Poly(methyl methacrylate) Toughening with Refractive Index-Controlled Core–Shell Composite Particles

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ABSTRACT: Poly(butylacrylate-co-styrene)/poly(methyl methacrylate) (PMMA) coreshell composite particles having different refractive indexes were prepared by a twostage consecutive emulsion polymerization. The refractive index of the core phase was controlled by varying the incorporated amount of divinylbenzene (DVB) which acted as a crosslinking agent as well as a refractive index enhancer. The blends of these core-shell composite particles with PMMA showed an impact strength increment of about three times compared with that of the pure PMMA. However, as the amount DVB increased, the impact strength showed a tendency toward decreasing. This was caused by the loss of the elastic property of the core phase. The toughened PMMA blended with core-shell composite particles having the core crosslinked with 1 wt % DVB showed the best transparency. However, the transparency was rather decreased, as the difference of the refractive index between the core phase and the pure PMMA increased. This suggested that in the case of using the core-shell composite particles as a toughening agent for PMMA the matching of the refractive index of the core phase with that of the pure PMMA was one of key factors in maintaining the transparency of the toughened PMMA. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1607–1614, 1999

Key words: refractive index of core phase; crosslinking agent; refractive index enhancer; loss of elastic property; transparency of toughened PMMA

INTRODUCTION

Poly(methy methacrylate) (PMMA) has been commonly used in the polymer fields requiring transparency. However, wide application has been limited because of its inherent brittleness. Therefore, there have been considerable efforts to increase its impact strength through various methods, including the copolymerization with another monomer, causing a low glass transition temperature, and blends with rubber polymers.^{1–6}

Recently, core-shell composite particles composed of a rubbery core and a glassy shell have received remarkable interest as a toughening agent for brittle polymers, such as epoxy resin, nylon, polystyrene, and PMMA. One of remarkable characteristics of their morphological structures is that the rubbery core phase was engulfed by the shell polymer having good compatibility with the matrix polymer. So, it was possible to disperse inner rubber particles successfully in a matrix polymer.

As related works to the toughening of PMMA, Riew and Kinloch examined the tendency of the impact strength for PMMA toughened with multiple-phase particles having radially alternating rubbery and glassy layers.⁷ They proposed that the properties of the toughened PMMA containing three- and four-layer toughening particles were superior to those containing two-layer toughening particles. Shah reported the effect of the content of

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composite particles consisting of PMMA/poly(butyl acrylate-co-styrene)/PMMA with three alternative layers.⁸ Wrotecki et al. also reported the effect of the size and the content of composite particles having the structure of a poly(butylacrylate-co-styrene)/ PMMA core-shell on the toughening of PMMA.^{9,10} They suggested that in the preparation of the toughened PMMA, for maintaining its transparency, it should be remembered that one of the next two parameters must be fixed by the essential requirements for transparency: One is that the refractive index of the rubber phase must be equal to that of the matrix PMMA. The other is that the particle size must be small to avoid turbidity. In the aspect of transparency, both cases showed a good result. On the contrary, in the aspect of toughening, the latter was not suitable for the toughening of PMMA, because the core-shell composite particles were too small to defend crack propagation.^{11,12} So, it could be said that the control of the refractive index of the core phase was more effective in the case of using core-shell composite particles for the toughening of PMMA requiring transparency. However, there are few studies to examine the effect of the refractive index of core-shell composite particles on the transparency of toughened PMMA in detail.

In this study, core-shell composite particles were prepared by varying their refractive indices, which was possible by the incorporation of divinylbenzene (DVB). DVB has a high refractive index and two vinyl groups in a molecule so that it can act as a crosslinking agent as well as a refractive index enhancer. To simplify the process, core-shell composite particles produced by twostage consecutive emulsion polymerization were suggested. The effect of the refractive index of the core phase and the content of the composite particles on the impact strength and transparency was investigated.

EXPERIMENTAL

Reagents

The inhibitors in butyl acrylate (BA, Junsei Chemical Co., Ltd., Japan), styrene (St, Junsei), and methyl methacrylate (MMA, Junsei) were removed through an inhibitor-removing column (Aldrich Chemical Co., USA). DVB (Fluka Chemica) was used without further purification. Potassium persulfate (KPS, Shinyo Pure Chemicals Co., Ltd., Japan) was used as an initiator, and Aerosol OT (A-OT, 10% solution, Sigma Chemical Co., USA), as an emulsifier. Magnesium sulfate (MgSO₄, Junsei) was used in deemulsifying.

Preparation of Core-Shell Composite Particles

The polymerization of seed latex was carried out in a round-bottomed glass reactor equipped with a reflux condenser, thermometer, nitrogen inlet, reagent inlet, Teflon stirrer, and water bath at 70 \pm 0.5°C. The stirring speed was fixed at 300 rpm. The distilled deionized water (DDI water) was charged into the reactor and nitrogen was bubbled through the DDI water for 10 min. The aqueous solution of KPS was added into the reactor. Then, by adding 20 wt % of the monomer–emulsifier mixture (BA, St, DVB, and A-OT), a seed latex was polymerized.

After the seed latex polymerization was completed, the rest of the mixture (80 wt %) was dropped into the reactor at the rate of 0.223 g/min. The emulsion polymerization of the core latex was carried out for 4 h. Because the half-life time of KPS was long enough, the initiator concentration in the core latex polymerization was approximately the same as that in the seed latex polymerization.^{13,14}

Shell polymerization was carried out continuously. The aqueous solution of KPS was added into the reactor, and then MMA was dropped into the reactor at the rate of 0.223 g/min. After MMA dropping, the shell polymerization was performed for 4 h at 70 \pm 0.5°C. Power-typed composite particles could be obtained by deemulsifying the latexes in a 1% MgSO₄ water solution at 70–80°C for 1 h and then filtering. Next, they were dried at 50°C for 48 h.

The composition for the preparation of core and core-shell latexes is summarized in Table I. To remove other effects except the refractive index on the particle composition, the quantity of the other ingredients but the core were fixed throughout the series.

Melt Blending and Molding

Core-shell composite particles and PMMA chips [LG Chemical, = 55,000 g/mol, polydispersity index (PDI) = 2.00] were blended in a sample mixer (S-25SM, Sinshang Industry Co.) at 250°C for 7 min with a rotation speed of 100 rpm. The content of the composite particles in PMMA was varied from 10 to 30 wt %. These mixtures were then molded with a Mini Max molder (CS-183MMX,

	Core Polymerization					Shell Polymerization			
Series ^a	BA	St	DVB	DDI Water	KPS	A-OT	MMA	KPS	DDI Water
$\rm D05^{b}$	39.80	9.95	0.25	380	0.25	5.00	50	0.25	20
D10	39.60	9.90	0.50	380	0.25	5.00	50	0.25	20
D15	39.40	9.85	0.75	380	0.25	5.00	50	0.25	20
D20	39.20	9.80	1.00	380	0.25	5.00	50	0.25	20
D30	38.80	9.70	1.50	380	0.25	5.00	50	0.25	20

Table I Recipe for Preparation of Poly(BA-co-St)/PMMA Core-Shell Latexes

All units are in grams.

^a This core series is defined according to the incorporating amount of DVB in the core phase.

Custom Scientific Instruments, Inc.) at 280°C. The dimension of all the samples molded was 62 \times 12.5 \times 3 mm. The composition for blending is summarized in Table II.

Measurements

The average sizes of the core latex and the coreshell latex were measured with a laser light scatter instrument of Brook Heaven Co. Ltd. (BI9000AT, argon laser). The fracture surface of the sample prepared at the liquid nitrogen temperature was examined with a scanning electron microscope (SEM, JSM-6300, JEOL). A conventional secondary electron-imaging technique was

Table IIComposition for the Preparation ofthe Toughened PMMA

	Core Series	Blended Weight		
Samples	of Core–Shell Composite Particles	Composite Particles	PMMA Chips	
$\mathrm{S00^{a}}$	_	_	10	
$S05-20^{b}$	D05	2	8	
S10-10	D10	1	9	
S10-20	D10	2	8	
S10-30	D10	3	7	
S15-20	D15	2	8	
S20-20	D20	2	8	
S30-20	D30	2	8	

All units are in grams.

^a S00 means the pure PMMA sample not containing any composite particles.

^b Sαβ-γδ is defined as follows: For example, S10-20 means that the core series used in the core–shell composite particles is D10 and the content of the core–shell composite particles is 20 wt % in the PMMA matrix.

^b $D\alpha\beta$ means the weight percentage of DVB in core phase (α,β wt %).

used. The fracture of the samples prepared at the liquid nitrogen temperature was coated with a thin layer of gold palladium to reduce any charge buildup on the fracture surface.

The Izod impact test was conducted using a Mini Max impact tester (CS-183TI, Custom Scientific Instruments, Inc.) at room temperature. The method of the unnotched Izod type was performed according to ASTM 256. The test was performed with five samples and the average value was taken. The thickness of all the samples was 3 mm.

The flexural modulus and the deflection at break for the samples were measured with a three-point bending tester (RS-232, Hounsfield Test Equipment Ltd.) at room temperature. The test method followed ASTM D790M.

Transmittance of each sample was measured by using a UV-visible spectrophotometer (Shimadzu UV-2010PC). The absorbency of the samples was measured at a 500-nm wavelength and then the transmittance was calculated through the following equation¹⁵:

$$T = \frac{P}{P_0} = e^{-A}$$
 (1)

where *T* is the transmittance of sample, *P* and P_0 are radiant powers after and before absorption, respectively, and *A* is the absorbency measured.

RESULTS AND DISCUSSION

Preparation of Poly(BA-*co*-St)/PMMA Core–Shell Composite Particles

In core latex polymerization, we used DVB as a crosslinking agent as well as a refractive index-

controlling agent. In general, it has been known that matching the refractive index of the rubbery core with that of PMMA is difficult, because rubbers have relatively low refractive indices.¹³ Therefore, the enhancement of the refractive index of the rubbery core has usually been achieved by copolymerizing with monomers of a high refractive index. Alternatively, however, these monomers of a high refractive index form glassy polymers. So, the elastic property of the rubbery core can be seriously diminished. In addition, a crosslinking agent employed in the core phase for the purpose of making the core-shell morphology more favorable in preparing core-shell latex and for maintaining the core morphology during blending also has lowered the final refractive index of the core phase. The DVB employed in this study was strongly expected to overcome these demerits, because it had an inherent high refractive index of 1.615.¹³ Moreover, owing to the two vinyl groups in its molecule, DVB also was expected to replace the role of the crosslinking agent. Table III shows the refractive index of the core latex in each series, which was calculated by the Gladstone–Dale relation as follows^{16,17}:

Refractive index (RI) =
$$\sum_{i} n_i v_i$$
 (2)

where n_i and v_i are the refractive index and the volume fraction of each component of the core latex, respectively. In Table III, the D10 core series was found to be the most similar refractive index to that of PMMA.

In preparing poly(BA-co-St)/PMMA core-shell latexes, semibatch polymerization, where the second-stage monomer is added gradually to the seed

Table IIIRefractive Index of Poly(BA-co-St)Core Latex in Each Series

	Volume Fraction (vol %)			
Series	BA	St	DVB	Refractive Index
D05 D10 D15 D20 D30	79.89 79.52 79.16 78.79 78.06	19.65 19.56 19.46 19.37 19.18	$0.46 \\ 0.92 \\ 1.38 \\ 1.84 \\ 2.76$	1.4887 1.4892 1.4898 1.4904 1.4915

Refractive index of each component: polyBA, 1.4630; polySt, 1.5900; polyDVB, 1.6150; PMMA, 1.4893.

Table IVParticle Size of Poly(BA-co-St) CoreLatex and Poly(BA-co-St)/PMMACore-Shell Latex

Series	Core Latex (nm)	Core–Shell Latex (nm)
D05	181	211
D10	188	211
D15	184	218
D20	187	220
D30	183	215

particles, was employed to minimize the level of the second-stage monomer present at any time during the polymerization. In so doing, the second phase will be presented primarily in the form of polymer molecules, which are relatively hindered in mobility compared with the monomer molecules. Therefore, the core–shell morphology could be more favorable.^{18–20}

The size of the core latexes and the core-shell latexes prepared in this study are summarized in Table IV. We could obtain the core latex over the size range of 181–188 nm. Even though the added amount of DVB in the core phase increased, the size of the core latex changed little. As two-stage consecutive emulsion polymerization was employed, if the core particle size were controlled, the size of the two-stage latex would depend on the amount of the shell monomer. As expected, the size of the core-shell latexes also changed slightly over the size range of 211-220 nm, as listed in Table IV. The outer-shell thickness was constant at about 15 nm. This thickness of the shell polymer was considered to be sufficient to prevent particle coalescence during blending. Figure 1(a,b)shows the size distribution of the D10 core latex and the resultant core-shell latex. As shown, the size distributions were considerably narrow and monodisperse.

These results mean that the core latexes and core-shell latexes having narrow and monodisperse size distributions could be prepared by varying the refractive index of the core phase. This similar size and monodisperse size distribution of the final core-shell latexes are important in that the impact strength seriously depends on the size and the dispersity of the rubber domain in the matrix polymer.^{5,7,21-23} Therefore, as the poly(BA-co-St)/PMMA core-shell latexes prepared in this study showed both a similar size and a monodisperse size distribution, we possibly ob-



Figure 1 Particle-size distribution for (a) D10 core latex and (b) its core–shell latex.

served the tendency of the impact strength of the toughened PMMA with the amount of DVB in the core phase and the content of the composite particles in the matrix PMMA, excluding the effect of the size and dispersity of the composite particles on the impact strength of the toughened PMMA.

Tendency of Impact Strength

The toughened PMMA samples were prepared by blending the core-shell composite particles with

PMMA chips. Figure 2 shows scanning electron micrographs for the toughened PMMA samples with an incorporating amount of DVB in the core [(a) 0.5 wt %, (b) 1.0 wt %, (c) 2.0 wt %, and (d) 3.0 wt %.] The content of the composite particles in the matrix PMMA was 20 wt \%. In all the micrographs, the core–shell composite particles were embedded well in the matrix PMMA and showed good dispersity, irrelevant of the amount of DVB. This suggested that these composite particles had good shell compatibility with the matrix PMMA.

Figure 3 shows the result of the Izod impact test as a function of the amount of DVB in the core phase at room temperature. The content of the composite particles was fixed at 20 wt % in the matrix PMMA. The improvement of the impact strength could be observed for all samples prepared in this study. For all samples except the pure PMMA (0.0 wt % DVB in Fig. 3), the appearance of a whitened zone of the fracture surface occurred. As is well known, this stress-whitening is obviously connected with an energy-absorbing yield process in the toughened PMMA, which contributes to the increase of the impact strength.⁵

The improvement of the impact strength was predominant especially for S05-20 and S10-20. The impact strength was increased about three times, compared with that of the pure PMMA. However, the impact strength was rather decreased with increase of the amount of DVB. Related to this trend, it was assumed that the DVB used to enhance the refractive index of the core phase eventually increased the crosslinking density of the core phase, which gave rise to the loss of the elastic properties of the core phase. To observe the elastic properties in detail, the flexural modulus and the deflection at break were measured by a three-point bending test and are shown in Figure 4. Overall, the flexural modulus for the toughened PMMA blended with the composite particles having different amounts of DVB was decreased dramatically, compared with that of the pure PMMA. However, it should be noted that the flexural modulus increased as the amount of DVB in the core increased. The deflection at break also showed the same trend: When the amount of DVB was high, the deflection at break was also decreased. These results of the flexural modulus and the deflection at break supported the assumption that the increase of the amount of DVB consequently made the rubbery core phase lose its elastic properties.

Figure 5 shows the impact strength of the toughened PMMA in relation to the content of the



Figure 2 SEM of the fracture surface of the toughened PMMA with an incorporating amount of DVB in the core phase: (a) 0.5 wt % DVB; (b) 1.0 wt % DVB; (c) 2.0 wt % DVB; (d) 3.0 wt % DVB. The content of the composite particles in the matrix PMMA was fixed at 20 wt %.

core-shell composite particles. The S10-20 sample was selected. The impact strength was increased, as the content of the core-shell composite particles increased. The extent of the stresswhitening of the fracture surface also increased with increase of the content of the composite particles. This seemed to be attributed to increase of the rubber phase in the matrix PMMA.⁵ For further examination of the elastic properties of the toughened PMMA in relation to the composite particle content, the flexural modulus and the deflection at break were measured and are shown in Figure 6. It could be easily seen that the elastic property increased as the content of the coreshell composite particles increased along with a decrease of the flexural modulus and an increase of the deflection at break.

Tendency of Transparency

The transparency of the toughened PMMA was observed by measuring the absorbency of all the samples with UV-visible spectroscopy at room temperature. The transmittance was calculated by eq. (1). The transparency for the toughened PMMA could be determined by converting the measured transmittance to the percentage of the transmittance of the pure PMMA.

Figure 7 shows the results determined by the above-mentioned method. S10-20 showed the best transparency. Ninety-five percent of the transmittance could be obtained for the toughened PMMA blended with the core-shell composite particles made of the D10 core series, which is significantly transparent. On the contrary, the transparencies showed the result, rather, of a de-





Figure 3 Impact strength for the toughened PMMA prepared with an incorporating amount of DVB in the core phase. The content of the composite particles in the matrix PMMA was fixed at 20 wt %. The plot of 0 wt % DVB was of the pure PMMA not containing any composite particles.

crease for the toughened PMMAs blended with the core-shell composite particles above and below the amount of DVB of the D10 core series. These results showed good agreement with those calculated in Table III; the D10 core series dis-



Figure 4 (-**■**-) Flexural modulus and (-•-) deflection at break for the toughened PMMA prepared with an incorporating amount of DVB in the core phase. The content of the composite particles in matrix PMMA was fixed at 20 wt %. The plot of 0 wt % DVB was the pure PMMA not containing any composite particles.



Figure 5 Impact strength for the toughened PMMA prepared with a composite particle content in matrix PMMA. S10-20 was selected.

played the most similar refractive index to that of the pure PMMA. However, the difference of the refractive index between the toughened PMMA and the pure PMMA was increased by varying the amount of DVB around the D10 core series. This explained well that the matching of the refractive index of the core phase with PMMA was one of the key factors in preparing the toughened PMMA which is transparent.



Figure 6 (-**I**-) Flexural modulus and (-**O**-) deflection at break for the toughened PMMA prepared with the composite particles contained in the matrix PMMA. S10-20 was selected.



Figure 7 Transmittance of the toughened PMMA prepared with an incorporating amount of DVB in the core phase. The content of the composite particles in the PMMA matrix was fixed at 20 wt %.

CONCLUSIONS

In this study, poly(BA-co-St)/PMMA two-layer core-shell composite particles were prepared by two-stage consecutive emulsion polymerization. Thus, the process of the preparation of core-shell composite particles could be simplified, compared with commercial three-layer core-shell composite particles. In preparing the core latexes, DVB was employed to control the refractive index of the final core-shell composite particles. Core-shell composite particles prepared with these core latexes showed narrow and monodisperse particlesize distributions. The impact strength was about three times larger than that of the pure PMMA for the samples of S05-20 and S10-20. However, the impact strength of the toughened PMMA was somewhat decreased, as the amount of DVB was increased. This was because the elastic properties of the core phase were reduced with increase of the DVB, acting as a crosslinking agent. The impact strength was also increased, as the content of the core-shell particles increased. The toughened PMMA with the core-shell composite particles made of the D10 core series showed the best transparency. However, the transparency was rather decreased, as the difference of the refractive index between the core phase and the pure PMMA increased. The tendency of the transparency measured matched well with the result calculated. This suggested that matching the refractive index of the core phase with PMMA played an important role in keeping the transparency of the toughened PMMA.

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