

Fracture Behavior of Epoxy Polymers Modified with Core-Shell Rubber Particles

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ABSTRACT: Physical and thermomechanical properties of BDMA-catalyzed DGEBA/Dicy epoxy toughened with core-shell particles were studied. Relationships between these properties and the level of toughening are reported. The blends have been made in well-defined processing conditions. In fact, the resulting properties depend on the state of dispersion of the particles in the prepolymer matrix before crosslinking and on the cure schedule. The considered core-shell particles were of two types: i) poly(butadiene-co-styrene) core/carboxy-functionalized poly(methyl methacrylate-co-styrene) shell. Such core-shell particles have been dispersed in the epoxy matrix at different volume fractions (from 9.5 to 24%); ii) poly(butyl acrylate) core/carboxy functionalized poly(methyl methacrylate-co-styrene) shell. These particles have been dispersed at a volume fraction of 24%. Static mechanical tests were performed in tension and compression modes on these core-shell polyepoxy blends. A slight decrease of Young's modulus and an increase of the ability to plastic deformation were noticed as the volume fraction of the core-shell particles increased. Using linear fracture mechanics (LEFM), an improvement of the fracture properties (K_{IC}) was measured. Fatigue crack-growth studied for blends demonstrates that the Paris's law can be used to describe the behavior of the materials. Increasing the volume fraction of core-shell particles leads to an improvement of the resistance to fatigue crack-propagation. The same trend is noted on the impact behavior studied by means of high-speed tests performed in a large range of temperatures. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 2419–2431, 1997

Key words: epoxy networks; core-shell particles; fracture toughness; impact; fatigue crack-propagation

INTRODUCTION

Numerous articles were written during the last decades on the modification of epoxies by addition of a low modulus component to improve the toughness and impact resistance without a substantial decrease in the stiffness and the thermal properties. Several approaches were developed for this purpose.

First, a modifier that is initially miscible in the

epoxy prepolymer/hardener reactive mixture separates during curing as the molar mass of the reactive system increases. Either reactive liquid polymers with low molar masses based on carboxy-terminated butadiene-acrylonitrile copolymers^{1–15} or thermoplastics¹⁶ such as polyether-sulfone or polyetherimide were used this a way. However, the characteristics of the separated phase depend on the competition between the phase separation process and the reaction kinetics. Thus, the final properties of the morphology of rubber or thermoplastics modified-epoxy networks depend on the cure schedule, the amount, and characteristics (chemical nature, type of func-

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tional groups, etc.) of the initial modifier. According to the fact that a part of the rubber remains dissolved in the epoxy continuous phase, a decrease in the thermal and mechanical properties of the final modified epoxies is generally observed. To avoid these problems, a second way consists in dispersing an immiscible polymer in a predefined shape (powder or latexes) into the epoxy matrix. This approach has been used during the last decade for toughening thermoplastics such as poly(methyl methacrylate) or polyamide and thermosets using pre-formed core-shell particles.^{17–41} These latexes are prepared by seed-emulsion polymerization, which allows designing of well-defined particles (core-to-shell ratio, chemical nature of the shell and core, reactive surface, and nature of the functional groups). Very few articles were devoted to the use of core-shell latexes (CSR) as modifiers for thermoset resins, especially for epoxies.^{18–21,29} In addition, structured core/shell particle toughening agents provide model systems that allow us to independently examine the role of the particle size, the particle–matrix interactions, and the cohesive strength of particles on the toughening mechanisms.^{41–43}

The mechanisms involved in the toughening depend on the intrinsic ductility of the matrix material,²³ on the morphology of the blend, and on the properties of the CSR particles such as particle size,²⁴ chemical structure, and state of dispersion.²⁵ Under a triaxial tensile stress field at low temperature and high strain rate, the occurrence of voids inside the components can not be avoided. Macroscopically, this phenomenon is defined as stress-whitening.²⁴ In rubber-modified materials under triaxial tensile stresses, voiding can occur in the matrix or can initiate inside the rubber particles (rubber cavitation inside the core-shell). Because the rubber particles cavitate, the hydrostatic tension in the material is released and the stress field inside the thin ligaments of matrix between the voids is converted from triaxial stress into almost uniaxial tension. As a consequence, the resulting initiates shear yielding. As demonstrated by the energy-based model developed by Bucknall et al.,³⁸ the cavitation of the rubber is the initial step in the toughening mechanism and is shown to accelerate the shear yielding of the matrix.

Most of the studies done on the fatigue behavior of rubber-modified epoxies were devoted to the CTBN/epoxy blends and especially the influence of the amount of reactive rubber and/or the crosslink density of the epoxy matrix.^{30–35} Fatigue data

were reported by Karger–Kocsis and Friedrich³⁰ comparing the nature of the rubber-dispersed phase. They showed that the nature of the dispersed phase is an important parameter for the fatigue crack growth because the toughening mechanisms are modified.

In this article, the static and fatigue crack propagation (FCP) resistances of core-shell–modified epoxy networks were investigated as a function of the volume fraction of the dispersed particles. The fatigue behavior of these CSR-modified blends are discussed from the toughening mechanisms proposed in the literature. The different FCP resistances for the CSR/epoxy and CTBN/epoxy blend are compared and discussed.

EXPERIMENTAL

Reagents and Processing of Blends

Epoxy Network and CSR Particles

The chemical reagents used are presented in Table I. A mixture of diglycidyl ether of bisphenol A (DGEBA) and dicyandiamide (Dicy) was used as the matrix. The catalyst used was the benzyl dimethylamine. The amino-hydrogen-to-epoxy ratio of 0.6 was chosen in order to obtain the maximum of the 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 were well described in other articles.^{15,20}

Processing of CSR/Epoxy Blends

Two core-shell latexes (Table I) were considered. The core-shell particles denoted CSR 1 (EXL 2611 from Rohm and Haas) were based on a polybutadiene core ($T_g = -80^\circ\text{C}$) and a poly(methyl methacrylate) shell ($T_g = 100^\circ\text{C}$). The average diameter of these CSR 1 particles was equal to 220 nm. The particles denoted CSR 2 (EXL 8866 from Rohm and Haas) were based on a poly(butyl-acrylate) core ($T_g = -56^\circ\text{C}$) and a poly(methyl methacrylate) shell ($T_g = 100^\circ\text{C}$). Their average diameter was 300 nm. According to the synthesis of the core-shell latexes used, the shell is slightly crosslinked and functionalized with carboxylic groups³⁹ for both the CSR 1 and CSR 2 particles.

The mixing of the DGEBA prepolymer, the hardener Dicy, and the core-shell particles was done under high speed mechanical stirring using a Ultraturax T50 mixer operating at 2800 rpm. Different volume fractions of CSR particles were

Table I Chemical Products Used in Synthesis of Materials

Name	Chemical Formula	Supplier
DGEBA		Bakelite 0164
Dicy	$\overline{M}_n = 380 \text{ gmol}^{-1}$ <p>Dicyandiamide</p>	Bakelite VE 2560
BDMA	<p>Catalyst or initiator</p>	Aldrich
CSR particles	<p>Core : CSR2 – Poly(butyl acrylate) a) CSR1 – Poly(butadiène-co-styrène) b)</p> <p>Shell : crosslinked poly(methy/methacrylate) ± COOH</p>	Rohm & Haas a) EXL 8866 b) EXL 2611

considered: from 9.5 to 24% for the CSR 1 particles and 24% for the CSR 2 particles. The cure schedule was 1 h at 120°C, followed by 1 h at 180°C. The detailed procedure was similar to that used in a previous study.¹⁵ During curing, the mold rotated, in order to prevent possible sedimentation of the CSR particles and Dicy.

Experimental Techniques for Characterization

Differential scanning calorimetry (DSC) measurements were performed using a METTLER TA 3000 calorimeter in a temperature range from 25 to 250°C under argon.

The dynamic mechanical behavior (DMS) of the neat resin and the CSR-modified epoxies was studied in shear mode using a Rheometrics RDA 700 at 10 Hz in a temperature range from -140 to 250°C. The heating rate was 1°C·min⁻¹ and the strain amplitude, 0.3%. Parallelepipedic spec-

imens (30 × 8 × 1 mm³) were machined in the molded plates.

The morphology of the CSR particles and their ability to be dispersed in the reactive epoxy mixture were checked by transmission electron microscopy (TEM) using a Hitachi HV12 microscope. Osmium tetroxide vapor was used to stain the core poly(butadiène) of CSR 1 on 10–80 nm thick samples for 24 h, whereas an aqueous solution of phosphotungstic acid (1 wt %) was used to stain the core poly(butyl acrylate) of the CSR 2 particles.

Mechanical Testing

Tensile tests were performed using a Adamel Lhomargy DY25 setup at room temperature. The measurements were performed on ISO 60 specimens. The strain was recorded using strain gauges at a crosshead speed of 10 mm·min⁻¹.

Thus, Young's modulus, E_{RT} , and Poisson ratio, ν , were determined for all materials.

The plastic strain behavior of the neat matrix and the CSR-modified epoxies was also studied using the same tensile machine equipped with a compression device. Yield stresses, σ_y was then measured.

Fracture toughness (critical strain energy release rate, G_{IC} , and the critical intensity stress factor, K_{IC} , were measured according to the procedure developed by the European Group on Fracture of Polymers.²⁶ All measurements were performed on single-edge notched three-point bending specimens ($60 \times 14 \times 7 \text{ mm}^3$). The span was 56 mm. A crosshead speed of $10 \text{ mm} \cdot \text{min}^{-1}$ was used. All fracture toughness measurements were performed at room temperature using a DY25 type Adamel Lhomargy tensile machine. At least five samples 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:

$$G_{IC} = \frac{K_{IC}^2}{E_{RT}} \cdot (1 - \nu^2)$$

The high-speed impact toughness, $G_{IC HS}$, was determined from the already reported method. The dimensions of the specimens were the same as for the previous tests and the crosshead speed was $1.1 \text{ m} \cdot \text{s}^{-1}$. Impact measurements were performed in a temperature range from -35 to $+100^\circ\text{C}$ using a Zwick Rel 1853 hydraulic tensile machine. At least five specimens were fractured for each test condition.

The Fatigue Crack Propagation tests (FCT) were performed on compact-tension (CT) specimens at room temperature. Sinusoidal cycling was performed at 5 Hz under load control in tension-tension mode between a minimum load of 10 N and a maximum load calculated to obtain $\Delta K \cong K_{IC}/2$. Crack growth was determined by using gauges VISHAY micrometers having 20 parallel conductors with 0.25-mm intervals placed perpendicular to the crack direction (as the crack grows, conductor lines are cut and, the resistance of the system increases). Thus, the crack length, a , was recorded without test interruption from the electric resistance, vs. of the number of cycles, N . The fracture crack propagation rate, da/dN , was determined graphically as the slope of the curve of the crack growth, da , as a function of number of cycles. The related stress intensity factor range,

ΔK , was calculated according the following equation²⁷:

$$\Delta K = \frac{\Delta P}{bw^{1/2}} \left[\frac{(2+A)}{(1-A)^{3/2}} \right] \\ \times (0.886 + 4.64A - 13.32A^3 - 5.6A^4)$$

where ΔP is the amplitude of the load at each cycle ($P_{max} - P_{min}$). w and b are the sample width and thickness of the specimen, respectively. A is the ratio of the crack length to the width of the specimen, a/w .

RESULTS AND DISCUSSION

Qian et al.²² recently showed that the state of dispersion of the CSR particles in the epoxy matrix governs the level of improvement of the fracture toughness. A good state of dispersion, i.e., the particles do not form aggregates, leads to a high value of the fracture energy. In order to have a reproducible state of dispersion with improvement of the fracture properties of the CSR-modified epoxies, the dispersion of the particles was done using a mechanical stirrer without solvent. In fact, as shown on the TEM micrographs (Fig. 1), a good state of dispersion of the particles within the epoxy was obtained and was not affected by further curing. The CSR particles kept their core-shell morphology and their spherical shape. Thus, using such a dispersion method, different parameters, such as the volume fraction and/or the nature of the phases of the particles can be varied.

The thermal and mechanical properties of the modified and unmodified epoxy systems are reported in Table II. In agreement with other studies,^{18–20} the glass transition temperature, T_g , is not affected by adding CSR particles in comparison with the CTBN-modified epoxy. The same conclusions can be derived from the dynamic mechanical spectra of the neat epoxy and the CSR-epoxy blends (Fig. 2). The temperature of the main relaxation of the epoxy network associated with its T_g (denoted α_e), is similar for the neat epoxy and the CSR-modified networks (Table II). In addition, on the DMS spectra the relaxation of the poly(butadiene-*co*-styrene) core the CSR-modified epoxies (Fig. 2) (denoted α_{core}) can be observed in the low temperature region as a shoulder on the secondary relaxation of the epoxy network, β_e . Unfortunately, the relaxation peaks of

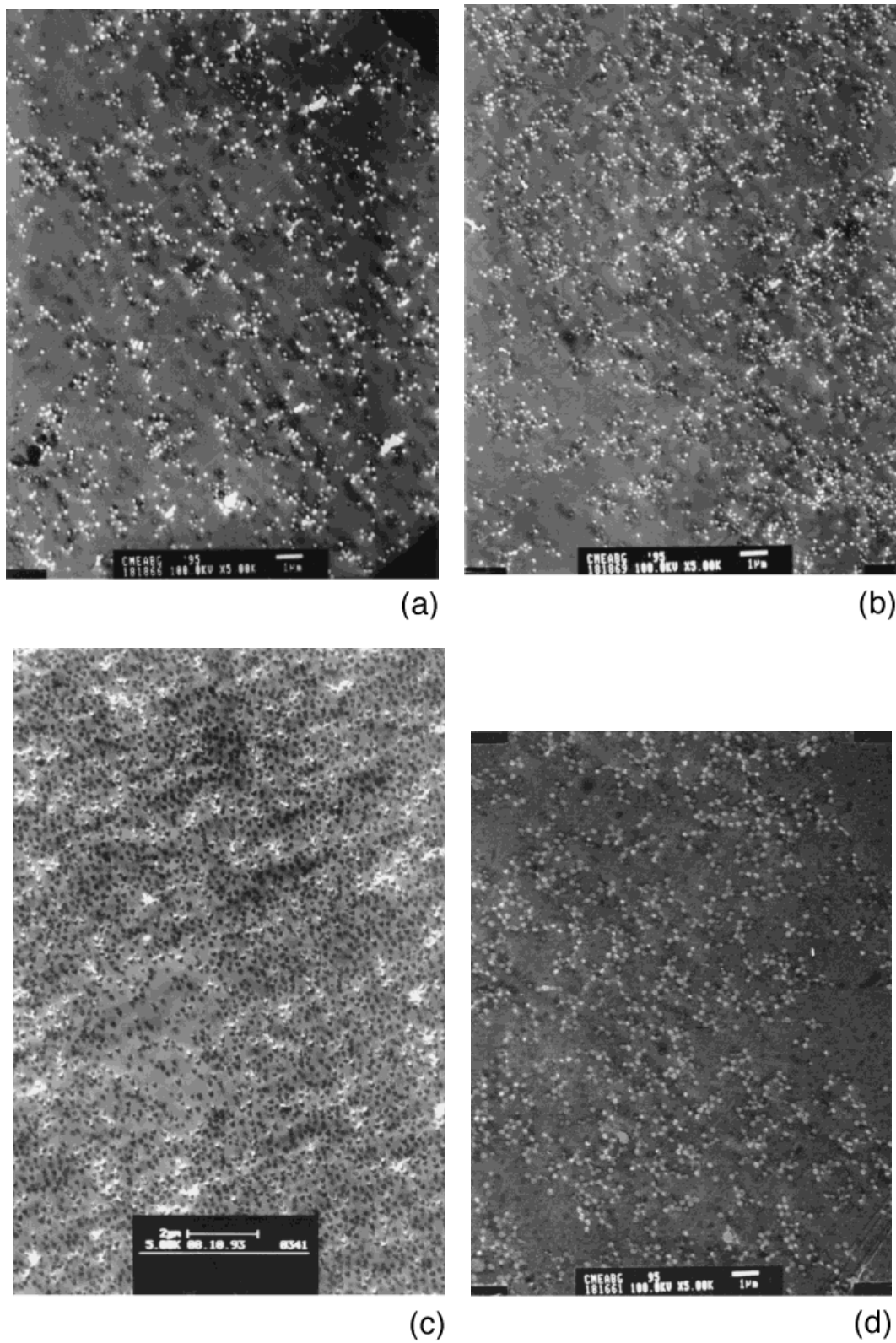


Figure 1 TEM micrographs after staining for CSR/epoxy blends for different volume fractions of the core-shell particles: (a) 9% CSR 1; (b) 17.5% CSR 1; (c) 24% CSR 1; (d) 24% CSR 2.

Table II Thermal and Mechanical Properties of Pure Epoxy and CSR or CTBN Blends

Material	Modifier Content (% vol)	T_g (°C)	E_{RT} (GPa)	σ_y (MPa)	T_{α_e} (°C) ^a
Neat epoxy	0	141	3.2	105	170
Epoxy + CSR 1	9.5	140	2.65	95	169
	17.5	142	2.67	85	170
	24	140	2.17	72	169
	24	139	2.2	71	170
Epoxy + CTBN (20)	17.5	135	1.8	76	159

^a Measured at the maximum of the $\tan \delta$ peak.

the PMMA shell and the epoxy continuous phase, respectively α_{shell} and α_e , occurred in the same temperature range. Thus, only α_e can be evidenced on the dynamic mechanical spectra. This overlapping of the relaxations of the dispersed phase and the matrix was also observed in epoxy networks modified by carboxy-terminated acrylonitrile butadiene copolymers (CTBN).^{30,31} In the later cases, dynamic mechanical spectroscopy evidences that part of the reactive rubber remains dissolved in the epoxy matrix. In the present study, the slightly constant α_e observed in neat epoxy and CSR blends indicate that the epoxy network is not plasticized by the CSR particules in opposition to CTBN–epoxy blends. As a consequence, the epoxy/CSR blends are model systems for the study of the toughening mechanisms of epoxy networks by a dispersed phase.

As expected, the Young's modulus at room temperature, E_{RT} , slightly decreases by introducing core-shell particles (Table II). In fact, according to different mechanical models, the addition of a component having a low modulus to a glassy polymer tends to decrease its stiffness. Nevertheless, the decrease in the glass transition temperature and in the Young's modulus are lower than those observed for the same epoxy network modified with a reactive rubber, which phase separates during curing, at the same volume fraction.²⁰ In fact, for the same epoxy matrix, the T_g of the epoxy phase decreases to 135°C and the Young's modulus decreases of about 38% at a volume fraction of reactive rubber of 17%. These effects in rubber-modified epoxies are due to the fact that part of the carboxy-terminated acrylonitrile–butadiene copolymers (CTBN) remains dissolved in the epoxy continuous phase.

The yield stress, σ_y , is also sensitive to the presence of soft particles in the epoxy matrix (Table II). The analysis of yielding for similar systems in different testing modes (tension, compression,

shearing, and plane strain compression) shows that the same mechanisms are involved in the deformation process of the CSR-modified epoxies.²⁰ Thus, the presence of the core-shell particles favors the plastic deformation of the surrounding epoxy network.

The fracture toughness, G_{IC} of the CSR 1-modified epoxy networks, determined at a rate of 10 mm · min⁻¹ and at room temperature, increases with the CSR content (Table III). These results are in agreement with those found on DGEBA/MDA (diamino-diphenyl methane)-CSR blends.⁴² The fracture properties are enhanced by modifying the epoxy network using such pre-formed particles in comparison to the use of CTBN reactive rubber. As discussed later, the structure of the dispersed particles can modify the toughening mechanisms involved in the fracture process. In fact, as the CSR particles have a well-defined structure, the particles in the CTBN-modified epoxy have a two phase structure (i.e., phase separation inside the particles). By using the CSR 2 latex as modifier, i.e., particles having a poly(butyl acrylate) core, the K_{IC} value is twice as high as for the neat matrix and is higher than for the CSR 1-modified epoxy. Because both types of core-shell particles have a common carboxy-functionalized shell, the same shell thickness-to-core radius ratio, same diameter, and the same dispersion state [Fig. 1(c) and (d)], the main difference is the cavitation resistance of the core polymers: poly(butadiene-*co*-styrene) or poly(butyl acrylate). The shear yielding of the epoxy matrix is not changed between the CSR 1 and CSR 2/epoxy blends as a consequence of the previous phenomenon. Shaffer et al.,³⁷ on CTBN and CSR-modified epoxy, observed by AFM experiments, a cooperative cavitation phenomenon of the rubber particles and a permanent deformation surrounding the particles. Nevertheless, they were not able to

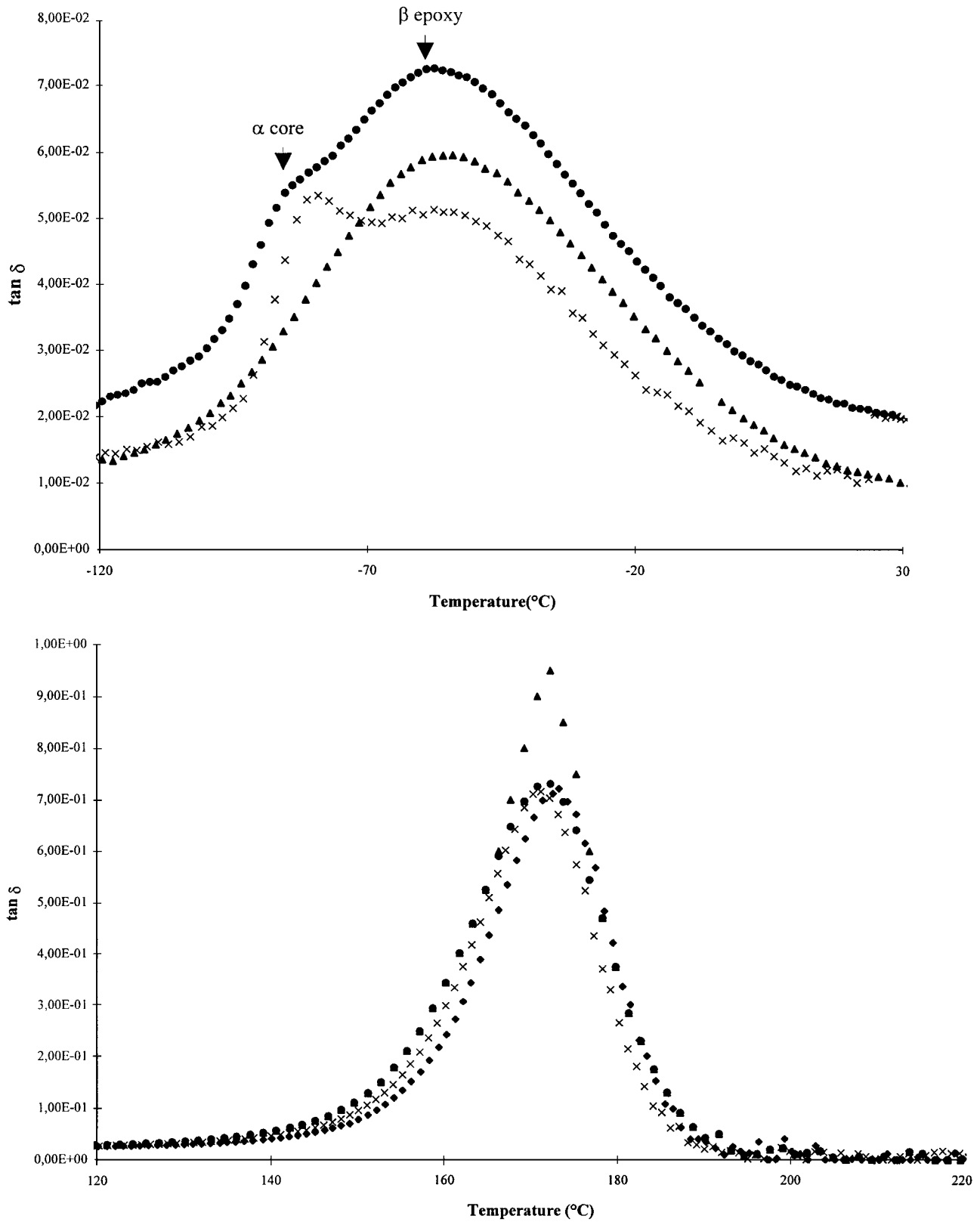


Figure 2 Dynamic mechanical spectra at 10 Hz of CSR 1/epoxy blends in the low temperature region (a) and in the glass transition region of the epoxy matrix (b). CSR 1 volume fractions: (\blacktriangle) pure epoxy (\bullet) 9.5%, (\blacklozenge) 17.5%, and (\times) 24%.

Table III Static Fracture Properties of the Pure Epoxy and Epoxy-CSR Blends Measured at Room Temperature

Composition Material	Modifier Content (% by vol)	K_{IC} (MPa \sqrt{m})	G_{IC} (J/m ²)
Pure epoxy	0	0.8	220
Epoxy + CSR 1	9.5	1.1	490
	17.5	1.1	450
	24	1.4	800
	24	1.7	1130
Epoxy + CTBN	17.5	1.3	800

quantitatively correlate these observations with the fracture toughness.

When increasing the crosshead speed, the critical stress intensity factor, K_{IC} , for all considered systems remained constant above the room temperature. At room temperature, a slight difference between the K_{IC} and G_{IC} values at low and high crosshead speed can be noticed (Table III and IV). So, the toughening mechanisms under static ($1.7 \times 10^{-4} \text{ m} \cdot \text{s}^{-1}$) or dynamic tests ($1.1 \text{ m} \cdot \text{s}^{-1}$) are similar for all the CSR-modified the epoxy networks (Fig. 3) and are in agreement with previous works done by Pearson and Yee²⁸ and Sue et al.²⁹ A slight increase of K_{IC} values of CSR-modified epoxy networks was observed at low temperature (-35°C) (Fig. 3) (see also Table IV). This suggest that the role of the rubber particles in the toughening process of glassy networks can be described as a two-step process: the relieving of the plane strain constraint, followed by the nucleation of

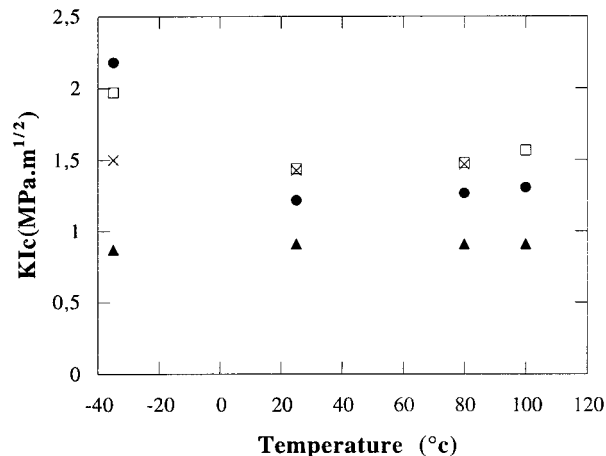


Figure 3 Dependence of the fracture toughness, K_{IC} , of CSR 1-modified epoxy as a function of the temperature for tests performed at $1.1 \text{ m} \cdot \text{s}^{-1}$: (▲): neat epoxy; (●): 9.5% vol; (□): 17.5% vol; (×): 24% vol.

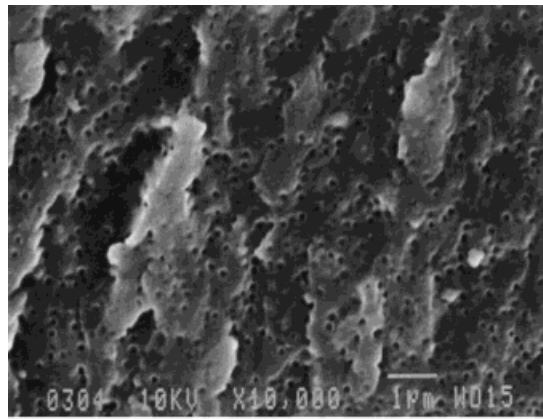
matrix shear bands from which cavitation results particles. The elongation level of the CSR particle, which is an indication of surrounding matrix plastic deformation around the crack-tip region in the epoxy matrix, is similar for both types of CSR particles (Fig. 4). Kim and co-workers,⁴² who studied CSR/epoxy blends, demonstrated that the toughening mechanisms are cavitation of the rubbery core and shear yielding in the matrix for epoxy based on DGEBA/piperidine, whereas only the cavitation process is involved for a DGEBA/diamino-diphenyl methane (MDA) matrix. Numerous articles also reported that the effect of crosslink density on the toughenability of rubber-modified epoxies.^{30,42,44} For a continuous epoxy phase having a high crosslink density, the shear yielding is restricted and the cavitation is the main energy absorbing mechanism.⁴²

The effects of the nature and the volume fraction of CSR-modified polyepoxy networks on the fatigue growth rates at room temperature are shown in Figure 5. The experimental data can be linearly fitted in a log-log diagram and are well-fitted by the Paris law:

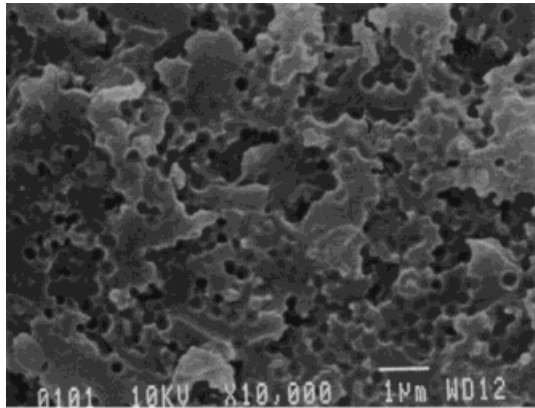
$$\frac{da}{dN} = C(\Delta K)^m$$

where C and m are material dependent constants reported in Table V. The same behavior was reported on other epoxy networks associated with hard (filler) and/or soft particles.³⁰⁻³⁴

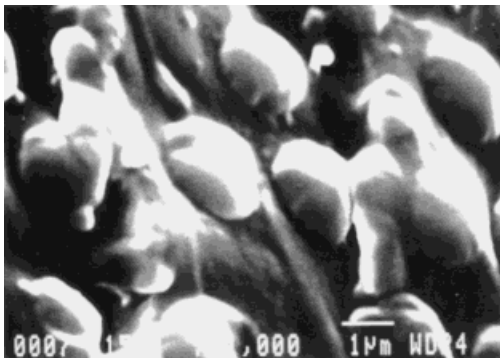
The presence of CSR particles shifts the FCP curve of the neat epoxy towards high ΔK values and improves significantly the resistance to fatigue crack propagation. In fact, a much higher ΔK is required to propagate the crack in the CSR-modified epoxy. Increasing the amount of the core-shell particles leads to the same effect. In addition, the m values decrease continuously from the



(a)



(b)



(c)

Figure 4 SEM micrographs of the static fracture surface of CSR and CTBN-modified epoxy (17.5% vol): (a) CSR 1-modified; (b) CSR 2-modified; (c) CTBN-modified.

neat epoxy to the 17.5% vol. CSR-modified epoxy and are in agreement with the values found by Lowe et al.⁴⁰ On the other hand, plotting the ΔK values at crack instability ΔK_{\max} as a function of the static fracture toughness values at low and

high crosshead speeds (cf. Tables III, IV, and V) yields acceptable linear correlations (Fig. 7). Considering the static K_{IC} values at different crosshead speeds, one can conclude that the crack growth is very closely matched when the former test is performed between $1.7 \times 10^{-4} \text{ m} \cdot \text{s}^{-1}$ and 1.1 m/s. These results are in the same range than those reported previously on filled^{32–34} and rubber-modified epoxies,^{30,40} indicating the strong influence of ΔK on FCP. In fact, crack propagation in such CSR-modified epoxies is easier than in linear polymers. As shown in Figure 6, the ΔK value necessary to achieve a given crack propagation rate (in our case chosen as $7.5 \times 10^{-4} \text{ mm} \cdot \text{cycle}^{-1}$) increases with increasing volume fraction of core-shell particles. The increasing of the FCP resistance with the introduction of CSR particles can be attributed to the toughening mechanisms detailed previously, i.e., the cavitation of the CSR particles followed by the formation of extended shear banding around the advancing crack. These results are also in agreement with other works done on core-shell particle-modified cross-linkable epoxy thermoplastics by Sue et al.²⁹ or on CTBN and siloxane-modified epoxy/anhydride networks.³⁰ Mai and Wu³⁵ applied two models to fit FCP results on rubber-modified epoxies as a function of the temperature: (a) a model in terms of crack-opening displacement and a Dugdale two-stage line zone in which fatigue damage accumulates; (b) a mechanistic model proposed by Wu³⁶ considering crack closure and damage accumulation due to the cyclic plastic strain in

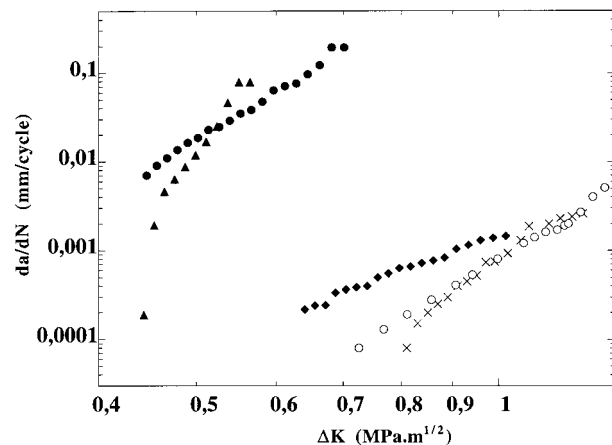


Figure 5 FCP curves for the neat epoxy and CSR 1/ epoxy blends—the same epoxy matrix modified with (17.5% vol) of CTBN is given as reference (○): (▲): neat epoxy; (●): 9.5% vol; (◆): 17.5% vol; (×): 24% vol.

Table IV Fracture Properties of the Pure Epoxy and Epoxy–CSR Blends, Determined at 1.1 m · s⁻¹ and for Different Temperatures

Composition Material	Modifier Content (% by vol)	Test Temperature (°C)	K_{IC} (MPa \sqrt{m})	G_{IC} (J/m ²)
Pure Epoxy	0	-35	0.9	170
		25	0.9	220
		80	0.9	220
		100	0.9	220
Epoxy + CSR 1	9.5	-35	2.2	1570
		25	1.2	480
		80	1.3	530
		100	1.3	560
	17.5	-35	2	1040
		25	1.4	650
		80	1.5	680
		100	1.6	770
	24	-35	1.5	1990
		-15	1.7	2230
		25	1.4	1900
		60	1.5	2150
Matrix + CSR 2	24	-35	1.3	590
		-15	1.6	1320
		25	1.4	1070
		60	1.5	1310

the crack tip reversed plastic zone. They claimed that the parameters C and m from the Paris power law cannot be easily associated to physical phenomena, and these models can be applied for describing the fatigue crack propagation of neat and CTBN-modified epoxies. Especially, according to the Williams' model,²⁷ the shear yielding at the advancing crack tip of the line zone might be the major fatigue mechanism.

The fatigue crack propagation behavior is enhanced by introducing 17.5% vol of CTBN rubber in the epoxy (Fig. 5). In fact, the FCP curve is shifted towards a higher value of ΔK , and the

resulting behavior is similar to that obtained with 24% vol of core-shell particles. This effect can be explained by the balance between the toughening mechanisms involved in such materials: cavitation of the particles and shear yielding of the matrix. In fact, the dissolved reactive rubber plasticizes the epoxy continuous phase in CTBN-modified epoxies.²⁰ As a consequence, the shear yielding of the epoxy matrix became easier. In addition, the diameter and the cavitation resistance are different in both types of particles. In fact, Sue et al.²⁹ demonstrated using optical and transmission electron microscopies that the relative size of the

Table V Fatigue Crack Propagation for Pure and Modified Epoxies: Determined Constants of the Paris Law at Room Temperature

Material	C ($\times 10^{-3}$)	m	Correlation Parameter r	ΔK_{max} , (MPa $\cdot m^{1/2}$)	ΔK (MPa $\cdot m^{1/2}$) ^a
Pure epoxy	437	8.90	0.991	0.6	0.43
Epoxy/CSR 1 (9.5% vol)	204	6.87	0.996	0.62	0.44
Epoxy/CSR 1 (17.5% vol)	1	4.23	0.994	1.01	0.85
Epoxy/CSR 1 (24% vol)	0.7	8.42	0.993	1.14	0.86
Epoxy/CSR 2 (24% vol)	0.7	8.22	0.994	1.20	0.88
Epoxy/CTBN (17.5% vol)	0.8	6.94	0.993	1.1	0.85

^a For $da/dN = 7.5 \times 10^{-4}$ mm per cycle.

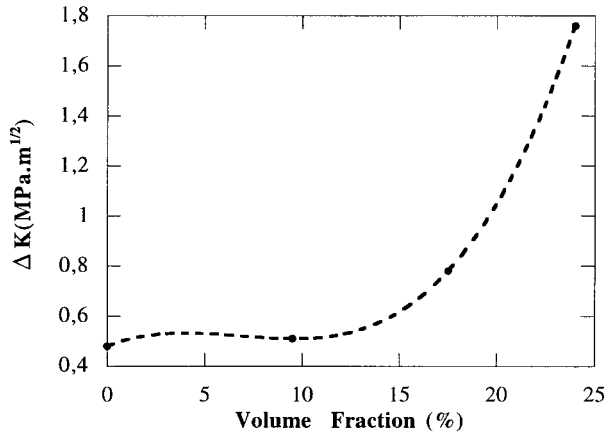


Figure 6 ΔK as a function of the volume fraction of CSR 1 in epoxy blends (at $da/dN = 7.5 \times 10^{-4} \text{ mm} \cdot \text{cycle}^{-1}$).

cavitation zone in CSR-modified epoxies is much smaller than the one in the CTBN-modified in both static and fatigue conditions.

Nevertheless, some changes were found to be slightly different under fatigue loading: the damage pattern is not progressive. The difference can be attributed to the local variation of dispersion of the CSR particles in the epoxy. These conclusions can also be made from the SEM analysis of the fracture surfaces of CTBN and CSR-modified epoxies (Fig. 4).

As reported in Table V, the fatigue crack propagation resistance for the blends including the CSR 1 and CSR 2 particles are the same. Thus, the nature of the core-poly (butyl acrylate) or poly (bu-

tadiene-*co*-styrene) does not govern the fatigue behavior in comparison with the fracture toughness. The SEM micrographs of the fracture surfaces of CSR 1 and CSR 2-based blends do not show large differences in the fracture mechanisms. Nevertheless, it can be observed on the fracture surface of both types of blends that the epoxy matrix surrounding the rubber particles undergoes plastic deformation. On the other hand, Karger-Kocsis and K. Friedrich³⁰ attributed the difference between fatigue and fracture failure to the dimension of the plastic and processing zone and on crack sharpness effects. No clear evidence of cavitated particles can be established in our experiments; thus, the cavitation resistance of rubber particles does not seem to be main mechanism involved in toughening. Such evidence requires specific experiments such as D.N-4 point bending.¹⁹ In these experiments, TEM micrographs show highly localized cavitated rubber particles linked by an array of voids to form a series of cracks. The toughening mechanism was denoted as a “croid” (from “crack” and “void” phenomena). Thus, as reported previously,⁴⁵ the shear matrix yielding between the cavitated particles and the resulting crack-tip blunting in addition to the cavitation of the particles are the main mechanisms involved in the toughening of modified epoxies.

CONCLUSIONS

The static and fatigue fracture behavior of epoxy matrix/core-shell particles blends were studied as

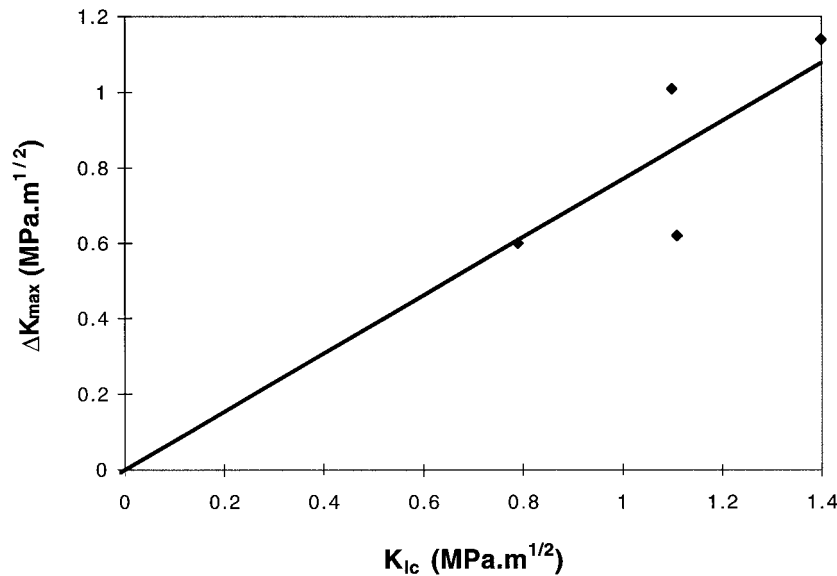


Figure 7 Plot of the onset of crack instability in fatigue, ΔK_{max} , as a function of K_{IC}

a function of the amount and the nature of the rubbery core of the CSR particles. The fracture toughness of the epoxy matrix can be largely improved by introducing predefined core-shell particles in comparison with the modification with reactive rubber such as carboxy-terminated acrylonitrile butadiene copolymers (CTBN). The toughening mechanisms that were reported in the literature for the rubber-modified epoxies, i.e., the cavitation of the rubbery particles followed by the shear yielding of the epoxy matrix, are verified. The most important toughening effect was obtained with the core-shell modifier having a poly(butyl acrylate) core instead of poly(butadiene-co-styrene). This result can be explained by the higher cavitation resistance of the PBuA core.

Work in progress deals with fracture and FCP behaviors in relation to the dispersion state of particles and will be published in a future article.

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