

# Preparation and Physical Properties of Rubber-Modified Epoxy Resin Using Poly(urethane acrylate)/Poly(glycidyl methacrylate-*co*-acrylonitrile) Core–Shell Composite Particles

JIN-WOONG KIM, JU-YOUNG KIM, KYUNG-DO SUH

Department of Industrial Chemistry, College of Engineering, Hanyang University, Seoul 133-791, Korea

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**ABSTRACT:** Poly(urethane acrylate)/poly(glycidyl methacrylate-*co*-acrylonitrile) core–shell composite particles were prepared using two-stage emulsion polymerization. Composite particle sizes were varied from 48 to 200 nm by introducing polyoxyethylene groups into the urethane acrylate molecules. The morphology of the two-stage composite latex was inferred using surface energy measurements and titration of the emulsion. In the two-stage latex, which was prepared using relatively small core particles (about 40 nm), an inverted core–shell morphology was obtained. It was believed that the high polarity of the core surface and the low stage ratio of core to shell made the core–shell morphology more unstable thermodynamically. When the core of the two-stage latex was more crosslinked, the morphology was perfectly prevented from inverting because a higher kinetic barrier between the core–shell and inverted core–shell structures was achieved. The impact strength of the modified epoxy resin increased with the decrease of composite particle sizes and the increase of the shell thickness. In particular, when the average size of the composite particle was 50 nm and the stage ratio was 70/30, the impact strength of the modified epoxy resin increased more than 20 times compared to that of pure epoxy resin. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **63**: 1589–1600, 1997

**Key words:** core–shell composite particles; particle size; impact strength; inverted; core–shell morphology

## INTRODUCTION

Epoxy resins are widely used as coatings, structural adhesives, and advanced composite matrices in many applications. In addition to their outstanding adhesive properties, their highly cross-linked network possesses excellent thermal and dimensional stability as well as high modulus and strength.<sup>1,2</sup> The widespread use of epoxies, however, is limited in many high performance applica-

tions because of their inherent brittleness. Several methods have been proposed to improve this epoxy resin attribute. The effect of elastomeric modifiers on the fracture behavior of epoxy polymers was described by Sultan et al.,<sup>3,4</sup> Siebert et al.,<sup>5–7</sup> Bascom et al.,<sup>8–10</sup> and others.<sup>11,12</sup> They investigated epoxy resins modified with liquid carboxy-terminated butadiene acrylonitrile. Pearson and Yee<sup>13,14</sup> also evaluated the toughening mechanism in elastomer-modified epoxies. They reported the effect of particle size and particle size distribution on the toughening mechanism in rubber-modified epoxies and proposed the importance of particle size on the toughening of epoxy resin. Recently, core–shell composite particles, comprising rubber phase and glassy polymer,

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Correspondence to: K.-D. Suh.

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were tried as toughening agents for epoxy resin.<sup>15–17</sup> As suggested by Pearson and Yee,<sup>13,14</sup> the toughness of the modified epoxy resin would also be affected by the particle sizes of core–shell composite particles. In epoxies toughened with core–shell composite particles, monomer-type rubber, styrene–butadiene rubber, poly(butyl acrylate), acrylonitrile–butadiene–styrene, and so on, were used as core polymers.

The goal of this study was to prepare composite particles made of polyurethane acrylate and poly(glycidyl methacrylate-*co*-acrylonitrile) according to the controlled particle sizes and to investigate the effect of the particle sizes on the toughening of epoxy resin. The effects of core particle sizes, the surface polarity of core particles, the crosslinking density of core polymer, and the stage ratio of core to shell on the morphology of the two-stage latex were investigated. In addition, the compatibility between shell polymer and epoxy matrix and the dispersity of composite particles in the epoxy matrix were examined when changing the stage ratio of core to shell and shell thickness according to the controlled particle sizes.

## EXPERIMENTAL

### Reagents

Polytetramethylene glycol (PTMG, MW 1000, Hysung BASF), 2,4-toluene diisocyanate (TDI, Junsei Chemical Co.), 2-hydroxyethyl methacrylate (2-HEMA, Aldrich Chemical Co.), and polyethylene glycol (PEG, MW 600, Junsei Chemical Co.) were used in the synthesis of PEG-modified urethane acrylate (PMUA). Inhibitor in glycidyl methacrylate (GMA) and acrylonitrile (AN) monomer was removed through a removing column (Aldrich Chemical Co.). 2,2'-Azobisisobutyronitrile (AIBN), an oil-soluble initiator, was recrystallized by absolute methanol and dried at 30°C in a decompressed condition for 3 days. Sodium laurylsulfate (SLS, Aldrich Chemical Co.) was used as an emulsifier. Epoxy resin (diglycidyl ether of bisphenol A, the commercial grade of YD-128, 11,500–13,500 cps at 25°C, MW 374) and polyamide-type curing agent were purchased from Kuck-Do Chemical Co., Ltd.

### Synthesis of PMUA

The reaction was carried out in a four-neck glass reactor equipped with a stirrer, a reflux con-

denser, thermocouples, and a nitrogen inlet system. In the first step, TDI was poured into the glass reactor than N<sub>2</sub> atmosphere. Then PTMG was dropped into the reactor at 35°C and the reaction temperature was raised to 45°C so that the isocyanate group of the TDI reacted with the hydroxy groups of the PTMG. This temperature was maintained for 7 h to retain an acceptable rate of reaction, then lowered slowly. The change of NCO value during the reaction was determined using the dibutylamine back titration method to find the end point of the reaction.<sup>18</sup>

In the second step, 2-HEMA was added slowly into the reactor to let the hydroxyl group of 2-HEMA react to the residual NCO group at 45°C for 4 h, which introduced the reactive vinyl group into the molecular end. The temperature was raised to 75°C to eliminate unreacted isocyanates. For the PMUA, in this step, the NCO value was not changed with reaction time.

In the third step, PEG was poured slowly into the reactor to react the hydroxy group of PEG to the residual isocyanate, which made it possible to introduce polyoxyethylene chains into the molecular ends as hydrophilic groups. To obtain a molecule having a polyoxyethylene chain on one side and a reactive vinyl group of 2-HEMA on the other, the reaction molar ratio of PEG to 2-HEMA was controlled (Table I). The reaction end point was determined by the disappearance of the NCO stretching peak (2270 cm<sup>-1</sup>) through IR spectroscopy. In our previous study, the molecular structure of PMUA was analyzed. When the molecular weight of PEG was 600, PMUA showed the best emulsification effects.<sup>19,20</sup>

### Preparation of Two-Stage Composite Particles

To prepare PMUA emulsion, the mixture of PMUA (10 g), AIBN (0.2 g), and SLS (0.1 g) were charged in a glass reactor equipped with a stirrer, a reflux condenser, and thermocouples. Then dis-

**Table I** Reaction Molar Ratio of Each Reagent for Synthesis of PEG-Modified Urethane Acrylate Oligomer (PMUA)

	PTMG (MW 1000)	TDI	2-HEMA	PEG (MW 600)
PMUA1	1	2	1.85	0.15
PMUA2	1	2	1.70	0.30
PMUA3	1	2	1.50	0.50
PMUA4	1	2	1.20	0.80

tilled deionized (DDI) water was dropped into the reactor at a 0.375 g/min rate at room temperature. When the preparation of emulsion was completed, the reactor was heated to the initiation temperature of AIBN, 55°C. When the polymerization was carried out for 6 h, the conversion was over 98%.

In the second-stage emulsion polymerization, the addition of GMA and AN was performed with the semibatch process where the monomer containing AIBN (1.5 wt %) was added continuously into the reactor from a microdropping funnel at a constant rate of 0.04 g/min. The shell polymerization was also carried out at 55°C for 6 h with an agitation speed of 150 rpm. The composition of two-stage latex is summarized in Table II.

The average particle size of two-stage latex particles was measured with laser light scattering (Brook Heaven Co. Ltd., BI9000AT, argon laser). To obtain the powder of composite particles, prepared latexes were deemulsified with CaCl<sub>2</sub> and filtered. Then it was dried at 50°C for 48 h.

### Surface Energy Measurements

DDI water and methylene iodide (CH<sub>2</sub>I<sub>2</sub>) (1 μL) were dropped on each sample film, and the contact angle was read with a contact angle meter (Erma contact angle meter, model G-1). With these contact angles of DDI water and CH<sub>2</sub>I<sub>2</sub>, surface tension ( $\gamma_s$ ), surface polarity ( $\gamma_s^p$ ), and surface dispersity ( $\gamma_s^d$ ) were calculated through the geometric-mean method.<sup>21</sup> Although there is some difference between harmonic-mean and geometric-mean methods, the geometric-mean method was used because it was possible to infer the morphology of the composite particle with only relative surface polarities. Daniels et al. suggested that core surface polarity has an effect on the morphology of a two-stage latex.<sup>22</sup> Therefore, by using

urethane core surface polarity ( $\gamma_s^p$ ), the morphology of the two-stage latex could be identified indirectly and the effect of core surface polarity on the morphology could also be investigated.

### Soap Titrations

To predict the morphology of the two-stage latex, the surface area occupied by a single surfactant molecule at critical micelle concentration (CMC) (Am value) was obtained with soap titration. Maron and colleagues suggested the following equation<sup>23</sup>:

$$Am = \frac{6 MW}{\rho d Es}$$

Here, MW is the molecular weight of the soap (SLS),  $\rho$  is the polymer density (g/cm<sup>3</sup>),  $d$  is the average particle diameter (Å), and Am is in Å<sup>2</sup>/molecule. Maron et al.<sup>23</sup> suggested that the amount of surfactant dissolved in the aqueous phase and the amount of surfactant on the polymer per unit weight of the polymer phase ( $Es$ ) could be determined by performing the titration on samples of latex containing different amounts of polymeric solids. To determine the weight fractions of surfactant and polymer in a latex for any constant value of the air-liquid interfacial tension, raw soap titration curves with the contents of polymers were used. The slope and intercepts of these lines give the area occupied by an adsorbed molecule and the aqueous phase surfactant concentration, respectively. Thus, Am value could be calculated using the above-mentioned equation.

### Scanning Electron Microscopy

Epoxy resin was mixed with a stoichiometric amount of curing agent (20 wt % to the epoxy

**Table II** Preparation of Poly(PMUA)/Poly(GMA-co-AN) Two-Stage Latex

	MUA	PMUA Latex	GMA	AN	DDI Water	AIBN	SLS
PMUA <sup>a</sup>	10	—	—	—	75	0.200	0.100
PMUA-80-20 <sup>b</sup>	—	85	2.000	0.500	50	0.025	—
PMUA-75-25 <sup>c</sup>	—	85	2.670	0.670	50	0.033	—
PMUA-70-30 <sup>d</sup>	—	85	3.430	0.860	50	0.043	—
Poly(GMA-co-AN) latex	—	—	8.000	2.000	125	0.200	0.100

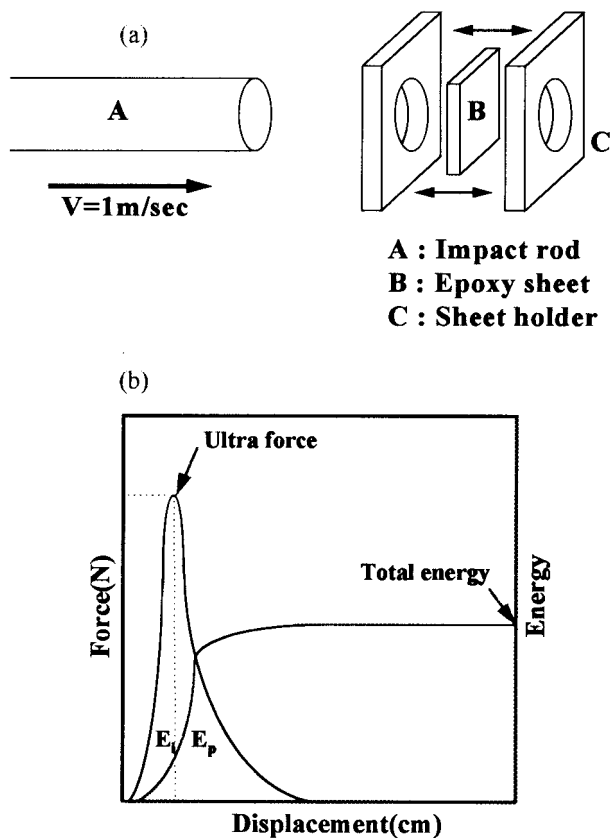
All values are in grams.

<sup>a</sup> The latex of the polymerized PEG-modified urethane acrylate.

<sup>b</sup> PMUA-80-20, poly(PMUA)/poly(GMA-co-AN) core-shell latex with 80-20 stage ratio.

<sup>c</sup> PMUA-75-25, poly(PMUA)/poly(GMA-co-AN) core-shell latex with 75-25 stage ratio.

<sup>d</sup> PMUA-70-30, poly(PMUA)/poly(GMA-co-AN) core-shell latex with 70-30 stage ratio.



**Figure 1** High-rate impact test. (a) The high rate impact testing method. (b) The schematic impact diagram.  $E_i$  is the initial energy before breaking and  $E_p$  is the postenergy after breaking.  $D_i = E_i/E_p$ .

resin) and composite particles. Foams were disposed of by decompressing the mixtures on the heating condition at 60°C. This mixture was cured in a mold at 80°C for 24 h and postcured at 150°C for 10 h to obtain a perfectly cured specimen. To ascertain the dispersity of composite particles in the epoxy matrix and the compatibility of the shell with the epoxy resin, the fracture surface of the specimen was analyzed with scanning electron microscopy (Philips C. XL-30). The conventional secondary electron imaging technique was used. Samples were coated with a thin layer of gold-palladium to reduce any charge buildup on the fracture surface.

### High-Rate Impact Test

A high-rate impact tester (Rheometric high rate impact tester, RIT-8000) was used to measure impact strength (ASTM, D 3763-92). A cured specimen (7 × 7 × 0.3 cm) was gripped tightly with a clamp [Fig. 1(a)]. Then, the specimen was hit

with a hemispherical impact rod of 1.58 cm diameter and 1 m/s velocity. This result is represented with the relationship of displacement (cm) and force (N). In the diagram in Figure 1(b), the occupied area means the energy (J). In our experiment, a ductile index ( $D_i$ ) was used to evaluate the impact strength, expressed as follows:

$$D_i = \frac{E_i}{E_p}$$

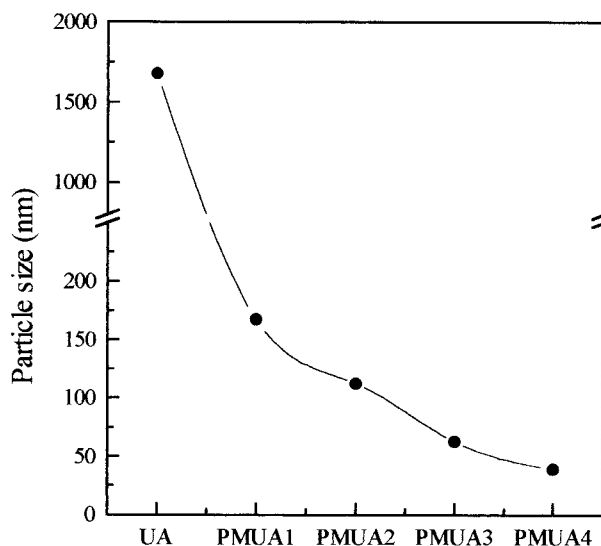
$E_i$  is the initial energy, meaning the energy before maximum load, and  $E_p$  is the postenergy, meaning the energy after maximum load.

## RESULTS AND DISCUSSION

### Preparation of PMUA and Its Emulsion Polymerization

According to our previous experiments,<sup>24</sup> it was very difficult to control the droplet size of UA emulsion using surfactants. Moreover, UA could not be emulsified easily with a single surfactant. The relatively stable emulsion could be obtained using the mixture of SLS and cosurfactants (cetyl alcohol and stearyl alcohol), which reduced the inherent incompatibility of UA with water. Thus, to improve the water dispersibility of UA, the hydrophilic group (polyoxyethylene group) was introduced into the molecule ends by the reaction of PEG with the residual isocyanate groups of the unmodified UAs.

Figure 2 shows the particle size change of



**Figure 2** Particle size change of PMUA latex with the reaction molar ratio of PEG to 2-HEMA. UA is the unmodified urethane acrylate emulsion.

**Table III Average Particle Sizes of PMUA Core Latexes and Poly(PMUA)/Poly(GMA-co-AN) Two-Stage Latexes**

Core Materials	PMUA Core Latex (nm)	Poly(PMUA)/Poly(GMA-co-AN) Core-Shell Latex (nm)		
		80–20 <sup>a</sup>	75–25 <sup>a</sup>	70–30 <sup>a</sup>
PMUA1	167.4	179.8	188.8	199.3
PMUA2	125.5	134.6	143.3	150.2
PMUA3	62.8	67.8	74.6	80.6
PMUA4	39.0	46.8	48.3	55.0

<sup>a</sup> Stage ratios.

PMUA latexes with the reaction molar ratio of PEG to 2-HEMA. Particle size of the PMUA latex was reduced with the reaction molar ratio of PEG and was much smaller than that of polymerized UA emulsion prepared using the mixture of SLS and cosurfactants. These results were due to the interfacial activity of PMUA. That is, the UA molecules containing polyoxyethylene groups as end groups might act as polymeric surfactants and assist the interfacial activity of SLS. The interfacial activity of PMUA was confirmed by another study.

These PMUA emulsions could be polymerized with AIBN without any coagulums, and four types of crosslinked PMUA latexes with different sizes were prepared to control the composite particle sizes. Droplet sizes of these latexes were in the 39–170 nm range and are summarized in Table III.

Particle size distributions of core latexes are shown in Figure 3. Crosslinked PMUA core latexes show narrow and fine size distributions.

#### Preparation of Poly(PMUA)/Poly(GMA-co-AN) Two-Stage Latex

The addition method of a second monomer and the crosslinking density of the core particle are known as kinetic factors. Therefore, in this study, the addition method of a second monomer was fixed with semibatch polymerization that imposed a higher kinetic barrier to obtain a more core-shell morphology favorable system.

The copolymer of GMA and AN was used as the shell. GMA has a glycidyl ether ring and a reactive vinyl group in both sides of the molecule so that the former can react with the diglycidyl ether rings of the epoxy resin in the course of curing; on the other hand, the latter can form a shell polymer with the radical initiator AIBN. As a shell polymer, AN was copolymerized with GMA. AN has a bulky CN triple bond in the mole-

cule so that it can confer the effect of polarity on the composite particle. The polar shell plays a role in dispersing the composite particles in the toughened phase.<sup>15,22</sup>

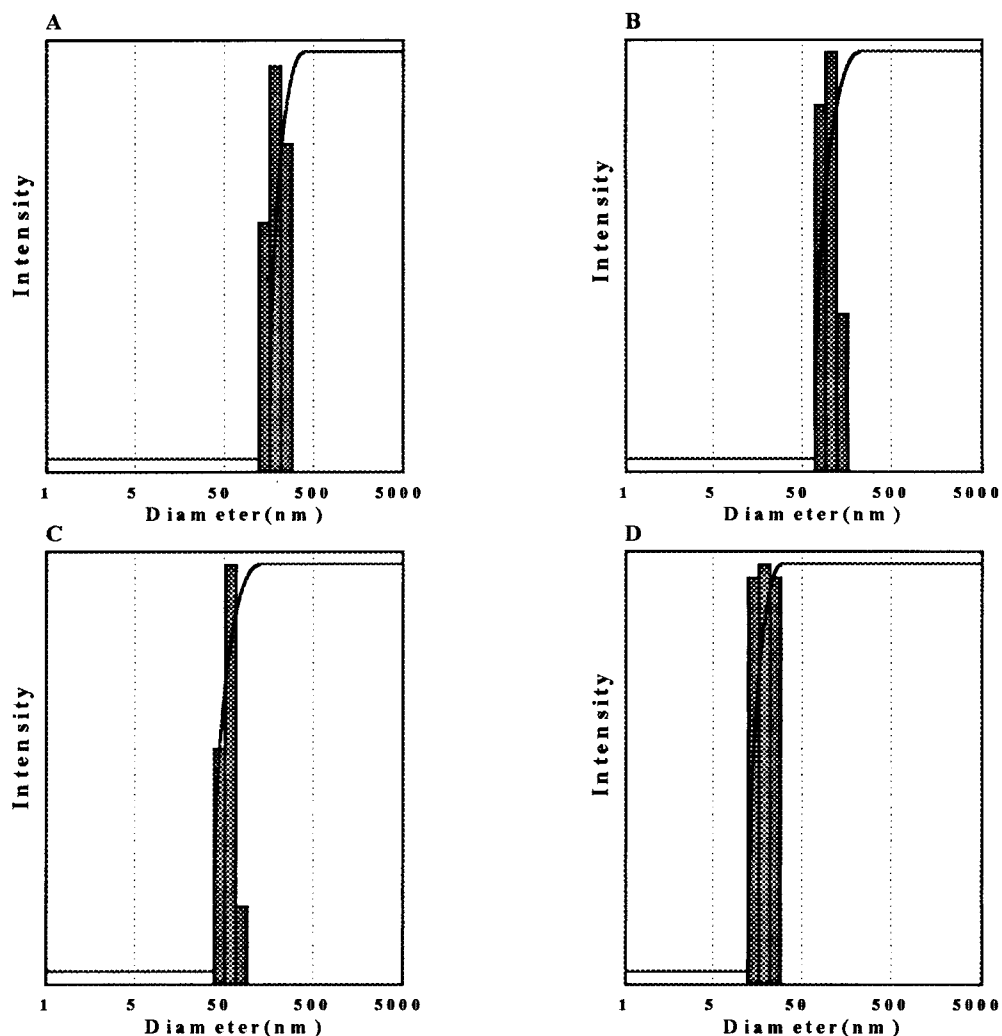
Figure 4 shows the particle size distributions of poly(PMUA)/poly(GMA-co-AN) two-stage latexes. Similar to the core size distributions, particle sizes of two-stage latexes were also narrow and monodispersed.

Particle size also increased as the stage ratio increased; that is to say, as the added amount of GMA and AN increased (Table III). Finally the composite particles sizes could be controlled from about 46 to 200 nm.

#### Identification of Two-Stage Latex Morphology Through Surface Polarity

To apply the poly(PMUA)/poly(GMA-co-AN) two-stage composite particle to an impact modifier of an epoxy resin, the core-shell morphology must be favorable. In other words, the core polymer must be urethane rubber and the shell polymer must be the copolymer of GMA and AN. In our study, contact angle and Am value were introduced to infer the morphology of the two-stage latex, because contact angles and Am value are dependent on the polymer surface characteristics. If core-shell morphology is formed, the characteristics of the shell polymer will be the same as those of the shell polymer latex only [in our study, poly(GMA-co-AN) latex].

When DDI water and methylene iodide (CH<sub>2</sub>I<sub>2</sub>) were dropped on the surface of the PMUA and composite latex film, the contact angle ( $\theta$ ) could be decided by the polymer surface properties, for example, surface polarity and surface dispersity. Especially the surface polarity with particle sizes is one of the factors influencing the morphology of the two-stage latex. Accordingly, the core particle



**Figure 3** Particle size distributions of PMUA core latexes: (A) PMUA1 core latex; (B) PMUA2 core latex, (C) PMUA3 core latex, and (D) PMUA4 core latex. Laser light scattering (Brook Heaven Co. Ltd., BI9000AT) was used to obtain particle size distribution.

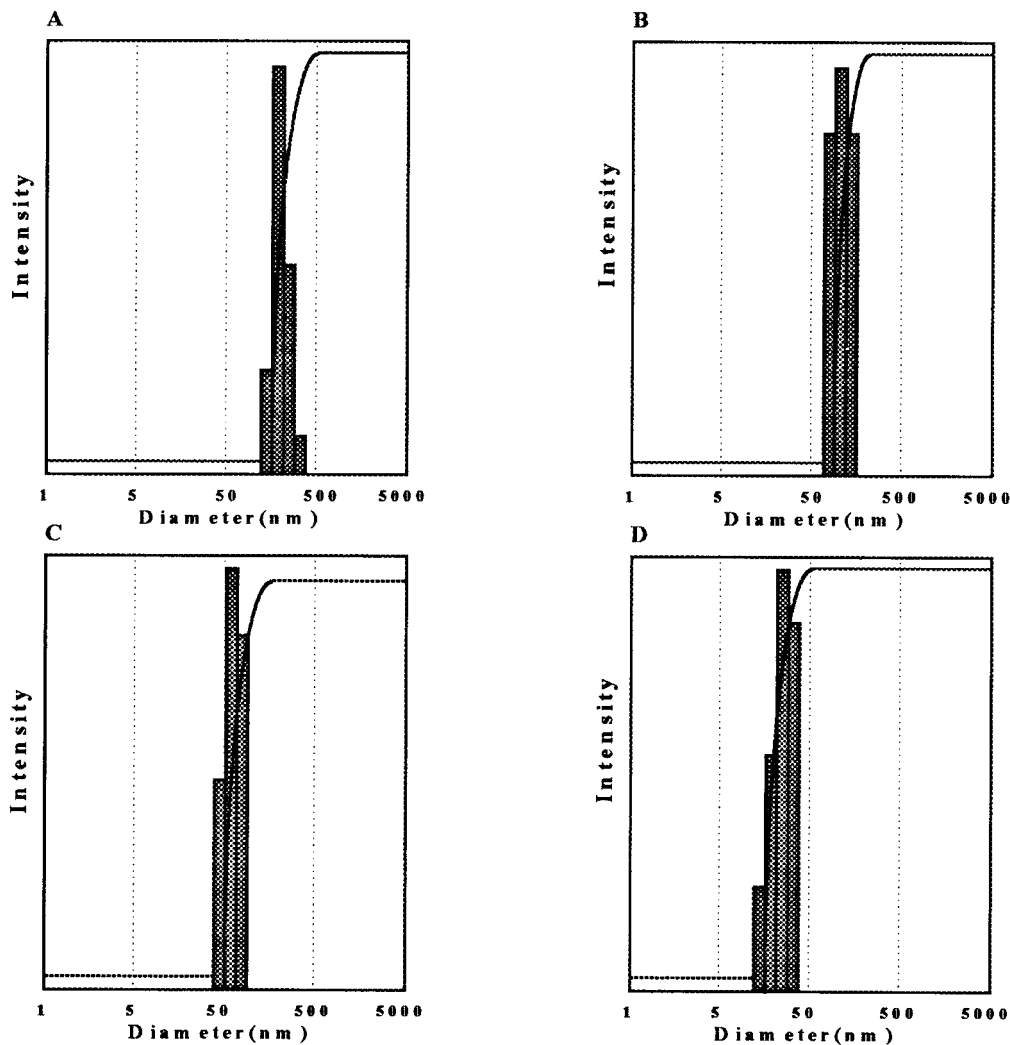
showing high surface polarity is more favorable for inversion, because the water phase is placed in the continuous phase in the emulsion system. So one can predict a priority that generally the most thermodynamically favorable arrangement will be an inverted morphology rather than a true core-shell structure.

In the poly(PMUA)/poly(GMA-co-AN) two-stage latex, three thermodynamic factors could be considered: surface polarity, the stage ratio of core to shell, and core particle size. Using contact angles of DDI water and  $\text{CH}_2\text{I}_2$ , surface polarity ( $\gamma_s^p$ ) could be obtained through Owens' equation.

Table IV shows surface polarities of poly(PMUA) and composite latex films. The surface polarity of the PMUA series increased as the reaction molar ratio of PEG to 2-HEMA increased in

regular sequence (Table I), indicating the increase of hydrophilicity with the introduction of polyoxyethylene groups. And most surface polarities of two-stage latex films were similar to that of poly(GMA-co-AN) film, being about 8–9 dyne/cm. Thus, it could be inferred from these results that poly(PMUA)/poly(GMA-co-AN) core-shell morphology was formed.

However, for PMUA4-80-20 and PMUA4-90-10 two-stage latexes, each surface polarity was about 14 and 20 dyne/cm, respectively, rather higher than that of poly(GMA-co-AN) film and closer to that of PMUA4 core film. This indicated that core-shell morphology was not formed and another type morphology was formed. PMUA4 core latex had considerably higher surface polarity (21.30 dyne/cm) than that of poly(GMA-co-AN)



**Figure 4** Particle size distributions of poly(PMUA)/poly(GMA-*co*-AN) two-stage latexes: (A) PMUA1-75-25 latex, (B) PMUA2-75-25 latex, (C) PMUA3-75-25 latex, and (D) PMUA4-75-25 latex.

(9.70 dyne/cm). So, the hydrophobe–water surface of GMA-*co*-AN polymer would be replaced with the hydrophile–water surface of PMUA4 polymer, resulting in the most favorable morphology being the inverted one. However, in that the surface polarity of PMUA4-80-20 did not coincide with that of the PMUA4 core polymer, it could be postulated that two phases of UA and poly(GMA-*co*-AN) coexist on the surface of composite latex, just as sandwichlike, acornlike, and octopus ocellatuslike composite latexes, rather than an exactly inverted one.

It is well known that when the added amount of the second monomer is small, say, the relative phase volume of the shell polymer is small, the morphology of the core–shell also tends to be inverted.<sup>22</sup> This could be identified with the composite latexes

using PMUA4 core polymer. As the stage ratio increased, the formation of core–shell morphology became favorable, which was due to the increase of the phase volume of the shell polymer.

#### Identification of Two-Stage Latex Morphology Through $A_m$ Value

For a more detailed identification of two-stage latex morphology,  $A_m$  value was also introduced. This value has been widely used as a method to identify various morphologies of latexes. As Maron et al.<sup>23</sup> and Syed et al.<sup>25</sup> suggested, hydrophilicity of a polymer can be evaluated by  $A_m$  value.

To obtain an  $A_m$  value for each latex, Maron's equation [ $A_m = (6 MW)/(\rho d E s)$ ] was used. If the

**Table IV Surface Polarities and Am Values of PMUA Core Latexes and Poly(PMUA)/Poly(GMA-co-AN) Two-Stage Latexes**

	Surface Polarity ( $\gamma_s^p$ , dyne/cm)	Am ( $\text{\AA}^2/\text{molecule}$ )
PMUA1 core latex	5.24	—
PMUA1-80-20	8.78	—
PMUA1-75-25	8.96	—
PMUA1-70-30	8.97	—
PMUA2 core latex	10.50	—
PMUA2-80-20	7.85	—
PMUA2-75-25	9.30	—
PMUA2-70-30	8.94	—
PMUA3 core latex	19.01	—
PMUA3-80-20	8.74	—
PMUA3-75-25	8.94	—
PMUA3-70-30	8.23	—
PMUA4 core latex	21.30	119.29
PMUA4-90-10	19.96	93.60
PMUA4-80-20	14.84	60.80
PMUA4-75-25	8.80	43.50
PMUA4-70-30	9.01	44.76
Poly(GMA-co-AN) latex	9.70	45.32

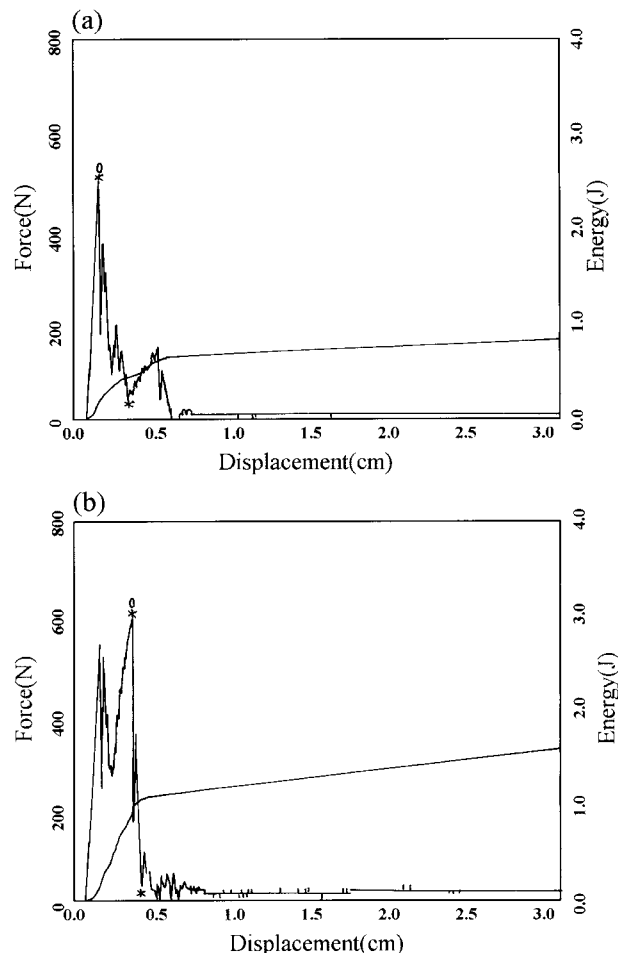
PMUA1, PMUA2, PMUA3, and PMUA4 are the polymerized PMUA series.

density of polymer ( $\text{g}/\text{cm}^3$ ), particle diameter ( $\text{\AA}$ ), and  $E_s$  were known, Am value ( $\text{\AA}^2/\text{molecule}$ ) could be calculated easily. The area covered by a single molecule was not a unique property of the surfactant but depended on the nature of the polymer surface. For example, surfactants would adsorb more strongly on the hydrophobic polymer surface than the hydrophilic polymer surface. As shown in Table IV, PMUA4 core latex had a higher Am value than poly(GMA-co-AN) latex,

**Table V Kinetic Effects on PMUA Core Latexes and Poly(PMUA)/Poly(GMA-co-AN) Two-Stage Latexes**

	Surface Porosity ( $\gamma_s^p$ , dyne/cm)	Am ( $\text{\AA}^2/\text{molecule}$ )
PMUA4 core latex	21.30	119.29
PMUA4-90-10	19.96	93.60
CPMUA4-90-10	15.31	80.08
PMUA4-80-20	14.84	60.80
CPMUA4-80-20	8.81	44.08
Poly(GMA-co-AN) latex	9.70	45.32

CPMUA4, more crosslinked PMUA4 with 3 wt % triethylene glycol dimethacrylate.

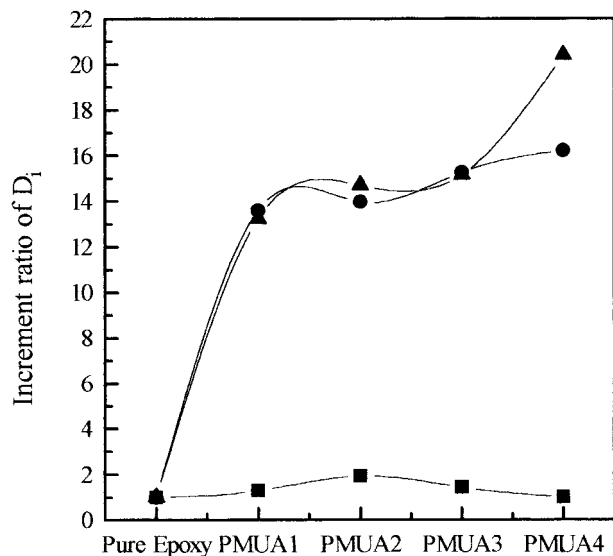


**Figure 5** High-rate impact diagrams of pure epoxy resin and modified epoxy resin. (a) Pure epoxy resin. (b) The modified epoxy resin with PMUA4-75-25 composite particles. The contents of composite particles were 12 wt %.

meaning that the PMUA4 core polymer was more hydrophilic than the shell polymer. When the stage ratio of core to shell was 80/20 (PMUA4-80-20), the Am value was rather closer to PMUA4 core latex, which had the same result with surface polarity, indicating that the morphology of the two-stage latex was partially mixed or another type morphology was formed. When the stage ratio was 90/10 (PMUA4-90-10), the Am value was similar to that of PMUA4 core latex, resulting in inverting of the two-stage latex.

PMUA2, PMUA3, and PMUA4 latexes showed higher surface polarities than poly(GMA-co-AN). However, morphology inverting, phase mixing, or other type morphology formation could not be found except poly(PMUA4)/poly(GMA-co-AN) two-stage latexes of low stage ratio, even though the core surface was more hydrophilic than the





**Figure 6** High-rate impact test versus the particle sizes. Core-shell stage ratio of (■) 80/20, (●) 75/25, and (▲) 70/30. The contents of core-shell composite particles were fixed with 12 wt % for epoxy resin. (Increment ratio of  $D_i$  was set at 1 in PMUA4-80-20 composite particles.)

shell polymer. These results were attributed to the highly crosslinked core particles, because PMUA had reactive vinyl groups at both ends. Thus, even though core particles were more hydrophilic, core-shell morphology could be formed successfully.

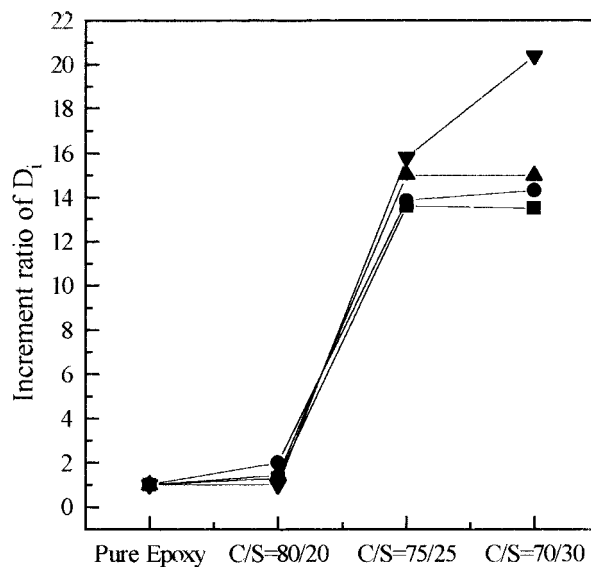
In this study, kinetic effects of the two-stage latex on their morphologies were also considered. As mentioned above, the addition method of a second monomer was fixed with semibatch polymerization that imposed a higher kinetic barrier in order to obtain a more core-shell morphology favorable system. Therefore, core particles were more crosslinked with crosslinking agent to consider the kinetic factor in our urethane core rubber system. Table V shows the kinetic effects on two-stage latexes.

When the core of the PMUA4-90-10 composite particle was more crosslinked with 3 wt % triethylene glycol dimethacrylate (TEGDMA), the morphology could be prevented from inverting slightly. For PMUA4-80-20 composite particles, however, the morphology was perfectly prevented from inverting by imposing a higher kinetic barrier between the core-shell and inverted core-shell morphology. These results indicated that the mobility of the phase decreased to such an extent that migration of the phase was prevented, and the core was essentially immobilized. Therefore, a crosslinked core was found to be necessary

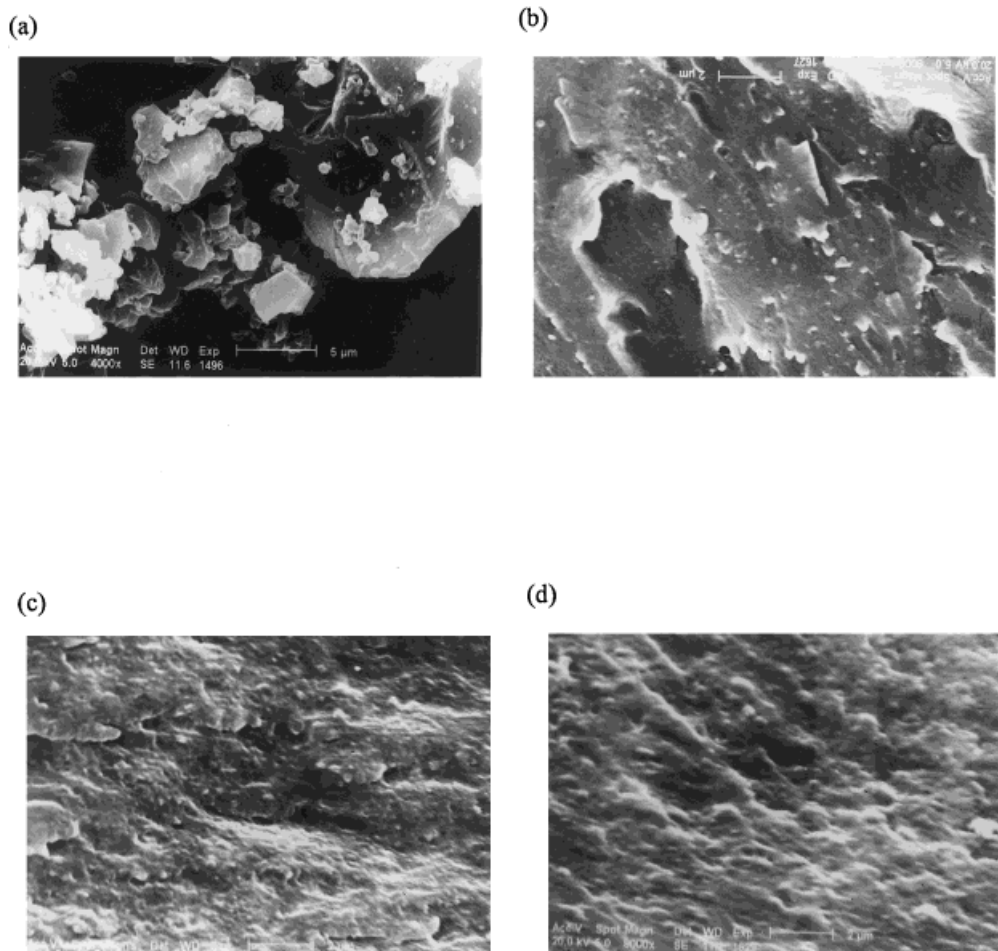
to eliminate phase mixing and other types of morphology formation.

### Impact Strength Tendencies

High-rate impact tests were employed to estimate the impact strength of epoxy resin blended with core-shell composite particles. A schematic impact diagram is shown in Figure 1(b). When the initial energy ( $E_i$ ) is high, the enduring capacity of the specimen for initial impact force is excellent; low  $E_i$  means the reverse. That is to say, the specimen of high  $E_i$  has the ability to absorb a large amount of energy before failure. This means that deformation mechanisms need to be used that absorb energy before crack propagation occurs. As proposed in theories,<sup>14,15,26,27</sup> smaller particles (<100 nm) provide a significant increase in toughness by cavitation-induced shear banding. In our experiment, particle sizes were varied from 46 to 200 nm; therefore, it was possible to observe the impact strength tendency in that particle size region where shear banding was dominant. On the basis of the above-mentioned postulation, high  $E_i$  means that the modifier has an excellent



**Figure 7** High-rate impact test with the stage ratio: (■) poly(PMUA1)/poly(GMA-co-AN) two-stage composite particle, (●) poly(PMUA2)/poly(GMA-co-AN) two-stage composite particles, (▲) poly(PMUA3)/poly(GMA-co-AN) two-stage composite particles, and (▼) poly(PMUA4)/poly(GMA-co-AN) two-stage composite particles. The contents of core-shell composite particles were fixed with 12 wt % for epoxy resin. (Increment ratio of  $D_i$  was set at 1 in PMUA4-80-20 composite particles.)



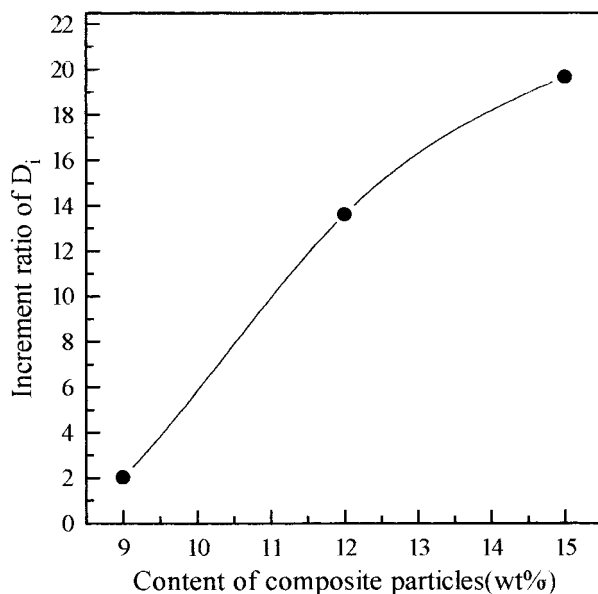
**Figure 8** Scanning electron microscopy with the stage ratio of poly(PMUA)/poly(GMA-co-AN) two-stage composite particles. The contents of composite particles was 12 wt %. (a) PMUA4-80-20 composite particles, (b) PMUA3-80-20 composite particles, (c) PMUA4-75-25 composite particles, and (d) PMUA4-70-30 composite particles.

ability to dissipate the energy through shear band formation before breaking.

Figure 5 shows the high rate impact diagrams of pure epoxy resin and rubber-modified epoxy resin. In the impact diagram, pure epoxy resin shows low  $E_i$ , meaning a poor energy dissipation ability for initial impact. So the specimen of pure epoxy resin was broken as soon as the impact was delivered. However, the rubber-modified epoxy resin by core-shell composite particles showed high  $E_i$  compared to that of pure epoxy resin, indicating that the ability to endure the initial impact was good. The ability to dissipate the initial impact was believed to be through the occurrence of massive shear banding.

Figure 6 shows the impact strength tendency (the increment ratio of ductile index) versus the particle sizes. As the particle sizes were reduced, ductile index ( $D_i$ ) increased. Especially for the

PMUA4-70-30 core-shell composite particle, the  $D_i$  ratio increased more than 20 times compared to that of pure epoxy resin. It has been generally accepted that the optimal rubber particle size for epoxy toughening using carboxy-terminated rubber particles is in the range of 0.1–5  $\mu\text{m}$ .<sup>14</sup> However, in our experiment, the smaller particles showed better impact strength. It could be assumed from this result that as the composite particle size was reduced, the dissipation of energy through shear banding was more favorable. Figure 7 shows the effect of the stage ratio of composite particles on the impact strength of rubber-modified epoxy resin. Impact strength for the 80/20 stage ratio showed a poor increment compared with those of 75/25 and 70/30. These results seemed to be attributed to the low dispersibility of composite particles in the epoxy matrix and the phase separation between composite particles and



**Figure 9** High-rate impact test with the contents of two-stage composite particles. PMUA4-75-25 composite particles were used.

epoxy matrix. As shown in the scanning electron microscopy of Figure 8, at the stage ratio of 75/25 and 70/30, composite particles were dispersed and imbedded well in the epoxy matrix. However, PMUA4-80-20 core-shell composite particles were separated from epoxy resin and aggregated with lumps, which caused a poor impact strength increment. According to the surface polarity and  $A_m$  value, however, composite particles prepared using PMUA1, PMUA2, and PMUA3 with the 80/20 stage ratio showed the core-shell morphology; nevertheless, there were no impact strength increments in high-rate impact tests. This phenomenon could be confirmed by scanning electron microscopy as shown in Figure 8(b). Core-shell composite particles could not retain their morphology and were agglomerated with lumps, which explained that the relatively thin shell formed by the low stage ratio could not maintain the morphology in the process of curing. However, the degree of the agglomeration of composite particles was slight compared to that of PMUA4-80-20, because the preference to form core-shell morphology was better in PMUAs of low polarity. Therefore, to maintain the morphology of a core-shell latex, the thicker shell was necessary. This was the reason that the modified epoxy resin with composite particles of high stage ratio showed better impact strength than those of low stage ratio. Figure 9 shows impact strength changes versus

the contents of composite particles. As the contents of composite particles increased, the impact strength increased. When the contents of core-shell composite particles were above 15 wt %, it was impossible to prepare the modified epoxy sheet because of the high viscosity of the mixture.

## CONCLUSIONS

In our study, droplet sizes of PMUA latex could be controlled by introducing polyoxyethylene groups into UA molecular ends. Moreover, it was possible to control the particle size of a two-stage composite latex by using PMUA latexes containing different particle sizes. Therefore, poly(PMUA)/poly(GMA-co-AN) two-stage latexes could be prepared within the range of 46–200 nm. A thicker shell made it easier to form a core-shell morphology; on the other hand, a core-shell was not favorable for small particles because of the high core surface polarity and low stage ratio. Kinetic barriers, however, prevented the morphology of the two-stage from inverting. This result indicated that the mobility of the phase decreased to such an extent that migration of the phase was prevented and the core was essentially immobilized. Therefore, crosslinked core was found to be necessary to maintain particle morphology in the blend and to prevent the formation of inverted core-shell morphology.

The impact strength of the modified epoxy resin increased as the shell thickness and contents of composite particles increased; when PMUA4 was used as a core polymer at the stage ratio of 70/30, impact strength was improved more than 20 times compared with that of pure epoxy resin. In our study, more, smaller particles showed a better impact strength increase. From this result, it could be assumed that as the composite particle sizes were reduced, the dissipation of energy through shear banding was more favorable.

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