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FTIR spectroscopy and physical properties of an epoxy/bismaleimide IPN system

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Blends of a tetrafunctional epoxy resin and a thermosetting bismaleimide (BMI) resin cured with 4,4′-diamino diphenyl sulfone were investigated. Information on the conversion of the reactive groups upon curing was obtained by Fourier transform infrared spectroscopy. Dynamic-mechanical tests carried out on both dry and wet samples indicated the formation of an IPN-like structure and a considerable reduction of the plasticizing effect of the water absorbed in the presence of BMI. Sorption measurements at 70 °C revealed a reduction of the equilibrium water uptake with respect to the neat epoxy matrix, and a slight increase of the apparent diffusion coefficient. Furthermore, the presence of BMI enhanced such properties as the flexural elastic modulus and the compressive yield stress while reducing slightly the fracture parameters K_{Ic}, and G_{Ic} (critical stress intensity factor and critical strain energy release rate, respectively), as a consequence of the reduced ability of the IPN network to be plastically deformed under loading. © *1998 Kluwer Academic Publishers*

1. Introduction

Polymeric composites for structural applications are generally made by stiff fibres embedded in a highly crosslinked matrix. Among the matrices normally used in this high technology field a lot of interest has been paid to epoxy and bismaleimide resins because of their very attractive properties in terms of thermal and thermo-oxidative stability and high glass transition temperatures. In particular, an epoxy based system widely used for carbon fibre reinforced composites in the aircraft and aerospace industries involves tetraglycidyl 4,4′-diamino diphenyl methane (TGDDM) cured by diamino diphenyl sulfone (DDS).

However, the performances of this system are limited by the intrinsic brittleness of the network structure and by the considerable amount of moisture absorbed at equilibrium, which adversely affects its mechanical properties [1, 2].

With respect to the first problem different approaches have been reported in the scientific and patent literature, based on the addition of thermoplastics [3, 7] or conventional liquid rubbers [8–16]. To overcome the second limitation a method has recently emerged, which consists of the formulation of thermoset–thermoset blends [17].

The systems obtained in this way exhibit some of the properties of both the component networks and often synergistic effects take place that improve certain characteristics with respect to those of the neat components. A careful choice of the blend components and of the processing parameters may therefore allow one to obtain materials with tailored end-properties.

In the present paper a blend system obtained by blending the TGDDM resin with a thermosetting bismaleimide monomer (BMI) is investigated. The mixture was cured in the presence of the DDS hardener. The BMI resin exhibits very high rigidity, coupled with an outstanding temperature stability; in addition it shows a negligible tendency to absorb water. However, the processing window of this resin is very narrow, because thermal curing starts just above the melting point.

The results obtained demonstrate that the addition of BMI improves such properties of the neat epoxy resin as the glass transition temperature, T_g, and the stiffness, while reducing, at the same time, its equilibrium water uptake.

2. Experimental procedure

2.1. Materials

The materials used were a commercial grade tetraglycidyl 4,4′-diamino diphenyl methane (TGDDM) supplied by Ciba Geigy, N,N′-bismaleimide-4,4′-diphenyl methane (BMI) and 4,4′-diamino diphenyl sulfone (DDS), both from Aldrich. The molecular structures of these components are (see Scheme 1).

2.2. Preparation of a typical TGDDM–DDS–BMI blend

TGDDM and DDS were mixed in a weight ratio of 100–30 at 120 °C under vigorous mechanical stirring to obtain a homogeneous, visually transparent

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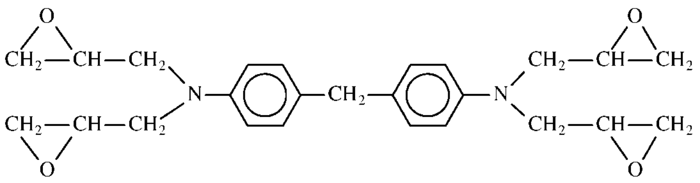
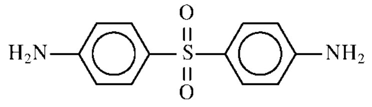
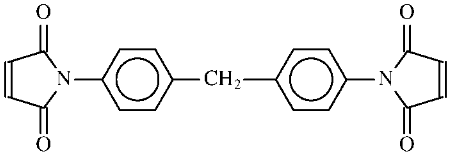


Tetraglycidyl 4,4 ′-diamino diphenyl methane (TGDDM)



4,4′-diamino diphenyl sulfone (DDS)



N,N′bismaleimide-4,4 ′-diphenyl methane (BMI)

Scheme 1

solution. The mixture was then degassed under vacuum and the appropriate amount of BMI was added. Mixing was continued at 100 °C up to complete dissolution of the bismaleimide powder.

The reactive mixture so obtained was poured in a glass mould and cured at 140 °C for 16 h. Post-curing was accomplished at 200 °C for 4 h.

2.3. Techniques

Fourier transform infrared (FTIR) analysis was performed on thin films (5–15 μm) of the reactive mixture using a Perkin Elmer System 2000 spectrometer with a resolution of 2 cm^{-1}. The scanned wave-number range was 4000–400 cm^{-1}. The instrument was equipped with a deuterated triglycine sulphate (DTGS) detector and a Ge–KBr beam splitter.

Dynamic-mechanical measurements were performed with a Polymer Laboratories DMTA model MK III apparatus using a single-cantilever bending mode at a fixed frequency (1 Hz).

Flexural moduli were measured with an Instron machine at room temperature and at a crosshead speed of 1 mm min^{-1}. Uniaxial compressive tests were performed on samples 6.0 mm long, 5.0 mm wide and 5.0 mm thick, using the same Instron apparatus and the same instrument parameters as for the flexural tests.

Fracture tests were carried out on three-point bending specimens 60.0 mm long, 6.0 mm wide and 4.0 mm thick at room temperature and at a crosshead speed of 1 mm min^{-1}. Prior to testing, the samples were sharply notched. Results were analysed applying the linear elastic fracture mechanics approach [18]. By using this theory, absolute fracture parameters were calculated such as the critical stress intensity factor, K_{Ic}, and the critical strain energy release rate, G_{Ic}. In particular, K_{Ic} was calculated by means of the following equation

$$K_{\text{Ic}} = Y\sigma(a)^{1/2} \tag{1}$$

where σ is the nominal stress at the onset of crack propagation, a is the initial crack length and Y is a calibration factor depending upon the specimen geometry. Values of this factor for three-point bending specimens are given by Brown and Srawley [19].

The critical strain energy release rate, G_{Ic}, was, instead, determined by the equation

$$G_{\text{Ic}} = \frac{U}{BW\phi} \tag{2}$$

where U is the fracture energy; B and W are, respectively, the thickness and the width of the specimen; and ϕ is a calibration factor, which depends on the a/W ratio. Values of ϕ were taken from Plati and Williams [20].

3. Results and discussion

3.1. FTIR characterization

In Figs 1–3 are shown the FTIR transmission spectra of a typical TGDDM–DDS–BMI blend composition (100 : 30 : 100 parts by weight) prior and after the curing process [traces a (thick line) and b (thin line) respectively].

In the wave-number range 4000–2500 cm^{-1} (see Fig. 1) the intensity of the well resolved doublet at 3475 and 3375 cm^{-1}, which is due to the asymmetric and symmetric stretching vibration of the NH_2 group, respectively, strongly decreases upon curing. A further peak characteristic of primary amine is found at 3236 cm^{-1} [first overtone of the $\delta(NH_2)$ fundamental at 1629 cm^{-1}). It is found that this peak completely disappears in trace b, thus indicating that the primary amino groups are completely reacted under the curing conditions employed. This is confirmed by inspection

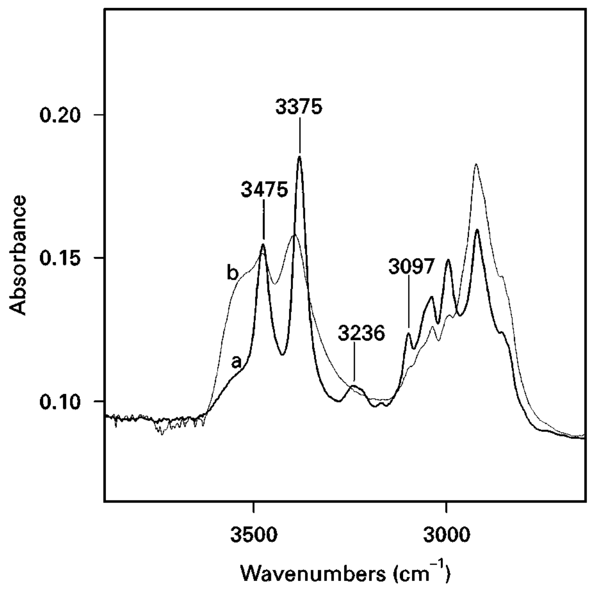


Figure 1 Transmission FTIR spectra of the 100:30:100 TGDDM–DDS–BMI blend in the wave-number range 3700–2700 cm^{-1} before curing (curve a, thick line) and after curing (curve b, thin line).

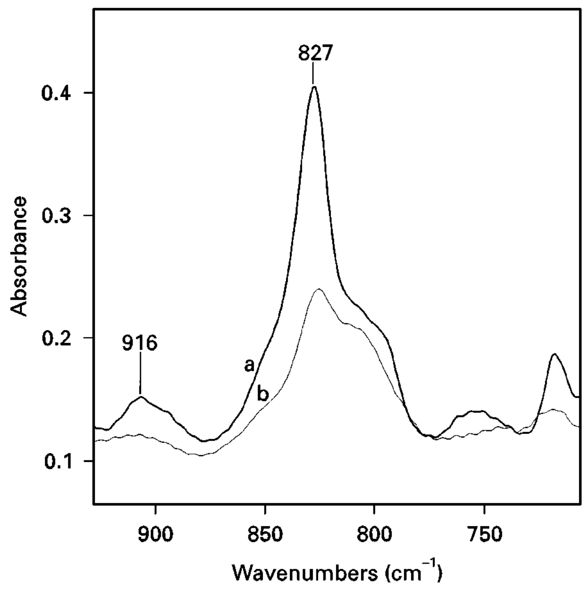


Figure 3 Transmission FTIR spectra of the 100:30:100 TGDDM–DDS–BMI blend in the wave-number range 950–700 cm^{-1} before curing (curve a, thick line) and after curing (curve b, thin line).

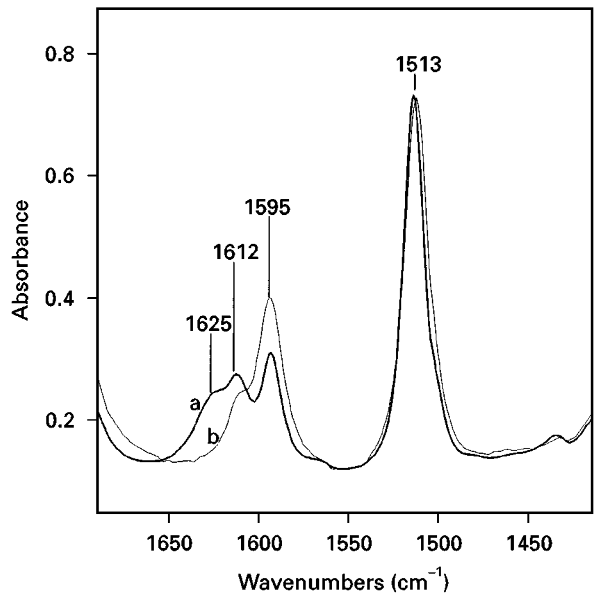


Figure 2 Transmission FTIR spectra of the 100:30:100 TGDDM–DDS–BMI blend in the wave-number range 1700–1400 cm^{-1} before curing (curve a, thick line) and after curing (curve b, thin line).

of Fig. 2, trace b, showing the complete disappearance of the shoulder at 1625 cm^{-1}, which is due to the $\delta(NH_2)$ mode.

In Fig. 1, trace b, the increase of the broad absorption bond in the range 3600–3200 cm^{-1} due to the formation of hydroxyl groups is also evident. In the same figure the two peaks at 3472 and 3395 cm^{-1} are attributed, respectively, to the BMI $\nu_{C=O}$ overtone, and to the ν_{NH} mode of the secondary amine. Thus, a considerable amount of secondary amine groups remain unreacted at the end of the process.

The peaks characteristic of BMI unsaturation occur at 3097 cm^{-1} (a $\nu_{\mathrm{H\text{-}C}}$ = vibration) and at 827 cm^{-1} (an out-of plane bending of the H–C=C unit). Fig. 1, trace b, and Fig. 3, trace b, show considerable reduction upon curing, which is due to the reactivity of BMI double bonds. The conversion of BMI unsaturation is incomplete, however, as evidenced by the presence of residual absorptions at 3097 and 827 cm^{-1}.

The spectral data reported in Figs 1–3 allow quantitative evaluation of the final conversion, C, of the various reactive groups

$$\alpha = \frac{C_0 - C_t}{C_0} = 1 - \frac{C_t}{C_0}$$

and, according to Lambert–Beer's law

$$\alpha = 1 - \frac{\bar{A}_t^{\mathrm{v}}}{\bar{A}_0^{\mathrm{v}}}$$

where $\bar{A}_t^{\mathrm{v}}$ and $\bar{A}_0^{\mathrm{v}}$ are the integrated absorbances of the analytical peak at times t and 0, respectively, corrected for the sample thickness. The thickness correction was accomplished by use of the invariant aromatic peak at 1513 cm^{-1}.

Conversion of the BMI double bonds was evaluated from the peak at 827 cm^{-1}. For epoxy group conversion the characteristic oxirane ring stretching at 916 cm^{-1} was employed.

For both the epoxy and the bismaleimide groups a final conversion of 70 per cent was evaluated; this value compares well with that obtained for the neat TGDDM–DDS resin cured in the same conditions. Also in this case 30 per cent of the epoxy groups initially present in the system remained unreacted. Moreover, the spectral features observed for the neat epoxy resin after curing were essentially the same as those discussed above.

Thus the curing mechanism of the TGDDM–DDS pair does not seem to be influenced by the presence of the BMI coreactive monomer, which may polymerize through a different and independent reaction mechanism (chain addition). A complete kinetic analysis of the curing process, by real time FTIR data collection, in the neat resin as well as in the blend, is currently under way to obtain further information on the reaction mechanism of this complex system.

3.2. Dynamic-mechanical properties and water sorption

Dynamic-mechanical spectra in terms of tan δ and storage modulus, G', relative to the TGDDM–DDS system and two typical blend compositions, are reported in Figs 4–6.

The plots of the dry resins (full lines) indicate the existence of a single, symmetrical damping peak, located at a temperature increasing with the BMI content. This observation points to the formation of a single phase, homogeneous system, at least up to the scale of the dynamic-mechanical test; i.e. the phase domain, if it exists, is smaller than the size of the segments that are responsible for the primary molecular relaxation. This conclusion is also supported by the morphological analysis carried out by scanning electron microscopy on the fracture surfaces of the investigated samples: no evidence of phase separated domains was found, even at very high magnification.

Based on these results, and on the spectroscopic analysis previously discussed, it may be assumed that an IPN-type of network structure is developed upon curing.

The neat TGDDM–DDS resin and the two blends containing, respectively, 50 and 100 parts by weight of BMI were tested for water absorption at 70 °C. A linear behaviour of the M_t/M_∞ data when plotted against $t^{(1/2)}/l$ was found, thus indicating that all the investigated materials behave according to Fick's law of diffusion. As usual, M_t and M_∞ represent the mass of penetrant absorbed at times t and at equilibrium, respectively, and l is the sample thickness. The results of sorption tests are summarized in Table I, where we report the equilibrium water uptake (W_∞, wt %) and the apparent diffusion coefficients (D_{app}, mm^2 s^{-1}).

It is noted that, by enhancing the BMI content in the blend, the equilibrium water uptake decreases, while the apparent diffusion coefficient increases. The reduction of water uptake with respect to the neat resin (19 per cent for the blend containing 100 parts of BMI) is lower than that expected on the basis of a simple additive rule. It is likely that a more defective network is formed in the presence of BMI, which enhances the water absorption through purely physical processes. This hypothesis would also explain the slight increase of the diffusion coefficients in the blends.

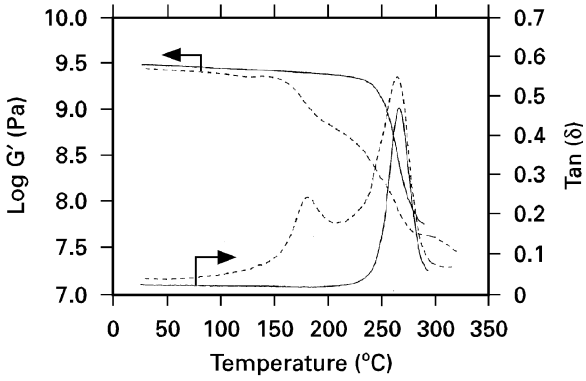


Figure 4 Dynamic-mechanical spectra of the neat epoxy resin: dry sample; sample after reaching the equilibrium water uptake.

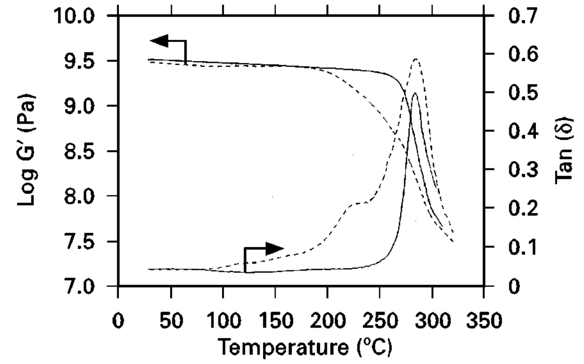


Figure 5 Dynamic-mechanical spectra of the TGDDM–DDS–BMI system of composition 100 : 30 : 50 parts by weight (—): dry sample; (- - -) sample after reaching the equilibrium water uptake.

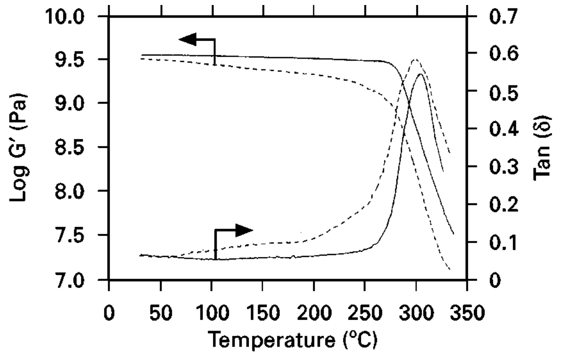


Figure 6 Dynamic-mechanical spectra of the TGDDM–DDS–BMI system of composition 100 : 30 : 100 parts by weight: (—) dry sample; (- - -) sample after reaching the equilibrium water uptake.

In Figs 4–6 are also reported the dynamic-mechanical spectra of the water saturated (wet) samples (dotted lines). The tan δ spectrum of the wet epoxy resin shows two well resolved peaks at 181.5 and 262 °C. This behaviour, already reported in the literature [21], is due to the strong plasticizing effect of water. By heating the sample during the test, its progressive drying is achieved. At about 210 °C the sample has lost all the absorbed moisture and produces a relaxation peak characteristic of the network in the dry state. This interpretation has been confirmed in a separate experiment performed on a thinner sample (0.5 mm). In this case the rate of desorption is strongly enhanced because of a thickness effect and the first peak is no longer detected.

The presence of BMI induces considerable changes in the tan δ spectra of the wet samples: the low temperature peak broadens and shifts at higher temperatures as the BMI content increases. For the composition containing 28 wt % BMI this component remains partially resolved from the principal relaxation, while in the blend with 43.5 wt % BMI becomes a barely detectable shoulder.

TABLE I Equilibrium water absorption, apparent diffusion coefficients and compressive yield stress values for the investigated blends

TGDDM (parts of weight)	DDS (parts of weight)	BMI (parts of weight)	W^{a}_{∞} (%)	$\bar{D}^{b}$ ($mm^2 s^{-1}$)	$\sigma^{c}_{c,y}$ (MPa)
100	30	–	5.2	2.14×10^{-6}	131.1
100	30	50	4.9	2.67×10^{-6}	136.9
100	30	100	4.2	2.82×10^{-6}	158.9

[a] W_{∞} is the equivalent water uptake at 70 °C.
[b] D_{app} is the apparent diffusion coefficient at 70 °C.
[c] $\sigma_{c,y}$ is the compressive yield stress.

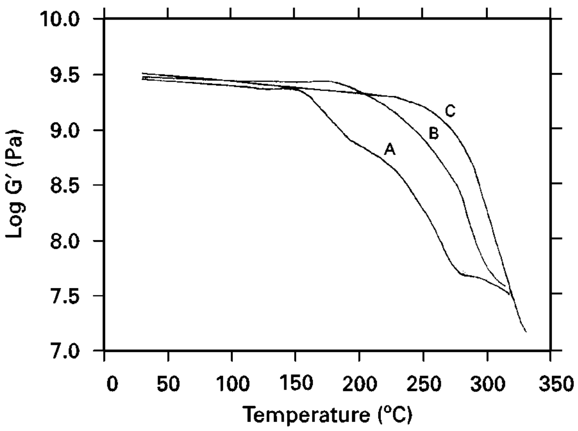


Figure 7 The storage modulus, G', as a function of temperature, for the water saturated samples. Curve A: TGDDM–DDS 100:30 part by weight. Curve B: TGDDM–DDS–BMI 100:30:50 parts by weight. Curve C: TGDDM–DDS–BMI 100:30:100 parts by weight.

An explanation of these features may be attempted by assuming that the specimens containing BMI lose the absorbed water at a higher rate than the neat epoxy resin, in the experimental conditions of the dynamic-mechanical test. This explanation is consistent with the above discussed increase of the diffusion coefficient, which occurs by enhancing the BMI content in the blend.

A direct comparison of the G' versus temperature curves of the wet samples (Fig. 7) evidences an important result related to the application of these materials. The considerable drop of the modulus due to water plasticization, which occurs about 100 °C below the main relaxation in the neat epoxy resin, takes place at higher temperatures by increasing the BMI content in the system and tends to merge with the main relaxation. Thus one of the main limitations of epoxy matrices, i.e. their decreased stiffness and thermal stability in the wet state, may be reduced in this way.

3.3. Mechanical and fracture properties

Young's modulus, E, of the various blend compositions investigated, was determined in flexural mode using the equation

$$E = \frac{L^3 P}{4dWB^3}$$

where d is the displacement; P is the load at the displacement, d; L is the span; and W and B are the width and the thickness of the specimen, respectively.

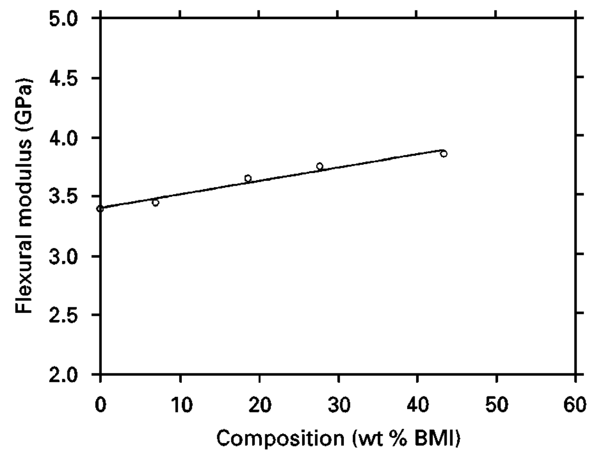


Figure 8 The elastic modulus, E, as a function of the composition of the reactive mixture.

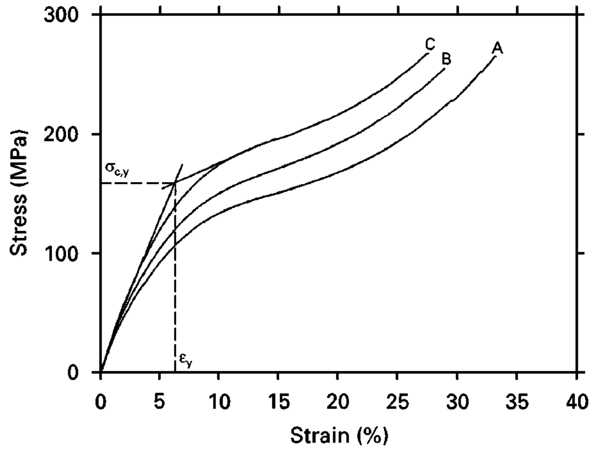


Figure 9 Compressive stress–strain curves for the neat epoxy resin (A), for the 100:30:50 blend composition (B), and for the 100:30:100 composition (C).

The E versus composition curve is shown in Fig. 8; E increases linearly with enhanced BMI content. This behaviour reflects the higher stiffness of the BMI containing network with respect to that of the TGDDM–DDS resin.

To predict large strain properties the yielding behaviour of some of the investigated blends was examined under uniaxial compression mode. The relative stress–strain curves, obtained at the same loading rate and temperature as for Young's Modulus (see experimental), are shown in Fig. 9. It can be observed that, when loaded in compression, the samples yield and

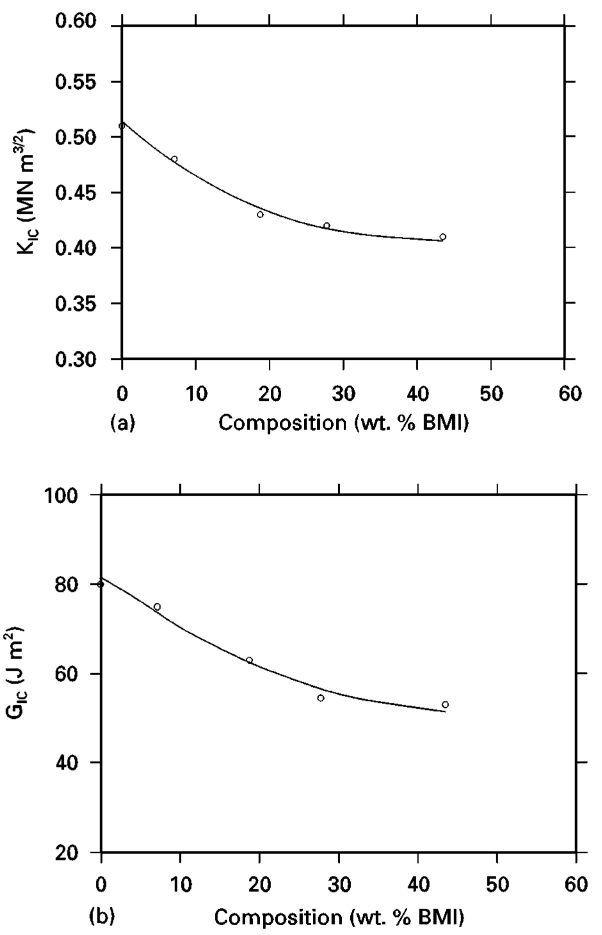


Figure 10 The critical stress intensity factor, (a) K_{Ic}, and the critical strain energy release rate, G_{Ic}, (b) as a function of the composition of the reactive mixture.

flow, contrary to what happens in tension [22], where they exhibit a brittle behaviour.

The compressive yield stress, $\sigma_{c,y}$, evaluated as in Fig. 9, is reported in Table I. The $\sigma_{c,y}$ values increase by increasing the BMI content in the blend, which indicates, in agreement with the behaviour of E, that the presence of bismaleimide enhances the rigidity of the three-dimensional structure and hence the stress required to permanently deform the network.

Fracture measurements were also performed and the experimental data were analysed according to the linear elastic fracture mechanics approach. The critical stress intensity factor, K_{Ic}, and the critical strain energy release rate, G_{Ic}, evaluated according to Equations 1 and 2, are reported in Fig. 10a and b, respectively, as a function of the BMI content in the blend.

Both the fracture parameters exhibit a gradual decrease with increasing amount of BMI in the blend. The observed reduction of toughness is consistent with the behaviour of the elastic modulus and of the compressive yield stess. It is due to the increased rigidity of the network, which renders the IPN structure less prone to undergo viscoelastic and plastic deformation processes.

4. Conclusions

In the present contribution information on the molecular structure and on the physico-mechanical properties of a thermoset–thermoset blend system is reported.

The spectroscopic analysis points to the formation, upon curing of an IPN-type network. The two thermosetting matrices, a tetrafunctional epoxy and a bismaleimide resin seem to undergo the curing process with minimum, or no interaction at all. The former resin crosslinks with its own hardener, DDS, while the latter polymerizes via a chain addition process.

The dynamic-mechanical measurements showed a single tan δ peak for all the investigated compositions, intermediate between those of the two components, thus suggesting the interpenetrated nature of the resulting network.

The same tests, carried out on samples having absorbed their equilibrium water content, demonstrated a considerable plasticization effect of the absorbed moisture into the neat epoxy resin. Such an effect was found to decrease gradually as the BMI content in the blend increased. The presence of BMI also yielded a decrease of the equilibrium water uptake and a slight increase of the apparent diffusion coefficient, for sorption measurements carried out at 70 °C.

With respect to the mechanical properties, the presence of BMI, which is a more rigid monomer than TGDDM, increased such properties as the flexural elastic modulus and the compressive yield stress. On the other hand, the enhanced stiffness caused a slight reduction of the fracture parameters K_{Ic} and G_{Ic}, as a consequence of the reduced ability of the IPN network to be plastically deformed under loading.

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