

Toughening of epoxy networks using pre-formed core-shell particles or reactive rubbers

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ABSTRACT

The influence of several additives (liquid reactive rubbers or core-shell particles-CSR) is studied on thermal and mechanical properties of an epoxy network based on diglycidyl ether of bisphenol-A (DGEBA) and dicy (DDA). Using high speed stirring, without any solvent, a good dispersion of the CSR is achieved. It is shown that the glass transition temperature (T_g) of the networks decreases when liquid rubbers are added but remains constant with the addition of CSR.

It is demonstrated that every kind of particles favors the shear yielding of the networks, and well fit a modified Von Mises criterion.

The fracture energies increase with the addition of rubbers, especially for the rubber with the higher acrylonitrile content. The same toughening effect is obtained with CSR if compared to the lower acrylonitrile content of liquid reactive rubbers but without any decrease in T_g of the epoxy network.

INTRODUCTION

Different ways of enhancing the fracture toughness of brittle epoxy thermosets have been investigated. The main way is to add a rubber or a thermoplastic which is initially miscible into the epoxy prepolymer and leads to a phase separation during curing.^{1,2}

The final morphology of the dispersed phase depends on the competition between the kinetic of separation phase process and the kinetic of the epoxy networks formation. For example, the nature of the reactants, the structure and the nature of the functional groups of the rubber, and the curing conditions influence the characteristics of the dispersed phase and the final properties of the rubber-modified epoxies.³⁻⁶ Another way is to add pre-formed particles into the reactive epoxy mixture.⁷⁻¹¹

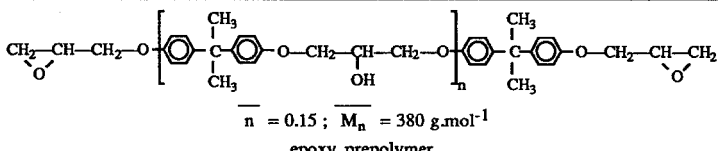
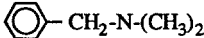
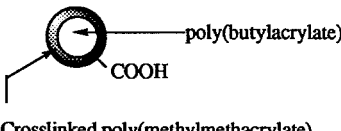
In this paper, an epoxy network based on diglycidylether of bisphenol-A (DGEBA) and dicyandiamide (Dicy) is modified with two kinds of rubber modifier : 1) an epoxy-terminated butadiene-acrylonitrile copolymer (ETBN) : 2) core-shell particles (CSR) constituted by a poly(butylacrylate) core and a carboxy-functionalized crosslinked poly(methyl-methacrylate) shell. In the first case, the morphology (sizes and composition) of the separated phase is strongly dependent on the curing conditions and initial amount of rubber, whereas, in the second case, the morphology is initially defined.

EXPERIMENTAL

Reagents - Materials

The chemical reagents used in this work are presented in Table I. A mixture of diglycidylether of bisphenol-A and dicyandiamide was used as the epoxy continuous phase. The amino-hydrogen-to-epoxy ratio of 0.6 was chosen in order to obtain the higher glass transition temperature, T_g , using benzyldimethylamine as a catalyst and a cure schedule of 1 hour at 120°C followed by 2 hours at 180°C .¹² The epoxy-terminated liquid rubber (ETBN) was obtained from the reaction between the DGEBA and a carboxy-terminated butadiene-acrylonitrile copolymer (CTBN) (carboxy-to-epoxy = 0.065).⁵

Table I Chemical products used in synthesis of materials

Name	Chemical formula	Supplier
DGEBA	 <p style="text-align: center;">$n = 0.15$; $\overline{M}_n = 380 \text{ g.mol}^{-1}$ epoxy prepolymer</p>	Bakelite 0164
DDA	$\text{H}_2\text{N}-\text{C}=\text{N}-\text{C}=\text{N}$ $\quad \quad \quad $ $\quad \quad \quad \text{NH}_2$ <p style="text-align: center;">Cyanoguanidine or dicyandiamide</p>	Bakelite VE 2560
BDMA	 <p style="text-align: center;">Catalyst or initiator</p>	Aldrich
CTBN	$\text{HOOC} \left[\left(\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2 \right)_x - \left(\text{CH}_2-\underset{\text{CN}}{\text{CH}} \right)_y \right]_z \text{COOH}$ <p style="text-align: center;">CTBN8 ($\overline{M}_n = 3500 \text{ g.mol}^{-1}$); CTBN13 ($\overline{M}_n = 3200 \text{ g.mol}^{-1}$); $\overline{F}_n = 1.8$</p>	Hycar CTBN BF Goodrich
CSR	 <p style="text-align: center;">Crosslinked poly(methylmethacrylate)</p>	Rohm & Haas Ref. EXL 3387

Two CTBN rubbers were used for this study in order to change the initial miscibility with DGEBA/Dicy mixture: the CTBN8 (leading to an ETBN denoted R8) and the CTBN13 (ETBN denoted R13) with acrylonitrile contents of 18 % and 26 % respectively.

A dried core-shell latex (Table 1) based on a poly(butyl-acrylate) core ($T_g \approx -56^\circ\text{C}$) and a carboxy-functionalized crosslinked poly(methyl methacrylate) shell ($T_g \approx 100^\circ\text{C}$) was used as CSR particles. The mean diameter of the CSR particles is equal to 300 nm.

Different amounts (from 0 to 15 % by weight) of reactive rubbers (R8 or R13) or CSR were added to the DGEBA/Dicy mixture. In the case of the CSR particles, the mixing was done using high speed stirring (UltraturaxT50).

Characterization

The viscosities, η , of the epoxy/rubber mixtures were measured as a function of shear rate, $\dot{\gamma}$, using a co-axial rheometer (Rheomat 115 Contraves) at 60°C.

The characteristics of the dispersed phase were studied by electronic microscopies (SEM and TEM) and differential scanning calorimetry, DSC, (Mettler TA3000 at 7.5°.(min⁻¹). In addition, dynamic mechanical spectroscopy was performed to obtain on parallelepipedic specimens the shear complex modulus G^* (storage modulus, G' , and loss factor, $\tan \delta$) using a RDA700 viscoelasticimeter from Rheometrics operating at 1.6×10^{-2} and 10 Hz.

The Young's modulus, E_{RT} , and the yield stress, σ_y , were measured at room temperature during tensile and compression tests respectively (strain rate : 8×10^{-4} s⁻¹). The fracture properties were studied using linear elastic fracture mechanics at room temperature on SEN8 specimens.⁵

RESULTS AND DISCUSSION

An important parameter for processing the reactive epoxy system is the initial viscosity of the mixture. Figure 1 clearly demonstrates that the introduction of rubber (CSR or ETBN) leads to an increase of the viscosity. The viscosity of the epoxy/CSR mixture significantly exceeds that of the pure DGEBA resin and of the DGEBA/ETBN mixture at low shear rates. Fortunately, at high shear rates, which is the case of most of the processes, the viscosities of epoxy/CSR and epoxy/ETBN are the same. This result indicates that, a good dispersion of the particles CSR is obtained using high speed mixing without any solvent or emulsifier in opposition to previous works.^{8,9}

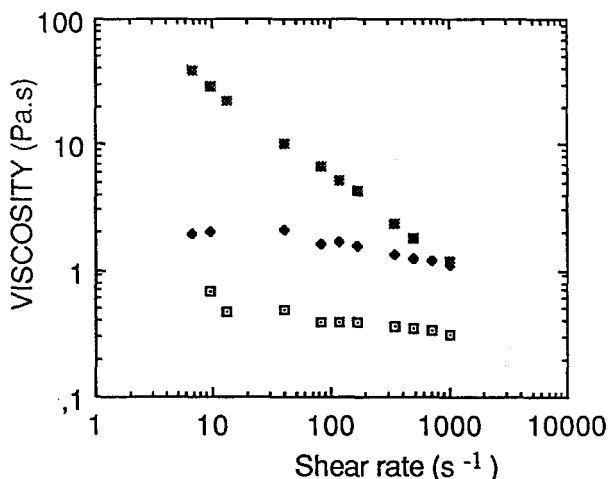


Figure 1 Dependence of the viscosity on the shear rate at 60°C : (□) : pure DGEBA ; (◆) : DGEBA + 15 % wt. R13 ; (■) : DGEBA + 15 % wt. CSR

The glass transition temperature of the cured epoxy matrix is about 144°C whereas the T_g of the pure rubbers are - 60°C and - 42°C for R8 and R13 respectively. The glass transition temperatures of the epoxy continuous phase and dispersed phase (denoted T_{gE} and T_{gR} respectively) of the cured modified epoxies are shown in Table II for all the systems. The

introduction of reactive rubbers (R8 or R13) leads to a decrease in T_{GE} . In addition, it could be noted that the glass transition temperature of the continuous phase decreases as the initial amount of rubber increases and by increasing the acrylonitrile content of the CTBN rubber (from R8 to R13). These effects are associated to a part of rubber which remains dissolved in the epoxy matrix and to the higher miscibility of the R13 rubber into the epoxy reactive mixture.³⁻⁵ From the glass transition temperature of the pure constituents and using the Fox's equation,¹³ the volume fraction of the rubber in the continuous phase, ϕ_R^c , and in the dispersed phase, ϕ_R^D can be calculated⁵ (Table II). As expected, the R13-modified epoxies display the higher ϕ_R^c values indicating a higher miscibility of the ETBN13 rubber. ϕ_R^c also increases with the initial amount of rubber as reported previously.

Using a home-made image analysis software on scanning electron micrographs, the distribution of the particle sizes is obtained which allows us to calculate the average diameter, \overline{D} (Table II). As reported in previous papers,³⁻⁵ \overline{D} increases as the amount of rubber increases and is lower for the more miscible rubber.

In the case of CSR modified-polyepoxy, the epoxy continuous phase displays a glass transition temperature which is close to those obtained on the pure epoxy network (Table II). Even a slight increase of T_{GE} is observed as the amount of CSR increases. The temperature of the maximum of the $\tan \delta$ curve (DMS) at the main relaxation, α , corresponding to the glass transition of epoxy, displays the same trends (Table II). Thus, these results demonstrate that, in opposition to the reactive rubber for which a part remains dissolved in the epoxy, no plasticization of the continuous phase is observed using CSR particles. The high temperature region of the dynamic mechanical spectra of the CSR-modified epoxies, could be analyzed by compare to the spectra of a film made by compression of CSR particles at 180°C under a pressure of 150 bars and of the epoxy network (Fig. 2). In fact, in the loss spectrum of the CSR/epoxy blend, the main relaxations of the PMMA shell and epoxy occur in the same zone. The slight increase of T_{GE} (or $T_{\alpha E}$) could be related to a decrease of the mobility of the macromolecular chains and/or to chemical changes in the vicinity of the epoxy functionalized CSR particles.

Table II Characteristics of the continuous and dispersed phases in the blends

Material (% wt.)	ϕ_R^o (%)	ϕ_R^c (%)	\overline{D} (μm)	ϕ_R^D (%)	DSC ^{a)}		DMS ^{b)}
					T_{GE} (°C)	T_{GR} (°C)	$T_{\alpha E}$ (°C)
Matrix	0	/	/	/	144	/	153
R8/5 %	6.29	0	1.53	23	144	- 62	153
R8/10 %	11.6	1.8	1.67	37	138	- 62	146
R8/15 %	17.3	2.7	1.90	54	135	- 62	145
R13/5 %	6.25	3.7	0.6	23	132	- 44	144
R13/10 %	11.6	5.6	1	39	126	- 44	140
R13/15 %	17.3	8.5	1.36	48	121	- 40	138
CSR/5 %	6.25	0	0.3	100	144	- 62	157
CSR/10 %	11.6	0	0.3	100	146	- 62	159
CSR/15 %	17.3	0	0.3	100	149	- 62	159

^{a)} 7.5 K.min⁻¹; ^{b)} at 0.016 Hz

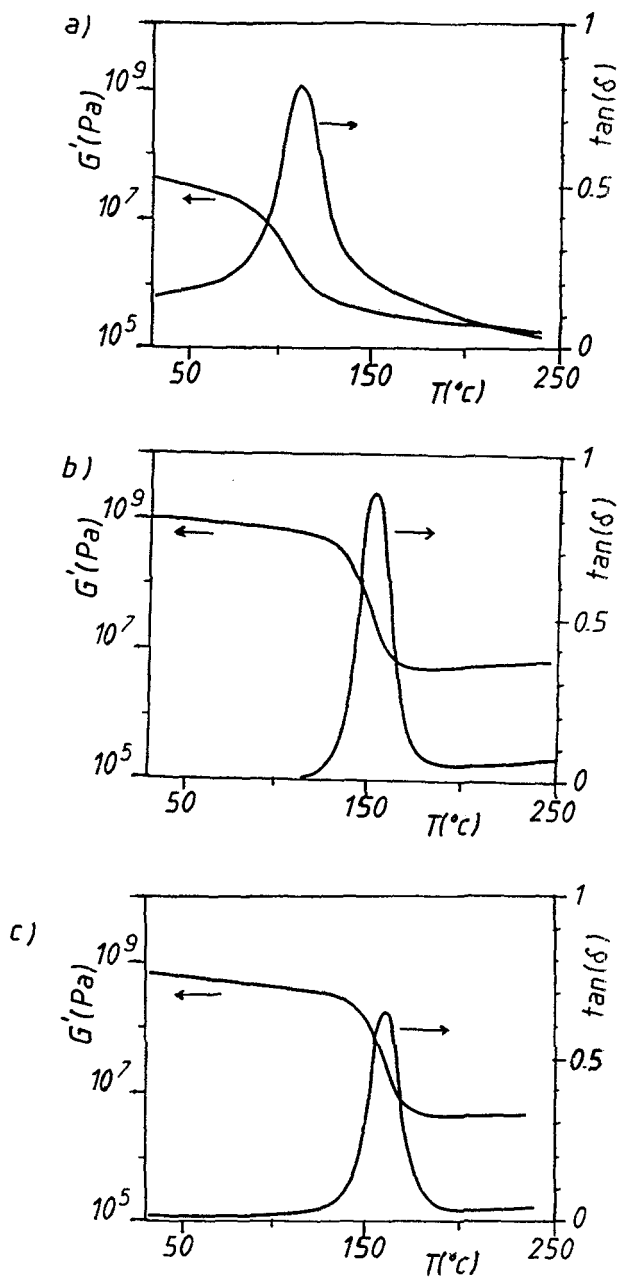


Figure 2 Dynamic mechanical spectra (G' and $\tan \delta$ vs. temperature) at 10 Hz of : (a) : CSR film (2 mm-thick) ; (b) : pure epoxy network ; (c) : CSR-modified (15 % wt.) epoxy network

In addition, it could be noted on the spectrum of CSR-films that a rubbery plateau exists indicating that the PMMA shell is really crosslinked and that the processing (temperature, pressure) does not affect the CSR particles structure.

TEM analysis clearly confirms that the dispersion of the CSR aggregates to single unitary particles is obtained (Fig. 3).

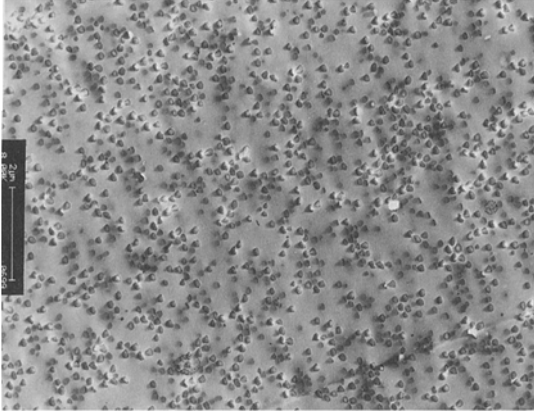


Figure 3 TEM micrograph of a CSR-modified (15 % wt.) epoxy network

Table III gives the mechanical properties of the various rubber/epoxy blends at room temperature. As expected, the tensile modulus decreases as the amount of rubber increases for the different kinds of rubbers (ETBN or CSR) according to the low modulus of the elastomeric dispersed phase. The decreasing of ERT is more pronounced in the case of the blends based on the R13 rubber. In fact, as reported previously, for R13, a higher amount of rubber remains dissolved in the continuous phase which acts as a plastifier.

Table III Mechanical properties, at 25°C, of the various materials

	ERT (GPa)	σ_y a) (MPa)	K_{Ic} (MPa.m ^{1/2})	G_{Ic} (kJ.m ⁻²)
matrice	2.9	102	0.7	0.13
R8/5%	2.6	95	1	0.35
R8/10%	2.3	83	1.26	0.60
R8/15%	1.8	70	1.33	0.87
R13/5%	2.6	94	1.3	0.57
R13/10%	2.3	86	1.5	0.84
R13/15%	1.8	76	1.6	1.35
CSR5%	2.7	94	0.95	0.29
CSR10%	2.3	85	1.3	0.64
CSR15%	1.8	76	1.3	0.8

a) corrected for volume variations ($\dot{\epsilon} = 8 \times 10^{-4} \text{ s}^{-1}$)

The same trend is observed for the plastic properties (Table III). In addition, the analysis of the yielding behavior carried out in different modes of testing (tension, compression, shear, and plane-strain compression) indicates that the shear yielding is the main mechanism involved in the deformation process and that the introduction of a rubber favors the plastic deformation. As a matter of fact, the yielding envelope could be fitted using the Von Mises criteria modified by Sternstein¹⁴ (Fig. 4) in plane-stress ($\sigma_3 = 0$).

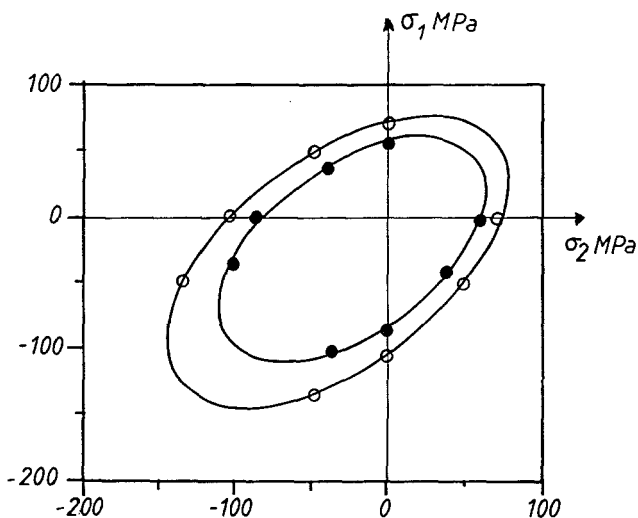


Figure 4 Yielding envelope at 25°C, $\sigma_3 = 0$, for : (●) : R8-modified epoxy (15 % wt.) ; (○) : pure epoxy network

Figure 5 shows the large increase of the fracture energy, G_{IC} , for the rubber-modified epoxies in comparison with the pure epoxy network. The largest improvement of the fracture properties is made using the R13 rubber, whereas the same effect is obtained with the R8 rubber and CSR particles. The toughening effect needs to be considered with the thermal behavior. In fact, even if a large improvement is obtained using a more miscible reactive rubber (R13), it induces a large decrease in the glass transition temperature and, as a consequence, an increase on the mechanical properties. A less pronounced effect is observed for a reactive rubber with a lower acrylonitrile content (R8). In the contrary, a similar fracture toughness improvement is obtained by introducing core-shell particles. These CSR particles keep their integrity during the processing of the epoxy system and as a consequence, no plasticization effect is noted. Using such a concept consisting of the introduction of pre-formed particles, the morphology of the dispersed phase is well-defined and the toughening effect proceeds from the same mechanism as for liquid reactive rubbers. This way of toughening leads to reinforced epoxies with a morphology which is not dependent on the nature of the rubber and/or on the curing conditions, i.e., on the phase separation process.

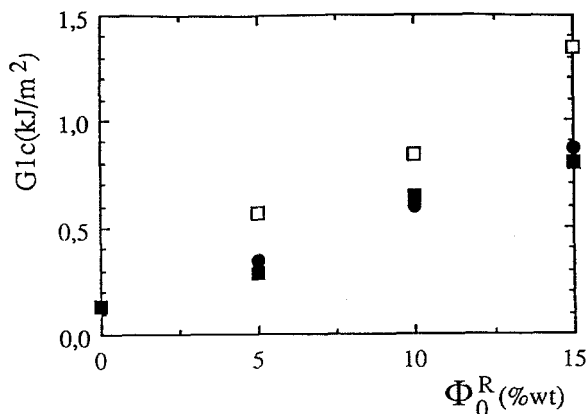


Figure 5 Fracture energy vs. the initial amount of rubber (ETBN or CSR) ; (●) : R8-modified epoxy ; (□) : R13-modified epoxy ; (■) : CSR-modified epoxy

Further investigations are in progress in order to study the effect of the CSR structure (thickness of the shell, nature of the phases, presence of functional groups,...) on the toughening of the epoxy networks.

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