copolymer emulsions at room temperature and then dried at 50° C for 24 h. They were conditioned in a 75% relative

humidity chamber at 25°C for 72 h before the measurements. Specimens were formed into dumbbell shapes of 1.2 \pm 0.1 mm thickness. The gauge length was 40 mm and the measurement was performed at a crosshead speed of 40 mm/min. Six specimens for each sample were taken, and the three measurements that showed the highest tensile strength were selected for calculating the mean value.

Gel Content

A known weight of oven-dried film was put into a Soxhlet extractor for a continuous extraction with tetrahydrofuran (THF) for 24 h. The polymer gel remaining after extraction was dried and calculated according to the test results. Three tests were carried out and averaged for each sample.

Contact Angle

The PU film was cast onto a clean glass plate from the PU dispersions and dried at room temperature. Distilled water droplets on the film surface were used for contact angle measurements. The dimensions of the droplets were measured at 25°C for about 10 s after placing the water droplets. Five measurements of each sample were performed and the three closest results were chosen and averaged for the mean value. Each contact angle was calculated by the following equation:

Contact angle=
$$2 \tan^{-1} (h/r)$$

where h is the height of the spherical segment of the water droplet and r is the radius of the spherical segment.

Water Uptake

A known weight (W_0) of the dried PU film with a sample dimension of $60 \times 60 \times 1$ mm was immersed in a distilled water bath for 8 days. The towel-wiped dry sample weight (W_1) and the ovendried film weight (W_2) were obtained. Three measurements were averaged for each sample. The water uptake $(W_A \%)$ and weight loss $(W_L \%)$ of the polymer films in water were calculated according to the following equations:

$$W_A\% = rac{W_1 - W_2}{W_2} imes 100\%$$

where W_A is the amount of water-uptake by the polymer film, and

$$W_L \ \% = rac{W_0 - W_2}{W_0} \ imes 100\%$$

where W_L is the amount of polymer dissolved into the water.

Dynamic Mechanical Behavior

Air-dried PU films were dried further in a 50°C oven for 24 h and then conditioned in a 75% relative humidity chamber at 25°C for 72 h before testing. Dynamic mechanical analysis measurements were carried out in a bending mode at a heating rate of 3°C/min from -80 to 150°C at a 1.0-Hz frequency for each sample.

Thermogravimetric Analyses

The conditioned samples were measured by a thermogravimetric analyzer at a heating rate of 20°C per minute from ambient temperature to 500°C under an argon gas atmosphere.

RESULTS AND DISCUSSION

The carboxylic groups containing aqueous-based PU dispersions were prepared by the PU prepolymer process mentioned in the Introduction. The resulting amino-terminated PU dispersions are solvent-free with 30% solid contents and had an average particle size of 100 nm and an average zeta potential at 55 mV.

The equivalent number of amino groups per 100 g of PU dispersions is 3.8×10^{-3} as determined by the styrene oxide titration method.³ Most of the PU amino end groups were generated by the partial EDA chain extension along with the hydrolysis of NCO-terminated PU prepolymers in the water dispersion (Scheme 1). These amino end groups served as the reaction sites of the PU. Fluorescence spectral evidence indicated that the reaction took place between the epoxide and the amino groups of the polymers inside the PU particles at ambient temperature.³⁻⁵

The epoxide groups of the GMA copolymer will react with the amino groups of aqueous-based PU after they are blended. The resulting hybridized copolymer from the blending of these two reactive polymers is an A–B type crosslinked copolymer.¹⁰



Scheme 1 Preparations of aqueous-based PU anionomers.

Carboxyl pendants, the other reaction sites of PU, come from one of the PU ingredients (2,2dimethylolpropanic acid), which consists of 1.5×10^{-2} equivalents of carboxyl groups per 100 g of the PU dispersion. The hydrophilic carboxyl ions on the PU particle surface extended toward the water phase after the formation of the aqueous PU dispersions. These ionic groups carry a particle surface charge and provide a repulsive force among the particles for stabilizing the final PU dispersion. However, the presence of these hydrophilic ionic groups causes a deficiency in the water resistance and weakens the PU quality. The reaction of PU carboxyl groups with an aziridinyl agent² or with a bivalent metallic ion (e.g., Ca^{+2}) to form a crosslinked polymer can solve this problem. Furthermore, the PU properties can be improved by hybridization with the GMA copolymer. The mechanical and physical properties as well as the thermal behavior of these crosslinked and hybridized copolymers were investigated in this report.

Model Curing Reaction of GMA Copolymer with EDA

The GMA copolymer emulsion contains 50% solids and 6.0% (w/w) of the GMA monomer. The

		GMA Copolymers with EDA (phr) ^a		
		Dos	ages	
Properties	GMA Copolymers	1.0	2.0	
Epoxy/amino ^b	_	1.25	0.63	
Gel content % ^c	0	96.5	96.5	
$W_A \ \%^{\mathrm{d}}$	5.7	8.6	14.6	
$W_L \%^d$	0.4	0.4	1.9	

Table I Properties of EDA-cured GMA Copolymers

 $^{\rm a}$ 0.5 and 1.0 phr EDA added into 50% solid GMA copolymer emulsion.

^b Epoxy/amino equivalent ratio.

^c Gel content %: THF is used with Soxhlet extraction for 24 h. ^d W_A % water uptake; W_L % polymer dissolved into water.

equivalent number of epoxide groups per 100 g of the GMA copolymer emulsion is 4.2 \times $10^{-2}.~A$ dried GMA copolymer film has a 5.7% water uptake but it is soluble in tetrahydrofuran (THF) because it is a thermoplastic linear polymer.

EDA is reactive toward the epoxide group of the GMA copolymer, serving as a curing agent. Two dosages of EDA (0.5 and 1.0 phr) were each added into the GMA copolymer emulsions. Their "amino/epoxide" equivalent ratios are 0.8 and 1.6



Figure 1 DMA curves of GMA copolymers cured with EDA: (-O-O-O) original GMA copolymers; $(-\star-\star-\star-)$ with 1.0 phr EDA and $(-\triangle-\triangle-)$ then heat-treated (100°C/30 min); (-+-+-) with 2.0 phr EDA and $(-\times - \times - \times -)$ heat-treated (100°C/30 min).



Figure 2 FTIR spectra of original PU and its calcium ion-exchange polymer.

with these two EDA-curing dosages. These EDAcured GMA copolymers have more than 96% gel contents after THF extraction (Table I) due to that these resulting crosslinked polymers have a polymeric network formation.

The GMA copolymer film had a damping peak at 41.0°C on its dynamic mechanical analysis (DMA) curve. The damping peaks were shifted to 43.4°C for these EDA-cured GMA copolymers, and each peak intensity became lower than that of the original GMA copolymer. Its damping peak intensity decreased further after each EDA-cured GMA copolymer was heated at 100°C for 30 min (Fig. 1), which is possibly due to the decrease of the polymer free volume and mobility as its curing density was increased after these curing treatments.

Infrared Spectra of Calcium Ion-bonded Aqueous-based PU

The infrared spectrum of the aqueous-based PU film had a carbonyl stretching of carboxylic acid at 1716 cm⁻¹, an amide I band (urethane and urea carbonyl stretching vibrations) at 1637 cm⁻¹, and an amide II band (N—H bending vibrations) at 1551 cm⁻¹. There was no change of the PU infrared spectrum after it was treated with diluted hydrochloric acid.^{6,7} The triethylamine was evaporated and the carboxylic acid remained free on the PU film after drying.

The PU infrared spectrum changed between the 1550 and 1720 cm⁻¹ range after the PU film was treated with a calcium chloride solution. Its absorption on 1656 and 1589 cm⁻¹ of the PU





		Ingredients							
		GMA Copolymer emulsions (phr) in 100 g PU Dispersions ^a						ns ^a	
			1.0	5	.0	7	.5	10).0
Properties	PU	PU–Ca ²⁺	_	_	$-Ca^{2+}$	_	$-Ca^{2+}$	_	$-Ca^{2+}$
			S	tress (kg/cı	m ²)				
Elongation									
100%	4.4	4.5	4.7	4.8	5.3	4.3	5.6	4.1	7.2
200%	6.9	7.3	7.5	8.0	8.4	7.3	9.4	7.3	11.3
300%	10.0	10.4	11.1	11.3	12.2	11.2	13.9	10.9	16.7
400%	14.5	14.9	16.0	16.2	17.1	16.1	20.1	15.5	25.4
500%	_	20.5	21.8		24.3				_
600%	_								_
Tensile strength									
$(\text{kg cm}^{-2}/\%)$	18.6/453	23.6/539	23.3/513	18.9/454	29.3/560	19.9/457	25.7/476	19.3/465	26.4/423
Gel Content (%)	85.4	94.2	94.3	92.4	92.2	92.0	95.2	91.5	92.6
W_A (%)	11.6	11.6	15.6	14.0	15.2	9.9	12.5	12.5	12.0
W_L (%)	0.8	1.1	1.2	0.8	1.1	0.7	0.9	0.5	1.1

Table II Properties of PU with GMA Copolymers and with Ca²⁺ Ionic Crosslinker

^a Solid contents of GMA copolymer emulsions and PU dispersions are 50 and 30%, respectively. There are 3.8×10^{-3} equivalents of the amino group in 100-g PU dispersion and 4.2×10^{-2} equivalents of epoxide groups in 100-g GMA copolymer emulsion.

carboxylate (CO₂⁻) carbonyl stretching frequencies increased and the absorption of the carboxylic acid (at 1716 cm⁻¹) decreased⁶ (Fig. 2). There was evidence of calcium carboxylate formation from the calcium ion-exchanged with the carboxylic acid of the PU system (Scheme 2).

Physical and Mechanical Properties of PU and GMA Copolymer

The aqueous-based PU had 85.4% gel contents after THF extraction but the GMA copolymer was soluble in THF completely. The blending of the aqueous-based PU dispersions with the GMA copolymer emulsions in various ratios and the resulting PU/GMA hybridized copolymer films had gel contents ranging from 91.5 to 94.3% (Table II), which indicated that the hybridization of PU with the GMA copolymer resulted in a polymeric network formation.

The hybridized copolymer's contact angle changed slightly as the dosage of the GMA copolymer increased. The PU film's contact angle changed from 73.6° to 82.8° after it was treated with 1.0-phr GMA copolymer emulsions.

The original aqueous-based PU film had a tensile stress at 14.5 kg/cm^2 with 400% elongation.

Its tensile strength was changed from 18.6 kg/ $\rm cm^2/453\%$ to 19.3 kg/cm²/465% after the PU was treated with 10.0-phr GMA copolymer emulsions (Table II), which was due to the polymeric network formation from the reactive blending of aqueous-based PU with the GMA copolymer.

Furthermore, the carboxylic groups on the PU backbone can be ion-exchanged with calcium ions and the resulting polymers had improved mechanical properties. For example, the ultimate tensile strength of the hybridized copolymer from

Table III	TGA Weight L	oss of PU	and Its	GMA
Copolyme	rs in Various D	osages		

	P Cop	IA phr)			
	7.5	5.0	1.0		
Temperature	Wt Loss (%)			PU	
300°C	12	13	14	15	
$350^{\circ}\mathrm{C}$	28	35	38	46	
400°C	69	83	86	88	



Figure 3 DMA curves of aqueous-based PU cured with GMA copolymers: (-+-+-+-) PU; $(-\times -\times -\times -)$ PU with 2.5 GMA copolymers; $(-\bigcirc -\bigcirc -\bigcirc -)$ PU with 10.0 phr GMA copolymers.



Figure 4 DMA curves of PU, GMA copolymer-cured PU, and their calcium ioncoordinated polymers: (-+-+-+-) PU; $(-\times-\times-\times-)$ PU with Ca²⁺); $(-\star-\star-\star-)$ PU/5.0 phr GMA copolymers; $(-\bigcirc-\bigcirc-\bigcirc-)$ PU with 5.0 phr GMA copolymers and with Ca²⁺).



Figure 5 DTA thermograms of PU and its GMA copolymers crosslinked polymers. U-Gc 7.5, U-Gc 2.5, and U-Gc 1.0 phr and PU with 7.5, 2.5, and 1.0 phr GMA copolymers, respectively.

the hybridization of PU with 5.0 phr of the GMA copolymer was 18.9 kg/cm²/454% and changed to 29.3 kg/cm²/560% after the copolymer was ion-exchanged with the calcium ion. Most of the calcium ion-exchanged hybridized copolymers had higher tensile strength than their original corresponding polymer, because a bivalent calcium ion will be coordinated with carboxylic groups containing PU, resulting in the formation of calcium ionic-crosslinked PU (Scheme II).

Dynamic Mechanical Analysis

The GMA copolymer had a damping peak shifted to 43.4° C and its peak intensity decreased as its curing degree with EDA increased, which demonstrated a curing behavior of epoxide groups of the GMA copolymer with EDA (Fig.1). The aqueous-based PU and GMA copolymer had their damping peaks at -38.7 and 41.0° C on the dynamic mechanical analysis (DMA) curves, respectively. The hybridized copolymer had a damping peak of the PU soft segment shifted to -34.8° C after the PU was treated with 2.5-phr GMA copolymer emulsions and also had a damping peak of the polyacrylate

segment shifted to 43.4° C. A higher dosage of the GMA copolymer resulted in a higher damping peak intensity (at 42.4° C) of the hybridized copolymer. For example, for the hybridized copolymer with 10.0-phr GMA copolymer emulsions, the damping peak of the PU segment shifted to -32.7° C with a lower peak intensity, but the damping peak intensity of the polyacrylate segment became higher than its low-dosage one (Fig. 3). Due to the limitation of the availability and the steric hindrance of the reaction sites on the PU and GMA copolymer, a higher dosage of the GMA copolymer could have resulted in an excess amount of epoxide groups left on the copolymer.

The PU carboxylic groups could be coordinated with the calcium ions after they were treated with a CaCl₂ solution (Scheme 2). The calcium ioncoordinated PU had a damping peak shifted to -34.2° C and with a lower peak intensity. The hybridized copolymer was treated with the CaCl₂ solution also showed a lower intensity on the DMA curves (Fig. 4), due to that the calcium ion had an ionic crosslinking formation with the PU carboxyl pendants of the aqueous-based PU or the hybridized copolymer system.

Thermogravimetric Analysis

The original aqueous-based PU had weight losses of 46 and 88% at 350 and 400°C on the TGA thermograms, respectively. The thermal stability of the hybridized copolymer was improved by increasing the GMA copolymer dosage (Fig. 5). For example, the resulting hybridized copolymers from the blending of PU with the 1.0-, 5.0-, and 7.5-phr GMA copolymers had weight losses at 400°C of 86, 83, and 69%, respectively (Table III). These phenomena indicated that the hybridized copolymer from the reactive blending of aqueousbased PU with the GMA copolymer could form a polymer network with a better thermal stability than that of its original polymer.

CONCLUSIONS

The amino-terminal groups of aqueous-based PU were generated by the NCO-terminated PU prepolymer process, and the amino contents of PU could be determined by the styrene oxide titration method. A reaction of EDA with an epoxide-containing GMA copolymer demonstrated that the curing reaction between them occurred at ambient temperature.

The reactive blend of the aqueous-based PU with the GMA copolymer resulted in a hybridized copolymer. These hybridized copolymers had improvements in the mechanical and the physical properties as well as in the thermal stability, due to that the reaction took place between the amino groups of the aqueous-based PU with the epoxide groups of the GMA copolymer and resulted in the formation of polymeric networks. The carboxylic acids on the aqueous-based PU and on the hybridized copolymer could be ionexchanged with the calcium ion. These resulting calcium ion-crosslinked polymer systems also had further improvements in their mechanical dynamic mechanical properties.

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