

# Preparation of Acrylic Copolymers and Crosslinking Agents and Properties as a Film

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**ABSTRACT:** Copolymers of butyl acrylate (BA)-methyl methacrylate (MMA)-acrylic acid (AA) and intraparticle crosslinking agents containing *N*-methylol acrylamide (NMA) and ethylene glycol dimethacrylate (EGDMA) were prepared by emulsion copolymerization. After that, films were prepared from the mixture of copolymers and the interparticle crosslinking agents. The interparticle crosslinking agents were prepared from hexamethylene diisocyanate and aziridine ethanol. Mixtures of the copolymer and the interparticle crosslinking agent were cast to films and crosslinked in a convection oven. The effects of the contents of the intra/interparticle crosslinking agents were also evaluated. By increasing the contents of EGDMA, rough-

ness of the films was increased because of the effects of EGDMA acting as an intraparticle crosslinking agent. By increasing the contents of the interparticle crosslinking agent, roughness was also increased by the reaction between the copolymers and interparticle crosslinking agent. Tensile strength and water and chemical resistance of the film were increased, whereas elongation of film was decreased by increasing the contents of interparticle crosslinking agents. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 1587–1594, 2009

**Key words:** emulsion polymerization; copolymerization; crosslinking; films

## INTRODUCTION

Polymers containing *N*-methylol acrylamide (NMA) and ethylene glycol dimethacrylate (EGDMA) prepared by emulsion copolymerization with other vinyl monomers have been widely used in various applications such as binders for nonwoven fabrics, protective coatings, latex paints, and adhesives.<sup>1–3</sup> The use of the NMA in small amount (3–7 wt % of the copolymer) and the EGDMA in small amount (1–5 wt % of the copolymer) acts as an intraparticle crosslinking agents, which form the films with increased tensile strength, impact strength, abrasion resistance, peel strength, water, detergent, alkali and solvent resistance, and dirt pickup resistance.<sup>4,5</sup> For film formation from latexes, the polymer molecules have to diffuse across the interface between the particles to give good interparticle adhesion or welding. It is desirable for polymer particles to contain the linear chains that can diffuse across during the film formation process, and then crosslinking occurs after the film is formed. If the latex particles are microgels, which means if they are containing crosslinked polymer chains, the resulting films will have poor

mechanical properties because of the poor interparticle welding.<sup>6</sup> The presence of crosslinkings limits the interdiffusion and the interparticle mixing of polymer.<sup>7–9</sup>

Polymer latex films are formed by casting method. The fundamental process involves the transformation of the particles in a stable latex dispersion into a continuous film. Early works on the mechanism of latex film formation were carried out by Dillon et al.,<sup>10</sup> Brown,<sup>11</sup> Voyutskii,<sup>12</sup> Bradford and Vanderhoff,<sup>13</sup> and Mason.<sup>14</sup> When an aqueous dispersion of soft latex particles is allowed to evaporate, a transparent void-free film is formed.<sup>15,16</sup> This process of the film formation is the basis of many latex coating technologies. Traditionally, the sequential steps of the film formation are as follows: (i) a linear cumulative water loss with time, the evaporation rate of which was close to the one of pure water [this step ends when irreversible contact between particles is adhered (particle volume fraction between 60 and 74%)]; (ii) particle deformation and close contact associated with a dramatic decrease of the water evaporation rate (this leads to a drying film presenting the so-called honeycomb structure where the particle boundaries, known as further gradual coalescence or autoadhesion, yielding a homogenous film).<sup>17–20</sup>

In this work, we describe the results of a study of the intraparticle crosslinking behavior of latexes

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TABLE I  
Basic Recipe for the Copolymer Using Emulsion Polymerization<sup>a</sup>

Component	Monomer (wt %)					Initiator (wt %)	Surfactant (wt %)
	BA	MMA	AA	NMA	EGDMA	KPS	SLS
A	50	46	1	3		1	3
B	50	45	1	3	1	1	3
C	50	44	1	3	2	1	3
D	50	43	1	3	3	1	3

<sup>a</sup> Total solid concentration is based on 25 wt % with DDI water.

prepared from butyl acrylate (BA), NMA, acrylic acid (AA), and EGDMA. The copolymers with functional carboxyl groups on the surface were prepared by semibatch emulsion polymerization. Also, synthesis of the interparticle crosslinking agent was prepared by the reaction between isocyanate monomer and aziridine derivatives. And then the film was prepared by casting of the mixture of the copolymer and the interparticle crosslinking agent and dried.<sup>21</sup> In this condition, the crosslinking reactions become possible between the carboxyl group of the copolymer and aziridine group of the crosslinking agent. The focus of this article is to investigate the effects of the contents of the crosslinking agent on the mechanical properties, the surface morphologies, water, and chemical resistance of the films.<sup>22</sup>

## EXPERIMENTAL

### Materials

BA (99.5% in purity) and methyl methacrylate (MMA) (99.9%) were purchased from Duksan Chemical (Ansan, Korea) and AA (99.0%), NMA (99%), EGDMA (98%) were purchased from Aldrich, USA. All materials were distilled under nitrogen and stored at  $-10^{\circ}\text{C}$  before use. Potassium persulfate (KPS) (99.5%) and sodium lauryl sulfate (SLS) were purchased from Duksan Chemical, and they were used as an initiator and as a surfactant, respectively. Deionized water was used for all polymerization and treatment processes. 1,6-Hexamethylene diisocyanate (HDI) was purchased from Needfill Chemical (Seoul, Korea) and aziridine ethanol (97%) were purchased from Aldrich. Dimethylformamide (DMF, 99.5% in purity; Duksan Chemical) was used as a solvent.

### Preparations of copolymers with functional carboxyl group

The mixtures of BA, MMA, AA, NMA, and EGDMA were emulsified in an aqueous solution of SLS and KPS and stirred with the magnetic stirrer for 1 h until the solution seemed to be homogeneous. The emulsion polymerization of the monomer solution was carried out as a semibatch process with drop-

ping the solutions continuously at  $70^{\circ}\text{C}$  under nitrogen. The reaction continued for 3 h and at 200 rpm. Poly(BA-*co*-MMA-*co*-AA-*co*-NMA) and poly(BA-*co*-MMA-*co*-AA-*co*-NMA-*co*-EGDMA) copolymers prepared by emulsion copolymerization had the functional carboxyl groups on their surface. The basic formulations for copolymers are shown in Table I. The copolymer particle size and morphology were measured using scanning electron microscopy (SEM, JSM-6700F; Jeol, Tokyo, Japan). Also, glass transition temperature,  $T_g$ , of copolymer was determined by differential scanning calorimeter (DSC Q1000, TA, New Castle, DE).

### Preparations of interparticle crosslinking agent

The interparticle crosslinking agents were prepared from HDI and aziridine ethanol. The heat liberated and viscosity increment from this exothermic reaction were controlled by DMF. The synthesis of interparticle crosslinking agent was performed in a 500-mL round-bottomed flask at  $60^{\circ}\text{C}$  under nitrogen. First, HDI and DMF mixture were transferred into the flask, and then aziridine ethanol was added. The reaction continued for 3 h and at 200 rpm. The prepared interparticle crosslinking agents were evaluated using Fourier transform infrared spectroscopy (FTIR, Bomem MB100, Hartmann & Braun, Germany).

### Preparations and characterizations of film from the copolymer and the interparticle crosslinking agent

The mixture of the copolymer and the interparticle crosslinking agent were cast to form the films and then dried in a convection oven at  $130^{\circ}\text{C}$ . In this

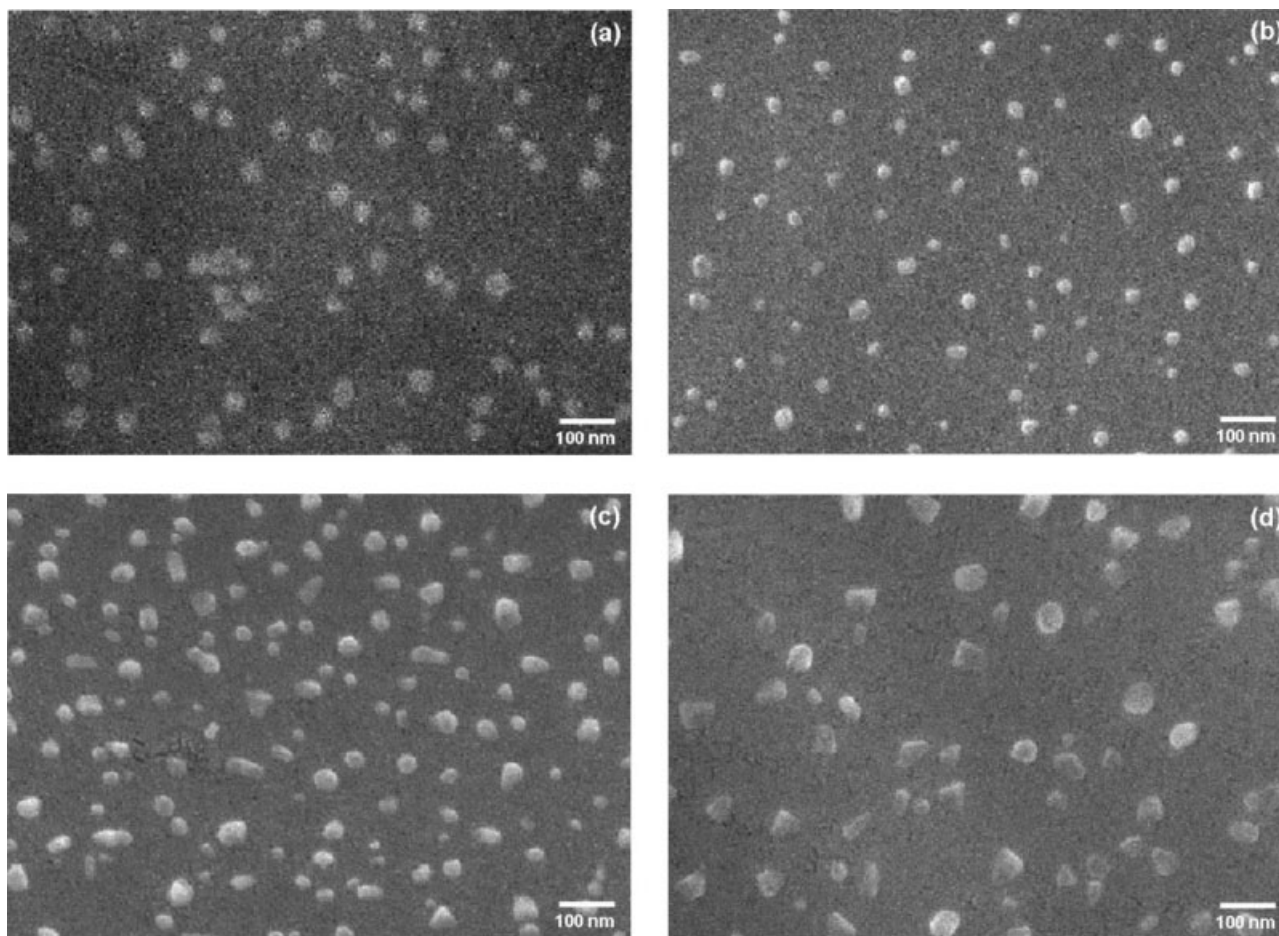
TABLE II  
Recipe for the Film Formation

Component	Copolymer (wt %)	Crosslinking agent (wt %)
E	A	100
F		99
G		97
H		95
I	C	97

condition, crosslinking reactions proceeded between carboxyl groups of copolymer and aziridine groups of interparticle crosslinking agent. To investigate the effects of the contents of the interparticle crosslinking agent on the mechanical properties, water resistance and chemical resistance, the contents of the crosslinking agents were varied as shown in Table II. The morphologies of film surfaces were observed using atomic force microscope (AFM; NanoScope IV, Plainview, NY). The mechanical properties of the film were measured by universal test machine (Instron 8516, Instron, Norwood, MA). Also, water and chemical resistance were characterized considering the swelling ratio of the film in water and toluene. To measure the swelling ratio of the film, dried film was dipped in water at 50°C and toluene at room temperature for 24 h. The swelling ratio of each sample was calculated using the following equation:

$$\text{Swelling ratio} = \frac{W_s - W_d}{W_d}$$

where  $W_s$  and  $W_d$  are the weights of fully swollen and dried films, respectively.



**Figure 1** SEM micrographs of the copolymer particles: (a) 0 wt % EGDMA (A); (b) 1 wt % (B); (c) 2 wt % (C); and (d) 3 wt % (D).

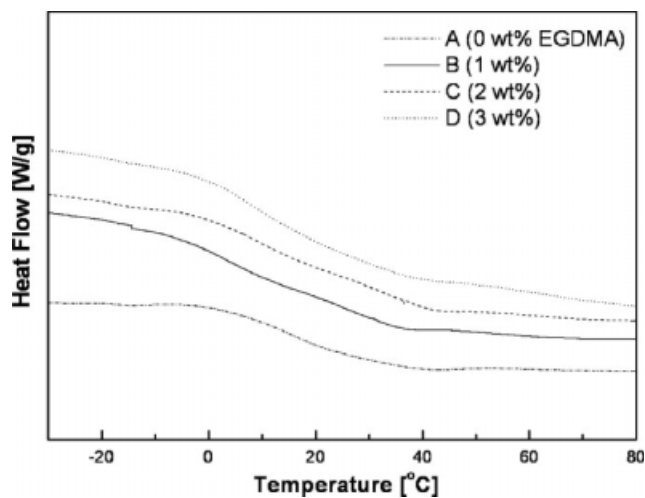
## RESULTS AND DISCUSSION

### Characterizations of the copolymer

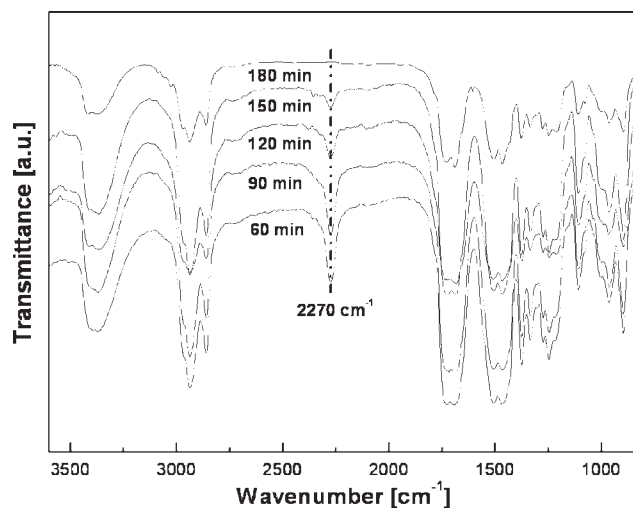
Figure 1 shows the micrographs of the prepared copolymers. Copolymer particles show uniform dispersion and generally round shape, and the average particle size was about 50 nm. The addition of small amount (1–3 wt % of the copolymer) of EGDMA shows that these polymer particles are self-crosslinkable. By increasing the EGDMA contents, the particle morphology are clearer because of the crosslinking, whereas the particles at low EGDMA contents are not. Glass transition temperature of copolymers was investigated at about 25°C and found that the glass transition temperatures of copolymers are constant regardless of EGDMA contents from DSC thermograms as shown in Figure 2.

### Characterizations of the crosslinking agent

Crosslinking agents were prepared from the isocyanate monomers that have two or three functional groups and aziridine ethanol. Synthetic process of crosslinking agent was confirmed using FTIR as



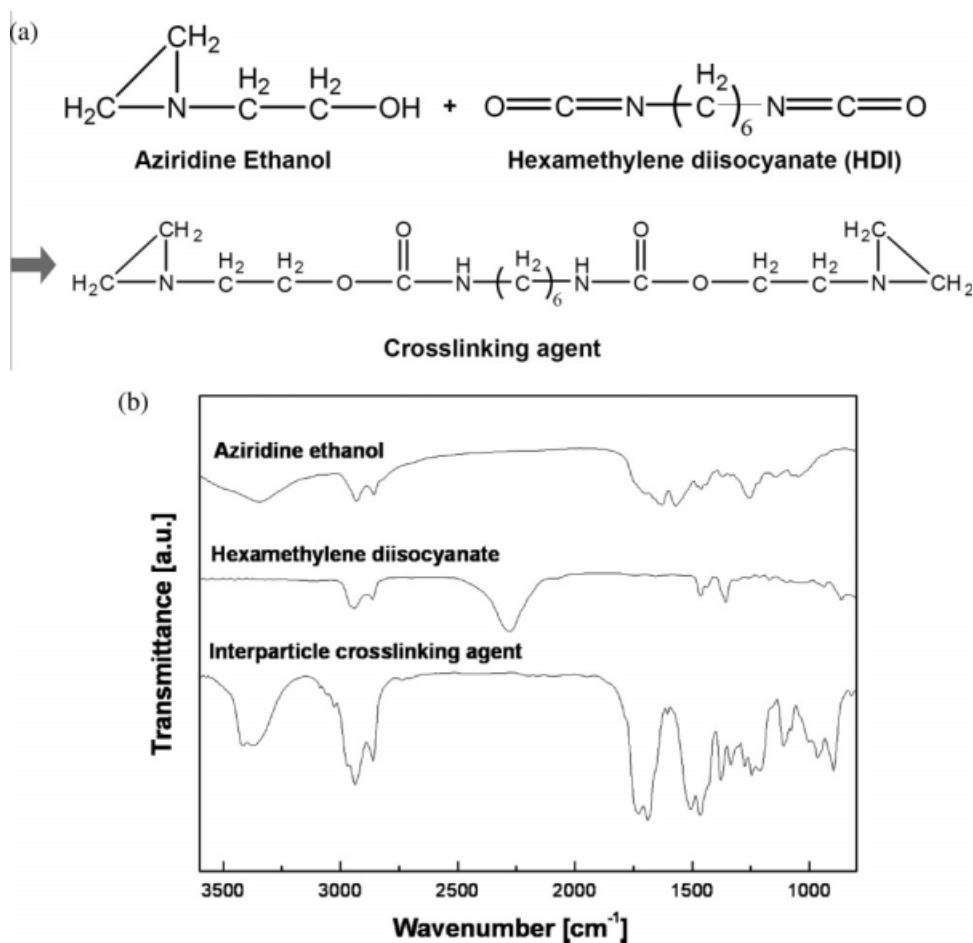
**Figure 2** Glass transition temperature ( $T_g$ ) of the copolymer particles A, B, C, and D from DSC thermograms.



**Figure 3** FTIR spectra in the N=C=O stretching region of the isocyanate monomer.

shown in Figure 3 by measuring the transmittance of  $2270\text{ cm}^{-1}$  band attributed to the N=C=O stretching of isocyanate monomers. Samples of the crosslinking agents were withdrawn every 30 min during the reaction, and the isocyanate band of the

FTIR was observed to decrease with the increase of the reaction time. The sampling was stopped when  $2270\text{ cm}^{-1}$  band was disappeared. As expected,  $2270\text{ cm}^{-1}$  band are totally disappeared after 3 h. It means that all isocyanate monomers reacted with



**Figure 4** The scheme (a) and FTIR spectra (b) of the interparticle crosslinking agent.

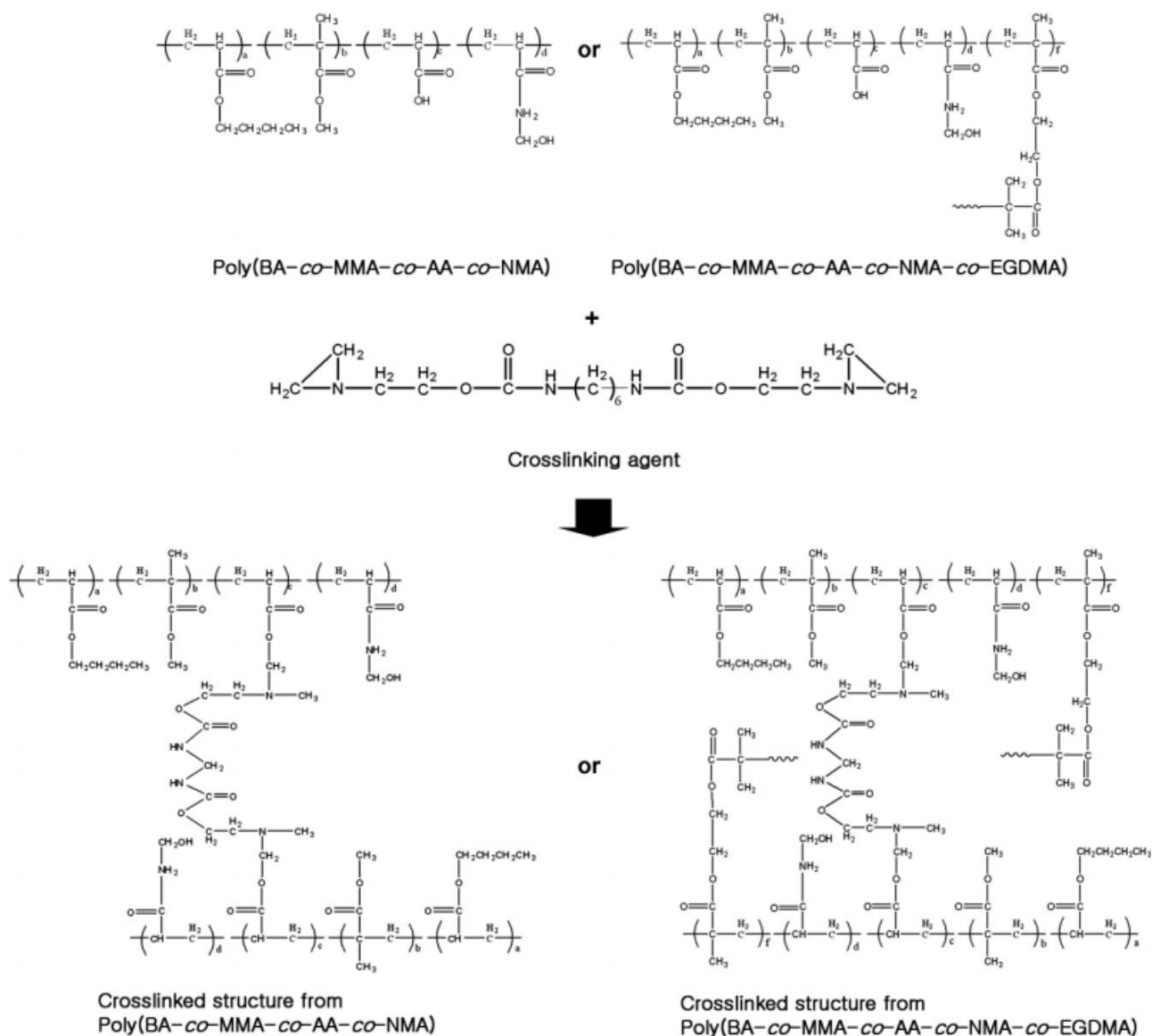


Figure 5 A schematic diagram of the inter/intracrosslinking reaction.

aziridine groups and there were no unreacted isocyanate monomers. This result proves that the synthesis of the crosslinking agent was well prepared by the reaction of isocyanate monomer and aziridine ethanol according to a scheme shown in Figure 4(a). This is also observed from FTIR spectra shown in Figure 4(b). Although there is still some  $1250 \text{ cm}^{-1}$  band for aziridine, there are no isocyanate monomers that can react with aziridine groups.

#### Properties of the film from copolymers and crosslinking agents

A schematic procedure of the intraparticle crosslinking reaction by the use of the EGDMA and the interparticle crosslinking reaction between carboxyl groups of copolymer and aziridine groups of the interparticle crosslinking agent are shown in Figure 5.

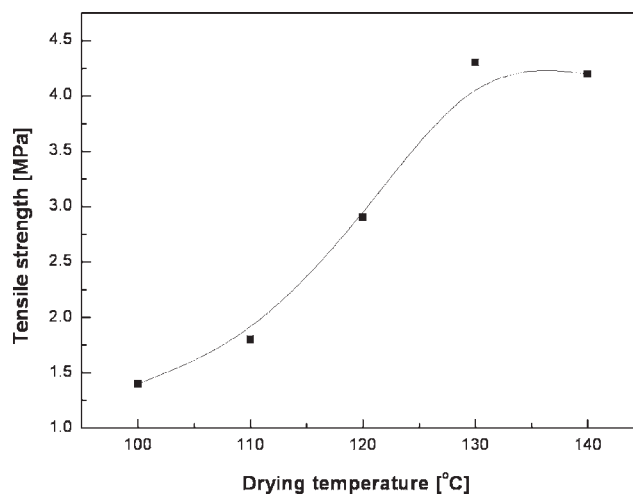
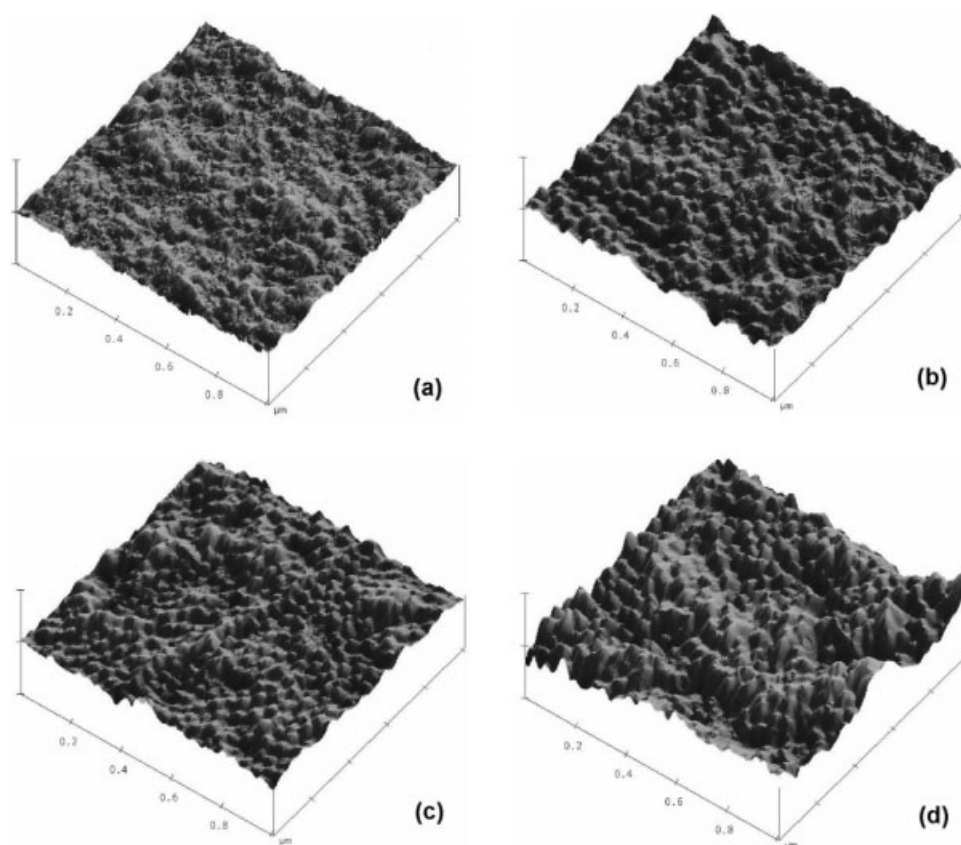


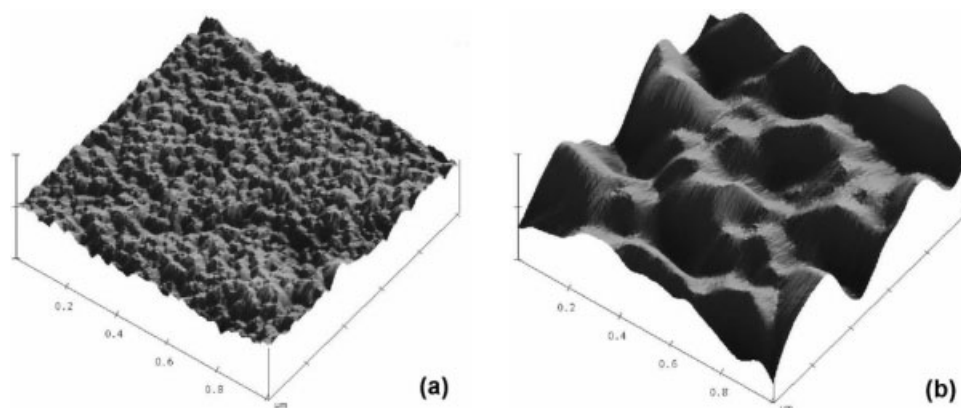
Figure 6 The effect of drying temperature on the tensile strength of the film.



**Figure 7** AFM image of the copolymer particles: (a) 0 wt % EGDMA (A), (b) 1 wt % (B), (c) 2 wt % (C), and (d) 3 wt % (D).

Tensile strength of the film increased with increasing drying temperature as shown in Figure 6. There was rapid increase in tensile strength below 130°C, and then there was no additional increase in tensile strength at drying temperature above 130°C. After this temperature, the tensile strength increment was retarded and then became constant. Therefore, it can be known that the optimum drying condition for the film formation with high tensile strength is 130°C.

AFM images of the copolymer film surface are shown in Figure 7 to investigate the effect of intraparticle crosslinking. The average sizes of the copolymer particles were measured to about 50 nm, and then uniform particle size distribution was observed, showing the relatively monodisperse particles. Any of the large aggregates of the particles are indiscernible. For the copolymer particles without EGDMA, the particle contour seems to be disappeared completely

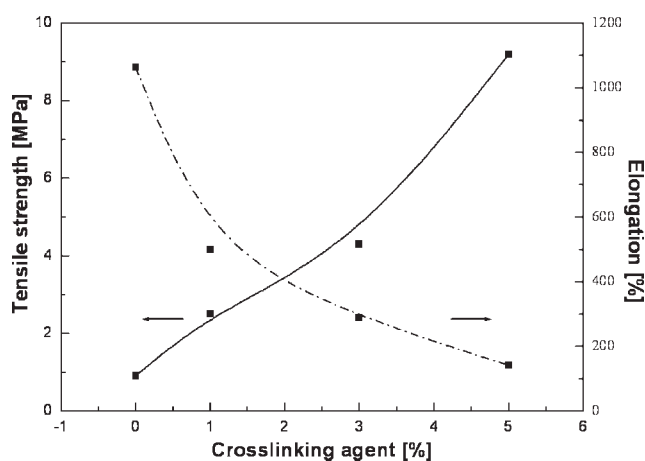


**Figure 8** AFM images of the interparticle crosslinked copolymer particle: (a) 0 wt % EGDMA (G) and (b) 2 wt % (I).

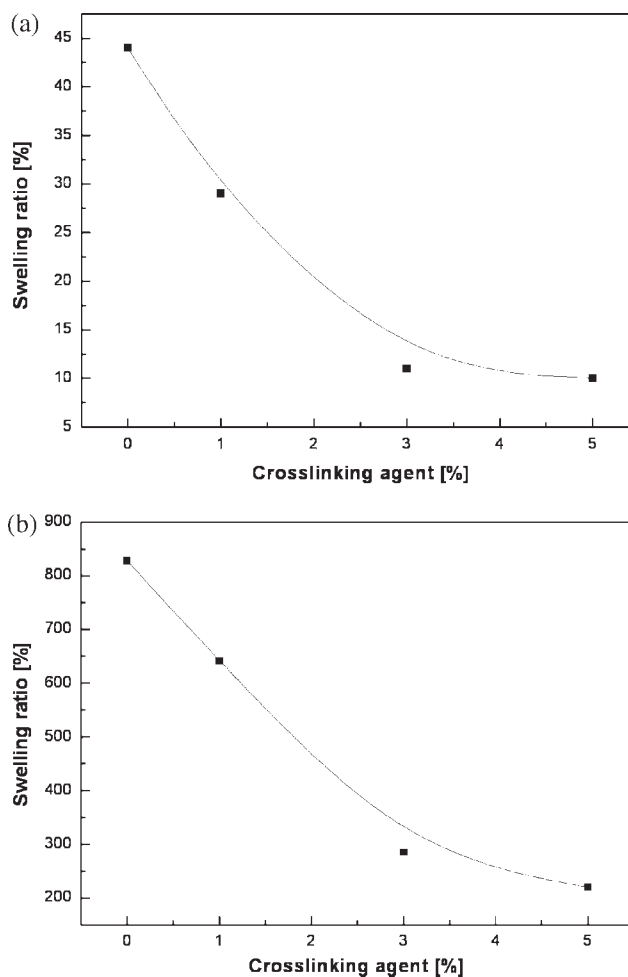
and then becomes rather flat and smooth as shown in Figure 7(a). By varying the contents of EGDMA, the variations of the particles inside the films and the variations of the roughness of the particles at the surface film were observed. Figure 7 shows that the roughness of the emulsion film was increased with increasing the contents of EGDMA. EGDMA belongs to the groups of the intraparticle crosslinking agent. Figure 8 also shows the AFM images of the film from the mixture of the copolymer and the interparticle crosslinking agent. Figure 8(a) shows the image for component (G), which has only 3 wt % of interparticle crosslinking agent, whereas Figure 8(b) shows the image for component (I), which has 3 wt % of EGDMA and interparticle crosslinking agent, respectively. The film made from EGDMA and interparticle crosslinking agent shows the higher roughness when compared with the film made only from interparticle crosslinking agent. Even if it is not shown here, the roughness was increased with increasing the contents of interparticle crosslinking agents. In conclusion, the film made from inter/intracrosslinked particle shows the highest roughness.

The effect of the content of interparticle crosslinking agent on the mechanical properties of the film is shown in Figure 9. Tensile strength of the film was increased considerably by increasing the content of interparticle crosslinking agent, but elongation of film was decreased. Moreover, the flexibility and tackiness of the film decreased as the content of interparticle crosslinking agent increased. It may be considered to be originated from the effect of interparticle crosslinking.

Swelling ratio of the film seemed to be affected generally by the content of interparticle crosslinking agent. Figure 10 shows the results that the swelling ratio of the film was decreased by increasing the content of interparticle crosslinking agent. It also



**Figure 9** The effect of the contents of the interparticle crosslinking agents on tensile strength and elongation of the films.



**Figure 10** Swelling behaviors of the film according to the content of interparticle crosslinking agent: (a) in water (24 h, 50°C) and (b) in toluene (24 h, room temperature).

shows that water and chemical resistance of the films were increased. It may be considered that swelling ratio was decreased because of the chemical bond of the film by crosslinking.

## CONCLUSIONS

As mentioned earlier, the copolymer and the interparticle crosslinking agent were prepared, and then films were prepared from the copolymer and the interparticle crosslinking agent. Poly(BA-co-MMA-co-AA-co-NMA) and poly(BA-co-MMA-co-AA-co-NMA-co-EGDMA) copolymer with functional carboxyl groups on the surface were prepared by emulsion polymerization. The interparticle crosslinking agents were prepared from HDI and aziridine ethanol. The mixture of the copolymer and the interparticle crosslinking agent was cast and dried in a convection oven. In this condition, crosslinking reaction was proven to be possible between carboxyl groups of copolymer and aziridine groups of interparticle crosslinking agent. The films prepared from the copolymer were

investigated to find out the effects of various contents of the interparticle crosslinking agent.

The effects of the contents of EGDMA and interparticle crosslinking agent on roughness were measured. By increasing the contents of EGDMA, roughness of the prepared film was increased. EGDMA belongs to the groups of the intraparticle crosslinking agent. By increasing the contents of interparticle crosslinking agent, roughness of the mixture from the copolymer and interparticle crosslinking agent was increased. In conclusion, the films made from inter/intracrosslinked particle show the highest roughness. The tensile strength of the film was increased by increasing the contents of interparticle crosslinking agent, but elongation of film was decreased. Similarly, addition of interparticle crosslinking agent decreased the flexibility and tackiness of the films. Also, water and chemical resistance of the film were increased by increasing the content of interparticle crosslinking agent.

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