

The effect of formulated molecular weight on temperature resistance and mechanical properties in polyimide based composites

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This experimental study examines the role of formulated molecular weight between crosslink sites on the temperature resistance and mechanical properties of composites based on a polyimide containing a diphenyl thioether unit (PTI). The composites are fabricated by *in situ* polymerization of monomer reactants (PMR) using three monomeric ingredients: bis(3,4-dicarboxyphenyl) sulfide dianhydride (TDPA); 4,4'-methylene dianiline (MDA); and the monomethyl ester of norbornene anhydride (NE). By changing monomeric molar ratio, three formulations are prepared, in which formulated molecular weight between crosslink sites varies from 1487 to 3446 g mol⁻¹. Unidirectional composite laminates from each formulation and T300 carbon fibres are compression moulded and cut into a series of test specimens. By measuring the glass transition temperature (T_g), Mode I interlaminar fracture toughness (G_{IC}) and other mechanical properties at room and elevated temperatures, the influences of formulated molecular weight on the temperature resistance and mechanical properties of PTI-based composites are investigated.

1. Introduction

The attraction of polyimides for advanced composite applications lies in their potential to operate successfully at high temperatures above the performance limit of the best multifunctional epoxy resins. However, two major obstacles stand in the way of the extensive exploitation of polyimides in composite structures. First, the inherent brittleness of the tightly cross-linked polyimides structures leads to low fracture toughness and poor damage resistance in the composites. The second problem is processability. For example, in condensation-type polyimides, the polyamic acid precursor solution is used to impregnate fibres and the intermediate is then thermally dehydrated to give the fully cyclized polyimide. This type of chemistry leads to considerable processing problems, such as poor degree of fibre wetting, and high pressure for moulding laminates.

A much improved process known as *in situ* polymerization of monomer reactants (PMR), developed at the NASA Lewis Research Center, provides an effective approach for composite fabrication based on polyimides [1]. In the PMR process, the low molecular weight and low viscosity monomers are dissolved in a low-boiling solvent. By using such monomeric solution to impregnate the reinforcing fibres and heat-activated *in situ* polymerization, high quality and void-free composites can be made.

Another significant aspect of the PMR approach is that, for a given set of monomer reactants, a series of

PMR polyimides with different formulations can be produced simply by varying the molar ratio $n:(n+1):2$ for aromatic dianhydride:diamine:the end group. As the n value is increased, the formulated molecular weight of the imide prepolymer also increases. In theory, the formulated molecular weight of the imide prepolymer, i.e. the molecular weight between the crosslink sites, determines the crosslink density of a PMR polyimide. On the other hand, it is known that for a given thermosetting resin, the higher the crosslink density, the higher is the glass transition temperature and the lower is the toughness. Although it is very difficult to attain a high glass transition temperature and high toughness in a single product, the PMR approach offers an opportunity to optimize these physical and mechanical properties of PMR polyimides in order to fulfill a design requirement by controlling material parameters. Thus, it is necessary to investigate the influence of the formulated molecular weight on the processing and performance of polyimide-based composites.

Several years ago, a linear polyimide containing the diphenyl thioether unit (PTI) was developed in this Institute. The composite laminates based on the PTI, which were fabricated through the PMR approach by using bis(3,4-dicarboxyphenyl) sulfide dianhydride (TDPA) and 4,4'-methylene dianiline (MDA) as monomers, show excellent mechanical properties and good processability [2]. In order to increase the temperature resistance of PTI, the third ingredient, the

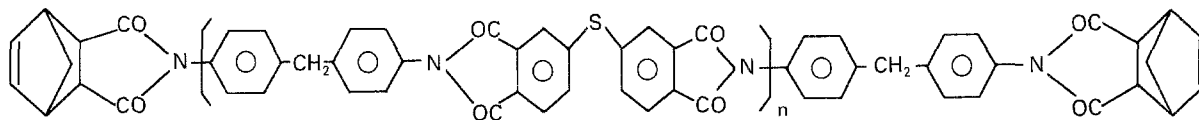


Figure 1 Chemical structure of thermosetting PTI.

TABLE I Molar ratio of monomers and their corresponding formulated molecular weight

	Molar ratio of monomers TDPA: MDA:NE	Formulated molecular weight of prepolymer
Matrix A	2.087:3.087:2	1487
Matrix B	4:5:2	2445
Matrix C	6:7:2	3446

monomethyl ester of norbornene anhydride (NE) is added. Since NE plays the part of an end group, the crosslink density will significantly affect the physical and mechanical properties of PTI and PTI-based composites. As mentioned above, the crosslink density is determined by the molecular weight of the imide prepolymer which can be controlled by changing the monomeric molar ratio. The aim of this study is to examine the influence of formulated molecular weight between crosslink sites on the physical and mechanical properties of PTI-based composites, especially glass transition temperature, T_g , and Mode I interlaminar fracture toughness, G_{IC} .

2. Experimental details

2.1. Materials

The studied thermosetting polyimide, PTI, for which the chemical structure is shown in Fig. 1, is formed from three monomeric ingredients: bis(3,4-dicarboxyphenyl) sulfide dianhydride (TDPA); 4,4'-methylene dianiline (MDA); and the monomethyl ester of norbornene anhydride (NE). The TDPA was esterified by boiling in alcohol for 4 h then, after cooling to room temperature, the MDA and NE were added whilst stirring to obtain a PMR-type solution with a solids content of 50%. To achieve different formulated molecular weights of imide prepolymer, the TDPA, MDA, and NE are combined in three different molar ratios. These molar ratios and their corresponding formulated molecular weight are listed in Table I.

2.2. Composite fabrication

Impregnation of the reinforcing fibres was performed on a small-scale winding machine. Carbon fibre (T300) continuously passed through the impregnation solution, and then through two metering bars to remove excess resin and to maintain a fibre volume content of about 60% in the prepregs. After the solvents in the prepregs were evaporated in an oven, the prepregs were cut into 120 mm × 170 mm sheets, stacked unidirectionally, and placed in a matched metal mould coated with a release agent. Then, this mould was put

in a vacuum oven and hot press and subjected to a cure cycle to complete the cure reaction. In order to distinguish the laminates fabricated from matrices A, B and C, these materials were designated composite A, composite B and composite C, respectively. Specimens for various tests were machined from the laminates. Note that none of the specimens were postcured further.

2.3. Dynamic mechanical analysis

A Du Pont DMA 982 with 9900 Thermal Analyzer was used at a heating rate of 5°C min^{-1} to measure the glass transition temperatures of the three composite laminates.

2.4. Interlaminar fracture tests

The double cantilever beam (DCB) testing geometry, 20 mm in width and 170 mm in length with an aluminium film crack starter, was used in the present fracture investigation. An Instron 1121 test machine was used to load the specimens in Mode I in a continuous monotonic fashion at a crosshead speed of 2 mm min^{-1} . No effort was made to produce a "natural precrack". The load and displacement were recorded continuously on an x - y plotter, and the crack length was observed in the specimen edge using a travelling microscope. When the tests were finished, the DCB fracture surfaces were examined directly, after gold coating, in a Hitachi S-570 scanning electron microscope (SEM).

The fracture toughness determination for the DCB specimens was performed by using the experimental compliance calibration method proposed by Berry [3].

$$C = Ka^n \quad (1)$$

where C is the compliance, a is the measured crack length, and K and n are empirical parameters. The Mode I interlaminar fracture toughness G_{IC} is then given by [4].

$$G_{IC} = nP\delta/2Ba \quad (2)$$

where P and δ are the critical load and displacement, respectively, at crack length a , and B is the width of the DCB specimen.

2.5. Mechanical properties tests

Flexural tests were carried out by three-point bending according to ASTM D790 with a span-to-depth ratio of 32:1 to measure the flexural strength and flexural modulus at room temperature and elevated temperatures for the three composite laminates. Interlaminar

shear strength tests were conducted in accordance with ASTM D3039 at room temperature and elevated temperatures by using a three-point loading fixture with a constant span-to-depth ratio of 4 to assess the fibre wetting and fibre matrix adhesion.

3. Results and discussion

3.1. Temperature resistance

One of the characteristics of high performance composites is their excellent temperature resistance. The glass transition temperature, T_g , is an important physical parameter for evaluating temperature resistance for polymeric composite materials, because T_g is an upper limit for the service temperature of the materials. This is simply due to the considerable drop in the matrix resin modulus, once the material transforms from a glassy to a rubbery phase when it reaches T_g .

The dynamic mechanical analysis (DMA) diagrams for the three composites are shown in Fig. 2. It can be seen that the positions of flexural loss modulus peaks (α transition) of the three composites are obviously different. From these diagrams, it is determined that the glass transition temperatures for composite A, composite B and composite C are 319, 288, and 265 °C, respectively. This result shows that the temperature resistance decreases with increasing formulated molecular weight between crosslink sites.

3.2. Interlaminar fracture toughness

From load-displacement curves for the DCB specimens of the three materials, linear elastic responses were observed. At the point of deviation from linearity, subcritical crack growth occurred, initiated from the aluminium foil, when the load reached a

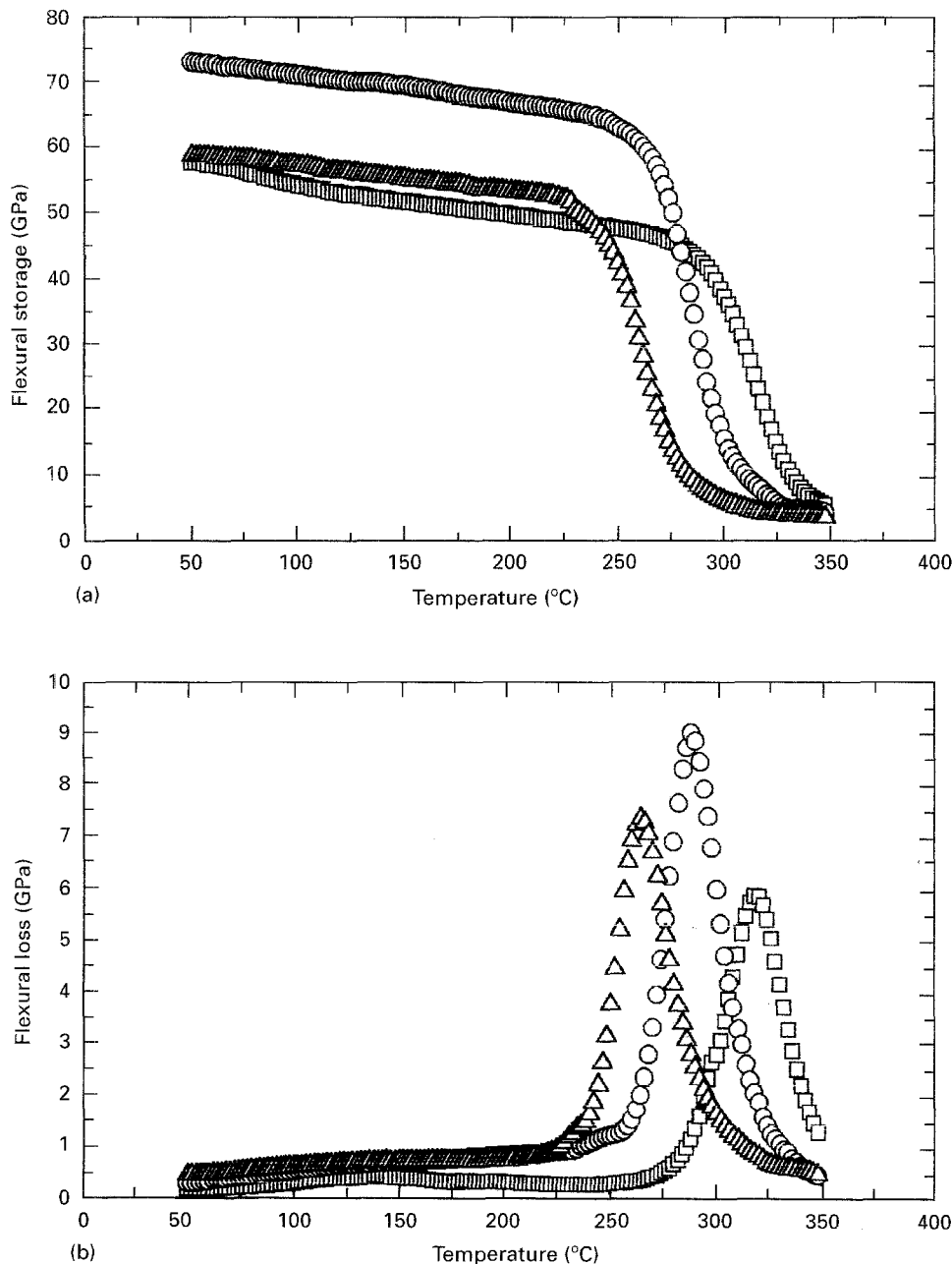


Figure 2 Dynamic mechanical analysis diagrams for the composites with different formulation. Key: □, composite A; ○, composite B; △, composite C.

maximum the interlaminar crack grew in a continuous, stable manner through the specimen. During the crack propagation, no obvious fibre bridging behind the crack tip was observed from the side views of the three composites. Based on the load–displacement traces and corresponding crack lengths, the relationship between compliance and crack length can be obtained. By the use of linear regression analysis, the exponent n in Equation 1 is determined. The results for the three composites are listed in Table II; the correlation coefficients are also given, and these indicate an excellent fit. The interlaminar fracture toughness, G_{IC} , is then calculated from Equation 2 for each composite.

Variations of the interlaminar fracture toughness with crack growth (R curves) for the three composites are shown in Fig. 3. The values of G_{IC} (init), corresponding to the crack initiation point determined by the deviation from the linear slope of the load–displacement curves were evaluated [5]. A distinctive difference in the R curves for the three composites, not only in the initial toughness but also in the propagation value, can be observed in Fig. 3. It is known that the interlaminar fracture in an unidirectional composite is a complicated process which involves the fracture of matrix resin, peeling of fibres, debonding of the matrix–fibre interface, breakage of bridging fibres

and extension of the damage zone [6, 7]. The propagation toughness values, G_{IC} (prop), should include contributions from all these sources. While there is no fibre peeling and fibre bridging during the crack initiation from the crack starter foil, the initial toughness G_{IC} (init) should result mainly from fracture and deformation of the matrix resin. However, in general G_{IC} (init) is not coincident with the fracture toughness of the bulk matrix resin because the fibres constrain the size of the plastic zone of the matrix. Due to the fibre volume fraction and aluminium foil thickness being almost identical for the three materials, G_{IC} (init) could be considered to be significantly related to the fracture toughness of the matrix resin. The results presented in Fig. 3 show that the larger the formulated molecular weight, the higher G_{IC} (init). Fig. 4 gives the SEM micrographs of the fracture surfaces at the end of starter foil for the three composites. These fracture surfaces correspond to the area of G_{IC} (init). Comparing the three fractographs, the following features can be found: the fracture surface of composite A is the most smooth, whereas the surface of composite B shows bigger differences in height, and the fracture surface of composite C is the most rough. This is a result of the fact that matrix C is more deformed than matrix B and matrix B is more deformed than matrix A. Therefore, it can be concluded that the fracture toughness of the matrix increases with formulated molecular weight between crosslink sites.

Fracture surfaces, 30 mm away from the starter foil in the three composites, were also examined; this corresponded to the area of G_{IC} (prop). Typical fractographs of these surfaces are shown in Fig. 5. It is clearly seen that for all three composites there were no detached fibres on the fracture surface and the fibres were almost coated with the matrix resin, indicating good impregnation and a strong fibre/matrix bond. Thus, the contributions to G_{IC} (prop) from fibre

TABLE II Values of the Berry exponent for the PTI-based composites with different formulations

Material	Berry exponent	Correlation coefficient
Composite A	2.89	0.99919
Composite B	2.85	0.99909
Composite C	2.92	0.99869

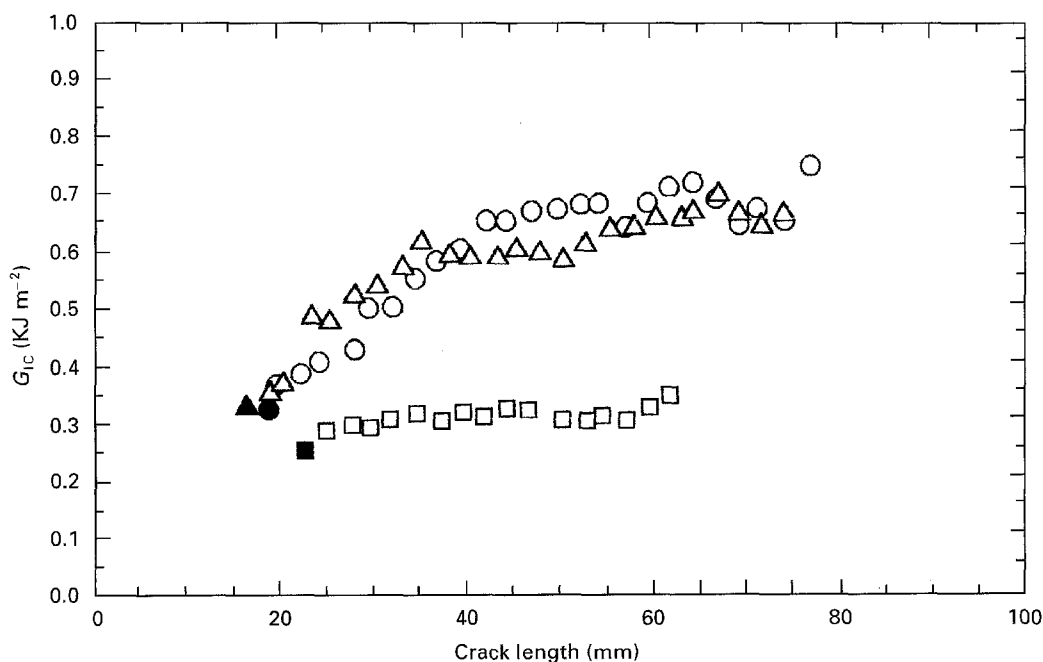


Figure 3 Variation of G_{IC} with crack length for the composites with different formulation. Key: \square , composite A; \circ , composite B; \triangle , composite C. Solid points represent initiation.

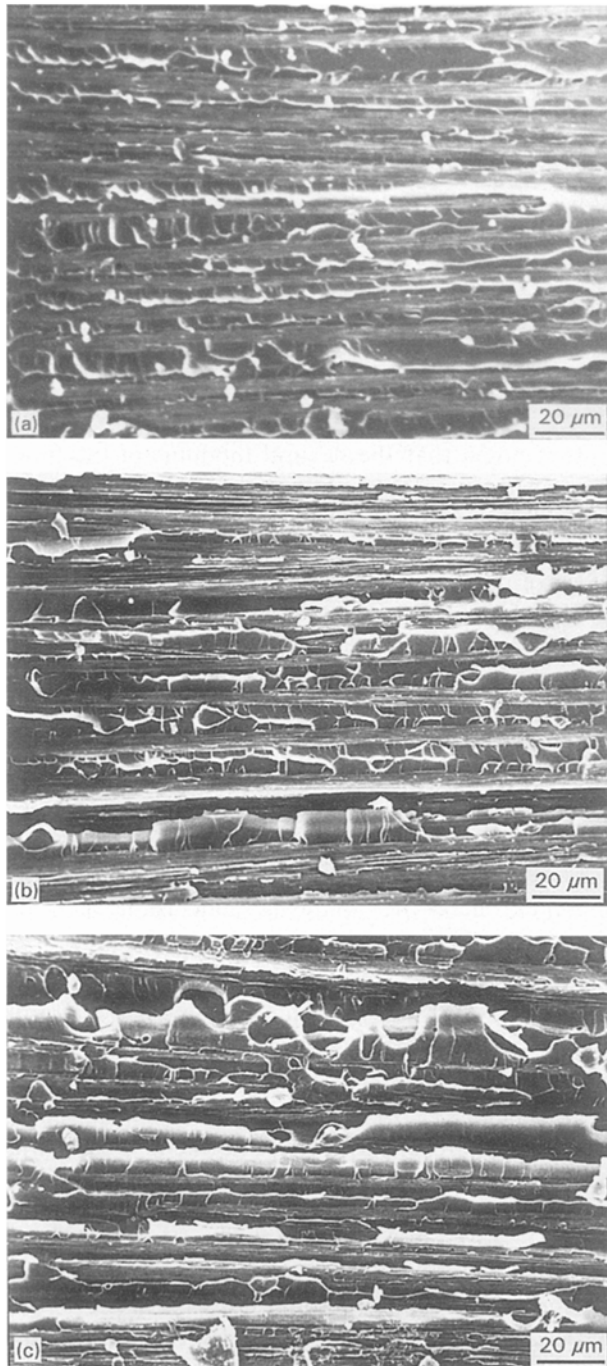


Figure 4 Scanning electron micrographs of fracture surfaces at the end of the starter foil; (a) composite A, (b) composite B, and (c) composite C.

peeling and fibre/matrix debonding appear to be neglectable. Examining the micrographs in Fig. 5, the level of deformation of the matrices and roughness of the fracture surfaces for three composites are seen to be different. Again, composite A has a relatively smooth fracture surface with the matrix showing fewer signs of ductility, while composites B and C have rather rough fracture surfaces with the matrices showing more evidence of plastic deformation. This is consistent with the observations in the area at the end of the starter foil (Fig. 4). It is noted that there are some microcracks at the fracture surface of composite A (see Fig. 5a), whereas there are none observed for composites B and C. This illustrates that matrix A is more brittle than matrices B and C.

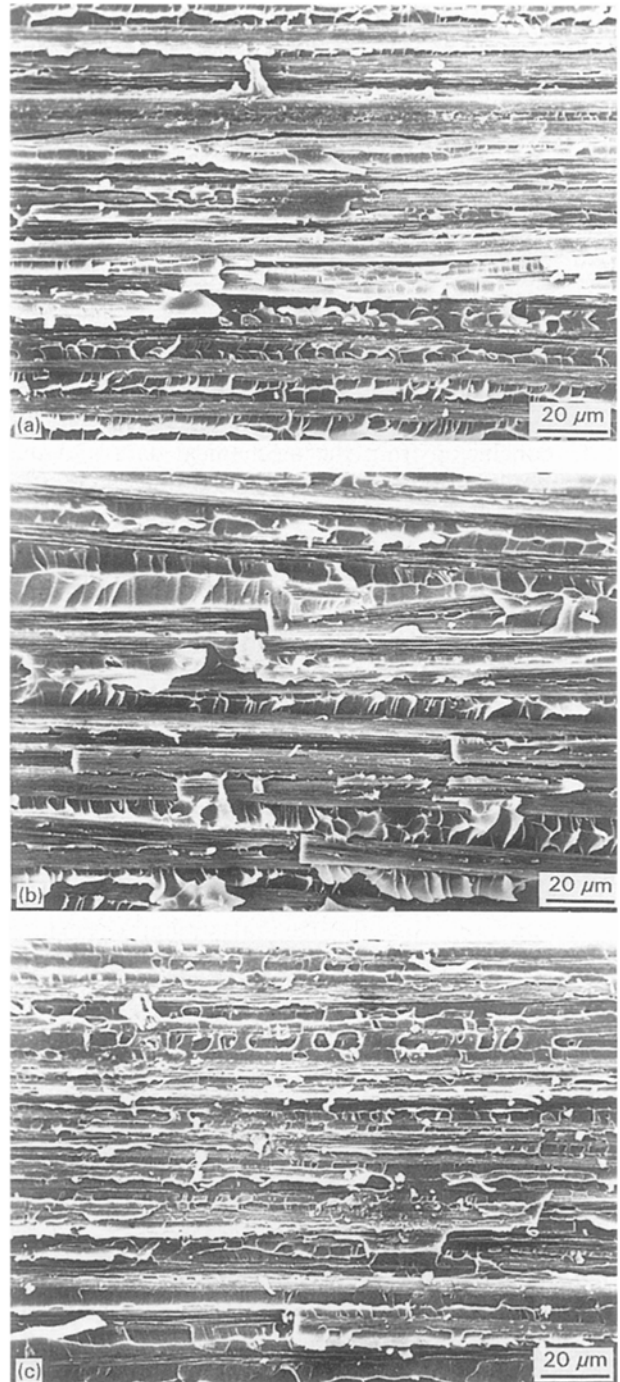


Figure 5 Scanning electron micrographs of fracture surfaces 30 mm away from the starter foil; (a) composite A, (b) composite B, and (c) composite C.

The results presented in Fig. 3 show that G_{IC} (prop) for composite B is slight higher than that for composite C. Comparing the fracture surfaces of the two composites (Fig. 4b and c), some broken fibre ends can be observed on the fracture surface of composite B, but few can be detected on the fracture surface of composite C. The reason for fibre breakage is that the fibres which are bridging a crack and cannot be peeled off their layer must break; their ends then lie in the opened fibre beds. These observations suggest that fibre breakage is involved in the fracture process of composite B and hence leads to greater energy dissipation. This may be the reason that G_{IC} (prop) for composite B is higher than composite C.

TABLE III Mechanical properties of PTI-based composites with different formulations at room temperature and elevated temperatures

	Composite A			Composite B			Composite C		
	R.T.	250 °C	Retention %	R.T.	220 °C	Retention %	R.T.	200 °C	Retention %
Interlaminar shear strength (MPa)	110	52.9	47.9	108	50.2	46.4	109	51.3	46.8
(Standard deviation)	(4.4)	(1.8)		(6.2)	(1.4)		(2.1)	(3.9)	
Flexural strength (MPa)	1619	797.0	49.2	1606	801	49.8	1502	833	55.4
(Standard deviation)	(98.4)	(56.3)		(51.1)	(21.3)		(44.6)	(61.7)	
Flexural modulus (GPa)	105	108	103	111	112	101	110	112.1	102
(Standard deviation)	(3.4)	(6.1)		(5.5)	(2.1)		(5.5)	(2.7)	

R.T. = room temperature

In conclusion from the mechanical data and the fractographic results, it can be stated that the matrix toughness and $G_{IC}(\text{init})$ of PTI-based composites increase with formulated molecular weight, and formulated molecular weight has a significant effect on $G_{IC}(\text{prop})$ of these composites, but it does not play a decisive role because other factors also influence the value of $G_{IC}(\text{prop})$ of the composites.

3.3. Mechanical properties

Table III lists mechanical properties at room temperature and elevated temperatures for unidirectional composites based on the three different formulations of PTI. From the data obtained at room temperature, it can be seen that the flexural strengths, flexural modulus and interlaminar shear strengths for the three laminates are nearly equal, especially the interlaminar shear strength. It is known that composite properties are governed by many factors, such as composites composition (e.g. fibre, resin and void content) and processing conditions (e.g. temperature, time and pressure). Since the reinforcing fibre and its content (0.60 ± 0.02 in volume) are the same and the processing cycles are identical for the three composites, the mechanical properties at room temperature indicate that changing the molecular weight between crosslink sites from 1487 to 3446 g mol^{-1} has no significant effect on the processing characteristics of their composites. For instance, from the almost identical values of interlaminar shear strength of the three composites, the resin flow can be considered adequate in the composites based on the three formulations under the processing conditions (temperature, time and pressure) used.

The interlaminar shear strengths and flexural strengths at elevated temperatures presented in Table III show that the formulated molecular weight has a significant effect on the performance. The elevated temperatures, at which the mechanical properties were measured for the three composites, were selected at about 70 °C below their glass transition temperatures as determined by DMA. It can be seen that the retention of interlaminar shear strength, flexural strength and flexural modulus are similar for the three composites at these selected temperatures. This suggests that the retention of mechanical properties at elevated temperatures is governed by the glass transition temperature.

It is noted that the flexural modulus of the three composites increases slightly at elevated temperatures, and this is not the first time this phenomenon has been observed [8]. The reason may be that it is due to the effect of postcuring during the tests (the temperature of each specimen is raised to the selected value and held to reach equilibrium).

4. Conclusions

An experimental study has been conducted to investigate the effect of formulated molecular weight on the temperature resistance and mechanical properties of PTI-based composites. From the results presented here the following conclusions can be drawn:

1. The glass transition temperature of PTI-based composites decreases with increasing formulated molecular weight between crosslink sites.
2. The matrix toughness and $G_{IC}(\text{init})$ of PTI-based composites increase with formulated molecular weight, and higher formulated molecular weight will considerably improve the $G_{IC}(\text{prop})$ of composites even though it does not play a decisive role.
3. The formulated molecular weight, in the range studied, has little influence on the processing characteristics of the composites and mechanical properties of the composites at room temperature, but the retention of mechanical strengths at elevated temperatures is significantly dependent on the formulated molecular weight.
4. The temperature resistance and fracture toughness of polymeric composite materials is governed by the chemical structure of the matrix resin. For a PMR-type polyimide-based composite, the performance can be changed and optimized to a certain extent by varying the molar ratio to fulfill design requirements.

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References

1. T. T. SERAFINI, P. DELVIGS and G. R. LIGHTSEY, *J. Appl. Polym. Sci.* **16** (1972) 905.
2. J. ZHOU, T. HE, J. ZHANG and M. DING, *SAMPE Q.*, **24** (1993) 31.
3. J. P. BERRY, *J. Appl. Phys.* **34** (1963) 62.
4. P.-Y. B. JAR, R. MULONE, D. DAVIES and H.-H. KAUSCH, *Compos. Sci. Technol.* **46** (1993) 7.
5. S. HASHEMI, A. J. KINLOCH and J. G. WILLIAMS, *ibid.* **37** (1990) 429.
6. R. A. CRICK, D. C. LEACH, P. J. MEAKIN and D. R. MOORE, *J. Mater. Sci.* **22** (1987) 2094.
7. J. ZHOU, T. HE, J. ZHANG and M. DING, *ibid.* **29** (1994) 2916.
8. T. HE and M. DING, 4,4'-oxydiphthalic anhydride and 3,4,3',4'-biphenyltetracarboxylic dianhydride based polyimides by polymerization of monomer reactants as matrices for advanced composites, Final Report to Occidental Chemical Corporation, Grand Island, New York (1992).

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