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# Effect of Poly(butyl acrylate)-Poly(methyl methacrylate) Rubber Particle Texture on the Toughening Behavior of Poly(methyl methacrylate)

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**Abstract:** Monodisperse composite latex particles with size of ca. 300 nm, which consist of *n*-butyl acrylate as a soft phase and methyl methacrylate as a hard phase with different morphology, were synthesized by seeded multi-stage emulsion polymerization. Three types of composite latex particles including random-, core/shell-, and gradient-type particles were obtained by using different monomer feeding methods during semi-batch emulsion polymerization. Effect of poly(butyl acrylate)-poly(methyl methacrylate) rubber particle morphology on the mechanical and rheological properties of rubber toughened poly(methyl methacrylate) was investigated. Among three different rubber particles, the gradient-type rubber particle showed better toughening effect than others. No significant variation of rheological property of poly(methyl methacrylate)/rubber blends was observed for the different rubber particle morphology.

## Introduction

Control of morphology in composite latex particle is important for many latex applications such as adhesives, coatings, impact modifiers, *etc.* Composite latex particles of different morphology can be prepared by multi-staged emulsion polymerization techniques where a second stage monomer is polymerized in the presence of preformed first polymer particles.[1-3] During the course of multi-staged emulsion polymerization, the equilibrium morphology of composite latex particles is mainly governed by thermodynamic factors, and kinetic factors also affect the final morphology which depends on thermodynamic factors.[4-6] The thermodynamic factors determine the equilibrium morphology of composite latex particle, and the kinetic factors determine the ease with which such a thermodynamically favored state can be achieved.

It has long been recognized that physical properties of composite latex particles largely depend on their particle morphology. Many of the polymerization parameters and conditions are known to affect the particle morphology.[7-11] The design of particle morphology for a specific application is of paramount importance and is the subject of many recent research efforts. Depending on the polymerization parameters, various composite latexes, from core/shell type to inverted core/shell type and other phase separated texture such as sandwich structures, hemispheres, raspberry-like structure, have been prepared by seeded emulsion polymerization techniques.

In spite of the intensive efforts related to the study of composite latex particles, relatively few attempts have been made to correlate the morphology of rubber particle with the performance of final properties of rubber for each application area.[12-14] The objectives of this study were to prepare monodis-

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perse poly(butyl acrylate)-poly(methyl methacrylate) (PBA-PMMA) composite latex particles having various morphology by the adjustment of monomer feeding method in emulsion polymerization, to investigate the effect of polymerization variables on the morphology of PBA-PMMA composite rubber particles, and finally to examine the effect of PBA-PMMA composite rubber latex particle morphology on the toughening behavior of PMMA.

**Table I. Typical Polymerization Recipe for the Preparation of Composite Latex**

| Ingredient | Amount(g) |
|---|---|
| BA | 197.40 |
| MMA | 131.60 |
| KPS | 0.35 |
| SLS | 5.38 |
| AMA | 1.65 |
| EGDMA | 1.65 |
| Water | 431.3 |

## Experimental

**Materials.** The monomers, *n*-butyl acrylate (Junsei Chemical Co., BA) and methyl methacrylate (Junsei Chemical Co., MMA), were used after purification by 2N NaOH solution to remove the inhibitor. After this treatment, these monomers were washed with distilled water several times. All other materials were used without further purification. Sodium lauryl sulfate (Aldrich Chemical Co., SLS) was used as an emulsifier. Potassium persulfate (Sigma Chemical Co., KPS) was used as an initiator. Allyl methacrylate (Aldrich Chemical Co., AMA) and ethylene glycol dimethacrylate (Aldrich Chemical Co., EGDMA) were used as crosslinking agents.

**Synthesis of Composite Latex Particle.** Polymerization reaction was performed in a 1 L jacket reactor purging with nitrogen gas during polymerization. The reactor was equipped with a mechanical stirrer, reflux condenser, thermocouple, and nitrogen gas inlet tube. Agitation speed was fixed at 170 rpm and polymerization temperature was controlled by circulating water. A typical polymerization recipe is given in Table I.

Seeded emulsion polymerization was carried out in this experiment to prepare latex particles with narrow particle size distribution. Batch polymerization reaction was used for polymerization of seed latex. The reactor vessel which contained water and emulsifier was heated to 55 °C. Then, the mixture of monomers and SLS was added with initiator. Polymerization was carried out for 1 hr. The amount of emulsifier was controlled below critical micelle concentration of SLS to prepare mono-disperse seed particles.

Semi-batch type reaction was employed for the polymerization of composite latex using the prepolymerized seed latex. Post-reaction was carried out for additional 2 hrs after complete addition of monomers for 10 hrs in order to eliminate residual monomers. To prepare core/shell type latex, poly (butyl acrylate) core phase was polymerized first and then shell phase of MMA was copolymerized onto the poly(butyl acrylate) core phase. Mixture of MMA and BA monomers was copolymerized to prepare random copolymer particle. Gradient type particle, which has gradual change of composition along the radial direction within the particle, was prepared using power-feed method.[15,16] Figure 1 shows the expected rubber particle texture which can be obtained by the different monomer feeding

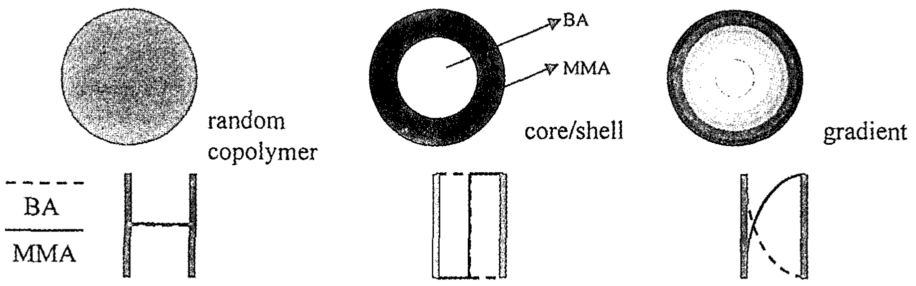


**Figure 1.** The expected morphology and composition of monomers within the particle.

methods in the semi-batch polymerization reaction.

**Blending and Specimen Preparation.** PMMA homopolymer ($M_w$ = 267,000, PDI = 2.8) was prepared separately by emulsion polymerization. The rubber latex and PMMA homopolymer latex were blended in latex state. Next, these blended latices were dried for melt blending. Melt blending was performed in a Haake mixer at 180 °C for 10 minutes. The contents of rubber phase were adjusted from 0 to 20 wt%. These PMMA/rubber blends were compression molded at 200 °C and 2,500 psi for tensile test and Izod impact test.

**Characterization.** Small amount of emulsion latices were taken out of the reactor and 1 wt% hydroquinone solution was added before measuring conversion. These latices were dried in a forced convection oven for 24 hrs at 70 °C and further dried in a vacuum oven for 2 hrs at 70 °C. The conversion was calculated based on the gravimetric measurement.

A light scattering apparatus (Particle Sizing Systems, Nicomp 370HPL) and a scanning electron microscopy (Leica, Model 440) were used to analyze the particle size and distribution of latex particles. The molecular weight of the polymers was measured using a gel permeation chromatography (Waters, Model 600E, GPC). Tetrahydrofuran was used as carrier solvent and the calibration curve was established by using a standard polystyrene.

Thermal analysis was carried out by differential scanning calorimetry (TA Instruments, DSC 2010). A dynamic mechanical analyzer(TA Instruments, DMA 2980) was used to examine the viscoelastic properties of rubbers. A mechanical spectrometer (Rheometrics, RMS 800) was used to measure melt viscosity of blends. Izod impact test (ASTM D256) was carried out by an impact testing machine (Yasuda Seiki Seisakusho, Impact Tester No. 225).

## Results and Discussion

**Effect of the Monomer Feeding Method on the Particle Morphology.** Same seed particles were used to synthesize three different rubber particles including PBA-PMMA random copolymer, PBA-PMMA core/shell type copolymer, and PBA-PMMA gradient type copolymer. The composition of BA/MMA in the final latex was chosen as 60/40. The particle size and the particle size distribution are shown in Figure 2. These results show that number-average particle size($D_n$) of latex is between 281 and 306 nm with polydispersity index of 1.02, which means very distinct monodispersity. This indicated that no new particles were generated during semi-batch type emulsion polymerization of three different rubber particles in our experiment.

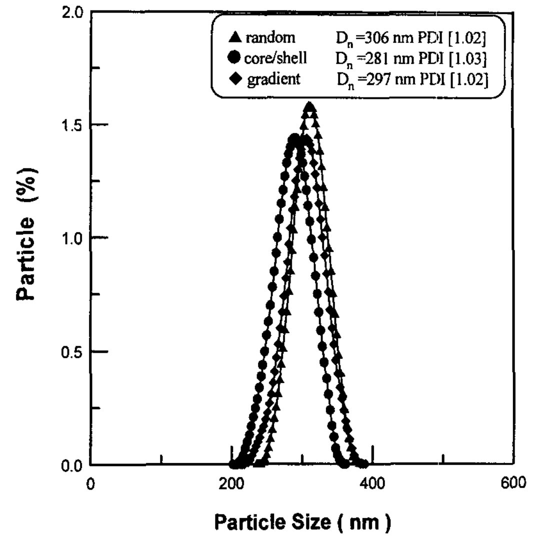
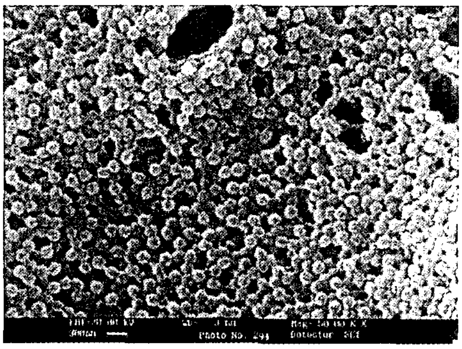
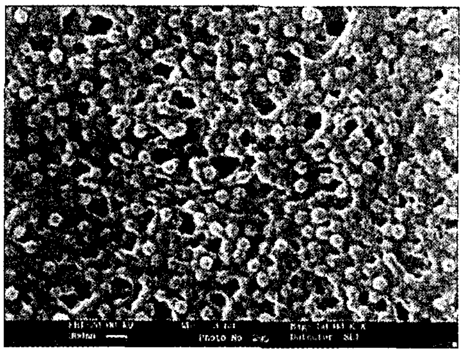


**Figure 2.** Particle size and particle size distribution of final latices prepared by various monomer feeding methods.

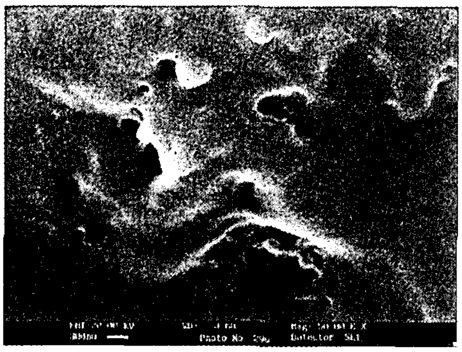
Figure 3 shows the SEM micrographs of latex particles. The PBA-PMMA core/shell type latex clearly shows the monodispersity of latex particles. However, one cannot confirm the monodispersity for other PBA-PMMA gradient type or PBA-PMMA random type particles as shown in Figure 3. The reason is because those latices formed films during sample preparation stage for SEM observation. It has been known that film formation of latex is largely dependent on the glass transition temperature ($T_g$) of outer layer of particles.[17] Therefore, the SEM micrographs of dried latex at room temperature reveal the glass transition temperature of latex qualitatively. We cannot use TEM for the direct observation of particle



(a) core/shell



(b) gradient



(c) random copolymer

**Figure 3.** SEM micrographs of PBA-PMMA composite latex prepared by various monomer feeding methods. (a) core/shell type; (b) gradient type; (c) random type.

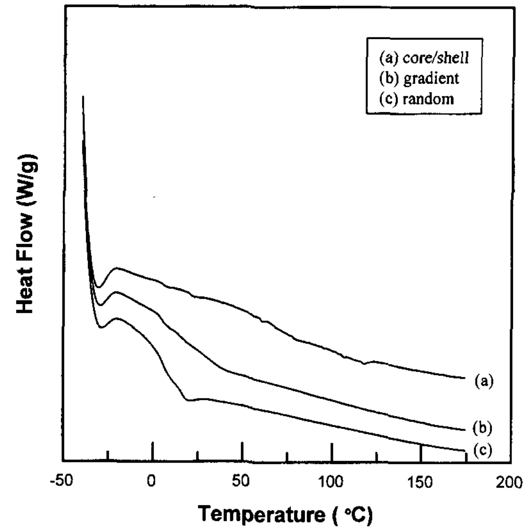


**Figure 4.** DSC thermograms of PBA-PMMA composite rubber particles.

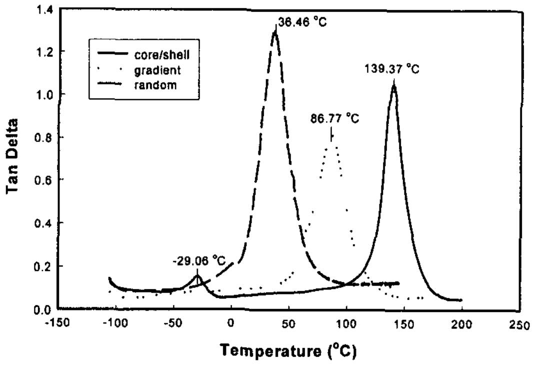


**Figure 5.** Loss tan $\delta$ as a function of temperature for PBA-PMMA composite rubber particles at 1 Hz and a heating rate of 2 °C/min.

morphology, because it is difficult to stain PBA and PMMA selectively using $OsO_4$ or $RuO_4$. Particle morphology may be predicted indirectly by the measurement of glass transition temperatures.

The DSC thermogram and the tan $\delta$ of PBA/PMMA composite latex particles of three different morphology are shown in Figure 4 and 5, respectively. Even though it is not clear enough, the DSC results show the general trend of glass transition temperatures of three different particles prepared in our experiment. The glass transition temperature, defined as the temperature corresponding to the peak of tan $\delta$ in the glass transition region, is near 36 °C for the random type particle. This $T_g$ value is about 20 °C higher than that observed from DSC measurements. It is also higher than the predicted value from the Flory-Fox equation. The core/shell type particle shows two separate glass transition temperatures, -29 and 139 °C. This implies that there are two distinct regions such as PBA-rich core and PMMA-rich

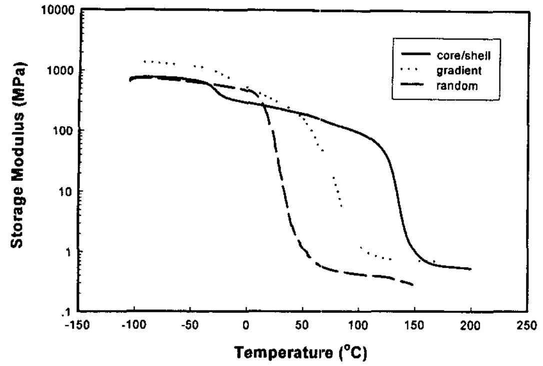


**Figure 6.** Storage modulus as a function of temperature for PBA-PMMA composite rubber particles at 1 Hz and a heating rate of 2 °C/min.

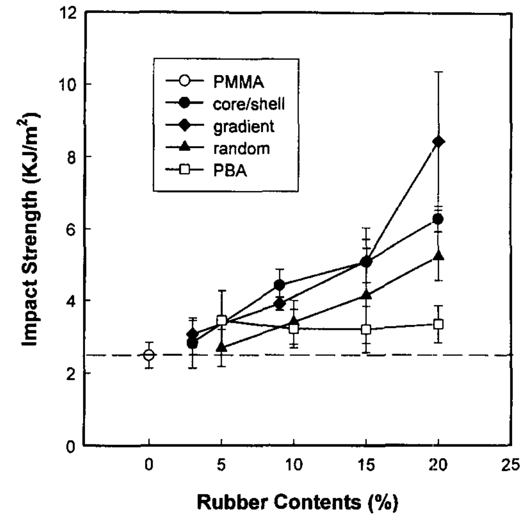


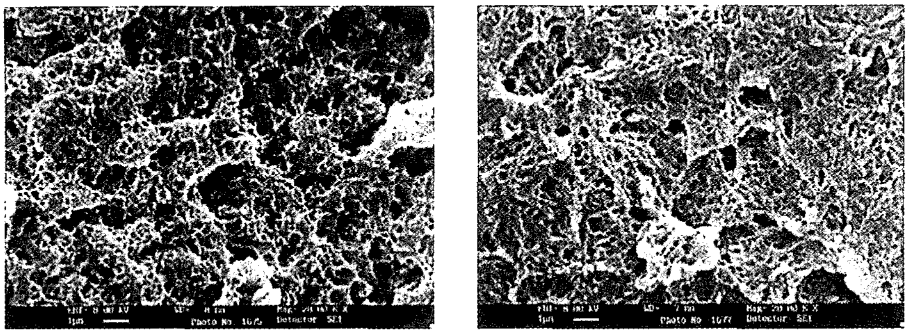
**Figure 7.** Impact strength of PMMA/rubber blends as a function of rubber contents for various type of rubber.

shell. The gradient type particle shows a broad peak between $T_g$'s of random type and core/shell type particles.

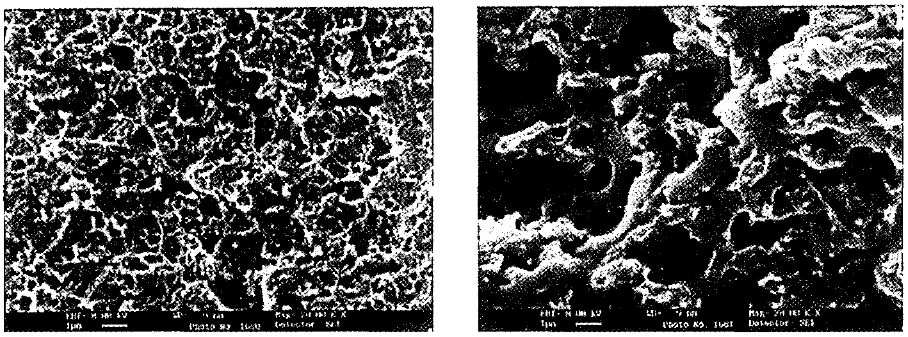
Figure 6 shows the storage modulus as a function of temperature for the hot pressed samples of PBA-PMMA composite latices. For the random type sample, a distinct single transition of storage modulus is observed, which is typical characteristics of random copolymers. Two well defined transitions are observed in the storage modulus of core/shell type sample, which correspond to the characteristics of the hard and the soft homopolymers, respectively. Gradient type sample is quite different from the others. The transition regions are broader than those observed with the random type sample or core/shell type sample. This broad transition behavior is due to the result of an alloying effect caused by the continuously changing composition. This indicates that the particles have gradual change of composition along the particle diameter.

**Impact Strength of PMMA/Rubber Blends.** It has been known that the toughness of PMMA can be considerably increased by the incorporation of rubber phase.[13,17-21] This toughening behavior of PMMA/rubber blends is mainly governed by interfacial adhesion, the rubber particle size, the amount of rubber phase and the morphology of the incorporated rubber particle.[13,20] Figure 7 shows the Izod impact strength of PMMA matrix blended with different rubber particles. Several authors have reported decrease of toughness when the rubber content is above a certain value which varies from 10 to 20 wt%, depending on the size of rubber particles.[21] However, as shown in Figure 7, the impact strength generally increases with rubber content up to 20 wt% except homo-PBA rubber particle. Lower toughening efficiency of homo-PBA rubber is largely related to the poor interfacial adhesion and the deformation and the coagulation of rubber particles during melt blending. The SEM micrographs in Figure 8, showing the fracture surface of the specimen containing 20 wt% of rubber particles for various morphology of rubbers, strongly support these facts. These results indicate that interfacial adhesion between rubber particle and the matrix polymer plays an important role in the toughening of rubber toughened polymers. The toughening efficiency of the different rubber particles examined in our experiment is improved in the order of the gradient type, core/shell type, random type, and PBA homopolymer.

**Rheological Behavior of PMMA/Rubber Blends.** It is convenient to characterize the viscoelastic response of polymer melts in terms of a complex viscosity, $\eta^*$. Numerous heterogeneous polymeric systems have been studied and it has been reported that the complex viscosity is influenced by various factors including the volume fraction of dispersed phase, interfacial tension,



(a) core/shell (b) gradient



(c) random copolymer (d) homo PBA

**Figure 8.** SEM micrographs of fracture surface of PMMA/rubber blends.(Rubber content = 20 wt%): Rubber type (a) core/shell type; (b) gradient type; (c) random type; (d) PBA homopolymer type.

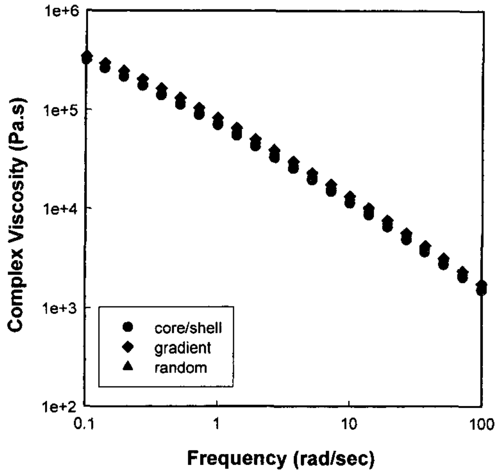


**Figure 9.** Complex viscosity of PMMA/rubber blends as a function of frequency at 220 °C and strain of 3%.

and the particle size, *etc.*[22,23] Figure 9 shows the complex viscosity of PMMA/rubber blends as a function of frequency for different morphology of rubber particles. The PMMA/rubber blends represent typical shear thinning behavior of polymer melts. It shows, however, that the complex viscosity of PMMA/rubber blends is not sensitive enough to reveal the effect of particle morphology examined in our study.

## Conclusions

We investigated the effect of rubber particle morphology on their mechanical and rheological properties. Various composite latices were synthesized by seeded emulsion polymerization using different monomer feeding methods. To examine the performance of these particles as an impact modifier for the brittle PMMA, the mechanical and the rheological properties of PMMA/rubber blends were examined.

Monodisperse PBA-PMMA composite latices with size of ca. 300 nm having various morphology, including random copolymer particle, core/shell type particle, and gradient type particle were prepared by seeded emulsion polymerization.

Detailed texture of rubber particles was confirmed using SEM micrographs and measurement of glass transition temperature. It was found that toughening efficiency could be enhanced by introducing gradient-type rubber morphology in designing rubber particle for PMMA/rubber blends. No significant variation of complex viscosity of PMMA/rubber blends for the different rubber particle morphology was observed in our system.

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