Fracture Behaviour and Deformation Mechanisms of Polyimide/Silica Hybrids

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Summary: Films of particulate polyimide-silica hybrids were produced by a sol-gel process and were examined in terms of morphological structure and fracture properties at different temperatures, varying from 20 to 250 °C.
The fracture toughness characteristics were studied by the "Essential Work of Fracture" method using double edge-notched specimens of different ligament lengths. The results showed that the fracture toughness, expressed through the essential (w_e) and non-essential work of fracture (βw_p) parameters increased when submicron silica particles were dispersed in the polyimide matrix. In particular, it was found that both w_e and βw_p increased with temperature to a larger extent than the parent polyimide. This enhancement in the fracture toughness was attributed to extensive cavitations and shear yielding originating at the particle interface and within the matrix.

Keywords: hybrids; morphology; polyimides; sol-gel; toughness

Introduction

Polyimides have gained considerable importance as high-performance polymers during the last two decades primarily because of their outstanding characteristics in terms of thermal stability, mechanical properties and resistance to solvents[1-4]. For some applications, however, properties such as modulus and fracture resistance need to be further enhanced. This can often be attained through the production of organic-inorganic hybrid systems [5-8]. The sol-gel method is commonly used for the preparation of these hybrids as a means of controlling the morphology of the inorganic phase[9-11].

In the present study composites consisting of a polyimide matrix and silica, as the dispersed phase, were prepared by the sol-gel method and examined in terms of morphological structure, deformation micro-mechanisms and fracture behaviour at different temperatures, from cast films. In particular, the failure process was studied using the Essential Work of Fracture (EWF) approach[12-18]. This method is based on the assumption that the total work of fracture, W_f, dissipated in a pre-cracked sample can be considered as the contribution of two energy terms:

$$W_f = W_e + W_p \qquad (1)$$

where W_e is the energy required to fracture the material in its inner process zone and W_p is the energy dissipated in the surrounding outer plastic deformation zone. Assuming that W_e is proportional to the ligament area and W_p is proportional to the volume of the plastic deformation zone the total work of fracture per unit ligament area can be written as

$$w_f = \frac{W_f}{Lt} = w_e + \beta w_p L \qquad (2)$$

where L is the ligament length, t is the specimen thickness, w_e is the specific essential work of fracture, w_p is the specific non-essential work of fracture and β is a shape factor associated with the volume of the plastic deformation zone. According to equation 2, a plot of w_f as a function of L should be linear with intercept and slope giving w_e and βw_p respectively. It has been proposed that w_e is a true material property, which characterizes the material fracture resistance under plane-stress conditions[19-21].

Experimental

The polyimide precursor used in this study was a polyamic acid, Pyre-ML RK 692 from I.S.T (Indian Orchard, MA). This has molecular weights $\overline{M}_w = 1.0 \cdot 10^5$, and $\overline{M}_n = 4.6 \cdot 10^4$, and is supplied as a 12 wt % solution in a mixture of N-methyl-2-pyrrolidone (NMP) and xylene (weight ratio 80/20). The polyamic acid is obtained by condensation of pyromellitic dianhydride (PMDA) and oxydianiline (ODA).

The silica precursor was a high purity grade of tetraethoxysilane (TEOS) obtained from Aldrich (Milwaukee, WI). Distilled water was used to induce hydrolysis of the alkoxysilane components using a 32 wt % HCl solution as catalyst and ethanol as solvent.

The polyamic acid and the tetraethoxysilane were formulated to produce composites with 10 and 15 wt% nominal silica content i.e. based on the assumption that the entire TEOS content is converted to S_iO_2. Details about the sol-gel procedure adopted for the preparation of these composites are reported elsewhere[22].

For EWF studies rectangular specimens 20 mm wide, 0.035 mm thick and 100 mm long were used. The specimens were sharply notched to produce series of double edge-notched samples (DENT) with ligament length, L, ranging from 3 to 15 mm. The measurement of the ligament length was performed prior to testing by using an optical microscope. The specimens were tested using a universal testing machine (Instron mod. 4505), equipped

with a temperature control chamber, at a cross-head speed of 2 mm min^{-1} and in a temperature range from ambient temperature to 250 °C. Dynamic mechanical measurements were performed in tensile mode at a heating rate of 5 °C min^{-1} and at an oscillating frequency of 1 Hz using a Pyris Diamond DMA apparatus from Perkin-Elmer. The morphology of the samples was examined on fractured samples by scanning electron microscopy (SEM). The apparatus used was a Philips SEM mod. XL20 and the fracture surfaces were coated with a gold-palladium layer by vacuum sputtering.

Results and discussion

Fracture behaviour

The fracture of the DENT specimens occurred in a stable and ductile fashion for both polyimide and silica composites producing load-displacement (L-D) curves an example of which is shown in Figure 1. The remarkable feature of these curves is their geometrical similarity, irrespective of the ligament length, which is an essential pre-requisite for the EFW analysis[23-28]. The actual requirement of the EWF theory is that the ligament length has to be fully yielded prior to the onset of crack growth. This behaviour was observed to occur in all samples.
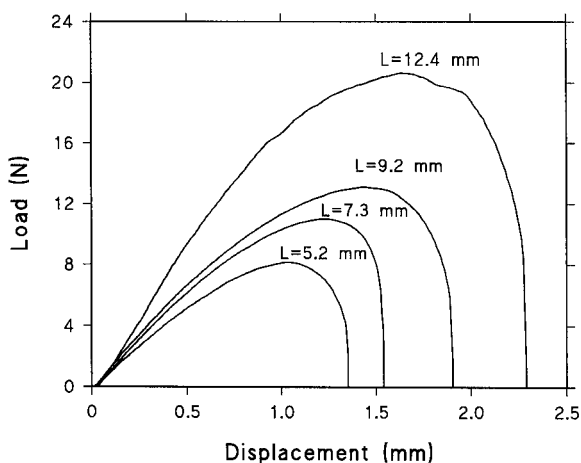

Figure 1. Typical DENT type load-displacement curves at various ligament lengths and at 20°C for the composite with 15 wt% of silica.
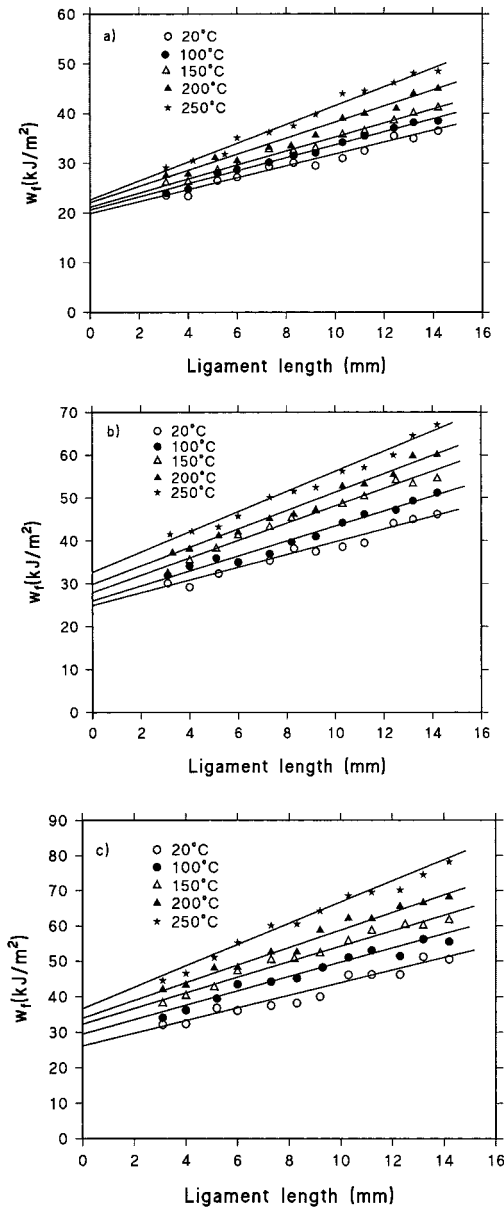
Figure 2. Specific total work of fracture, w_f, versus ligament length as a function of temperature: a) polyimide; b) composite with 10 wt% of silica; c) composite with 15 wt% of silica.

Plots of the specific total work of fracture, w_f, computed from the area under the L-D curves, versus the ligament length (L) for all the materials and temperatures investigated are reported in Figure 2 (a, b and c). These show that the variation of w_f with L is linear for all values of L (correlation coefficients are always higher than 0.97). From these straight lines the essential work of fracture, w_e, and the non essential work of fracture, βw_p, were evaluated according to equation 2. The values of w_e and βw_p so evaluated are shown as a function of the testing temperature in Figure 3 (a and b).

These plots show that the incorporation of the silica phase in the polyimide strongly enhances the fracture toughness. Both w_e and βw_p parameters increase linearly with increasing temperature. At any given temperature the enhancement of fracture toughness is related to the silica content. However, this temperature dependence is lower for the pure polyimide and increases with increasing silica content in the particulate composites.

There are two factors that are generally considered relevant for the interpretation of temperature effects on the fracture toughness. These are, respectively, the molecular relaxation processes occurring in the material, and the adiabatic heating at the crack-tip, which causes blunting of the crack through excessive yielding. In the tests carried out in this study the latter effect is not applicable owing to the low strain rate and the very small sample thickness, which do not allow the temperature to rise appreciably. Therefore, an explanation based on molecular relaxations seems reasonable to understand the experimental fracture results.
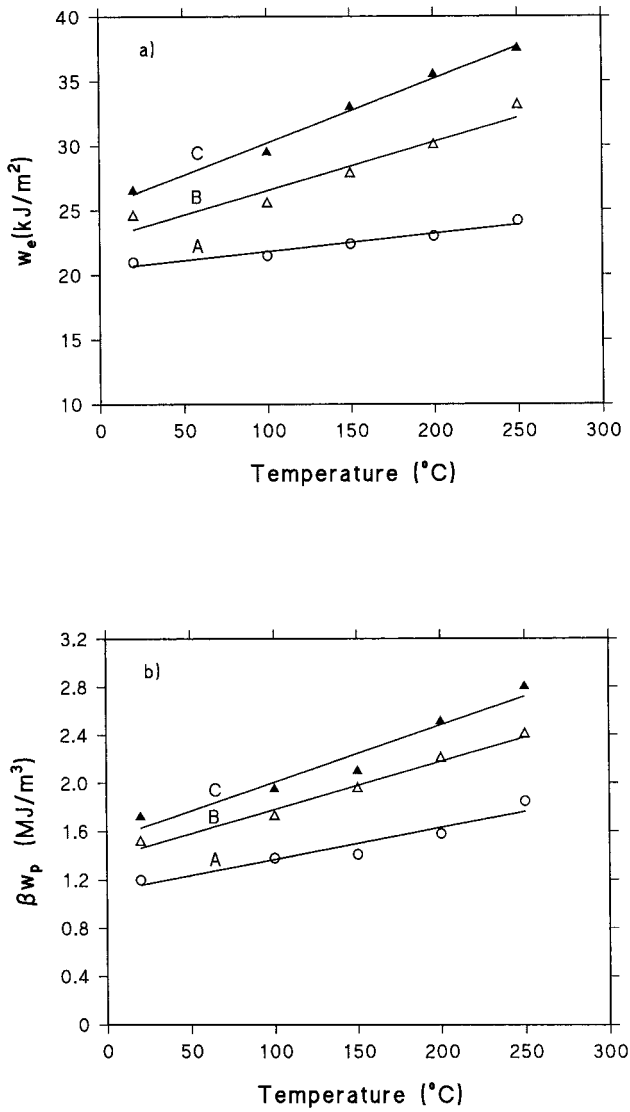
Figure 3. (a) Essential work of fracture, w_e, and (b) non-essential work of fracture, βw_p, as a function of temperature: A) polyimide; B) composite with 10 wt% of silica; C) composite with 15 wt% of silica.

In figure 4 are shown the dynamic mechanical spectra in term of tanδ for the hybrid samples and the parent polyimide as a function of temperature. This plot reveals the occurrence of a well defined primary relaxation peak around 400°C, corresponding to the T_g, and a broad secondary relaxation (β transition) at lower temperature. Since this transition covers the range from 0 °C to 200 °C for all three systems, it can be deduced that the contribution to the energy absorption for pure polyimide arises mainly from the molecular relaxations associated with the β transition.
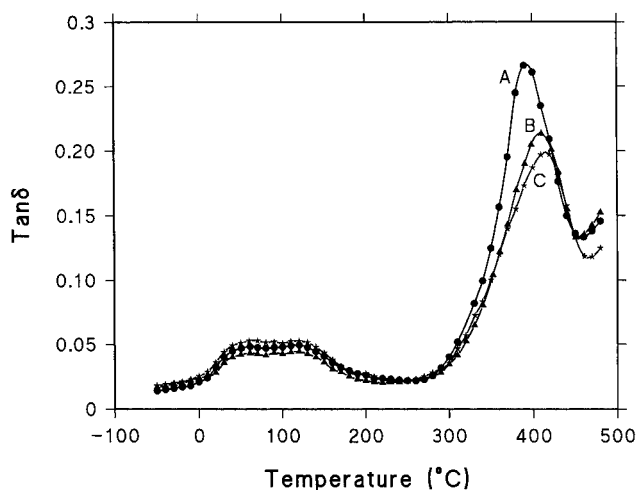

Figure 4. Tanδ as a function of temperature: A) polyimide; B) composite with 10 wt% of silica; C) composite with 15 wt% of silica.

Because of the rigidity of polyimide chains, and their associated tendency to assume a planar orientation, it is possible that the onset of yielding is controlled by this β transition. Accordingly, the small effect of temperature on w_e may be attributed to the broadness of the secondary transition, which covers the entire temperature range of the tests. The more pronounced dependence of the plastic parameter, βw_p, with temperature (Fig. 3b), on the other hand, is likely to arise from larger scale chain motions during yielding, which require

a high activation energy.

For the case of polyimide-silica systems some additional energy absorption mechanisms have to be invoked to explain the higher values of the work-fracture parameters, relative to those of the parent polyimide. A deeped understanding of these mechanisms and their dependence on temperature is given in the next paragraph where the results of a fractographic analysis performed on the hybrid composites are reported.

Morphological analysis

In Figure 5 (A, and B) are shown the SEM micrographs of the fracture surfaces of the ligament area of composites with 10, and 15 wt% of silica tested at ambient temperature. These reveal that the adhesion between polyimide and silica particles is very low and that the size of the particles increases slightly with increasing silica content. In particular the average diameter of particles was found to be 0.31 μm (standard deviation ± 0.15) for the composite with 10 wt% of silica and 0.47 μm (standard deviation ± 0.11) for that containing 15 wt% of silica.

The SEM micrographs in Figure 5 also show that the silica particles bring about failures dominated by interface-initiated cavitations. This mechanism is known to take place in particulate composites with spherical particles when the matrix modulus is lower than that of the particles[29]. In particular, due to poor adhesion between particles and matrix, the debonding process takes place at both equator and pole regions of the particles. The debonding of the matrix from the particles relaxes the local interfacial stresses and may be considered to be responsible for a change to plane stress conditions within the matrix, thereby promoting shear yielding. Therefore two deformation mechanisms are effective in these composites, cavitations and shear yielding.

A mixed mode of fracture dissipates a large amount of energy. This becomes operative when the interparticles distance or the matrix ligament thickness is small. According to the Wu's criterion when, the distance, τ, between the outer surfaces of two particles is below a critical value, there is an overlapping of the localized stress fields around adjacent particles, which causes yielding of the matrix and interfacial cavitations[30]. The surface-to-surface critical distance is a function of the particle diameter, d, and volume fraction, V_f of the particles, and can be determined from the following equation:

$$\tau_c = d\left[\left(\frac{\pi}{6V_f}\right)^{\frac{1}{3}} - 1\right] \qquad (3)$$
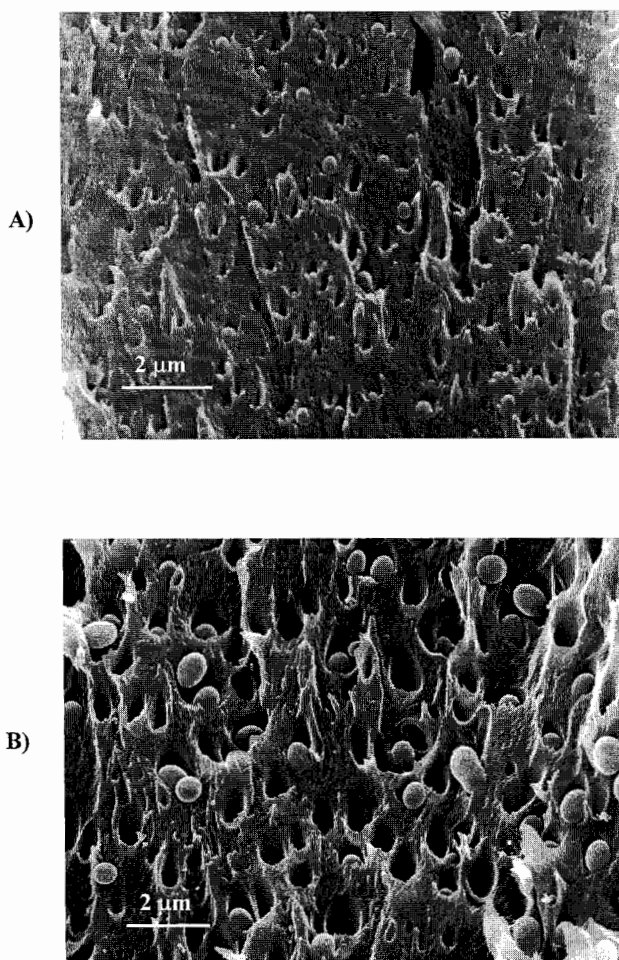

Figure 5. SEM pictures of fractured surfaces of composites tested at ambient temperature: A) composite with 10 wt% of silica; B) composite with 15 wt% of silica.

The volume fraction of silica, V_f, can be calculated from the weight fraction, W_f, using the relationship[31]:

$$V_f = \frac{\rho_m W_f}{[(\rho_m - \rho_s)W_f + \rho_s]} \qquad (4)$$

where ρ_m and ρ_s are the densities of polyimide (1.409 g cm^{-3}) and the silica phase (1.974 g cm^{-3}) respectively. These were experimentally determined at 20 °C, using a hydrostatic balance, on films produced from the two separate components.

For the systems examined, $W_f = 0.1$ corresponds to $V_f = 0.073$ and $W_f = 0.15$ corresponds to $V_f = 0.117$. By substituting these values and the corresponding average particles diameters in equation 7, the critical surface to surface distance values obtained are respectively $\tau_c = 0.28$ μm for the composite with 10 wt% of silica and $\tau_c = 0.30$ μm for the composite with 15 wt% of silica.

Since the two values for τ_c are very close, any difference in fracture toughness between the two systems has to be connected to the difference in energy consumed through microcavitations rather than plastic deformations.

A comparison of the fractographs in Figure 6 for samples tested at 200 °C with those in Figure 5 for the same samples tested at room temperature, suggests that the fracture energy contribution from plastic deformations may be greater at higher temperature.

The plots in Figure 3, however, show that the rate of increase in w_e values on temperature, for the particulate composites relative to the parent polyimide, is much higher than the respective rate of increase of βw_p with temperature, i.e.

$$(\mathrm{d}w_e/\mathrm{d}T)_{\mathrm{composite}}/(\mathrm{d}w_e/\mathrm{d}T)_{\mathrm{polyimide}} > (\mathrm{d}\beta w_p/\mathrm{d}T)_{\mathrm{composite}}/(\mathrm{d}\beta w_p/\mathrm{d}T)_{\mathrm{polyimide}}$$

Since energy absorption through cavitations is more likely to have a larger effect on the w_e values than the βw_p values, it can be deduced that these may constitute the main mechanism responsible for the enhancement of fracture toughness in particulate composites where the interfacial adhesion is very low.

Accordingly, the embrittlement often observed at higher filler loadings could be attributed to a large reduction in energy absorbed through yielding, owing to the inability of achieving conditions for plane-stress. This reduces the extent of cold drawing of the matrix during yielding, due to the onset of the fracture process taking place at lower strains. Such low strain failure would also reduce the total amount of energy used for cavitations as the surface area of the cavities at fracture would be smaller.
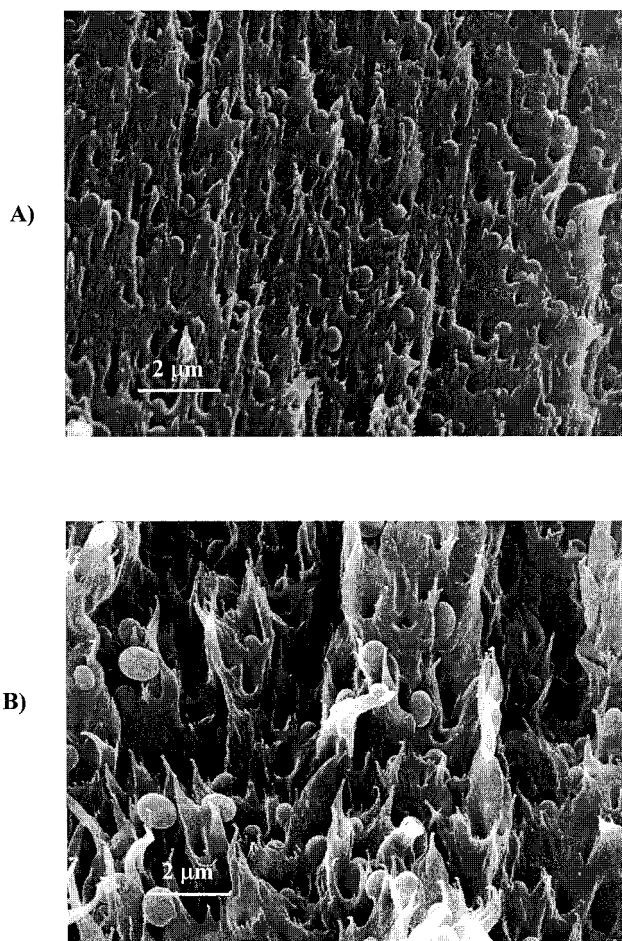
Figure 6. SEM pictures of fractured surfaces of composites tested at 200°C: A) composite with 10 wt% of silica; B) composite with 15 wt% of silica.

Conclusions

The main conclusions that can be drawn from this study are as follows:

- The incorporation of submicron silica particles in the polyimide matrix, by the sol-gel method, brings about a considerable enhancement in fracture toughness

- The effect of testing temperature on the values of the EFW parameters is much greater when silica particles are present. In all cases, however, both the essential work, w_e, and the non-essential work, βw_p parameters increase

linearly with temperature.

- The above trend for the toughness parameters is reflected by the failure behaviour of the materials. For the case of composites the silica particles induce interfacial cavitations and shear yielding of the polyimide matrix. The contribution of each of the two energy dissipative mechanisms depends on temperature. The results suggest that interface-initiated cavitations may be the major factor responsible for the enhancement of fracture toughness exhibited by particulate composites

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