

New semi-interpenetrating polymeric networks from linear polyimides and thermosetting bismaleimides:

2. Mechanical and thermal properties of the blends

Thierry Pascal, Régis Mercier and Bernard Sillion*

CEMOTA, BP 3, 69390 Vernaison, France

(Received 14th November 1988; revised 19 April 1989; accepted 26 April 1989)

Two linear polyimides, BAPPY-BTDA and BAPB-BTDA, prepared by condensation of 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) with 3,3'-[2,6-pyridinediylbis(oxy)]bisbenzene amine (BAPPY) and 3,3'-[1,3-phenylenebis(oxy)]bisbenzene amine (BAPB), and three thermosetting bismaleimides (BMI), PPY-BMI, PB-BMI and MDA-BMI, synthesized from the two preceding aromatic diamines and 4,4'-methylenebis(1,4-phenylene) (MDA), were blended to obtain the following mixtures: BAPPY-BTDA/PPY-BMI, BAPPY-BTDA/MDA-BMI and BAPB-BTDA/PB-BMI. These three types of mixture were cured up to 300°C to give semi-interpenetrating polymeric networks (IPNs). Thermomechanical and dynamic mechanical analysis of semi-2-IPN films essentially pointed out a phase separation between the linear polyimide and the crosslinked bismaleimide with probably partial miscibility between the polyimide and oligomeric or unreacted bismaleimide compounds. Thermogravimetric analysis showed that the thermal resistance of semi-IPNs was dramatically decreased as the bismaleimide concentration increased. Compared to the free linear polyimides, the semi-interpenetrated structure led to a reduction of the room-temperature adhesive joint strengths but allowed the conservation of adhesive and mechanical tensile properties in the region of the glass transition temperature of the linear polyimide.

(Keywords: 3,3'-[2,6-pyridinediylbis(oxy)]bisbenzene amine; 3,3'-[1,3-phenylenebis(oxy)]bisbenzene amine; polyimide; bismaleimide; semi-interpenetrating polymeric network; thermomechanical analysis; phase separation)

INTRODUCTION

New semi-interpenetrating polymeric networks obtained by mixing a thermostable linear polymer and a thermostable crosslinked polymer were recently studied to develop matrix resins for high-performance composites¹⁻⁵.

In a previous paper⁶ we have described the synthesis and characterization of two linear polyimides, BAPPY-BTDA (I) and BAPB-BTDA (II), respectively prepared by polycondensation of 3,3'-[2,6-pyridinediylbis(oxy)]bisbenzene amine (BAPPY, 1) or 3,3'-[1,3-phenylenebis(oxy)]bisbenzene amine (BAPB, 2) with 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA, 7).

Three bismaleimides, PPY-BMI (4), PB-BMI (5) and MDA-BMI (6), coming from the precedent aromatic diamines, 1 and 2, and another diamine, 4,4'-methylenebis(1,4-phenylene) (MDA, 3), were also prepared.

These thermoplastic and thermosetting imide structures were blended in *N*-methylpyrrolidone solution, cast and thermally dried at temperatures limited to 200°C in order to obtain films free of crosslinked bismaleimides.

The following blends were studied:

blend PPY/PPY:	polyimide	BAPPY-BTDA and bismaleimide	PPY-BMI
blend PPY/MDA:	polyimide	BAPPY-BTDA and bismaleimide	MDA-BMI
blend PB/PB:	polyimide	BAPB-BTDA and bismaleimide	PB-BMI

The main conclusion of this study was given by the thermomechanical analysis of the films, which showed a plasticizing of the polyimides by the unreacted bismaleimides in agreement with a good miscibility of the blend components.

The present paper deals with the study of semi-2-IPNs resulting from these three types of blends cured up to 300°C. The following points were examined:

(a) Evolution of mechanical and thermal properties of the semi-IPNs as a function of the proportion of bismaleimide in the starting blend.

(b) Study of adhesive and mechanical tensile properties of semi-IPNs.

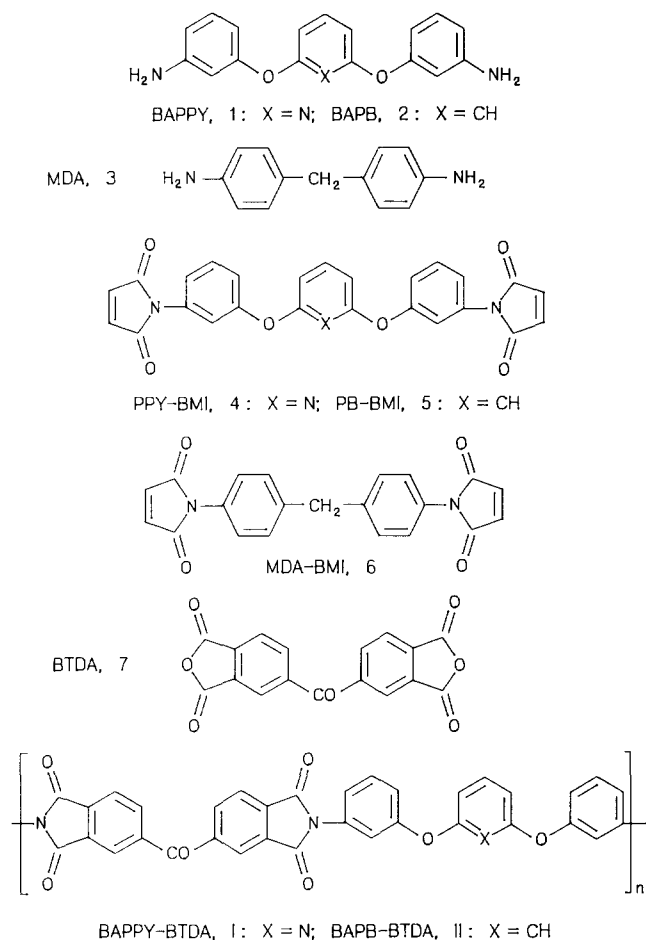
EXPERIMENTAL

Instrumentation

T.m.a. spectra were recorded at a heating rate of 5°C min⁻¹ on films of 0.05 mm thickness with a 0.3 N penetrating strength using a Mettler TMA 40 thermo-mechanical analyser.

Dynamic mechanical spectra were recorded at a heating rate of 5°C min⁻¹ with an 11 Hz oscillating

*To whom correspondence should be addressed



frequency on films of about 0.2 mm thickness using a Rheovibron spectrometer.

T.g.a. data were obtained from 100 mg samples in a nitrogen or air atmosphere at a heating rate of $5^{\circ}\text{C min}^{-1}$ using a Setaram TG85 thermogravimetric analyser.

Mechanical tensile tests were recorded at 1 mm min^{-1} crosshead speed with an Instron 1175 apparatus equipped with an Instron temperature cabinet and an Instron self-adaptive temperature controller.

Adhesive joint strengths were determined using the overlap shear test as outlined by ASTM D 1002-72 for aluminium to aluminium (Alloy 2024, Temper T-3).

The aluminium specimens were degreased with methyl ethyl ketone (MEK), then acid etched in a 2.44% sodium dichromate/24.4% sulphuric acid bath at 70°C for 10 min, sprayed with dionised water, then air dried.

N-methylpyrrolidone solutions with 30 wt% of free polyimide or 40 wt% of polyimide/bismaleimide blend were cast on the aluminium specimens and were dried at 100°C for 20 min before assembling.

The cure schedule for lap shear specimens was 30 min at 150°C and 60 min at 275°C .

Preparation of polyimide films

An *N*-methylpyrrolidone (NMP) solution with 40 wt% of polyimide/bismaleimide blend was cast on a glass plate using a doctor blade ($e=0.2 \text{ mm}$ for t.m.a., $e=0.8 \text{ mm}$ for dynamic mechanical test). The solvent was evaporated in a convection oven at 100°C for 1 h and at 150°C for 1 h. Then, final cure was performed at 300°C for 1 h. The film was removed from the glass plate by soaking it in cold water. The final film thickness was about 0.05 or 0.2 mm.

RESULTS AND DISCUSSION

Thermal and mechanical characteristics of the blend components

The analytical data from previous studies⁶ of the two linear polyimides and the three bismaleimides are reported in Tables 1 and 2.

Behaviour of the crosslinked blends

The polyimide/bismaleimide blends in *N*-methylpyrrolidone solution were cast and cured for 1 h at 100°C , 1 h at 150°C and 1 h at 300°C in order to polymerize the maleimide groups. The resulting systems were called semi-IPN PPY/PPY, semi-IPN PPY/MDA and semi-IPN PB/PB.

Thermomechanical analysis and dynamic mechanical analysis. Figure 1 compares the thermomechanical analysis profiles of linear polyimides and corresponding semi-IPNs coming from blends with an equal weight of each component. Two distinct mechanical transitions were observed on the t.m.a. spectra of the semi-IPNs: the first, T_{g1} , was related to the glass transition temperature of the linear polyimide and the second, T_{g2} , corresponded to the softening point of the crosslinked bismaleimide structure. T_{g1} and T_{g2} are given in Table 3 as a function of the concentration of bismaleimide. The relative deformation ε_T measured by t.m.a. between 100 and 300°C is also reported.

Table 1 Thermal and mechanical characteristics of the linear polyimides

	η_i^a (g dl^{-1})	T_g^b ($^{\circ}\text{C}$)	T_d^c ($^{\circ}\text{C}$)	ΔP^d at 500°C (%)
BAPPY-BTDA, I	0.53	198	377	6.3
BAPB-BTDA, II	0.48	191	385	3.1

^aInherent viscosities determined from NMP solutions with a concentration of 1 g dl^{-1}

^bGlass transition temperature from t.m.a. determined on films obtained from NMP solutions cast and cured 1 h at 100°C , 1 h at 150°C and 1 h at 300°C

^cOnset of degradation temperature from dynamic t.g.a. on precipitated powders with a heating rate of $5^{\circ}\text{C min}^{-1}$ under a nitrogen atmosphere

^dWeight loss at 500°C from t.g.a.

Table 2 Thermal and mechanical characteristics of the bismaleimides and corresponding networks

	Bismaleimide		Network ^a		
	T_f^b ($^{\circ}\text{C}$)	T_{exo}^c ($^{\circ}\text{C}$)	T_r^d ($^{\circ}\text{C}$)	T_d^e ($^{\circ}\text{C}$)	ΔP^f at 500°C (%)
PPY-BMI, 4	137	258	386	400	32.5
PB-BMI, 5	116	277	372	386	30.2
MDA-BMI, 6	159	205	390	410	27.5

^aCure cycle of 1 h at 100°C , 1 h at 150°C and 1 h at 300°C

^bMelting point from d.s.c. with a heating rate of $2^{\circ}\text{C min}^{-1}$

^cMaximum temperature of polymerization exotherm from d.s.c. with a heating rate of $2^{\circ}\text{C min}^{-1}$

^dSoftening point of the network from t.m.a. with a heating rate of $5^{\circ}\text{C min}^{-1}$

^eOnset of degradation temperature from dynamic t.g.a. on grinding samples with a heating rate of $5^{\circ}\text{C min}^{-1}$ under a nitrogen atmosphere

^fWeight loss at 500°C from t.g.a.

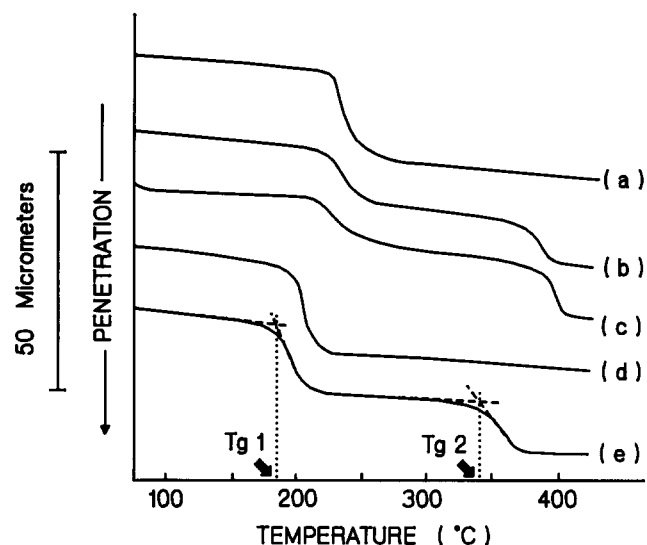


Figure 1 T.m.a. diagrams of free linear polyimides and corresponding semi-IPNs with 1/1 bismaleimide/polyimide weight ratio (weight ratio: weight of bismaleimide/weight of polyimide): (a) BAPPY-BTDA; (b) semi-IPN PPY/PPY; (c) semi-IPN PPY/MDA; (d) BAPB-BTDA; (e) semi-IPN PB/PB

Although the cured films always showed good homogeneity and good transparency, the thermo-mechanical analysis pointed out two mechanical transitions. As shown in *Table 3*, the glass transition temperatures T_{g1} of the linear polyimides in the semi-IPNs were about 10°C lower than the glass transition temperatures of the corresponding free polyimides. In addition, the softening point T_{g2} due to the crosslinked structure decreased about 10°C to 60°C as a function of the bismaleimide content relative to the neat bismaleimide network.

These observations are consistent with the partial miscibility of the two components and probably this miscibility is due to the presence of low-molecular-weight bismaleimide polymers. However, the existence of two well defined transitions is in agreement with the presence of an incompatible crosslinked phase resulting from the polymerization of bismaleimides^{7,8}. Therefore the semi-IPNs could be described as a dispersion of reticulated microdomains in a linear matrix.

Considering the good miscibility of the starting components⁶, it should be noticed that phase separation between the linear polyimides and the polymerized bismaleimides occurs during the crosslinking period probably owing to the growth of the molecular weight of the network.

As shown in *Figure 2*, the relative deformation ϵ_T was reduced when the bismaleimide concentration increased. Therefore, the incorporation of the reticulated structure led to an enhancement of mechanical rigidity. However, an increase of ϵ_T was observed for low concentrations of bismaleimide, below about 0.9 bismaleimide/polyimide molar ratio, compared with the values corresponding to the free polyimides. In that case, it seems that bismaleimides produced mainly a plasticizing effect probably caused by their high dilution in the polymeric matrix allowing the presence of residual unreacted molecules or low-molecular-weight oligomers.

The analogy of chemical structure between the linear polyimide BAPPY-BTDA and the bismaleimide PPY-BMI blended in the semi-IPN PPY/PPY did not induce a better compatibility in comparison with the semi-IPN

PPY/MDA whose components did not show molecular similarity. So the intermolecular associative properties due to the pyridinic ring⁶ present in BAPPY-BTDA and PPY-BMI are not sufficient to produce a homogeneous system.

Figure 3 shows dynamic mechanical spectra obtained with films of about 0.1 mm thickness using a Rheovibron spectrometer. The figure compares the spectra of free polyimide BAPPY-BTDA and two corresponding semi-IPNs PPY/PPY. A progressive decrease of the $\tan \delta$ peak relating to the T_g of the linear polyimide was correlated to the increase of bismaleimide concentration. A concomitant broadening towards low temperatures of the $\tan \delta$ peak was noticed, in agreement with a plasticizing effect due to oligomeric or unreacted maleimide compounds.

Table 3 Thermomechanical characteristics of the semi-IPNs^a

Weight ratio bismaleimide/polyimide ^b	Molar ratio bismaleimide/polyimide ^c	T_{g1}^d (°C)	T_{g2}^d (°C)	ϵ_T (%)
Semi-IPN PPY/PPY				
0		198	1	52.0
0.246	0.314	187	320	68.7
0.495	0.633	192	335	56.1
0.654	0.886	186	340	52.1
1.011	1.292	189	339	39.9
1.250	1.597	189	348	31.7
1.511	1.931	184	346	29.2
1.770	2.262	187	357	31.6
1.992	2.546	187	353	24.8
2.444	3.123	190	370	14.0
2.918	3.729	198	372	4.6
2.918	3.729	198	372	4.6
			386 ^e	2.8
Semi-IPN PPY/MDA				
0		198	1	52.0
0.186	0.300	192	342	62.0
0.356	0.576	192	340	59.0
0.612	0.990	194	350	59.2
0.655	1.059	192	347	57.7
0.902	1.459	190	348	47.2
0.994	1.607	186	350	35.5
1.115	1.803	190	350	25.9
1.295	2.094	191	352	34.0
1.456	2.354	192	371	22.0
1.797	2.906	188	385	21.1
2.522	4.078	190	390	11.1
3.104	5.019	194	390	9.1
			399 ^e	0
Semi-IPN PB/PB				
0	0	191	1	56.5
0.290	0.371	180	315	60.0
0.379	0.485	180	322	62.5
0.725	0.927	184	330	58.4
1.086	1.390	182	335	47.8
1.445	1.848	180	350	41.5
1.845	2.360	185	352	30.8
2.173	2.779	178	350	32.7
2.495	3.191	181	360	21.6
2.893	3.700	178	364	14.9
3.236	4.139	180	365	12.8
			372 ^e	4

^a T.m.a. on films of about 0.05 mm in thickness with a heating rate of 5°C min⁻¹

^b Weight ratio: weight of bismaleimide/weight of polyimide

^c Molar ratio; mole of bismaleimide/mole of repeating unit of polyimide

^d T_{g1} and T_{g2} were determined with the intersection of the base line tangent and the inflection point tangent on the t.m.a. curve

^e T_{g2} corresponds to the softening point of the neat bismaleimide network

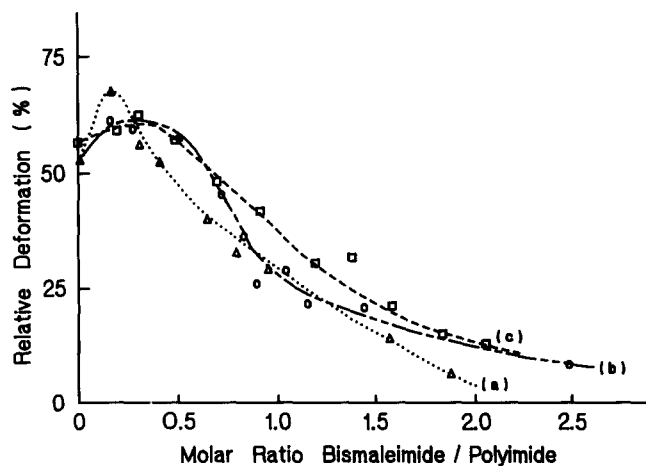


Figure 2 Evolution of the relative deformation ϵ_T between 100 and 300°C of semi-IPN films versus the bismaleimide concentration (molar ratio: mole of bismaleimide/mole of repeating unit of polyimide): (a) semi-IPN PPY/PPY; (b) semi-IPN PPY/MDA; (c) semi-IPN PB/PB

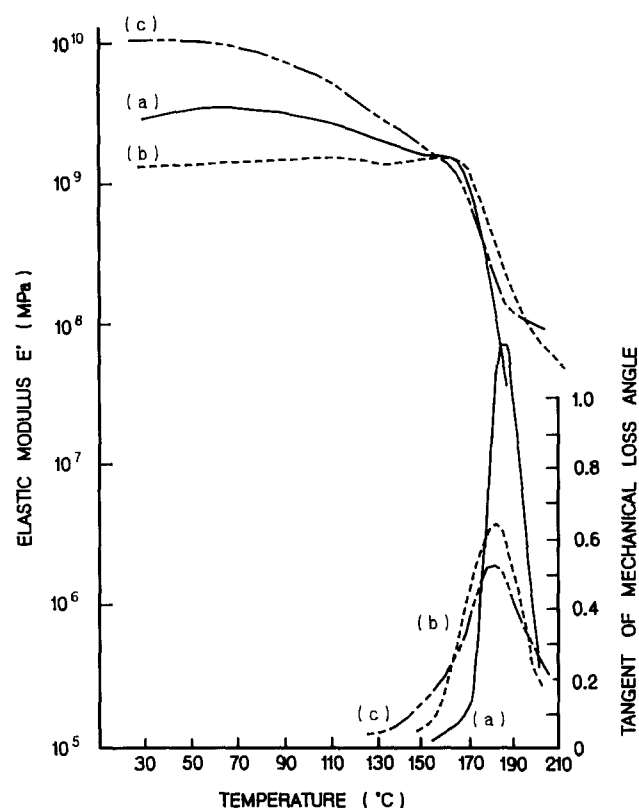


Figure 3 Dynamic mechanical spectra of polyimide and semi-IPN films from Rheovibron spectrometer: (a) BAPPY-BTDA; (b) semi-IPN PPY/PPY with 1/1 bismaleimide/polyimide weight ratio; (c) semi-IPN PPY/PPY with 2/1 bismaleimide/polyimide weight ratio

Thermogravimetric analysis. The dynamic t.g.a. curves in a nitrogen atmosphere are presented in Figures 4–6 for polyimide films and semi-IPN films with different compositions. The weight losses at 400°C and 500°C reported in Table 4 show that the thermal stability of the semi-IPNs is governed by the concentration of the less stable polymerized maleimide structure.

Mechanical tensile tests and adhesive tests. The mechanical tensile properties of linear polyimides and corresponding semi-IPNs formed with equal weight proportion of each component were studied at 20 and 160°C. The analytical data reported in Table 5 were

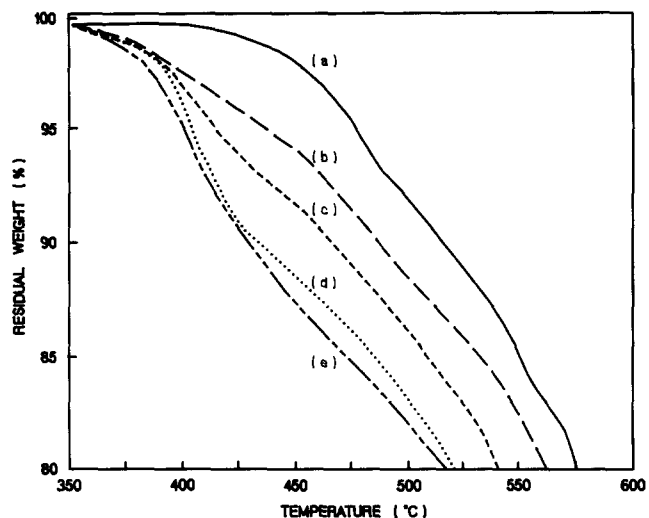


Figure 4 T.g.a. thermograms of free linear polyimide and corresponding semi-IPN with different weight ratio bismaleimide/polyimide, R : (a) BAPPY-BTDA; PPY/PPY with (b) $R=0.495$, (c) $R=1.011$, (d) $R=1.511$, (e) $R=2.444$

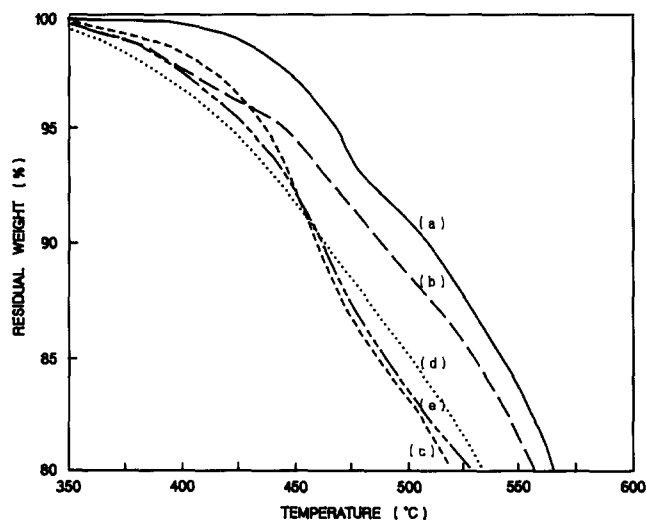


Figure 5 T.g.a. thermograms of free linear polyimide and corresponding semi-IPN with different weight ratio bismaleimide/polyimide, R : (a) BAPPY-BTDA; PPY/MDA with (b) $R=0.356$, (c) $R=0.612$, (d) $R=0.902$; (e) $R=1.295$

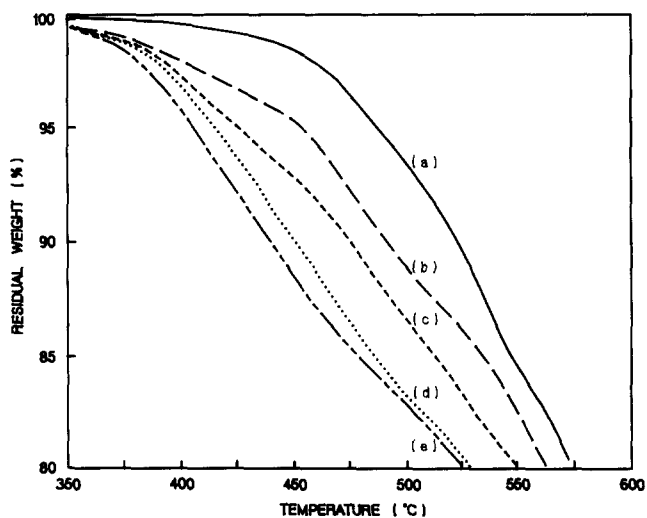


Figure 6 T.g.a. thermograms of free linear polyimide and corresponding semi-IPN with different weight ratio bismaleimide/polyimide, R : (a) BAPPY-BTDA; PB/PB with (b) $R=0.379$, (c) $R=1.086$, (d) $R=1.445$, (e) $R=2.495$

obtained from the classical stress-strain curves recorded with an Instron 1175. Typical curves at 160°C are given in Figure 7 with polyimide BAPPY-BTDA and the corresponding semi-IPN PPY/PPY. The linear polyimide showed a viscoelastic behaviour with high elongation at break at 160°C when the semi-IPN always exhibited elastic-type character.

The tensile moduli of semi-IPNs were higher than those of free polymers; as can be seen in Table 5, an increase of 30% at 20°C was obtained with the semi-IPN PPY/MDA. However, the most important property due to the semi-interpenetrated structure was the conservation of mechanical characteristics at 160°C in the vicinity of the glass transition temperature of polyimide.

From Table 5, it can be noted that the residual tensile moduli of semi-IPNs at 160°C reached about 70% of the initial moduli of the linear polymers at 20°C.

Adhesive joint strengths were determined using the lap shear test as outlined by ASTM D 1002-82 for aluminium to aluminium with a cure schedule of 30 min at 150°C and 60 min at 275°C. The average lap shear strengths

determined at 20, 160 and 200°C are given in Table 6. In all cases, a cohesive failure was observed.

Performing best at 20°C were the free linear polyimides for which the average lap shear strengths were higher than those of the majority of known processable polyimide resins⁹. Bearing in mind the cohesive mode of failure, the weaker adhesive properties of the semi-IPNs at 20°C could be due to the lower plasticity of the bond layer. Therefore, the low lap shear strength of the semi-IPN PPY/MDA was probably due to its high crosslink density.

In addition, residual mechanical stresses due to shrinkage during crosslinking probably reduce the adhesive properties, particularly when the crosslink density is high.

The semi-IPNs showed the higher lap shear strengths at 160 and 200°C, as the linear polyimides underwent a dramatic decrease of their adhesive properties due to their viscoelastic character in this temperature range. The adhesive strengths of semi-IPNs at 160°C were even higher than those determined at 20°C for the same products. This improvement is attributed to a reduction of the residual mechanical stresses, which could probably

Table 4 Thermogravimetric characteristics of the polyimides and semi-IPNs^a

Weight ratio bismaleimide/polyimide ^b	Molar ratio bismaleimide/polyimide ^c	ΔP at 400°C (%)	ΔP at 500°C (%)
Semi-IPN PPY/PPY			
0	0	0.55	8.15
0.495	0.633	2.5	11.45
1.011	1.292	3.25	13.95
1.511	1.931	4.2	18.0
2.444	3.123	5.0	16.95
Semi-IPN PPY/MDA			
0	0	0.55	8.15
0.356	0.576	2.1	10.4
0.612	0.990	2.1	15.3
0.902	1.459	2.8	13.8
1.797	2.906	2.2	15.5
Semi-IPN PB/PB			
0	0	0.5	6.5
0.379	0.485	2.1	10.95
1.086	1.390	2.8	13.3
1.445	1.848	3.15	16.5
2.495	3.191	4.1	17.1

^aDynamic t.g.a. on films with a heating rate of 5°Cmin⁻¹ under a nitrogen atmosphere

^bWeight ratio: weight of bismaleimide/weight of polyimide

^cMolar ratio: mole of bismaleimide/mole of repeating unit of polyimide

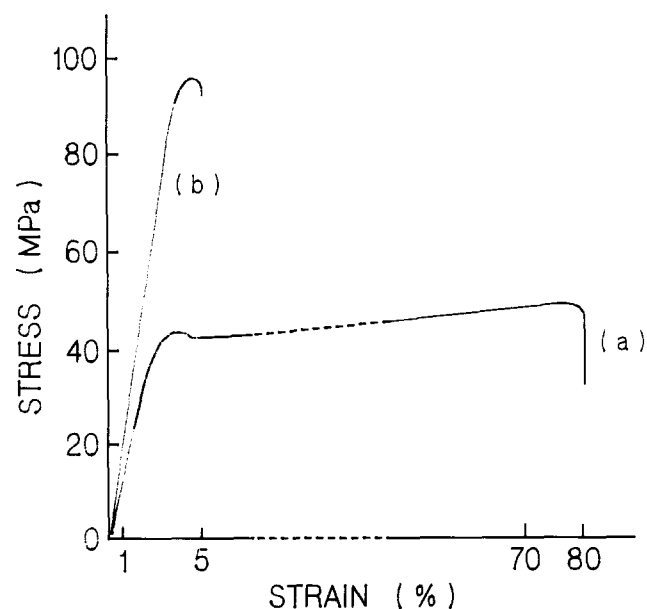


Figure 7 Stress-strain curve obtained from mechanical tensile test at 160°C: (a) polyimide BAPPY-BTDA; (b) semi-IPN PPY/PPY with 1/1 bismaleimide/polyimide molar ratio

Table 5 Mechanical tensile properties of the polyimides and semi-IPNs

Film ^a	Molar ratio bismaleimide/polyimide	Tensile modulus (GPa)		Tensile strength at break (MPa)		Elongation at break (%)	
		20°C	160°C	20°C	160°C	20°C	160°C
BAPPY-BTDA		2.12	0.72	93.3	23.4	5.4	80
Semi-IPN PPY/PPY	1.278 [1] ^b	2.6	1.47	96.6	46.6	5.2	6.1
Semi-IPN PPY/MDA	1.617 [1]	2.81	1.56	110.5	58.7	4.1	5.7
BAPB-BTDA		1.95	0.58	87.2	18.2	7.3	100
Semi-IPN PB/PB	1.279 [1]	2.35	1.23	94.8	42.1	4.8	11.3

^aFilms prepared from N-methylpyrrolidone solution with initial concentration of 40 wt%. Cure cycle: 1 h at 100°C, 1 h at 150°C and 1 h at 300°C

^bValues in square brackets correspond to the bismaleimide/polyimide weight ratio

Table 6 Adhesive properties of the polyimides and semi-IPNs^a

Product	Molar ratio bismaleimide/ polyimide	Average lap shear strength (MPa)		
		20°C	160°C	200°C
BAPPY-BTDA		23.0	11.3	6.6
Semi-IPN PPY/PPY	1.278 [1] ^b	16.4	16.7	13.8
Semi-IPN PPY/MDA	1.617 [1]	6.5	7.9	7.4
BAPB-BTDA		22.8	11.0	2.2
Semi-IPN PB/PB	1.279 [1]	18.0	19.7	15.8

^a Determined according to ASTM standard D 1002-72 starting from *N*-methylpyrrolidone solutions of polyimides or blends with concentrations of 40 wt%

^b Values in square brackets correspond to the bismaleimide/polyimide weight ratio

be decreased by a post-cure treatment of the lap shear specimens at a temperature higher than the polyimide T_g .

CONCLUSIONS

The study of blends between linear polyimides and thermosetting bismaleimides prepared from the same aromatic diamines showed the rather heterogeneous structure of semi-IPNs obtained after thermal polymerization of maleimide double bonds.

The thermomechanical analysis of the semi-IPNs pointed out two mechanical transitions: the first corresponded to the T_g of the linear polyimide and the second was related to the softening point of the crosslinked bismaleimide phase.

Although phase separation does exist, partial and local

miscibility could occur in agreement with the reduction of these two transition temperatures compared with the same temperatures obtained from the free linear polymer and bismaleimide network.

These results concerning the incompatibility of two polymeric imide structures are evidently valid for a given molecular mass of linear polymer ($\eta_{inh} \approx 0.5 \text{ dl g}^{-1}$) and for a given cure cycle of blend (final $T = 300^\circ\text{C}$).

The heat resistance of the semi-IPNs was dramatically influenced by the crosslinked bismaleimide content. Therefore the resulting thermal stability ranged between the stability of the linear polyimide and the stability of the neat crosslinked bismaleimide.

The room-temperature adhesive properties of the semi-IPNs were lower than those of the linear polyimides but the semi-IPNs exhibited an elastic behaviour up to 160°C , leading to improved mechanical and adhesive properties compared with the polyimides, which showed only a viscoelastic character at the same temperature.

REFERENCES

- 1 Manson, J. A. and Sperling, L. H. 'Polymer Blends and Composites', Plenum Press, New York, 1976
- 2 Cooper, S. L. and Estes, G. M. 'Multiphase Polymers', Adv. Chem. Ser. No. 176, American Chemical Society, Washington DC, 1979
- 3 Zeng, H. M. *Su chiao* 1979, No. 3, 1; 1981, No. 1, 51
- 4 Frisch, K. C. and Klempner, D. *Polym. Eng. Sci.* 1982, **22**(17), 1143
- 5 Sperling, L. H. *Chemtech* 1988, February, 104
- 6 Pascal, T., Mercier, R. and Sillion, B. *Polymer* 1989, **30**, 739
- 7 Shyu, S. S. and Chen, D. S. *J. Appl. Polym. Sci.* 1987, **34**, 2151
- 8 Hartness, J. T. 'Toughened Composites', ASTM STP 937, American Society for Testing and Materials, Philadelphia, 1987, pp. 453-62
- 9 Burke Driscoll, S. and Walton, T. C. *Sampe J.* 1987, July/August, 9-17