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PREPARATION OF IMPACT MODIFIED EPOXY RESIN BY USING POLY(BUTYL ACRYLATE)/POLY (GLYCIDYL METHACRYLATE) CORE-SHELL COMPOSITE PARTICLES

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ABSTRACT

Poly(butyl acrylate)/poly(glycidyl methacrylate) core-shell latex was prepared by a two stage consecutive emulsion polymerization. It was possible to get narrow and monodispersed particles with an increase of shell thickness. This was done by changing the stage ratio of core to shell. The formation of core-shell morphology was confirmed by contact angle measurements, using the characteristics of composite particles e.g., surface tension, surface dispersity, and surface polarity in our research. At low stage ratio of core to shell, the morphology showed a tendency toward not forming core-shell morphology because of the thermodynamic instability, especially the effect of phase volume. The blend of poly(butyl acrylate/poly-(glycidyl methacrylate) core-shell composite particles with epoxy resin showed an impact strength increment of about 1.6 times compared with that of epoxy resin itself. In the toughening mechanism, it was assumed that the crazing effect is preferred to shear banding understanding poly(butyl acrylate)/poly(glycidyl methacrylate) core-shell composite particles as an impact modifier for epoxy resins.

INTRODUCTION

Epoxy resins are widely employed as the basis for adhesive compositions and as the matrix material for glass-polyamide and carbon-fiber composites. When cured, epoxy resins are highly crosslinked, amorphous thermoset polymers and this structure results in many useful properties, such as high modulus, low creep and good performance at elevated temperature. However, it also means that the unmodified epoxies are relatively brittle polymers with poor resistance to crack growth. Several methods have been proposed to increase the toughness of epoxies and one of the most successful involves the addition of a suitable rubber to the uncured epoxy resin and then controlling the polymerization reactions in order to induce phase separation [1-3].

Core-shell composite particles were recently employed to elevate the impact strength of epoxy resin. J. Jonson *et al.* have prepared core-shell latexes by consecutive two-stage emulsion polymerization and other workers have identified the morphology of the two-stage latex [4-6]. Previous workers, M. Okubo *et al.* [7], I. Cho *et al.* [8], and D. I. Lee *et al.* [9] have reported a number of morphologies including core-shell morphology, e.g., raspberry-like, confetti-like, snowman-like, octopus ocellatus-like, sandwich-like and inverted particles. However, in order to employ these two-stage composite particles as an impact modifier for epoxy resin, core-shell morphology must be favorable, that is, core polymer must be a rubber and the shell a glassy polymer having compatibility with epoxy resin.

The goal of this study is to confirm the morphology of the core-shell latex and to investigate the compatibility of the shell polymer with the epoxy matrix as to the shell thickness. Poly(butyl acrylate)/poly(glycidyl methacrylate) two-stage composite particles were prepared by consecutive two-stage emulsion polymerization and investigated as an impact modifier for epoxy resin, instead of blending rubbery or thermoplastic polymers with epoxies. Generally, rubbery polymers used as cores have mobility, resulting in the unfavorability of core-shell morphology. However, by elevating the kinetic barrier between core-shell and inverted core-shell structures, it is possible to be favorable forming core-shell morphology. In our study, semi-batch polymerization was employed to elevate the kinetic barrier.

In particular, glycidyl methacrylate using as a shell polymer has glycidyl ether ring on its one side, the same functional group with epoxy resin, it is expected that the compatibility of shell polymer with epoxy matrix be good. Therefore, the compatibility of shell polymer with epoxy matrix is investigated through the stage ratio of core to shell, that is, shell thickness.

EXPERIMENTAL

Materials

The inhibitors in butyl acrylate monomer (Junsei Chemical Co., Ltd.) and glycidyl methacrylate (GMA) monomer (Aldrich Chemical Co.) were removed through an inhibitor removing column (Aldrich Chemical Co.). Potassium persulfate (KPS) of Kanto Chemical Co. was used as an initiator. NaSS (sodium styrenesulfate), ionic comonomer (Aldrich Chemical Co.), was used as a reactive surfactant. Epoxy resin (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 Ind. Co., Ltd.

Preparation of Two-Stage Composite Particles

In order to prepare poly(butyl acrylate) (PBA) seed latex, the mixture (Run 1 in Table 1) of KPS, NaSS, and deionized distilled water was charged into a glass reactor equipped with a mechanical stirrer, a reflux condenser, a dropping funnel, and thermocouples under a nitrogen purge. Polymerization temperature was fixed at 70°C and maintained during the polymerization. Agitation speed was 190 rpm during the entire process. Semibatch emulsion polymerization was used in our system, that is, 10% of butyl acrylate monomer was added and polymerized. Then the remaining 90% of butyl acrylate monomer was added continuously at a rate of 0.5 g/min, and polymerized.

The addition of GMA monomer to PBA seed latex was also performed with the semibatch polymerization process in which the monomer was added continuously to the reactor from a micro-dropping funnel at a constant rate of 10 g/hour (Run 2-6 in Table 1). The polymerization was conducted for 120 minutes at 70°C.

In order to obtain the average particle size of composite particles, laser light scattering (Brook Heaven Co. Lid. (Bi9000AT)) was used. Powder of composite particles could be obtained by coagulating latexes with $CaCl_2$, and filtering. Then, this coagulum was dried at 50°C for 48 hours. These composite particles were used as an impact modifier for epoxy resins.

Contact Angle Measurements

DDI water and methylene iodide (CH_2I_2) (1 μl) were dropped on each sample film and the contact angle read with contact angle meter (Erma contact angle meter, model G-1). From these contact angles of DDI water and CH_2I_2, surface

TABLE 1. Recipe for the Preparation of Poly(butyl acrylate) Seed Latex and Poly(butyl acrylate)/poly(glycidyl methacrylate) Two-stage Latex.

Run No.	1	2	3	4	5	6
BA (g)	100	-	-	-	-	-
PBA latex (g)	-	50	50	50	50	50
KPS (g)	0.4	0.04	0.07	0.1	0.23	0.3
GMA (g)	-	4.285	6.667	10	23.33	30
NaSS (g)	0.01	-	-	-	-	-
Water (g)	400	88.565	110	140	260	320
Temp. (°C)	70	70	70	70	70	70
Time (min)	180	120	120	120	120	120

Run No.1 : PBA seed latex
No.2 : PBA/PGMA = 70/30 two-stage latex
No.3 : PBA/PGMA = 60/40 two-stage latex
No.4 : PBA/PGMA = 50/50 two-stage latex
No.5 : PBA/PGMA = 30/70 two-stage latex
No.6 : PBA/PGMA = 25/75 two-stage latex

tension (γ_s), surface polarity (γ_s^p), and surface dispersity (γ_s^d) were calculated through Owens' equation [10]. It has been suggested that surface characteristics of particles e.g., surface tension, surface polarity, and surface dispersity, could be employed to identify the morphology of two-stage latexes. Especially, the polarity of core surface has a considerable effect on the morphology of two-stage latex considerably [11]. Therefore, by considering the surface polarity and dispersity of latex particles, the morphology of the two-stage latex could be identified indirectly, and the effect of surface polarity of seed particle on the morphology of two-stage latex could be investigated.

Impact Strength Measurements

Epoxy resin was mixed with stoichiometric amounts of curing agent and composite particles in a ball mill at moderate temperature. Foams generated in the course of mixing were broken down under vacuum at 50°C. This mixture was cured in a mold at a temperature of 80°C for 24 hours and then post cured at 150°C for 5 hours to obtain a cured specimen. The specimen of 3 mm thickness was cut to make it correspond to the ASTM D256 test method. This specimen was not notched because of the concern that a crack might be generated in the course of making a notch. Then, impact strength was measured with an izod type impact tester.

RESULTS AND DISCUSSION

Preparation of Poly(Butyl Acrylate)/Poly(Glycidyl Methacrylate) Two-Stage Latexes

The semibatch emulsion polymerization, where the second-stage monomer is added gradually to seed particles, was employed to minimize the level of second-stage monomer present at any time during the polymerization. In so doing, the second phase will be present primarily in the form of polymer molecules, which are relatively hindered in mobility compared with monomer molecules. Therefore, semibatch polymerization is more favorable than batch polymerization in the core-shell formation [11].

Figure 1 shows the conversion-time curves of poly(butyl acrylate) seed latex and poly(butyl acrylate)/poly(glycidyl methacrylate) two-stage latex. The maximum conversion of seed latex reached about 98%, and that of shell polymer did about 86%. As shown in Figure 1, the conversion of shell polymer reached above 80%, only after the addition of glycidyl methacrylate monomer was completed. As semibatch polymerization was employed, the second-stage monomer, glycidyl methacrylate, was polymerizing during the addition. Therefore, it could be said when the addition of glycidyl methacrylate monomer was completed, about 80% of shell monomer was already polymerized.

Poly(butyl acrylate) core latex had an average particle size of 118.7 nm as shown in Figure 2. The size distribution was narrow and monodisperse. As two-stage consecutive emulsion polymerization was employed, if core particle size were controlled, the size of two-stage latex would increase as the amount of shell monomer was increased. Figure 3 shows the resultant average sizes of two-stage latex particles. As expected, the average sizes of two-stage latex particles increased according to the stage ratio of core to shell. However, when the stage ratio was high, new particles appeared in the region of 90 nm. These particles were assumed to be

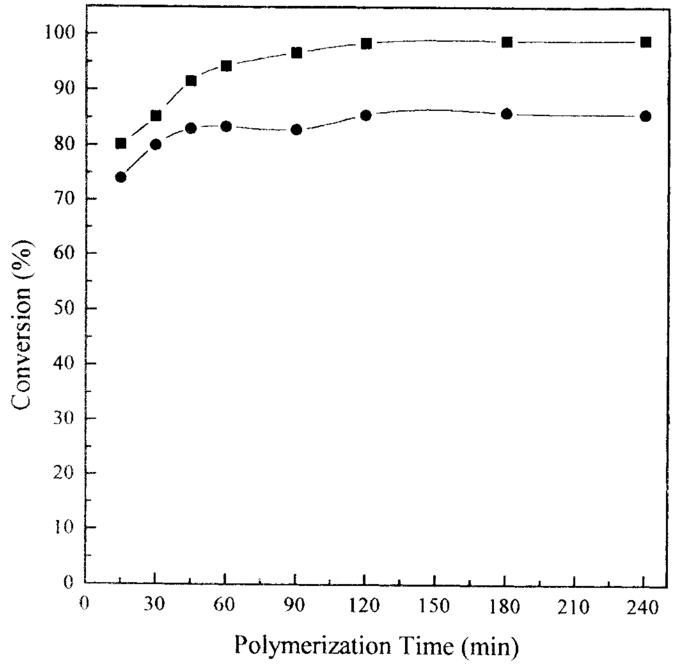

Figure 1. Conversion versus polymerization time. Conversion of poly(butyl acrylate) core latex (-■-) and poly(butyl acrylate)/poly(glycidyl methacrylate) two-stage latex of which stage ratio of core to shell is 50 to 50 (-●-).

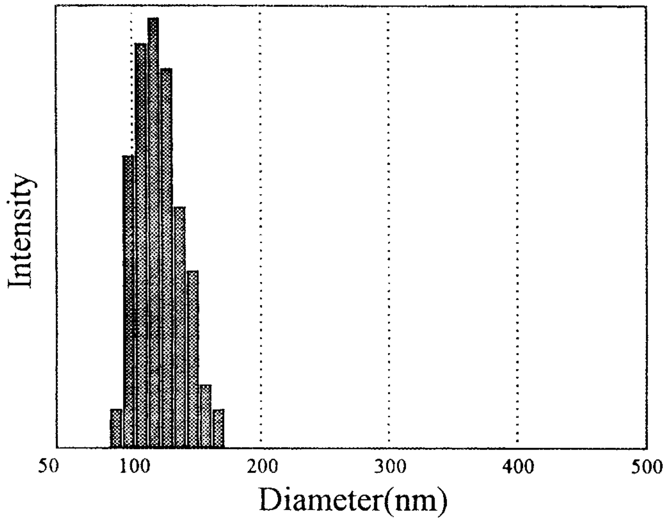

Figure 2. Particle size distribution of poly(butyl acrylate) coVre latex. Average particle size was 118.7 nm. We used laser light scattering to obtain particle size distribution (Brook Heaven Co. Ltd. (Bi9000AT)).

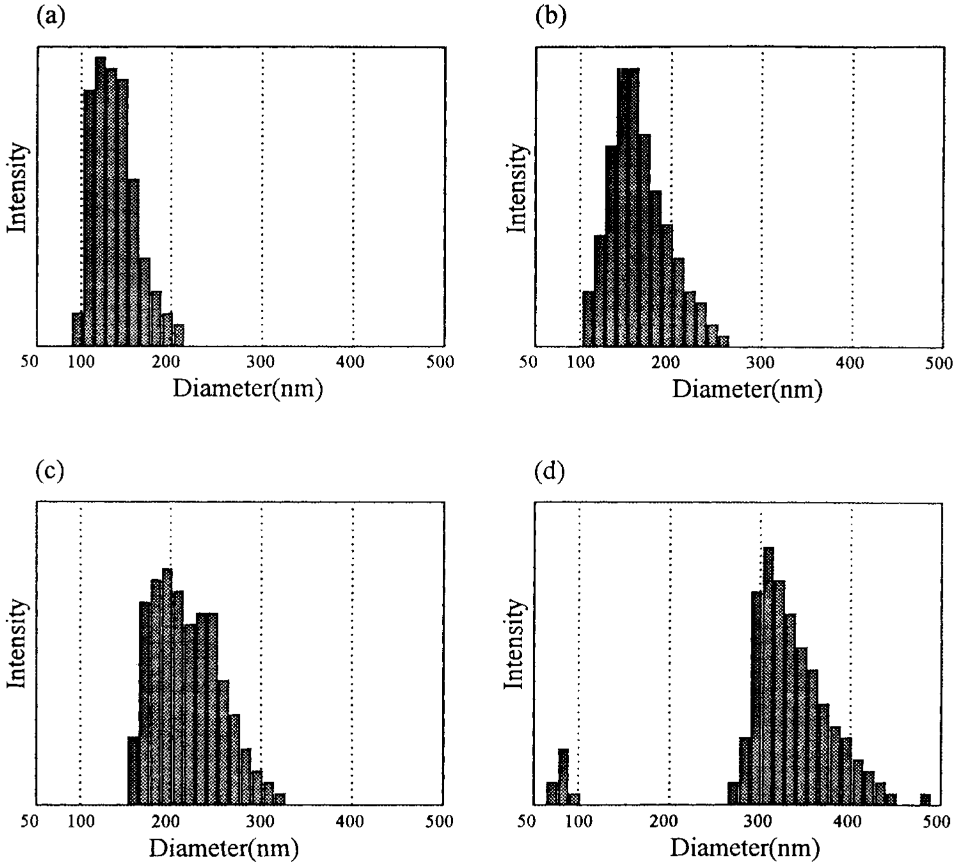

Figure 3. Particle size distributions of poly(butyl acrylate)/poly(glycidyl methacrylate) two-stage latexes. Here, average particle size of PBA/PGMA=60/40 was 128.6 nm (a), PBA/PGMA=50/50 (b) was 139.4 nm, PBA/PGMA=30/70 (c) was 233.1 nm, and PBA/PGMA=25/75 (d) was 327.5 nm. We used laser light scattering to obtain particle size distribution (Brook Heaven Co. Ltd. (Bi9000AT)).

the homopolymer of poly (glycidyl methacrylate) latex, generated in the course of shell formation. The size distribution of two-stage latex particles showed the tendency of broadening with the stage ratio increase. This might be due to particle agglomeration and homopolymer formation of poly(glycidyl methacrylate) latex.

The Identification of Two-Stage Composite Particle Morphology

In order to apply a poly(butyl acrylate)/poly(glycidyl methacrylate) core-shell composite particle as an impact modifier for epoxy resin, the core-shell morphology must be favorable. In other words, the core polymer should be poly(butyl acrylate) rubber and the shell should be the polymer of glycidyl methacrylate. Therefore, the identification of two-stage composite particles morphology is an inevitable course prior to the application of these composite particles for impact modification of epoxy resin. In this paper, contact angle was introduced to identify the morphology of two-stage composite particles.

When DDI water and methylene iodide (CH_2I_2) are dropped on the polymer surface, the contact angle are determined by the polymer surface properties, e.g., surface polarity and surface dispersity. Therefore, if core-shell morphology was formed, the characteristics of the shell polymer would be the same as those of the shell polymer latex only, poly(glycidyl methacrylate) latex.

Surface polarity is one of the factors influencing core-shell morphology. The first-stage seed particle showing high surface polarity is more favorable to be inverted, because the water is in the continuous phase of the emulsion system. Therefore, one can predict that, generally, the most thermodynamically favorable orientation will be an inverted morphology rather than a true core-shell structure [11]. In our system, however, since the surface polarity of poly (butyl acrylate) seed particle was much lower than that of poly(glycidyl methacrylate) shell polymer surface (with a difference of about 31 dyne/cm-Table 2), the core-shell structure is the more favorable morphology.

In the poly(butyl acrylate)/poly(glycidyl methacrylate) two-stage latex system, two thermodynamic factors can be considered; the surface polarity and the stage ratio of core to shell. From the contact angles of DDI water and CH_2I_2, surface polarity (γ_s^p) and surface dispersity (γ_s^d) could be obtained through Owens' equation. As shown in Table 2, surface polarities of two-stage latex films showed similarities to that of poly(glycidyl methacrylate) film at or above the stage ratio of 50/50, and surface dispersities also showed the same trend. It could be deduced from these results that a poly(butyl acrylate)/poly(glycidyl methacrylate) core-shell morphology was formed.

However, at or below the stage ratio of 60 to 40, surface polarities were more or less reduced and close to that of poly(butyl acrylate) film. This result seemed to be caused by the effect of phase mixing or the formation of another type morphology e.g., sandwich-like, acorn-like, and raspberry-like, etc. [7]. In our poly(butyl acrylate)/poly(glycidyl methacrylate) two-stage latex, the core-shell morphology would be thermodynamically more favorable. However, when the relative phase volume of shell polymer was small, the morphology of the two-stage latex had a tendency to be inverted. For this reason, the morphology of the

TABLE 2. Contact Angle Measurement. γ_s is the Surface Tension, γ_s^d the Component of Dispersity, and γ_s^p the Component of Polarity.

Sample	Contact angle		γ_s	γ_s^d	γ_s^p
	Water	CH_2I_2	dyne/cm	dyne/cm	dyne/cm
PBA latex	97.13	64.50	26.01	1.51	24.50
[a]PBA/PGMA=70/30	87.25	58.72	30.07	4.01	26.06
PBA/PGMA=60/40	84.89	58.38	30.73	5.00	25.73
PBA/PGMA=50/50	73.78	43.75	40.06	7.92	32.14
PBA/PGMA=30/70	73.79	44.01	39.95	7.96	31.99
PBA/PGMA=25/75	74.21	43.27	40.12	7.60	32.52
[b]PGMA latex	74.38	43.07	40.14	7.46	32.68

[a] PBA/PGMA=70/30 means poly (butyl acrylate) / poly (glycidyl methacrylate) two-stage latex of which stage ratio of core to shell is 70 to 30, and so forth.

[b] PGMA latex means poly (glycidyl methacrylate) latex.

poly(butyl acrylate)/poly(glycidyl methacrylate) two-stage latex was not formed at low stage ratio of core to shell. However, when the stage ratio of core to shell increased, core-shell morphology was well again formed, since the phase volume of shell polymer increased in comparison with that of core polymer.

Impact Strength Measurements

Some theories propose a correlation between the toughening mechanism and morphology in the case that carboxy-terminated rubber particles were used as a modifier [12-15]. For example, small particles (<100nm) are said to promote shear banding, and large particles (>50 μm) crazing. In general, shear banding was reported to be much superior to crazing in epoxy impact modification. In our research, as particle sizes were in abovementioned range, it was possible to investigate which effect was more dominant in improving impact strength when using core-shell composite particles as an impact modifier.

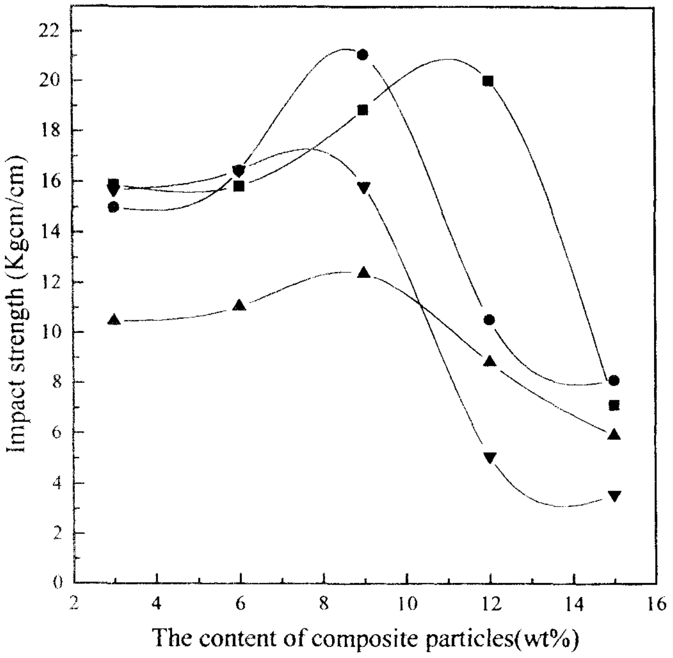

Figure 4. Impact strength versus the content of core-shell composite particles (wt%). PBA/PGMA=50/50 (-■-), PBA/PGMA=40/60 (-●-), PBA/PGMA=30/70 (-▼-), and PBA/PGMA=25/75 (-▲-).

Impact strength was measured as a function of the concentration of composite particles and the stage ratio of core to shell, As shown in Figure 4, the overall impact strength increased with increasing concentration of composite particles, and then decreased. The decrement of impact strength above 9 wt% of core-shell composite particle content appeared to be related to a phase separation, resulting from the excess of composite particles. With respect to the core-shell stage ratio, 40 to 60 (-●-) showed the best impact strength (the original impact strength of epoxy resin was 15 kgcm/cm), an indicator of the good interface compatibility between poly(glycidyl methacrylate) shell polymer and the epoxy matrix. However, above this stage ratio the impact strength decreased. This seemed to be caused by the fact that the relative amount of poly(butyl acrylate) decreased as the amount of shell increased. Also bearing a negative effect was the formation of poly GMA homopolymer in the latex at high stage ratio, as shown in Figure 3 (d).

In our study, the impact strength increased only about 1.6 times comparing with that of epoxy resin itself. This suggests that the crazing effect is a more dominant mechanism than shear banding in the impact modification of epoxy resin using poly(butyl acrylate)/poly(glycidyl methacrylate) core-shell composite particles.

CONCLUSIONS

Poly(butyl acrylate)/poly(glycidyl methacrylate) core-shell latex was prepared by a two stage consecutive emulsion polymerization process. The particle size distribution of two-stage latex was broader as the shell thickness of the composite particles increased. This is probably caused by the generation of poly(glycidyl methacrylate) homopolymer and the agglomeration of particles.

The morphology of the core-shell composite particles was confirmed by contact angle measurements. This shows the formation of a mixed or other-type morphology below the stage of 40 to 60 (core/shell), because the amount of shell monomer was small; i.e., the relative phase volume of shell polymer was small. However, when the stage ratio of core to shell increased, core-shell morphology was formed well again, for the phase volume of shell polymer increased in comparison to that of core polymer.

In our study, the increase in impact strength was not good. This means that although the particle size of the composite particle was located in the range of shear band formation, the crazing mechanism is predominant. With respect to the compatibility of shell polymer with the epoxy matrix, a suitable stage ratio was suggested; i.e., when the core-shell morphology was formed, the compatibility of shell polymer was improved as the shell thickness increased. However, above this stage ratio of core to shell the impact strength was somewhat diminished, because the content of rubber polymer was relatively reduced.

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