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Mechanical properties of high strength and high toughness metallic filament composites with epoxy and poly(ether ether ketone) matrices

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High strength and high toughness metallic filament was produced by glass-coated melt spinning. The mechanical properties of the composite consisting of the filaments uniaxially aligned in brittle epoxy resin, ductile epoxy resin with plasticizer and poly(ether ether ketone) matrices were investigated. It was found that the Young's modulus (E_c) and tensile strength (σ_{cu}) of the composite consisting of uncoated filaments in brittle epoxy matrix were higher than those predicted by a linear function of the filament content (V_f), and the filaments fractured tightly in contact with the matrix. On the other hand, no improvement of the mechanical properties of the composite consisting of glass-coated filaments in brittle epoxy matrix was detected, due to the weak interfacial force between metallic filaments and the coating glass. The composite consisting of filaments in a ductile matrix was a high toughness material with a long range of plasticity deformation, and the experimental values of E_c and σ_{cu} against V_f agreed with the simple law of mixtures.

1. Introduction

Many composite materials usually rely for their reinforcement upon fibres which, although strong and stiff, are seldom ductile. This lack of ductility is often carried over into the composite and leads to problems of low fracture toughness and difficulty in the design of structures [1]. High strength and high toughness filaments can be employed for making composites which are inherently stable, so that progressive deformation occurs under rising-load conditions. We have studied the preparation of high strength and high toughness metallic filaments using the method of glass-coated melt spinning [2–4]. This method gives filament at a cooling rate of more than 10^5 K sec^{-1} from the molten state with micrograins of a grain size of less than 100 nm, depending on the exact alloy composition. It was found in a previous experiment that high toughness $Fe_{57.5}Co_5Cr_{15}Mn_{10}Cu_2B_{10}Ti_{0.5}$ filaments having a high tensile strength (σ_{fu}) of 2 GPa with high elongation of 10% could be produced by this method [4]. This paper describes the mechanical properties of this high toughness filament composite. The aim has been to understand how the properties of composites consisting of the filament in brittle and ductile matrices depend on the elastic and plastic properties of the filaments and matrix. The filament–epoxy resin, filament–(glass + epoxy resin), filament–(epoxy resin with plasticizer) and filament–poly(ether ether ketone) (PEEK) systems were chosen for this investigation because the composites may be easily made and there is no chemical interaction between the two constituents.

2. Experimental procedure

2.1. High toughness filament

The high strength and high toughness filaments were produced using a method similar to that described earlier [4]. The chemical compositions in (wt %) of the parent alloy used was as follows: 0.057 C, 0.01 Si, 11.01 Mn, 0.005 P, 0.004 S, 2.25 Cu, < 0.01 Ni, 15.2 Cr, < 0.01 Mo, 5.64 Co, 0.45 Ti, 1.75 B and 63.62 Fe. About 0.7 g alloy was placed in a Pyrex glass tube and melted by r.f. induction heating in an argon atmosphere. When the glass tube containing the molten alloy was drawn, the alloy was stretched to form a glass-coated metallic filament and was coiled on a winding drum. The glass coating was removed in a hydrogen fluoride aqueous solution (HF solution). The filaments produced by this method were embedded in a matrix of epoxy resin or PEEK. In addition the glass-coated metallic filaments were embedded in a matrix of epoxy resin.

2.2. Composite fabrication

2.2.1. Epoxy resin composite

Specimens were made by a filament winding method: the glass-coated filaments were coiled on a winding drum which was coated with a sheet of polytetrafluoroethylene (PTFE) release agent. The glass coating was then removed in HF solution while still wound on the PTFE drum. Our initial studies were made with a resin composed of 100 parts by weight of resin (Araldite Type XB 3052 A) and 38 parts hardener (Araldite Type XB 3052 B). A layer of resin was spread on the drum and was de-aerated under reduced pressure and was cured at 373 K for 18 ksec. The ductile epoxy matrix was also studied. In spite of a decrease of the strength, the resin could be modified in such a way as to increase the failure strain by adding 60 parts plasticizer (Araldite DY 040). The curing was made at 323 K for 54 ksec in this case. A series of composites was made with filament volume fraction (V_f) in the

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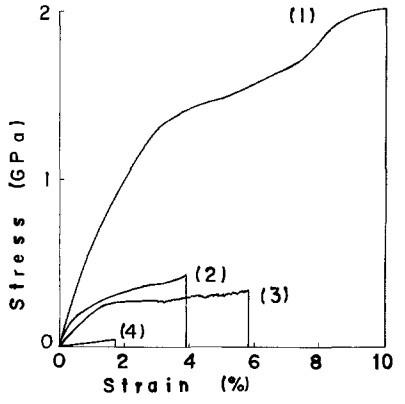

Figure 1 Apparent stress–strain curves of the composite in brittle matrix: (1) filament, (2) filament–epoxy resin composite with $V_f = 0.22$, (3) glass-coated filament–epoxy resin composite with $V_f = 0.12$, (4) epoxy resin.

range from 0.02 to 0.50 by varying the winding time and thickness of the layers. A single strip could be peeled from the drum by making an axial cut through the composite cylinder, and specimens of 50 mm length for tensile testing were cut out.

2.2.2. PEEK composite

PEEK is a semi-crystalline thermoplastic with a melting point of about 607 K and a glass transition temperature of about 416 K [5]. The composite in PEEK was made by a hot-press method [6]: the filaments were laid between PEEK film of 25 μm thickness (Talpa 2000, Mitsui Toatsu Kagaku Co Ltd., Tokyo). The laminate was placed between aluminium foil pretreated with a release agent (Daifree A541, Daikin Kogyo Co. Ltd., Osaka) and then the sandwich was placed between mirror-finished press plates and put into a hot-plate press operating at 653 K. When thermal equilibrium at 653 K had been achieved, a consolidation pressure of 1 MPa was applied for 600 sec. The sandwich was transferred to a cool press at about 463 K, applying a consolidation pressure of 2 MPa. The laminate was removed after 600 sec.

2.3. Tensile tests

The tensile strength of the composite produced by this method was measured with an Instron type machine at room temperature. All tests were performed at room temperature with a crosshead movement of 0.0333 mm sec^{-1} and the gauge length was 30 mm. The apparent stress was chosen as the load divided by the fracture area of the material, and the apparent strain was chosen as the displacement divided by the gauge length. The fracture morphology of the composites was observed by scanning electron microscopy (SEM).

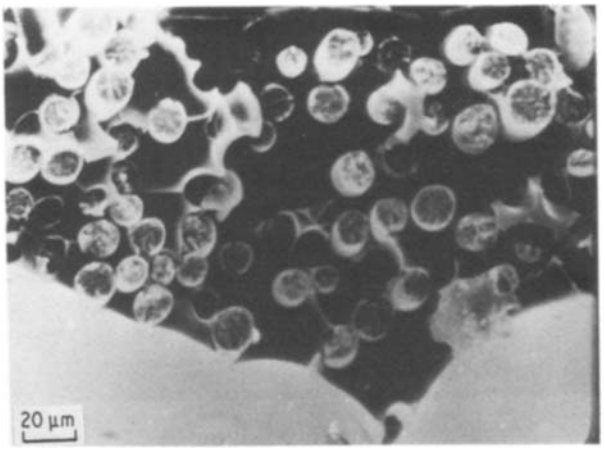

Figure 2 Fracture morphology of filament–epoxy resin composite.

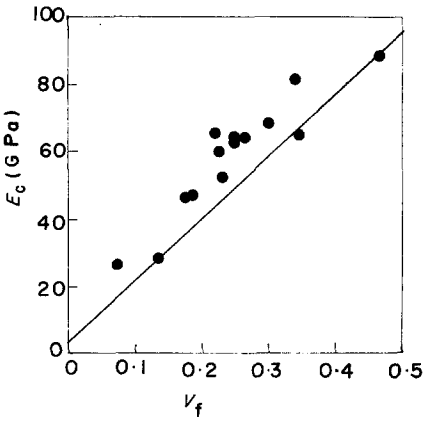

Figure 3 Young's modulus of filament–epoxy resin composite against volume fraction of filaments. (——) Equation 1.

3. Results and discussion

Continuous high strength and high toughness filaments, which had a tensile strength of 2 GPa and an elongation of 10%, were obtained from the molten state at 1600 K for a winding speed of 0.95 m sec^{-1}. The diameter of the filament obtained varied for every spinning time from 12 to 18 μm because of the strict spinning conditions. Therefore the diameter of the filament in the composite was measured by SEM every time. On the preparation of the filaments, the volume fraction of the coated glass (V_g) is very important due to the cooling rate during the spinning process and high toughness filament could only be obtained with $V_g/V_f < 1$.

3.1. Brittle matrix

The epoxy resin was initially used as for the brittle matrix. The apparent stress–strain curve (S–S curve) for the composite containing the filaments in brittle epoxy resin is shown in Fig. 1. The composite exhibited a distinct range of plasticity. Fig. 1 shows S–S curves of both filament and matrix. A noticeable feature of the S–S curve of the filament was that rapid hardening to a high stress level of more than 1.5 GPa was reached in the first few per cent of tensile elongation, while the matrix was stretched uniformly to the breaking point with a tensile strength (σ_{mu}) of 0.05 GPa. The Young's modulus of the filament (E_f) and matrix (E_m) were determined at 190 and 3 GPa, respectively, from the initial slopes of the S–S curves. The fracture morphology of the composite was observed by SEM with representative example shown in Fig. 2. The filaments fractured tightly in contact with the epoxy matrix.

The filaments were incorporated to various V_f in epoxy resin. The Young's modulus (E_c) and tensile strength (σ_{cu}) of the composite against V_f were

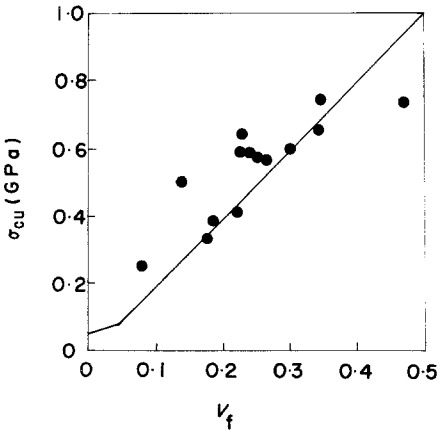

Figure 4 Tensile strength of filament–epoxy resin composite against volume fraction of filaments. (——) Equations 2 and 3.

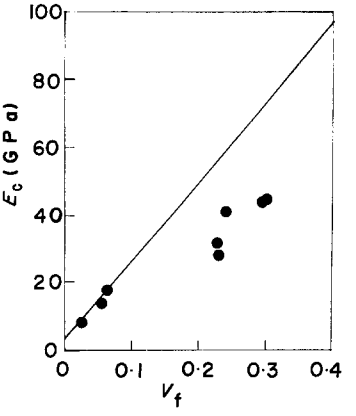

Figure 6 Young's modulus of glass-coated filament–epoxy resin composite against volume fraction of filaments. (——) Equation 4 for $K = 0.78$.

measured and are plotted in Figs 3 and 4, respectively. Each point shows the average value of several tests of the samples through the same operation in the fabrication of the composite.

A simple theory was developed to predict the tensile properties of a single tough filament composite from the mechanical properties of the filament and matrix [7]. When very strong continuous filaments are embedded in a matrix which is a brittle material with a breaking stress very much less than the tensile strength of the filament, such as Fig. 1 [8], E_c will be given by

$$E_c = E_f V_f + E_m(1 - V_f) \quad (1)$$

Below a critical volume fraction V_f^* given by $V_f^* = \sigma_{mu}/(\sigma_{fu} - \sigma_f' + \sigma_{mu})$, the fracture strength of the matrix is greater than that of the filament and the tensile strain in filament and matrix is taken to be equal and we have

$$\sigma_{cu} = \sigma_{mu}(1 - V_f) + \sigma_f' V_f \quad (2)$$

where σ_f' is tensile stress of the filaments at the fracture point of the matrix. Above V_f^*, the filament can work-harden sufficiently after fracture of the matrix to bear the applied load alone and the tensile strength is then given by

$$\sigma_{cu} = \sigma_{fu} V_f \quad (3)$$

In the present case, Equation 3 should hold for case of $V_f > 0.04$. Although there is considerable scatter, the experimental values of E_c and σ_{cu} in Figs 3 and 4 are higher than those of the prediction of Equations 1, 2 and 3, which are shown by straight lines in Figs 3 and 4. The scatter of the datum points is considered to be due to the following reason: it was difficult to obtain exactly the value of V_f because the alignment of the filament was often disturbed during removal of the coated glass and spreading of a layer of resin. Moreover, as we did not pay special attention to the surface of the filaments, the microscopic condition of the interface between the filaments and resin was variable according to each operation in the fabrication of the composite.

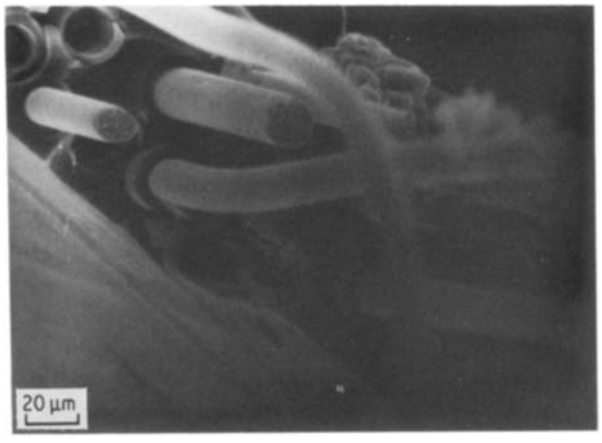

Figure 5 Fracture morphology of glass-coated filament–epoxy resin composite.

The main overall elastic moduli of fibre composites with transversely isotropic phases were shown by Hill [9] to be connected by simple universal relations which are independent of the geometry at a given concentration. The enhancement of E_c from the prediction of Equation 1 was discussed as due to the energy of the plane field of internal strain that would be produced by interfacial dislocations needed to close gaps opened by different transverse linear contractions.

Thornton and Thomas [10] have discussed the theoretical strengthening effects of brittle zones on ductile fibre composites, making the assumption of uniform shear stress at the interface. The enhancement of E_c and σ_{cu} in Figs 3 and 4 is considered to be due to the high compressive strength of a brittle matrix on a ductile filament [8–11].

The composite of the glass-coated filament in epoxy resin was examined to study the effect of the interface between filaments and matrix. In this case the interfacial force between metallic filament and coated glass is considered to be relatively weak [7, 12]. The S–S curve for the composite consisting of glass-coated filament in epoxy matrix are also shown in Fig. 1. The composite has a longer range of plasticity than that for the composite without glass, and the S–S curve shows serration in the region of plasticity related to multiple crazing of the coated glass [7]. The fracture morphology of the composite is shown in Fig. 5. The metallic filaments were pulled out from the coated glass and epoxy matrix. E_c and σ_{cu} for composites with various values of V_f were also measured and the results are shown in Figs 6 and 7, respectively.

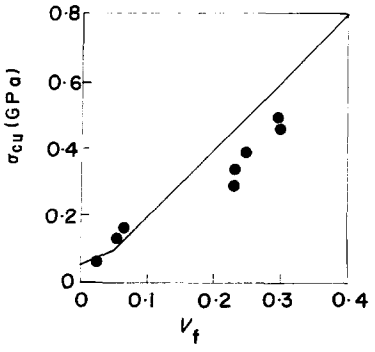

Figure 7 Tensile strength of glass-coated filament–epoxy resin composite against volume fraction of filaments. (——) Equations 3 and 5 for $K = 0.78$.

Putting $K = V_g/V_f$, E_c is given by

$$E_c = (E_f - KE_m - E_m + KE_g)V_f + E_m \quad (4)$$

where E_g is Young's modulus for the glass, given as 69 GPa for Pyrex glass [13]. The straight line in Fig. 6 shows Equation 4 for $K = 0.78$, which was the experimental value of V_g/V_f. Equation 4 agrees with the experimental values for low volume fractions. The fall-off in E_c at high volume fractions is probably due to buckling of the filament during the strengthening of the matrix [14].

For the composite with glass, V_f^* is given by $\sigma_{mu}/(\sigma_{fu} + \sigma_{mu} + K\sigma_{mu} - \sigma'_f - K\sigma'_g)$. Below V_f^*, σ_{cu} is given by

$$\sigma_{cu} = \sigma_{mu} + [\sigma'_f + \sigma'_g K - (1 + K)\sigma_{mu}]V_f \quad (5)$$

where σ'_g is the tensile stress of the coated glass at the breaking point of the epoxy matrix. Above V_f^*, σ_{cu} is given by Equation 3 for $K < 1$. The experimental value of σ_{cu} for low volume fraction is approximately fitted by Equations 3 and 5 as shown in Fig. 7. Thus, the enhancement of the mechanical properties as found for the composite without glass was not detected for the composite with weak contact between the metallic filament and coating glass.

3.2. Ductile matrix

The composite of the filament in ductile epoxy resin matrix with plasticizer was initially examined. The typical S–S curve of the composite is shown in Fig. 8. A long range of plasticity, as found for the filament, is observed and the composite with $V_f = 0.19$ fractured at a high tensile strength of 380 MPa, whereas the

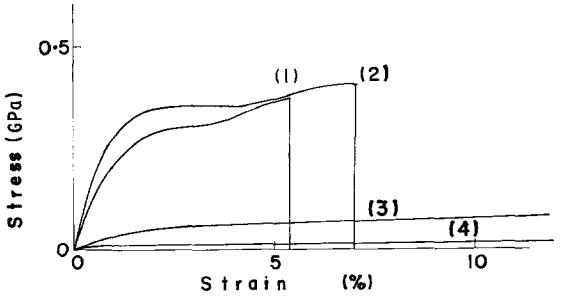

Figure 8 Apparent stress–strain curves of the composite in ductile matrix: (1) filament–epoxy resin with plasticizer composite with $V_f = 0.19$, (2) filament–PEEK composite with $V_f = 0.18$, (3) PEEK, (4) epoxy resin with plasticizer.

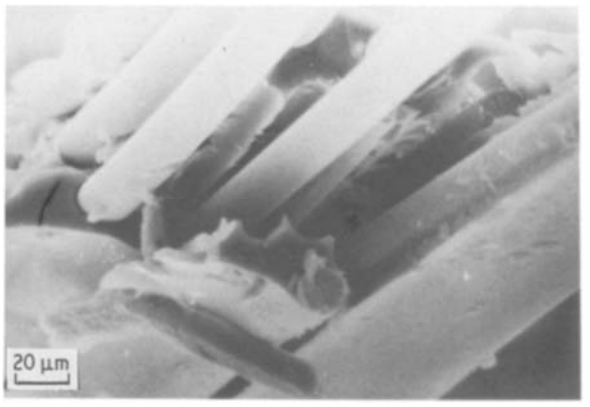

Figure 9 Fracture morphology of filament–epoxy resin with plasticizer composite.

matrix has a low tensile strength of 13 MPa. The debonding and pull-out of the filament are observed in the fracture morphology of Fig. 9.

The E_c and σ_{cu} of the composite with various values of V_f are shown in Figs 10 and 11. When very strong continuous filaments are embedded in a matrix which has a ductile material with high elongation, E_c will be given by Equation 1 and V_f^* is given by $V_f^* = (\sigma_{mu} - \sigma'_m)/(\sigma_{fu} + \sigma_{mu} - \sigma'_m)$. Below V_f^*, we have

$$\sigma_{cu} = \sigma_{mu}(1 - V_f) \quad (6)$$

Above V_f^*, σ_{cu} is given by

$$\sigma_{cu} = \sigma_{fu}V_f + \sigma'_m(1 - V_f) \quad (7)$$

where σ'_m is the tensile stress of the matrix at the fracture point of the filament. In the present case, the value of σ'_m is approximately equal to σ_{mu} as shown in Fig. 8 and then V_f^* becomes nearly zero and σ_{cu} is given by Equation 7. The predictions of Equations 1 and 7 for various values of V_f of the composite are shown by straight lines in Figs 10 and 11, respectively. The experimental values agree with these equations.

PEEK is a typical high-temperature engineering thermoplastic with high toughness having a tensile strength of 93 MPa and elongation of more than 100% [5]. The composite of the filaments in PEEK matrix was made by a hot-press method. Fig. 12 is a magnified section cut through a consolidated sample and illustrates the void-free impregnation, but the filaments are loosely in contact with the matrix. The tensile test of the composite was examined and the S–S

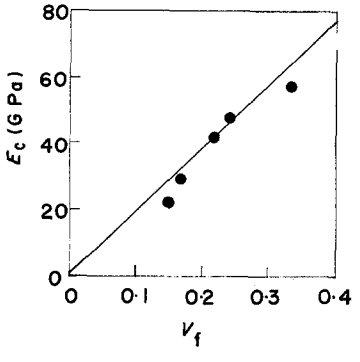

Figure 10 Young's modulus of filament–epoxy resin with plasticizer composite against volume fraction of filaments. (——) Equation 1.

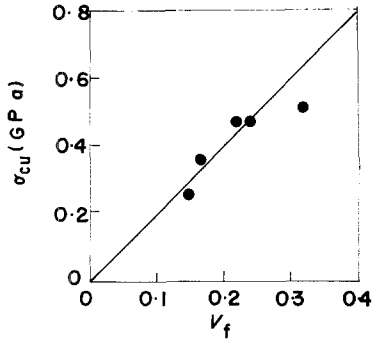

Figure 11 Tensile strength of filament–epoxy resin with plasticizer composite against volume fraction of filaments. (——) Equation 7.

curve is shown in Fig. 8. The composite has a high toughness with a long range of plasticity as for the filament, whereas the composite of unidirectional continuous carbon fibre in PEEK matrix was a brittle material with a low elongation of 1.45% [6]. The debonding and pull-out of the filaments are observed in the fracture morphology of Fig. 13. The E_c and σ_{cu} of the composite against V_f are shown in Figs 14 and 15, respectively. Although a composite with high V_f could not be made, the experimental values of E_c and σ_{cu} are slightly low compared with the predictions of Equations 1 and 7 due to the loose contact between the filament and PEEK.

As described above, the composite consisting of high toughness filament in ductile matrix was a high toughness material with a long range of plasticity deformation, and the E_c and σ_{cu} of the composite against V_f agreed with the simple law of mixtures.

4. Conclusion

High strength and high toughness metallic filaments were produced by a glass-coated melt-spinning method, and tensile tests were carried out on composites consisting of the filaments uniaxially aligned in a brittle epoxy resin and a ductile epoxy resin with plasticizer and PEEK matrices.

It was found that the E_c and σ_{cu} of the composite consisting of filaments in a brittle matrix were higher than those predicted by a linear function of V_f, and the filaments fractured tightly in contact with the matrix. On the other hand the improvement of the mechanical properties of the composite consisting of glass-coated filaments in brittle epoxy matrix was not detected, due to the weak interfacial force between the metallic filaments and coating glass.

The composite consisting of filaments in a ductile matrix was a high toughness material with a long range of plasticity deformation, and the experimental values of E_c and σ_{cu} against V_f agreed with the simple law of mixtures. Debonding and pull-out of the filaments were observed in the fractography of the composite in ductile matrix.

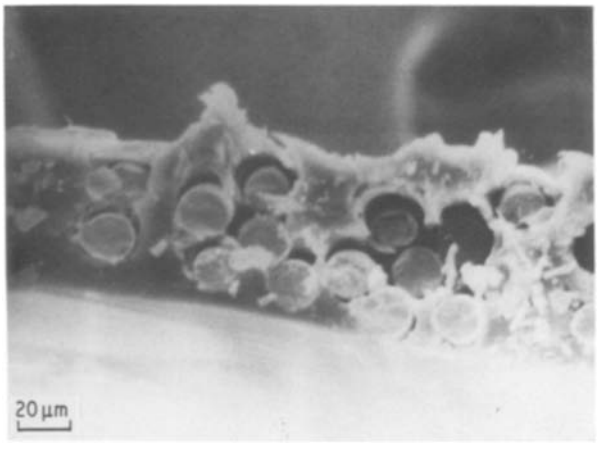

Figure 12 Cross-section of filament–PEEK composite.

Figure 13 Fracture morphology of filament–PEEK composite.

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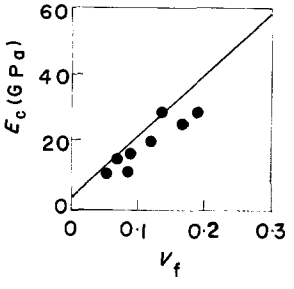

Figure 14 Young's modulus of filament–PEEK composite against volume fraction of filaments. (——) Equation 1.

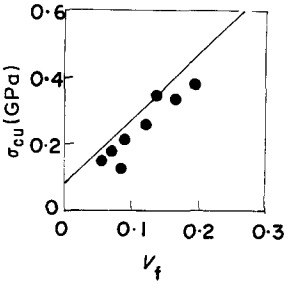

Figure 15 Tensile strength of filament–PEEK composite against volume fraction of filaments. (——) Equation 7.

References

1. G. A. COOPER and J. M. SILLWOOD, *J. Mater. Sci.* **7** (1972) 325.
2. T. GOTŌ and T. TOYAMA, *ibid.* **20** (1985) 1883.
3. T. GOTŌ and A. YOSHINO, *Trans. Jpn Inst. Met.* **26** (1985) 557.
4. *Idem, J. Mater. Sci.* **21** (1986) 1809.
5. O. B. SEARLE and R. H. PFEIFFER, *Polym. Eng. Sci.* **25** (1985) 474.
6. ICI Petrochemicals and Plastics Division, Publication No. APC-2 PD 2 and 3 (1984).
7. T. GOTŌ and K. NISHIO, in Proceedings of International Symposium on Composite Materials and Structures, Beijing, 1986, edited by T. T. Loo and C. T. Sun (Technomic Publishing Co., Inc, Lancaster, U.S.A., 1986) p. 62.
8. A. KELLY and W. R. TYSON, *J. Mech. Phys. Solids* **3** (1965) 329.
9. R. HILL, *ibid.* **12** (1964) 199.
10. J. S. THORNTON and A. D. THOMAS, *Metall. Trans.* **3** (1972) 637.
11. S. OCHIAI and Y. MURAKAMI, *Metal. Sci.* **10** (1976) 401.
12. T. GOTŌ, *Trans. Jpn Inst. Met.* **21** (1980) 219.
13. E. B. SHAND, "Glass Engineering Handbook" (McGraw-Hill, New York, 1958) p. 36.
14. A. KELLY, "Strong Solids" (Oxford University Press, 1966) p. 154.

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