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Influence of the addition of thermoplastic preformed particles on the properties of an epoxy/anhydride network

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An anhydride/epoxy system is modified by the introduction of thermoplastic microparticles (ORGASOL®). The influence of the presence of polyamide (PA) particles is evaluated on the reactivity of the epoxy/anhydride system below the melting temperature of the thermoplastic. Networks containing various amounts of polyamide are prepared using a cure schedule in order to keep the PA particles below their melting point. Both thermomechanical and mechanical behaviours (glass transition temperature, elastic, plastic and fracture properties) are studied and discussed as a function of the polyamide nature, the particle content and the adhesion between the particles and the matrix.

1. Introduction

To improve the toughness of glassy thermoset resins, especially epoxy networks, the most useful way consists of incorporating initially miscible elastomers in the reactive epoxy system [1–5]. During the network formation and before gelation [6], a part of the elastomer separates and forms discrete particles in the matrix. The morphology of the dispersed rubber phase is largely dependent on the molecular weight, the chemical nature of the chain ends [1, 3, 7] and on the cure schedule. Many studies [7–11] have shown how the morphology of the elastomer toughened epoxy networks relates to their mechanical properties and their fracture behaviour.

Thus it is very important in these systems to control the competition between the cure kinetics and the phase separation phenomenon because it conditions the final morphology of the network and hence its fracture behaviour. Indeed, the phase separation process is complex and the composition of the two phases may vary. Especially a part of the rubber remains dissolved in the matrix, leading to the decrease of the glass transition temperature. This fact represents the main drawback of the toughening of thermosets using liquid reactive rubbers. In order to avoid this disadvantage, high T_g thermoplastics initially miscible are added in the primary stage [12–16]. The phase separation process occurs due to the increase in molecular weight and the final morphology is difficult to monitor for the same reasons as in the preceding case.

For this reason, it appears very interesting to initially incorporate non-miscible particles with a well defined size. Core-shell particles have already been used for this purpose [17–20] but only a few studies are reported in the literature that concern the use of thermoplastic fillers.

In this preliminary work, we will study the influence of adding non-miscible thermoplastic particles to an epoxy matrix. Contrary to another study concerning polybutylene terephthalate (PBT) and nylon toughened epoxy [21], the cure cycle used to prepare the networks will be chosen in order to keep the polyamide particles below their melting point and thus keep their initial shape and size.

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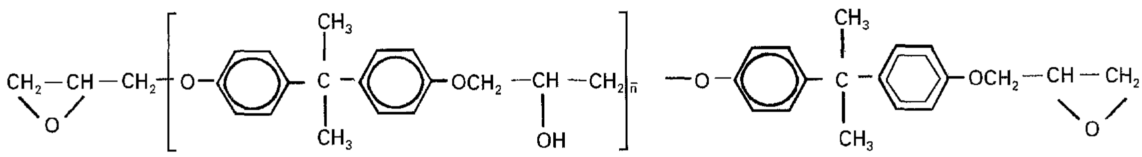
(a) diglycidyl ether of bisphenol A (DGEBA) :



(b) methyl tetrahydrophthalic anhydride (MTHPA) : (c) methyl imidazole (MIA) :

Figure 1 Structural formulae of the diepoxy prepolymer, the comonomer and the initiator.

2. Materials

2.1. Epoxy reactive system

Fig. 1 displays the structural formulae of the chemical reagents.

The aromatic epoxy prepolymer used was a diglycidyl ether of bisphenol A with $\bar{n} = 0.03$ (DGEBA "DER 332" from Dow Chemical). The comonomer used as curing agent was methyl tetrahydrophthalic acid anhydride (MTHPA "EPICLON B570" from Anchor). The initiator introduced in the reactive system was methyl imidazole (MIA from Aldrich). The anhydride: epoxy ratio was equal to 0.85. The initiator quantity was fixed at 1 wt % of the DGEBA/MTHPA system. The choice of these conditions was explained in a previous study [22].

2.2. Thermoplastic fillers

The thermoplastic particles chosen in this study are the polyamide type powders: ORGASOL® manufactured by Elf-Atochem. They are obtained directly by an anionic polymerization process of ε-caprolactam and ω-laurolactam, the polymer precipitates in an organic solvent. Due to this original polymerization process, no grinding and selecting process is necessary to adjust the particle size of ORGASOL®. The powders are very fine microporous polyamide powders with a narrow particle size distribution. As we can see on Fig. 2, the particles have a round shape with a porous structure like gypsum flower [23] and a very large specific surface area (from 1 to 10 $m^2 g^{-1}$). The nature of the polyamide (PA6, PA12, copolymer 6–12), and the average particle size (from 5–60 μm) may be chosen.

For this study, we have chosen two types of particles:

(i) a PA6 powder (reference 1002 D Nat 1)

The average particle size in this case is 20 μm with a specific area of about 3 $m^2 g^{-1}$. The melting peak determined by DSC at a scan rate of 10 K min^{-1} goes from 185°–225 °C. T_f (the temperature at the maximum of the endothermic peak) is 214 °C.

(ii) a PA12 powder (reference 2001 UD Nat 1)

The average particle size is 5 μm with a specific area of about 10 $m^2 g^{-1}$. The melting peak determined by DSC with similar conditions as for PA6 goes from 150–180 °C, T_f being equal to 176 °C.

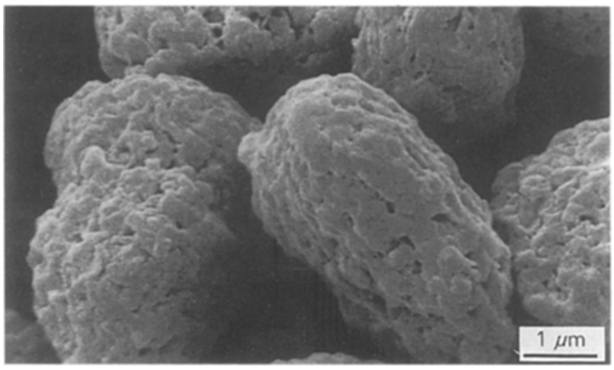


Figure 2 ORGASOL® particles observed by SEM.

In order to improve the particle-matrix adhesion, a chemical treatment with ammonium persulfate is applied on PA12 particles.

In all these studies, the ORGASOL® content in the formulations will be expressed as a percentage mass fraction of the reactive system (DGEBA/MTHPA/MIA).

2.3. Cure schedules

For each formulation the appropriate amounts of the compounds were mixed and degassed at room temperature under mechanical stirring for almost 2 h. The mixture was poured into a PTFE coated mould, cured in a forced air oven for 1 h at 100 °C and 5 h at 160 °C so that the ORGASOL® particles remained below their melting point. The plate was then cooled slowly to room temperature.

3. Experimental procedure

3.1. Elastic properties

Young's moduli and Poisson's ratio at room temperature were obtained in tension mode using an Adamel Lhomargy DY25 testing machine. Dog-bone H_2 type specimens were tested using an EX10 extensometer and strain gauges (Vishay Micromeasures) at a strain rate $\dot{\varepsilon} = 1.67 \times 10^{-3} s^{-1}$.

3.2. Yielding behaviour

The compression stress–strain curves were obtained with an Adamel Lhomargy DY25 testing machine equipped with a compression rig. Yield stresses (σ_y) were measured at room temperature at the strain rate of $\dot{\varepsilon} = 8 \times 10^{-4}\ \mathrm{s}^{-1}$.

3.3. Linear elastic fracture mechanics

Single-edge notched specimens (SEN) (thickness $t = 6$ mm and width $w = 12$ mm) were machined in plates and tested in three-point bending mode (span-to-length = 48 mm) at 25 °C.

Cracks of length a were made at ambient temperature using a diamond saw and finished with a razor blade. The crack length was measured by optical microscopy and was in the range 5–8 mm. About 12 notched specimens with various a/w were fractured (crosshead speed = 1 mm min^{-1}). The stress–deflection curves are typical of a stick–slip propagation. The critical stress intensity factor (K_{Ic}) was calculated using the following formula:

$$K_{\mathrm{Ic}} = \sigma_c (\pi a)^{1/2} f(a/w)$$

where σ_c is the critical stress for crack propagation and $f(a/w)$ the form factor [24].

The critical strain energy release rate G_{Ic} can be related to the stress intensity factor K_{Ic} in plane–strain conditions by the equation:

$$G_{\mathrm{Ic}} = (K_{\mathrm{Ic}}^2/E)(1 - \nu^2)$$

where ν is the Poisson's coefficient and E the Young's modulus of the material. ν is constant in the range 0.36–0.37 for all formulations.

4. Results and discussion

We first studied the influence of the introduction of ORGASOL® on the reactivity of the (DGEBA/MTHPA/MIA) system with differential scanning calorimetry using a Mettler TA 3000 apparatus. DSC specimens (10–15 mg) were heated from 0–250 °C with a heating rate of 10 °C min^{-1}.

A first scan allowed us to determine the temperature at the maximum of the exothermic peak (T_p). The enthalpy of polymerization was not calculated because, as we can see on Fig. 3, the ORGASOL® melting peak is superimposed on the polymerization peak.

A second scan on the same sample allowed us to determine the glass transition temperature of the network formed during the first scan. T_g was taken as the temperature corresponding to the onset of the heat capacity base-line change.

The results are presented in Table I. We can see that introducing ORGASOL® into the reactive system does not modify either the temperature at the maximum of the exothermic peak or the glass transition temperature, whatever the polyamide nature. This demonstrates that the ORGASOL® particles do not influence the chemistry of the network formation, below the melting point of the thermoplastic.

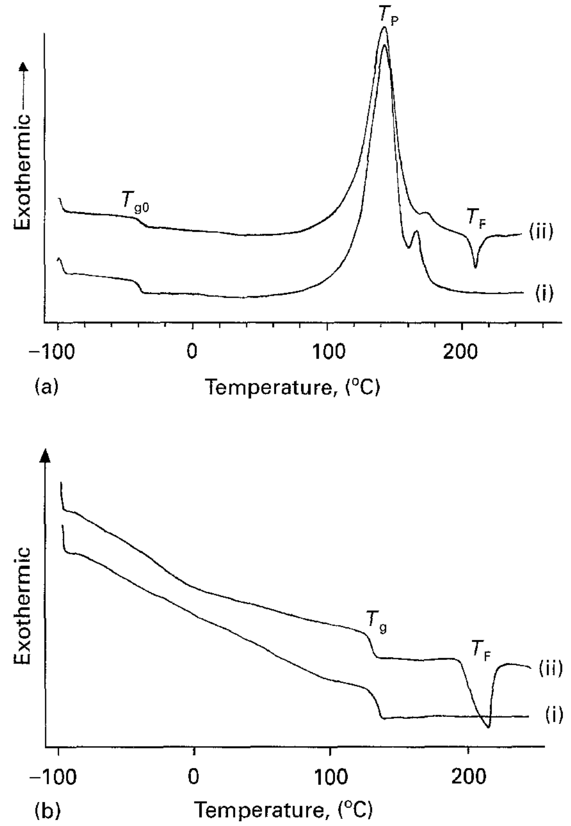


Figure 3 Differential scanning calorimetry thermograms of the reactive systems: (a) first scan and (b) second scan for: (i) the neat system, (ii) the system modified by the introduction of 15 phr PA6.

TABLE I Characteristics of the reactive systems modified by introduction of ORGASOL® particles

	T_p(°C)	T_g(°C)
Pure matrix	146	128
15 phr PA6	144	123
15 phr PA12	145	126
15 phr treated PA12	146	126

T_p = temperature at the maximum of the polymerization peak
T_g = glass transition temperature of the network formed during the first DSC scan.

We will now examine the properties of the networks modified by the incorporation of different amounts and types of ORGASOL®. The results obtained are presented in Table II. We will discuss first the evolution obtained with ORGASOL® particles used as received.

For ORGASOL® percentages less than 15 phr, we can see that the glass transition temperature stays roughly constant at about 133 °C whatever the nature of the powder. For higher percentages (30 phr of PA6), T_g decreases down to about 125 °C. This observation leads us to think that the polyamides are partially miscible with the epoxy matrix. In order to estimate the amount of polyamide dissolved in the matrix, the Fox equation may be applied [25]:

$$1/{}_{\mathrm{E}}T_g = (1 - W_p)/T_{gE} + W_p/T_{gp}$$

where W_p is the mass fraction of ORGASOL® dissolved in the matrix, $T_{gE} = 135$ °C is the glass transition temperature of the pure matrix $\mathrm{E}T_g$ is the

TABLE II Characteristics of the ORGASOL®-modified epoxy-anhydride-networks compared to the neat system

	T_g(°C)	E(GPa)	σ_y(MPa)	K_{Ic}(MPa m$^{1/2}$)	G_{Ic}(J m^{-2})
Pure matrix	136	3.2	107	0.87	200
15 phr PA6	131	3.4	108	0.99	264
30 phr PA6	126	3.2	98	1.2	380
15 phr PA12	133	3.3	98	0.89	210
15 phr persulfate treated PA12	126	3.1	102	0.91	228

T_g = glass transition temperature of the networks determined by DSC
E = Young's modulus measured at 25°C
σ_y = compressive yield stress at 25°C
K_{Ic} = critical stress intensity factor at 25°C
G_{Ic} = critical strain energy release rate at 25°C.

glass transition temperature of the modified network and T_{gp} is the glass transition temperature of the PA6 ORGASOL® (T_{gp} = 35 °C). For the 30 phr PA6-modified-network, W_p is equal to 7%.

Concerning the elastic and plastic behaviour of the modified networks, we can see that introducing ORGASOL® in the anhydride matrix has no influence on the Young's modulus but has a small but significant effect on the compressive yield stress. For PA6-modified-networks a relatively high amount of particles is necessary (30 phr) to decrease σ_y. For PA12-modified-networks, only 15 phr are needed to decrease the yield stress by 10%. Thus, the introduction of ORGASOL® microparticles favours the plastic deformation of the networks, which is the only deformation mechanism with cavitation, crazing not being possible.

Concerning the toughness of the networks, we can see in Table II, that the 15 phr PA12 modified network has a critical stress intensity factor value similar to that of the basic network. On the other hand, the introduction of 15 phr PA6 leads to an increase of K_{Ic} from 0.87 to 0.99 MPa m$^{1/2}$ and increasing PA6 amount in the anhydride network leads to an improvement of the critical stress intensity factor. The same kind of evolution was noted by Shi *et al.* [26] on an epoxy thermoplastic CET resin with various amounts of PA12 type ORGASOL® particles. The relation between K_{Ic} and the polyamide content introduced in the system is linear as generally observed [27] (Fig. 4).

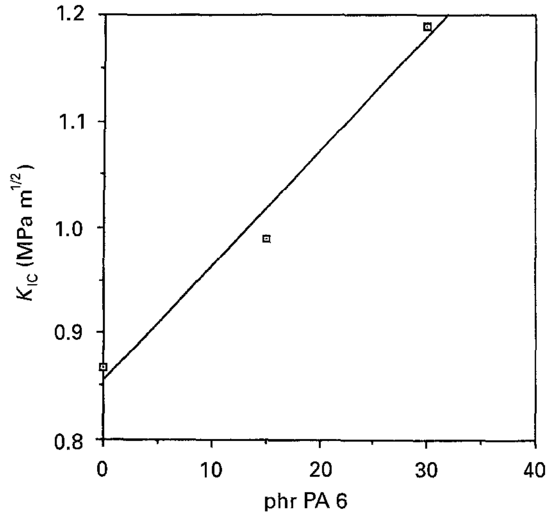


Figure 4 Relationship between the critical stress intensity factor and the phr of PA6.

The difference in the fracture behaviour of the two types of networks cannot be explained by a difference in the contraction process of the particles during the cooling of the networks from 160 °C to ambient temperature. Indeed a thermo–mechanical analysis allowed us to determine the linear thermal dilatation coefficient of the two polyamides and of the (DGEBA/MTHPA/MIA) network. The following results were obtained:

$$\alpha \text{ PA6}(60°\text{C} < T < 165\,°\text{C}) = 190 \times 10^{-6}\,\text{K}^{-1}$$

$$\alpha \text{ PA12}(60\,°\text{C} < T < 165\,°\text{C}) = 190 \times 10^{-6}\,\text{K}^{-1}$$

for the DGEBA/MTHPA/MIA network:

$$\alpha(25\,°\text{C} < T < 130\,°\text{C}) = 70 \times 10^{-6}\,\text{K}^{-1}$$

$$\alpha(T > 135\,°\text{C}) = 175 \times 10^{-6}\,\text{K}^{-1}$$

Since the two polyamides have similar linear dilatation coefficient values in the explored temperature range, this cannot explain the differences observed in the fracture behaviour of the modified networks.

We notice that the values of the DGEBA/MTHPA/MIA network dilatation coefficient in the vitrous and in the rubbery states conform to those found in the literature for other epoxy networks [28]. We can also see that above T_g, the DGEBA/MTHPA/MIA network has an α value similar to those of the two polyamides. On the other hand, in the vitrous state the linear dilatation coefficient of the basic network is lower than those of the polyamide. The values of the linear expansion coefficients imply that the ORGASOL® particles are in a triaxial tensile stress field [13] and justify that a good adhesion has to be obtained between the particles and the epoxy matrix to avoid a decohesion phenomenon between the particles and the matrix.

Thus, to understand the difference between the fracture behaviour of the networks modified by PA6 and those modified by PA12, the cleaved surfaces of SEN specimens were analysed by SEM. We can immediately notice that in both cases the particle dispersions seem correct. Indeed the agglomerate particles are not numerous.

In the case of the PA12 modified networks, the rupture seems to be of the adhesive type because the particles are debonded from the matrix (Fig. 5). On the contrary, in the case of PA6, we note the presence of debonded particles and also a lot of broken particles (Fig. 6). In that case, there is enough adhesion between the particles and the matrix and crack propagation occurs either in the particles or around them. Thus the bridging mechanism proposed in the literature for thermoplastic modified epoxy networks [29] can be applied in the case of PA6 reinforced anhydride networks.

The wettability of the particles by the reactive system could be an important parameter in order to obtain high fracture properties in the modified networks. To verify this hypothesis, a PA12 powder was treated with an ammonium persulfate solution which leads to an increase in the powder's hydrophily. The SEN cleaved surfaces were examined by SEM. We can see from Fig. 7, that contrary to the network modified by untreated PA12, a lot of particles are broken, showing the existence of better adhesion between the treated ORGASOL® and the anhydride matrix. On the other hand the particle dispersion observed by SEM isnot as good as in the case of the non treated PA12. These two opposing effects could explain the low K_{Ic} increase for this network (see Table II).

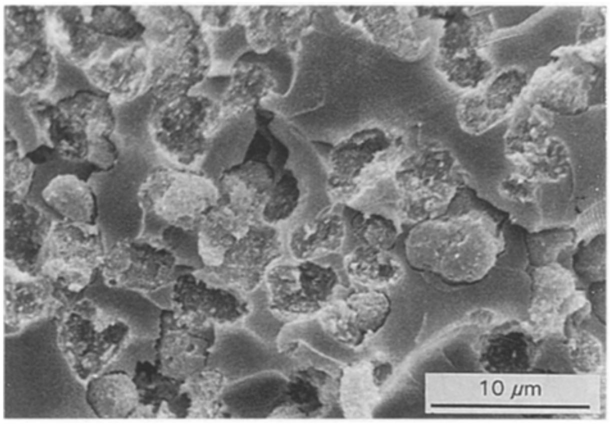


Figure 5 Cleaved surface of PA12-modified-network observed by SEM.

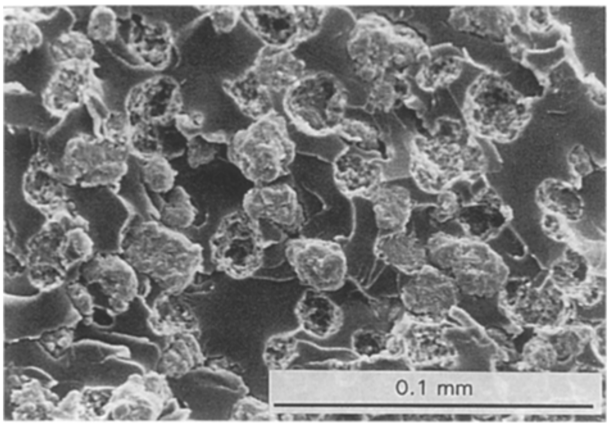


Figure 6 Cleaved surface of PA6-modified-network observed by SEM.

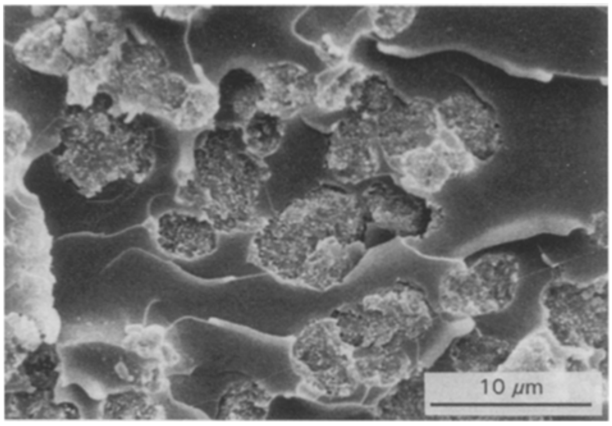


Figure 7 Cleaved surface of persulfate-treated PA12-modified-network observed by SEM.

5. Conclusions

ORGASOL® particles were introduced into an anhydride/epoxy matrix and then networks containing various amounts of polyamide were prepared, keeping the thermoplastic particles below their melting point.

(i) The reactivity of the (DGEBA/MTHPA/MIA) system was not affected by the presence of polyamide particles whatever their nature (6 or 12).

(ii) Concerning the mechanical properties, we have seen that introduction of polyamide powders has no influence on the elastic behaviour of the modified networks, whatever the nature or the percentage of the polyamide.

(iii) On the other hand, the type of polyamide is very important for compressive and fracture behaviour. Indeed the introduction of PA12 particles does not produce a significant increase of K_{Ic} whereas the introduction of 15 phr PA6 leads to an increase of K_{Ic} from 0.87 to 0.99 MPa $m^{1/2}$. We have found a linear relation between K_{Ic} and the PA6 content. This evolution is in accordance with the results concerning thermoplastic reinforced networks found in the literature [29, 30]. We have shown that a better adhesion between the particles and the matrix could be noticed in the case of a PA6 modified network and that a chemical treatment performed on PA12 which increases the hydrophily can improve adhesion between the particles and the matrix.

The perspectives of this work will then consist in improving our comprehension of the interfacial phenomena in these systems and of their relations with the fracture properties and in improving adhesion between ORGASOL® particles and the matrix. Work is also now in progress in order to study the influence of a cure schedule at temperatures higher than the melting point of the thermoplastic additives.

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