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High temperature mechanical properties of high toughness metallic filament composites with polyimide and epoxy matrices

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High toughness metallic filament was produced by glass-coated melt spinning. The high temperature mechanical properties of the composite consisting of the filaments uniaxially aligned in polyimide and epoxy matrices were investigated at the temperature range from 423 K to 573 K.

The Young's modulus of the composite (E_c) of the polyimide composite at temperatures up to 573 K was higher than that predicted by the linear function of the filament content (V_f) and the filaments fractured tightly in contact with the matrix. The epoxy resin composite had a excellent high temperature mechanical properties in spite of the low T_g of the resin and large thermal expansion mismatch between the filaments and the resin. The value of E_c at 573 K was higher than that of a linear function of the V_f and tensile strength of the composite (σ_{cu}) at 573 K agreed with the simple law of mixture. It is considered that some heat reaction of the resin occurred by incorporating the metallic filaments.

1. Introduction

We have studied the preparation of high strength and high toughness metallic filaments using the method of glass-coated melt spinning and 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 [1]. The high strength and high toughness filaments can be employed for making composites which have high fracture toughness and are inherently stable. In the previous paper the mechanical properties of the composite consisting the filaments uniaxially aligned in brittle epoxy resin and ductile poly(ether ether ketone) matrices were investigated and it was found out that the composites obtained were high toughness materials with a range of plasticity deformation [2]. This paper describes the high temperature mechanical properties of the composite consisting of high toughness metallic filaments in the polyimide and epoxy matrices at the temperature range from 423 K to 573 K.

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 [1]. 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 polyimide or epoxy resin.

2.2. Composite fabrication

2.2.1. Polyimide composite

Polyimide is a super heat-resistant polymer. Then the polyimide composite was made by using varnish polyamide acid solution type LARC-TPI (Mitsui Toatsu Kagaku Co Ltd) [3]. The filaments were laid on aluminium foil pretreated with a release agent (Daifree A-541, Daikin Kogyo Co Ltd). A layer of resin was spread on the filaments and de-aerated under reduced pressure and reacted by heating up to 493 K [3]. Then the laminate was put into a hot plate press operating at 613 K and subsequently at 553 K. A consolidation pressure of 4 MPa was applied for 300 sec.

2.2.2. Epoxy resin composite

Epoxy resin composite was made as described before [2]. The composite was made by a filament winding method with a resin composed of 100 parts by weight of resin (Araldite Type XB 3052 A) and 38 parts

TABLE I The T_g and linear expansion of the component of the composite

Component	T_g (K)	Linear expansion $\times 10^{-5}$ (1/K)
metallic filament	–	1.5–2.0
polyimide	533	3.5
epoxy resin	348	7.1

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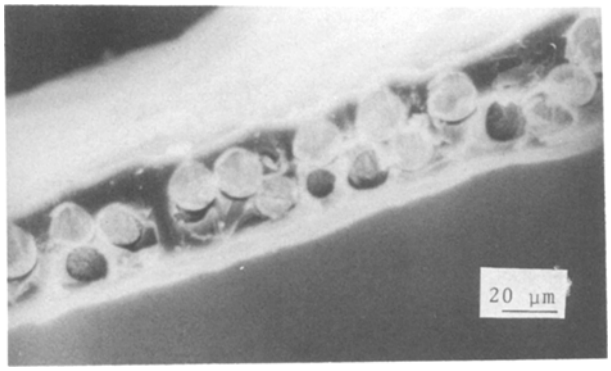

Figure 1 Cross-section of the polyimide composite.

hardener (Araldite Type XB 3052 B). A layer of resin was spread on the filaments which were coiled on a polytetrafluoroethylene drum, de-aerated under reduced pressure and cured at 373 K for 18 ksec.

2.3. Tensile test

The tensile strength of the composite produced by this method was measured with an Instron type machine with a heating furnace at room temperature, 423 K, 473 K, and 573 K, respectively. All tests were performed after 300 sec reaching the sample at each test temperature. A cross-head movement was 0.0333 mm sec^{-1} and the gauge length was 30 mm. The apparent stress was chosen as the load divided fracture area of the material and the apparent strain was as the displacement divided by the gauge length. The Young's modulus was determined from initial incline of the apparent stress–strain curve (SS curve). The fracture morphology of the composite was observed by scanning electron microscopy (SEM).

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 μm to 18 μm because of the strict spinning conditions. Therefore the diameter of the filament in the composite was measured by SEM every time to estimate the V_f of the composite. The

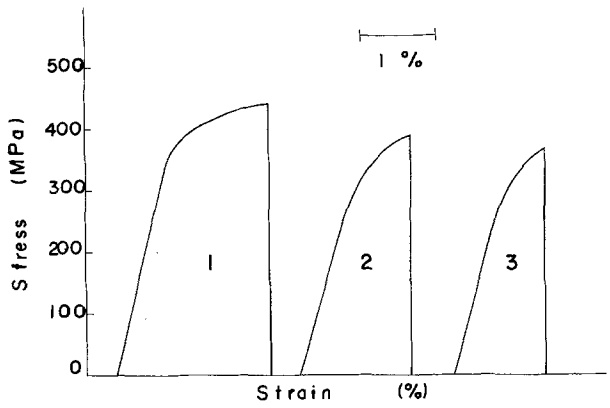

Figure 2 Apparent stress–strain curves of the polyimide composite at various temperatures. (1) with V_f = 0.28 at 423 K, (2) with V_f = 0.21 at 473 K, (3) with V_f = 0.28 at 573 K.

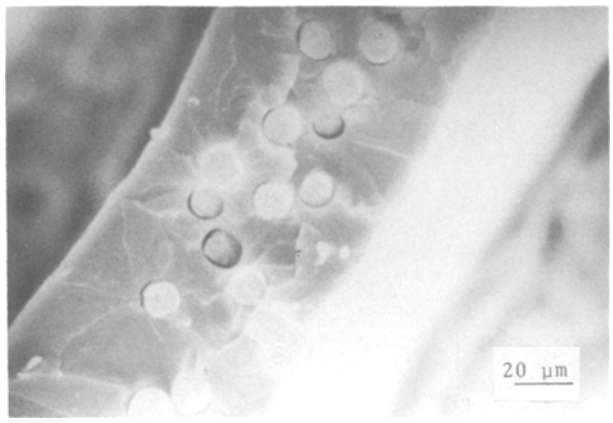

Figure 3 Fracture morphology of the polyimide composite at 573 K.

glass-transition temperature and thermal expansion of the components used are shown in Table I.

3.1. Polyimide composite

LARC-TPI is the first super heat-resisting thermoplastic polyimide adhesive developed by NASA (USA) and has a starting point of heat decomposition of 673 K [3]. Then the polyimide composite was initially examined to easily make a heat resisting composite. Fig. 1 is a cross section of the composite and shows the void free impregnation of the resin and the filaments are tightly in contact with the matrix. The tensile test of the composite was measured at various temperatures and typical SS curve for the composite are shown in Fig. 2. The composite exhibited a distinct range of plasticity at all test temperatures. As the temperature increases, the tensile strength, elongation and the range of plasticity slightly decrease. The fracture morphology of the composite was observed by SEM with representative example shown in Fig. 3. The filaments fractured tightly contact with matrix at all test temperatures. The filaments were incorporated

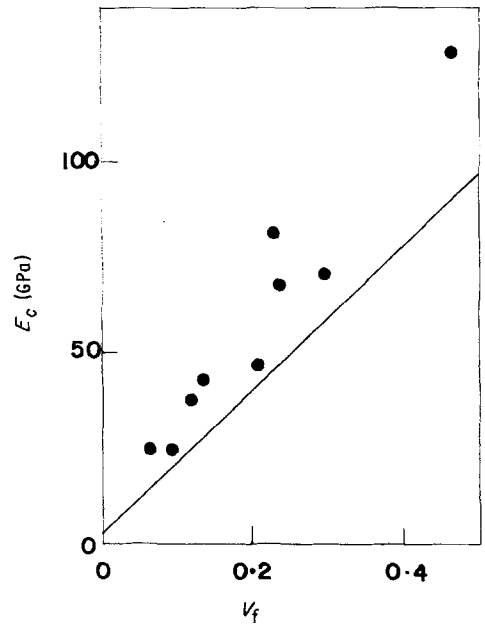

Figure 4 Young's modulus of the polyimide composite plotted against volume fraction of filaments measured at room temperature. (Equation 1).

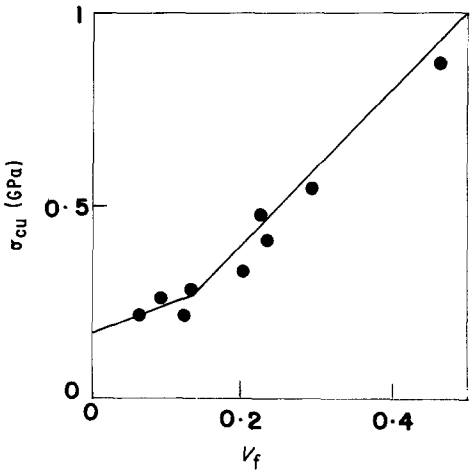

Figure 5 Tensile strength of the polyimide composite plotted against volume fraction of filaments measured at room temperature (Equations 2 and 3).

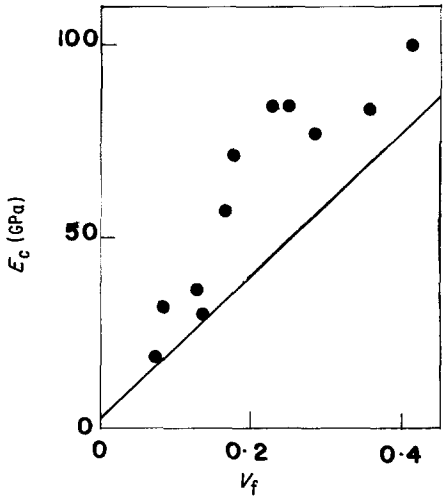

Figure 6 Young's modulus of the polyimide composite plotted against volume fraction of filaments measured at 423 K (Equation 1).

to various V_f in polyimide matrix. The E_c and σ_{cu} of the composite against V_f at various temperatures were measured and are plotted in Figs 4–11. A simple theory was developed to predict the tensile properties of the high toughness filaments composite in the previous paper [2] and E_c and σ_{cu} are given by

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

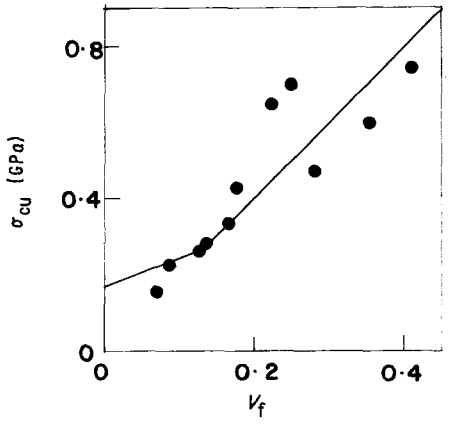

Figure 7 Tensile strength of the polyimide composite plotted against volume fraction of filaments measured at 423 K (Equations 2 and 3).

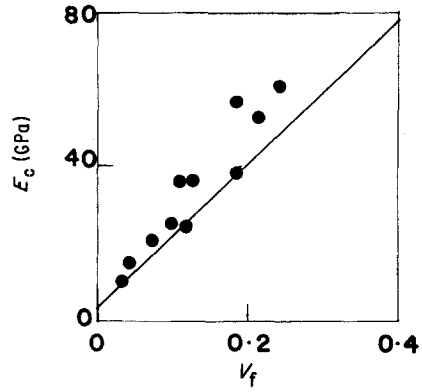

Figure 8 Young's modulus of the polyimide composite plotted against volume fraction of filaments measured at 473 K (Equation 1).

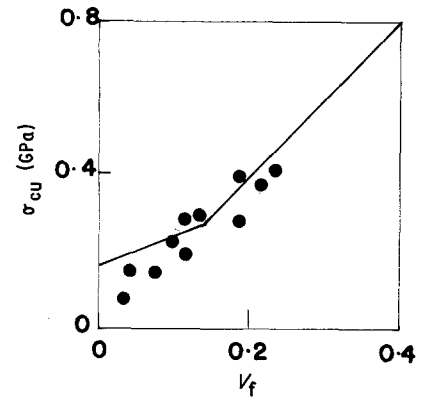

Figure 9 Tensile strength of the polyimide composite plotted against volume fraction of filaments measured at 473 K (Equations 2 and 3).

Below a critical volume fraction V_f^*, given by $V_f^* = \sigma_{mu}/(\sigma_{fu} - \sigma_f' + \sigma_{mu})$,

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

Above V_f^*,

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

where σ_f' is tensile stress of the filaments at the fracture point of the matrix. In the present case, Equation 3 should hold for case of $V_f > 0.13$ at room temperature. Assuming the values of E_m and σ_{mu} at up to 473 K are same as those of room temperature and zero above T_g, the experimental values of E_c in Figs 4, 6, 8

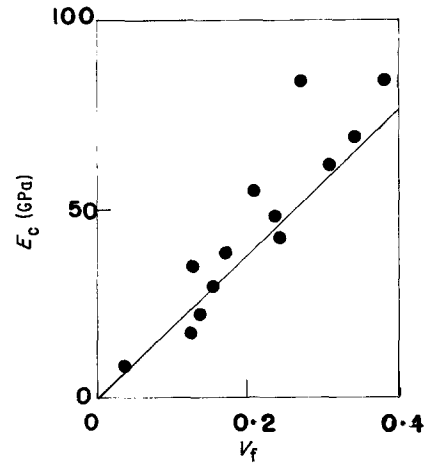

Figure 10 Young's modulus of the polyimide composite plotted against volume fraction of filaments measured at 573 K (Equation 1).

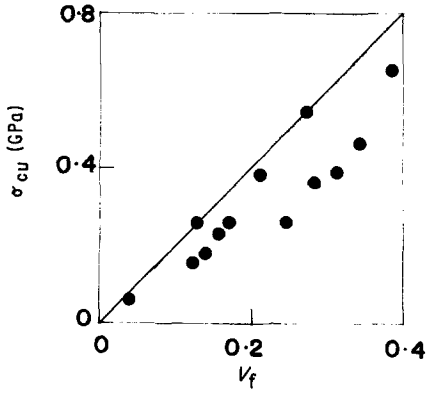

Figure 11 Tensile strength of the polyimide composite plotted against volume fraction of filaments measured at 573 K (Equations 2 and 3).

and 10 are higher than those of the prediction of Equation 1. This was discussed as being 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 as described for the epoxy composite [2, 4]. Equations 2 and 3 agree with the experimental values of σ_{cu} in Figs 5, 7 and 9. On the other hand a fall-off in σ_{cu} at high temperature of 573 K is probably due to the thermal expansion mismatch.

3.2. Epoxy composite

It was discovered in the previous paper that the E_c and σ_{cu} of the epoxy composite at room temperature were higher than those of prediction of Equations 1, 2 and 3 and the filaments were fractured tightly contact with matrix. The mechanical properties of the epoxy composite at high temperature were also examined. The apparent SS curves for the epoxy composite at various temperatures are shown in Fig. 12. Although the epoxy resin has low T_g of 348 K and large thermal expansion mismatch, the stress propagation through the matrix is completely performed and the SS curve of the composite showed a range of plasticity at high temperature such as 573 K. The fracture morphology of the composite at 573 K is shown in Fig. 13. While the pull out of the filament from the matrix was slightly observed, the filaments fractured tightly contact with epoxy resin and the debonding of the composite was

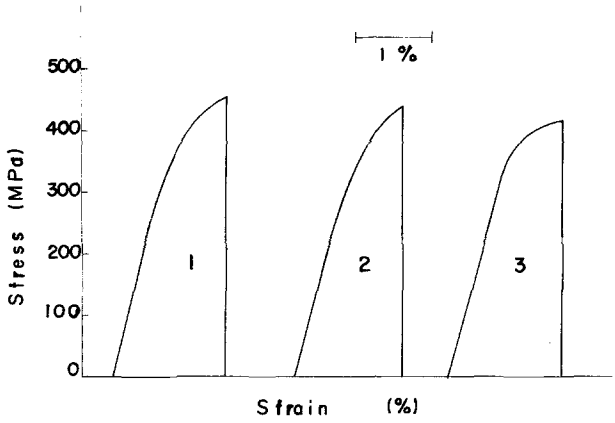

Figure 12 Apparent stress–strain curves of the epoxy composite at various temperatures. (1) with V_f = 0.26 at 423 K, (2) with V_f = 0.25 at 473 K, (3) with V_f = 0.26 at 573 K.

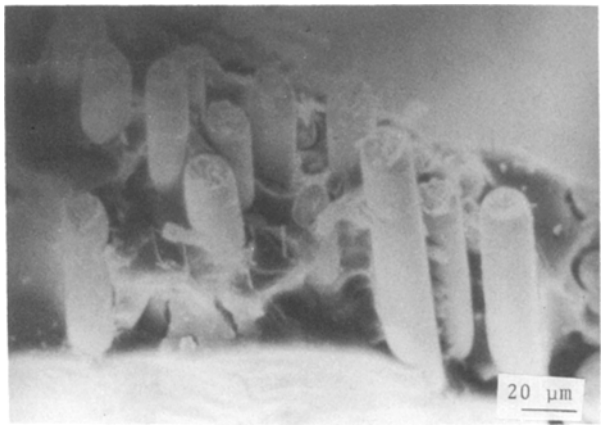

Figure 13 Fracture morphology of the epoxy composite at 573 K.

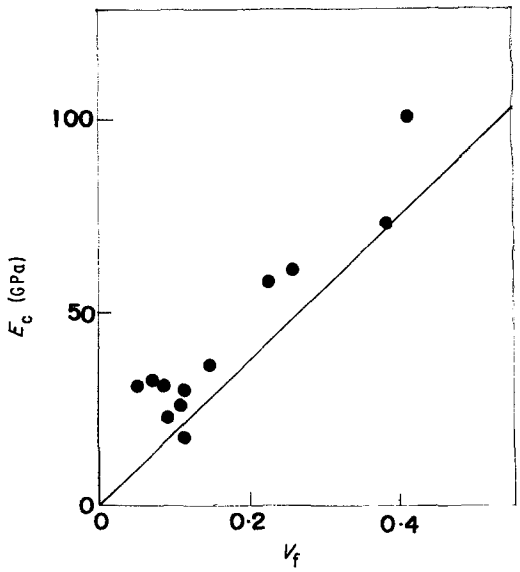

Figure 14 Young's modulus of the epoxy composite plotted against volume fraction of filaments measured at 423 K (Equation 1).

not detected. E_c and σ_{cu} for composites with various values of V_f at 423 K and 573 K were also measured and the results are shown in Figs 14, 15, 16 and 17, respectively. Assuming that E_m and σ_{mu} are zero above the T_g, the experimental values of E_c are higher than those of the prediction of Equation 1 and the values of σ_{cu} are approximately fitted by Equations 2 and 3. The

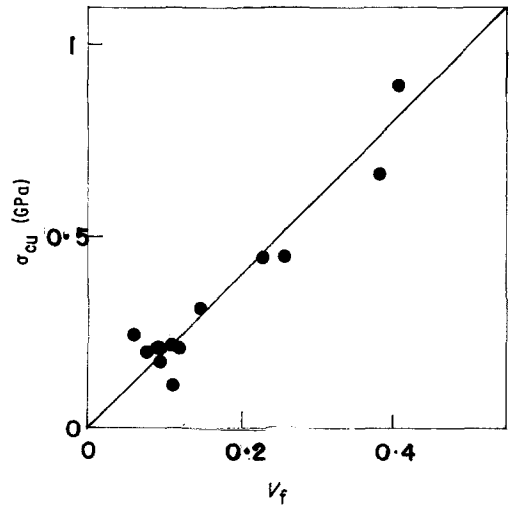

Figure 15 Tensile strength of the epoxy composite plotted against volume fraction of filaments measured at 423 K (Equations 2 and 3).

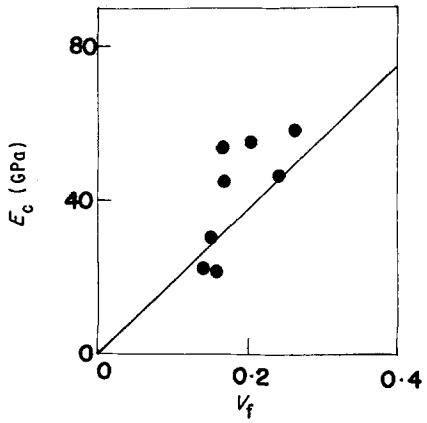

Figure 16 Young's modulus of the epoxy composite plotted against volume fraction of filaments measured at 573 K (Equation 1).

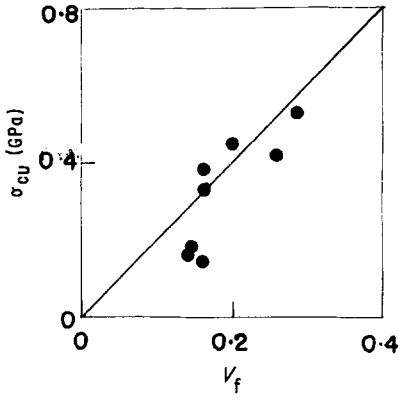

Figure 17 Tensile strength of the epoxy composite plotted against volume fraction of filaments measured at 573 K. (Equations 2 and 3).

DSC curves of the epoxy resin, the composite and the filaments were measured to clarify the excellent high heat resistance of the composite and shown in Fig. 18. The curve of epoxy resin shows the endothermic peak at 345 K due to the T_g. The curve of the composite shows the endothermic peak at 390 K and broad exothermic peak from 460 K. The endothermic peak was considered to arise from the T_g, the T_g of the composite was increased at 390 K by incorporating the filaments due to a hindrance of the molecular motion. The exothermic peak at 460 K for the composite was not reproduced after the first heating treatment. The IR spectra of the epoxy resin as-cured and after heating at 573 K, and the epoxy resin of the

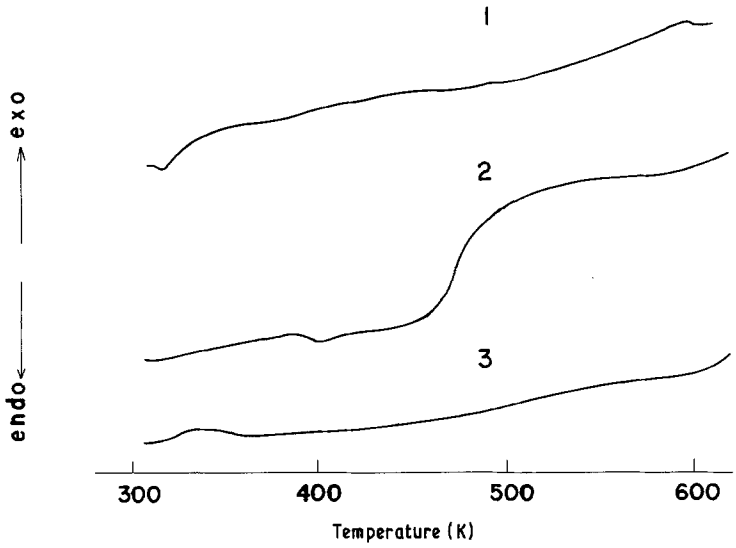

Figure 18 DSC curve of the composite (1) metallic filament (2) epoxy composite (3) epoxy resin.

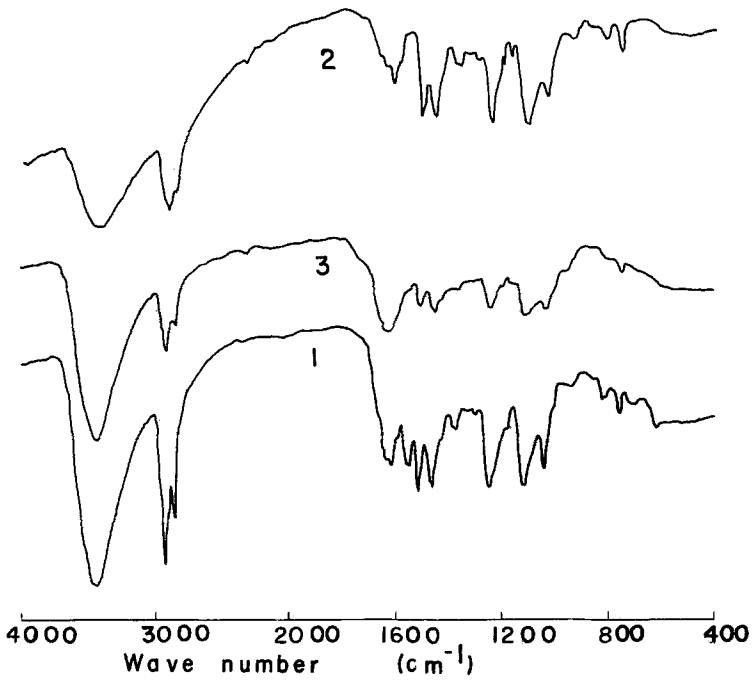

Figure 19 IR spectra of the epoxy resin (1) as-cured epoxy resin (2) epoxy resin after heating at 573 K (3) epoxy resin of the composite after heating at 573 K.

composite after heating at 573 K are shown in Fig. 19. The absorption at 1550 cm^{-1} attributable to amino group is disappeared by heating at 573 K. This is considered as the degradation of amino group which arose from the cross-linking by hardener. The broad peak at 1620 cm^{-1} is remarkably appears for the epoxy resin of the composite after heating at 573 K. It is most likely from these results that some heat reaction of the epoxy resin took place by incorporating the metallic filaments and the excellent heat resistance composite could fortunately be prepared.

4. Conclusion

High strength and high toughness metallic filaments were produced by glass-coated melt spinning. The mechanical properties of the composite consisting of filaments uniaxially aligned in polyimide and epoxy resin matrices at 423 K, 473 K and 573 K were investigated.

It was found that the E_c of the polyimide composite was higher than that of the linear function of the V_f at all test temperatures and the σ_{cu} of the polyimide composite agreed with the simple law of mixture.

The epoxy composite exhibited an excellent thermal mechanical properties in spite of a low T_g of the resin such as 345 K and large thermal expansion mismatch between the filaments and epoxy resin. The E_c of the composite at 573 K was higher than that of the linear function of the V_f and the σ_{cu} at 573 K agreed with the simple law of mixture. It is considered that some heat reactions of the resin occurred by incorporating the metallic filaments and an excellent heat resistance composite was prepared.

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