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Structure–property relationships as a tool for the formulation of high-performance epoxy-amine networks[†]

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Abstract: Inspection of the structure–property relationships already established for epoxy-amine networks allows the design of some novel formulations leading to high-performance materials. This was achieved by choosing an additive, miscible in the mixture of monomers, but which gives rise to phase nanoseparation along the network construction. As a result, small domains, consisting of additive molecules trapping some network chains, are dispersed in the polymer matrix which also contains residual additive molecules. The main effects of this special morphology on the properties of the networks are the depression of the main relaxation temperature, T_α, of the matrix and the appearance of some damping (so-called μ relaxation) in the temperature range intermediate between the secondary relaxation and T_α. The networks prepared in this way exhibit a lower water uptake at equilibrium, and present higher modulus and higher toughness around room temperature than conventional systems without additive. Friction experiments showed that the increase in toughness drastically delays crack propagation within the contact and, in turn, can improve the wear resistance of the material.

Keywords: epoxy; water uptake; toughening; phase separation; secondary relaxation; fracture; fretting; contact fatigue

INTRODUCTION

Epoxy-amine networks are very attractive materials, widely used as adhesives, coatings and matrixes for fibre-reinforced composites. Their main advantages are: (i) easy processing at low cost, based on a quite simple chemistry (namely, the opening of the epoxide rings of multifunctional monomers by primary and secondary diamines); (ii) great versatility, resulting from a glass transition temperature, T_g, adjustable over a broad range from -20 up to 220 °C by choosing the chemical nature of the reactants; (iii) a strength-to-weight ratio favorable to aeronautic applications. However, three main characteristics of these epoxies leave much to be desired. The excessive sensitivity to moisture (up to 5 wt% of water uptake at equilibrium) induces a dramatic depression of T_g. The Young's modulus at room temperature is rather low. Finally, the toughness is quite poor, being marked by a critical stress intensity factor, K_{IC}, of about 0.7 MPa m$^{1/2}$. All the above features are apparent from the abundant literature (see for instance refs 1 and 2).

There have been many approaches to modifying the formulation of epoxy resins. Daly *et al*[3] reported that the use of small molecule additives was a successful way to 'fortify' the room temperature modulus. Unfortunately, no reduction in brittleness and water uptake at equilibrium resulted from this approach.[4] Production of two-phase materials, in which the second phase may consist of rubbery particles,[5] thermoplastic polymers,[6] or, in a more sophisticated way, preformed, multilayer particles,[7] proved to be a successful method to enhance toughness. Among other disadvantages, this strategy greatly complicates the cure procedure and leads to a penalizing increase in processing cost.

Thus, for industrial applications, there remains a need for novel epoxy-amine formulations, likely to yield high-performance materials without changing the usual processing procedure. As crucial requirements, the materials produced in this way should combine increased Young's modulus and toughness with reduced sensitivity to moisture. The purpose of the present publication is to show how these objectives have been attained by designing a new formulation route which is deduced from the inspection of previously published structure–property relationships of epoxy-amine networks.

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BASIS FOR THE DESIGN OF NOVEL FORMULATIONS

Let us suppose that the formulation of modified epoxy networks exhibiting a T_g value not lower than about 100 °C would be a suitable choice. The selection of the reactants should account for the established relationships between T_g, chain flexibility and crosslink density[8] on the one hand, and for the drop of T_g which results from network hydration[9] on the other. Accordingly, appropriate candidates could be new formulations based on diglycidylether of bisphenol A (DGEBA) fully cured in the presence of a stoichiometric amount of aromatic diamine. Either diaminodiphenylmethane (DDM) or diaminodiphenylsulfone (DDS) are suitable hardeners for this purpose.

Secondly, an increase in room temperature modulus is desired. As previously shown,[10,11] this goal can be achieved by reducing the mechanical losses associated with the sub-T_g β relaxation, ie by decreasing network crosslink density either by undercure of diepoxy–primary diamine formulations or by use of momoamines or secondary diamines as the co-hardener. As a matter of fact, none of these procedures is convenient here, because they would lead to an excessive decrease in T_g. Fortunately, the modulus fortifiers previously proposed by Daly *et al*[3] offer an interesting alternative. In particular, the role of the so-called EPPHAA acetamide additive (see Table 1) has been understood on a molecular basis:[12,13] the β relaxation motions were shown to be partly hindered by unreactive additive molecules dispersed within the network.

A solubility parameter calculation[14] provided an opportunity to explain why EPPHAA is still miscible in the monomer mixtures and remains miscible in the polymer networks despite unfavorable entropic contributions when the chain length increases. In both cases, the solubility parameter of the additive is close to that of the surrounding medium. Bearing in mind that epoxy network toughening systematically results from phase separation, two homologues of EPPHAA, presenting lower solubility parameters, were synthesized and included in the formulations. These additives, subsequently called AM and AO, correspond to diarylethers of glycerol. The decrease in polarity from EPPHAA to AM resulted from the replacement of the acetamide moiety by a methyl group. A further decrease in polarity from AM to AO was achieved by synthesizing the triether of glycerol resulting from the substitution of the alcohol function of the hydroxypropylether moiety by a methoxy group. As sketched in Fig 1, the additives AM and AO remained miscible in the monomer mixtures, but gave rise to nanoscale phase separation during the network construction step.[4,15] Reference 18 details how phase separation can be quantified from T_g measurements. It was also demonstrated from NMR measurements that the additives did not react chemically with the networks. As will be shown in the Results and discussion section, the networks with additives may present a higher room temperature modulus than their unmodified homologues. Indeed, the decrease in modulus resulting from the presence of the additive-richer phase (μ relaxation) is balanced here by the increase in modulus resulting from the partial hindrance of the β relaxation motions. The formulae of the chemicals mentioned in this section are shown in Table 1. Values of the relevant solubility parameters are given in Table 2.

EXPERIMENTAL

Chemicals

The DGEBA and DDM monomers are commercial chemicals, purchased from Bakelite, Duisberg, Germany (grade Rutapox 162) and Acros Organics, France, respectively. The additives EPPHAA, AM, and AO were synthesized in our laboratory according to methods detailed elsewhere.[4]

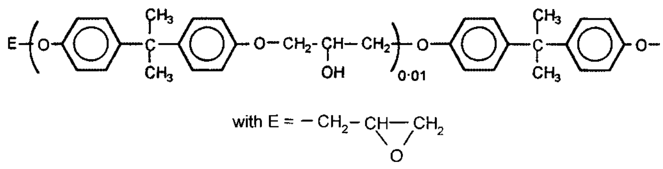
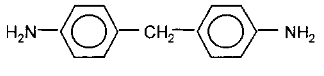
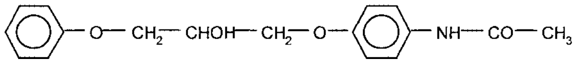
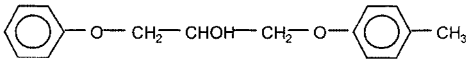
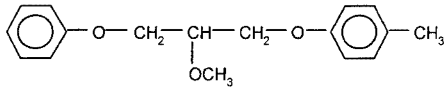
Chemical	*Formula*
DGEBA	
DDM	
EPPHAA	
Additive AM	
Additive AO	

Table 1. Formulae of the chemicals used in this study

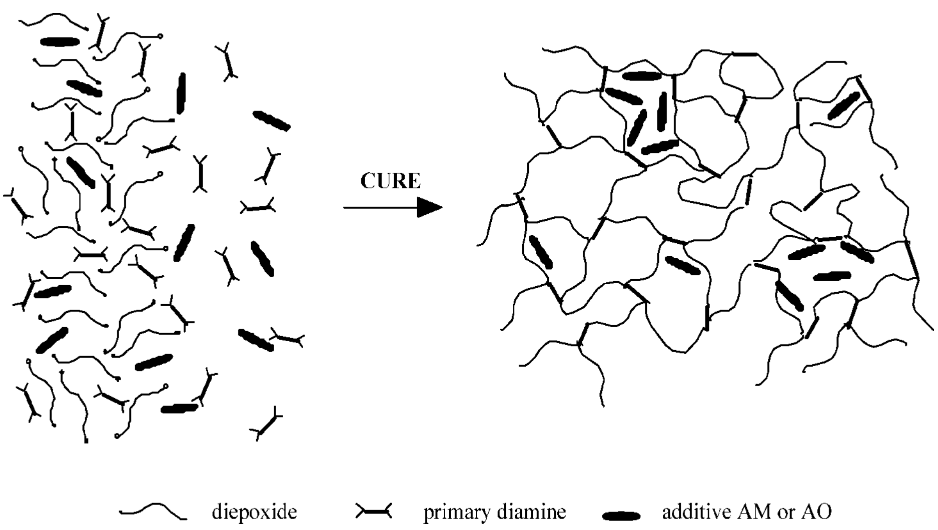


Figure 1. Sketch of the nanoscale phase separation occurring during network construction.

Sample preparation

Each additive was incorporated into stoichiometric mixtures of monomers (based on two moles of diepoxide for one mole of primary diamine) before cure. Relative molar ratios of additive to diamine were fixed at 0.29, 0.62 and 0.96 mole/mole. Code names for the samples refer to the network acronym, followed when relevant by the additive acronym and the two digits corresponding to the relative amount of additive in the initial mixture.

The DGEBA–DDM networks were cured for 12 h at 80 °C, and then post-cured for 24 h at 200 °C in the case of the reference system without additive, and at 160 °C for the new formulations.

Viscoelastic measurements

Dynamic mechanical experiments were performed on a MTS 831 testing system (Minneapolis, USA). Samples were subjected to a tensile sinusoidal strain of low amplitude and frequency of 1 Hz. Values of the storage modulus, E', and loss modulus, E'', were calculated as the real and imaginary components of the complex modulus, E^*, determined under isothermal conditions at various temperatures. Inspection of peaks of E'' allows the identification of the mechanically active relaxations, whereas E' can be regarded as the Young's modulus of the network at the considered temperature.

Fracture measurements

Toughness of the materials was characterized by the value of the critical stress intensity factor, K_{IC}. This quantity was deduced from three-point bending experiments, performed on thick razor-notched samples by using a MTS 810 testing system, according to a protocol detailed elsewhere.[4] Only the samples presenting a sufficiently sharp notch, and a ratio of notch length over bar thickness ranging from 0.45 to 0.55, were subjected to fracture tests.

Table 2. Values of the solubility parameters used to predict the compatibility between epoxies and additives

Chemical	*δ (MPa$^{1/2}$)*
DGEBA + DDM (monomer mixture)	21.7
DGEBA–DDM (network)	26.5
EPPHAA	26.5
AM	24.0
AO	20.8

Tribological characterization

The contact fatigue behaviour of the materials was analysed under small amplitude oscillating micromotions, ie fretting loading. Using a specific device mounted on a MTS 810 testing system, cyclic tangential displacements in the micrometer range (± 50 µm) were applied to a polymer plane in contact with a glass hemisphere with a 48 mm radius. Under the selected normal load ($P = 100$ N), the diameter of the contact area (about 2 mm) was much larger than the magnitude of the imposed tangential displacement. Due to the reduced slip amplitude within the contact area, such fretting conditions have been shown to be a peculiarly relevant tool to investigate the generation of fatigue cracks without the complications arising from particle detachment and wear.[16,17] Accordingly, the fretting contact under consideration may be viewed as a model single asperity contact simulating, at an observable scale, the contact fatigue processes which may occur within polymers contacting rough rigid counterfaces. In addition to the continuous monitoring of the tangential load, Q, and displacement, δ, the fretting device allowed microscopic observations of the contact area to be performed *in situ* through the glass counterface. Crack initiation and propagation within the epoxy materials were monitored as a function of the number of cycles (up to 5×10^3). The frequency of the imposed tangential displacement (1 Hz) prevented any thermal fatigue effects to be induced within the contact.

Water uptake studies

To reach the anhydrous state, the samples were first dried for 48 h under vacuum at a temperature equal to $T_g + 30\,^\circ$C. Then, pieces of anhydrous material were placed for 2 weeks in a water saturated atmosphere at 100 °C. Weighing at regular intervals allowed the monitoring of the water uptake, $w(t)$, as a function of time, until a constant equilibrium value, w_∞, was reached. For each formulation, it was verified that w_∞ is independent of the sample thickness (between 0.8 mm and 4 mm). Therefore, w_∞ values are actually representative of the hydration of the materials at equilibrium.

RESULTS AND DISCUSSION

The results discussed in the present investigation are focused on the DGEBA–DDM–additive systems. It should, however, be noted that very similar features have been observed for the analysis of the DGEBA–DDS–additive systems, as reported in part elsewhere.[18]

Relaxation behavior

Figure 2 presents typical plots of E'' as a function of temperature relative to the pure DGEBA–DDM resin and to the DGEBA–DDM–additive resins. The plots relative to DGEBA–DDM and DGEBA–DDM–EPPHAA/62 show two mechanically active relaxations, namely the α relaxation at high temperature, in the glass transition region, and the β relaxation, at lower temperature, which mainly involves hydroxypropylether motions. Presence of the additive EPPHAA is marked by plasticization effects in the glass transition region (substantial depression of T_α), and by antiplasticization effects in the secondary relaxation region (dramatic reduction of the E'' peak). Inspection of the β relaxation of the samples DGEBA–DDM–AM/62 and DGEBA–DDM–AO/62 reveals the same antiplasticizing effect. In addition, these samples present a splitting of the high temperature relaxation into two peaks, so called α and μ. The origin of these two relaxations has been ascribed[4,15] to the nanoscale phase separation (Fig 1).

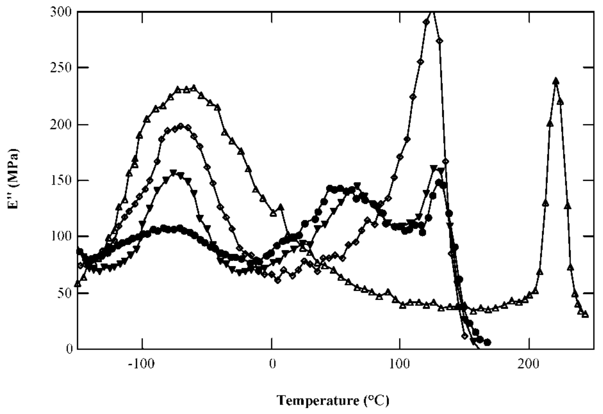


Figure 2. Temperature dependence of E'' (1 Hz) for the networks DGEBA–DDM (△), DGEBA–DDM–EPPHAA/62 (◇), DGEBA–DDM–AM/62 (▼) and DGEBA–DDM–AO/62 (●).

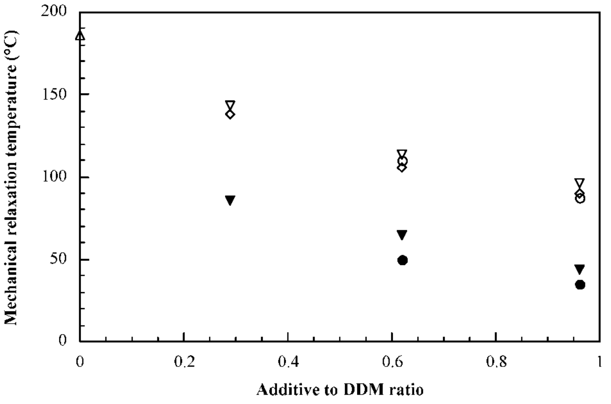


Figure 3. Shift of the characteristic temperatures of the mechanical relaxations α (open symbols) and μ (filled symbols) at 1 Hz as a function of the additive to DDM ratio: △, DGEBA–DDM; ◊, DGEBA–DDM–EPPHAA/62; ▽, DGEBA–DDM–AM/62; ○, DGEBA–DDM–AO/62.

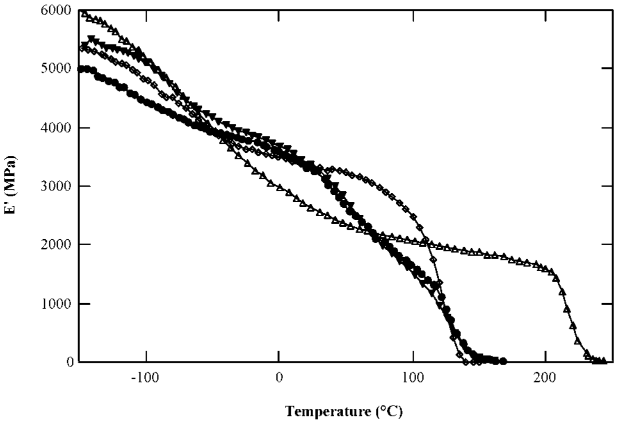


Figure 4. Temperature dependence of E' (1 Hz) for the networks DGEBA–DDM (△), DGEBA–DDM–EPPHAA/62 (◇), DGEBA–DDM–AM/62 (▼) and DGEBA–DDM–AO/62 (●).

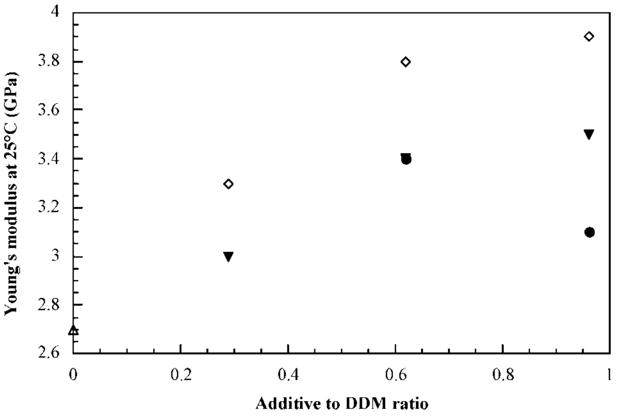


Figure 5. Change of the room temperature modulus as a function of the additive to DDM ratio: DGEBA–DDM (△), DGEBA–DDM–EPPHAA/62 (◇), DGEBA–DDM–AM/62 (▼) and DGEBA–DDM–AO/62 (●).

All the above observations are qualitatively true whatever the amounts of additive in the range under study. From the formulation viewpoint, it is useful to plot the temperatures, T_α and T_μ, at which these relaxations pass by a maximum, as a function of the additive to DDM ratio (Fig 3). According to the requirement of a T_g larger than about 100 °C, it turns out that the additive to DDM ratio should not be larger than 0.62.

As far as the E' traces are concerned (Fig 4), the antiplasticizing effect of the three additives EPPHAA, AM and AO shows up. In each case, an increase in E' is observed upon addition of additive in the temperature range from T_β to T_α. Again, inspection of the plots of room temperature modulus as a function of the additive to DDM ratio (Fig 5) shows that the choice of an additive to DDM ratio equal to 0.62 is convenient.

Toughness

Because a number of samples have to be submitted to fracture tests to obtain representative values of K_{IC}, we restricted this part of the study to the most interesting formulations, namely DGEBA–DDM, DGEBA–DDM–EPPHAA/62 and DGEBA–DDM–AM/62. DGEBA–DDM–AO/62 was disregarded because it was difficult to synthesize the additive.

Table 3 shows the values of K_{IC} determined over the temperature range 0–60 °C. The pure resin DGEBA–DDM presents a poor toughness that reflects the well-known poor crack resistance of highly crosslinked materials at temperatures below T_g. The resin DGEBA–DDM–EPPHAA/62 behaves in almost the same way, despite a moderate increase in K_{IC} values. By contrast, the resin DGEBA–DDM–AM/62 presents much greater K_{IC} values over the entire temperature range studied. The strong toughening effect observed for the AM formulation is assigned to the very special morphology of the material. Tentatively, a realistic mechanism might involve a stress concentration localized in the μ domains, able to favour plastic flow in the matrix, in agreement with the toughening mechanism involved in rubber-modified epoxy systems. However, because the network spreads over the entire resin volume, localized cavitation at the aggregate–matrix interface cannot exist, and therefore a possible deformation process might be shear yielding. This idea is corroborated by the absence of any stress whitening effect on the fractured samples.

Table 3. Values of K_{IC} (MPa m$^{1/2}$), determined at various temperatures for some DGEBA–DDM and DGEBA–DDM–additive networks

	Temperature (°C)			
Network	*0*	*20*	*40*	*60*
DGEBA–DDM	0.8	0.7	0.7	0.7
DGEBA–DDM–EPPHAA/62	0.9	1.0	1.2	1.3
DGEBA–DDM–AM/62	2.1	2.1	2.0	1.9

Contact fatigue behaviour

The contribution of the fracture properties of polymers to their wear behaviour against rigid counterfaces has long been recognized and has been extensively reviewed by Lancaster.[19] According to the general idea that the abrasive wear rate of a polymer is correlated to a measure of the reciprocal of its work to rupture, Rey *et al*[20] and Chitsaz-Zedeh and Eiss[21] independently reported that the enhancement of the fracture toughness of polysiloxane-modified epoxies resulted in an increased wear resistance of the materials. Due to the uncertainty regarding the nature of the deformation processes within the contact, the physical interpretation of such a correlation is still largely unsolved. For polymer materials, considerations regarding the ratio of the modulus to the yield properties indicate that the damage process is likely to be of the fatigue type rather than unitary in nature. Accordingly, fatigue wear models have been largely derived in order to account for the wear resistance of polymer substrates sliding against rigid counterfaces which are insufficiently rough for the elastic limit of the polymer to be exceeded during asperity deformation (see for instance refs 22 and 23). Direct experimental evidence of such contact fatigue processes is, however, scarce: propagating cracks in polymers are difficult to detect on a micro-asperity scale because of elastic recovery.

In this investigation, the cracking micromechanisms within the DGEBA–DDM and DGEBA–DDM–AM/62 resins have been compared under identical fretting conditions. The behaviour of the unmodified network was dominated by the early nucleation and propagation of two main cracks located close to the edge of the contact and at two approximately symmetrical locations along the sliding direction (Fig 6(a)). Contact mechanical approaches[25] reveal that these cracks can be attributed to the maximum values of the tensile stress which are achieved at the contact edge during the fretting cycle. In that respect, the two observed cracks can be essentially considered as mode I opening cracks. After an initiation stage of about 500 cycles, the propagation of these cracks occurred within a few tens of cycles, in a quasi-brittle manner, as indicated by the optical observations and the rapid decrease in the measured contact tangential stiffness, K (see Fig 7(a)). As shown in Fig 7, the latter was determined from the initial slope of the tangential load–displacement fretting loops, ie when the sliding direction was reversed. Under such conditions, the extent of slip

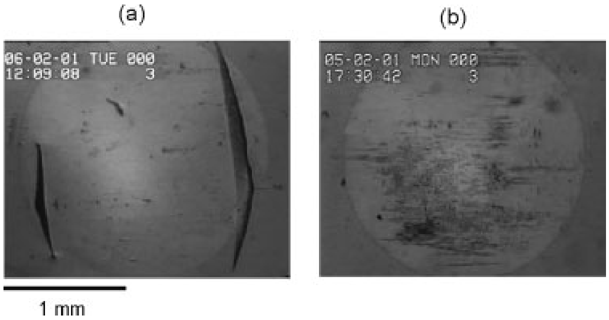


Figure 6. Optical micrographs of the contact area after 5×10^3 fretting cycles: (a) DGEBA–DDM; (b) DGEBA–DDM–AM/62 ($P = 100$ N; $\delta = \pm$ 50 μm).

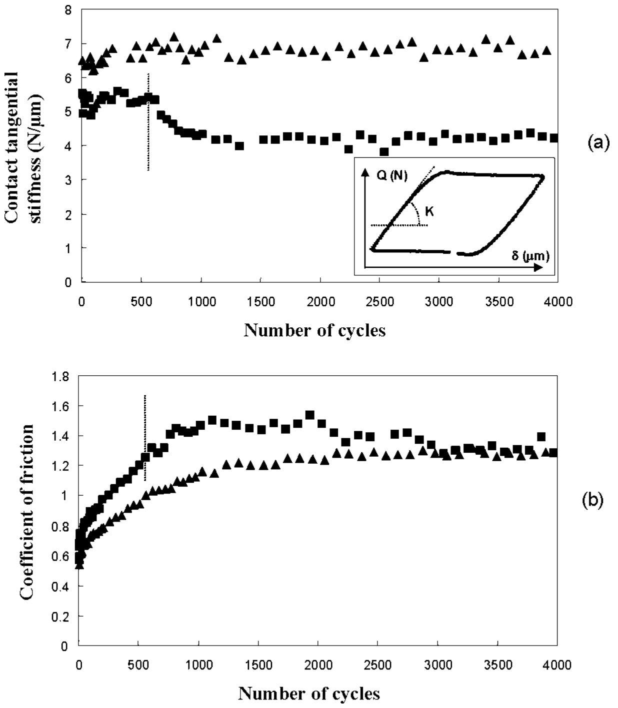


Figure 7. Changes in (a) the contact tangential stiffness and (b) the coefficient of friction as a function of the number of fretting cycles: (■) DGEBA–DDM; (▲) DGEBA–DDM–AM/62. The dashed lines indicate the crack initiation time for the DGEBA–DDM system. A typical tangential load/displacement fretting cycle is represented in the insert box, together with the determination of the tangential contact stiffness.

within the contact is strongly restricted and the measured stiffness is mostly a measure of the elastic accommodation of the epoxy substrate. After crack propagation, the observed decrease in K can be explained by the additional accommodation mechanism associated with the opening and the closing of the cracks. For the modified DGEBA–DDM–AM/62 system, no significant crack propagation processes were detected up to 5×10^3 cycles (Fig 6(b)), which could be related to the improved fracture toughness properties. A relevant comparison of the contact fatigue behaviour of the resins requires, however, an estimate of the local contact conditions which result from a combination of the contact loading parameters, the contact geometry, the elastic properties of the contacting bodies and the magnitude of the friction coefficient. For a given contact loading (normal load, imposed displacement), the induced contact stresses may vary due to changes in the coefficient of friction or in the elastic properties of the contacting materials. As a result, variations in the contact fatigue behaviour do not necessarily reflect a change in the intrinsic crack propagation resistance of the material. For a sphere-on-flat contact, the magnitude of the maximum tensile stress at the edge of the contact, $\sigma_{xx}^{\max}$, can be expressed as follows:[24]

$$\sigma_{xx}^{\max} = \frac{3P}{2\pi a^2}\left[\frac{1-2\nu}{3} + \frac{4+\nu}{8}\pi\mu\right] \qquad (1)$$

where P is the normal load, a is the radius of the contact area, μ is the coefficient of friction and ν is the Poisson coefficient of the epoxy material. According to eqn (1), two separate effects must be taken into account for the calculation of $\sigma_{xx}^{\max}$.

The first one is the changes in the contact radius which may result from the increased room temperature Young's modulus of the modified epoxy. The measured contact radius were respectively 1.0 mm and 1.1 mm for the DGEBA–DDM and DGEBA–DDM–AM-62 systems. From a Hertzian analysis, the corresponding quasistatic Young's moduli can be estimated to be 2.6 GPa and 3.3 GPa, which are consistent with the values of the storage modulus, E', measured by DMA at 1 Hz (2.8 GPa and 3.4 GPa for DGEBA–DDM and DGEBA–DDM–AM-62 resins, respectively).

The second effect concerns the evolving nature of the coefficient of friction. During the early stages of the fretting process, a progressive increase in μ is usually observed (Fig 7(b)). For the unmodified epoxy, $\sigma_{xx}^{\max}$ was calculated using the value of the coefficient of friction at the onset of crack initiation ($\mu = 1.3 \pm 0.1$). As mentioned above, no cracks were detected for the DGEBA–DDM–AM-62 system and the maximum value of μ was considered in the calculation of the maximum tensile stress, ie $\mu = 1.2 \pm 0.1$.

When applying eqn (1), it appeared that the differences in the contact radius (ie in the Young's modulus) were balanced by the slight differences in the mean coefficient of friction. As a result, the same average value of the tensile stress at the edge of the contact, $\sigma_{xx}^{\max} = 100 \pm 10\,\text{MPa}$, was obtained for the two epoxy systems. The improved contact fatigue resistance of the modified epoxy system can therefore be attributed unambiguously to the enhanced resistance of this material to mode I crack propagation and not to changes in the local contact stress conditions.

Sensitivity to moisture

Figure 8 summarizes the influence of additive chemical nature and amount on water uptake at equilibrium.

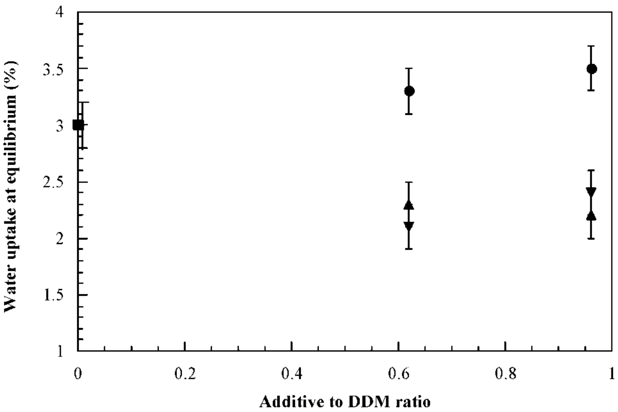


Figure 8. Change of the water uptake at equilibrium as a function of the additive to DDM ratio: ■, DGEBA–DDM; ●, DGEBA–DDM–EPPHAA/62; ▲, DGEBA–DDM–AM/62; ▼, DGEBA–DDM–AO/62.

The networks formulated with the compatible polar additive EPPHAA present a slightly larger sensitivity to moisture than the neat DGEBA–DDM network. In contrast, the two-phase networks, formulated with the less polar additives AM and AO, are much less likely to absorb water. As reported recently[19] epoxy network sensitivity to moisture is controlled by both chain polarity and topology. Probably these two effects contribute to explain our data.

CONCLUSIONS

A novel strategy for the formulation of epoxy resins, toughened using small molecule additives, has been reported. Two main messages can be retained from this study in anticipation of future work on high-performance thermosetting materials. First, these formulations were not optimized by empirical step procedures, but according to a comprehensive analysis of the structure–property relationships available in the literature for epoxy-amine networks and from the use of the solubility parameter concept. Secondly, thanks to this strategy, the performance of the materials was upgraded to a significant extent. Two network formulations, namely DGEBA–DDM–AM/62 and DGEBA–DDS–AM/62 (data not shown here), actually deserve to be tested in practical application conditions. They can be processed using the usual epoxy-amine cure cycle, and incorporate an additive, AM, which is synthesized very easily. The characteristics of the DGEBA–DDM–AM/62 network are the following: T_α (1 Hz) = 114 °C, E' (1 Hz, 25 °C) = 3.4 GPa, K_{IC} (20 °C) = 2.1 MPa m$^{1/2}$, and $w = 2.3\%$. They are very similar to those obtained in a twin study[19] on the network DGEBA–DDS–AM/62: T_α (1 Hz) = 125 °C, E' (1 Hz, 25 °C) = 3.4 GPa, K_{IC} (20 °C) = 2.4 MPa m$^{1/2}$, and $w = 3.4\%$. In both cases, the price to be paid is a depression of T_g, which is fortunately contained in proportion compatible with potential applications. A detailed investigation of the toughening effect was carried out. It is not only based on K_{IC} determinations, which may be sometimes regarded with reservation, but also on a careful analysis of contact fatigue experiments. Furthermore, crack initiation and growth were observed in the networks without additive, whereas no damage was detected under the same contact loading conditions for the modified networks.

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