Polyimide-modified epoxy system: time–temperature–transformation diagrams, mechanical and thermal properties

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A hot-melt processable thermoset was prepared by blending tetraglycidyl-4,4′-diaminodiphenylmethane/4,4′-diaminodiphenylsulfone epoxy resin and a high-T_g thermoplastic polyimide. The polyimide was synthesized from 3,3′,4,4′-benzophenonetetracarboxylic dianhydride and 4,4′-(9*H*-fluoren-9-ylidene)bisphenylamine to form a linear structure initially miscible with the neat epoxy resin. The thermal polymerization study, including determination of time–temperature–transformation cure diagrams, pointed out a lowering in crosslink density of epoxy network probably due to the polyimide viscosity effect. After cure, no phase separation could be observed by scanning electron microscopy and only one T_g was detected by dynamic mechanical analysis, showing full miscibility between the blend components. The consequences of the thermoplastic incorporation (polyimide concentration = 10 wt%) were a slight increase in T_g value ($\Delta T_g = +5°C$) and rather limited improvements in stress at rupture (50%) and strain-energy release rate G_{Ic} (27%) compared to the unmodified epoxy matrix.

(Keywords: modified epoxy resin; epoxy–thermoplastic blend; toughness improvement)

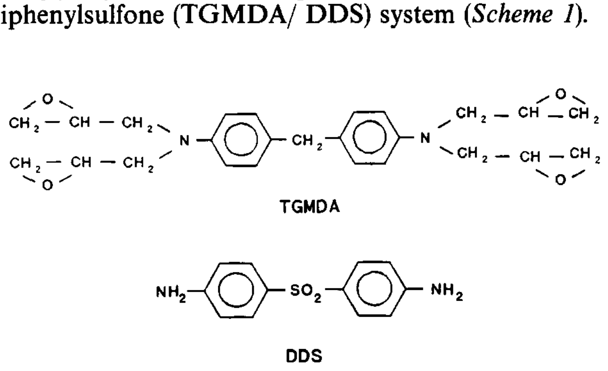
INTRODUCTION

Motivated by the increasing demands of the aerospace industry for new high-performance composite materials, many laboratories have undertaken considerable efforts to develop new thermosetting resins leading to matrices with high end-use temperature. Epoxy resins are one of the most important classes of thermosetting polymers used for structural or adhesive applications. They show various desirable properties such as high tensile strength and modulus, easy processing, good thermal and chemical resistance and dimensional stability. However, in many applications, their brittleness is a major drawback. Over the last decades, methods of appropriately mixing two or more different polymers to obtain a new material with desirable features have been developed[1–7]. Brittle epoxy resins have been modified by mixing with liquid CTBN (carboxyl-terminated butadiene–acrylonitrile) rubbers. Improved materials with enhanced fracture toughness were obtained. But significant deterioration of the bulk properties, i.e. elastic modulus, T_g and moisture absorption, were observed. Moreover, it has been demonstrated[8] that if rubber toughening is effective for difunctional resins (such as the diglycidyl ether of bisphenol A), when the functionality of epoxy monomers is higher, inducing a higher crosslink density, toughening capability decreases.

Much attention has recently been given to the toughening of thermosets by blending with high-performance aromatic thermoplastic polymers. In the case of epoxy resins, poly(ether sulfone) or poly(ether imide) has been used owing to their solubility or miscibility with the uncured starting resin[8–19]. These thermoplastics show high T_g, close to that of the crosslinked polyepoxy network (near 200°C), so significant improvement in damage tolerance has been achieved without compromising other critical laminate properties and hot/wet performance.

Our approach consists of modifying an epoxy thermoset by a soluble thermoplastic polyimide exhibiting a very high T_g. So, apart from the toughening effect, we expect to increase the blend T_g taking advantage of possible miscibility between the two components after thermal polymerization.

The epoxy resin corresponds to the high-temperature tetraglycidyl-4,4′-diaminodiphenylmethane/4,4′-diaminodiphenylsulfone (TGMDA/ DDS) system (*Scheme 1*).



Scheme 1

The polyimide was synthesized from 3,3′4,4′-benzophenonetetracarboxylic dianhydride (BTDA) and 4,4′-

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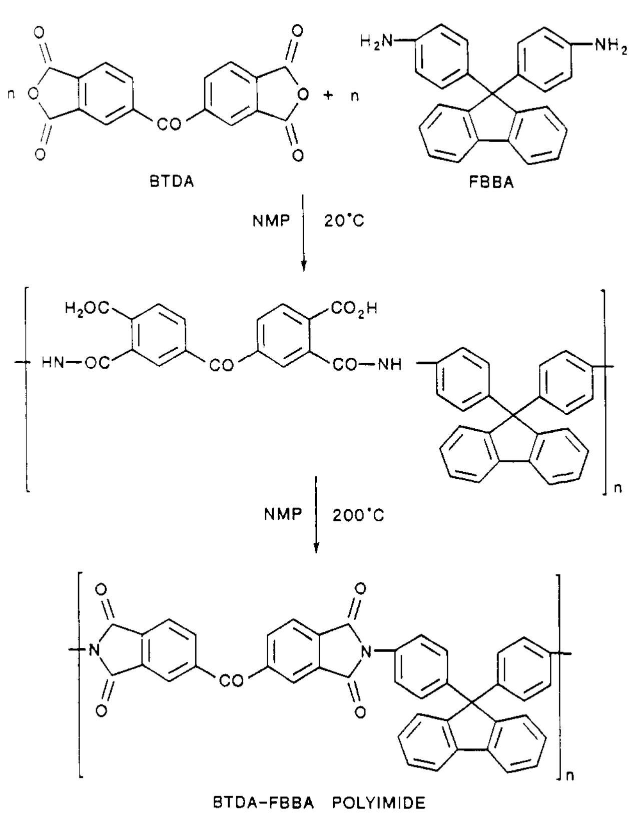


Scheme 2

(9*H*-fluoren-9-ylidene)bisphenylamine (FBPA) as shown in *Scheme 2*.

The hindered backbone due to lateral fluorene groups (cardo structure) leads to a polymer exhibiting a very high T_g (near 350°C) and a good solubility in many organic solvents, such as *N*,*N*-dimethylformamide, anisole, chloroform and dioxane[20]. An efficient blending of the two components was achieved by dissolution in a common solvent followed by a careful striping. Two polyimide concentrations in the epoxy thermoset were investigated. In order to understand the influence of the polyimide on the thermal polymerization process, we determined the TTT (time–temperature–transformation) cure diagrams[21] of pure and modified resins. The mechanical properties, i.e. tensile and flexural moduli, and the fracture resistance were examined in comparison to the unmodified TGMDA/DDS network. Thermal stability properties were also studied.

EXPERIMENTAL

Starting materials

The epoxy resin was CIBA-Geigy MY720 resin, which consists essentially of tetraglycidyl-4,4′-diaminodiphenylmethane. The resin was cured with 4,4′-diaminodiphenylsulfone (CIBA-Geigy hardener HT976). The cardo polyimide was prepared according to a reported procedure[20].

Blend preparation

The formulations were prepared on the basis of one epoxy group per 0.85 amine hydrogens. Pure resin compositions were obtained by a standard procedure. The TGMDA was heated in an oil bath to 80°C and the DDS hardener was added slowly with stirring for about 20 min. Resin compositions containing 5 and 10 wt% of thermoplastic polyimide were prepared by the following method. The powered polyimide was dissolved in dioxane at 20 wt% concentration at room temperature. The solution was then heated to 80°C. TGMDA was added and stirred at 80°C for 1 h. Dioxane was then boiled off, first with a rotavapor apparatus for 30 min and then in a primary vacuum oven at 100°C for about 4 h. The solution was then heated in an oil bath to 120°C and the DDS hardener was added with stirring over about 45 min.

Cure

The determination of TTT diagrams was achieved by using four isothermal curing temperatures: 120, 135, 150 and 170°C. The resin was poured into test-tubes and cured by immersion in a thermoregulated oil bath. After curing, tubes were quenched into ice-water to stop the reaction. Specimens for mechanical properties measurements and thermal characterization were cured for 4 h at 120°C, 4 h at 150°C and 7 h at 200°C in a press with 1°C min^{-1} heating rate.

Techniques

TTT diagrams. The polymerization kinetics up to the gelation point were 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 and tetrahydrofuran (THF) as elution solvent were used. The samples were initially dissolved in *N*-methylpyrrolidone (NMP) to prevent any precipitation of the polyimide into the s.e.c. columns. So the gel point was determined during the sample preparation from the appearance of insoluble product in NMP.

The kinetics of the pre-gel state may be determined by following the decrease in the area of basic monomer peaks (TGMDA, DDS). The overall conversion of monomer functions is given by:

$$x = 1 - (h_t/h_0)^{1/4}$$

for TGMDA functions, and

$$x = 1 - (h_t/h_0)^{1/2}$$

for primary amine functions of DDS, where h_t/h_0 is the ratio of the peak area at any time with respect to the initial peak area.

Glass transition temperatures were measured with a Mettler TA 3000 thermomechanical analyser. The penetrating probe exerted a 0.2 N force. A 10°C min^{-1} heating rate was applied and T_g was determined after a first scan up to 200°C to prevent any error due to stress release. Vitrification time was assigned to be the time at which the T_g becomes equal to the cure temperature. The $T_{g,\mathrm{gel}}$ value was determined at the break of slope of the degree of conversion *versus* T_g curve.

Viscoelastic analysis. Viscoelastic analyses were performed by a Rheometrics RMS 800 apparatus. Resin gelations were studied with 4 mm radius parallel plates with a 10 rad s^{-1} frequency (strain 10%) from 150 to 220°C.

Solid-state analyses were made using $3 \times 8 \times 45\ \mathrm{mm}^3$ specimens at 0.1 rad s^{-1} (strain 0.1%) from 50 to 350°C. The sample temperature was increased by steps of 5°C with a heating rate of about 1°C min^{-1}.

Mechanical and thermal properties. Mechanical tests were performed by an Instron 1175 analyser. Fracture toughness (K_{Ic}) was determined according to ASTM E-399 standard. Flexural and tensile properties were measured following ASTM D-638M normalization. T.g.a. data were obtained from 50 mg samples using a Setaram TG 85 thermogravimetric analyser. The heating rate was 5°C min^{-1} with a flow rate of 100 ml min^{-1} of air or argon.

POLYIMIDE PROPERTIES: RESULTS AND DISCUSSION

The cardo polyimide was synthesized by polycondensation between 4,4′-(9*H*-fluoren-9-ylidene)bisphenylamine (FBPA) and 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA) in *N*-methylpyrrolidone (NMP). The reaction was conducted with a slight excess of anhydride functions, allowing the obtention of a phenylimide end-capped polymer after treatment with aniline.

A detailed study of polyimide including chemical structure determination from ^{13}C n.m.r. analysis and molecular-weight calculation from s.e.c. was previously published. The thermal and mechanical properties of polyimide films were investigated too[20]. *Table 1* summarizes the main results.

EPOXY–POLYIMIDE BLENDS: RESULTS AND DISCUSSION

Study of thermal polymerization

The cure behaviour of commercial-grade TGMDA/DDS mixtures has already been investigated in order to understand the polymerization mechanisms leading to gelation and vitrification[22,23]. The possibility of chemical interaction between the epoxy functions of diglycidylamine groups, and the low reactivity of amine groups of DDS explain the high complexity of the chemical transformations involved during the reaction. The curing of TGMDA/DDS system implies, besides the conventional addition of primary amines on oxirane groups, secondary reaction mechanisms occurring to different extents, i.e. (i) addition of secondary amines, (ii) intermolecular etherification by reaction of hydroxyl groups on neighbouring epoxy groups, and (iii) intramolecular etherification leading to a morpholine-type cyclic structure.

Table 1 Characterization of polyimide from BTDA and FBPA

Molecular weight (s.e.c. from model compound study)	$M_n = 10\,000$ $M_w = 26\,000$
Glass transition temperature (t.m.a., 5°C min^{-1})	$T_g = 350°C$
Thermal stability (t.g.a., 5°C min^{-1} under argon)	Onset of degradation, $T_d = 401°C$
	Weight loss at 500 and 600°C (air) $\Delta P_{500} = 0.7\%$ $\Delta P_{600} = 18.6\%$
Tensile properties (samples: polyimide films)	Room temperature $E = 2.3$ GPa $\sigma_R = 67.5$ MPa $\varepsilon_R = 3.93\%$ At 200°C $E = 1.4$ GPa $\sigma_R = 47.2$ MPa $\varepsilon_R = 3.4\%$
Water uptake (24 h at 25°C with 65% relative humidity)	0.8%

Table 2 T_g of TGMDA/DDS systems with different stoichiometric ratios (SR = amine hydrogen/epoxy function)

$SR = 0.7$	$SR = 0.85$	$SR = 1.0$
217°C	239°C	198°C

In agreement with the various publications, the network seems to be less dense than expected from the relative functionalities of starting components. Thus the existence of intramolecular reactions and the partial conversion of weakly reactive DDS secondary amines decrease the potential crosslink density. Moreover, chain-growth mechanisms, essentially involving the preferential reaction of primary amines, occur during the first polymerization steps.

Stoichiometry. A preliminary study of TGMDA/DDS systems with various molar ratios of amine hydrogen per epoxy group (*Table 2*) has shown that the stoichiometric ratio value of 0.85 hydrogen/epoxy led to the highest T_g. This formulation should lead to the highest crosslink density by minimizing the possibility of intramolecular etherification[24]. Numerous industrial TGMDA/DDS resins use this stoichiometric ratio.

Epoxy–polyimide blend preparation. The same stoichiometric ratio has been selected for the blends assuming that the polyimide is chemically inactive towards the TGMDA/DDS polymerization. The blends were obtained by mixing TGMDA with a solution of polyimide in dioxane. After removing dioxane, DDS was added and the mixture was stirred to give clear solutions (dioxane weight content = 0.4% measured by t.g.a.). The blends had respectively 5 and 10 wt% of polyimide.

Preliminary d.s.c. study and rheological behaviour. The position of the polymerization exotherm and the related enthalpy were quite similar for the pure TGMDA/DDS resin and the 10% polyimide-modified blend ($T_{max} = 180°C$, $\Delta H = 130$ kJ mol^{-1}). *Figure 1* reports the corresponding rheological profiles. The temperatures of gelation (determined from the point of intersection between G' and G'') were 191 and 195.5°C respectively for the neat and modified resins. This points out the rather limited influence of the polyimide component on the initial polymerization stage. However, there was an important increase of $|\eta^*|$ (about three orders of magnitude) due to the polyimide incorporation.

TTT cure diagrams. The 10% polyimide-modified system was compared to the pure TGMDA/DDS resin. Four curing temperatures were explored: 120, 135, 150 and 170°C. No phase separation was observed at these different temperatures from cloud-point measurement with visible light.

Gel time. The influence of polyimide addition on the TGMDA/DDS system is presented in *Table 3*. The isothermal curing experiments confirm that there was no great modification of gelation times caused by the addition of polyimide. The reproducibility of the gelation-

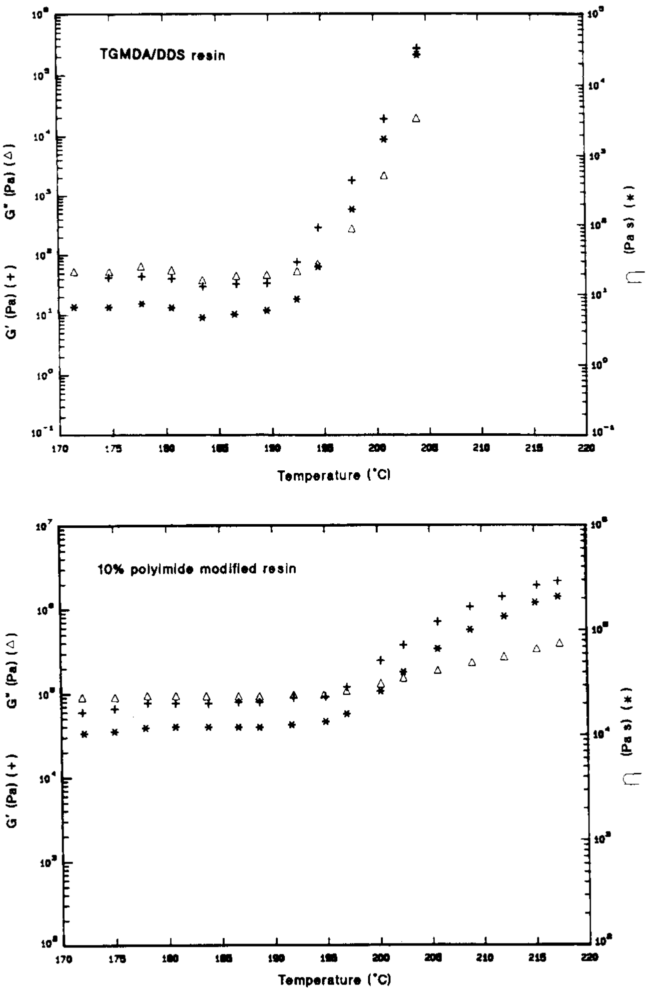
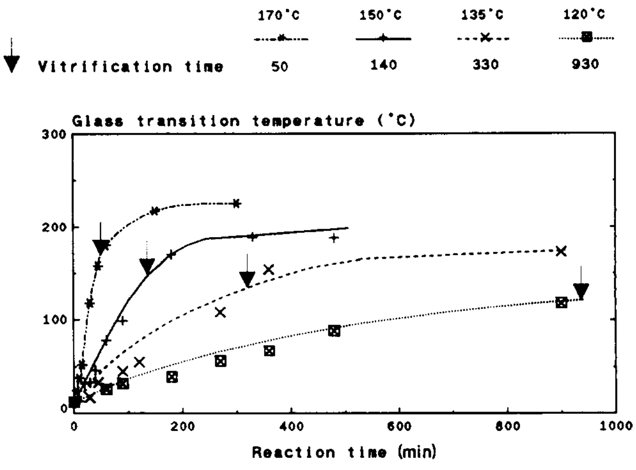
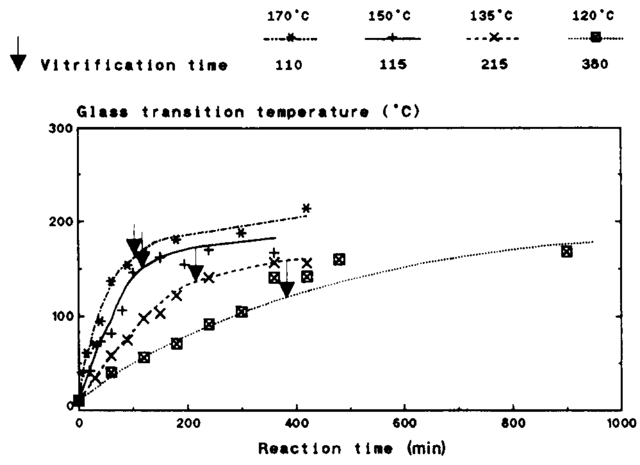


Figure 1 Rheological profile of TGMDA/DDS and 10% polyimide-modified systems



TGMDA/DDS system



10% PI modified system

Figure 2 T_g *versus* time of TGMDA/DDS and 10% polyimide-modified systems

Table 3 Gelation times (min) of TGMDA/DDS and 10% polyimide-modified systems at 120, 135, 150 and 170°C

	170°C	150°C	135°C	120°C
TGMDA/DDS	10–15	30–35	70–75	165–170
TGMDA/DDS/PI	10–15	40–50	75–90	150–180

time measurements is poor for the polyimide-modified resin. This was probably due to the greater difficulty in dissolving the polyimide–epoxy mixture into NMP.

Vitrification. The T_g *versus* time curves of both TGMDA/DDS and 10% modified systems are reported in *Figure 2*. Referring to the high T_g of the polyimide, a classical mixture behaviour should lead to an increase in blend T_g compared to the neat epoxy resin. However, two separate trends are observed depending on the curing temperature. Surprisingly, the presence of thermoplastic polymer provided a decrease in glass transition temperature at 170°C isothermal cure.

The great increase in viscosity due to the polyimide incorporation probably affects the selectivity of the epoxy-group polymerization, the intramolecular etherification reactions being promoted instead of crosslink formation. This effect is essentially visible for the high cure temperatures because the mobility is strongly reduced at high conversion degrees. A lowering of the reaction kinetics could also be obtained. This is not apparent for the gelation curves presented in *Figure 3*, but, in this case, the polymerization process is only observed for low conversion degrees ($x_{epoxy} \leq 0.3$).

Concerning the 120 and 135°C vitrification curves, a classical miscibility effect seems to operate. In this case, the T_g of the polyepoxy network is limited and its evolution includes chain-growth mechanisms less dependent on the medium viscosity. For the polyimide-modified resin, isothermal curing at 200 and 220°C was investigated. The first vitrification curve showed the possibility to obtain high blend T_g ($T_g = 220$°C after 1 h at 200°C). The second curve showed a lowering of T_g after a maximum value at 200°C due to thermodegradation.

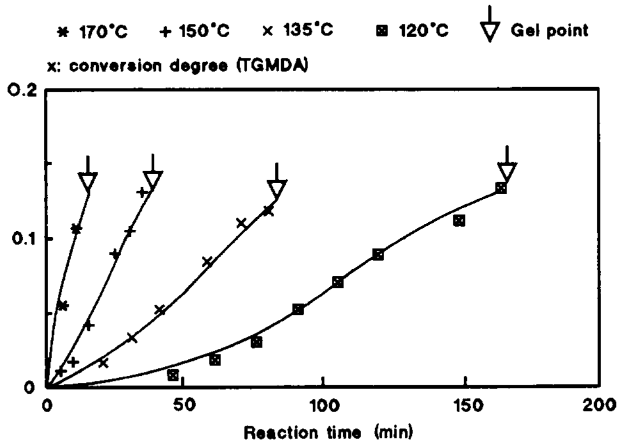
Gelation. Gelation curves were determined from the conversion *versus* time of reactive components (TGMDA, primary amines of DDS). Theoretical degrees of conversion at the gel point were calculated from Flory's equations:

$$x_A x_B = \frac{1}{(f_A - 1)(f_B - 1)}$$

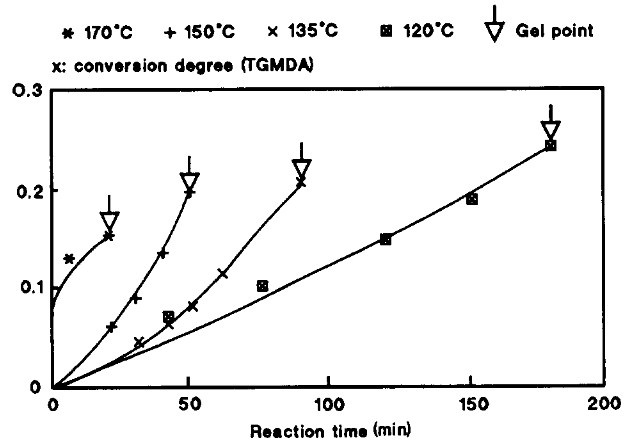
where x_i is the conversion degree at the gel point and f_i is functionality of species i. If r is the stoichiometric ratio, then:

$$x_B = \left(\frac{r}{(f_A-1)(f_B-1)}\right)^{1/2}$$

$$x_A = \left(\frac{1}{(f_A-1)(f_B-1)r}\right)^{1/2}$$



TGMDA/DDS System



10% PI modified system

Figure 3 Conversion *versus* time of TGMDA/DDS and 10% polyimide-modified systems (TGMDA functions)

TGMDA epoxy resin is tetrafunctional, but the functionality of DDS has been disputed, especially during the first stage of polymerization. This is related to the low intrinsic reactivity of secondary amines, which could be amplified by steric hindrance[25] due to the crosslinking of initial primary amine groups. Conversion degrees at the gel point were calculated using both difunctional and tetrafunctional DDS:

$$f_{\mathrm{TGMDA}} = 4, f_{\mathrm{DDS}} = 2, r = 0.425 \quad \Rightarrow \quad x_{\mathrm{TGMDA}} = 0.376$$

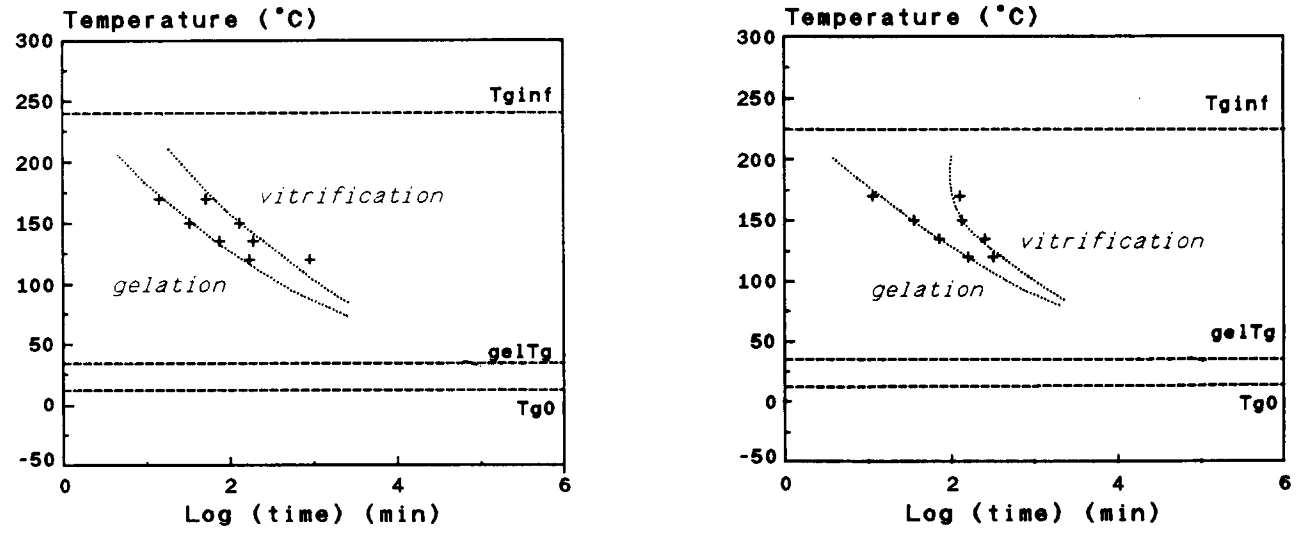
and

$$f_{\mathrm{TGMDA}} = 4, f_{\mathrm{DDS}} = 4, r = 0.850 \quad \Rightarrow \quad x_{\mathrm{TGMDA}} = 0.307$$

Figure 3 shows the epoxy function conversion *versus* time of TGMDA/DDS and polyimide-modified systems. We notice that experimental degrees of conversion at the gel point are well below theoretical values in both cases. Although the experimental determination is only based on the formation of insoluble products in NMP, which could be criticized, Flory's equations do not seem directly usable to describe the TGMDA/DDS behaviour. Moreover, the blending procedures used for the two systems were not strictly similar and the starting polymerization degrees were probably slightly different, resulting in a displacement of conversion curves with and without polyimide. Except for this displacement of curves due to experimental conditions, gelation curves for the two systems seemed to be similar up to $x = 0.15$, showing that the reaction behaviour is the same at low conversion.

The evolution of conversion degree at the gel point for the polyimide-modified system shows that the polymerization mechanism is temperature-dependent. This might be explained by a simple viscosity effect: the lower the isothermal cure temperature, the higher is the blend viscosity, which could promote the chain-growing processes instead of gel formation.

Figure 4 reports the TTT diagrams of TGMDA/DDS with and without polyimide, revealing a slight modification in the vitrification curve, which is shifted to longer times in the presence of thermoplastic modifier. $T_{g,0}$ was determined by t.m.a. before cure. $T_{g,\mathrm{inf}}$ was measured after an isothermal cure at 200°C for 7 h leading to maximum T_g values for the neat and modified resins (respectively 240 and 225°C).



TGMDA/DDS System

10% PI Modified System

Figure 4 Isothermal time–temperature–transformation cure diagrams of TGMDA/DDS and 10% polyimide-modified systems

The temperature at which gelation and vitrification take place simultaneously, $T_{g,gel}$, is practically the same for the pure and polyimide-modified resin (i.e. close to 20°C). These temperatures have been determined from the variation of conversion degree in TGMDA *versus* T_g ($T_{g,gel}$ corresponds to the temperature of slope change).

Considering the TTT diagrams, we have selected a curing cycle with a final step at 200°C to optimize the T_g of the epoxy–polyimide blend.

The curing temperature cycles for the bulk samples were: 2 h at 80°C, 2 h at 120°C, 4 h at 150°C, 7 h at 200°C for TGMDA/DDS; and 4 h at 120°C, 4 h at 150°C, 7 h at 200°C for TGMDA/DDS–polyimide blends.

Epoxy–polyimide matrix properties

Morphological features. Blends were clear solutions before cure. No cloud point was observed during the cure from light diffusion study and cured samples were transparent. SEM observations on fracture surface did not show the presence of segregated microdomains.

Dynamic mechanical properties. Figure 5 shows the viscoelastic behaviour of TGMDA/DDS compared to polyimide-modified resin. A single tan δ peak could be identified for the epoxy–polyimide blend. This result confirms the full miscibility of the blend components. In addition, there was an increase of glass transition (maximum of tan δ peak) owing to the contribution of the high T_g of thermoplastic polymer.

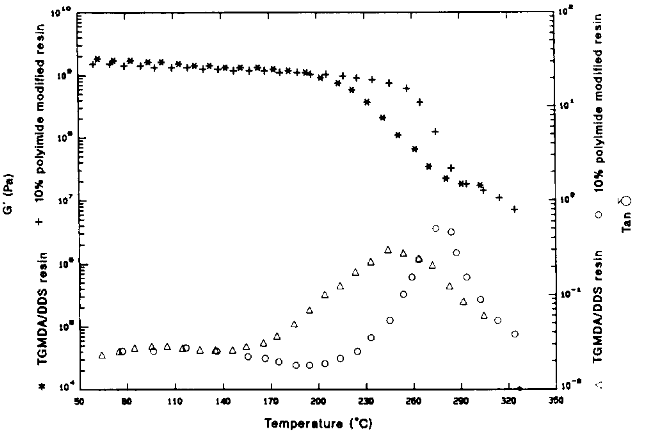


Figure 5 Viscoelastic behaviour of TGMDA/DDS and 10% polyimide-modified systems

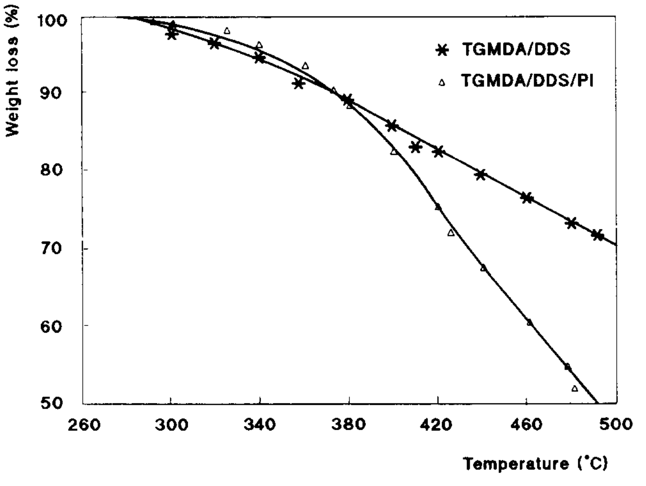


Figure 6 Thermogravimetric behaviour of TGMDA/DDS and 10% polyimide-modified system

Table 4 Mechanical properties[a] of TGMDA/DDS, 5 and 10% polyimide-modified systems

	Cardo polyimide	TGMDA/DDS pure	TGMDA/DDS/PI 5% PI	TGMDA/DDS/PI 10% PI
T_g (°C)	350	225	227	230
Flexural modulus (GPa)		3.3	3.4	3.2
Tensile modulus (GPa)		3.8	4.3	4.2
Elongation at rupture (%)		0.35	0.48	0.51
Stress at rupture (MPa)		140	190	210
K_{Ic} (MPa m$^{1/2}$)[a]		0.69	0.67	0.82
G_{Ic} (J m^{-2})[a]		110	90	140

[a] K_{Ic} = stress intensity factor; G_{Ic} = fracture energy

Thermogravimetric properties. Figure 6 shows the thermogravimetric behaviour in argon atmosphere of pure TGMDA/DDS and 10% polyimide-modified systems. We can see that the onset of decomposition of the polyimide-modified system is shifted to higher temperature but the corresponding decomposition profile is more pronounced above 400°C.

Mechanical properties. Mechanical properties of 5 and 10% polyimide-modified blends are presented in *Table 4*, compared to pure TGMDA/DDS system and BTDA/FBPA polyimide. Referring to the dynamic mechanical analysis spectrum reported above, the increase in T_g for the 10% polyimide-modified blend seemed much more limited in this case (ΔT_g near 5°C). However, the considered T_g values are determined from thermomechanical analysis in penetrating mode and cannot be compared with the tan δ maximum temperatures. The flexural modulus, the tensile modulus and the corresponding elongation at rupture were very similar for the different matrices. However, the presence of polyimide modifier induced a notable enhancement in stress at rupture. Concerning the toughness improvement, only the 10% polyimide concentration was able to bring a slight increase in K_{Ic} and G_{Ic} values. Surprisingly, the 5% polyimide-modified blend seemed more brittle than the pure TGMDA/DDS resin.

Considering this set of results, we could not assume that the toughening effect observed for the 10% polyimide-modified blend was really due to the contribution of the thermoplastic polymer. A decrease in crosslink density of the polyepoxy network could lead to the same behaviour[8]. So the resulting lowering in T_g could be compensated by full miscibility between the two blend components.

CONCLUSION

The BTDA–FBPA thermoplastic polyimide could be successfully blended with TGMDA/DDS epoxy resin to give homogeneous mixtures before curing. This demonstrated the possibility of preparation of hot-melt-processable resins including a high-T_g thermoplastic polyimide with bulky cardo groups. After epoxy polymerization, no phase separation could be detected by SEM and only one glass transition was obtained from d.m.a., showing full miscibility between the polyimide structure and the polyepoxy network. A rather slight increase in fracture toughness and T_g was observed only for the 10% polyimide-modified resin.

This limited improvement of properties probably resulted from the high miscibility between the components, leading to high-viscosity blends. First of all, this could affect the kinetics and the selectivity of the polymerization reaction, inducing a lowering of the crosslink density. Secondly, this prevents the formation of a phase-separated morphology, which is generally required to obtain a notable toughening effect[4,16].

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