Influence of a two-step process and of different cure schedules on the generated morphology of a rubber-modified epoxy system based on aromatic diamines

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Toughened epoxy networks based on diglycidyl ether of bisphenol A (DGEBA) prepolymer, 4,4′-diamino diphenyl sulphone (DDS) curing agent and epoxy-terminated butadiene–acrylonitrile copolymer–2,2′-bis(4-aminophenoxy)phenyl propane (ETBN–BAPP) adduct were prepared using a two-step process and compared to DGEBA–DDS–ETBN networks prepared using a one-step process. The kinetics of the reaction was followed by size exclusion chromatography and differential scanning calorimetry: the extent of reaction was found to be higher at the cloud point and lower at gelation in the two-step process. The morphology was studied by transmission and scanning electron microscopy. For the same initial rubber content, large differences were observed: when a two-step process was used, the dispersed particles showed irregular contours with a broad diameter distribution, but the volume fraction of dissolved rubber in the rigid matrix was independent of the process. The effect of the cure cycle on the morphology, mechanical and viscoelastic properties was examined. All of the samples had the same impact strength ($\simeq 30$ kJ m^{-2}) with an identical modulus and glass transition temperature. These results confirm that the most important parameter is the volume fraction rather than the diameter of the dispersed-phase particles.

(Keywords: epoxy; amine; toughened networks; two-step process; morphology, phase separation)

INTRODUCTION

Thermosets have often been modified by the incorporation of a rubbery second phase[1,2]. Rubber-toughened epoxies have been the most extensively studied of these polymers, owing to their wide use as structural adhesives and in fibre composites. The multiphase microstructure of such a system can be observed by scanning or transmission electron microscopies (SEM or TEM). The microstructural features, particle size and particle size distribution are still to be conclusively established[3].

Several authors have analysed the influence of cure schedule and rubber content on the resulting morphologies[4–12]. The cure cycle is chosen based on the facts that initially (conversion $x=0$) the system is homogeneous, phase separation starts at the cloud point conversion, x_{cp}, and the final morphology is arrested at gelation, x_{gel} (in fact well before gelation). It is therefore only necessary to gel at a prescribed temperature to develop the intended morphology. The system may then be cured at a second higher temperature to attain the maximum glass transition temperature, T_g. Analysis of experimental results shows that the concentration of dispersed particles decreases as temperature increases[5,6,9,10]; the volume fraction of the dispersed phase remains practically constant[8–10], then goes through a maximum[5] or decreases[5,6] as temperature increases, and the average diameter of the dispersed-phase particles goes through a maximum[5,9], or increases[8,10], as temperature increases. Regarding the influence of initial rubber concentration it is agreed that increasing the rubber content leads to higher values for the volume fraction and the average diameter of the dispersed-phase particle[4,7–10].

Other authors prefer to use epoxy network modifiers to increase fracture toughness. The most important modifier used is bisphenol A (BPA). It acts as a toughener partly because the volume fraction of the separated phase tends to be higher than in binary epoxy–rubber blends; subinclusions are easily visible in ternary BPA–epoxy–rubber blends. In the case of the epoxy system based on diglycidyl ether of bisphenol A (DGEBA) and piperidine, this effect is produced without any change in the T_g of the matrix by the reaction with BPA[13]. Other phenols such as 1,5-dihydroxy naphthalene or 2,2-bis(4-hydroxyphenyl)sulphone[14] can be used instead of BPA.

Romanchick *et al.*[15] have prepared two phases in cured solid materials with the help of a pre-reaction (chain extension) between BPA and liquid DGEBA. The material can then be post-cured with imidazole-accelerated dicyandiamide. The morphology of the pre- and post-cured samples has been determined. In the pre-cured sample, the two phases occur as core–shell structures, with the interior consisting of epoxy, the shell of phase-separated elastomer and the matrix of epoxy. The final morphology of the post-cured sample is controlled by the morphology of the pre-cured sample and by the gelation time during the second step of the reaction.

Similar two-step reactions have been proposed using liquid diamines instead of phenols[16].

Recently we have studied the curing of a DGEBA epoxy prepolymer with different aromatic diamines[17],

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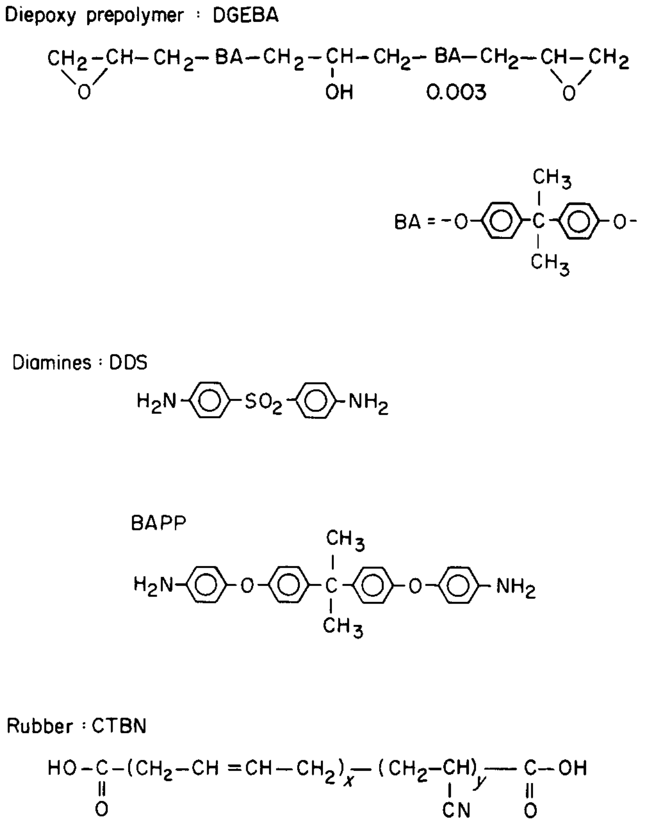

Figure 1 Chemical structures of the diepoxy, diamines and rubber

including 4,4′-diamino diphenyl sulphone (DDS) and 2,2′-bis(4-aminophenoxy)phenyl propane (BAPP). Rubber-toughened epoxies based on DGEBA and DDS have been studied by different authors[18,19], but always using a simple one-step reaction. The purpose of this work is to investigate the role of a two-step reaction procedure using a BAPP diamine for controlling the morphology of a rubber-modified DGEBA–DDS system.

Unlike the case with diphenol, it is possible with diamines (amino hydrogen functionality $=4$) to decrease the extent of reaction at gelation, x_{gel}, while keeping the same final network. The model for this is presented in a paper by Williams *et al.*[20].

EXPERIMENTAL

Materials

The chemical structures of the different reagents are shown in *Figure 1*. The DGEBA-based epoxy prepolymer used was DER 332 (Dow), with an equivalent weight of epoxy groups equal to 175 g eq^{-1} ($\bar{n}=0.03$). The diamines were DDS (Fluka) and BAPP (Mallinkrodt). The carboxy-terminated butadiene–acrylonitrile copolymer (CTBN) rubber used was Hycar 1300 × 13 (Goodrich), with a number average molecular weight close to 3600, a 26% acrylonitrile (AN %) content and a COOH functionality $=1.8$. The epoxy terminated butadiene–acrylonitrile copolymer (ETBN)–DGEBA ($\bar{n}=0.03$) adducts were prepared following a procedure previously described[10,11].

Techniques

The polymerization kinetics up to gelation was followed by size exclusion chromatography (s.e.c.) of the partially reacted samples at a selected temperature. A Waters apparatus with a refractive index detector was used with tetrahydrofuran (THF) as elution solvent.

A Mettler TA3000 microcalorimeter was used to measure the T_g values of different samples using a 10°C min^{-1} heating rate, under an argon atmosphere. The onset value was always taken as the T_g.

The time at which phase separation began, i.e. the cloud point for a particular sample and cure temperature, was recorded with a light transmission device described previously[10]. The use of light in the visible region led to an observable alteration of the dispersed particles having diameters of the order of 0.1 μm.

Fracture surfaces were observed using a scanning electron microscope (Jeol 840 A) after gold sputtering the surface. The detection level was close to 0.1 μm. Transmission electron micrographs were obtained for the specimens that had been stained with ruthenium chloride and microtomed at room temperature to give a thickness of 500 Å (0.05 μm). A Philipps EM 301 was used at magnifications of 20 800, 28 800 and 44 800.

Relaxations of both phases were determined from dynamic mechanical measurements. A dynamic mechanical thermal analyser (Polymer Laboratories) was used at a frequency of 0.1 Hz. The samples were tested in a double cantilever bending mode with a fixed displacement.

Unnotched instrumented Charpy impact characterization was carried out as described elsewhere[10].

DESCRIPTION OF THE POLYMER SYNTHESIS

The steps involved in the synthesis of the rubber-modified epoxy networks based on DDS and BAPP are summarized in *Table 1* together with the weight per cent of the different monomers introduced at each step.

To prepare the ETBN adduct, the CTBN rubber (Hycar 1300 × 13) was reacted at 85°C with an excess of DGEBA, using a carboxyl-to-epoxy (c/e) ratio $=0.065$. This reaction was carried out in the presence of 0.18 wt% triphenylphosphine[10].

For the two-step process, only BAPP is introduced during the first step at 135°C.

The amino hydrogen to epoxy (a/e) ratio was chosen to be 0.3 to prevent the system from gelling. Only 36.5% of the DGEBA was introduced in the first step.

Initially, at 135°C, the system is miscible but phase separation can occur during the reaction. In the second step, the remaining DGEBA (63.5%) and the DDS were introduced, with the following two conditions:

$$15\,\text{wt\%}\ \text{CTBN (R)}$$

and

$$a/e = \frac{4[\text{DDS}]+4[\text{BAPP}]}{2[\text{DGEBA}]_{\text{total}}} = 1$$

If we introduce even 36.54% of the DGEBA in the first

Table 1 Weight per cent of different monomers introduced at each step for the rubber-modified epoxy systems based on DDS hardener and with or without a chain-extender step with BAPP

	Adduct ETBN		First step	Second step	
	CTBN	DGEBA	BAPP	DGEBA–DDS	
	(c/e = 0.065)		(a/e = 0.3)	(a/e = 1)	
R-BAPP-DDS	15	22.4	4	38.9	19.7
R-DDS	15	22.4	0	40	22.6

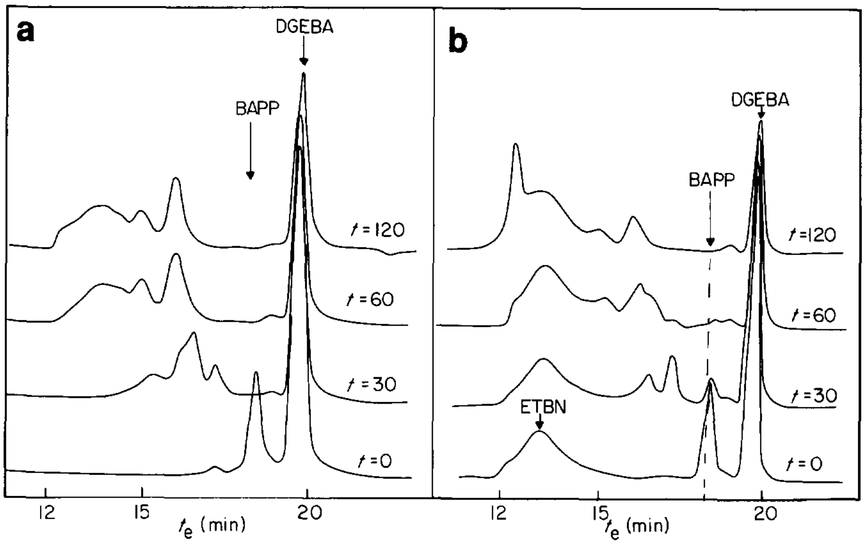

Figure 2 Evolution of the reaction of DGEBA with the diamine BAPP at 135°C, a/e = 0.3 (a) without and (b) with 36.6 wt% rubber (see text)

step, the per cent of BAPP compared to the overall (DDS + BAPP) would be 11 wt%.

The two-step network will be denoted R-BAPP-DDS.

In *Table 1*, the monomer proportions used for a one-step process, without BAPP, are also given for comparison. The one-step network will be denoted R-DDS.

RESULTS

In order to control the two-step and one-step processes, it is first necessary to know the chemistry of the systems: the extent of reaction as a function of time, and also the times at which phase separation, gelation and vitrification occur.

Kinetics of the first reaction step

In order to control the first step and also to analyse the influence of rubber on the kinetics, conversion *versus* time curves for the epoxy–BAPP mixture, with a/e = 0.3, isothermally cured at 135°C, were determined by s.e.c. *Figure 2* shows an example of the s.e.c. chromatograms for mixtures without and with 36.2 wt% (15/41.4) rubber.

As explained previously[11,17] the overall conversion of epoxy is given by:

$$x_e = 1 - (h_t/h_o)_e^{1/2}$$

where $(h_t/h_o)_e$ is the ratio of the peak height of the DGEBA monomer at any time with respect to the initial peak height.

With the aromatic diamine it is also possible to use s.e.c. to determine the conversion of BAPP monomer[17]:

$$X_a = 1 - (h_t/h_o)_a$$

where $(h_t/h_o)_a$ is the ratio of the peak height of the diamine monomer at any time with respect to the initial peak height.

The conversion, x_e, *versus* time, t, curves for the neat and the rubber-modified systems are given in *Figure 3*. The experimental points are on the same curve for the first part of the reaction but after $t = 75$ min, x_e for the rubber-modified system becomes higher than x_e for the neat system.

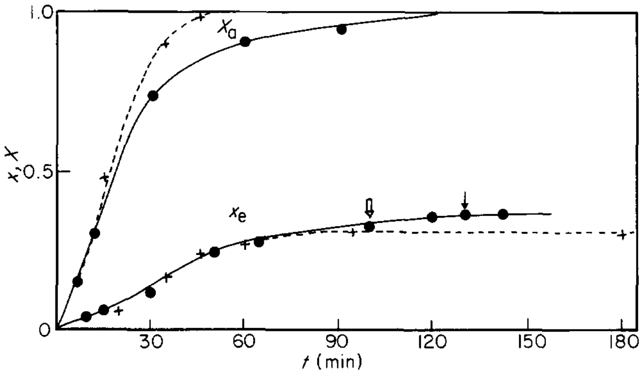

Figure 3 Extent of reaction measured by s.e.c. for DGEBA–BAPP with the stoichiometric ratio a/e = 0.3: (●) with 36.6% R; (+) without rubber. Epoxy conversion, x_e; diamine conversion, X_a; gelation, ↓; cloud point, ⇓

For the neat system after $t = 90$ min, x_e is constant and equal to 0.305. This result is consistent with the fact that the initial a/e ratio = 0.3. It also means that in this case there is no secondary reaction such as etherification, at 135°C for $t < 180$ min, even with a large excess of epoxy.

For the rubber-modified system, after $t = 75$ min, x_e still increases. The time at which phase separation begins, i.e. the cloud point as determined with a light transmission device, occurs at $t = 100$ min and for a conversion of $x_{cp} = 0.32$. Gelation occurs after the cloud point, at $t = 130$ min and $x_{gel} = 0.364$. We repeated this experiment several times and each time gelation occurred at $x_{gel} = 0.365 + 0.05$. For the same time, X_a is lower in the rubber-modified system than in the neat system. The phase separation phenomenon probably disturbs the reaction but this still does not explain why a higher value is obtained.

It is evident that epoxy groups are consumed by another reaction other than that of amino hydrogen with epoxy. The fact that triphenylphosphine has been previously used to catalyse the carboxy–epoxy reaction and can also catalyse the hydroxy–epoxy reaction can explain this result. For this reason, and to prevent gelation, the first step was then stopped after 60 min by introducing

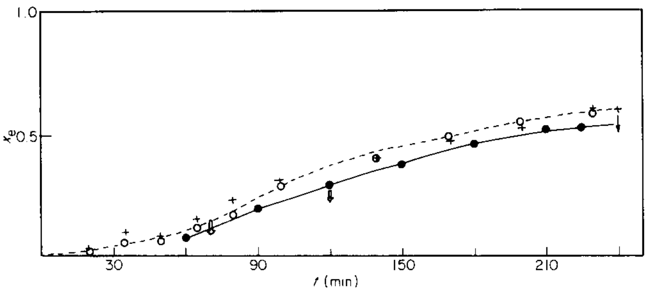

Figure 4 Extent of reaction determined by s.e.c. for different systems at 135°C: (+) DGEBA–DDS; (○) DGEBA–DDS and 15% R, system R-DDS; (●) the second step of the two-step system, R-BAPP-DDS with 15% R (see *Table 1*). Arrows: (↓) gelation; (⇓) cloud point

further DGEBA and dissolving the DDS (*Table 1*). At 60 min the mixture is clear and no phase separation has occurred.

Kinetics of the second reaction step

First, s.e.c. was used to determine the influence of adding 15 wt% rubber on the kinetics of the samples based only on DDS (one-step system) with a/e = 1. *Figure 4* shows the results for a cure temperature of 135°C. It can be seen that the experimental points for the neat and rubber-modified systems fall on the same curve. Verchère *et al.*[11] observed a higher reactivity at the first stage of the reaction for the rubber-modified system based on a cycloaliphatic diamine. The higher reactivity was explained by an autocatalytic mechanism of the initial hydroxyl groups $(OH)_0$ [higher concentration of $(OH)_0$ in the case of the rubber-modified system] and also the catalytic effect of impurities such as triphenylphosphine. However, their experiments were done at lower temperatures, 50–75°C, and these effects were not observed with DDS at 135°C.

The gelation, vitrification and phase separation times were determined as described in the Experimental section. Gelation and then vitrification occur at the same times for the neat and rubber-modified systems, and at the same conversion x_e. The value of $x_{gel} = 0.62$ has been discussed elsewhere[17].

For the rubber-modified system, R-DDS, phase separation was completed very rapidly at $t = 70$ min, well before gelation, in agreement with previous results for systems based on cycloaliphatic diamines[10,11]. The conversion at the cloud point, x_{cp}, is equal to 0.14 (0.17 for the DGEBA-3DCM system[11] but with CTBN × 8).

Vasquez *et al.*[18] have found quite a different value at 120°C, $x_{cp} \approx 0.40$, which would be even higher at 135°C. This value was determined theoretically from an experimental determination of the Flory–Huggins interaction parameter, χ, and the calculation of the binodal and spinodal curves, assuming χ is a simple function of temperature with no dependence on composition or conversion. To obtain experimental values of χ, cloud point values have been determined for formulations containing various amounts of CTBN × 13 in a DGEBA–DDS mixture having a large excess of DGEBA (a/e = 0.286).

Similar experiments have been done by Roginskaya *et al.*[21]. In these cases the large difference in the solubility parameters between DGEBA and DDS monomers ($\delta = 20.45$ and 23.31 MPa$^{1/2}$ respectively[22]) leads to a lower χ value than the useful one with a/e = 1.

Figure 4 shows a comparison of the behaviour of rubber-modified systems for a two-step reaction (R-BAPP-DDS) and a one-step reaction (R-DDS).

For R-BAPP-DDS, the kinetics of the first step is described in *Figure 3*. After 1 h (first step) at 135°C, the mixture was clear (no phase separation) and $x_e = 0.27$ with respect to the initial fraction of DGEBA introduced. Then liquid DGEBA and DDS powder were introduced (*Table 1*). The new conversion at the beginning of the second step, expressed with respect to the total DGEBA, was then $x_e = 0.075$.

After 30 min the DDS was totally dissolved and the solution became clear again. A phase separation phenomenon appeared after 120 min (60 min during the second step), for a conversion $x_{cp} = 0.27$. Gelation, defined by the time at which the presence of an insoluble fraction in THF was first detected, took place at a conversion of $x_{gel} = 0.52$ ($t_{gel} = 250$ min, *Table 2*).

The behaviour of a two-step reaction, R-BAPP-DDS, compared to a one-step reaction, R-DDS, can be described in the following way. If we assume that the reactivity of the epoxy group of ETBN and DGEBA molecules are the same, the probability for the ETBN rubber to react with diamine molecules and to be chain-extended is higher in a two-step procedure than in a classical one-step system (being equal to 6% in the first case and only 2.2% in the second case).

Rubber chain extension induces a copolymer effect on the miscibility of the rubber in the epoxy system, and can explain the high x_{cp} value for the two-step process, $x_{cp} = 0.27$, compared to the one-step process, $x_{cp} = 0.14$.

At the end of the first step, we have increased the functionality of the epoxy oligomers, because some molecules now have a functionality $\geqslant 4$. The profile of the increase in viscosity during the second step and the conversion at the gel point will be different[20].

Initially BAPP had been chosen because its reactivity is 12 times higher than the reactivity of DDS[17]. However, we think that using BAPP instead of DDS during the first step had a secondary effect; the trends are the same using a two-step reaction, R-(DDS)-DDS. This will be verified later.

The effect of a two-step process is to increase x_{cp} and to decrease x_{gel}. Therefore, for a given system, we can modify the viscosity at the cloud point, η_{cp}, and the time $\Delta t = (t_{gel} - t_{cp})$ for the phase separation process. These effects will influence the morphology of the two-phase system.

Table 2 Characteristics of the reaction for epoxy networks with and without rubber (15 wt%) at 135°C

System	DDS	R-DDS (one step)	R-BAPP-DDS (two steps)
Phase separation			
t_{cp} (min	–	70	120
x_{cp} (%)	–	14	27
Gelation			
t_{gel} (min)	240	250	250
x_{gel} (%)	62	62	52
Vitrification			
t_{vit} (min)	400	405	390

Table 3 Glass transition temperatures and mechanical properties for different epoxy networks without rubber

Systems	T_g (°C)	T_α[a] (°C)	E_{20} (GPa) (±0.05)	R_s (kJ m^{-2}) (±4)
DDS	218	226	2.80	13
BAPP (11) DDS (89)	206	-	2.50	14
BAPP	168	172	2.45	20

Curing cycle: 15 min at 135°C and 2 h at 180°C and 2 h at 230°C
[a] Determined at 0.1 Hz

Effect of the two-step process on the morphology of the rubber-modified epoxy network

Further details comparing the networks based on DGEBA and different aromatic diamines are given elsewhere[23]. Since two different diamines were used during the two-step process, the effects of using different amounts of BAPP on the properties of a DGEBA–DDS network without rubber are given in *Table 3*. As the per cent of BAPP increases, the T_g and the Young's modulus at room temperature, E_{20}, decrease. The impact strength, R_s, is constant, except for the pure DGEBA–BAPP network for which a rather high value is obtained, due to the higher molecular weight and flexibility of BAPP units compared to DDS units.

A phase separation model[12] was used to simulate the morphologies obtained in a system consisting of DGEBA cured with a cycloaliphatic diamine in the presence of an ETBN. This model is based on a thermodynamic description through the Flory–Huggins equation and constitutive equation for polymerization and phase separation rates. A nucleation growth mechanism is believed to take place because of the very low values of interfacial tension for this type of system. In this case the final morphology is arrested well before gelation (x_{gel}) due to the large increase in viscosity with conversion and the corresponding high decrease in the phase separation rate. In a first approach the systems under study are expected to follow a similar model.

Scanning and transmission electron microscopies, differential scanning calorimetry (d.s.c.) and dynamic mechanical analysis (d.m.a.) were used to characterize the generated morphologies. The details of the analyses using these techniques are reported elsewhere[11].

In order to visualize the resulting morphology *Figure 5* shows SEM micrographs and TEM micrographs of samples containing 15% R and pre-cured at 135°C with a one-step, R-DDS, or a two-step, R-BAPP-DDS, process. The average particle diameter, $\bar{D}$, and the volume fraction of the dispersed phase V, can be obtained from SEM micrographs:

$$\bar{D}\ (\mathrm{SEM}) = \frac{\Sigma nD}{\Sigma n}$$

where n is the number of particles having a diameter D, and

$$V\ (\mathrm{SEM}) = (\pi/4)\,\frac{\Sigma nD^2}{A_\mathrm{T}}$$

where A_T is the area of the micrograph region under analysis.

Table 4 compares the morphological parameters obtained with these different techniques.

For the one-step, R-DDS, system the results in *Table 4* are independent of the pre-curing time at 135°C and are consistent with the values found in the literature[18,19] with the same rubber, CTBN x 13, and the same hardener, DDS. The dispersed particles are well defined with $\bar{D} = 3 + 0.5$ μm. With a pre-curing temperature of 120°C Vazquez *et al.*[18] found $\bar{D} \cong 2$ μm; a higher value would be expected for a higher isothermal pre-curing temperature[12], 135°C. These D values are larger than those observed by Montarnal *et al.*[10] and Verchères *et al.*[11]; in the case of a ETBN (18% AN)-modified epoxy system based on cycloaliphatic diamines these authors found values on the order of 0.5 μm.

Figures 5a and *b* clearly illustrate the primary morphological differences between particles in rubber-modified epoxies, prepared with the same initial mass fraction of rubber (15%) using a one-step, R-DDS, or two-step, R-BAPP-DDS, process.

For the R-DDS sample, the essentially circular cross-

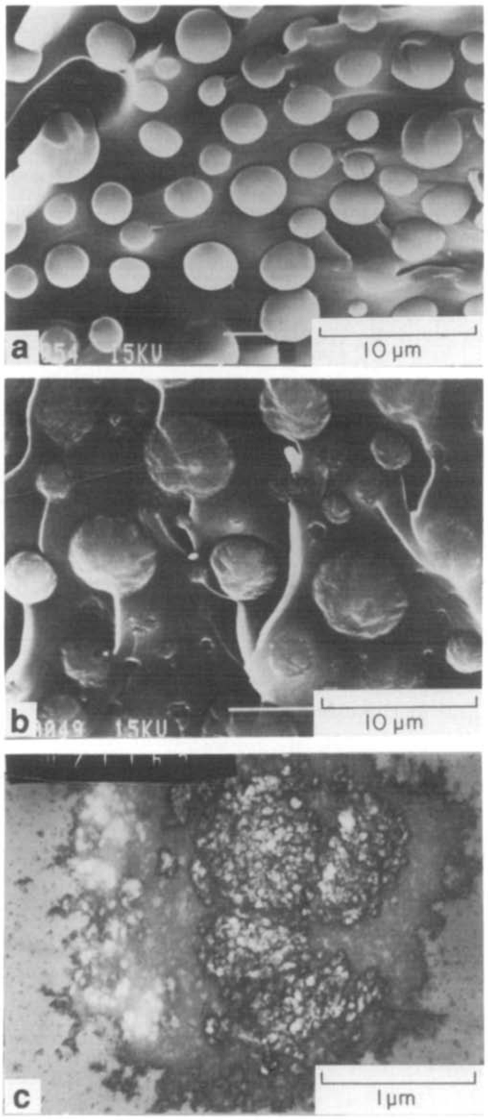

Figure 5 (a) and (b) SEM and (c) TEM micrographs of rubber-modified epoxy networks: (a) one-step R-DDS (15 min at 135°C; 2 h at 180°C and 2 h at 230°C); (b) and (c) two-step R-BAPP-DDS (60 min at 135°C, BAPP; 60 min at 135°C, DDS, and 2 h at 180°C and 2 h at 230°C)

Table 4 Glass transition temperatures, morphologies and mechanical properties for different epoxy networks with 15 wt% rubber

Systems	${}_{\mathrm{E}}T_g$	${}_{\mathrm{E}}T_\alpha{}^a$	${}_{\mathrm{R}}T_\alpha{}^a$ (°C)	$\phi_R c$ (%)	$\bar{D}$ (μm)	V (%)	E_{20} (GPa) (± 0.05)	R_s (kJ m^{-2}) (± 4)
R-DDS[b]	199	207	−42	4.5	3±0.5	35	1.8	21
R-DDS[c]	203	–	–	4.3	3±0.5	35	17	18
R-BAPP-DDS[d]	188	196	−32	4.6	2–6	28	1.6	31

[a] Determined at 0.1 Hz

[b] Curing cycle: 25 min at 135°C, before the cloud point, then post-cured for 2 h at 180°C and 2 h at 230°C

[c] Curing cycle: 210 min at 135°C, after the cloud point before gelation, then post-cured for 2 h at 180°C and 2 h at 230°C

[d] Curing cycle: 60 min at 135°C for the first step (BAPP), 60 min at 135°C for the second step (DDS), after the cloud point but before gelation, then post-cured 2 h at 180°C and 2 h at 230°C

sections of the dispersed particles indicate a nearly spherical shape. In contrast, for the R-BAPP-DDS sample, the dispersed particles show highly irregular contours which appear as agglomerated groups of small particles (*Figure 5c*).

Curiously similar differences have been observed by Kunz *et al.*[7] when they compared carboxyl- and amine-terminated, CTBN and ATBN, modified epoxies. This difference was not well understood, but the authors supposed that the surface irregularities of the dispersed particles in the ATBN system act as stress concentrator defects which initiate low-strain tear failure giving rise to flat fracture surfaces. Compared to the neat system (*Table 3*), the impact strength of the rubber-modified epoxy (*Table 4*) increases, but the rise is more important in the case of the two-step process, R-BAPP-DDS, and can be correlated to the irregular contours of the observed morphology.

Values of the T_g of the epoxy network, ${}_{\mathrm{E}}T_g$ are shown in *Table 4*. The samples were always post-cured at 180 and 230°C to achieve the maximum T_g. The T_g of the matrix without rubber is ${}_{\mathrm{E}}T_{g,\mathrm{pure}} = 206$°C (*Table 4*), while the T_g of the pure rubber (CTBN × 13) is ${}_{\mathrm{R}}T_{g,\mathrm{pure}} = -45$°C. Since the values of ${}_{\mathrm{E}}T_g$ reported in *Table 4* are lower than ${}_{\mathrm{E}}T_{g,\mathrm{pure}}$, some of the rubber must remain in solution in the matrix at the end of the cure. The mass fraction of rubber dissolved in the matrix, $W_R c$, may be calculated if we assume that the Fox equation is valid[11]:

$$\frac{1}{{}_{\mathrm{E}}T_g} = \frac{(1 - W_R c)}{{}_{\mathrm{E}}T_{g,\mathrm{pure}}} + \frac{W_R c}{{}_{\mathrm{R}}T_{g,\mathrm{pure}}}$$

$W_R c$ is in turn expressed as a volume fraction, $\phi_R c$, by:

$$\phi_R c = \frac{W_R c/\rho_R}{W_R c/\rho_R + (1 - W_R c)/\rho_E}$$

where $\rho_R = 0.960$ g cm^{-3} and $\rho_E = 1.233$ g cm^{-3}.

The $\phi_R c$ values are ~4.5% and independent of the process used.

Table 4 gives the average diameters and volume fractions of the dispersed particles. In a two-step reaction the distribution of the diameters is very large with two different maxima at ~2 and 6 μm. For the two systems, the volume fractions of the dispersed phase are nearly double those predicted using the amount of rubber added (15 wt% or 18.4 vol%). We have $V = 35\%$ for R-DDS and $V = 28\%$ for R-BAPP-DDS.

The composition of the dispersed phase may be obtained by performing a mass balance of the rubber in the total system. The details of the calculation have been given previously[11] but it is easy to estimate that more than half of the volume fraction of the dispersed domains consists of the epoxy–amine copolymer (or terpolymer).

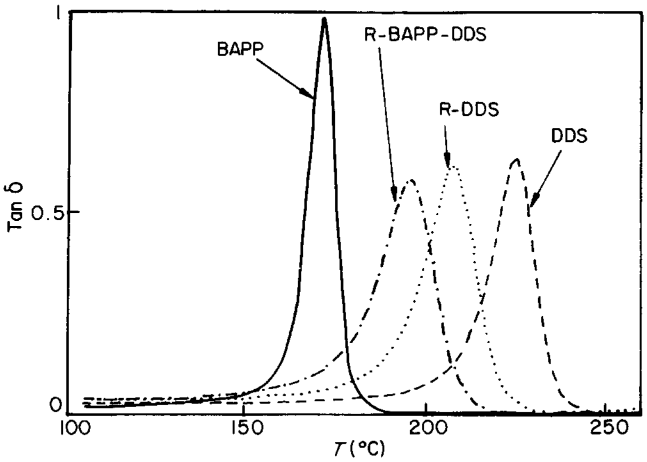

Figure 6 The α relaxation at 0.1 Hz of the epoxy networks described in *Tables 3* and *4*

Several authors have reported the presence of unstained regions inside the dispersed phase observed in TEM micrographs[7,24,25] giving direct evidence of a phase separation inside the dispersed domains. This seems to be the case for the sample prepared via the two-step process, R-BAPP-DDS, but on the contrary, we were not able to reveal a phase separation inside dispersed domains for the one-step sample, R-DDS.

Recently Verchère *et al.*[11] performed d.m.a. at a very low frequency to observe and quantify the interphases. They assumed that epoxy copolymer segments present in dispersed domains relax near, but in the lower temperature region, of the α relaxation of the matrix, ${}_{\mathrm{E}}T_\alpha$. These epoxy copolymer segments are responsible for the asymmetry of the α relaxation peak, the asymmetry increases with the overall volume fraction of epoxy copolymer segments in the dispersed domains.

Figure 6 shows a comparison of the α relaxations appearing in samples without rubber and containing 15 wt% rubber. In our case the fact that we can introduce one or two hardeners, DDS or BAPP and DDS, complicate the relaxation peaks, and we are not able to say if the asymmetry of the ${}_{\mathrm{E}}T_\alpha$ relaxation is due only to the epoxy copolymer segments present in the dispersed particles.

The rubber relaxation, ${}_{\mathrm{R}}T_\alpha$, is superimposed onto the β relaxation of the epoxy, ${}_{\mathrm{E}}T_\beta$. *Figure 7* shows a comparison of the β relaxations appearing in samples without rubber and the $(\beta + \alpha)$ relaxations appearing in

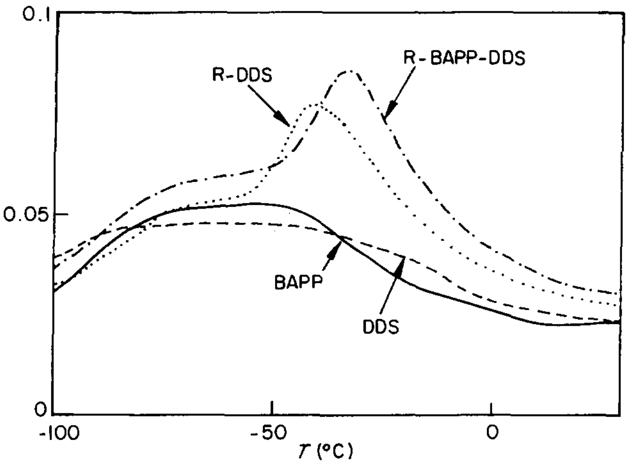

Figure 7 Low-temperature relaxations at 0.1 Hz of the same epoxy networks as in *Figure 6*

Table 5 Glass transition temperatures and morphologies for different rubber-modified epoxy networks

Second step of pre-curing cycle	$_{E}T_g$ (°C)	$_{R}T_\alpha$ (°C)	ϕ_Rc (%)	D_{max} (μm)	V (%)
1 h 135°C 20 h 90°C	190	−30	4.4	2.8	34
5 h 125°C	188	–	4.6	2, 4.5	28
1 h 135°C	188	−32	4.6	2, 4.5	28
3 h 135°C	187	–	4.7	2, 6	29.5
3 h 145°C	185	–	4.9	2, 9	–
3 h 165°C	184	−32	5.0	4, 7, 10	30

First step of 60 min with BAPP with second step for pre-curing shown in table, and post-curing for 2 h at 180°C and 2 h at 230°C

samples containing 15 wt% rubber. For the same reason as for the $_{E}T_\alpha$ relaxation it is difficult to correlate the intensity of the rubber damping peak in d.m.a. with the volume fraction of the dispersed phase but they are in the same range. It is important to note that the $_{R}T_\alpha$ peak is shifted along the temperature axis.

The $_{R}T_g = -45$°C (onset value). The maximum of the α relaxation peak measured at 0.1 Hz of this CTBN x 13 was estimated to be ~ -38 to -35°C (using a torsional braid analysis, Romanchik *et al.*[25] found a higher value of $T_\alpha = -30$°C). The same α relaxation at 0.1 Hz of the rubber, measured at the maximum of the peak in the one-step sample, R-DDS, is $_{R}T_\alpha = -42$°C. This value is lower than that of the pure rubber confirming previous results[6,11,25]. This is attributed to differences in the coefficients of thermal expansion between the glassy epoxy matrix and the rubber-rich phase. The larger coefficient of thermal expansion of the rubber results in a constraining of the rubber domains upon cooling below the T_g of the matrix. This effect depends on the morphology of the system[26].

For the two-step sample, R-BAPP-DDS, the α relaxation of the rubber is found at $_{R}T_\alpha = -32$°C, which is now higher than the relaxation of the pure rubber. This result means that we have no thermal stresses inside the dispersed particles, different morphologies or eventually a partial mixing of $<2\%$ of epoxy copolymer chains with CTBN. This result must now be related to the morphological differences observed in *Figure 5* between the constrained particles formed in the one-step, R-DDS, process and the unconstrained particles of the two-step, R-BAPP-DDS, samples.

Effect of high temperature curing cycles for the two-step process on the morphology of the rubber-modified epoxy network

To examine the effect of curing temperature on the morphology of our two-step R-BAPP-DDS polymers, we prepared different samples with a first-step as before (BAPP, a/e = 0.3, 60 min, 135°C) and a second step with different pre-curing but the same post-curing (2 h at 180°C and 2 h at 230°C) cycles (*Table 5*). For every curing schedule, except that with 60 min at 135°C, phase separation and gelation occur during the pre-curing of the second step. The results are given in *Table 5*. There is no difference in the T_g of the matrices and for all the samples, ϕ_Rc is in the range of 4.5–5.0%.

The obtained morphologies have a very broad particle diameter distribution (*Figure 8*), so in these cases an average diameter has no real sense. Therefore, to characterize the samples we prefer to give the different maxima of the distributions and to highlight the most important one. There is no clear tendency of the dependence of the morphology and composition of the disperse phase with the pre-curing schedule. The volume fraction of the dispersed phase is $\sim 31+3\%$ for all samples.

Verchères *et al.*[11] concluded from their studies that when the morphology is controlled by the phase separation rate rather than by the polymerization rate, increasing the cure temperature leads to an increase in the average size of the dispersed domain. It seems, in our case, that we are in a range of cure temperatures where phase separation and polymerization rates are in competition.

Two other experiments have been done by using another mixing method. As before after the first step (BAPP, 60 min, 135°C), DDS powder is introduced, but at room temperature instead of at 135°C. The DDS is then dissolved at different heating rates, $q = 2$ or 10 K min^{-1} from room temperature to 180°C, followed by a curing cycle of 2 h at 180°C and 2 h at 230°C.

Curiously in these cases, a narrower rubber particles distribution is observed, with $\bar{D} = 1.9 \pm 0.4$ μm when

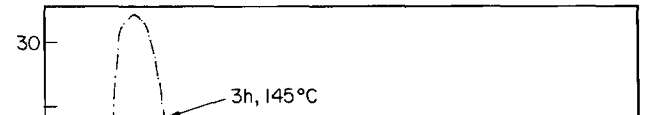

Figure 8 Particle diameter distribution curves of the rubber-modified epoxy networks with different pre-curing cycles during the second step (DDS)

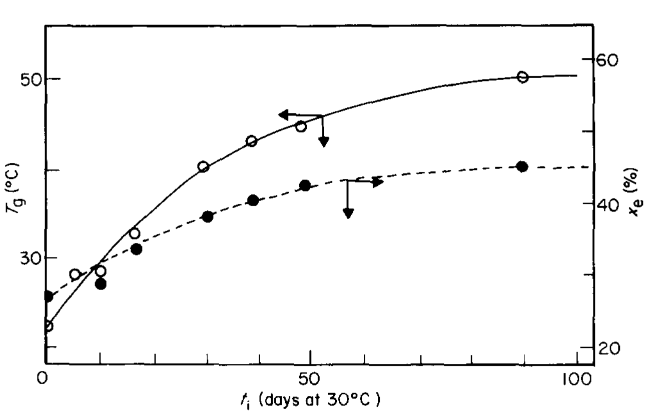

Figure 9 Evolution at 30°C of ${}_ET_g$ and x_e for a pre-cured rubber-modified epoxy network. Pre-curing schedule: first step 1 h at 135°C (BAPP); second step 1 h at 135°C (DDS)

$q=2\ \mathrm{K\ min^{-1}}$ and $\bar{D}=4\pm1\ \mu\mathrm{m}$ when $q=10\ \mathrm{K\ min^{-1}}$. With a lower heating rate of $q=2\ \mathrm{K\ min^{-1}}$, phase separation occurs at a lower temperature, T_{cp}, and smaller particles are obtained.

All the samples have the same $E_{20}=1.48\pm0.06\times10^9$ Pa and the same $R_s=28\pm5\ \mathrm{kJ\ m^{-2}}$.

Effect of low temperature curing cycles in the two-step process on the morphology of the rubber-modified epoxy network

The temperature at which gelation and vitrification take place simultaneously, ${}_{gel}T_g=75$ and 81°C for DGEBA-BAPP and DGEBA-DDS, respectively[23]. So, at $T>75$°C or $T>81$°C gelation takes place before vitrification and the opposite occurs at $T<75$°C or $T<81$°C. To control prepregs based on the two-step rubber-modified epoxy system, we have examined the effect of keeping the samples at room temperature T_i.

The schedule of the first step was as previously described (BAPP, a/e = 0.3, 60 min, 135°C). For the second step, we also begin as before by introducing new DGEBA monomer and dissolving DDS at 135°C, with an overall a/e ratio = 1 (*Table 1*). The mixture is reacted for 60 min in order to reach the cloud point but not gelation (*Figure 4*). Then the mixture is cooled and kept at $T_i=30$°C. The reaction at this temperature was characterized by d.s.c. and s.e.c.

The evolution of ${}_ET_g$ and x_e as a function of time at $T_i=30$°C are plotted in *Figure 9*.

Just after cooling, ${}_ET_g=20$°C and $x_e=0.27$, vitrification (${}_ET_g=30$°C) occurs after 8 days for $x_e=0.34$. Then the reaction progresses slowly in the vitreous state and reaches a plateau around ${}_ET_g=52$°C and $x_e=0.45$ after 90 days. Between 1 month and 3 months, the reaction rate is very low with a $\Delta x_e\sim0.06$. After 3 months $\Delta T_g=22$°C and $\Delta x_e=0.18$ ($x_e<x_{gel}$), thus the mixture is still ungelled and can be processed like a thermoplastic.

Since ${}_{gel}T_g\simeq80$°C, it is correct to observe vitrification and no gelation at $T_i=30$°C. For a DGEBA–cycloaliphatic diamine system, Verchère *et al.*[27] determined that vitrification only affects the kinetics but not the statistics of network formation, and this implies that the decrease in segmental mobility, due to vitrification is the same for molecules of different sizes. Since we have determined, T_g *versus* t_i and x *versus* t_i for $T_i=30$°C, it is now easy to correlate T_g and x. Our results of T_g as a function of x for this rubber-modified system correspond well with our previous results for a DGEBA–DDS system[23].

Just after cooling to $T_i=30$°C, the mixture was opaque. We were very surprised to observe that the opacity decreased with time, t_i, and the sample became translucent after 1 month.

After different curing times at $T_i=30$°C, three samples were post-cured for 2 h at 180°C and 2 h at 230°C, and characterized as before (*Table 6*). The first sample taken after 2 days at 30°C ($\Delta x\sim2$–3%) was opaque and still in a liquid state before the post-curing process.

The two other samples taken after 1 and 3 months at 30°C were translucent and in a vitreous state before the post-curing process with $\Delta x=16$ and 22%, respectively.

After post-curing we confirmed the translucent aspect of the last two samples but the two-phase structure was evident because the α relaxation of the rubber was observed (*Figure 10*). The two-phase structure is also clearly seen in the TEM micrographs (*Figure 11*).

The results are given in *Table 6*, and the per cent of rubber dissolved in the matrix is constant at ~4.8–4.9%. The intensity of the α relaxation of the rubber (dispersed phase) is also constant but the maximum of the relaxation peak shifts to a lower temperature, from −32 to −37°C (*Figure 10*).

The volume fraction of the dispersed particles is difficult to evaluate because the particles are not spherical but look like small cylinders with lengths of several hundred Ångströms, but less than the wavelength of the light since the samples are translucent. The dispersed particles seem to be smaller for the sample of $t_i=30$ days,

Table 6 Glass transition temperature and morphologies for different rubber-modified epoxy networks

Second step of pre-curing cycle	${}_ET_g$ (°C)	V_{RC} (%)	${}_RT_\alpha$	D_{max} (μm)	V (%)
1 h 135°C	188	4.6	−32	2, 4.5	28
1 h 135°C +48 h 30°C	185	4.9	−32	<1, 4.5	–
1 h 135°C +30 days 30°C	186	4.8	−35	<1	–
1 h 135°C +90 days 30°C	185	4.9	−37	<1	–

First step of 60 min at 135°C with BAPP, and for the second step DDS is dissolved during 60 min at 135°C and the sample is then kept frozen at $T_i=30$°C for different periods of time, and then post-cured for 2 h at 180°C and 2 h at 230°C

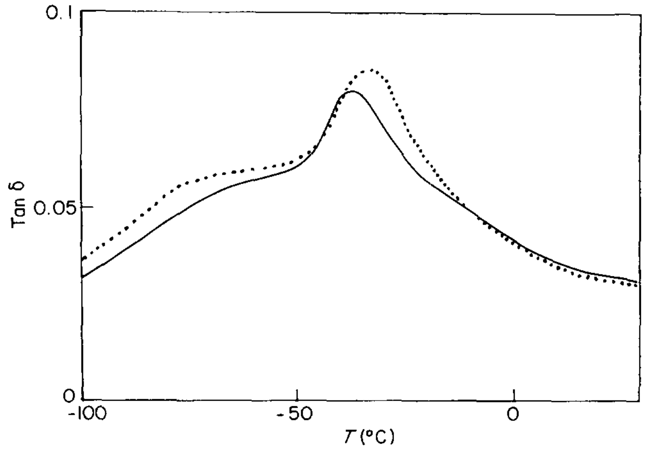

Figure 10 Low-temperature relaxations of the epoxy networks described in *Table 6*: (······) 1 h at 135°C; (———) 1 h at 135°C and 3 months at 30°C

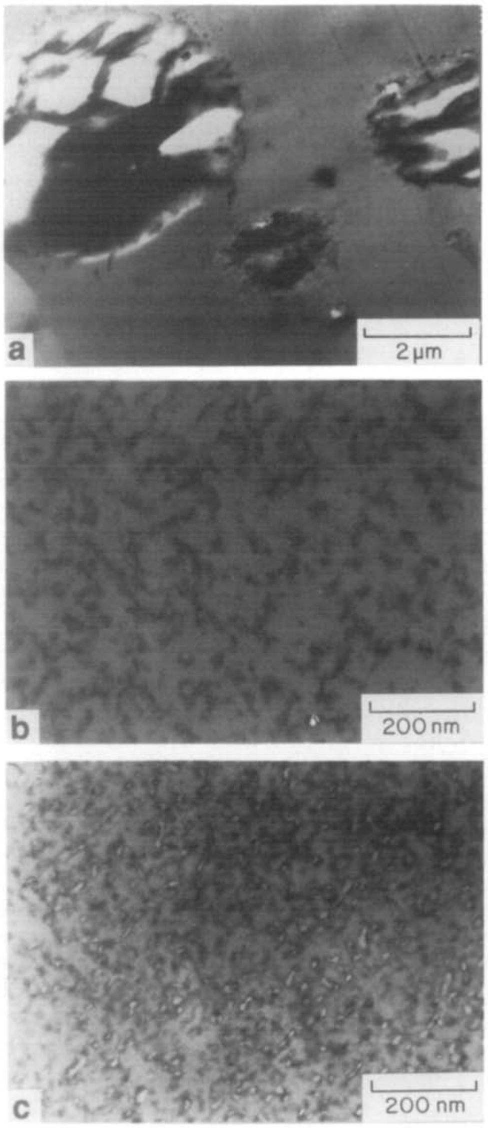

Figure 11 TEM micrographs of rubber-modified networks kept at $T_i = 30°C$ (*Table 6*): (a) 1 h at 135°C; 1 h at 135°C and 46 h at 30°C; post-cured; (b) 1 h at 135°C; 1 h at 135°C and 30 days at 30°C; post-cured; (c) 1 h at 135°C; 1 h at 135°C and 90 days at 30°C; post-cured

and in this case we can distinguish a core–shell structure with the interior consisting of epoxy and the shell the phase-separated rubber.

The interface between the rubber and epoxy copolymer is more significant in this case. In *Figure 12* we compared the α relaxation of the matrix, ${}_E T_\alpha$, for samples R-BAPP-DDS without and with reaction at $T_i = 30°C$. If we assume that epoxy copolymer segments present at the interface relax near but in the lower temperature region of ${}_E T_\alpha$ it is evident that the interface is more significant for the sample reacted at $T_i = 30°C$.

It seems that the morphology observed previously (*Figure 5c*) is destroyed during the conversion at $T_i = 30°C$.

To better understand the behaviour of our system, we determined the cloud points and x_e for various isothermal curing temperatures. The cloud point curve is plotted in *Figure 13; Y* represents the sample after 3 months at $T_i = 30°C$ ($x_e = 0.45$) and is inside the two-phase area of the diagram so it is not possible to redissolve the dispersed phase and have a new phase separation during the heating run from 30 to 180°C, before the post-cure process at 180°C, and then at 230°C. Therefore we think that the morphologies observed in *Figure 11* were obtained during the slow evolution of the system during the reaction at $T_i = 30°C$ in the vitreous state.

This phenomenon is the opposite of a coalescence process, and the surface area of the dispersed phase increases without an important change in the volume fraction of the dispersed phase (see the α relaxation of the rubber in *Figure 10*). We do not have an explanation for the thermodynamic phenomenon responsible for this increase in the surface area of the dispersed phase. Several questions can be asked: what is the role of the chain extension caused by BAPP during the first step? What is the role of the high viscosity and the conversion in the vitreous state? Is there always a nucleation growth mechanism or is spinodal decomposition the cause of the phase segregation process? To try and answer these questions further experiments will be performed on model systems.

Finally we determined R_s of our translucent samples. For all our samples, R_s is in the range of 30 ± 5 kJ m^{-1}. This confirms that the dispersed particle diameters have no effect on the toughness of rubber-modified epoxies[3] and that the volume fraction of the dispersed phase is in the same range for all our samples.

CONCLUSIONS

The influence of the curing schedule and the role of a two-step process on the morphologies generated in a DGEBA-based-epoxy DDS-ETBN system were discussed. An aromatic diamine, BAPP, was recommended as the modifier for a first step. The main conclusions from this study are:

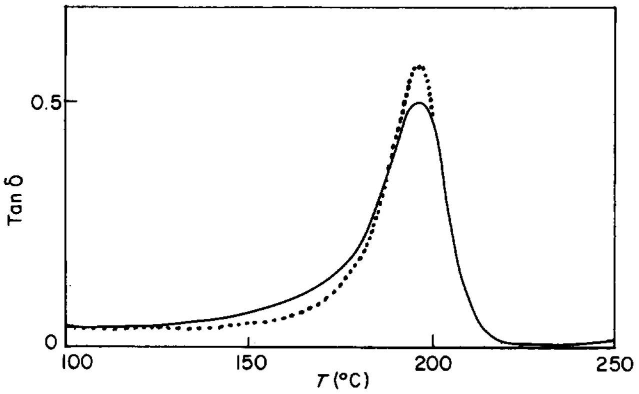

Figure 12 The α relaxations at 0.1 Hz of the same epoxy networks as in *Figure 10*

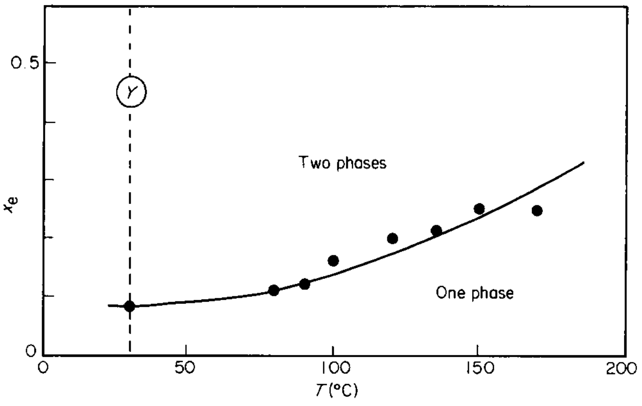

Figure 13 Cloud-point curve x_e *versus* T for our two-step system R-BAPP-DDS. *Y*, sample after 3 months at $T_i = 30°C$ ($x_e = 0.45$)

1. The chemistry of a two-step process with R-BAPP-DDS as compared to a classical one-step, R-DDS, system can be described in two ways: a higher miscibility of the rubber due to the chain extension (copolymer effect) during the first step, resulting in a higher x_{cp} value for the two-step process, $x_{cp}=0.27$ compared to $x_{cp}=0.14$ for the one-step process; and a decrease in the conversion at the gel point; $x_{gel}=0.52$ instead of $x_{gel}=0.62$. This effect can be explained by a higher molecule functionality after the first step[20].

2. There are large morphological differences between particles in rubber-modified epoxies prepared with the same initial mass fraction of rubber, 15 wt% (CTBN x 13), but with a one-step, R-DDS, or a two-step, R-BAPP-DDS, process.

In the first case, the dispersed particles have a well defined spherical shape with $\bar{D}=2\pm0.5$ mm. In the second case, the dispersed particles show highly irregular contours which appear as agglomerated islands of small particles, and the distribution of the diameters is very broad with two maxima in the range of 2–6 μm.

The volume fraction of dissolved rubber, calculated from the decrease in ${}_ET_g$ is independent of the process, $W_{RC}\sim 4$–5%.

Compared to the initial rubber volume fraction, 18.4 vol%, the high volume fraction of the dispersed phase, $V=35\%$ for R-DDS and 28–30% for R-BAPP-DDS, can be explained by the fact that >50% consists of the epoxy–amine copolymer. Unstained regions inside the dispersed phase are observed in TEM micrographs but only for R-BAPP-DDS.

The area of the damping peak of the rubber is not very different for the two rubber-modified networks. But it seems that the rubbery phase is constrained in the R-DDS sample and not in the R-BAPP-DDS sample.

3. We examined the effects of different curing temperatures and heating rates on the morphology of the two-step samples, R-BAPP-DDS. No clear tendency of the evolution of the morphology on the curing schedule appeared. The volume fraction of the dispersed phase is $31\pm3\%$, and generally we observe a broad particle diameter distribution (except when DDS is dissolved with a heating rate of 2 or 10 K min^{-1} from room temperature to 180°C).

4. After dissolving the DDS at 135°C, we examined the effects of keeping the two-step samples, R-BAPP-DDS, at $T_i=30$°C. In this case, the reaction progresses slowly in the vitreous state to values of $x=0.45$ and ${}_ET_g=52$°C. After 90 days the mixture had still not gelled (${}_ET_g<{}_{gel}T_g$ and $x<x_{gel}$) and could be processed like a thermoplastic.

After cooling to $T_i=30$°C, the mixture was opaque but at $T_i=30$°C the opacity decreases with time, t_i, and the sample is translucent after 1 month. Translucent samples were obtained after the post-curing process but the two-phase structure is evident because we have observed the α relaxation of the rubber. Stained dispersed domains of several hundred Ångströms are observed in TEM micrographs. A core–shell structure with an unstained area on the inside of the dispersed domains is discernible.

From these results several questions can be asked about the role, of the chain extension of the ETBN during the first step, the viscosity, η_{cp}, and the high conversion, x_{cp}, at the cloud point during the second step, and the nature of the phase separation phenomenon (nucleation and growth or spinodal decomposition). Before responding to these questions we wish to perform some additional experiments to better characterize the evolution of the morphology of a two-phase system in an ungelled vitreous state.

5. All our samples have an impact strength in the same range (30 ± 5 kJ m^{-1}). We confirmed that the principal parameter for the toughness of rubber-modified epoxies is the volume fraction and not the diameter of the dispersed phase particles.

From a practical point of view, the two-step system is more complicated to process, but the fact that we can obtain dispersed particles with sizes of several hundred Ångströms can be very useful, especially in composite materials.

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