

Fracture behaviour of long fibre reinforced thermoplastics

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This paper deals with the fracture performance of injection moulded long glass fibre composites based on polybutylene terephthalate (PBT) and polypropylene (PP) matrices. The tensile behaviour of these composites is analysed using the shear lag theory taking into consideration the interfacial shear strength, fibre length distribution and fibre orientation in the mouldings. The fracture performance is investigated using the post yield fracture mechanics approach. The crack growth resistance of the PP and PBT long fibre composite was found to increase with increasing fibre volume content up to 35%. Above 35% a plateau in the fracture performance was observed. A combination of high fibre degradation and a change in the fibre orientation pattern of the moulded pieces is found to be responsible for the plateau region in the performance of the high concentration system. In fact, the dependence of the maximum crack growth resistance of the composites on fibre length and fibre orientation is also controlled by testing temperature. The competition between fibre-induced matrix deformation and the fibre pull-out determines the ability of the composites to resist crack propagation.

1. Introduction

Previous investigations carried out on discontinuous fibre thermoplastic composites [1–7] processed by injection moulding have shown that longer fibres lead to an increase in stiffness, strength and impact properties of the materials. Moreover, taking into account the fibre degradation, fibre orientation and interfacial shear strength in the material, it has been found that the shear lag theory is adequate to predict the tensile strength of the injected long fibre composites [2]. It is also well known that the addition of fibres to a thermoplastic matrix results in a reduction of strain at break, and therefore a relatively brittle material. Consequently, fracture toughness is an engineering property of great interest. Factors affecting the toughness of thermoplastic composites have been extensively investigated [8–14]. The toughness of these composites has been found to be strongly governed by the competition between shear yielding and voiding in the matrix. Shear yielding occurs around the reinforcement, due to debonding at the reinforcement–matrix interface, and results in a stretching effect of the matrix which leads to an increase in the crack growth resistance of the composite. Voiding occurs in the matrix and dissipates much less energy. The reinforcement content can be optimized in order to maximize the matrix stretching. The shape of the reinforcement is another major parameter in the fracture process. Two-dimensional fillers (flakes) act in the same way as three-dimensional fillers (spheres) and, for these classes of reinforcement, a unique relationship between the maximum crack growth resistance and the average distance between particles has been observed, regard-

less of the nature of the filler [12]. In the case of the fibres, preliminary work [14] suggested that there is a critical fibre length which results in a lowest crack growth resistance. Below the critical length, the matrix stretching seems to be dominant and above the critical length, fibre pull-out enhances the dissipation of energy in the fracture process. However, while injection moulding of the long fibre pellets leads to a composite in which fibre length is much higher than that in conventional injection grades of reinforced thermoplastic matrices, significant fibre breakage occurs during injection moulding [15–19]. In fact, the long fibre composite is characterized by a wide distribution of fibre lengths ranging from 0.3 to 10 mm. Recent works of Friedrich and coworkers on polyamide [20] and polypropylene [21] reinforced with short and long glass fibre have shown that the addition of longer fibres generally increased the toughness of the material over shorter fibre filled material, although the magnitude of the increase was found to be highly test dependent.

In this work the fracture behaviour of glass fibre reinforced polypropylene (PP) and polybutylene terephthalate (PBT) is investigated. The effects of fibre length, fibre content and testing temperature on crack growth resistance is discussed in terms of crack growth resistance during quasi-static crack propagation [8, 9].

2. Experimental procedure

The long fibre composites investigated in this study are based on two different thermoplastic matrices:

polybutylene terephthalate (PBT) and polypropylene (PP), supplied by Baycomp, Canada. The glass fibre diameters were, respectively, 21.46 and 17.9 mm for the PBT and the PP materials.

Long fibre pellets were supplied in a concentrated form, the compositions being 54% by volume for the PBT composite and 36.4% by volume for the PP composite. In order to study the effects of fibre concentration in these materials, samples of various compositions were obtained by dry blending the concentrated long fibre pellets with pellets of pure resin. Long fibre pellets of PBT and PP of 12 and 13 mm lengths, respectively, were processed using a standard injection moulding press. In order to prevent extensive fibre breakage during the moulding, a nozzle of 7.9 mm diameter, a runner system of 6.4 mm diameter, and large rectangular gates of 6.4 × 3.2 mm were used. Tensile test pieces of ASTM D-638 Type 1 were moulded.

Three-point bend specimens of 3 × 12 × 80 mm, cut from the gauge length section of the injection moulded tensile bars were used for all fracture tests. The initial crack length, a_0 , was 4.8 mm, giving a ratio of initial crack length to specimen width, a_0/D , of 0.4. A pre-notch was first made by a saw cut and the final crack was created by forcing a razor blade into the specimen in a special jig on a laboratory press, giving a crack tip radius of less than 30 μm.

Fibre degradation during the injection moulding process was characterized by measuring the fibre length distribution in the moulded samples. Due to the wide range of fibre lengths present in the sample (0.3–13 mm), two different techniques were used to construct the complete distribution. Glass fibres were isolated from the samples by burning off the resin in an oven and separating it into two portions (< 1 and > 1 mm) by sieving. The amount of fibre in each fraction was weighed and analysed to determine the number and length. The fraction of short fibre (< 1 mm) was analysed with an automatic particle size analyser PA-720 adapted for fibre analysis [22]. The fraction of long fibre (> 1 mm) was analysed with a semi-automatic image analyser developed in the laboratory. The two fibre length distributions were combined, taking into account their relative weights. The complete fibre length distribution was obtained after analysing approximately 5000 fibres < 1 mm and 2000 fibres > 1 mm.

A scanning electron microscope (type Jeol 35CF) was used for the microstructural analysis. The fracture tests were performed on a standard testing machine (Instron, Model 1125).

3. Results and discussion

For isotropic materials, the stress intensity factor in three-point bend samples has been well established and is given by

$$K_I = \frac{PS}{BD^{3/2}} f\left(\frac{a}{D}\right) \quad (1)$$

where P is the load, S is the support span, B is the specimen thickness, D is the specimen width, a is the

crack length and $f(a/D)$ is a calibration factor defined in [23].

It is well known that injection moulding of fibre reinforced thermoplastics results in preferential orientation of the fibres in the moulded part, due to laminar flow during filling of the mould. Consequently, for these rather anisotropic materials, the above equation must be verified in order to characterize the material's fracture toughness. From the above equation, the calibration factor includes the effect of crack length on specimen compliance. With the definition of the strain energy release rate

$$G_I = \frac{1}{2} P^2 \frac{dC}{dA} \quad (2)$$

and

$$EG_I = (1 - \nu^2) K_I^2 \quad (3)$$

in which C is the specimen's compliance, E is the material's modulus, A is the crack area and ν is Poisson's ratio, the specimen compliance can be determined.

$$C = C_0 + \frac{9(1 - \nu^2)}{2EB} \left(\frac{L}{D}\right)^2 \int_0^{a/D} f\left(\frac{a}{D}\right) d\left(\frac{a}{D}\right) \quad (4)$$

where C_0 is the specimen's compliance when $a = 0$.

In the case of three-point bending tests on orthotropic materials, it is reasonable to use an effective flexural modulus instead of the material's true Young's modulus in order to calculate the specimen's compliance. Fig. 1 shows the comparison between the calculated and the measured compliances as a function of crack length for the injection moulded three-point bend samples. The results suggest that the above calibration factor reflects reasonably well the effect of the crack in these samples. Equation 1 is thus used to determine the critical stress intensity factor. Since it has been shown for several thermoplastic composites [8, 10, 13] that the role of fillers on fracture performance is rather essential during the crack propagation period, the critical stress intensity factor was

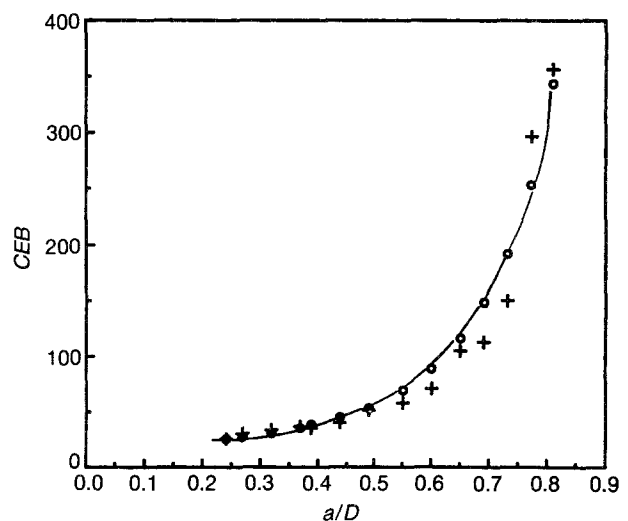


Figure 1 Variation of the calculated (○) and the measured (+) compliance as a function of crack length for the injection molded three-point bend samples of PP long fibre composite of 15.7% V_f .

determined as a function of crack growth, in the same manner as that discussed previously [8–11], and the maximum crack growth resistance in the composite, K_{Rmax} , is used to represent the material's fracture performance.

Fig. 2 shows the variation of the maximum crack growth resistance, K_{Rmax} , at 25 °C, of the long fibre reinforced PP and PBT as a function of fibre volume fraction, V_f . It can be seen that the addition of long fibre in the PP matrix leads to substantial increase in K_{Rmax} . However, in the PBT matrix, the addition of a small fraction (4.9%) of long fibre first reduces the fracture performance, but a subsequent increase of fibre content results in a significant increase in K_{Rmax} as in the case of PP composites. In both cases, it can also be observed that the composite crack growth resistance increases with increasing fibre content up to about 35% by volume. Above 35%, increasing fibre content seems to result in very little change in fracture performance of the composites. While it has been shown that at very high filler concentration the fracture toughness of composites can decrease abruptly due to the lack of matrix material [8, 9, 14, 24], a combination of high fibre attrition and change in fibre orientation in the flow direction could also be responsible for the observed levelling off in fracture performance. The variation of fibre orientation in the composites of various fibre contents can be observed by microscopic examination of the polished transverse section of the injection moulded samples.

The micrographs of the polished transverse sections of moulded samples (ASTM-D638 Type 1) of the PBT composite with two different fibre contents are shown in Fig. 3. It can be seen that layers of different fibre orientations are present across the thickness of the injected specimen in a classical skin–core structure, as often observed in injection molded fibre reinforced thermoplastics [20, 21, 25–30]. The micrographs show that an increase in fibre concentration produces an increase in the dimension of the core section.

The effect of fibre concentration on fibre attrition is reported in Table I, in which the number average fibre

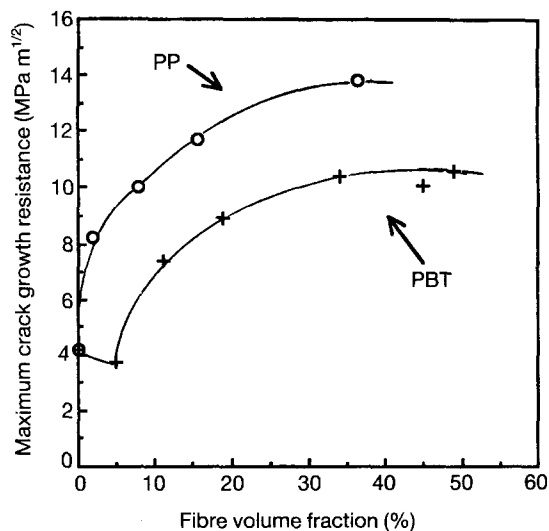


Figure 2 Variation of K_{Rmax} of long fibre reinforced PP and PBT as a function of V_f , at 25 °C.

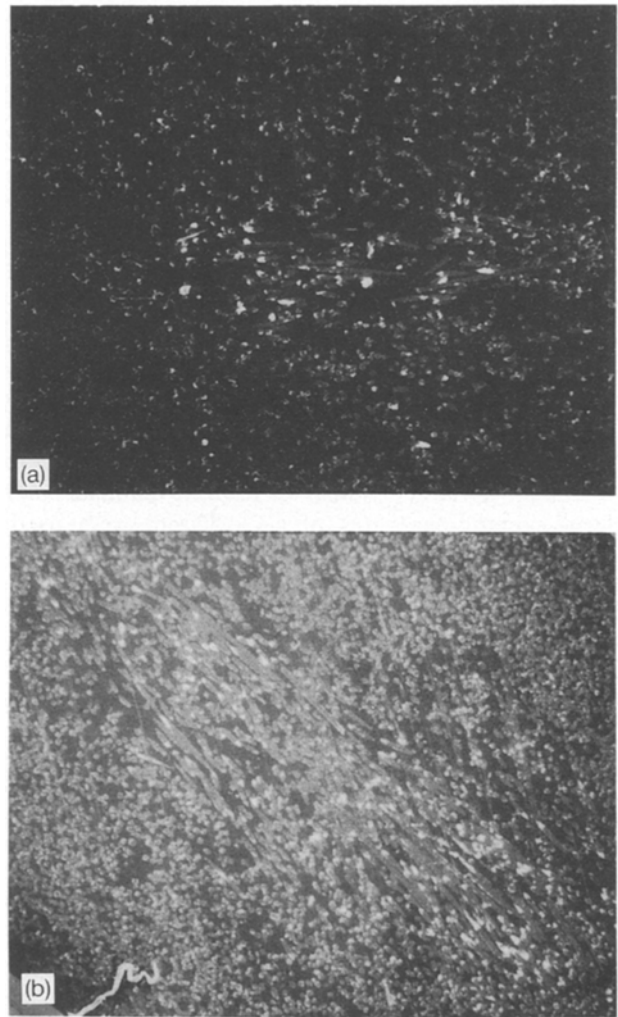


Figure 3 Micrographs of polished transverse sections of tensile specimens (ASTM-D638 Type 1) of PBT long fibre composites with two different fibre volume fractions: (a) 11.1%, and (b) 49%.

TABLE I Number average fibre length in PBT and PP reinforced by long glass fibres

PBT composite		PP composite	
V_f	l (mm) Average (number)	V_f	l (mm) Average (number)
4.9	1.77	2.0	–
11.1	1.40	7.9	2.18
19.0	1.18	15.7	1.68
33.9	1.00	36.4	0.88
45.0	–	15.7	0.80
49.0	0.72	15.7	0.20

length is shown for both composites at various fibre concentrations. It is clear that increasing fibre content results in more severe fibre degradation in the composites. Higher melt viscosity, as well as higher fibre contact during injection moulding of the concentrated system, could be responsible for the more severe damage. It is worth noting that, in spite of the strong reduction of average fibre length in the highly filled system, fibres of up to 10 mm length are still present in

these samples. Thus, the increase in the core region, along with greater fibre degradation, should also play an important role in the levelling off in the fracture performance of the composites at high fibre concentration.

The effect of fibres at low concentration on the fracture performance of PP and PBT is rather surprising, since it is in contradiction with the results observed by Friedrich [25] which showed that a decrease in fracture toughness could occur at low fibre concentration if the matrix is ductile. In fact, the neat PP and PBT exhibit an elongation at fracture of about 400% and 7%, respectively. The drop in fracture performance at low fibre concentrations would therefore be expected to be more pronounced in PP. It should be noted, however, that the reported data [25] are based on the fracture toughness at crack initiation, whereas in this work, fracture performance is discussed in terms of maximum crack growth resistance. In the presence of a sharp crack, there is a strong difference between the fracture processes in PP and PBT. The macroscopically ductile PP breaks in a purely brittle manner at a constant deflection, without any visible plastic deformation; whereas in the more brittle PBT, stable crack propagation occurred before unstable fracture. On the microscopic scale, it is well known that the fracture behaviour of discontinuous fibre reinforced thermoplastics can result from various micromechanisms of the failure process associated with the three basic components in the composite: the fibres, the matrix and the interface. The failure mechanisms related to the fibres are either fibre debonding and pull-out, or fibre fracture. In addition, the fibre ends can act as a sites of stress concentration in the matrix, inducing voids at fibre ends from which crazing or shear yielding of the polymer matrix may initiate. It is well known that the occurrence of these mechanisms depends on many factors, such as fibre tensile strength, matrix ductility, interfacial adhesion, fibre geometry and orientation. The difference in fracture behaviour between the PP and the PBT composites with low fibre content (Fig. 2) might be

explained by the microscopic plastic deformation behaviour of these matrices. The reduction in K_{Rmax} with a small addition of fibres observed for the case of PBT matrix suggests that, as opposed to the case of PP, the amount of microscopic plastic deformation by shear stresses around the voiding regions, initiated at fibre ends, is not sufficient to prevent the formed voids from propagating under triaxial stresses. Fracture becomes completely unstable.

Fig. 4 shows that augmenting the amount of shear yielding in the matrix by increasing the temperature results in a more significant drop of K_{Rmax} at low fibre concentration, although the fracture process in the neat PBT becomes more stable. The results would suggest that plastic deformation in the PBT matrix is rather related to voiding and/or crazing which, at low fibre concentration, are very localized around fibre matrix debonding at fibre end regions, and are not able to prevent the initiated microcracks from propagating, resulting in unstable fracture and low K_{Rmax} values.

The competition between the microcracks initiated by fibre-matrix debonding at the fibre ends and the microscopic deformation in the matrix can also be observed in the case of PP as shown in Fig. 5. In this figure, the variation of K_{Rmax} in PP reinforced by 15.7 vol % glass fibre is plotted as a function of the average fibre length, at 25°C. As the number average fibre length increases, the number of fibre ends decreases and the amount of microscopic plastic deformation initiated by fibre matrix debonding around fibre end regions is reduced, resulting first in a reduction in K_{Rmax} . As discussed in previous works [8], the PP matrix is prone to stretch under shear or uniaxial stresses, but triaxial stresses result in coalescence of voids and unstable fracture. There is therefore a critical number of voids required in order that the amount of plastic deformation by shear stresses around the formed voids becomes efficient to prevent void coalescence and unstable fracture. At low fibre length, K_{Rmax} increases as the number of voids initiated augments. At higher fibre length, although the number of formed

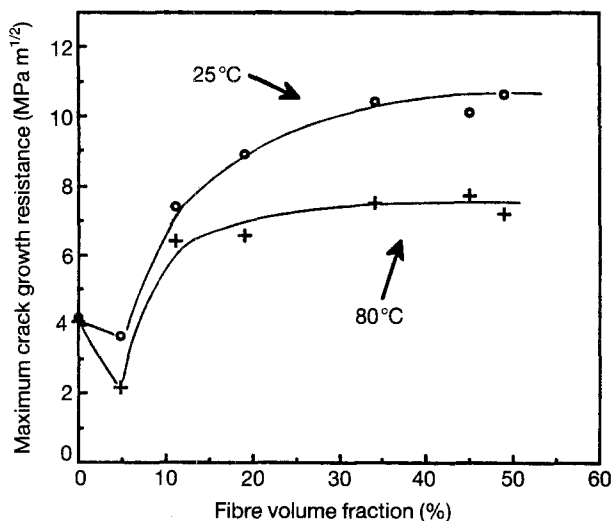


Figure 4 Variation of K_{Rmax} of long glass fibre reinforced PBT as a function of V_f , at 25 and 80°C.

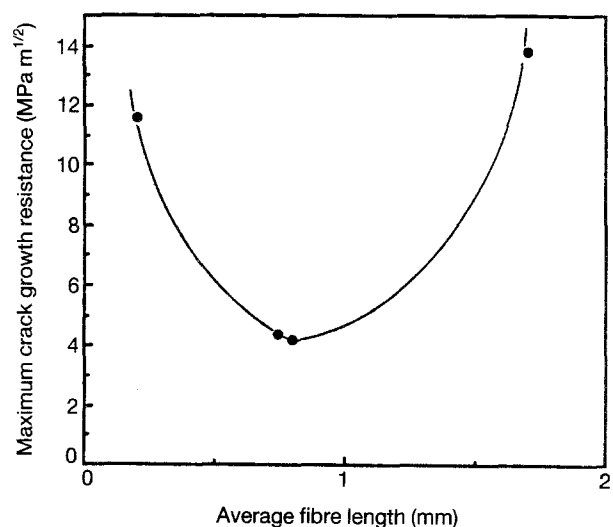


Figure 5 Variation of K_{Rmax} of glass fibre-PP composites at 15.7% V_f as a function of average fibre length, at 25°C.

voids is reduced, fibre rupture and pull-out may become predominant, resulting in an increase in K_{Rmax} with fibre length. The SEM micrographs of the fracture surfaces of the PP composites of various average fibre lengths are shown in Fig. 6. From this figure, it can be observed that the fracture surfaces in the cases of long (Fig. 6a) and very short (Fig. 6c) fibres are characterized by a high level of matrix deformation with respect to the case of medium average fibre lengths. These microscopic observations show that for the shorter fibre composite, characterized by a high number of fibre ends, matrix stretching is very significant. In the case of very long fiber composite, fiber pull-out also seems to enhance matrix deformation. The

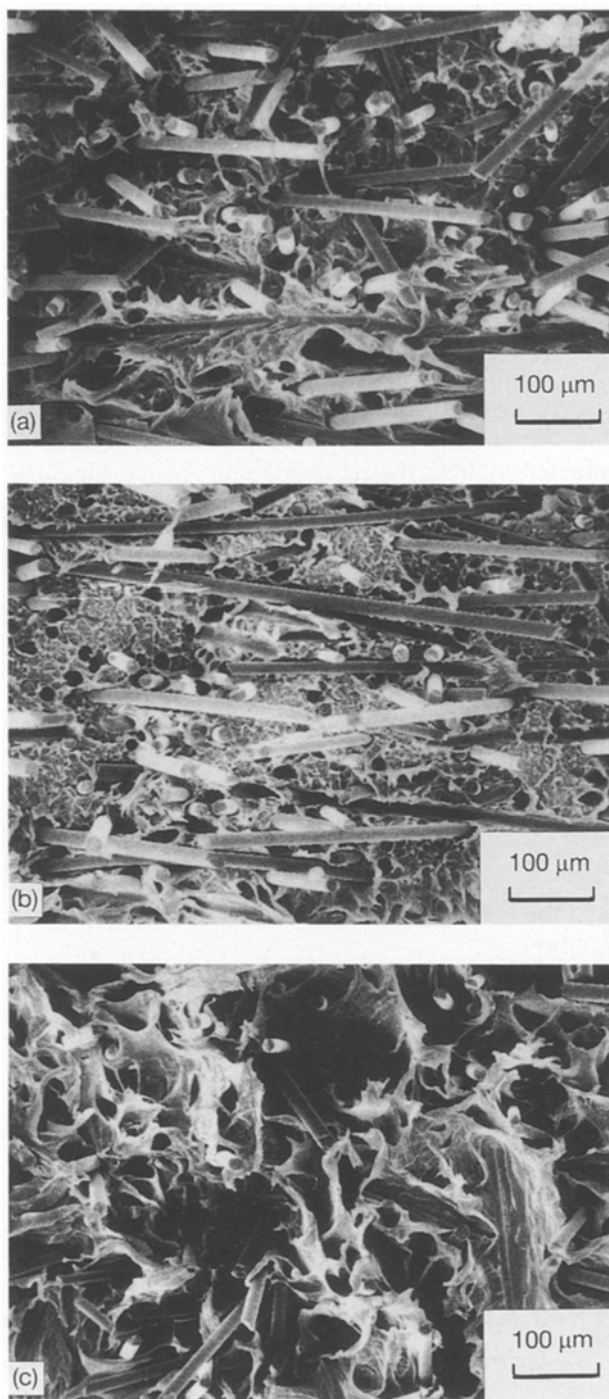


Figure 6 Micrographs of the fracture surfaces of glass fibre PP composites with 15.7% V_f , glass fibres of different number average lengths: (a) 1.68 mm, (b) 0.8 mm, and (c) 0.2 mm.

observed reduction of microscopic stretching of the matrix at intermediate fibre lengths suggests that there exists a critical competition between the initiated voids and shear yielding, resulting in a minimum microscopic stretching of the matrix which, in general, is the most energy dissipating mechanism of plastic deformation.

In order to verify the role of the microscopic stretching of the matrix in the cases of short and long fibre composites, fracture tests were carried out at low temperature. Fig. 7 shows the variation of K_{Rmax} as a function of fibre length at -30°C . Decreasing the testing temperature from 25 to -30°C leads to a decrease of K_{Rmax} of the very short fibre composite from $11.63^{1/2}$ to $5.96 \text{ MPa m}^{1/2}$ and a slight increase in K_{Rmax} of the long fibre composite. The results demonstrate that with very short fibres, the crack growth resistance of the composite is mainly governed by the matrix. With long fibres, although matrix stretching is more important than in the case of intermediate fibre length, fibre pull-out plays a more important role in the fracture process.

From the above results, it appears important to further analyse the effect of temperature on the competition between fibre induced matrix deformation and the fibre pull-out process. Fig. 8 shows the variation of K_{Rmax} as a function of temperature for PP containing various long glass fibre concentrations. It can be seen that as the temperature varies, the maximum crack growth resistance of PP and PP composites with low fibre volume fractions remains almost constant. However, at high fibre volume fractions the maximum crack growth resistance of the composite varies strongly with temperature. Furthermore, in the range of temperatures investigated, the fracture performance of the composite increases with increasing fibre content and the effect of fibre concentration is more and more pronounced as the temperature is lowered. It is obvious that in the case of high fibre volume fractions the maximum crack growth resistance in the composite is controlled by the fibres, via fibre breakage and fibre pull-out processes. When the

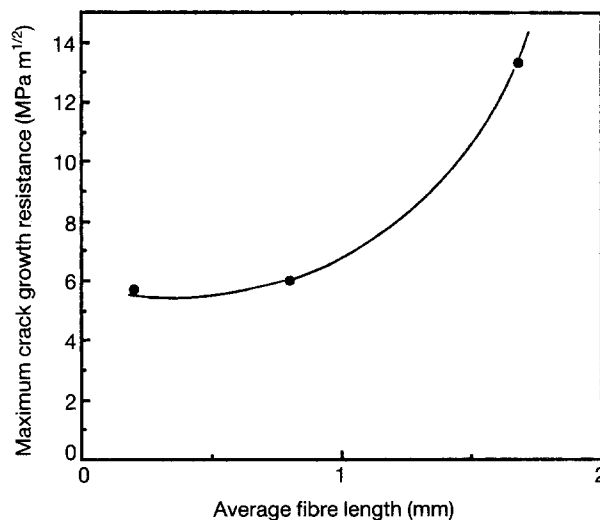


Figure 7 Variation of K_{Rmax} of glass fibre PP composite at 15.7% V_f as a function of the number average fibre length, at -30°C .

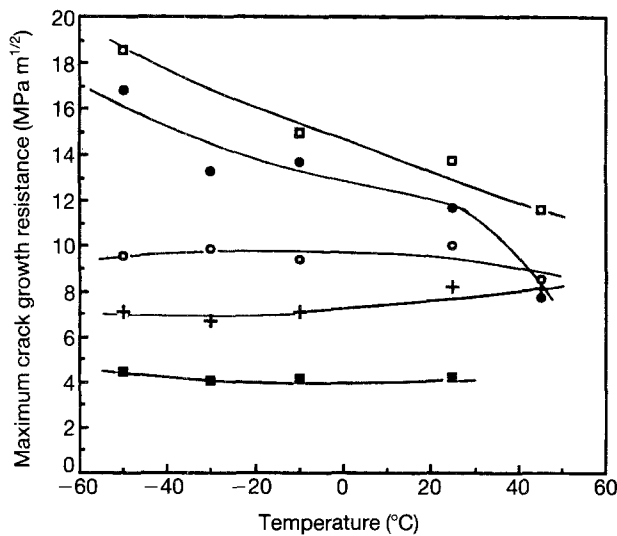


Figure 8 Variation of K_{Rmax} as a function of testing temperature for pure PP (■) and PP composites of various fibre volume contents: (+) 2%, (○) 7.9%, (●) 15.7%, and (□) 36.4%.

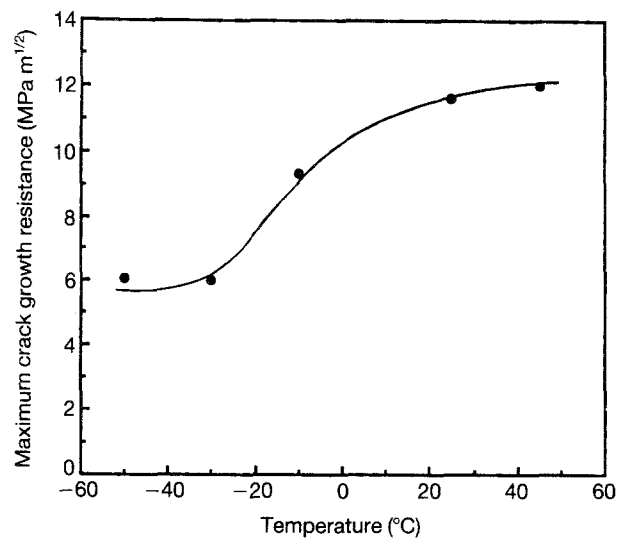


Figure 9 Variation of K_{Rmax} as a function of testing temperature for a glass fibre PP composite at 15.7% V_f with a number average fibre length of 0.2 mm.

temperature is reduced, the toughness improving effect due to the fibre has been shown to be enhanced [24] because of higher thermal contraction of the matrix compared to that of the fibres, resulting in a higher pull-out energy. In this composite, the number average fibre lengths vary between 2.18 and 0.88 mm (see Table I). As discussed above, the fracture toughness of the composite in the case of relatively long fibres is mainly controlled by the pull-out process and the higher crack growth resistance at lower temperature can be explained by the same mechanism as that suggested [24]. However, the fact that the maximum crack growth resistance in the composite with low fibre volume fraction does not augment with decreasing temperature is rather surprising. Since significant improvement in fracture performance is observed at low fibre volume fraction, the role of the fibres can be explained in the same manner as that in the case of high fibre volume fraction and one can also expect an increase in fracture performance with decreasing temperature. A possible explanation of the observed constant K_{Rmax} as a function of temperature is the competition between the role of the matrix and that of the fibres. As shown in Fig. 6, the microscopic stretching of the PP matrix is found to be more significant in the cases of very short and relatively long fibres. Consequently, it should also contribute significantly to the fracture process. When the temperature decreases, the toughness improving effect due to microscopic stretching of the matrix must be reduced since the shear yield stress of the matrix increases. This reduction probably compensates for the increase in the toughness improving effect due to fibre pull-out when the temperature is lowered, resulting in an insignificant change in the maximum crack growth resistance.

The reduction of microscopic stretching of the matrix with decreasing temperature can be demonstrated by Fig. 9 where the maximum crack growth resistance of PP containing 15.7 vol % very short fibres is plotted as a function of temperature. The results clearly show that when the fibres are short, the pull-out

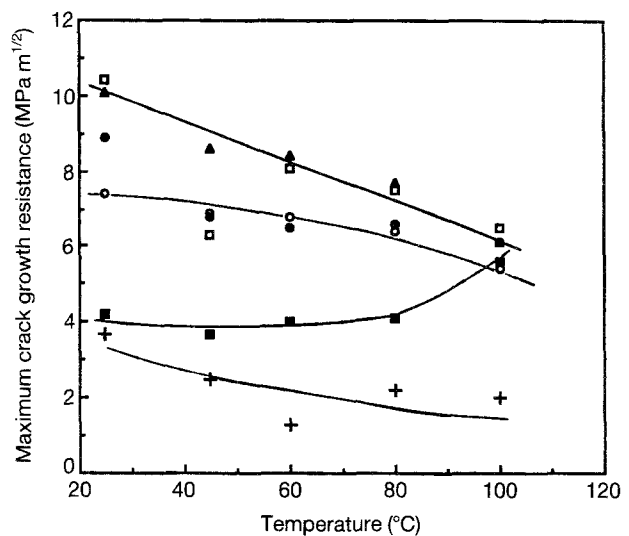


Figure 10 Variation of K_{Rmax} as a function of testing temperature for pure PBT (■) and PBT composites of various fibre volume contents: (+) 4.9%, (○) 11.1%, (●) 19.0%, (□) 33.9%, and (▲) 45.0%.

process is not significant and the improvement in toughness with fibre addition is rather due to the microscopic stretching of the matrix, induced by fibre-matrix debonding. When the temperature decreases this mechanism is reduced, resulting in a strong reduction in the maximum crack growth resistance. The result thus supports the above hypothesis on the competition between the matrix and the fibres at low fibre volume fraction.

The variations of the maximum crack growth resistance as a function of temperature in PBT composites with various fibre concentrations are shown in Fig. 10. In this case, except for the neat PBT, regardless of fibre content, the maximum crack growth resistance of the composites increases as the temperature decreases. The results suggest therefore that fibre pull-out controls the crack propagation process. As opposed to the case of PP matrix, the microscopic plastic deformation in the matrix induced by the fibres is detrimental

in preventing crack propagation. At low fibre concentration, when the fibre pull-out process is not dominant, the maximum crack growth resistance is reduced and this reduction is more important when the temperature increases. The crack propagation in the neat PBT matrix is stable, but with the addition of a small amount of glass fibres it becomes unstable. The minimum in the K_{Rmax} value would therefore correspond to the critical fibre volume fraction below which the matrix controls the fracture process and above which the role of the fibres becomes effective.

4. Conclusions

When the glass fibres are relatively long and at high concentration, fibre pull-out governs the crack propagation process in both PP and PBT matrices. However, at low fibre concentration, although the same mechanism exists, the microscopic plastic deformation in the matrix, induced by the presence of the glass fibre, can play a dominant role. Depending on their nature, the microscopic plastic deformations can be beneficial or detrimental to the composite's toughness. There is critical competition between fibre induced local plastic deformation and fibre pull-out, which leads to a minimum crack growth resistance in the composite.

The minimum crack growth resistance in the long glass fibre reinforced PBT corresponds to a critical fibre volume fraction which is required in order for the fibres to contribute significantly to the fracture process. Below this critical volume fraction, the fibres induce local plastic deformation in the matrix and become detrimental in terms of fracture toughness.

In the case of the PP matrix, the microscopic plastic deformation in the matrix induced by the glass fibres is always beneficial with respect to the crack growth resistance of the composite. However, the fibre length can affect the extent of the local stretching in the matrix. At a certain range of fibre lengths, the local stretching in the matrix can be a minimum and the composite's toughness can be reduced.

References

1. M. G. BADER and W. H. BOWYER, *Composites* **4** (1973) 150.
2. D. A. CIANELLI, J. E. TRAVIS and R. S. BAILEY, *Plast. Technol.* **34** (1988) 83.
3. W. H. BOWYER, and M. G. BADER, *J. Mater. Sci.* **7** (1972) 1315.
4. M. G. BADER and J. F. COLLINS, Proc. 4th Int. Conf. Compos. Mater., ICCM-IV, edited by T. Hayashi, K. Kawata and S. Umekawa (Tokyo, 1982) p. 1067.
5. P. T. CURTIS, M. G. BADER and J. E. BAILEY, *J. Mater. Sci.* **13** (1978) 377.
6. F. RAMSTEINER and R. THEYSON, *Composites* **10** (1979) 111.
7. M. W. DARLINGTON, B. K. GLADWELL and G. R. SMITH, *Polymer* **18** (1977) 1269.
8. T. VU-KHANH, B. SANSCHAGRIN and B. FISA, *Polym. Compos.* **6** (1985) 249.
9. J. DENAULT and T. VU-KHANH, *ibid.* **9** (1988) 360.
10. T. VU-KHANH and B. FISA, *ibid.* **7** (1986) 375.
11. *Idem*, *ibid.* **7** (1986) 219.
12. T. VU-KHANH, *J. Thermoplast. Compos. Mater.* **4** (1991) 46.
13. T. VU-KHANH and B. FISA, *Theoretical and Appl. Fract. Mech.* **13** (1990) 11.
14. T. VU-KHANH, Proc. Fifth Techn. Conf. of the American Society for Composites (Technomic Publishing, East Lansing, MI, 1990) p. 309.
15. J. DENAULT, T. VU-KHANH and B. FOSTER, *Polym. Compos.* **10** (1989) 313.
16. B. SCHIMD, *Kunstst Plast.* **79** (1989) 39.
17. R. BAILEY and H. KRAFT, *Intern. Polym. Process.* **2** (1987) 94.
18. R. BAILEY, Proc. SPE 36th Annual Techn. Conf. (ANTEC '90, Dallas, TX, 1990) p. 1339.
19. T. VU-KHANH, J. DENAULT, P. HABIB and A. LOW, *Compos. Sci. Technol.* **40** (1991) 423.
20. J. KARGER-KOCSIS and K. FRIEDRICH, *ibid.* **32** (1988) 293.
21. D. E. SPAHR, K. FRIEDRICH, J. M. SCHULTZ, and R. S. BAILEY, *J. Mater. Sci.* **25** (1990) 4427.
22. B. FISA, *Polym. Compos.* **6** (1985) 232.
23. E-399 Standard Test Method for Plane Strain Fracture Toughness of Metallic Material, Annual Book of ASTM Standards (1983).
24. K. FRIEDRICH, *Plast. Rubber Process. Appl.* **3** (1983) 255.
25. *Idem*, *Compos. Sci. Technol.* **22** (1985) 43.
26. J. KARGER-KOCSIS and K. FRIEDRICH, *Composites* **19** (1988) 105.
27. K. FRIEDRICH, R. WALTER, H. VOSS and J. KARGER-KOCSIS, *ibid.* **17** (1986) 205.
28. M. W. DARLINGTON, P. L. MCGINLEY and G. R. SMITH, *J. Mater. Sci.* **11** (1976) 877.
29. P. F. BRIGHT, R. J. CROWSON and M. J. FOLKES, *ibid.* **13** (1978) 2497.
30. P. F. BRIGHT and M. W. DARLINGTON, *Plast. Rubb. Process. Appl.* **1** (1981) 139.

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