JOURNAL OF MATERIALS SCIENCE **29** (1994) 3658–3664

Temperature dependent torsional properties of high performance fibres and their relevance to compressive strength

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A simple arrangement for the measurement of torsional moduli of high performance fibres as a function of temperature has been reported. Torsional moduli and damping factors have been measured on a number of polymeric [Kevlar^{TM}, poly(p-phenylene benzobisoxazole) (PBO), poly(p-phenylene benzobisthiazole) (PBZT) and Vectran^{TM}] and carbon fibres [pitch and PAN based, and one bromine intercalated pitch based carbon fibre] as a function of temperature (room temperature to 150 °C, range) and as a function of vacuum level (1.1–80 $\times$ 10^3 Pa). At these vacuum levels damping in the fine fibres is mainly due to aerodynamic effects. In general PAN based carbon fibres have higher torsional moduli than pitch based carbon fibres. Kelvar^{TM} 149, PBO and PBZT fibres have comparable room temperature torsional moduli, while the torsional modulus of Vectran^{TM} fibre is very low, probably due to the torsional flexibility of the –COO– group. In the above temperature range, torsional moduli of both pitch and PAN based carbon fibres do not change significantly, while for polymeric fibres they decrease; a small decrease is observed for PBO and PBZT, and a significantly higher decrease is observed for Vectran^{TM}. Relationships between compressive strength and torsional moduli have been discussed

1. Introduction

Evaluation of the properties of high performance fibres is critical, as many of the composite properties of these fibres are limited due to the properties of the fibres themselves. For example, the axial compressive strength of composites made from polymeric fibres and from pitch-based carbon fibres is limited due to the low compressive strength of the fibres themselves [1–3]. Accurate determination of the axial compressive strength of the fibre has been critical in research programmes either attempting to improve the compressive strength or to understand the compression failure mechanisms in polymeric and carbon fibres. A theoretical relationship between fibre shear modulus and compressive strength has been suggested [4]. A theoretical framework has also been developed, coupling the axial normal stresses and torsional shearing stresses for anisotropic fibres [5]. The linear relationship between compressive strength and torsional modulus has been experimentally demonstrated on a number of fibres. These fibres included Kevlar^{TM}, PBO, PBZT and one pitch based carbon fibre, P75. However, investigations on a larger number of samples seriously brings this relationship into question [3]. The list of larger number samples includes: the number of rigid-rod polymeric fibres with variations in processing conditions, fibres from modified rigid-rod polymers, PBZT fibres crosslinked to various degrees, and PAN based carbon fibres. However, considering the difficulties and uncertainties involved in the measurement of single fibre compressive strength, torsional moduli values are generally used as a double check for the determination of compressive strength, as has been reported in a recent study on crosslinked PBZT fibres [6]. It has also been suggested [7] that torsional moduli can be used to understand the role of cross linking in polymers with low visco-elasticity.

The wide use of a torsional modulus measurement technique for fine fibres is hampered due to the simultaneous vacuum requirement (below 6.7 $\times$ 10^3 Pa) and the ability to give torsional oscillations without any lateral vibrations. Tokita [8] used an oil damper, to avoid unfavourable vibrations of the pendulum and excitation of electromagnets, to impart torsional oscillations. Gloor [9] employed a pendulum bob, resting on a rotatable pedestal while the torsional strain was imposed, and a mirror was used to record the amplitude, to measure shear modulus and damping characteristics of poly(p-phenylene terephthalamide) (PPTA). DeTeresa [4] and Allen [5] used an apparatus similar to that used by Gloor, but without the pedestal for resting the pendulum bob. Room temperature torsional moduli measurements on PPTA, poly(p-phenylene benzobisthiazole) (PBZT), poly(p-phenylene benzobisoxazole) (PBO), and on P75 carbon fibres were reported by DeTeresa. Allen reported the torsional moduli of Kevlar^{TM} 49 and a glass fibre as a function of axial tensile load. The only literature report on the measurement of torsional modulus as a function of temperature for fine diameter fibres is by Seshadri [10], where a specially designed system for vacuum, temperature and for isolating the vibrations, has been used for measurements on carbon fibres.

In the present work a simple experimental set-up for measuring torsional moduli of small diameter fibres (5–20 μm) as function of temperature has been put together. The essential feature being that the measurements are carried out in a vacuum oven with a glass door. Use of a vacuum oven takes care of both the vacuum and the temperature requirements. Comprehensive torsional moduli data of various high performance polymeric and carbon fibres are reported as a function of temperature. Chemical structures of various polymers used in this study are given in Fig. 1. Results are discussed from the point of view of understanding the compression failure mechanisms in high performance fibres.

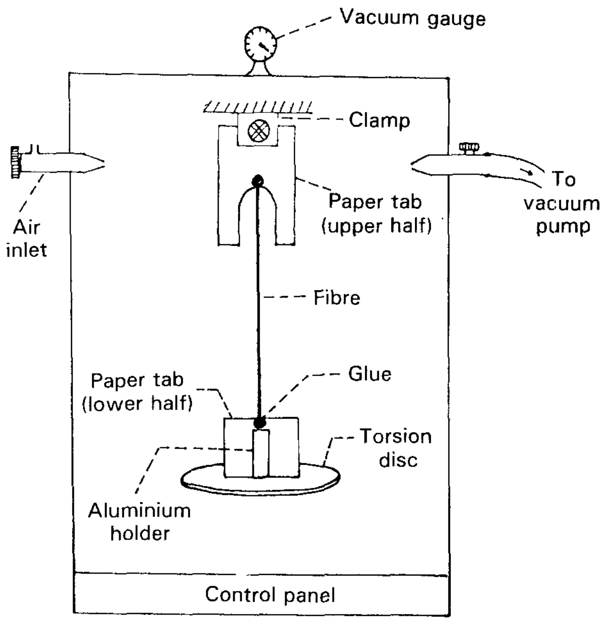

Figure 2 Schematic diagram of the torsional pendulum set-up.

2. Experimental procedure

Torsional moduli, *G*, of high performance fibres as a function of temperature were measured using a free-torsional pendulum placed inside a vacuum oven. A schematic of the apparatus is shown in Fig. 2. A brief description of the set-up is given here. The fibre samples were mounted on cardboard tabs of 2.54 cm gauge length. For room temperature studies, fibres were mounted on tabs using Quick-gel™ glue (cyanoacrylate ester), and the glue was allowed to set for 12–24 h. Adhesion between the fibre and Quick-gel™ glue was not good at higher temperatures. For higher temperature work a two-component epoxy system (No. 10–347) was selected. The torsional pendulum was prepared using a cardboard disc. At the centre of this disc, a round head aluminum fastener was inserted for holding the paper tab on which the fibre samples were mounted. After the paper tab containing the sample was carefully mounted onto the pendulum, the top end of the paper tab was clamped on a stand placed inside the vacuum oven. Both sides of the mounted paper tab were then carefully cut without straining the fibre. Now, the fibre was freely attached to the torsional pendulum. After mounting the specimen, the vacuum oven was closed and the vacuum pulled to the level of 0.8×10^3 Pa. Reduced oscillation amplitude at higher pressures, reduced the accuracy of the measurement. The oscillations were obtained by letting a very small amount of air into the vacuum oven chamber (which reduced the vacuum to about 1.1×10^3 Pa) through the air inlet. No significant lateral motions of the pendulum were observed. The pendulum's moment of inertia was calculated by incorporating the contributions of the cardboard disc, the fastener and the lower portion of the cardboard tab used for fibre mounting. The moment of inertia of the pendulum was 0.0924 g cm^{-2}, and the total weight of the pendulum was less than 0.75 g, which is only a small fraction of the breaking load required for such fibres.

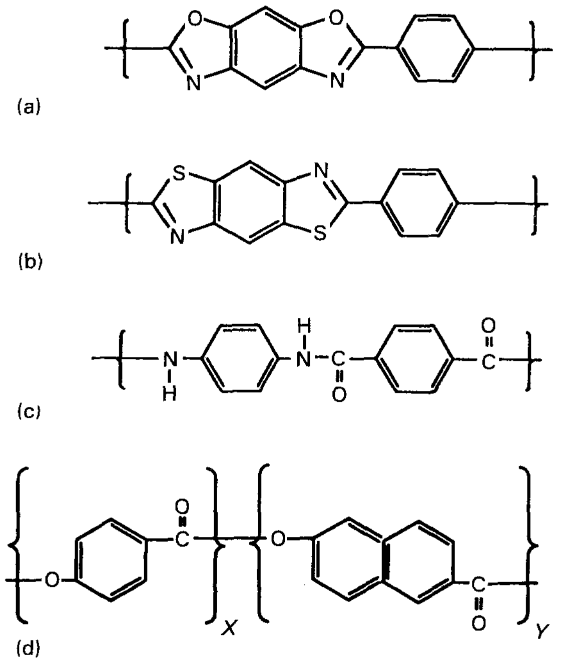

Figure 1 Chemical structure of various polymers: (a) poly(p-phenylene benzobisoxazole), (b) poly(p-phenylene benzobisthiazole), (c) poly(p-phenylene terephthalamide), and (d) copolyester from HBA and HNA.

For circular fibres, the torsional modulus is given by

$$G = 8\pi IL/T^2r^4 \quad (1)$$

where *I* is the moment of inertia of the torsion pendulum, *L* the fibre sample length, *r* the fibre radius and *T* the corrected oscillation period, which is given by

$$T = T_0/[1 + (\Delta/2\pi)^2]^{\frac{1}{2}} \quad (2)$$

where T_0 is the measured period of oscillation; and Δ the logarithmic decrement, given by $\ln(A_0/A)$, A_0 and A being amplitudes in two successive oscillations.

For each fibre the measurements were made on six samples, with four readings on each sample.

The radius term appears as a fourth power in Equation 1, therefore small errors in the measurement of r will affect moduli values significantly. The radius of each individual fibre mounted on the tab was measured at five different places randomly chosen along the 2.54 cm gauge length using a laser (He–Ne) beam diffraction method [11]. The radius of the fibre is given by

$$r = \lambda S/\delta \qquad (3)$$

where λ is the wavelength of the laser used (632.8 nm for the He–Ne laser), S the distance between the fibre and the projection screen, and δ the distance between the first intensity minima from the centre.

3. Results and discussion

3.1. Effect of vacuum level

First, the effect of vacuum level on torsional moduli and on the damping factor is examined. A systematic study of the effect of the vacuum level (1.1–80 × 10^3 Pa) on the torsional modulus and on the damping factor for Kevlar™ 49 was carried out. The results of this study are presented in Fig. 3. This figure shows that when the vacuum decreased from 1.1 to over 80 × 10^3 Pa, the torsional modulus decreased by about 6% and the damping factor increased by about 12%. It has been previously reported [12] that even at pressures as low as 0.13 Pa aerodynamic damping contributes significantly to the measured damping, and that for fibre damping measurements it is necessary to use high vacuum (of the order of 10^{-4} Pa), and even then a correction for aerodynamic damping is necessary. In the same study, it was further concluded that for pressures greater than about 13 Pa, aerodynamic damping is almost independent of pressure. The room temperature values of damping factors presented in Table I (measured at 1.1 × 10^3 Pa) indicate that the damping factor values are significantly different for different fibres. For example, the damping factor for the Kevlar™ 149 fibres is almost three times that for Vectran™ HS. Therefore, the question is, whether the damping factor observed at these vacuum levels is mostly due to aerodynamic effects.

TABLE 1 Room temperature shear moduli and damping factor data for various high performance fibres

Fibre	Fibre Diameter[a] (μm)	Shear Modulus (GPa)	Damping Factor
Polymeric fibres			
Kevlar™ 29	12.6	1.9	1.20
Kevlar™ 49	13.0	1.4	1.20
Kevlar™ 149	12.2	1.1	1.80
PBZT	19.0	1.2	0.60
PBO	17.2	1.0	0.80
Vectran™ HS	24.0	0.6	0.60
Pitch-based carbon fibres			
E-35	10.6	8.0	0.70
E-75	10.0	5.7	1.00
E-105	10.0	5.0	1.00
P-55	10.5	6.6	0.85
P-75	10.5	8.0	0.85
P-100	10.6	4.7	1.00
PAN-based carbon fibres			
T-40	5.6	14.0	2.00
T-50	7.0	14.0	1.50
T-300	7.0	15.0	1.30
AS-4	7.2	17.0	1.10

[a] Fibre diameter values, as measured using laser diffraction on the samples tested for torsional modulus.

Aerodynamic damping will depend on the number of gas molecules hitting the various parts of the torsional pendulum due to the Brownian motion of the air molecules. The number of molecules hitting the pendulum during one cycle will be proportional to the oscillation period. Therefore, if the measured damping factor is essentially due to aerodynamic effects, then it should be proportional to the oscillation period. Such a plot of observed damping factor versus oscillation period for various fibres is given in Fig. 4. This figure clearly supports the findings of Adams and Lloyd [12] that at vacuum levels such as the ones used in this study (1.1 × 10^3 Pa), damping is essentially due to aerodynamic effects.

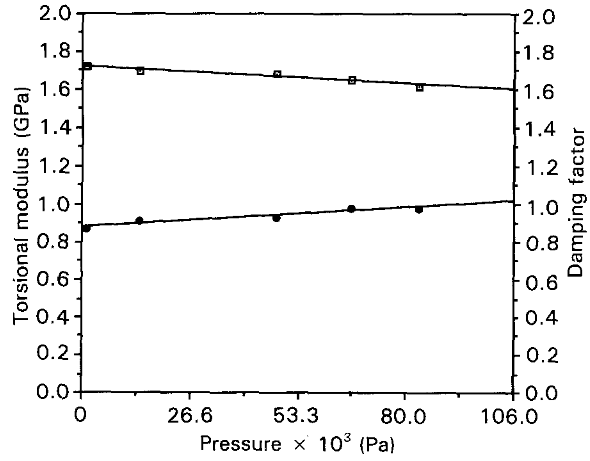

Figure 3 Effect of vacuum level on torsional modulus (□) and on the damping factor (●).

3.2. Torsional moduli

Room temperature torsional moduli of various fibres are listed in Table I. Polymeric fibres in order of decreasing torsional modulus are: Kevlar™ 29, Kevlar™ 49, PBZT, Kevlar™ 149, PBO and Vectran™ HS. The values for PBZT, Kevlar™ 149 and PBO are comparable. The shear modulus is a function of conformational rigidity, intermolecular interaction and fibre morphology. In spite of the chain rigidity of PBO and PBZT, there is some comformational flexibility present in these structures due to permissible rotations about the p-phenylene groups [13]. In PPTA and in copolyester (Vectran™ HS), the flexibility comes from the amide or ester groups, respectively. Significantly higher values of G for PPTA than for Vectran™ can be attributed to hydrogen bonding in Kevlar™. The

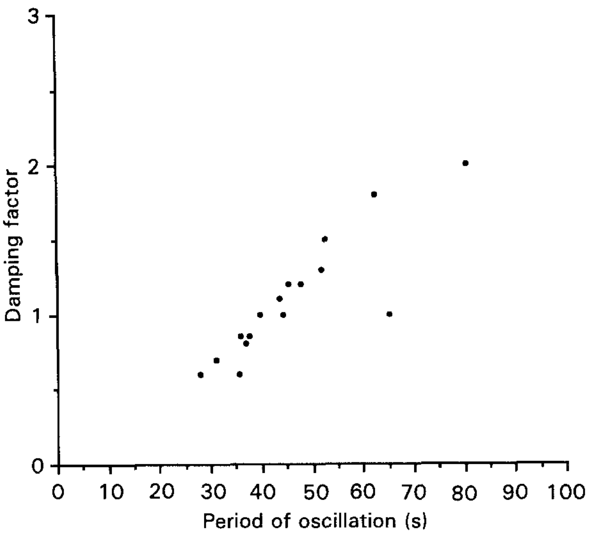

Figure 4 Observed damping factor as a function of oscillation period. Data for different polymeric and carbon fibres.

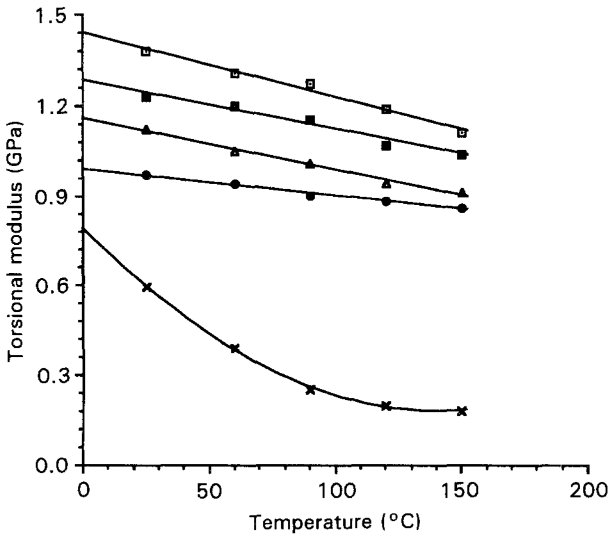

Figure 5 Torsional modulus of polymeric fibres as a function of temperature: (□) Kevlar™ 49, (■) PBZT, (△) Kevlar™ 149, (●) PBO, (×) Vectran™ HS.

torsional moduli differences between various Kevlar™ fibres arise from differences in fibre microstructure and morphology. Welsh *et al.* [14], using the Buckingham potential function and Columbic interactions [15], pointed out that intermolecular attractions are somewhat larger for trans-PBZT chains than for cis-PBO. This is due to the fact that sulfur atoms give rise to larger van der Waals' attractions than oxygen atoms because of the much higher polarization of sulfur. This can account for slightly higher torsional moduli values for PBZT as compared to PBO. However, differences in fibre morphologies and molecular orientation can also be responsible for the torsional moduli differences between PBO and PBZT. Vectran™ HS, a copolyester, represents the other extreme, in which there are no significant secondary interactions except for weak dipolar attractions. Vectran™ also has flexible –COO– swivel groups. As a result, the torsional modulus of the Vectran™ HS fibre is significantly lower than those for Kevlar™, PBO and PBZT fibres. The potential barrier for internal rotation in Kevlar (6–12 kcal mol^{-1}) is relatively higher than in polyethylene terephthalate (3 kcal mol^{-1}), suggesting higher rigidity in Kevlar [16].

Fig. 5 shows the temperature dependence of torsional moduli for polymeric fibres in the temperature range of 25–150 °C. Kevlar™, PBO and PBZT exhibit 10–20% reduction in torsional moduli in this temperature range. This observation is consistent with the observation of Heijboer [17], who indicated that for polymers with phenylene rings in the main chain, a decrease of 0.1% in torsional moduli per degree Celsius is likely. A slightly higher decrease was observed for Kevlar (about 18%) than for PBO and PBZT (about 10%). In this context, it is useful to note that the hydrogen bonds in PPTA are believed to be stable at least up to 200 °C. This was concluded by Termonia and Smith [18] in a temperature dependent tensile strength study of PPTA fibres. A much higher decrease in torsional modulus was observed for Vectran™, a fibre derived from liquid crystalline copolyester.

Carbon fibres, in general, have very high torsional moduli when compared to polymeric fibres. Pitch-based carbon fibres have lower shear moduli, generally in the range of 4–9 GPa, and those for PAN based carbon fibres range from 8 to 20 GPa (Seshadri [10] reports values up to 35 GPa). The theoretical value of basal plane shear modulus (C_{44}) in graphite, free of disorder is in the 4–5 GPa range [19]. It is also reported that PAN-based carbon fibres have a relatively higher amount of sp^3 hybridization (D line) in the mainly sp^2 bonded system. [20]. This probably is a significant factor responsible for higher torsional moduli in PAN-based carbon fibres. Torsional moduli of bromine-intercalated [21–23] P-100 fibres (approximately 1 Br atom per 37 carbon atoms) as a function of temperature have also been measured. Shear moduli for intercalated fibres are about 25% lower than those for pristine fibres (Fig. 6). Since on intercalation, no other structural changes are expected, the reduction in shear moduli may suggest a reduction in van der Waals' attraction between graphitic sheets due to the presence of Br atoms. However, it must be kept in mind that the intercalated and pristine fibres were obtained from different, batches, which can also contribute to the variation in torsional moduli. Torsional moduli of carbon fibres are almost independent of temperature in the room temperature to 150 °C range.

The torsional moduli of Kevlar™, PBZT and PBO extrapolate to zero value at 675, 900 and 1070 °C, respectively. The extrapolated temperature value for Kevlar™ compares well with the value obtained (600 °C) from extrapolation of tensile strength as a function of temperature [18]. This value is taken to be the glass transition temperature for Kevlar™. On this basis, the glass transition temperature for PBZT and PBO fibres may be predicted to be in the range of 900–1070 °C.

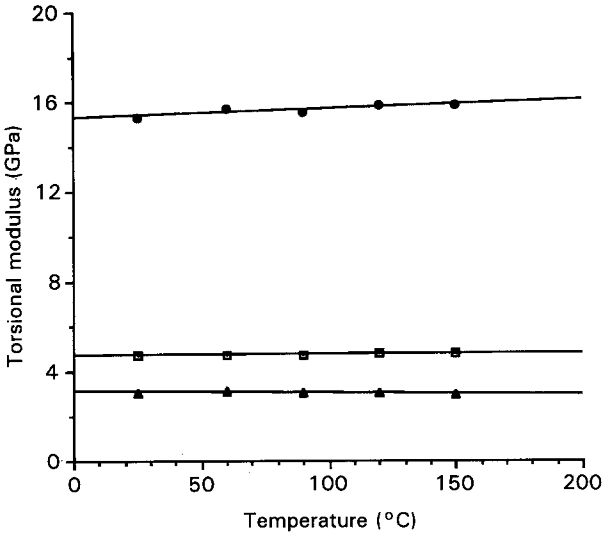

Figure 6 Torsional modulus of carbon fibres as a function of temperature. Data is given for: (●) PAN-based T-40, (□) pitch based pristine P-100, and (▲) bromine intercalated P-100 fibres.

3.3. Relevance to compressive strength

Compressive strength versus shear moduli of both pitch and PAN-based carbon fibres are plotted in Fig. 7. The compressive strength of all carbon fibres [24] is lower by a factor of five to ten compared to their shear moduli. For high modulus pitch based carbon fibres, compressive strength increases with increasing shear moduli, with the exception of the P75 fibre. On the other hand, correlation between compressive strength and shear moduli for the relatively less anisotropic PAN-based carbon fibres is poor. For example the PAN-based carbon fibre T-50, with almost half the compressive strength of T-40 and T-300, has a comparable torsional modulus. However, in this regard two factors must be borne in mind:

(i) that the structure of pitch-based fibres is sheet-like, while a sheet-like structure is not observed in most PAN-based carbon fibres [25]; and

(ii) the compressive strength values of the high compressive strength PAN-based carbon fibres obtained from composite tests are underestimated and despite the fact that numerous literature data exist for these fibres from other single filament tests, the unequivocally true axial compressive strength of these fine fibres (5–7 μm diameter) is not known [3].

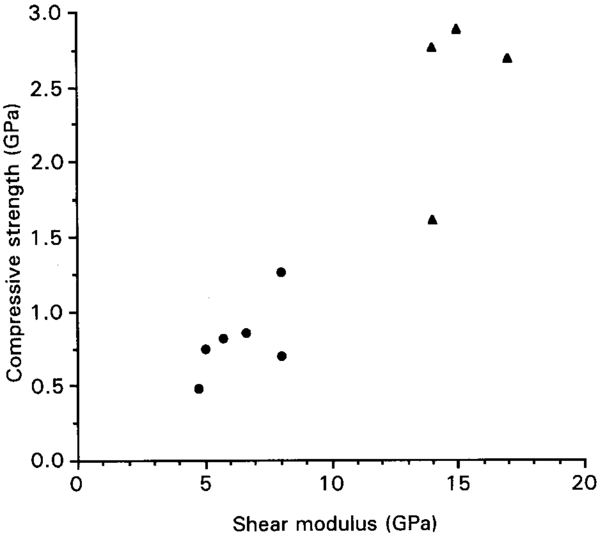

Figure 7 Compressive strength as a function of torsional modulus for various carbon fibres: (▲) PAN-based, (●) Pitch-based.

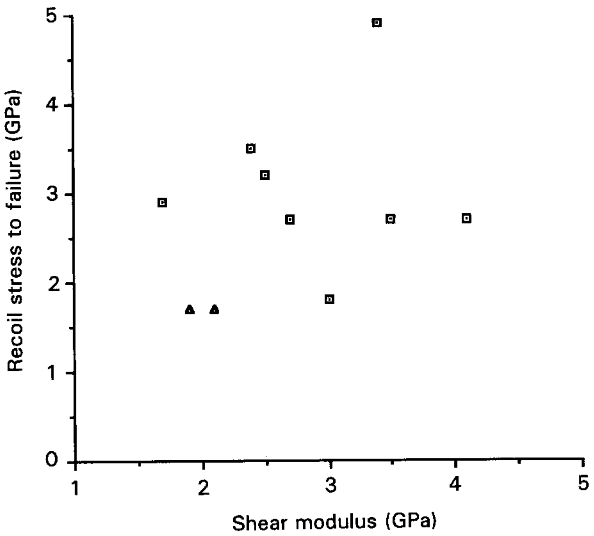

Figure 8 Recoil compressive stress of (□) crosslinked and (△) control PBZT fibres as a function of shear modulus. Data from Reference [6].

Recently, room temperature values of recoil compressive strength and torsional moduli were reported for a series of crosslinked PBZT fibres [6]. A plot of recoil stress as a function of shear modulus for these fibres is given in Fig. 8. It is quite apparent that for this set of fibres there is no relation between torsional modulus and compressive strength. Thus, it can be seen that the compressive strength–torsional modulus relationship has not been established in PAN-based carbon fibres, nor in the crosslinked PBZT fibres. However, due to random crosslinking in both of these types of fibres, the model on the basis of which the compressive strength–torsional modulus relationship has been suggested [4] may not be applicable for these fibres. Therefore, it was decided to test this relationship only on one type of fibre as a function of temperature. Kevlar^{TM} 49 was chosen for this purpose, as literature data for compressive strength as a function of temperature is available for the Kevlar^{TM} 49 epoxy composites [26]. Even though temperature dependent compressive strength data is also available for carbon fibre composites, however, these fibres were not chosen for the following reasons:

(i) for PAN-based carbon fibres the model might not be applicable due to random crosslinking;

(ii) most PAN-based carbon fibres–epoxy composites fail due to fibre buckling, which does not yield true fibre compressive strength [27]; and

(iii) pitch-based carbon fibres do not exhibit significant temperature dependent compressive strength in the room temperature to 200 °C range [27].

It has been shown that during compression testing at room temperature, Kevlar^{TM} epoxy composites fail due to fibre kinking [1, 3]. A change from the in-fibre

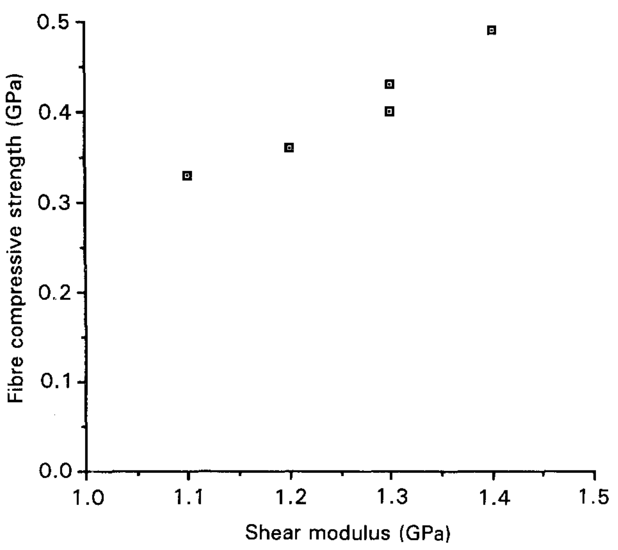

Figure 9 Compressive strength as a function of shear modulus for a Kevlar™ 49 fibre. Data from room temperature to 150 °C. Compressive strength data from [26].

failure mode to the fibre buckling mode results in a change in slope of the plot of compressive strength as a function of temperature [28]. Temperature dependent data on Kevlar™–epoxy composite do not exhibit such a change of slope [26]. Therefore, it is reasonable to assume that the reported experimental compressive strength of the Kevlar™–epoxy composite is limited due to low fibre compressive strength and not due to interfacial or matrix properties. Therefore, the compressive strength of the composite can be used to calculate fibre compressive strength.

Fibre compressive strength from composite is calculated using the rule of mixture for iso-strain model

$$(\sigma_c)_c = \sigma_{fc}V_f + \sigma_{mc}(1 - V_f)$$

where $(\sigma_c)_c$ is the composite compressive strength, V_f is the fibre volume fraction, σ_{fc} and σ_{mc} are the compressive stresses in the fibre and in the matrix, respectively, at the failure strain. For the Kevlar™–epoxy system, $\sigma_{mc} \ll \sigma_{fc}$, and therefore σ_{mc} can be neglected, which leads to

$$(\sigma_c)_c = \sigma_{fc}V_f$$

Therefore, the fibre compressive strength obtained from the composite is

$$\sigma_{fc} = (\sigma_c)_c/V_f \qquad (4)$$

Using this relation, Kevlar™ 49 fibre compressive strength is obtained using the composite data of Wilfong and Zimmermann [26] at various temperatures and these values are plotted as a function of corresponding shear moduli in Fig. 9. From this figure, it can be seen that there is a linear relationship between G and σ_c. These observations, it seems, supports buckling instability as the operating compressive failure mechanism in polymeric fibres such as Kevlar™ 49. The reason that a linear relationship between compressive strength and torsional modulus has not been observed for the crosslinked PBZT fibres and PAN-based carbon fibres may be due to the fact that the model on which DeTeresa's buckling instability theory has been derived may not be applicable to these systems due to the presence of random crosslinking.

4. Conclusions

A simple method has been used to measure torsional modulus as a function of temperature for high performance polymeric and carbon fibres. Torsional modulus of high performance polymeric fibres decreases in the temperature range 25–150 °C, whereas for pitch- and PAN-based carbon fibres there is no appreciable change in this temperature range. A comparison between the temperature dependence of G and compressive strength of the Kevlar™ 49 fibre supports DeTeresa's buckling instability theory. However, such a relationship has not been observed for crosslinked PBZT- and PAN-based carbon fibres.

Acknowledgements

Torsional modulus measurement on the Vectran™ fibre was carried out by Munish Shah.

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Received 28 September 1993
and accepted 21 January 1994