Epoxy Networks Toughened by Core–Shell Particles: Influence of the Particle Structure and Size on the Rheological and Mechanical Properties

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ABSTRACT: The core–shell particles considered were poly(butyl acrylate) core/epoxy groups functionalizing the poly(methyl methacrylate) shell. Physical and thermomechanical properties of benzyl dimethylamine (BDMA)-catalyzed diglycidyl ether of bisphenol A (DGEBA)/dicyandiamine epoxy networks toughened with core–shell particles were studied. The blends were prepared under well-defined processing conditions. The resulting properties were found to depend on the state of the dispersion of the particles in the prepolymer matrix before crosslinking. These particles were dispersed at different volume fractions in order to vary the interparticle distance. The relationships between the size of the core–shell particles and the level of toughening are reported. Static mechanical tests were performed in tension and compression modes on these core–shell polyepoxy blends. A slight decrease in the Young's modulus and an increase in the ability to plastic deformation were observed. Using linear fracture mechanics (LEFM), an improvement of the fracture properties (K_{IC}) was measured. By varying the volume fraction of core–shell particles, an optimum toughness improvement was found for an interparticle distance equal to 400 nm (with an average particle size of 600 nm). © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 849–858, 1999

Keywords: epoxy networks; core–shell particles; particle size; fracture toughness

INTRODUCTION

Much attention has been paid to the modification of epoxies by the addition of a low-modulus component in order to improve the ductility and impact resistance without a substantial decrease in the thermal properties. In the first method, a modifier is initially miscible in the epoxy and the comonomer hardener. Phase separation is induced by an increase of the molar mass of the reactive system during the curing process. For this purpose, reactive liquid polymers with low molar masses based on a carboxy-terminated butadiene–acrylonitrile copolymer[1–7] or thermoplastics[8,9] such as polyethersulfone or polyetherimide have been used in this way. However, the characteristics of the separated phase were found to depend on the competition between the rate of the phase-separation process and the reaction kinetics. Thus, the final properties of the rubber- or thermoplastic-modified epoxy networks depend on the cure schedule, the amount of the initial modifier, and its characteristics (chemical nature, functional groups, etc.). Considering that part of the rubber remained dissolved in the epoxy continuous phase, a decrease in the thermal and

mechanical properties of the final modified epoxies was generally observed.

To overcome these undesirable phenomena, a second method that consisted of dispersing an immiscible polymer in a predefined form (powder or latexes) into the epoxy matrix was used. During the last decade, this approach has been largely investigated using preformed core–shell particles[10–29] for toughening thermoplastics such as poly(methyl methacrylate) or polyamide and thermosets. Generally, these latexes were obtained by seeded emulsion polymerization, a technique allowing good control of the characteristics of the final particles: size, ratio of shell thickness (t) to core radius (R): t/R, and also functionalization of the particle surface. It is now well recognized that both thermodynamic and kinetic parameters play a predominant role in the formation of the particles. As a result, particular attention was devoted to several parameters such as the reactivity of the monomers, polarity, mode of the addition of the monomers, type of process (seed or batch emulsion process), and the monomer-to-polymer phase ratio for the conception of well-defined particles. A few articles have reported on the use of core–shell latexes (CSR) as modifiers for thermoset resins, especially for epoxies.[10–16] In addition, structured core/shell particle toughening agents provide model systems that enable the independent examination of the role of the particle size, the particle–matrix interactions, and the cohesive strength of particles on the toughening mechanisms.[28–35]

In this article, we show the influence of functionalized core–shell particles with different sizes and surface functionalities on the toughening of epoxy resin. First, poly(butyl acrylate) (PBuA)/poly(methyl methacrylate) (PMMA)-functionalized glycidyl methacrylate (GMA) core–shell particles were prepared using a shell thickness-to-core radius ratio $t/R = 0.3$. Second, after dispersion of the particles into the epoxy resin, the rheological and mechanical behavior of the two phases system was examined.

EXPERIMENTAL

Reagents

Methyl methacrylate (MMA) and butyl acrylate (BuA, from Janssen) are commercial products. They were distilled under reduced pressure for 2

days and stored at $-18°C$ before performing the polymerization. The initiator (potassium persulfate, $K_2S_2O_8$), the surfactant (sodium dodecyl sulfate, SDS), the reactive monomer (GMA), and ethylene glycol dimethacrylate (EGDMA) were used as received (RP products from Janssen). Deionized water was boiled in a nitrogen atmosphere just before use.

Reagent for Epoxy Network

Diglycidyl ether of bisphenol A (DGEBA) and dicyandiamine (DDA) as a hardener were used as the matrix. The catalyst used was benzyl dimethylamine (BDMA). The aminohydrogen-to-epoxy ratio of 0.6 was chosen to obtain the maximum glass transition temperature, T_g (140°C for the fully cured neat epoxy matrix). The chemical pathways and the resulting architecture of such a network have already been well described in other articles.[13]

Preparation of Latexes

Various emulsion polymerization protocols were performed with a view to synthesizing three epoxy-functionalized acrylic core–shell latexes with a shell-to-core ratio roughly constant but differing in their overall particle size.

Synthesis of Core–Shell Latexes with an Average Particle Size of 300 nm and a Shell-to-Core Ratio $t/R = 0.3$

First, a seed PBuA latex (CS0) was prepared by SDS emulsified batch emulsion polymerization of BuA according to the recipe given in Table I. As reported in a previous article,[29] it was found that a high monomer conversion was reached after about 0.5 h of reaction. Then, for the synthesis of functionalized core–shell latex, the following protocol was used:

The reactor was purged with nitrogen for 1 h before feeding it with a given amount of seed PBuA batch latex. The SDS and 1/6 of the overall of MMA + BuA charge were introduced for a preswelling step of the seed particles for 2 h at 40°C. This allows the introduction of a thin layer of the P[MMA-*co*-Bu] copolymer, which was more appropriate for promoting the core–shell morphology.[29] After increasing and equilibrating the reactor temperature at 60°C, the initiator solution was then added and the monomer mixture remaining (MMA–EGDMA) was added sequen-

Table I Recipes for Core Latex and CS1 Latex Samples

Component (g)	CS1
Seed latex	
Water	1500
BuA	500
SDS	0.7
$K_2S_2O_8$	3
Shell latex	
BuA	9.77
MMA	9.77 + 134.42
SDS	0.35
EGDMA	10
GMA	2.5
Water	400
$K_2S_2O_8$	1.46
K_2CO_3	150

Table II Batch Emulsification Recipes for CS2

Component (g)	CS2
Seed latex	
Water	964
BuA	321.3
SDS	1.63
$K_2S_2O_8$	1.93
Shell latex	
PBuA seed latex	434
BuA	10.84
MMA	10.84
MMA	131.7
EGDMA	10.17
GMA	2.57
SDS	0.608
$K_2S_2O_8$	1.023
Water	427.5

tially at five time intervals of 23 min. In one case (CS1), GMA was introduced with the last addition of MMA–EGDMA so as to favor surface functionalization with the epoxy groups. The recipes for the core latex and CS1 latex samples are fully described in Table I.

Synthesis of Core–Shell Latexes with Large Average Particle Size

Two different procedures were performed to ensure the preparation of large particles: (i) the growth of an initial seed latex upon successive monomer swelling and polymerization stages; and (ii) the direct formation of the seed latex by emulsification polymerization of BuA, providing a final size of 600 nm:

In the first case, a seed PBuA batch latex was prepared with an average size of 150 nm. Then, staged polymerization was performed comprising two swelling steps with the BuA monomer so as to obtain a particle size around 460 nm. The final step consists of the formation of the P(MMA-co-EGDMA) shell according to the already-described procedure, providing a final core–shell size around 600 nm (CS2).

In the second case, batch emulsification free polymerization of BuA was carried out according to recipes given in Tables II and III. Using these processes requires special attention to be paid to the stirring rate at the beginning of the polymerization. Particles are created via a homogeneous nucleation process within a very short period of

time; therefore, it is sometimes difficult to obtain good reproducibility of this synthesis for latexes prepared under identical conditions. In any case, an average particle diameter of 600 nm was obtained. For improving the colloidal stability of the latex, a small amount of the surfactant (SDS) was added, thus preventing particle flocculation at the end of the polymerization stage. All the latexes were freeze-dried to remove water before carrying out the addition to the epoxy prepolymer.

Preparation of the Core–Shell/Epoxy Blends

Dried latex particles were added to the epoxy prepolymer (DGEBA) and DDA hardener reactive

Table III Batch Emulsification Recipes for CS3

Component (g)	CS3
Seed latex	
Water	696.3
BuA	55.83
$NaHCO_3$	0.47
$K_2S_2O_8$	0.54
PBuA seed latex	600
Monomers	
BuA	5.2
MMA	5.2
MMA	94.8
EGDMA	7.14
GMA	0.52
SDS	0.31
$K_2S_2O_8$	1
Water	480

system without any solvent. Mixing was carried out under high-speed mechanical stirring using an Ultraturax T50 mixer operating at 2800 rpm: The weight fraction of the core–shell particles was usually 24% by volume. The cure schedule was 1 h at 120°C, followed by 1 h at 180°C.[7] During curing, the mold was rotated to prevent possible sedimentation of the core–shell particles and the solid hardener (DDA).

Characterization

Core–Shell Latexes

The monomer conversion rate was determined by gravimetry. For both the seed and the shell, the conversion yield was estimated by evaluating the ratio of the solid content to the theoretical final one (according to the total amount of the monomer added in each step). A surfactant concentration of 0.8 g/L was chosen to ensure an average size of seed particles of 150 nm.

The particle size was measured by using either quasielastic light scattering (QELS, N4 from Coultronics) or transmission electron microscopy (TEM, Hitachi HU 12), providing the hydrodynamic particle size ($\overline{Dz}$) and number ($\overline{Dn}$) and weight ($\overline{Dw}$) average particle size, respectively, according to

$$\overline{Dn} = \frac{\sum NiDi}{\sum Ni}; \quad \overline{Dw} = \left(\frac{\sum NiDi^6}{\sum NiDi^3}\right)^{1/3} \quad (1)$$

where Ni is the number of species i of diameter Di. The polydispersity ratio I was defined as

$$I = \frac{\overline{Dw}}{\overline{Dn}} \quad (2)$$

Core–Shell Particle-toughened Epoxy Networks

Measurements of the viscosity of the core–shell/epoxy prepolymer mixtures as a function of the shear rate at 60°C were conducted in a Couette from Rheometer (Rheomat 115). The glass transition temperatures, T_g's, of the fully cured samples were determined using a differential scanning calorimeter (DCS Mettler TA 3000) in an argon atmosphere with a heating rate of 10 K/min. The dynamic mechanical behavior (DMS) of the neat resin and core–shell-modified epoxies was studied in the shear mode using a Rheometrics RDA700 at 10 Hz in a temperature range

from 25 to 250°C. The heating rate was 1°C min^{-1}, and the strain amplitude, 0.3%. Parallel-epipedic specimens (30 × 8 × 1 mm^3) were machined from the molded plates.

The Young's modulus, E_{RT}, and the Poisson ratio, ν, were obtained from an uniaxial tensile test at room temperature and 1 mm · min^{-1} ($\dot{\varepsilon}$ = 3.3 × 10^{-4} s^{-1}) on an Adamel Lhomargy (DY25) testing machine with an ISO 60 specimen, using cross-strain gauges (from Vishay Micromeasures) giving both longitudinal and transversal strains. On the same machine, the uniaxial compression behavior of parallelepiped specimens (section 6 × 9 mm^2, height 20 mm) was investigated (25°C, $\dot{\varepsilon}$ = 8 × 10^{-4} s^{-1}) to determine the upper yield stress, σ_y.

Critical strain energy release rate, G_{Ic}, and the critical stress intensity factor, K_{Ic} were measured according to the procedure developed by the European Group on Polymer Fracture.[36] All measurements were performed on single-edge notched three-point bending specimens (60 × 14 × 7 mm^3) with a span of 56 mm. A crosshead of 10 mm · min^{-1} was used. All fracture toughness measurements were performed at room temperature using a DY25 type Adamel Lhomargy machine. At least five samples with a crack length/width ratio close to 0.5 were fractured to obtain the average value of K_{Ic} from the maximum load at failure. The fracture energy, G_{Ic}, was calculated using the following equation:

$$G_{Ic} = \frac{K_{Ic}^2}{E_{RT}} (1 - \nu^2) \quad (3)$$

The morphology of the CSR particles and their ability to be well dispersed in the epoxy matrix were checked by TEM (Hitachi, HUR microscope) on 70–80-nm-thick specimens. Osmium tetraoxide vapor was used to stain positively the matrix of the thin samples on a grid for 24 h. Moreover, an aqueous solution of phosphotungstic acid (1% wt) was used to stain the core of the preformed particles.

The dispersion state of the particles in the matrix was studied by image analysis. This system was composed of a 512 × 512-square pixel CCD camera (PULNIX TM 760), a frame grabber (Digital vision cyclope), and home-made software. The dispersion state was characterized by the first-neighbor proximity (FNP), which is the average of reciprocal values of the first-neighbor distance.

Table IV Characteristics of the Final Latexes

Latex Code	Exp Seed Latex $\overline{Dp}$ (QELS) (nm)	Exp Final Latex $\overline{Dp}$ (QELS) (nm)	$\bar{D}$ Theoretical (nm)	Exp Final $\overline{Dp}$ (TEM) (nm)	I (Polydi)	% BuA (wt %)	Shell Thickness (t) (nm)	t/R (%)
CS1	226	301	285	290	1.03	41	37.5	33
CS2	462	601	600	492	1.02	43	69.5	30
CS3	650	900	887	801	1.04	37	125	37

This parameter is compared to the interparticle distance (IPD), because the closer the neighbor is to the particle, the more the interaction is pronounced and the higher the FNP is.

RESULTS AND DISCUSSION

To investigate the effect of particle size on the toughening of the epoxy network, different latexes were synthesized with an average particle diameter varying from 300 to 900 nm. For particles with an average size of 900 nm, we used a soap-free polymerization process. This method is highly affected by the stirring rate in the early polymerization time. The particles are created by a homogeneous nucleation process. By increasing the stirring rate, we favor the coagulation of initial particles which are not yet stable, leading to a decrease in the initial number of particles. Due to the short nucleation period with BuA, it is sometimes difficult to get a good reproducibility of the synthesis as exemplified by the variation in the final particle size of latex prepared under identical conditions.

A small quantity of surfactant has to be added to prevent the flocculation of the latex particles during the process. The seed latex is then swollen by the MMA/BuA monomer mixture in order to obtain a final average particle size of 900 nm. The characteristics of the final latexes are reported in Table IV.

The technique shows that latexes have a very low dispersity index. This result confirms that no secondary nucleation occurs during the polymerization of the shell. We can assume that the time of preswelling was sufficient to favor the core–shell morphology.

Core–Shell Particle-modified Epoxy Networks

The stability of the unreacted blend was checked before any curing. The presence of a second phase in the epoxy prepolymer mixture can affect the processing conditions of the blends. Thus, the dependence of the viscosity of the CSR/DGEBA prepolymer mixture as a function of the shear rate was studied. No hysterisis was observed by increasing and decreasing the shear rate. Thus, the structure of the dispersion is not further modified by the processing conditions which generally induce a significant shear stress. The pure DGEBA prepolymer displays a Newtonian behavior, which is not the case for blends (Fig. 1).

A high viscosity is observed for low shear rates for these dispersions and, in addition, the viscosity increases for the blends with lower diameters (300 and 600 nm), that is, the interactions between the matrix and the high specific surfaces are probably favored (as illustrated in Fig. 1). In the case of the blends based on core/shell particles having a diameter equal to 900 nm, they display a lower viscosity than that of the CS1 and CS2

Figure 1 Log(viscosity) as a function of Log(shear rate) of epoxy core–shell blend (24% volume) and different particle sizes at $T = 60°C$: (–+–) neat epoxy; (—) 900 nm; (–●–) 300 nm; (– – –) 600 nm.

Figure 2 TEM micrographs of core–shell epoxy blends (24% by volume) with average size of (a) 300, (b) 600, and (c) 900 nm.

blends. This difference is due to the level of particle–particle and/or particle–matrix interactions. A previous study[29] has already shown the influence of the dispersion state on the blend viscosity. In the present study, as shown by the TEM micrographs (Fig. 2), a good dispersion of particles, (that is, the particles do not form aggregates within the epoxy), was obtained by using a high-speed mechanical stirrer without any solvent.

On the other hand, Qian et al.[15] recently showed that the dispersion state of the CSR particles in the epoxy matrix governs the level of improvement of the fracture toughness. If these conditions prevail, a high value of fracture energy is obtained. The CSR particles keep their core–shell morphology and their spherical shape. Thus, using this dispersion method, different parame-

ters, such as the structure of the CSR particles or their interparticle distances of the CSR modifiers, could be varied.

Dynamic Mechanical and Thermal Behaviors of the Blends

Figure 3 shows the temperature dependence of the storage modulus (G') for the pure epoxy network as well as for the epoxy blends prepared with (24% vol) of the core–shell particles. It was found that the G' of all the samples decreases rapidly in the range 10^6 and 10^7 Pa when $T = 140°C$. However, between 30 and 100°C, the epoxy matrix exhibits the highest values of G', followed by both the CS1 and CS2 blends.

The thermal and mechanical properties of the modified and unmodified epoxy systems are shown in Table V. In agreement with other studies,[11–13] the glass transition temperature, T_g, is not affected by adding CSR particles. This indicates that the epoxy network is not plasticized by the core–shell presence. As a consequence, the epoxy/CSR blends are a model system for the study of the toughening mechanisms of epoxy networks having a well-defined dispersed phase.

As expected, the Young's modulus at room temperature, E_{RT}, slightly decreases when introducing the core–shell particles (Table V). In fact, according to different mechanical models, the ad-

Figure 3 G' of blends (24% vol) as a function of temperature at $N = 10$ Hz: (—) matrix; (– – –) CS1; (–●–) CS2.

Table V   Thermal and Mechanical Properties of Modified and Unmodified Epoxy Systems

Materials	Neat Matrix	CS1	CS2	CS3
Core diameter (QELS) (nm)		226	462	650
Core-shell diameter (nm)	—	301	601	900
IPD (nm)	—	279	497	690
FNP (nm)	—	207	400	620
T_g of the matrix (°C)	141	140	140	140
E (GPa)	3	2.5	2.4	2.4
σ_y (MPa)	101	74	72	78
K_{Ic} (MPa $\cdot$ m$^{0.5}$)	0.8 ± 0.08	1.55 ± 0.05	2.01 ± 0.12	1.26 ± 0.01
G_{Ic} (kJ $\cdot$ m^{-2})	0.2	0.8	1.4	0.5

dition of a component having a low modulus to a glassy polymer tends to decrease its stiffness.

The yield stress, σ_y, is also sensitive to the presence of soft particles in the epoxy matrix (Table V). The yield analysis for similar systems in different modes (tension, compression, pure shear, and plain strain compression) shows that the same mechanisms are involved in the deformation process of CSR-modified epoxies.[13] Thus, the presence of the core–shell particles favors the plastic deformation of the surrounding epoxy network.

Toughening Behavior

Much research in the last decade showed that the main toughening mechanism is particle cavitation. One of the first studies dealing with variable particle sizes was made by Sultan and McGarry[1] on a blend of butadiene-*co*-acrylonitrile (CTBN) elastomer particles dispersed in a crosslinked epoxy matrix. At a rubber particle size of ~400 nm, the plastic deformation, the fracture toughness, and mechanical properties in uniaxial and biaxial tests appeared to be very similar to the unmodified matrix material. On the other hand, in the CTBN/epoxy blends with a rubber particle size of ~1200 nm, yielding deformation was reached at a lower stress level, fracture toughness increased considerably, and the material whitened, while scanning electron microscopy revealed cavity formation at the rubbery particle sites. These data confirm that for particle cavitation with associated yielding and ductile behavior the particle size needs to have a minimum value. The effect of the rubber particle size on the cavitation behavior has also been studied on many blends based on thermoplastics: Breuer et al.[33] demonstrated this phenomenon on blends of PVC with methyl

methacrylate–butadiene-styrene (MBS) graft copolymers using TEM. Moreover, the electron micrographs of the stress–whitened zones obtained from an uniaxial tensile test at a strain rate of 1m s^{-1} revealed that the MBS rubber particles with a size of 160 nm or larger showed internal cavitation, while only a few cavities were found in the blend with a particle size of 80 nm. The Izod impact strength of PVC/MBS blends was also investigated.[34] It was found that the impact resistance increases considerably with increasing particle size, up to a particle diameter of 200 nm. On the other hand, the data presented by Wu[35] on the notched Izod impact toughness of PMMA/rubber blends with 20 wt % rubber might be reconsidered in the light of these ideas. Wu found that the notched Izod impact strength is nearly the same as that of unmodified PMMA when the rubber particle diameter is smaller than 100 nm or larger than 500 nm. Toughness reaches a maximum at 250 nm.

In our case, the toughening behavior of core–shell particles is discussed in light of this literature. The values of the critical stress intensity factor, K_{IC}, and of the fracture energy, G_{IC}, are shown in Table V. The results show clearly that there is an optimal toughness (K_{IC} = 2.01 MPa $\cdot$ m$^{1/2}$) of the material for particles with an average diameter of 600 nm, whereas after the optimum, K_{IC} and G_{IC} decrease, retaining a high level of toughness (K_{IC} = 1.26 MPa m$^{1/2}$). The results shown here are very similar to data obtained on rubber-modified thermoplastics as are those described below. For constant core–shell particle volume-modified epoxy materials, the toughening mechanism reported in the literature[9,12] is shear yielding governed mainly by the cavitation of the particles.

However, Kim et al.[28] showed, for a highly crosslinked matrix, that K_{IC} was little dependent on the particle size. Dompas and Groeninckx[17] modeled the cavitation phenomenon on a PVC matrix modified by elastomers, taking into account the size of the particles introduced. They established an internal cavitation criterion for the particles. According to this model, cavitation occurs when the total energy stored during defor-

mation decreases, this being related to particle size.

Therefore, when the particles have a greater size, cavitation occurs later. The cavitation resistance of particles increases with decreasing their size. In fact, cavitation is thus dependent on the elastic and molecular properties of the rubbery particles and their size. This, moreover, depends on the applied volume deformation and the intrin-

Figure 4   Evolution of the K_{Ic} and G_{Ic} value, as a function of (a) the core particle diameter or (b) the FNP.

sic ductility of the matrix. Dompas and Groeninckx[17] defined the critical size for cavitation as the particle size at which an efficient improvement in matrix toughening and shear yielding appeared. This particle size was estimated at 200 nm in PVC, Nylon 6, PMMA, and polycarbonate (PC).[34,35] Van der Sanden and Meijer[16] coupled this phenomenon to the concept of the critical ligament thickness of the matrix and they demonstrated that toughening is efficient when the interparticle distance is lower than the ligament. In addition to the influence of the particle size on toughening, the first-neighbor number proximity (FNP) is a critical parameter which controls the matrix toughness level. This value is close to the interparticle distance (IPD) (Table V). As shown in Figure 4 and Table V, K_{IC} and G_{IC} reach a maximum value at a critical FNP and also at a critical IPD which is given by the following relation[37]:

$$IPD = d_0\left[\left(\frac{\pi}{6\phi_r}\right)^{1/3} - 1\right] \qquad (4)$$

where d_0 is the particle diameter and ϕ_r is the CSR volume fraction. The main reinforcement was obtained for an FNP and IPD equal, respectively, to 400 and 497 nm. This result agrees with the literature previously discussed.

CONCLUSIONS

The critical core particle size, in order to obtain a high level of improvement to the fracture properties in the DGEBA/DDA/BDMA epoxy system, modified with CSR particles during fracture tests, is 462 nm. The results were discussed according to the viewpoints of the literature and this showed that the mechanism involved is cavitation. In addition to the CSR size, IPD is equally important. It was shown that an IPD equal to 497 nm exhibits a high level of improvement to these epoxy systems.

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