Core-Shell Particles Designed for Toughening the Epoxy Resins. II. Core-Shell-Particle-Toughened Epoxy Resins

KING-FU LIN, YOW-DER SHIEH

Institute of Materials Science and Engineering, National Taiwan University, Taipei, Taiwan 10617, Republic of China

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ABSTRACT: The diglycidyl ether of bisphenol A–*m*-phenylene diamine (DGEBA–M-PDA) epoxy resin was toughened with various sizes and amounts of reactive core-shell particles (CSP) with butyl acrylate (BA) as a core and methyl methacrylate (MMA) copolymerized with various concentration of glycidyl methacrylate (GMA) as a shell. Ethylene glycol dimethacrylate (EGDMA) was used to crosslink either core or shell. Among the variables of incorporated CSP indicated above, the optimal design was to obtain the maximum plastic flow of epoxy matrix surrounding the cavitated CSP during the fracture test. It could be achieved by maximizing the content of GMA in a shell-crosslinked CSP, the particle size, and the content of CSP in the epoxy resin without causing the large-scale coagulations. The incorporation of reactive CSP could also accelerate the curing reaction of epoxy resins. Besides, it was able to increase the glass transition temperature of epoxy resins if the particle size ≤ 0.25 μm and the dispersion was globally uniform. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 2313–2322, 1998

Key words: epoxy resins; core-shell particles; toughness; emulsion

INTRODUCTION

Core-shell particles (CSP) with rubbery-type materials as a core prepared by two-stage emulsion polymerization have been recently employed to toughen the epoxy resins.[1–4] There are several advantages, such as (1) to increase the toughness of epoxy resins without significant deterioration in thermomechanical properties[5]; (2) to reduce the internal stress of incorporated epoxy resins[6]; and (3) to cater easily to the design variables of CSP, such as changing the compositions, crosslinking status, and particle size of CSP.[7]

To optimize the design variables of CSP for maximizing their toughening effects, it is important to understand their toughening mechanism in the modified epoxy resins. It has been reported that among many toughening mechanisms of incorporating rubber particles documented in the literature, shear yielding and cavitation to absorb the strain energy are the major reasons to increase the toughness of epoxy resins.[8–11] Others were regarded as the minor reasons. Since the extent of local deformation of materials under stress in the crack tip are strongly dependent on the local texture of epoxy resins, the characteristics of incorporated CSP, such as the particle size, interphasial bonding to the epoxy matrix, and their content, will be the key factors to regulate the toughening performance. Moreover, those factors would also affect the curing and thermomechanical properties of epoxy resins. Nevertheless, researchers have paid little attention to those issues.

In the first part of this study, we have employed a two-stage but multistep emulsion polymerization to prepare various sizes of the reactive CSP with butyl acrylate (BA) as a core

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Correspondence to: K.-F. Lin.

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Table I Recipes of First-Stage Soapless Emulsion Polymerization for The Preparation of BA Core With and Without EGDMA Crosslinking Agent

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

and methyl methacrylate (MMA)–glycidyl methacrylate (GMA) copolymers in various composition as a shell.[12] Ethylene glycol dimethacrylate (EGDMA) was used to crosslink either the core or shell. In the second part of this study, we have employed those CSP particles to toughen the diglycidyl ether of bisphenol A–meta-phenylene diamine (DGEBA–MPDA) epoxy systems. Their effects on the curing, thermomechanical properties, and fracture toughness of the epoxy resins were investigated in terms of their reactivity (the content of GMA), crosslinking status, particle size, and their contents in the epoxy resins.

EXPERIMENTAL

Materials

The DGEBA difunctional epoxy resin used was Shell's EPON 828 with an epoxy equivalent weight (EEW) of 193 g/mol, determined by titration. *M*-phenyldiamine (MPDA, reagent grade, Janssen Chemica, Japan) was used as the curing agent for DGEBA. MMA, *n*-butyl acrylate (BA), and GMA monomers from Janssen Chimica were purified by vacuum distillation. The EGDMA crosslinking agent from Merck, potassium persulfate (KSP) initiator from Mallinckrodt Inc., and hydroquinone inhibitor from Nacalei Tesque Inc. were used for preparation of CSP.

Sample Preparation

1. Two-stage soapless emulsion polymerization to prepare a BA–MMA CSP is as follows. Table I shows the recipes of the first-stage soapless emulsion polymerization to prepare the BA cores with and without containing EGDMA crosslinking agent, which were designated as C-BA and L-BA, respectively. The prepared BA core particles were used as a seed for the second-stage emulsion polymerization. The recipes to prepare a variety of CSP particles were listed in Table II. C-series in the table are product symbols for shell-crosslinked CSP, and L-series are for core-crosslinked. The detailed preparation procedures have been provided in the first part of this study.[12]
2. Two-stage multistep soapless emulsion polymerization to prepare a large CSP is as follows. Table III lists the recipes of the first-stage soapless emulsion polymerization to prepare the various sizes of BA core. Table IV lists the recipes of the second-stage emulsion polymerization to prepare the C3-series CSP of various particle sizes. The detailed preparation procedures were also provided in the first part of this study.
3. CSP-incorporated epoxy resins were prepared as follows. The CSP particles were precipitated from the latex by adding small amount of NaCl aqueous solution. After

Table II Recipes of Second-Stage Seeded Emulsion Polymerization for the Preparation of a Variety of BA–MMA CSP With Either A Crosslinked Core or A Crosslinked Shell

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

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

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

being centrifuged to remove water, being washed with distilled water several times and being dried under vacuum at room temperature, they were ground to powder in order to eliminate the possible coagulation. The CSP powders were then mixed with DGEBA epoxy resin in various phr at 70°C until homogeneous (phr stands for parts of CSP powders per hundred parts of resin by weight). Afterwards, the MPDA curing agent was added to the CSP-incorporated epoxy resins in stoichiometric quantity with the epoxy groups in DGEBA resin (not including the epoxy groups in CSP) and stirred vigorously until homogeneous. The resins were then degassed under vacuum, cast to the molds, and cured according to the following cure cycle: 2 h at 75°C plus 2 h at 125°C plus 6 h at 175°C for the postcure.

Analytical Techniques

The curing exotherm of CSP-incorporated epoxy resins was measured by differential scanning calorimetry (DSC), using a DuPont 9900-910 model DSC analyzer. Tests were run at a heating rate of 10°C/min. Dynamic mechanical analysis (DMA) of the cured samples was performed in a DuPont model 983 DMA analyzer. Tests were run at a heating rate of 10°C/min and under a mixed mode of tensile and bending load at an oscillation amplitude of 0.1 mm peak to peak.

The fracture toughness of cured specimens was measured by compact tension specimen (CTS) techniques.[13] A precrack was cut at a temperature about 10°C above the T_g of the specimens by using the device suggested in the literature.[14] Fracture tests were performed in an Orientic TRM-IT model tensile tester at a crosshead speed of 0.5 cm/min. The value of linear elastic strain energy release rate, G_{IC}, in joules per metre square (J/m^2) was calculated from[13]

$$G_{IC} = Y^2 P_c^2 a / b^2 w^2 E \qquad (1)$$

where P_c is the load at crack initiation, a is the crack length, E is Young's modulus, w is the width of specimen, b is the thickness of specimen, and Y is the geometry factor given by

$$Y = 29.6 - 186\,(a/w) + 656(a/w)^2 - 1017\,(a/w)^3 + 639\,(a/w)^4$$

The experimental data of fracture toughness, that is, the G_{IC} value, were averaged from 6 tested specimens. Their fracture surface morphology was investigated by scanning and transition electron microscopies (SEM and TEM) and atomic force microscopy (AFM). Samples for SEM were gold-sputtered and investigated in a Philips model SEM-515 scanning electron microscope. Those for TEM were prepared by one-stage carbon–platinum (C–Pt) replication of fracture surface and investigated in a Hitachi model H-600 transmission electron microscope. A Digital Instrument model Nano Scope III atomic force microscope was also used to investigate the three-dimensional fracture surface morphology.

RESULTS AND DISCUSSION

Curing and Thermal Properties

Figure 1 shows the DSC spectra of DGEBA–MPDA, DGEBA–MPDA–10 phr C0, and DGEBA–

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

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

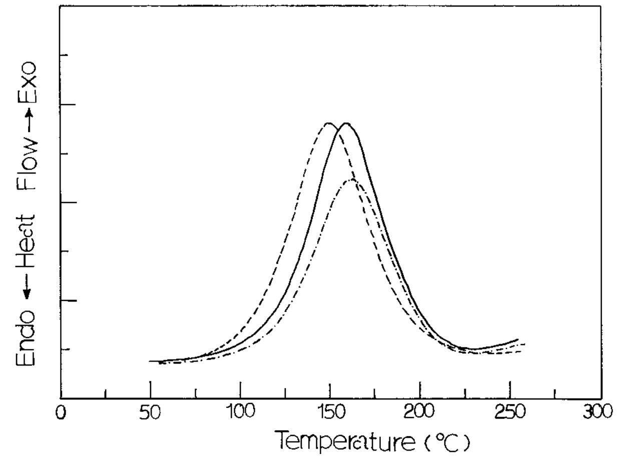


Figure 1 DSC spectra of (——) DGEBA–MPDA, (— · —), DGEBA–MPDA–10 phr C0, and (– – –) DGEBA–MPDA–10 phr C3 epoxy formulations.

MPDA–10 phr C3 epoxy formulations. It can be found that the CSP with epoxy groups did involve the curing reactions of DGEBA–MPDA while those without epoxy groups did not. The DSC results also indicate that the epoxy groups in CSP were more reactive than those in DGEBA because they accelerated the curing reactions. Figure 2 shows the changes in curing exotherm and peak temperature of DGEBA–MPDA–C3 as a function of the C3 CSP content. The initial increase of the curing exotherm indicates that the extent of curing reaction could be promoted by CSP rather than depressed. The less curing exotherm at high content of CSP was due to the fact that the amount of MPDA curing agent was decreased, and much less than the stoichiometric quantity with the total amount of epoxy groups (DGEBA + CSP) in the curing systems.

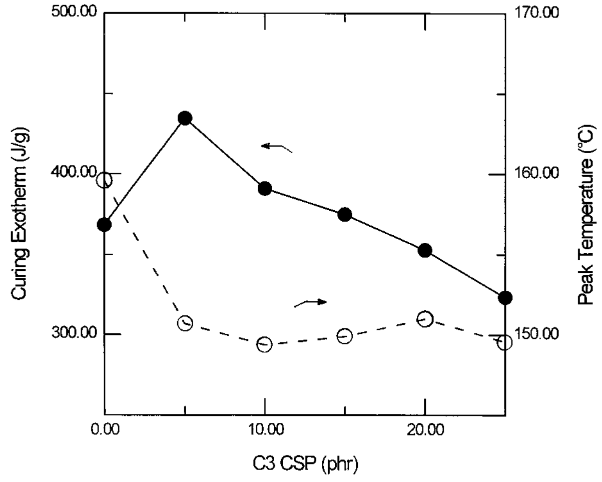


Figure 2 (●) Curing exotherm and (○) peak temperature of DGEBA–MPDA–C3 epoxy formulations as a function of the C3 CSP content.

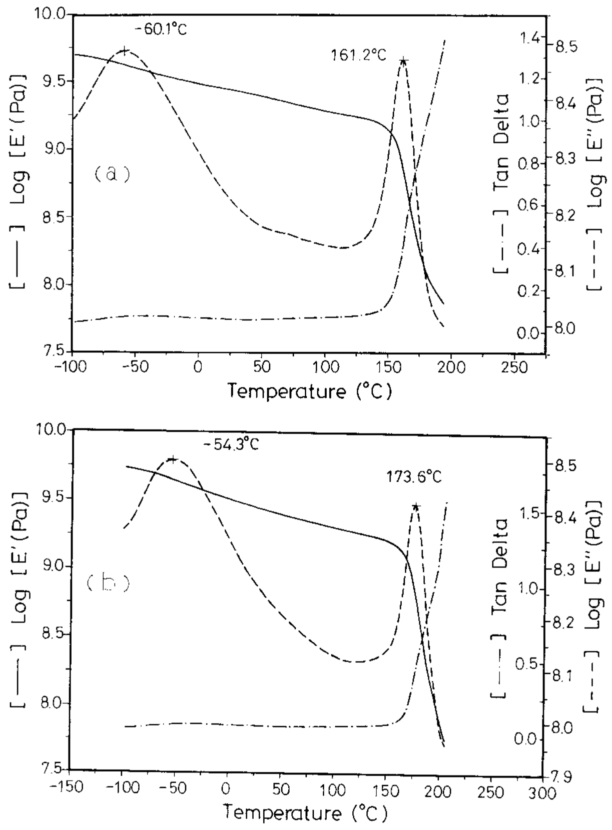


Figure 3 DMA spectra of cured (a) DGEBA–MPDA and (b) DGEBA–MPDA–10 phr C3 epoxy resins.

Figure 3 shows the DMA spectra of cured DGEBA–MPDA and DGEBA–MPDA–10 phr C3 epoxy resins, respectively. The glass transition temperature (T_g) of cured DGEBA–MPDA–10 phr C3 epoxy resins measured from the peak of loss modulus spectrum was 173.6°C higher than that of the neat DGEBA–MPDA epoxy resin by 12°C. The T_β peak was −54.3°C, also higher than the latter by 5.8°C. However, the width of T_g was not obviously changed by the addition of CSP. The increase of T_g was believed due to the different thermal expansion coefficient between the epoxy matrix and CSP. The T_g of BA core, interphasial region, and MMA–GMA–EGDMA crosslinked shell in a C3 CSP were measured as −43, 65, and 124°C, respectively,[12] which is much lower than the T_g of epoxy matrix. Thus, upon heating in DMA tests, the CSP particles expanded more than the epoxy matrix and introduced a compression force to the epoxy ma-

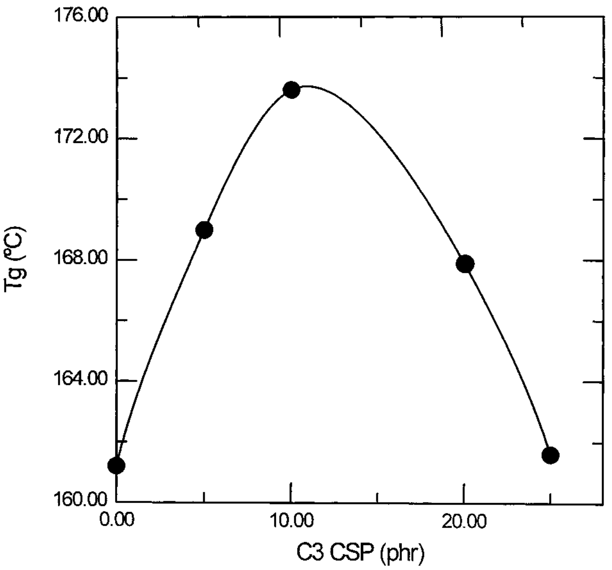


Figure 4 T_g of DGEBA–MPDA–C3 CSP epoxy resins as a function of the C3 CSP content.

trix. As a result, they depressed the increase of free volume of epoxy networks during heating and increased its T_g. The increase of T_g with the content of C3 CSP in DGEBA–MPDA was found until 10 phr was reached, and then the trend was reversed, as shown in Figure 4. The decrease of T_g with the content of C3 CSP after 10 phr was attributed to the incomplete cure of epoxy resin (see Fig. 3) and the coagulation of CSP particles, which had been found in their fracture surface of CTS specimens.

When we increased the size of C3 CSP from 0.25 to 0.6 μm (C3-0 to C3-3) by using multistep soapless emulsion polymerization, but maintained the same molar percentage of epoxy groups in the shell regions, both T_g and T_β of DGEBA–MPDA epoxy resins incorporating 10 phr C3-series CSP was decreased, as shown in Figure 5. In spite of that, the width of T_g and T_β peaks and entire DMA spectra were not significantly changed. Although the reason behind the decrease of T_g and T_β was not clear, it implies that when the content of C3 CSP was increased, their local coagulation to larger particles will decrease the T_g of incorporated epoxy resins. The detailed discussion on the local coagulations and their fusion into large particles will be given in the next section.

So far in this study, the DGEBA–MPDA epoxy resin incorporating 10 phr C3 CSP had the highest T_g. A further increase in the number of epoxy groups in a CSP particle, such as C4 and C5 CSP, was found to lower the T_g of incorporated epoxy resins. Again, it was due to the enhancement in coagulation of CSP particles. On the other hand, for the DGEBA–MPDA incorporating L-series CSP with a crosslinked BA core, the highest T_g was 170°C, obtained by the DGEBA–MPDA–10 phr L3 epoxy formulation. Otherwise, the trends of change in T_g for L-series incorporated epoxy resins as functions of CSP particle size, GMA content in a CSP, and CSP content in the epoxy resins were similar to those of the C-series but milder.

Fracture Toughness and Morphology

Figure 6 shows the fracture energy of DGEBA–MPDA epoxy resins incorporating 10 phr C-series and L-series CSP, respectively, as a function of their GMA content in the shell region. Apparently, shell-crosslinked CSP (C-series) has a higher toughening effect than the core-crosslinked (L-series), although the latter had been used by many researchers to toughen the epoxy resins.[15,16] The CSP without containing epoxy groups (no chemical reaction with epoxy matrix) did not have much toughening effect on the epoxy resins. By increasing the content of GMA in the C-series CSP, the fracture energy of incorporated epoxy resins was increased until 16 mol % GMA (C3 CSP) was reached.

In general, the shell-crosslinked CSP with more content of GMA had a higher tendency to

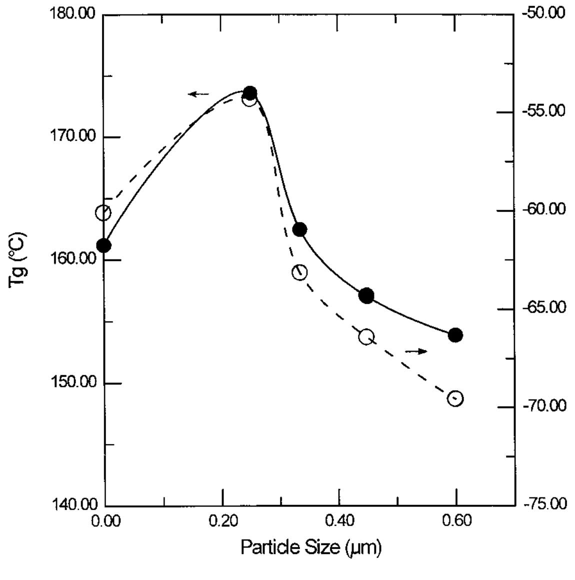


Figure 5 (●) T_g and (○) T_β of DGEBA–MPDA incorporating 10 phr C3-series CSP as a function of their particle size.

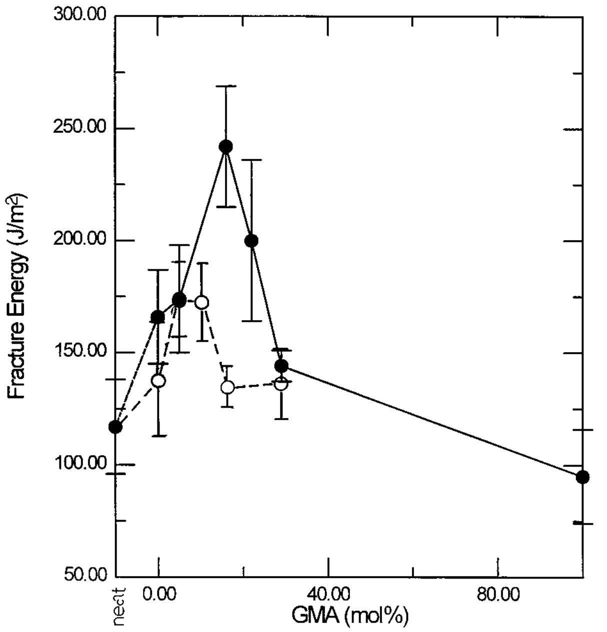


Figure 6 Fracture energy of DGEBA–MPDA epoxy resins incorporating 10 phr (●) C-series and (○) L-series CSP, respectively, as a function of their GMA content in the shell region.

coagulate, as indicated from the SEM investigations on the CTS fracture surfaces of their incorporated DGEBA–MPDA epoxy resins shown in Figure 7. From the TEM investigation on the one-stage C–Pt replication of the fracture surface illustrated in Figure 8, we found that the C-series CSP with a small content of GMA (less than 10 mol %) were coagulated locally in a cluster with a size range of 0.5–1 μm [see Fig. 8(a)]. The coagulated CSP in a cluster did not completely fuse together. However, when the GMA content in a CSP was increased to 16 mol %, the clusters tended to fuse into large particles, which have a clear boundary with the epoxy matrix, as shown in Figure 8(b). On the other hand, no cluster was found for the core-crosslinked CSP incorporated in the epoxy resins, as illustrated in Figure 9. Thus, the higher toughening effect of C-series CSP on the epoxy resins compared to the L-series CSP was believed to be at least partly due to their small-scale coagulations uniformly dispersing in the epoxy network. It had also been reported by Sue et al.[16] that when the CSP particles cluster locally, they can be mechanically treated as a large particle, and, consequently, the crack-deflection mechanism can be enhanced. Their observations were consistent with our experimental results that the toughening phase is better to disperse in such a way that it is globally randomly dispersed and locally coagulated in a small scale. Moreover, based on our observations,

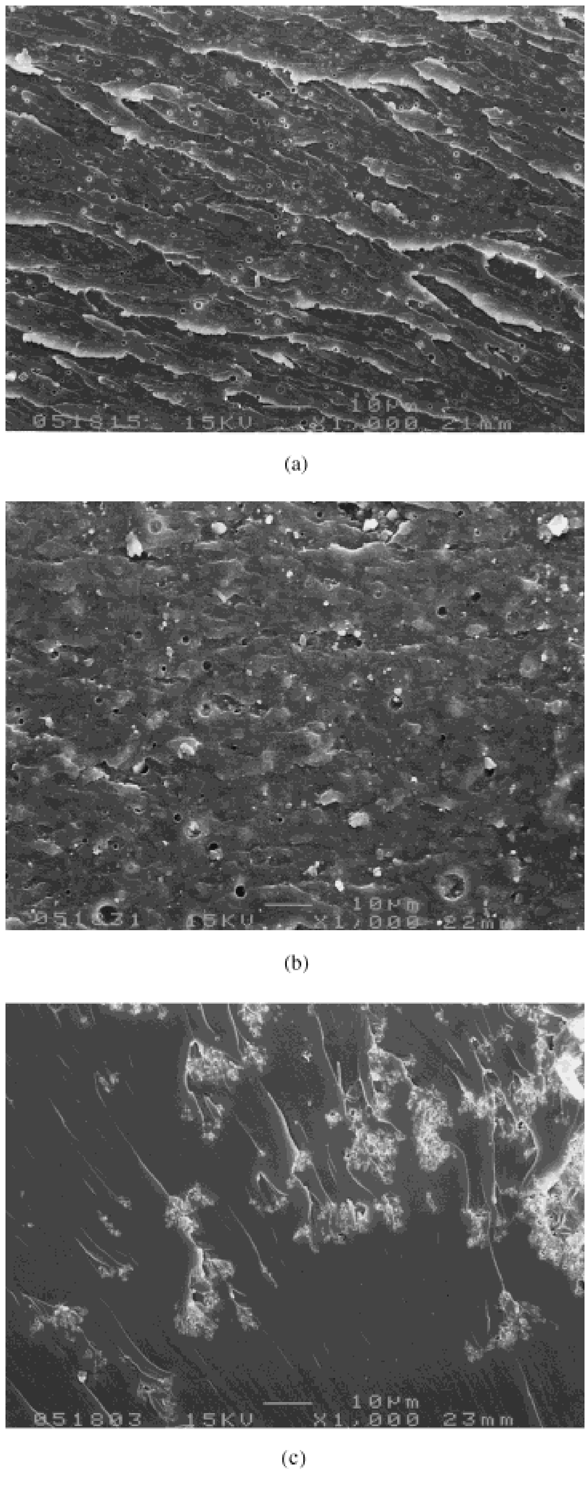
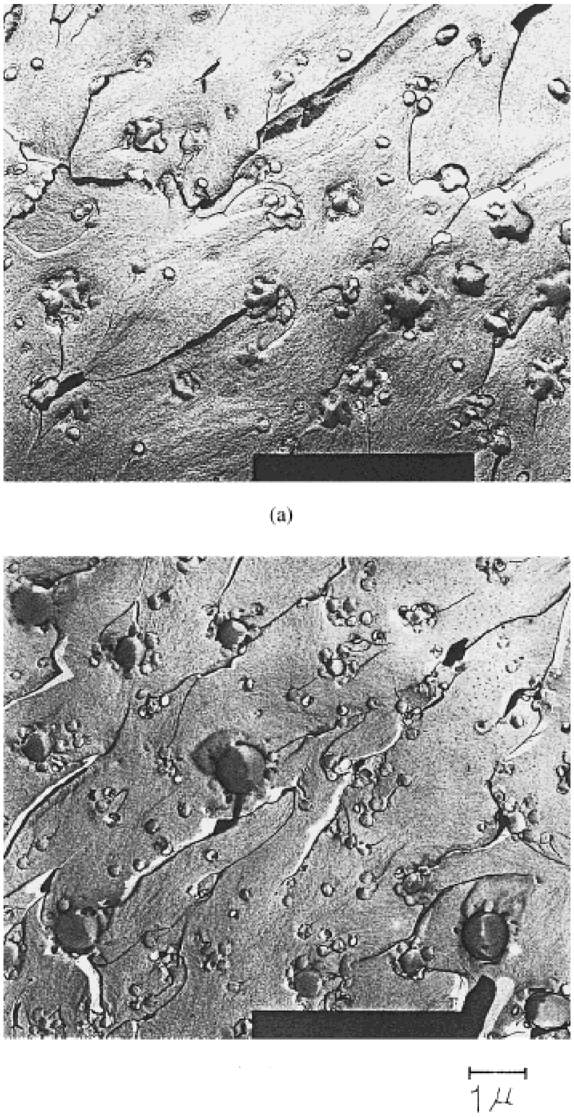


Figure 7 SEM micrographs of CTS fracture surfaces of (a) DGEBA–MPDA–10 C0 CSP, (b) DGEBA–MPDA–10 C3 CSP, and (c) DGEBA–MPDA–10 C5 CSP epoxy resins.



(a)

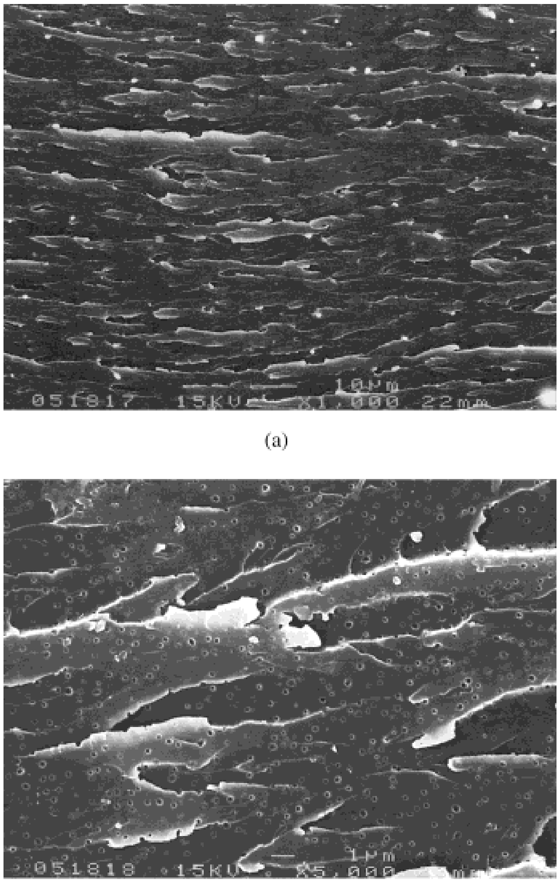
(b)

Figure 8 TEM micrographs of one-stage C–Pt replica of CTS fracture surfaces of (a) DGEBA–MPDA–10 C2 CSP and (b) DGEBA–MPDA–10 C3 CSP epoxy resins.

it would be better if the locally coagulated phase could be fused into large particles.

When the C-series CSP contained more than 16 mol % GMA, they turned to form large-scale coagulations, as seen in Figure 8(c), and their toughening effect was significantly reduced (Fig. 7). The large-scale coagulation might be due to the fact that the T_g in the shell region of CSP particles was lowered by increasing the GMA content. Similar large-scale coagulations were also found in the L-series CSP with the GMA content higher than 16 mol %, as seen in Figure 10, and their toughening effects were also significantly reduced (Fig. 7). In brief, the uniformly distributed small-scale coagulations of CSP could enhance the toughening performance, whereas the nonuniform large-scale coagulations reduced it.

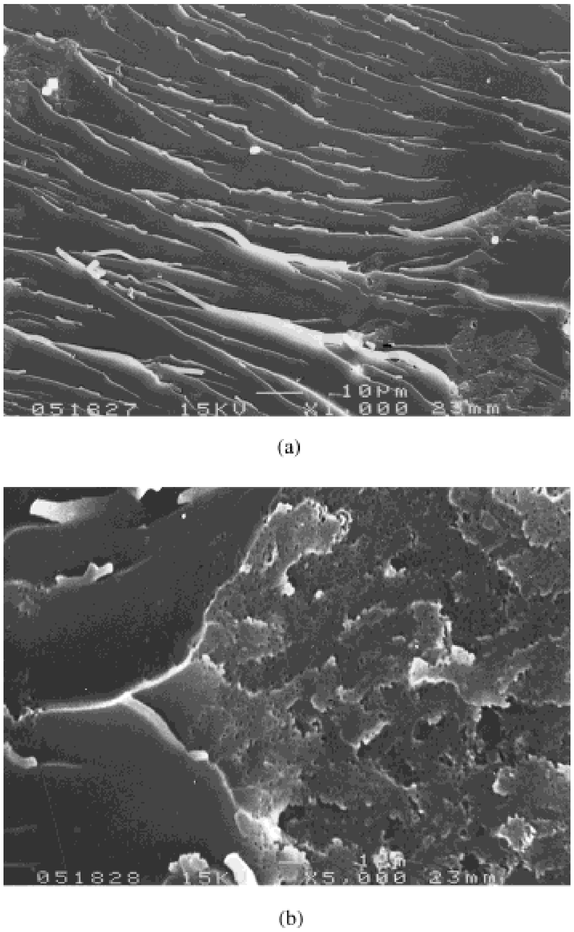
The fracture energy of C3 CSP-incorporated DGEBA–MPDA epoxy resins was increased with the content of CSP until 20 phr was reached; by then, the fracture energy was about 3 times that of the neat resin, as indicated in Figure 11. On the other hand, by maintaining the content of C3 CSP in 10 phr but increasing the particle size, we found that the fracture energy of incorporated epoxy resins was increased to 380 ± 21 J/m^2 when 0.33 μm was reached, as shown in Figure 12. Figure 13 shows the fracture surfaces of the C3-series CSP incorporated epoxy resins observed by SEM. By carefully investigating the fracture surface of all the samples (see Figs. 7, 9, 10, and 13), we can resolve that higher fracture energy of the



(a)

(b)

Figure 9 SEM micrographs of CTS fracture surface of DGEBA–MPDA–10 L1 CSP epoxy resin with magnifications of (a) ×1000 and (b) ×5000.



(a)

(b)

Figure 10 SEM micrographs of CTS fracture surface of DGEBA–MPDA–10 L4 CSP epoxy resin with magnifications of (a) ×1000 and (b) ×5000.

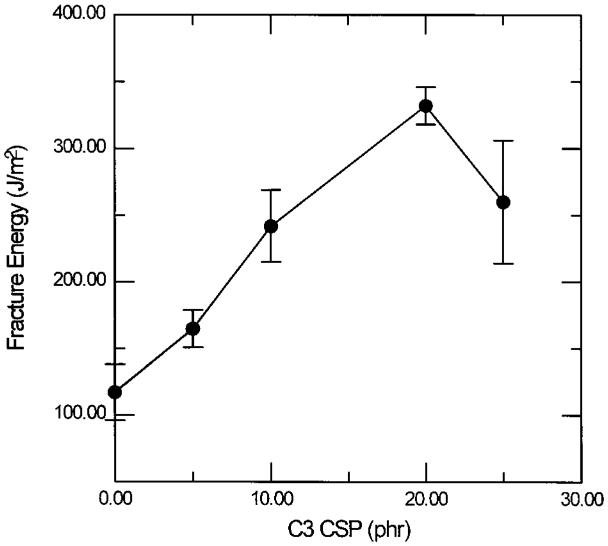


Figure 11 Fracture energy of DGEBA–MPDA–C3 CSP epoxy resins as a function of their CSP content.

CSP-incorporated epoxy resins usually have the rougher fracture surface.

By using the AFM to investigate the three-dimensional morphology of the fracture surface, we found that the CSP-incorporated epoxy resins with higher fracture energy exhibited more plastic flow of epoxy matrix surrounding the particle-cavitated areas, as illustrated in Figure 14. Cavitation of CSP particles occurred, resulting from the CSP particles experiencing the high triaxial stresses in the crack tip during fracture. The epoxy resin incorporating 10 phr C0 CSP, which have no epoxy groups to react with the epoxy matrix, shows a rather flat fracture surface and, barely, plastic flow surrounding the particle-cavitated areas [see Fig. 14(a)]. Its fracture energy was only 166 ± 20 J/m^2, slightly larger than that of the neat resin. When the epoxy resin was incorporated with 10 phr C3 CSP, the fracture surface exhibited the plastic flow in the epoxy matrix, especially surrounding the cavitated area [see Fig. 14(b)]. Its fracture energy was 242 ± 27 J/m^2. Apparently, because of the chemical bonding between C3 CSP and the epoxy matrix, when the CSP particles experienced the high local triaxial stresses in the crack tip prior to cavitation, their excess deformation than the epoxy matrix should have a tendency to trigger the plastic flow

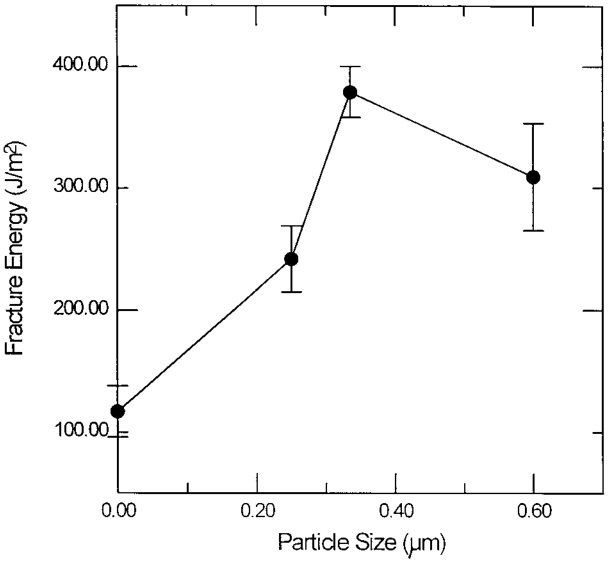
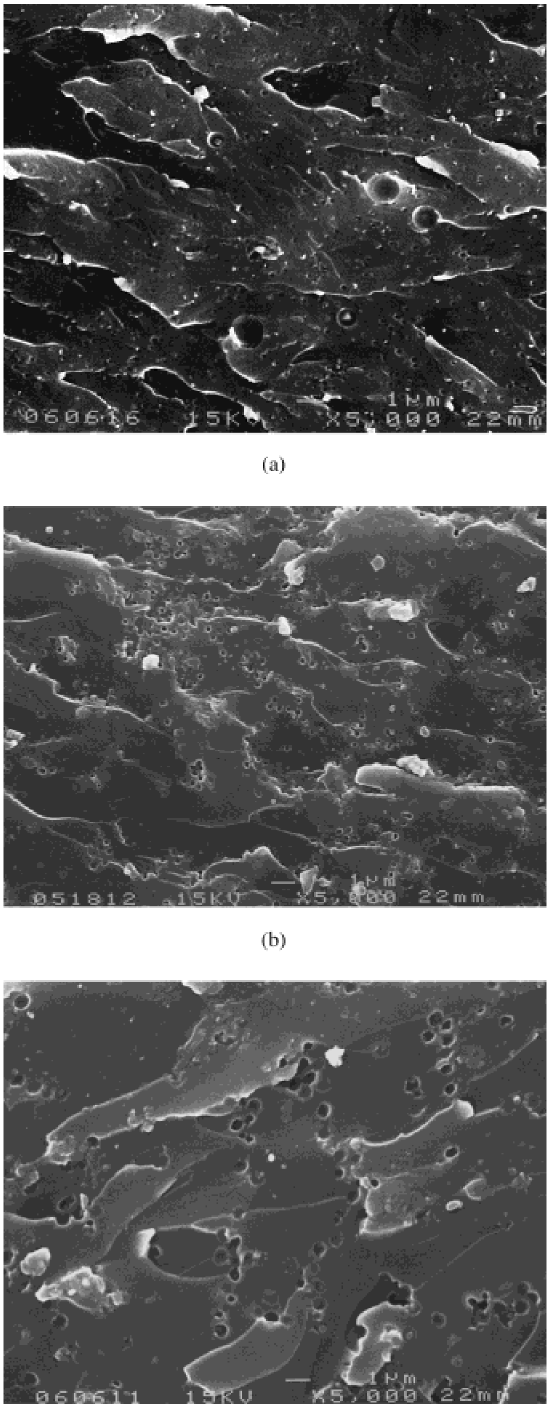


Figure 12 Fracture energy of DGEBA–MPDA incorporating 10 phr C3-series CSP as a function of their particle size.



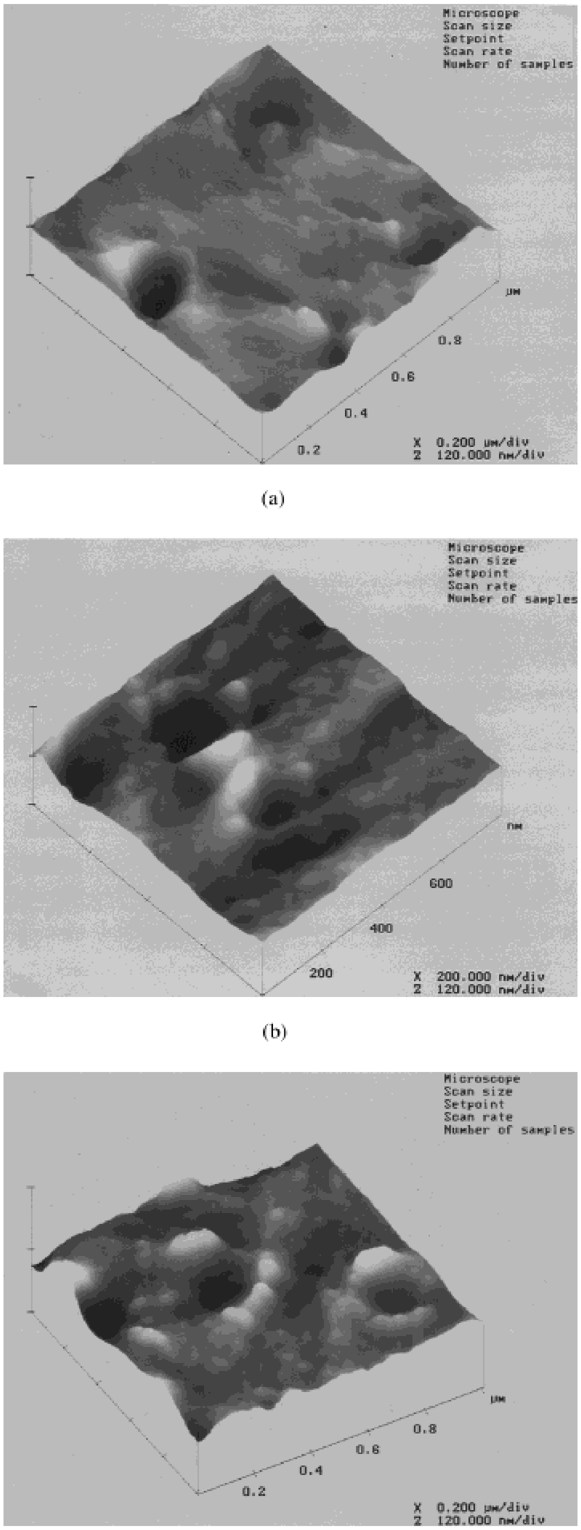
(a)

(b)

(c)

Figure 13 SEM micrographs of CTS fracture surfaces of (a) DGEBA–MPDA–10 C3-0 CSP, (b) DGEBA–MPDA–10 C3-1 CSP, and (c) DGEBA–MPDA–10 C3-3 CSP epoxy resins.

of epoxy resins in the interphasial region and, also, the surrounding areas. Thus, larger particles tended to trigger longer plastic flow and ab-



(a)

(b)

(c)

Figure 14 AFM micrographs of CTS fracture surfaces of (a) DGEBA–MPDA–10 C0 CSP, (b) DGEBA–MPDA–10 C3-0 CSP, and (c) DGEBA–MPDA–10 C3-1 CSP epoxy resins.

sorb more strain energy. Figure 14(c) shows the AFM micrograph of fracture surface of the epoxy resin incorporating 10 phr C3-1 CSP, the particle size of which is 1.32 times that of the C3 CSP. Its fracture surface did reveal longer plastic flow and, also, rougher surface compared to that incorporating C3 (or C3-0) CSP. The fracture energy was also much higher than that of the latter (see Fig. 12). Thus, based on our experimental results, it was the extent of chemical bonding between CSP and the epoxy matrix to determine whether the excess deformation of CSP was capable to trigger the plastic flow of epoxy matrix during fracture test. However, it seemed to contradict with Sue's observation that chemical bonding of CSP to the epoxy matrix did not significantly contribute to the toughening performance.[16] Noteworthily, the systems they used were the core-crosslinked CSP instead of the shell-crosslinked CSP. The core-crosslinked CSP were more rigid and deformed less prior to fracture. According to our study on L-series CSP incorporated epoxy resins, their fracture surface was rather flat (see Fig. 9) and had much less plastic flow compared to the one incorporating C-series CSP.

So far, we have investigated the effects of design variables such as the reactivity, the crosslinking status, the particle size, and the number of CSP on the fracture toughness of epoxy resins. The experimental results indicated that the optimal design of CSP as a toughening agent was to obtain the maximum plastic flow of the epoxy matrix. To achieve this, we have to maximize the content of GMA in a shell-crosslinked CSP, the particle size and the number of CSP incorporated in the epoxy resins but without causing the large-scale coagulations.

CONCLUSIONS

The GMA in the shell region of CSP was more reactive than the DGEBA epoxy resin. The incorporation of reactive CSP with a particle size $\leq 0.25\ \mu$m was able to increase the T_g of epoxy matrix if they were dispersed uniformly. The shell-crosslinked CSP had higher toughening effect than the core-crosslinked due to the fact that they could coagulate in a cluster locally and still maintain a good global dispersion. In addition, the toughening effect of CSP could be enhanced by introducing the epoxy groups in the shell region to react with the epoxy matrix because the excess deformation of CSP than the epoxy matrix prior to cavitation could trigger the plastic flow of surrounding epoxy matrix. Thus, the higher fracture energy of reactive CSP-incorporated epoxy resins usually have a rougher fracture surface. In brief, to design the CSP as a toughening agent, we should maximize the content of GMA in a shell-crosslinked CSP, the particle size, and the content of CSP in the epoxy resins without causing the large-scale coagulations.

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REFERENCES

1. H. J. Sue and R. J. Young, *J. Mater. Sci.,* **31,** 275 (1991).
2. D. E. Henton, D. M. Pickelman, C. B. Arends, and V. E. Meyer, U.S. Pat. 4,778,851 (1988).
3. H. J. Sue, E. I. Garcia-Meitin, and N. A. Orchard, *J. Polym. Sci., Polym. Phys. Ed.,* **31,** 595 (1993).
4. H. J. Sue, *Polym. Eng. Sci.,* **31,** 270 (1991).
5. A. Maazouz, H. Sautereau, and J. F. Gerard, *Polym. Bull.,* **33,** 67 (1994).
6. Y. Nakamura, H. Tabata, H. Suzuki, K. Iko, M. Okubo, and T. Matsumoto, *J. Appl. Polym. Sci.,* **32,** 4865 (1986).
7. K.-F. Lin and L.-D. Shieh, *Polym. Mater. Sci. Eng.,* **76,** 358 (1997).
8. H.-J. Sue, *Polym. Eng. Sci.,* **31,** 275 (1991).
9. A. B. Yee and R. A. Pearson, *J. Mater. Sci.,* **21,** 2462 (1986).
10. A. J. Kinloch, S. J. Shaw, D. A. Tod, and D. L. Hunston, *Polymer,* **24,** 1341 (1983).
11. A. C. Garg and Y. W. Mai, *Compos. Sci. Technol.,* **31,** 179 (1988).
12. K.-F. Lin and Y.-D. Shieh, *J. Appl. Polym. Sci.,* to appear.
13. R. Y. Ting and R. L. Cottington, *J. Appl. Polym. Sci.,* **25,** 1815 (1980).
14. S. A. Thompson and R. J. Farris, *SAMPE J.,* **24,** 47 (1988).
15. D. E. Henton, D. M. Pickelman, C. B. Arends, and V. E. Meyer, U.S. Pat. 4,778,851 (1988).
16. H.-J. Sue, E. I. Garcia-Metin, D. M. Pickelman, and P. C. Yang, in *Rubber-Toughened Plastics: Science and Engineering,* C. K. Riew and A. J. Kinloch, Eds., Advances in Chemistry Series 233, American Chemistry Society, Washington, DC, 1993, p. 259.