Time-Dependent Mechanical Properties of 3-D Braided Graphite/PEEK Composites

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ABSTRACT

Poly(ether-ether-ketone) or PEEK, was developed as a high performance engineering material. In this study, 3-D braided AS4 graphite/PEEK (graphite/PEEK) composites were preformed and processed to investigate the combined performance of this new system. These manufactured composites were then characterized, using matrix digestion and wide angle x-ray diffraction, to determine their fiber volume fractions and degrees of crystallinity. After physical characterization, the mechanical response of these composites were evaluated at various temperatures.

Experimental results from tensile measurements are compared to a fabric geometry model (FGM). This model predicts tensile strength based upon fiber and matrix properties, fiber volume fraction, and braiding angle. The model and experimental results are given here, and are in good agreement with each other.

In order to study the time-dependent mechanical properties of these 3-D braided graphite/PEEK composites, their stress relaxation and dynamic mechanical properties were evaluated. The dynamic mechanical properties of PEEK composites are compared to short fiber and continuous fiber reinforced PEEK composites to determine the effects of fiber geometry.

INTRODUCTION

Fiber-reinforced thermoplastic matrix composites are gaining in popularity for a number of applications. In these applications, their popularity stems from an improved combination of characteristics: from lowered processing temperatures and weight, to increased repairability, strength, and toughness.[1-5] Among thermoplastic matrix materials, PEEK, or poly(ether-ether-ketone) is one of a newer generation of high performance engineering materials. PEEK is a semicrystalline aromatic polymer with a glass transition temperature of 144°C, and a melting point of 335°C. PEEK has very good chemical resistance and retains its good mechanical properties up to 300°C. Compared to most thermoplastic materials, PEEK can be used at higher temperatures (to 250°C).[6-9] However, before it can be successfully used at higher temperatures, its behavior must be understood. Like most materials, PEEK exhibits time-dependent properties such as creep, stress relaxation, and energy dissipation. These time and temperature-dependent properties are not unique to polymeric materials, but they make the study of the long-term performance of PEEK composites at elevated temperatures essential.

Depending upon the final application, many reinforcing fiber geometries are used to make PEEK composites. For example, carbon fiber composites have been developed with short fibers,[9] laminates,[10] woven fabrics,[11,12] and three-dimensional braided structures.[13] Among these reinforcement geometries, 3-D braided structures are known for their high damage tolerance and delamination resistance.[14] Studies at room temperature show that 3-D braided Graphite/PEEK composites have very good damage tolerance and tensile properties.[13] In standard compression after impact tests,[15] these materials show higher compression after impact strength, and damage tolerance than laminated APC-2 (a 61% continuous graphite fiber reinforced PEEK composite). In this way, 3-D braided PEEK composites may be used to improve damage tolerance and delamination problems which are often associated with APC-2 composites.

In order to increase the commercial application of thermoplastic materials, their long-term behavior must be well understood. However, thermoplastic composites have a relatively short history of application compared to other materials.[4] In the case of 3-D braided composites, long-term properties have not been examined until now. In this paper, the tensile, stress relaxation, and dynamic mechanical properties of 3-D braided graphite/PEEK composites are studied. First, a series of tensile tests are described to demonstrate the stress-strain behavior of these composites. Second, tensile properties of these materials are compared to a fabric geometry model (FGM)[14,16] in order to demonstrate the usefulness of this predictive tool. Third, stress relaxation results are described, in experiments at various temperatures and strain levels. Finally, the dynamic mechanical properties of 3-D braided composites are investigated and compared to other PEEK composites with various types of fiber-reinforced geometries.

MATERIALS

In this study, Victrex® 150 G PEEK was used for the polymer matrix, and Magnamite® AS4 graphite was used for the reinforcing fiber. The physical and mechanical properties, as supplied by the manufacturers of these materials, are presented in Table 1.[9,17]

In order to ensure good matrix distribution in the final composites, commingled yarns were used. The yarns consist of 150G PEEK in filament form and AS4 graphite fibers. The commingled yarns contain approximately 280 PEEK fibers and 6,000 graphite fibers. Ignoring voids, the graphite fiber volume fraction in each yarn is 62.7%.[11]

EXPERIMENTS & THEORY

Experiments

The commingled yarns were braided into 3-D preforms at the Fibrous Materials Research Center at Drexel University. The 3-D braided preforms were 1.25 cm wide, 0.2 cm thick, with a surface braiding angle of ± 20°. A detailed description of the preforming process can be found in reviews by Ko or Chu.[14,18]

Consolidation of the 3-D braided preforms was carried out in a Wabash® hydraulic hot-press using a carbon steel matched die mold. Before consolidation, the 3-D braided preforms were carefully cut into 25 cm lengths. The time-temperature and time-pressure history of a typical sample during processing is shown in Figure 1.

After processing, composite fiber volume fractions were determined using a matrix digestion technique.[18,19] The fiber volume fraction in these processed composites was determined to be 63.60% (± 1.20%).

The crystallinity index for the PEEK matrix in these processed composites was determined to be 32%, using wide-angle x-ray diffraction. This method requires subtracting the diffraction from the fibers, and scaling the x-ray scattering from amphorous PEEK by a factor which is related to the crystallinity index. This method is detailed by Blundell.[20] More on the particular methods used here is reported by Chu.[18]

Tensile Properties Characterization

Static tensile tests (according to ASTM standard D-3039-76) were conducted to obtain the ultimate tensile strength, modulus, and Poisson's ratio of the 3-D braided composites. These tests were conducted using an Instron 1127 Universal Tester. The dimensions of the specimens were 25.4 x 1.25 x 0.254 cm. A schematic of a test specimen is shown in Figure 2. The strain induced from the applied stress was measured using strain gages. A strain gage conditioner/amplifier system (manufactured by Measurements Group Inc.) was connected with an x-y plotter to record the strain data. The cross-head speed of the Instron was 0.05 cm/min.

Tensile tests were conducted at 25, 60, 120, and 180°C. To reduce experimental error, 10 specimens were tested at each temperature. The results of these static tensile tests are summarized in Table 2.

These results show that 3-D braided graphite/PEEK composites retain their tensile strength to at least 180°C. Table 2 also shows that the Poisson's ratio increases with temperature. After failure, the test specimens were cut using a diamond

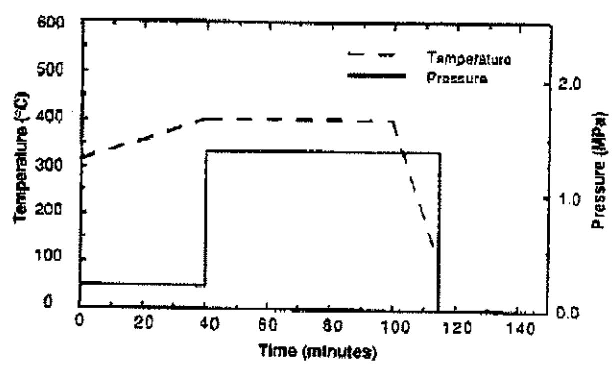

Figure 1. Hot press processing history of 3-D braided graphite/PEEK composites.

Properties	150G PEEK	AS4 Graphite Fiber
Density (g/cm³)	1.32†	1.80
Tensile Strength (MPa)	95	3,795
Tensile Modulus (GPa)	4.5	235
Poisson's Ratio	0.37	—
†semicrystalline		

Table 1. Material properties of PEEK and graphite fiber

Temp (°C)	Stress (MPa)	Modulus (GPa)	Poisson's Ratio
25	930.51 (± 47.78)	88.75 (± 5.50)	0.38 (± 0.02)
60	822.13 (± 79.94)	79.62 (± 2.39)	0.45 (± 0.04)
120	1027.59 (± 58.38)	83.67 (± 1.31)	1.14 (± 0.02)
180	1021.45 (± 102.15)	87.72 (± 12.79)	1.29 (± 0.16)

Table 2. Summary of the tensile test properties of 3-D braided AS4 grahpite/PEEK composites

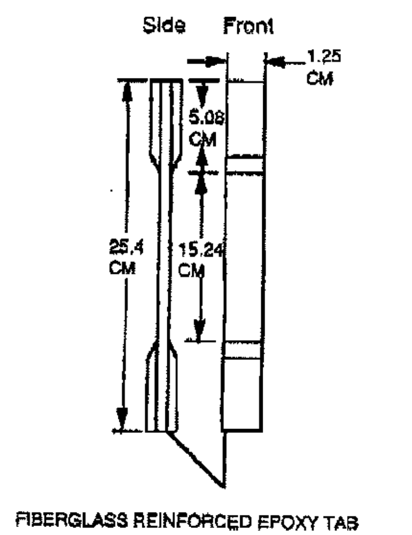

Figure 2. A schematic of a tensile test specimen.

blade to examine their fracture surfaces using a scanning electron microscope (SEM). Figures 3 and 4 show the SEM micrographs from a 25°C and a 180°C tensile test fracture surface, respectively. The fracture surface from the 180°C tensile test specimen shows more matrix flow than the 25°C specimen.

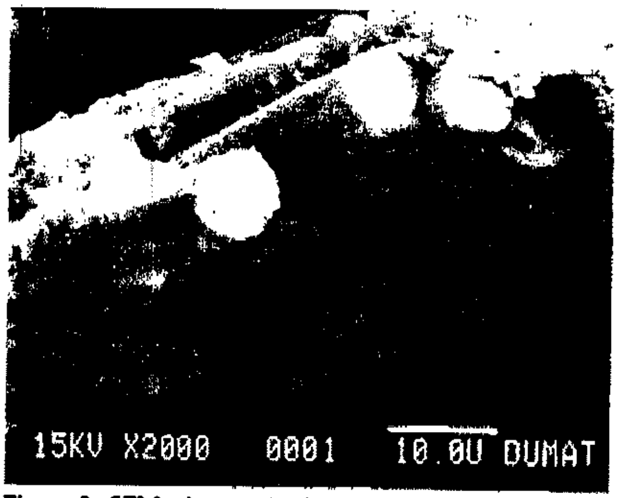

Figure 3. SEM micrograph of 25°C tensile test fracture surface.

Figure 4. SEM micrograph of 180°C tensile test fracture surface.

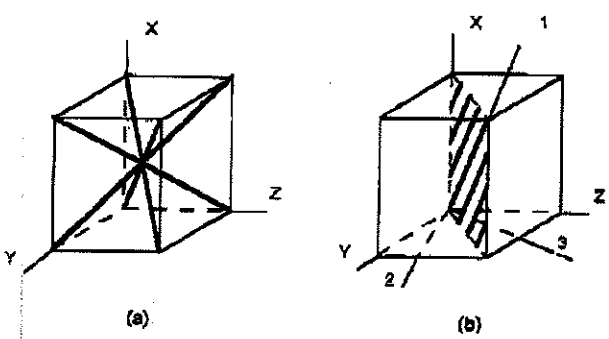

Figure 5. (a) The unit cell structure for 3-D braided composites. (b) A yarn system in the unit cell is treated as unidirectional lamina: (1, 2, 3) is the yarn coordinate system, (x, y, z) is the unit cell coordinate system.

From a theoretical point of view, a fabric geometry model (FGM) was developed which allows one to predict the tensile modulus of 3-D braided composites.[14] This model was employed here to estimate the tensile modulus of 3-D braided graphite/PEEK composites. Through a modified laminate theory, the model relates the modulus of the 3-D braided composite to its fiber and matrix properties, plus fiber orientation and volume fraction. In using this model, a unit cell is first identified. This forms a basis for the entire analysis. Figure 5a shows a typical unit cell for a 3-D braided composite.[16] In its simplest form, the unit cell is represented by a set of diagonal rods representing individual yarns. The rod orientations depend upon the braiding angle.

The FGM assumes that each yarn in the unit cell is a unidirectional lamina (Figure 5b). The overall material property of a unit cell is the sum over all the yarn contributions. The objective of FGM analysis is to calculate the elasticity matrix for the unit cell. The elasticity matrix for each lamina in the yarn coordinate system (labelled as 1-2-3 axes in Figure 5b), C, is determined by the fiber and matrix properties and fiber volume fraction. The elasticity matrix of the lamina in the unit cell coordinate system (labelled as X-Y-Z axes in Figure 5b) is determined through a coordinate transformation. Therefore, the elastic matrix of the i^{th} system of yarns, $[C_i]$, in the unit cell coordinate system is expressed as

$$[C_i] = [T_{\sigma,i}]\,[C]\,[T_{\varepsilon,i}]^{-1}, \qquad [1]$$

where $[T_{\sigma,i}]$ is the coordinate transformation tensor of stress and strain for the i^{th} system of yarns, respectively.

Finally, the elasticity matrix of the unit cell, $[C_s]$, can be obtained by summing over the individual lamina elasticity matrices,

$$[C_s] = \Sigma\, k_i\, [C_i], \qquad [2]$$

where k_i is the fractional volume of the i^{th} system of yarns.

The FGM can be incorporated into a general finite element analysis program for solving the elastic matrix of complex braided composite structures and shapes.[16] Figure 6 compares the 25°C experimental stress-strain relation for 3-D braided graphite/PEEK composites with the FGM analysis. As Figure 6 shows, the FGM analysis and experimental results are in good agreement. Therefore, FGM may be used as a method of predicting the modulus of these kinds of 3-D braided graphite/PEEK composites.

Stress Relaxation Properties Characterization

Stress relaxation experiments (according to ASTM standard D 2991-84) were conducted using an Instron 1127 Universal Tester. The geometry and specimen dimensions were the same as in the tensile tests. The load was instantaneously (within 2 seconds) applied to the specimen. Tests were conducted at 3 different strain levels, each at 3 different temperatures: 0.68, 0.82, and 0.96% elongation and 60, 120, and 180°C. Figure 7 shows the stress level as a function of time at various temperatures.

A common way to describe stress relaxation behavior is to use a normalized stress relaxation function G(t).[21-23] G(t) can be defined as

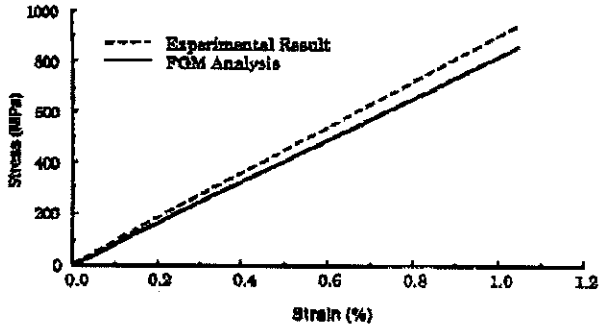

Figure 6. Room temperature stress-strain relation of 3-D braided AS4 graphite/PEEK composites.

$$G(t) = \frac{T(t)}{T(0)}, \quad G(0) = 1, \qquad [3]$$

where T(t) is the stress level necessary to give the corresponding strain at time t.

Referring to Equation [3], G(t) is an indication of the fractional stress retained in the specimen. Figure 8 plots the average G(t) at the 3 testing strain levels as a function of time for 3-D braided Graphite/PEEK composites at 60, 120, and 180°C. This figure shows that the stress relaxation behavior is relatively temperature insensitive in the temperature range of 60 to 180°C.

Dynamic Mechanical Analysis

A Dynamic Mechanical Analyzer (TA Instrument Inc, Model DMA-983) was used to investigate the effect of fiber geometry

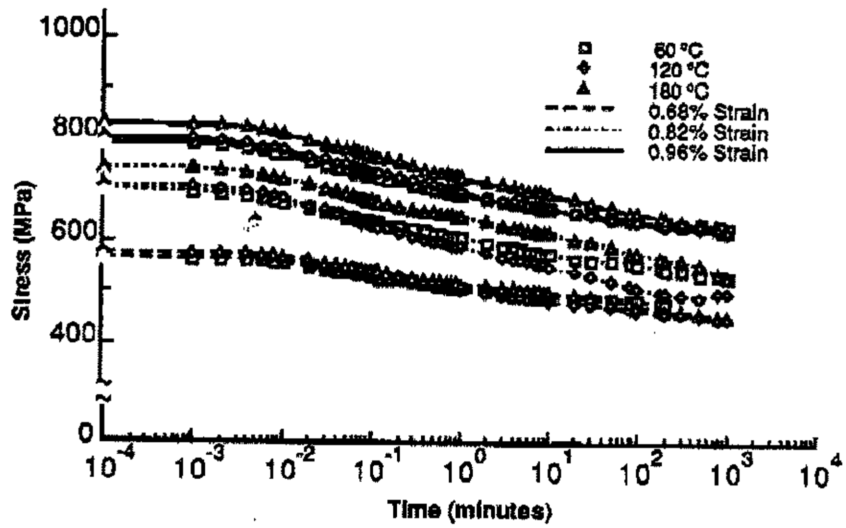

Figure 7. Stress relaxation behavior of 3-D braided AS4 graphite/PEEK composites.

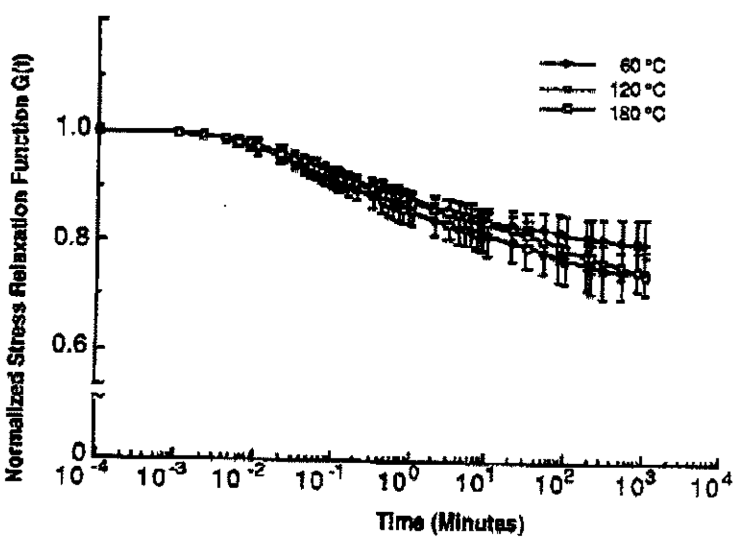

Figure 8. Normalized stress relaxation function of 3-D braided AS4 graphite/PEEK composites.

on the dynamic mechanical properties of the 3-D braided PEEK composites. The specimen dimensions were 40 x 12.6 x 2.28 mm. Tests were conducted at temperatures between 60 and 240°C. In general, during a dynamic experiment, the resulting stress is out of phase with the applied strain. Due to this fact, the modulus can be separated into two components: one in-phase (real), and one out of phase (imaginary) component. For example, the shear modulus (G*) may be represented as

$$G^* = G' + iG'' \qquad [4]$$

where G' is the real component of the shear modulus (also called the shear storage modulus), and G" is the imaginary part of the shear modulus (also called the shear loss modulus). G" is often associated with the dissipation or loss of energy during deformation.[24]

The phase angle that reflects the time lag between the applied stress and strain is generally defined as the angle δ. The tangent of δ is called the damping factor, and is often written as tan δ. The damping factor is associated with, among other things, internal friction, and is the ratio of energy dissipated per cycle to the energy stored per cycle. DMA results were obtained at 1 Hz frequency to compare results with literature data on bulk PEEK, 20 and 30% short glass fiber reinforced PEEK, and continuous fiber-reinforced PEEK composites (i.e., quasi-isotropic APC-2 8 ply). Figures 9, 10 and 11 show a comparison of fiber geometry effects on shear storage modulus (G'), shear loss modulus (G"), and damping factor (tan δ), respectively, in PEEK composites. These figures show that fiber geometry has a profound effect on the dynamic mechanical behavior of PEEK composites. 3-D braided PEEK composites enjoy higher shear storage and loss moduli relative to the various other composites shown in Figures 9 and 10. The

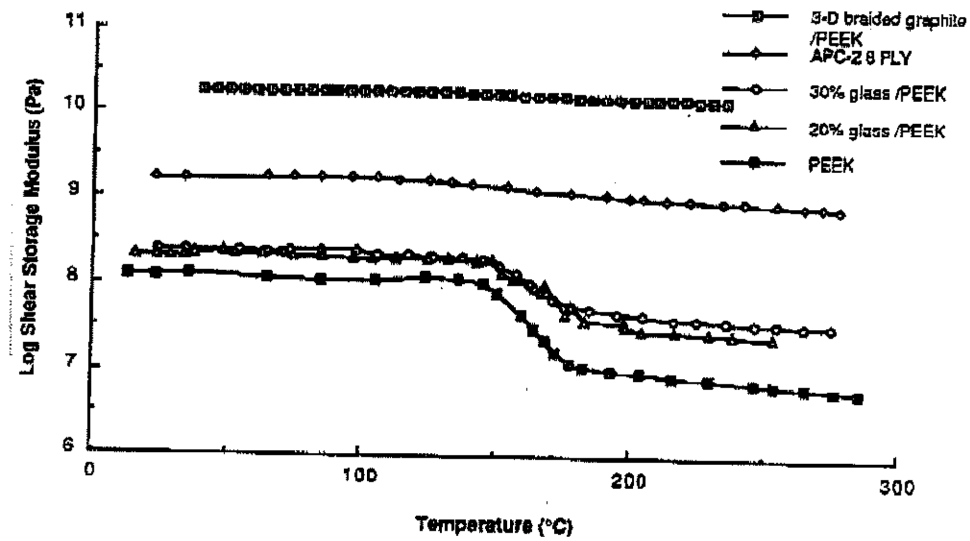

Figure 9. Effect of fiber geometry on shear storage modulus of PEEK composites.

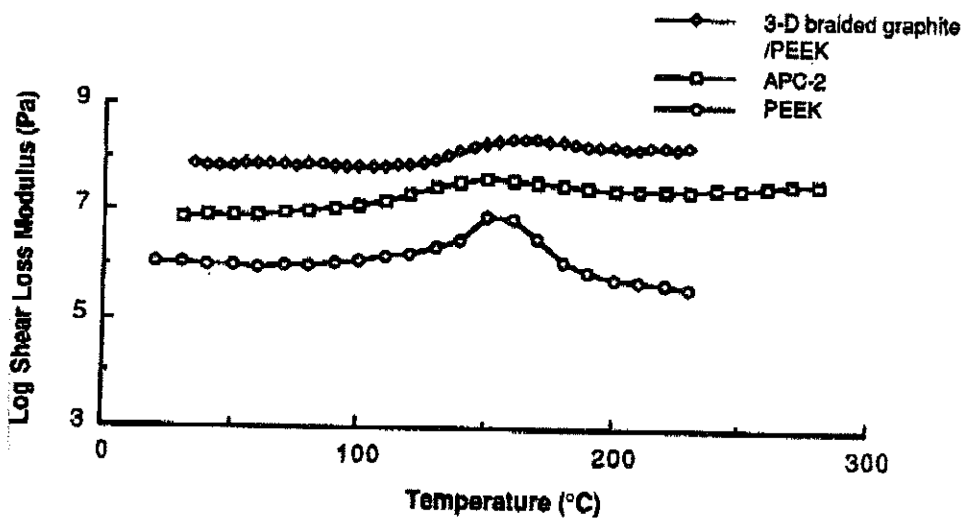

Figure 10. Effect of fiber geometry on shear loss modulus of PEEK composites.

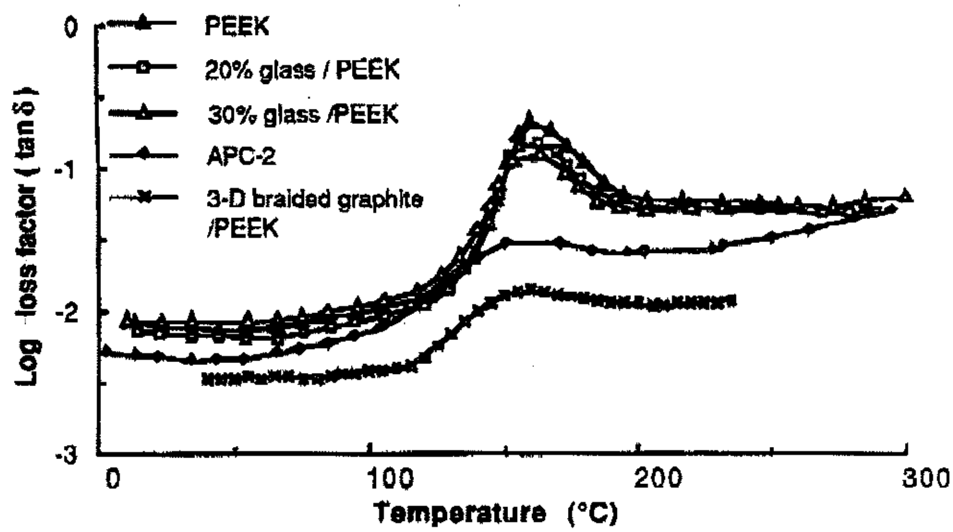

Figure 11. Effect of fiber geometry on loss factors of PEEK composites.

lower tan δ shown in Figure 11 implies that, in use, these composites may resist permanent changes.

CONCLUSIONS

The tensile properties of 3-D braided graphite/PEEK composites were studied at various temperatures. Experimental results indicate that 3-D braided PEEK composites retain their tensile strength to at least 180°C. Results from these tensile measurements compare well with predictions from a fabric geometry model (FGM). The FGM is therefore a good semi-empirical method for predicting the tensile properties of 3-D braided graphite/PEEK composites.

Results from stress relaxation studies show that 3-D braided graphite/PEEK composites are viscoelastic materials. Under constant strain, the stress relaxation behavior of these composites is relatively temperature insensitive in the temperature range of 60 to 180°C.

Dynamic mechanical properties of the 3-D braided graphite/PEEK composites were also investigated. It was found that fiber geometry has a profound effect on the dynamic mechanical properties of PEEK composites. Experimental results show that 3-D braided graphite/PEEK composites have higher shear storage and loss moduli, and lower damping factors relative to various other types of fiber reinforced composites. The lower damping factor in 3-D composites also implies that these materials may resist permanent change in use.

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