

Core–Shell Particles Designed for Toughening Epoxy Resins. I. Preparation and Characterization of Core–Shell Particles

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ABSTRACT: A two-stage, multistep soapless emulsion polymerization was employed to prepare various sizes of reactive core–shell particles (CSPs) with butyl acrylate (BA) as the core and methyl methacrylate (MMA) copolymerizing with various concentrations of glycidyl methacrylate (GMA) as the shell. Ethylene glycol dimethacrylate (EGDMA) was used to crosslink either the core or shell. The number of epoxy groups in a particle of the prepared CSP measured by chemical titration was close to the calculated value based on the assumption that the added GMA participated in the entire polymerization unless it was higher than 29 mol %. Similar results were also found for their solid-state ^{13}C -NMR spectroscopy. The MMA/GMA copolymerized and EGDMA-crosslinked shell of the CSP had a maximum glass transition temperature (T_g) of 140°C, which was decreased with the content of GMA at a rate of $-1^\circ\text{C}/\text{mol } \%$. However, the shell without crosslinking had a maximum T_g of 127°C, which decreased at a rate of $-0.83^\circ\text{C}/\text{mol } \%$. The T_g of the interphasial region between the core and shell was 65°C, which was invariant with the design variables. The T_g of the BA core was -43°C , but it could be increased to -35°C by crosslinking with EGDMA. The T_g values of the core and shell were also invariant with the size of the CSP. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 2069–2078, 1998

Key words: core–shell particles; emulsion polymerization; glycidyl methacrylate; epoxy resin; toughness

INTRODUCTION

Epoxy resins are brittle in nature. Researchers usually blend them with liquid rubber to improve their toughness.¹ The toughening mechanism has been studied well and associated with phase separation during cure by which a randomly dispersed rubber-rich phase was separated from the epoxy-rich mother phase.^{2–6} Although the toughness of the epoxy resins can be significantly improved, their high temperature properties are sacrificed

due to the epoxy-rich mother phase plasticized by the dissolved liquid rubber.

Recently, core–shell particles (CSPs) with rubbery-type materials as a core were prepared by two-stage emulsion polymerization and were employed to toughen epoxy resins.^{7–10} The samples were prepared by directly dispersing the CSP in the epoxy matrix without undergoing phase separation, so that no rubbery-type molecules dissolved in the epoxy matrix. However, the size of CSPs, their contents, and the interfacial bonding with the epoxy matrix strongly affect their toughening behaviors. For example, the particle size should be large enough to allow their deformation energy to be higher than their interfacial bonding to the epoxy matrix. Otherwise, no cavitation will occur during fracture.¹¹ Once the cavitation oc-

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curs, if the interparticle distance is short enough, the following local yielding would produce a thin matrix ligament.¹² As a result, the formation of a thin matrix ligament transforms the local material in the crack tip from brittle to tough thus increasing the fracture toughness.

The CSPs size and their interfacial properties with the epoxy resins can be designed and prepared by emulsion polymerization techniques. In the first part of this study, we used a two-stage, multistep soapless emulsion polymerization to prepare a variety of butyl acrylate/methyl methacrylate (BA/MMA) CSPs. The CSPs were copolymerized with various concentrations of glycidyl methacrylate (GMA) in the shell area to provide reactive epoxy groups. Ethylene glycol dimethacrylate (EGDMA) was used to crosslink either the BA core or MMA shell in the CSP. In the second part of this study, the prepared CSPs were employed as a toughening agent for the diglycidyl ether of bisphenol A/meta-phenylene diamine (DGEBA/MPDA) epoxy systems. Their toughening effect was evaluated as a function of the crosslinking state of the CSP, the number of epoxy groups in a particle, the particle size, and the content of the CSP in the epoxy resins. Then the toughening mechanism was investigated with respect to the observed plastic flow of the epoxy matrix surrounding the cavitated CSP.¹³

EXPERIMENTAL

Materials

MMA, BA, and GMA monomers (Janssen Chimica) were purified by vacuum distillation. EGDMA crosslinking agent (Merck), potassium persulfate (KPS) initiator (Mallinckrodt Inc.), and hydroquinone inhibitor (Nacalei Tesque Inc.) were used as received.

Sample Preparation

Two-Stage Soapless Emulsion Polymerization to Prepare BA/MMA CSP

Table I shows the recipes of the first-stage soapless emulsion polymerization to prepare the BA cores with and without EGDMA as the crosslinking agent, which are designated as C-BA and L-BA, respectively. The BA monomer and/or EGDMA crosslinking agent and the deionized water were loaded in a batch-type reactor with stirring

Table I Recipes of First-Stage Soapless Emulsion Polymerization for Preparation of BA Core with and without EGDMA Crosslinking Agent

Component	L-BA	C-BA
BA (g)	30	30
Water (g)	820	820
KPS (g)	0.87	0.87
EGDMA (g)	0	0.6

under nitrogen. The reactor was then heated to 70°C in a water bath. Then the KPS initiator was added, and the reaction was maintained at 70°C for 1 h. The conversion of soapless emulsion polymerization at this stage was > 95%.

The prepared BA-core particles were used as a seed for the second stage of the emulsion polymerization. The recipes to prepare a variety of CSP particles are listed in Table II. The C series in Table II are product symbols for shell-crosslinked CSPs and the L series are for core-crosslinked CSPs. The general preparation procedure is as follows: 780 g of solution taken from the first stage was loaded to a batch reactor; then the desired amount of MMA, GMA, and/or EGDMA crosslinking agent was added. The solution was maintained at room temperature for 12 h under agitation, allowing the monomers to swell the seeds. After that, the reactor was heated to 70°C under nitrogen with a stirring speed of 300 rpm. KPS was then added to the solution and reacted at 70°C for 2 h. At the end of the reaction, most of the CSP products had a conversion of over 95%, except those with 100 mol % GMA.

Two-Stage Multistep Soapless Emulsion Polymerization to Prepare Large CSP

Table III lists the recipes of the first-stage soapless emulsion polymerization to prepare the different sizes of large BA cores, designated as LBA-1, LBA-2, and LBA-3. In general, BA and deionized water were added to the LBA latex and stirred for 12 h at room temperature. After that, the solution was heated to 70°C under nitrogen with a stirring speed of 300 rpm. Then the KPS initiator was added. LBA-1 latex was obtained after the solution was reacted for 2 h at 70°C. Similar steps were also used to prepare the LBA-2 and LBA-3 latexes.

Table IV lists the recipes of the second-stage

Table II Recipes of Second-Stage Seeded Emulsion Polymerization for Preparation of Variety of BA/MMA CSPs with Either Crosslinked Core or Crosslinked Shell

Component	C Series						L Series					
	C0	C1	C2	C3	C4	C5	C6	L0	L1	L2	L3	L4
L-BA (g)	780	780	780	780	780	780	780	—	—	—	—	—
C-BA (g)	—	—	—	—	—	—	—	780	780	780	780	780
MMA (g)	27.5	25.5	23.5	21.5	19.5	15.5	0	27.5	25.5	23.5	21.5	15.5
GMA (g)	0	2	4	6	8	12	27.5	0	2	4	6	12
(mol %) ^a	(0)	(5)	(10)	(16)	(22)	(29)	(100)	(0)	(5)	(10)	(16)	(29)
EGDMA (g)	0.6	0.6	0.6	0.6	0.6	0.6	0.6	—	—	—	—	—
KPS (g)	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2

^a Molar percentage of GMA.

emulsion polymerization to prepare various sizes of the C3-series CSPs with a crosslinked shell. Similar to the preparation procedure of the C3 CSP latex, the LBA-1, LBA-2, or LBA-3 latexes were loaded with MMA, GMA, and EGDMA cross-linking agent in a batch reactor and stirred at room temperature for 12 h. The solutions were then heated to 70°C under nitrogen with a stirring speed of 300 rpm. C3-1, C3-2, and C3-3 latexes were obtained after reaction with KPS at 70°C for 2 h.

Tests

Monomer contents in the seeds of the second-stage solution prior to polymerization but after swelling the seeds for various times at room temperature were measured by the following method: the samples were taken from the solution at various swelling times and then centrifuged at 10°C to remove the monomer droplets in the latex. After that, they were divided into two parts with equal weight. One part of the samples was added to the hydroquinone/CH₃OH (0.25 g/100 mL) so-

lution to stop the reaction and then vacuum dried at 60°C to a constant weight (*P*). The other part of the sample was added to the KPS (0.2 g/100 mL) solution and then reacted at 100°C for 72 h. After that, it was dried at 60°C to a constant weight (*Q*). Then the monomer contents in the seeds and in the water phase could be calculated separately. The monomers diffused out of the water, and the swelling of the seeds per unit weight of water, X_p (g/g H₂O), was calculated by

$$X_p = \frac{Q - P}{P} \times \frac{S}{W} \quad (1)$$

where *S* is the weight of seeds in the solution (g) and *W* is the weight of water in the solution (g). In addition, the monomers remained in the water phase, X_w (g/g H₂O), and were calculated by

Table III Recipes of First-Stage Soapless Emulsion Polymerization for Preparation of Various Sizes of BA Cores for Large CSPs

Component	LBA-1	LBA-2	LBA-3
L-BA (g)	283	—	—
LBA-1 (g)	—	283	—
LBA-2 (g)	—	—	283
BA (g)	20	20	20
Water (g)	547	547	547
KSP (g)	0.2	0.2	0.2

Table IV Recipes of Second-Stage Soapless Emulsion Polymerization for Preparation of Various Sizes of C3-Series CSPs

Component	C3 or			
	C3-0	C3-1	C3-2	C3-3
L-BA (g)	780	—	—	—
LBA-1 (g)	—	780	—	—
LBA-2 (g)	—	—	780	—
LBA-3 (g)	—	—	—	780
MMA (g)	21.5	21.5	21.5	21.5
GMA (g)	6	6	6	6
(mol %) ^a	(16)	(16)	(16)	(16)
EGDMA (g)	0.6	0.6	0.6	0.6
KPS (g)	0.2	0.2	0.2	0.2

^a Molar percentage of GMA.

$$X_w = (M - \frac{Q - P}{P} \times S) / W \quad (2)$$

where M is the weight of the monomer used to swell the seeds (g).

The content of the epoxy groups in the CSPs was measured by IR and solid-state ^{13}C -NMR spectroscopies and chemical titration of the epoxy groups. IR spectra were recorded on a Hitachi model 270-30 spectrometer with dried CSP samples in the form of KBr disks. The solid-state ^{13}C -NMR spectra were recorded on a Bruker model MSL200 spectrometer equipped with a cross-polarization accessory by which a cross-contact time of 1 ms was set for the transfer of proton polarization to the carbon nuclei. Proton decoupling was achieved at a frequency of 50.4 MHz. A magic angle of 54.7° was set with a spin rate of 4 kHz at 25°C . The chemical titration of the epoxy groups was conducted by the following method: 0.5 g of the dried CSPs was suspended in 20 mL of HCl/acetone (1.2/80 by volume) solution. After 10 min, at which time the epoxy groups were fully opened by the HCl, the solution was titrated with 0.1N NaOH to determine the number of epoxy groups.

The particle morphology and size of the CSPs were investigated by transmission electron microscopy (TEM). In general, a drop of CSP latex was put in a carbon coated copper grid and vacuum dried. After that, a Hitachi model H-600 TEM microscope was used to investigate the CSPs and measure their size. The core-shell structure was investigated by TEM with the CSP samples embedded in the DGEBA/EDA epoxy resin, and they were microtome sectioned by the usual method.¹⁴ The sectioned specimens were stained by exposing them to the vapor from the ruthenium tetroxide/tetrahydrofuran (RuO_4/THF) solution (1 g/L) at room temperature for 72 h and then they were examined by TEM.

Differential scanning calorimetric (DSC) plots of the vacuum dried CSPs were recorded on a Du Pont model 910 differential scanning calorimeter by dynamic scanning from -100 to 300°C at a scanning rate of $10^\circ\text{C}/\text{min}$. The glass transition temperature (T_g) of the core, shell, and its interphasial regions in a CSP were determined from the corresponding inflection points of the heat flow curve in the DSC plots.

RESULTS AND DISCUSSION

In the preparation of CSPs, the saturation of monomers in the swelled BA seeds during the sec-

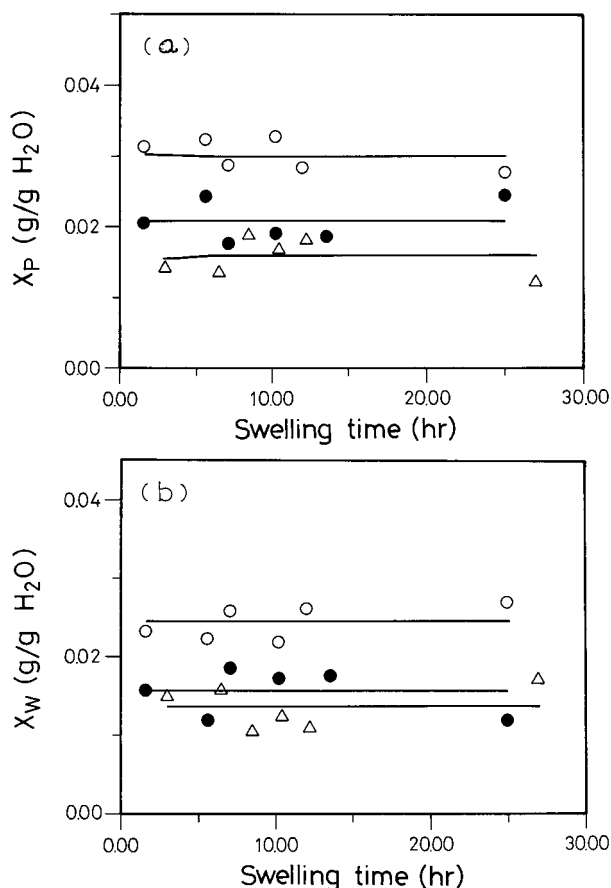


Figure 1 MMA/GMA/EGDMA (77 : 21 : 2 by weight) monomer contents (a) in the BA seeds and (b) in the water phase versus swelling time at room temperature for various monomer/seed weight ratios: (○) 1.5, (●) 1.0, and (△) 0.8.

ond-stage soapless seeded emulsion polymerization was desired. This was because the polymerization usually takes place in the shell region and the dissolved monomers inside the core will diffuse out to supply the reaction in the shell once the monomer droplets in the latexes are depleted.^{15,16} To estimate the time to swell the BA seeds by the MMA/GMA/EDGMA (77 : 21 : 2 by weight) monomers, we measured the monomer contents in the seeds (X_p) at various swelling times at room temperature; the results are shown in Figure 1(a).

The monomer concentration in the BA seeds was saturated rapidly at less than 1 h of swelling time. By changing the monomers/seed weight ratio from 0.8×1.0 to $1.5 : 1$ in preparation for the second-stage seeded emulsion solution, the saturated contents of the monomers in the BA seeds

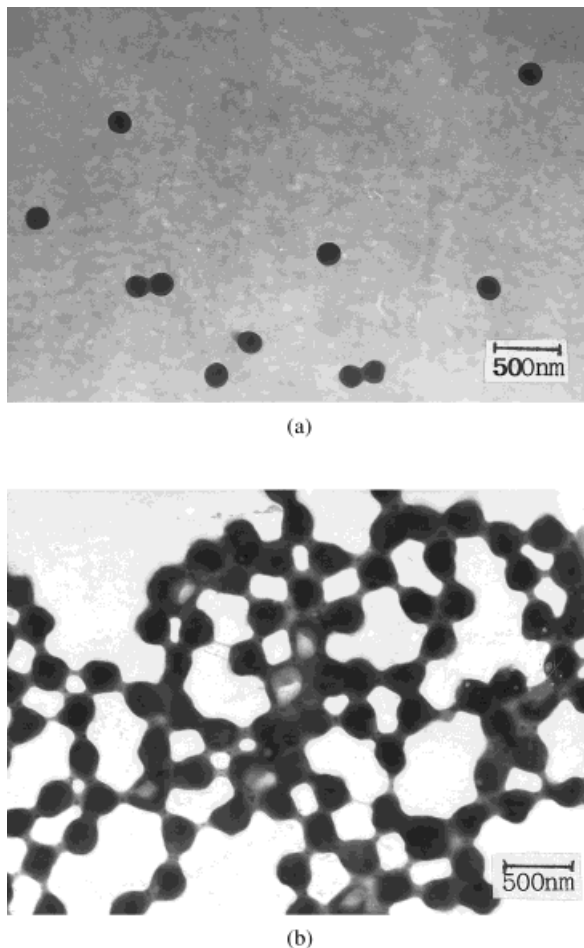


Figure 3 TEM micrographs of vacuum dried (a) C0 and (b) C6 CSP.

The intensity of the resonance peak of C₁ appearing at 66 ppm was increased by increasing the GMA content in the CSPs. However, by dividing their intensity with that of the inert peak of C=O carbon atoms and plotting their ratio versus the GMA content, we found that the data deviated from the linearity after the GMA content was higher than 29 mol % as shown in Figure 5. The results indicate that some of the GMA monomers did not join the polymerization in the shell region of the CSPs. Similar results were also found for the resonance peak of C₂ that appeared at 48 ppm. The resonance peak of C₃ in the epoxy groups of the CSPs is overlapped by that of the quaternary carbons in the main chains of the acrylic polymers.

Figure 6 shows the chemical titration results of the epoxy groups for the C-series CSPs. Similar to the results of the solid-state ¹³C-NMR, the num-

ber of epoxy groups in a CSP, N_e , began to deviate from the theoretical value after the GMA content was higher than 29 mol %. The theoretical value was calculated by the following equation, based on the assumption that the added GMA participated in the entire polymerization in the shell region:

$$N_e = \frac{\pi d^3 \rho n_G N}{6W} \quad (3)$$

where d is the average diameter of CSP particles, ρ is the density of the CSP, n_G is the moles of GMA component used in the recipes, N is Avogadro's number, and W is the weight of the total ingredients (except water) in the recipes. According to the titration results, when 100 mol % GMA was

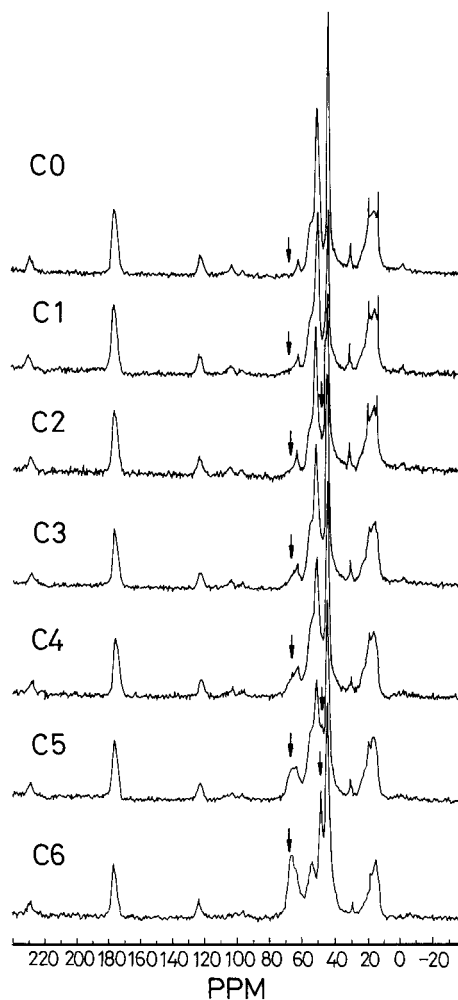


Figure 4 Solid-state ¹³C-NMR spectra of the C-series CSP.

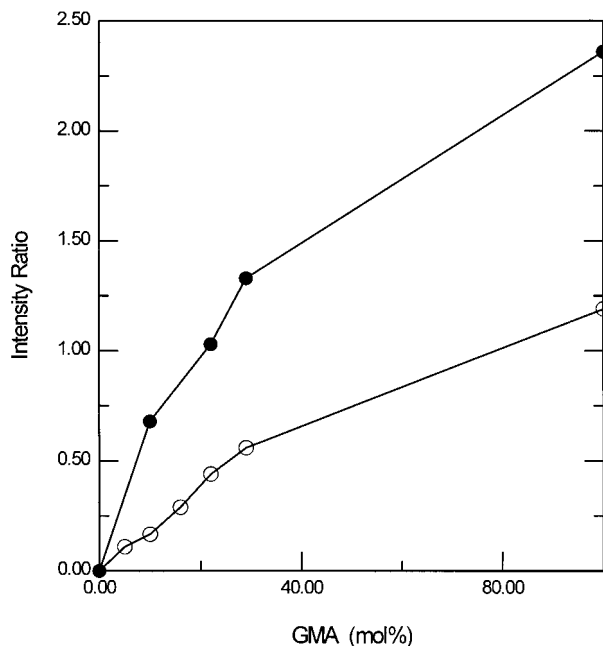


Figure 5 Intensity ratio of (○) $I_{C1}/I_{C=O}$ and (●) $I_{C2}/I_{C=O}$ in the solid-state ^{13}C -NMR spectra of the C-series CSP versus the GMA contents used to prepare the CSP.

used in the second stage of the soapless emulsion polymerization, about 40% of the GMA monomers did not join the reactions, indicating that the reactivity of GMA is much lower than that of MMA if it is used alone. Thus, a high content of GMA is not a good choice for preparing a reactive CSP, because it not only lowered the T_g of the CSP but also lowered the degree of conversion in the shell regions.

Thermal Properties of CSP

Figure 7 shows the DSC spectrum of the L3 CSP, a reactive CSP with a crosslinked BA core, and an MMA/GMA copolymerized shell. It can be seen that the T_g of the crosslinked BA core and MMA/GMA copolymerized shell are -35 and 113°C , respectively. In addition, another transition appeared at 65°C , which was believed to be the T_g of the core-shell interphase region where polymers interpenetrated with each other. The epoxy groups started to react after the glass transition of the shell region and had a reaction peak at 215°C . On the other hand, for the C3 (or C3-0) CSP, which has the same composition as L3 but with a EGDMA crosslinked shell instead of a crosslinked core, the T_g of the core region was at

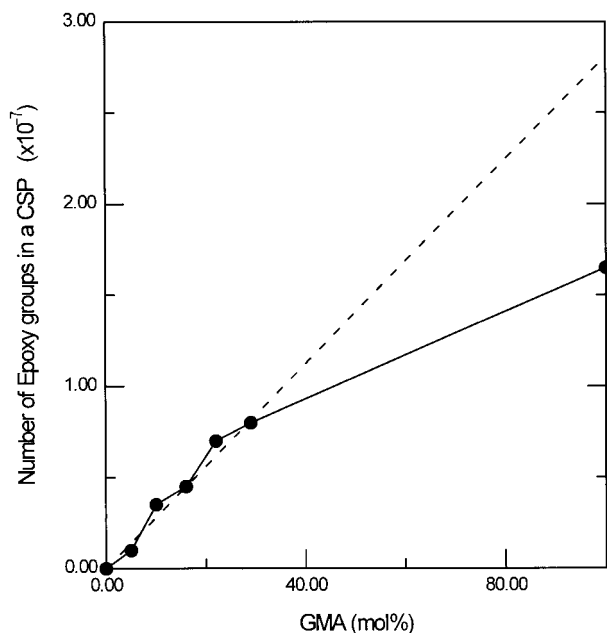


Figure 6 Number of epoxy groups in a particle of the C-series CSP (—) measured by the chemical titration and (---) estimated by eq. (3) as a function of GMA content in the formulations to prepare the shell of the CSP.

-43°C , which is lower than that of L3, but the T_g of the shell region at 122°C was higher as shown in Figure 8. Apparently the crosslinking increased the T_g . However, the T_g in the interphase region of the CSP for C3 was 65°C , which was not changed by switching the crosslinking area from

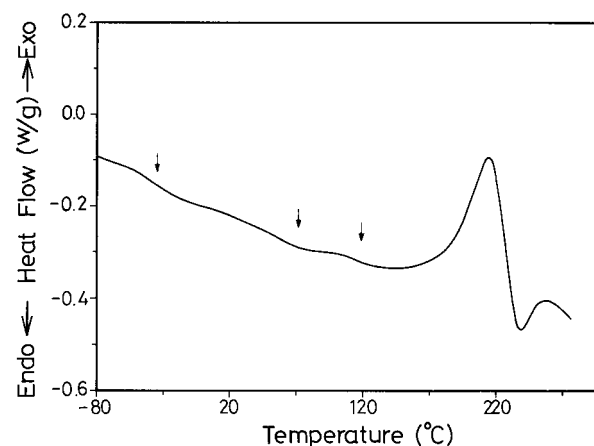


Figure 7 DSC spectrum of the L3 CSP. Arrows denote the glass transition regions.

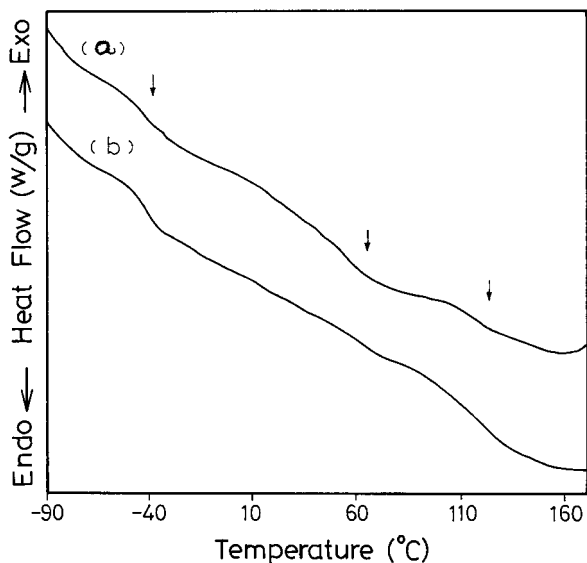


Figure 8 DSC spectra of (a) C3-0 and (b) C3-1 CSP. Arrows denote the glass transition regions.

core to shell. Figure 9 shows the T_g of the shell region of the C-series and L-series CSPs as a function of their GMA content. As seen in the figure, both T_g s were decreased with increasing GMA content. However, the decreasing rate for the C3 series was approximately -1°C per molar percentage of GMA whereas it was -0.83°C for the L3 series.

By using the two-stage, multistep soapless emulsion polymerization to prepare the different sizes of the C3-series CSPs from C3-0 (i.e., C3) to C3-3, their particle size was increased from 0.25 to $0.6\ \mu\text{m}$ in diameter with a near constant rate of 1.34 per size promotion step as seen in Figure 10. However, if the density of the CSP was kept constant and the monomers all participated in the core-shell polymerization, the size should change from 0.25 to $0.75\ \mu\text{m}$ with an increasing rate of $3^{1/3} = 1.442$. The difference between the sizes might be due to the secondary nucleation in which the dissolved monomers in the aqueous phase were initiated, polymerized, and formed the particles by themselves during the multistep emulsion polymerization. Smaller particles generated by the secondary nucleation were indeed observed around the prepared CSP as seen in Figure 9(c,d).

The DSC spectrum of C3-1 shows that the glass transition of the BA core and MMA/GMA copolymerized shell took place at the same tem-

perature as those of C3-0, but they involved more of a change in the heat capacity as seen in Figure 8. Although the glass transition of the interphase region took place at the same temperature between the two CSPs, the heat capacity of C3-1 is smaller than that of C3-0. Because the magnitude of the change of the heat capacity in the glass transition depends on the content of involved polymer segments, the interphase region per unit weight of C3-1 should be less than that of the C3-0. The similar glass transition temperature of the C3-0 and C3-1 CSPs in the BA core, MMA/GMA shell, and their interphase regions indicates that their characteristics (chemical structure, molecular weight, etc.) made no difference.

To investigate the core-shell structure, a C3-1 CSP was embedded in the DGEBA/EDA epoxy resin and microtome sectioned. After that the specimen was exposed to the vapor from the RuO_4/THF solution ($1\ \text{g/L}$) for staining and observed by TEM. Figure 11 shows the stained morphology of the C3-1 CSP; the BA core appears as a gray region, and the MMA/GMA copolymerized shell appears as a dark region. The staining reaction of RuO_4 was reported to associate with the crosslinking reactions of ester

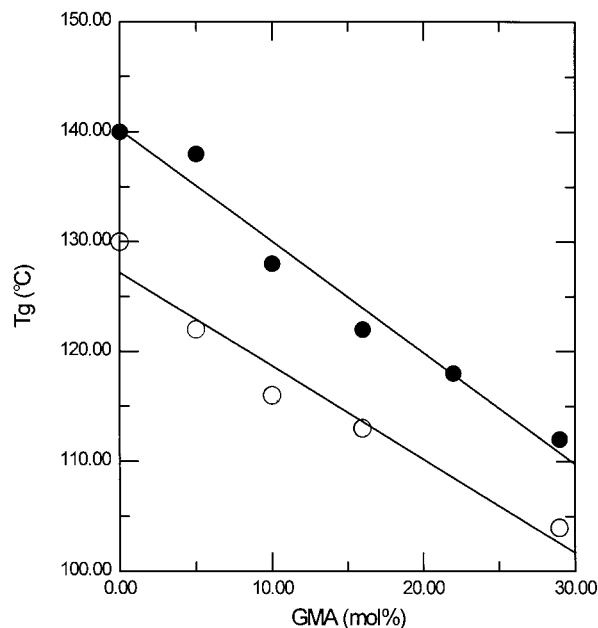


Figure 9 T_g of the shell regions of the (●) C3-series and (○) L3-series CSP as a function of GMA content in the formulations to prepare the shell of the CSP.

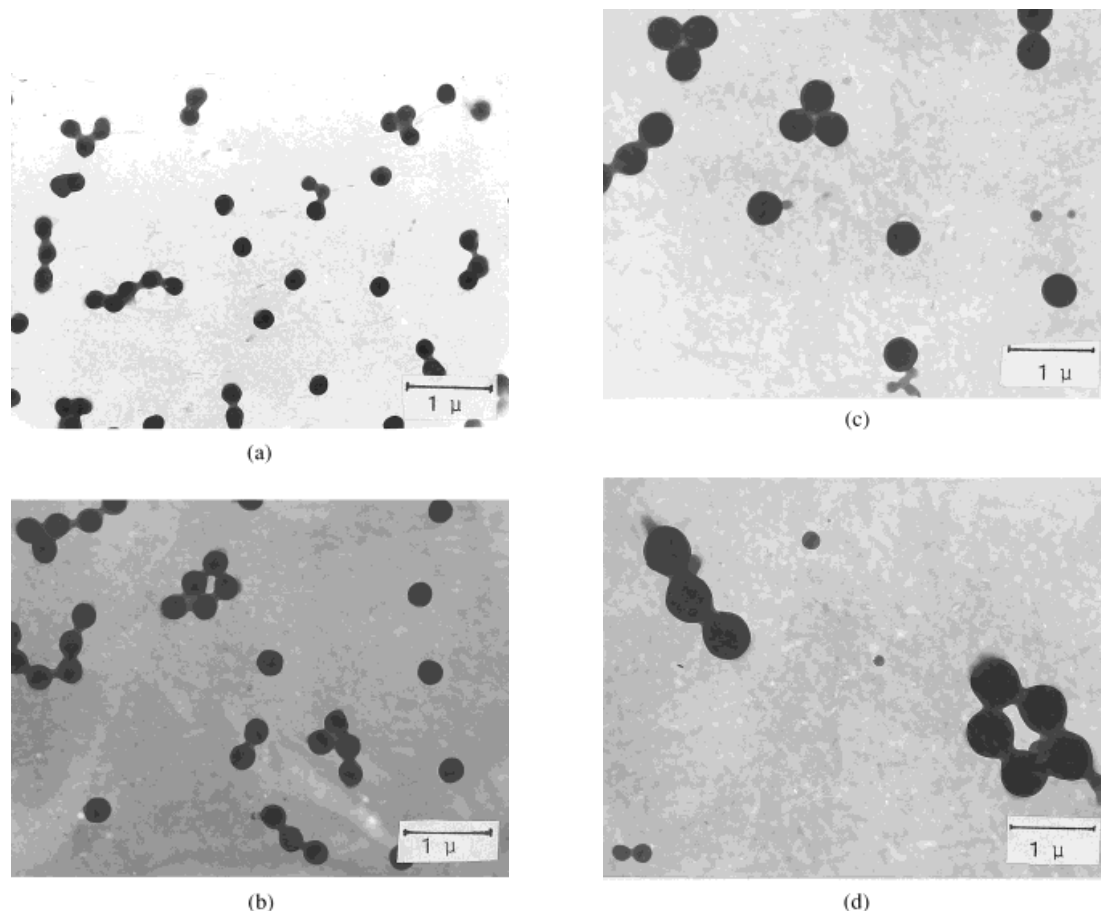


Figure 10 TEM micrographs of vacuum dried (a) C3-0, (b) C3-1, (c) C3-2, and (d) C3-3 CSP.

groups of the acrylate polymers.¹⁹ Thus, the contrast between core and shell should result from the different concentrations of the ester groups between the BA polymerized core and the MMA/GMA copolymerized shell. Besides, the size of the microtome-sectioned C3-1 CSP was 10% smaller than that of the free-dried C3-1 particles shown in Figure 10, which was believed to result from the fact that the shrinkage of the epoxy matrix during cure compressed the embedded CSPs.

CONCLUSIONS

In the beginning of the second-stage seeded emulsion polymerization, the BA core soaked up 55 wt % of the total input of the MMA/GMA/EDGMA monomers independently of the input ratio of the

monomers to seed. When the GMA content was less than 29 mol %, the number of epoxy groups in the CSP measured by chemical titration was equivalent to the calculated value, based on the assumption that the added GMA participated in the entire polymerization. A higher content of GMA lowered the conversion of polymerization in the shell region. Similar results were also found in the solid-state ¹³C-NMR spectroscopy of the CSP. The T_g of the MMA/GMA copolymerized shell in a CSP was decreased with the content of GMA, whereas the T_g of the interphase region between the core and shell was invariant. The T_g of the BA core was -43°C , but it could be increased to -35°C if it was crosslinked with EG-DMA. The T_g s of the core and shell were also invariant with the size of the CSP. In the multistep soapless emulsion polymerization, the particle size of C3 CSP was increased from 0.25 to 0.6 μm

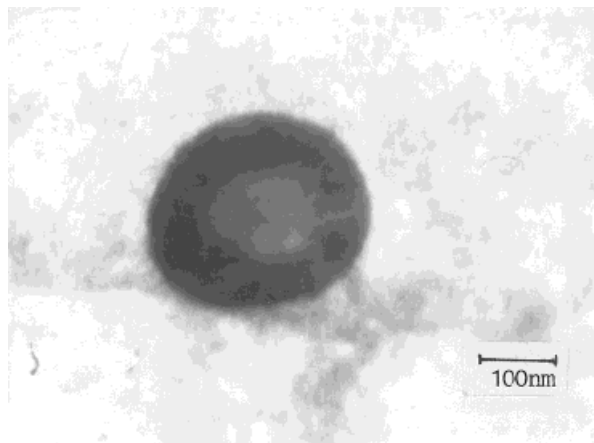


Figure 11 TEM micrograph of RuO_4 stained C3-1 CSP embedded in the epoxy resin, featuring the core-shell structure of the CSP.

in diameter at a near constant rate of 1.34 per size promotion step.

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