

# Synthesis of Nanophase-Separated Poly(urethane-co-acrylic acid) Network Films and Their Application for Magnetic Nanoparticle Synthesis

Ju-Young Kim,<sup>1</sup> Dong-Hyun Shin,<sup>1</sup> Jee-Hyun Ryu,<sup>2</sup> Gyung-Hyun Choi,<sup>3</sup> Kyung-Do Suh<sup>2</sup>

<sup>1</sup>Department of Advanced Materials Engineering, Samcheok National University, Samchok 245-711, South Korea

<sup>2</sup>Division of Chemical Engineering, College of Engineering, Hanyang University, Seoul 133-791, South Korea

<sup>3</sup>Department of Industrial Engineering, College of Engineering, Hanyang University, Seoul 133-791, South Korea

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**ABSTRACT:** Poly(urethane-co-acrylic acid) films were synthesized by the copolymerization of urethane acrylate nonionomer (UAN) and acrylic acid (AA) under different conditions. Poly(urethane-co-acrylic acid) films exhibited very different mechanical properties, attributed to the microstructural difference with the type of solvents used in the film preparation. The film synthesized using UAN/AA/water mixture had a relatively highly nanophase separated structure compared to that of the other films prepared using UAN/AA/dioxane mixture, resulting in higher mechanical property and glass-transition temperature. The nanostructural differences could be also confirmed by atomic force microscopy measurements. Magnetic nanocomposite films

synthesized based on UAN/AA/water and UAN/AA/dioxane mixtures showed different sizes of magnetic nanoparticles, attributed to the differences of size of hydrophilic nanodomains. The higher the degree of nanophase separation within poly(urethane-co-acrylic acid) films, the larger the size of hydrophilic nanodomains, resulting in formation of larger nanoparticles. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 3549–3556, 2004

**Key words:** poly(urethane-co-acrylic acid) film; urethane acrylate nonionomer (UAN); nanophase separation; magnetic nanoparticle; hydrophilic nanodomain

## INTRODUCTION

Recently, a number of investigations on nanoparticles dispersed within polymer matrix have been carried out because these materials can provide various new properties that result from the combination of properties both from inorganic components and polymers. The polymeric matrix provides the processability and the flexibility, whereas, at the same time, inorganic nanosized particles confer unique properties that differ from their bulk materials and atoms. As a consequence, nanocomposite films having novel catalytic, magnetic, and optical properties can be obtained.<sup>1–18</sup>

Most of polymers used in the synthesis of nanocomposite films have hydrophilic segments and hydrophobic segments at the same molecules (amphiphilic polymer). Hydrophilic segments can solubilize or adhere to inorganic materials through dipolar interaction, hydrogen bonding, complex formation, or covalent bonding and stabilize the formed nanosized particles through steric or electrosteric stabilization.<sup>1–5</sup> Hydrophobic segments can lead to smaller particle size with narrow size distributions and high colloidal

stability. There are several types of amphiphilic polymers used in the nanocomposite matrix such as nonionic, anionic, or cationic homopolymers, random copolymer, and diblock copolymer. The use of amphiphilic block becomes increasingly attractive because methods of synthesizing nanoparticles in microphase-separated diblock copolymer provide greater control over particle formation.<sup>3–10,17,18</sup> However, amphiphilic block copolymers, which are very expensive materials, can be obtained only by an extremely difficult synthetic process, and some amphiphilic homopolymers lack desirable mechanical properties, leading to limiting the application of polymer films containing metal nanoparticles.

Although amphiphilic urethane acrylate chains having hydrophilic moieties, such as carboxylic, sulfonic acid, amino groups, and polyoxyethylene (POE) groups, have been widely used as water-borne UV coatings,<sup>19,20</sup> little work has been reported on the use of these chains as nanocomposite matrix. In our previous works, we could synthesize nanophase-separated amphiphilic polyurethane networks through crosslinking polymerization of urethane acrylate nonionomers (UANs) as well as magnetic nanoparticles within these polyurethane networks.<sup>21,22</sup> Morphology and size of magnetic nanoparticles formed within these networks were largely changed with type of solvent used in the synthesis of networks.

Correspondence to: K.-D. Suh (kdsuh@hanyang.ac.kr).

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However, amphiphilic polyurethane network films based on amphiphilic UANs did not have greater mechanical properties compared to those of crosslinked urethane acrylate films. In addition, highly viscous urethane acrylate nonionomers made it difficult to control film thickness. This led us to synthesize amphiphilic polymer network through copolymerization of hydrophilic monomer, acrylic acid, and UAN to easily control film thickness and viscosity of UAN, and to obtain improved mechanical property of amphiphilic polymer networks without sacrificing their nanophase-separated structure.

We present here the synthesis of amphiphilic polymer networks through copolymerization of UAN and acrylic acids in the presence of various solvents. We also present the difference in morphology and mechanical properties of various amphiphilic polymer networks examined by atomic force microscopy (AFM) and dynamic mechanical analysis, and discuss it in relation to the different microstructures anticipated for these networks. Finally, formation of nanosized iron oxide particles within the polymer matrix was characterized using transmission electron microscopy (TEM) measurement, and the magnetic property of magnetic composite films was also investigated using a vibrating sample magnetometer.

## EXPERIMENTAL

### Materials

In the synthesis of amphiphilic urethane acrylate nonionomer (UAN) precursor chains, poly(propylene oxide triol) (PPO triol,  $M_w = 1000$ ; Korea Polyol Co.), 2,4-toluene diisocyanate (TDI; Aldrich Chemical Co., Milwaukee, WI), 2-hydroxyethyl methacrylate (2-HEMA; Aldrich), and polyethylene glycol (PEG,  $M_w = 1500$ ; Aldrich) were used. PPO triol and PEG were dried and degassed at 80°C and 3–5 mmHg for 2 days. Potassium persulfate (KPS; Wako Pure Chemicals, Osaka, Japan) and 2,2-azobisisobutyronitrile (AIBN; Aldrich) were used as water-soluble initiator and oil-soluble initiator, respectively. Acrylic acid (AA), dioxane, tetrahydrofuran (THF), and iron trichloride hydrate ( $\text{FeCl}_3$ ), purchased from Aldrich Chemical, were used as received.

### Synthesis of UAN chains and UAN networks

Amphiphilic UAN precursor chain was synthesized by using an established three-step process as described in a previous publication.<sup>22,23</sup> Each reaction was performed in a 500-mL four-neck vessel equipped with stirrer, thermometer, and an inlet system for nitrogen gas. NCO-capped intermediate precursor chains that were initially synthesized by the reaction between PPO triol and TDI were reacted with 2-HEMA (2nd step), followed by reaction with PEG

(3rd step) to obtain a UAN chain having reactive vinyl groups and hydrophilic polyethylene oxide chains as well. The molar ratio of TDI/PPO triol/2-HEMA/PEG was 3/1/2/1. The molecular weight of UAN precursor chains was measured by a Model 410 GPC equipped with Styragel HR1–4 column (Waters Chromatography Division/Millipore, Milford, MA) at 25°C. The flow rate of the carrier solvent THF was 0.5 mL/min. The weight-average molecular weight of synthesized UAN chains was 6700 with a polydispersity of 2.01. Characterization of synthesized UAN chains based on  $^1\text{H-NMR}$  spectra was reported in our previous study.<sup>22,23</sup> The expected molecular structure of the UAN chain is schematically illustrated at Figure 1.

Amphiphilic polyurethane networks [i.e., poly(urethane-*co*-acrylic acid)] were synthesized through crosslinking polymerization of UAN chain and AA at three different conditions: (1) thermal curing of UAN/AA mixture without a solvent, (2) crosslinking copolymerization of UAN/AA/water mixture, and (3) crosslinking copolymerization of UAN/AA/dioxane mixture. For thermal curing of UAN chains, an oil-soluble initiator (AIBN) and UAN/AA mixture were mixed and poured into a silicone-packed mold, after which crosslinking copolymerization was carried out at 85°C for 3–4 h to obtain polymer film with 0.1 mm thickness. For the preparation of network films using UAN/AA/water or UAN/AA/dioxane mixtures, distilled deionized (DDI) water or dioxane was slowly added into UAN/AA mixture with vigorous stirring (380 rpm). Then, the mixtures containing AIBN were poured into a silicone-packed mold and crosslinking polymerization proceeded for 4 h at 65°C. After the completion of polymerization, the obtained gel films were immersed in acetone for purification, then dried, and denoted as UANW and UAND gels, respectively. The recipe for the synthesis of these gel films is illustrated in detail in Table I. The gel content of the networks prepared under different conditions was determined by the Soxhlet extraction method using acetone for 2 days. The insoluble materials were dried under vacuum for about 2 days and weighed to determine the gel contents. The gel contents of the networks were determined from the difference in weight before and after the extraction experiment as follows: gel content (%) = the network weight after extraction  $\div$  the network weight before extraction. Several runs were carried out for each network, and average values were taken. Gel contents of the networks were in the range of 95.45–97.43%.

### Preparation of composite films

For the preparation of magnetic composites, two kinds of dried poly(urethane-*co*-acrylic acid) films were first immersed in  $\text{FeCl}_3$ -THF at room temperature for 24 h to load  $\text{FeCl}_3$  into network matrix, and then swollen gel films were washed with excess water and dried for

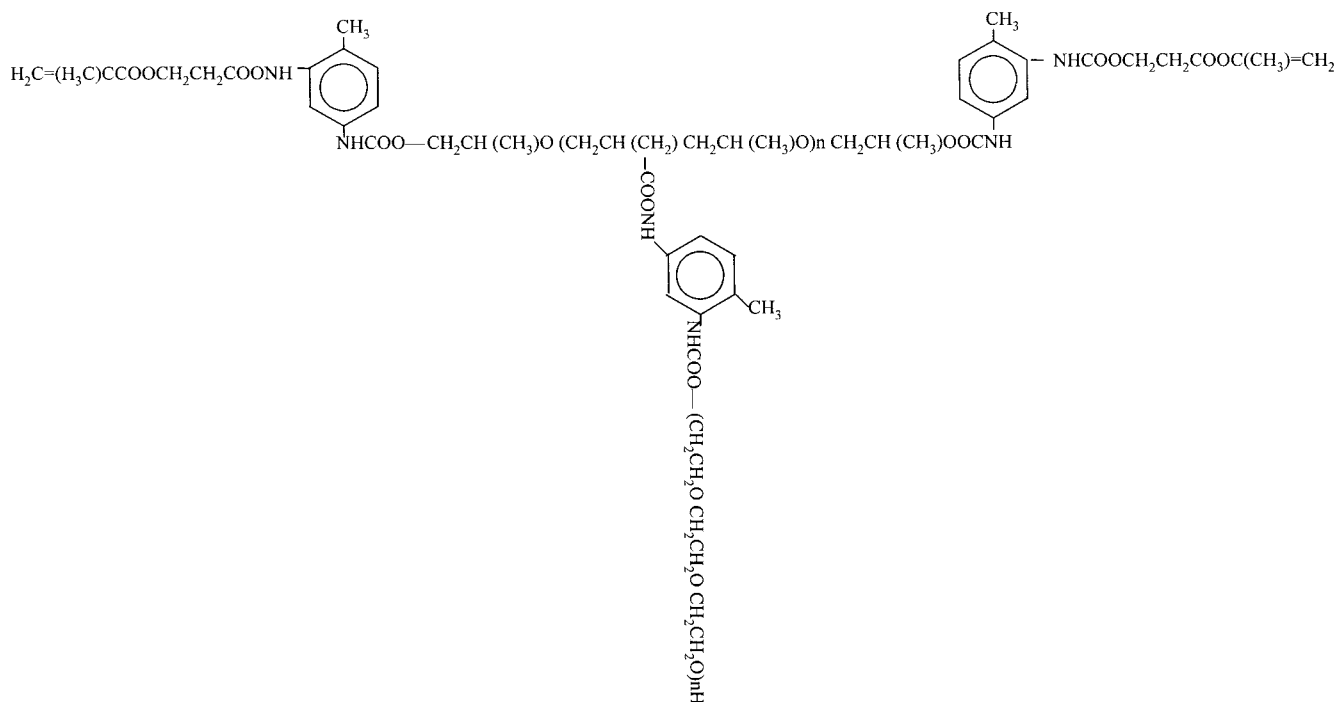


Figure 1 Schematic figure of chemical structure of UAN chains.

24 h. To make iron oxide particles, dried gel films containing  $\text{FeCl}_3$  were transferred into 2M NaOH aqueous solution and stirred at room temperature for 24 h.<sup>17,21,24,25</sup> After that, to wash out residual NaOH and NaCl, reswollen gel films were stirred in deionized distilled water at room temperature for 4 days and then dried under vacuum. To determine the amount of  $\text{FeCl}_3$  loaded within the gel films, the change of weight of the gel films before and after immersion in  $\text{FeCl}_3$  solution and reduction was measured.  $\text{FeCl}_3$  uptake within the gel films was represented as (weight of dried composite film after immersion at a  $\text{FeCl}_3$  solution and reduction  $\div$  weight of dried UAN gel films) (g/g). UAND and UANW gel films used showed 0.03–0.041 g/g of  $\text{FeCl}_3$  uptake.

### Measurements

A transmission electron microscope (TEM, JEM 2020CX; JEOL, Tokyo, Japan), applying an acceler-

ation voltage of 200 kV, was used to clarify the nanostructure of composites films. The nanocomposite films were embedded in an epoxy resin of Epon-812 supplied by SPI. Ultrathin sections of the nanocomposites with thickness of 70 nm were prepared at 60°C by a ultramicrotome of Ultracut R made by Leica (Cambridge, MA). Carbon was vacuum-evaporated on the thin sections to prevent accumulation of electrons during TEM observation. The particle sizes were determined with a comparator based on the measurement of at least 150 particles.

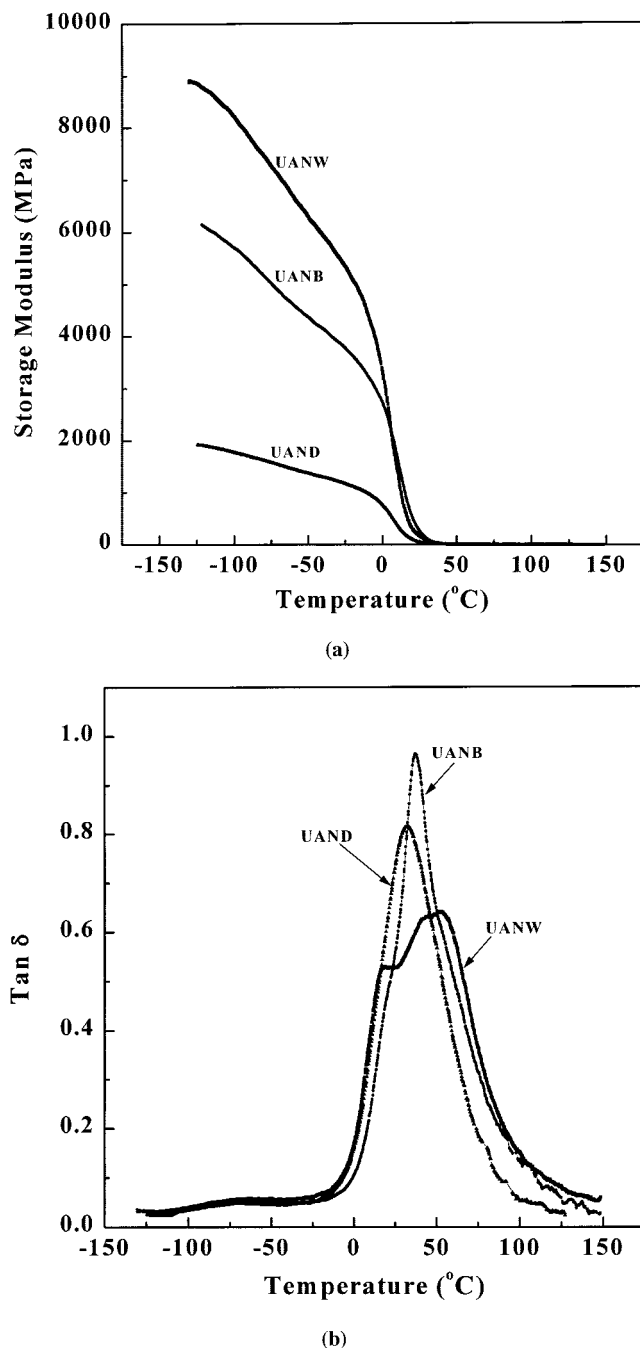
Atomic force microscopy (AFM, NanoScope III; Digital Instruments, Santa Barbara, CA) was used to examine the surface topology. The AFM was operated with silicon probes in the tapping mode. The AFM-E piezoelectric scanner can scan a surface area  $10 \times 10 \text{ mm}^2$ . The spring constant of the silicon cantilever was 50 N/m. In the tapping mode, the cantilever on which the tip is mounted was oscillated at a frequency of about 250 kHz.

The magnetic property of nanocomposites was studied using a vibrating-sample magnetometer (VSM, Model VSM-5-15; Toei Industry Co., Japan). The samples were vibrated within magnetic field of up to 15 kOe at room temperature. The response of the samples (magnetization) was obtained as a function of the applied magnetic field.

The tensile properties of dried gel films were measured using a Hounsfield Model Instron (No. R10001231) at a crosshead speed of 1 mm/min. All samples were measured five times. Dynamic

TABLE I  
Recipe for the Synthesis of Poly(urethane-co-acrylic acid) Gel Films

Symbol	Ingredient					Gel content (%)
	UAN	AA	Water	Dioxane	AIBN	
UANB	6g	4 g	—	—	0.001 g	97.43
UAND	6g	4 g	—	4 g	0.001 g	95.45
UANW	6g	4 g	4 g	4 g	0.001 g	96.37



**Figure 2** Storage modulus (a) and  $\tan \delta$  (b) of crosslinked poly(urethane-*co*-acrylic acid) films as a function of temperature.

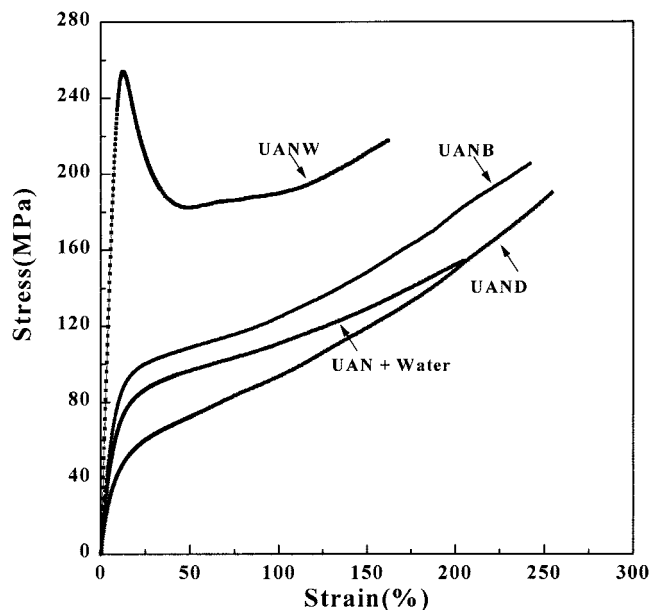
mechanical measurements on the dry networks were performed by using a DMA 2980 (TA Instruments, New Castle, DE) in the extension mode at 1 Hz and a heating temperature of 2°C/min in the temperature range -150 to 200°C. X-ray scattering experiments for the dried composite films were conducted with a Rigaku D/Max-2200 (copper radiation, 40 kV, 100 mA, nickel filter; Rigaku Denki, Japan).

## RESULTS AND DISCUSSION

### Nanophase-separated structure of poly(urethane-*co*-acrylic acid) networks

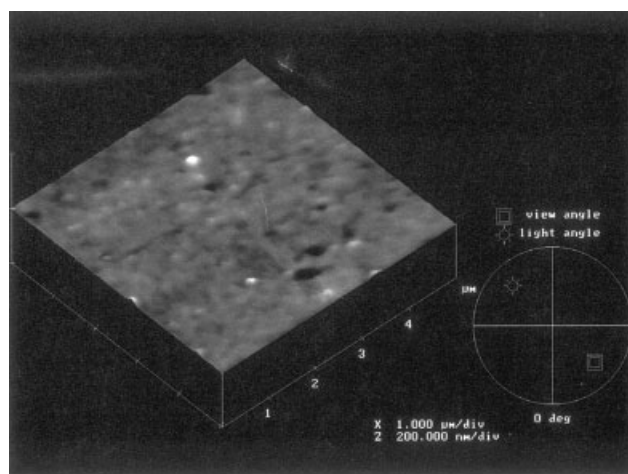
It was previously reported that nanophase separation in crosslinked urethane acrylate films strongly influences the mechanical properties of its film.<sup>26-33</sup> Unlike macrophase separation, tensile strength, elongation, and glass-transition temperature of crosslinked polyurethane films increases concomitantly with the degree of nanophase separation between the soft segment and the hard segment. For amphiphilic urethane acrylates such as urethane acrylate anionomer, and urethane acrylate nonionomer, nanophase separation between hydrophilic and hydrophobic segment or between soft and hard segments strongly influence the mechanical properties of their crosslinked films; this is attributed to the nanophase separation, which causes an increase of chain entanglement in each segment, and nanophase-separated hydrophilic or hard segments act as physical fillers.<sup>26-33</sup>

In our previous study, the mechanical property of crosslinked amphiphilic urethane acrylate (AUA) films was largely changed with the type of solvent used in the network preparation. For the crosslinked film synthesized using a water/AUA mixture, the film exhibited a higher mechanical property than that of the other films synthesized using DMAc/AUA mixture and neat crosslinked AUA film. This result was attributed to the higher degree of hydrophilic/hydrophobic nanophase separation in the AUA/water mixture.<sup>26-31</sup> Thus, the mechanical property of poly(urethane-*co*-acrylic acid) films was examined to investigate nanophase separation in UAN/acrylic acid mixture under various conditions.

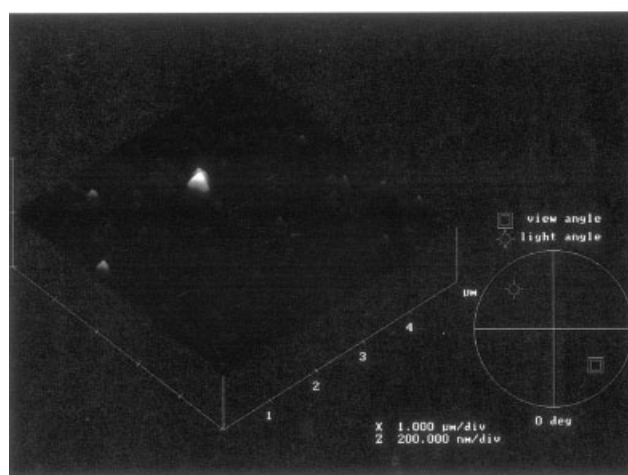


**Figure 3** Stress-strain curves of crosslinked poly(urethane-*co*-acrylic acid) films synthesized under different conditions.

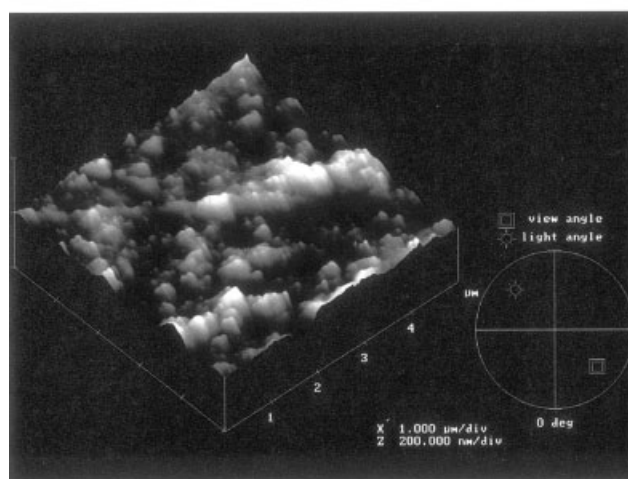




(a)



(b)



(c)

**Figure 4** Atomic force microscopy image of dried poly(urethane-*co*-acrylic acid) films: (a) UANB; (b) UAND; (c) UANW gel film.

Figure 2 shows the storage modulus and  $\tan \delta$  of poly(urethane-*co*-acrylic acid) films synthesized under different conditions as a function of temperature. Even

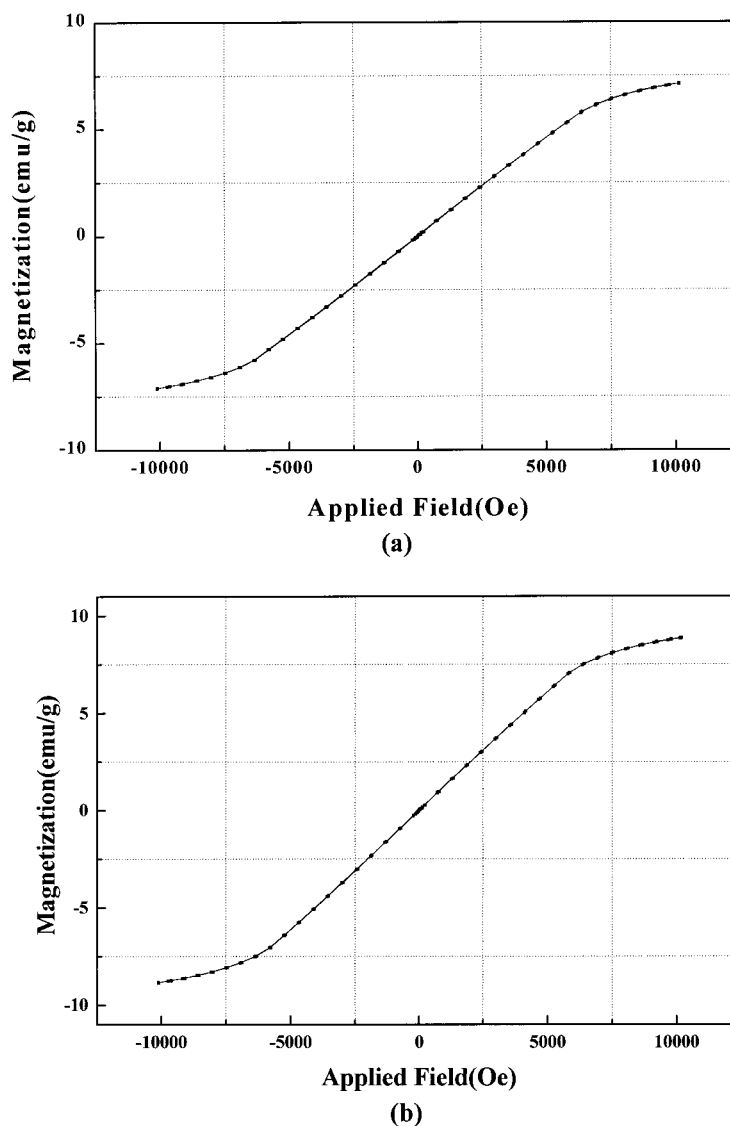
though all the poly(urethane-*co*-acrylic acid) films were synthesized using the same UAN chain and the same weight ratio of UAA/AA, these films showed very different storage modulus and maximum  $\tan \delta$  values at different temperatures. That is, UANW film synthesized using UAN/AA/water mixtures exhibits a greater storage modulus than that of either UANB or UAND film synthesized using neat UAN/AA and UAN/AA/dioxane mixture, respectively. The glass-transition temperature of UANW film was also higher than that of either UAND or UANB film.

In general, the mechanical property of the crosslinked film synthesized in the absence of a solvent was higher than that of the film synthesized in the presence of a solvent because of a decrease in chain entanglement, by using a solvent in the network synthesis. However, UANW film was prepared with the use of solvent (water), and its storage modulus was greater than that of UANB film synthesized without the use of solvent.

Figure 3 shows stress-strain curves of poly(urethane-*co*-acrylic acid) films prepared under different conditions. As expected, three kinds of crosslinked films exhibited very different tensile properties. UANW film, having greater storage modulus, exhibited higher tensile strength and modulus than those of UAND and UANB films. UAND film has greater elongation than that of UANW and UANB films. Thus, very different mechanical properties of the poly(urethane-*co*-acrylic acid) films can be interpreted as being attributed to the difference of degree of nanophase separation among the films. In other words, the films synthesized using UAN/AA mixtures would have a very different nanostructure depending on the type of solvent used in the crosslinking polymerization.

UAN chains used in synthesis of the films have a hydrophobic polypropylene oxide (PPO)-based segment and a hydrophilic polyethylene oxide (PEO)-based segment at the same backbone. Because these two segments are completely dissolved in acrylic acid, the degree of nanophase separation of UANB film synthesized using UAN/AA mixture would be very low. For the UAN/AA/dioxane mixture, dioxane is a solvent for AA as well as for the whole UAN chain, so that this mixture could also form a relatively homogeneous solution; as a consequence, the film synthesized using this mixture would have a low degree of nanophase-separated structure.

Given that water is a good solvent for both the AA and PEO segments of UAN chain but a nonsolvent for the PPO-based segment, AA and PEO segments are highly nanophase separated from the PPO-based segment on mixing with water. In the course of nanophase separation, AA and PEO segments are associated with each other to form hydrophilic domains, whereas PPO-based segments form their own domains. This highly nanophase separated structure is



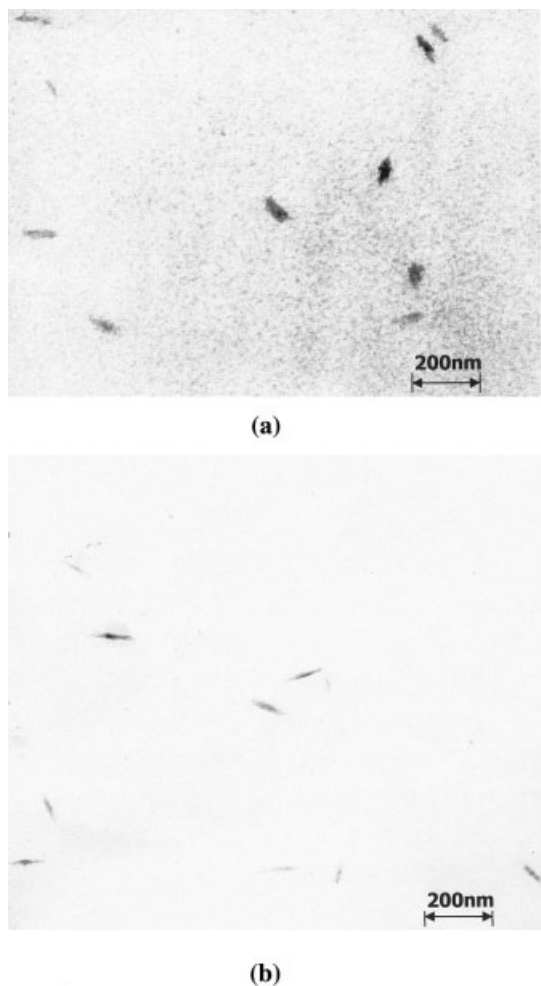
**Figure 5** Magnetization of composite films as a function of applied magnetic field at room temperature.

permanently locked in by crosslinking copolymerization; as a consequence, UANW film would have a higher degree of nanophase-separated structure than that of UANB and UAND films. Consequently, higher tensile strength and storage modulus of UANW film could be explained by its highly nanophase separated structure.

Recently, AFM has been considered as a powerful surface characterization technique and has been widely used to study surface morphology of homopolymer, blockcopolymer, and polymer blends. Nanophase separation and nanostructural changes in polymer films have been being investigated through measuring surface morphology using AFM because formation of nanoaggregates in polymer films can be monitored by changes in surface roughness at the nanoscale.<sup>34–38</sup> Figure 4 shows AFM images of three kinds of poly(urethane-*co*-acrylic acid) gels. These two films showed very different surface morphologies, indicat-

ing that the microstructure of poly(urethane-*co*-acrylic acid) film was largely changed with the type of solvent used in the network preparation.

The smooth, flat surface of neat polymerized UAN/AA and UAN/AA/dioxane films indicates that the degree of nanophase separation between acrylic acid and UAN is relatively low. Synthesis of the film using UAN/AA/water mixture revealed a relatively rough surface. This irregular surface for polymer films is generally observed for microphase-separated block copolymers or solvent-cast homopolymer films or immiscible polymer blend films. As mentioned earlier, in the course of mixing water with UAN/AA, the hydrophilic moiety PEO and AA are nanophase separated from hydrophobic PPO-based segments to form nanosized hydrophilic domains. After copolymerization, a nanophase-separated structure is formed by crosslinking polymerization. Thus, the rough surface of the film can be



**Figure 6** Transmission electron micrograph of magnetic composite films: (a) magnetic composites prepared with UAND film; (b) magnetic composites prepared with UANW film.

explained by its higher degree of hydrophilic/hydrophobic nanophase separation.

#### Formation of magnetic nanoparticles in nanophase-separated poly(urethane-co-acrylic acid) films

Figure 5 shows the magnetization of composite films as a function of applied magnetic field at room temperature. Two kinds of composite films synthesized using UAND and UANW gel films exhibited extremely small hysteresis loop and coercivity. This lack of hysteresis and coercivity is characteristic of superparamagnetic particles or some single-domain particles.<sup>17,24</sup> It has been established that magnetic particles, smaller than some critical particle diameter, can be designated as single domains. As the particles size continues to decrease below the single-domain value, particles exhibit superparamagnetic property, that is, no hysteresis and coercivity. Thus, results for magnetic property of composite films indicate the forma-

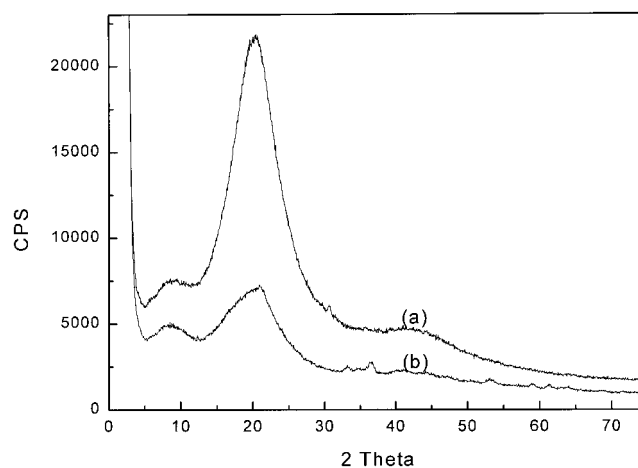
tion of nanosized magnetic particles within the crosslinked poly(urethane-co-acrylic acid) matrix.

Transmission electron microscopy images of two composite films, illustrated in Figure 6, also show that nanosized particles (145–160 nm) are dispersed within the crosslinked polymer matrix. This result supports the superparamagnetic property of composite films attributed to the formation of nanosized magnetic particles within the UAN matrix. Also, distinct peaks of X-ray diffraction patterns for composites, illustrated in Figure 7, correspond to characteristic peaks of  $\gamma$ - $\text{Fe}_2\text{O}_3$  (maghemite).<sup>21,25,39–41</sup>

Although magnetic composite films were prepared within the polymer matrix synthesized using the same chemicals, they had different particle morphologies. The composite films based on UAND gels have a smaller particle size than that of films synthesized using UANW gel film. This result is mainly attributed to the nanostructural differences between UAND and UANW gel films.

It has been reported that size and morphology of metal or semiconductor particles formed at amphiphilic polymer matrix can be controlled by several factors such as ratio of hydrophilic/hydrophobic segment in amphiphilic polymer chain, chain length of hydrophilic or hydrophobic segments, the metal precursor type, ionic or complex interactions of the metal precursor with the hydrophilic segment, and the reduction conditions.<sup>1–11</sup> For the preparation of nanosized metal or semiconductor particles in the presence of amphiphilic polymer, hydrophilic and hydrophobic segments in amphiphilic polymer chains should be nanophase separated at specific solvents to form nanosized hydrophilic domains, given that dissolved metal salts are exclusively sorbed at nanosized hydrophilic domains and reduction of sorbed metal salts mainly occurs within these domains.

Consequently, under the same reduction conditions using the same metal salts, the morphology and size of



**Figure 7** X-ray diffraction angle patterns of (a) UANW film and (b) magnetic composite film based on UANW film.



hydrophilic domains, formed by hydrophilic/hydrophobic nanophase separation, strongly influence the size and morphology of nanoparticles formed. As the ratio of hydrophobic segments in amphiphilic polymer increases, the size of microphase-separated hydrophilic domains decreases, causing the formation of smaller particle sizes within the polymer matrix. Because the crosslinked polymer matrix used in our study was synthesized with the same reactants (UAN/AA mixture), all polymer matrices had the same ratio and chain length of hydrophilic/hydrophobic segments. Thus, the formation of gel films, having very different size and morphology of magnetic particles, can be interpreted as being attributed to the microstructural difference of crosslinked UAN matrix prepared with different solvents. As mentioned earlier, UANW gel film has a relatively higher degree of nanophase separation, causing the formation of relatively larger size hydrophilic nanodomains in the polymer matrix; as a consequence, larger magnetic nanoparticles were formed in the UANW gel film.

### CONCLUSIONS

We synthesized nanophase-separated poly(urethane-co-acrylic acid) films under different conditions. Mechanical properties of these films were much better than those of neat crosslinked UAN films. In addition, the thickness of films could be more easily controlled. The nanostructure of poly(urethane-co-acrylic acid) was varied by the solvent type used in the preparation process. The gel film synthesized using UAN/AA/water mixture had a relatively highly nanophase separated structure compared to that of other gels prepared using UAN/AA/dioxane mixture.

The nanophase-separated structure of poly(urethane-co-acrylic acid) films strongly influenced their mechanical properties. That is, a higher degree of nanophase separation increased the storage modulus, tensile modulus, and glass-transition temperature because nanophase-separated hydrophilic domains could act as a physical filler. Magnetic nanoparticles could be also formed within hydrophilic nanodomains formed in poly(urethane-co-acrylic acid) films. Two kinds of magnetic nanocomposite films had different size of magnetic nanoparticles, attributed to the differences of size of hydrophilic nanodomains. The higher the degree of nanophase separation within poly(urethane-co-acrylic acid) films, the larger the size of hydrophilic nanodomains, resulting in formation of larger nanoparticles.

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