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Fracture propagation in particulate-filled polypropylene composites

Part 2 *Influence of mica concentration*

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Isotactic polypropylene (PP) with different concentrations of mica (20, 40 and 60% by weight) were prepared by injection moulding under identical conditions. The influence of mica concentration on the microstructure and fracture propagation in the composites was investigated. Microstructural studies revealed that mica concentration influences the flake orientation and alters the skin–core zone thicknesses. Virgin PP and its composites with mica exhibited brittle failure at −30° C. At 25° C, all the composites showed stable crack growth, even with 60% mica loading. At 80° C the composites exhibited stable crack growth but the ductility decreased with increasing mica concentration. The influence of mica content, as well as temperature, on normalized modulus and the fracture toughness (K_c) of the composites were studied. This study attempts to correlate mica concentration and polymer morphology with fracture propagation.

1. Introduction

Mica, in recent years, has been widely used as a reinforcing filler for several commodity polymers. In comparison to the other two fillers (talc and $CaCO_3$), considered in Part 1 of the present investigations [1], mica has been given more importance, because of its advantages when used as a filler. In this and in Part 3 [2], investigations related only to mica-filled polypropylene composites will be reported.

Several workers [3, 4] have investigated the mechanical properties [5], processability [6] and morphology [7] of polypropylene–mica composites. The degradation of mica flakes during processing [8], their orientation in moulded plaques [9], the influence of different surface treatments on processing of the composites [10], for example, have already been investigated. Besides these factors, the toughness of a composite material, from a practical point of view, is an important engineering property, but unlike strength and stiffness, it is a very difficult parameter to predict. The property advantages offered by the mica composites, coupled with their economic benefits, have inspired the investigation of the fracture mechanics of these composites. Vu-Khanh *et al.* [11, 12] have recently studied the crack initiation and propagation resistances at room temperature in polypropylene composites containing different mica concentrations. In an earlier publication [13] the influence of mica concentration (10, 20, 30, 40, 50 and 60% by weight) on the mechanical properties and morphology was reported in detail. The present paper discussed the fracture propagation in polypropylene–mica composites at −30, 25 and 80° C. Here, our concern is only with variation in mica concentration, at 20, 40 and 60% by weight. These concentrations were selected (based on our earlier investigations) in order to cover both the ranges where the composites exhibited properties dominated by the matrix and later by the filler.

2. Experimental procedure

The preparation of the composites and the methods followed in studying the fracture propagation are described in Part 1 [1].

3. Results and discussion

3.1. Microstructure

Scanning electron micrographs of the polished sections of the composites consisting of 20, 40 and 60% mica, by weight, are presented in Fig. 1. These sections are obtained in the same manner as described elsewhere [1] and the polished surfaces always contain the melt flow direction (MFD) and the thickness direction. In all three composites, the mica flake orientation in the skin areas (Figs 1a, b and c) is parallel to the mould wall, and in the core regions (Figs 1d, e and f) it is perpendicular to the wall. A typical view of the gradual orientational changes (from one end to the other) in mica flakes is presented in the preceding part. Further, the changes in the mica flake orientation angle ($|\theta°|$) with respect to the mould wall, measured

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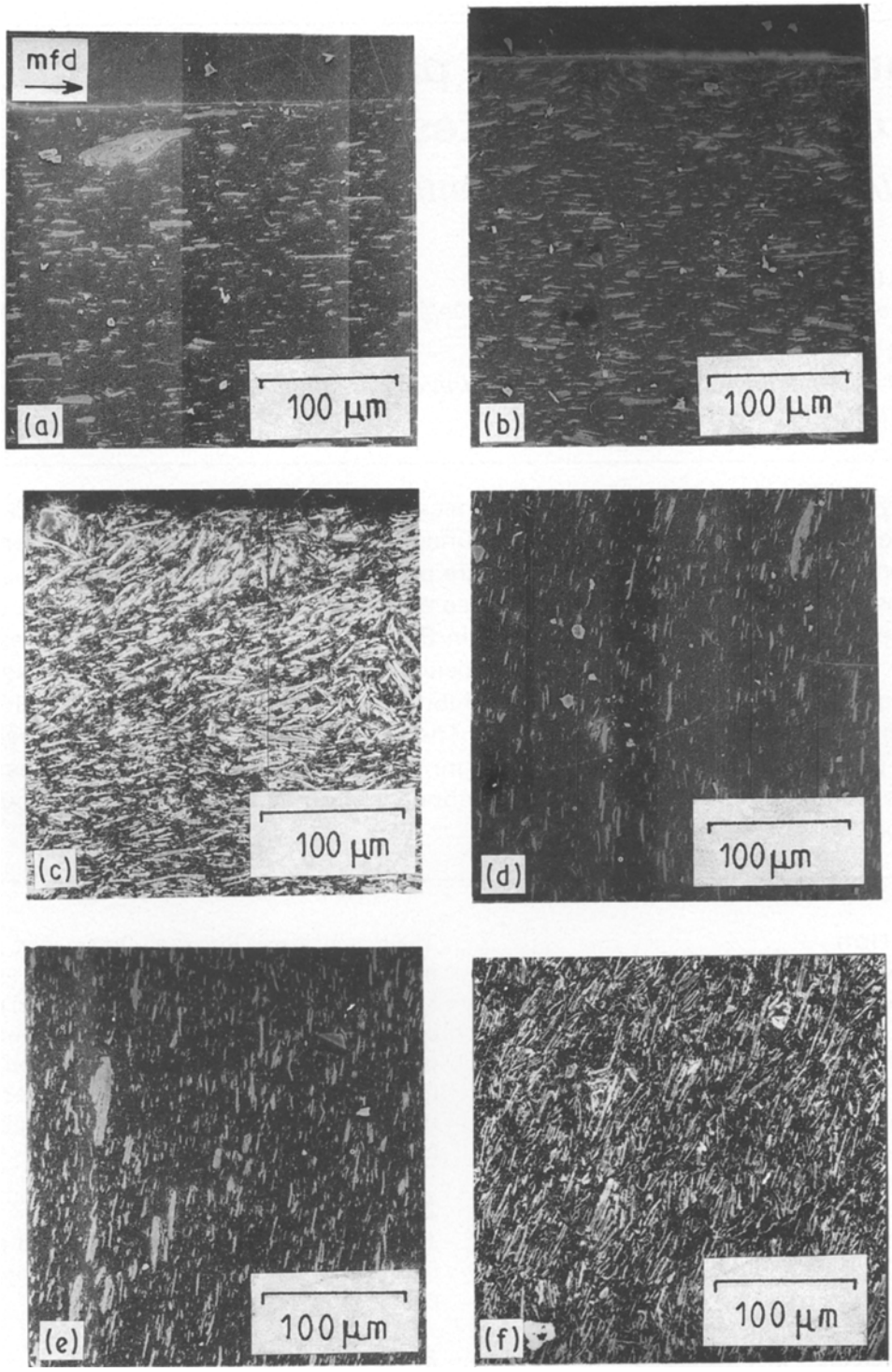


Figure 1 Scanning electron micrographs of mica flake orientation in the skin zones of (a) PP/mica, 20%, (b) PP/mica, 40%, (c) PP/mica, 60%; and mica flake orientation in the core regions of (d) PP/mica, 20%, (e) PP/mica, 40% and (f) PP/mica, 60%. The mould-fill direction (MFD) is indicated by an arrow.

from the scanning electron micrographs, taken across the thickness of the sample, are presented in Fig. 2. Confining discussion to the same definition of the skin–core regions presented elsewhere [1], it is evident that increasing mica concentration increases the thickness of the core regions considerably. Similar results were observed in the case of short glass fibre-reinforced polyethylene terephthalate [14]. In addition to this, with increasing mica concentration, the mica orientation angle ($|\theta°|$) in the skin also increased; i.e. a disorientation of the flakes from the plane that is parallel to the mould wall gradually develops. This phenomenon is dominant in the case of the composite with 60% mica; this material exhibits a flake misorientation of approximately 17° at the mould walls, gradually falling to 10° symmetrically on either side. Remillard and Fisa [15] observed, in the processing of mica-reinforced polypropylene, that air from small intragranular pores in the molten composite finds it extremely difficult to escape, especially because of the disc-like shape of the mica flakes, which can prevent the air from escaping. Pressure from this entrapped air builds up during the injection moulding process. This pressure may be sufficient to disorient the flakes to some extent. Because of this disorientation phenomenon, the moulded product loses its surface gloss.

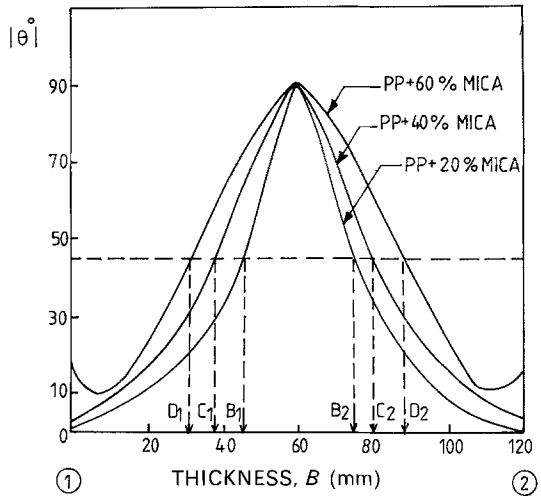


Figure 2 Variation of mica flake orientation ($|\theta°|$) as a function of thickness of the composites with 20%, 40% and 60% mica.

3.2. Fracture properties

The flexural stress–strain curves of virgin PP and its composites with 20, 40 and 60% (by weight) of mica (1000 mesh), tested at three different temperatures, are presented in Figs 3 to 5. The effect of mica content on the mechanical behaviour of the composites, both below and above the glass transition temperature of PP, is evident from these curves. From Fig. 3 it is clear that virgin PP, as well as all its composites with different concentrations of mica, exhibit brittle failure at $-30°$ C. With increasing mica concentrations, the maximum stress level at which the composite undergoes catastrophic failure gradually decreases. It was pointed out in Part 1 [1] that incorporation of a filler in PP matrix enhances the plastic deformation of the matrix and the degree of deformation was found to be

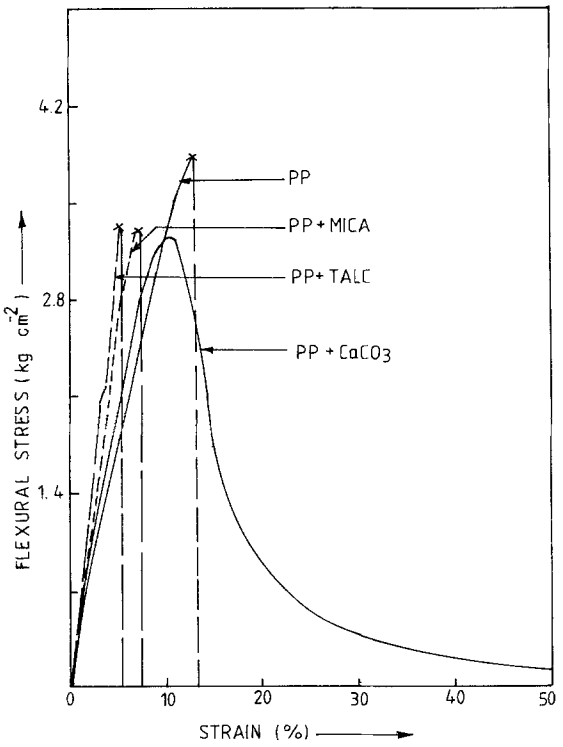


Figure 3 Flexural stress–strain curves of PP and its composites with 20%, 40% and 60% mica, obtained at $-30°$ C. (X indicates catastrophic failure.)

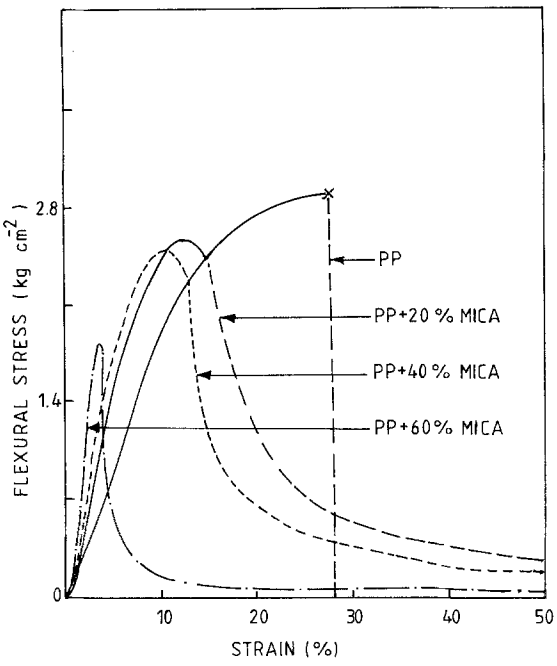


Figure 4 Flexural stress–strain curves of PP and its composites with 20%, 40% and 60% mica, obtained at 25° C. (X indicates catastrophic failure.)

dependent on the nature, as well as the size, of the filler. Crack-pinning at the particulates/mica-flakes is responsible for the enhanced crack ductility. However, by reducing the temperature (to $-30°$ C), the plastic zone size is reduced, even with the introduction of fillers such as talc and mica. In addition, increasing mica population reduces the spacing between pinning points and consequently the crack front bows forward less in order to break off from the pinning points. This would also result in a reduced plastic zone in front of the crack tip, thus causing reduction in the maximum stress level.

At 25° C, only the virgin PP exhibits brittle failure (Fig. 4), while all the mica composites show stable crack propagation. Incorporation of mica into PP has evidently helped in avoiding the brittle failure of PP at room temperature. With increasing mica concentration, the stress level at the yield point gradually

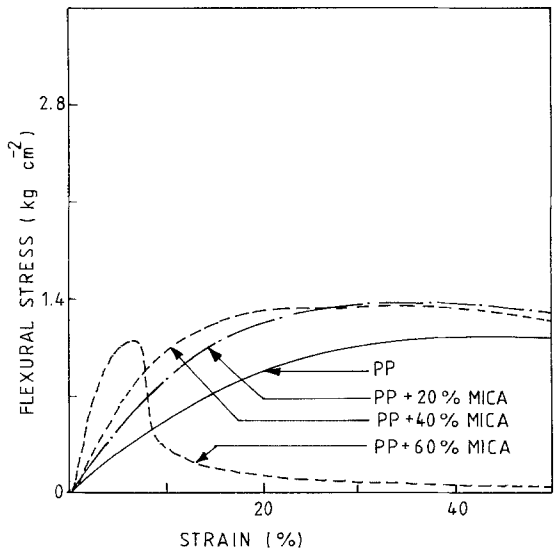


Figure 5 Flexural stress–strain curves of PP and its composites with 20%, 40% and 60% mica, obtained at 80° C.

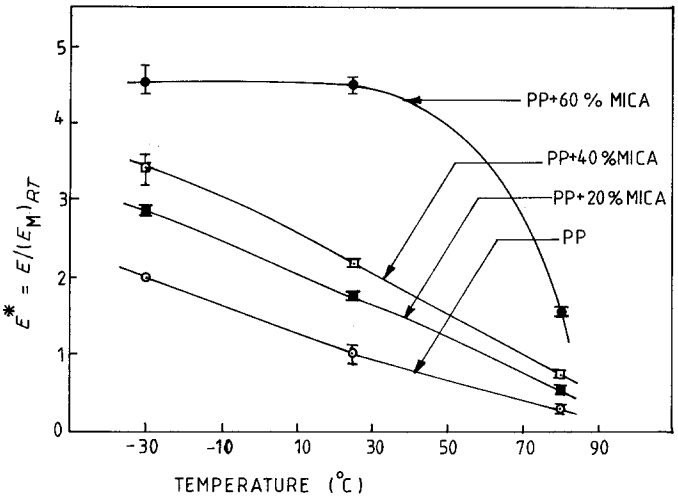


Figure 6 Variation of specific modulus (E^*) with temperature, for PP and its composites with 20%, 40% and 60% mica.

decreases. At 80° C, the mechanical behaviour of virgin PP and its composites with mica (Fig. 5) is entirely different from that at lower temperatures. With low filler concentrations (0 < mica % < 20%) the response of the composite is dominated by the matrix and there is no clear-cut yield point. In the moderate concentrations (20% < mica % < 40%) the trend is of mixed nature and at high filler concentrations (40% < mica % < 60%) the composite behaviour is dominated by the filler and the material exhibits a clear yield point but, nevertheless, with a stable crack growth.

The flexural moduli of the notched samples were calculated as described in Part 1 [1] and were normalized with the modulus of PP at room temperature. The variation of normalized moduli (E^*) with testing temperature is presented in Fig. 6. With decreasing testing temperature, the E^* values of PP, as well as its composites, increase. In addition, the incorporation of mica has increased E^* throughout the temperature range studied. The normalized modulus of the composite increases with increasing mica content. In the case of the PP–mica (60%) composite, E^* remains almost constant in the temperature range -30 to $+25$° C, but above this range the fall in E^* is rather rapid.

The variation in fracture toughness (K_c) with different mica contents at -30 as well as $+25$° C is presented in Fig. 7. The fracture toughness calculations were done in the same manner as in Part 1 of this work [1]. The fracture toughness at 25° C, in the case of the composite with 20% mica, is reduced in comparison to that of virgin PP. Vu Khanh *et al.* [11, 12] observed that crack initiation resistance increased with increasing mica content up to 20% (by weight) and above this concentration there was a drop in the resistance to crack growth. At -30° C, the composite with 20% mica exhibited a slightly higher K_c value and above this concentration the fall in K_c is quite rapid, whereas at 25° C, the fall in K_c is rapid beyond 40% mica. In other words, at -30° C, the reduction in the effective amount of matrix materials becomes influential beyond 20% mica content; at 25° C, it is influential above 40% mica.

3.3. Fractography

The PP–mica (20%) composite, fractured at -30° C, exhibits maximum matrix deformation (Fig. 8a) close to the notch. It is likely that mica flakes act as preferred sites for microvoid coalescence and eventually form a continuous fracture surface with cup-like markings, or "dimples", on the surface. The extent of microvoid nucleation determines the shape and size of the dimples present in Fig. 8a. It is also likely that the dimples of larger size are nucleated by particles of wider spacing. However, the matrix on the portion of the fracture surface lying opposite the notch, shown in Fig. 8b, appears relatively undeformed during the

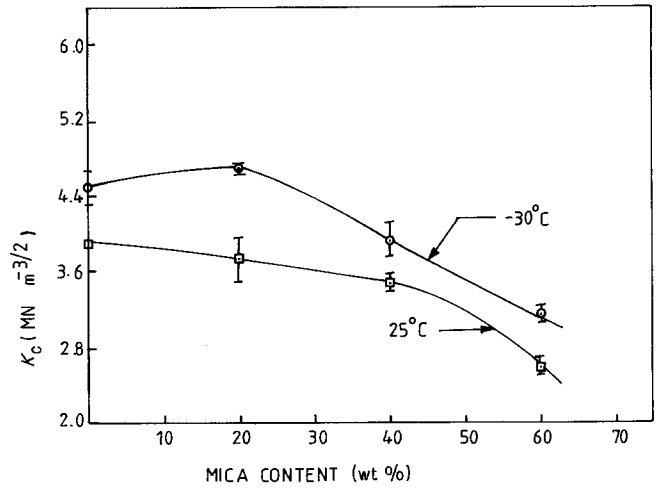


Figure 7 Variation of fracture toughness (K_c) with mica concentration, obtained at -30 and 25° C.

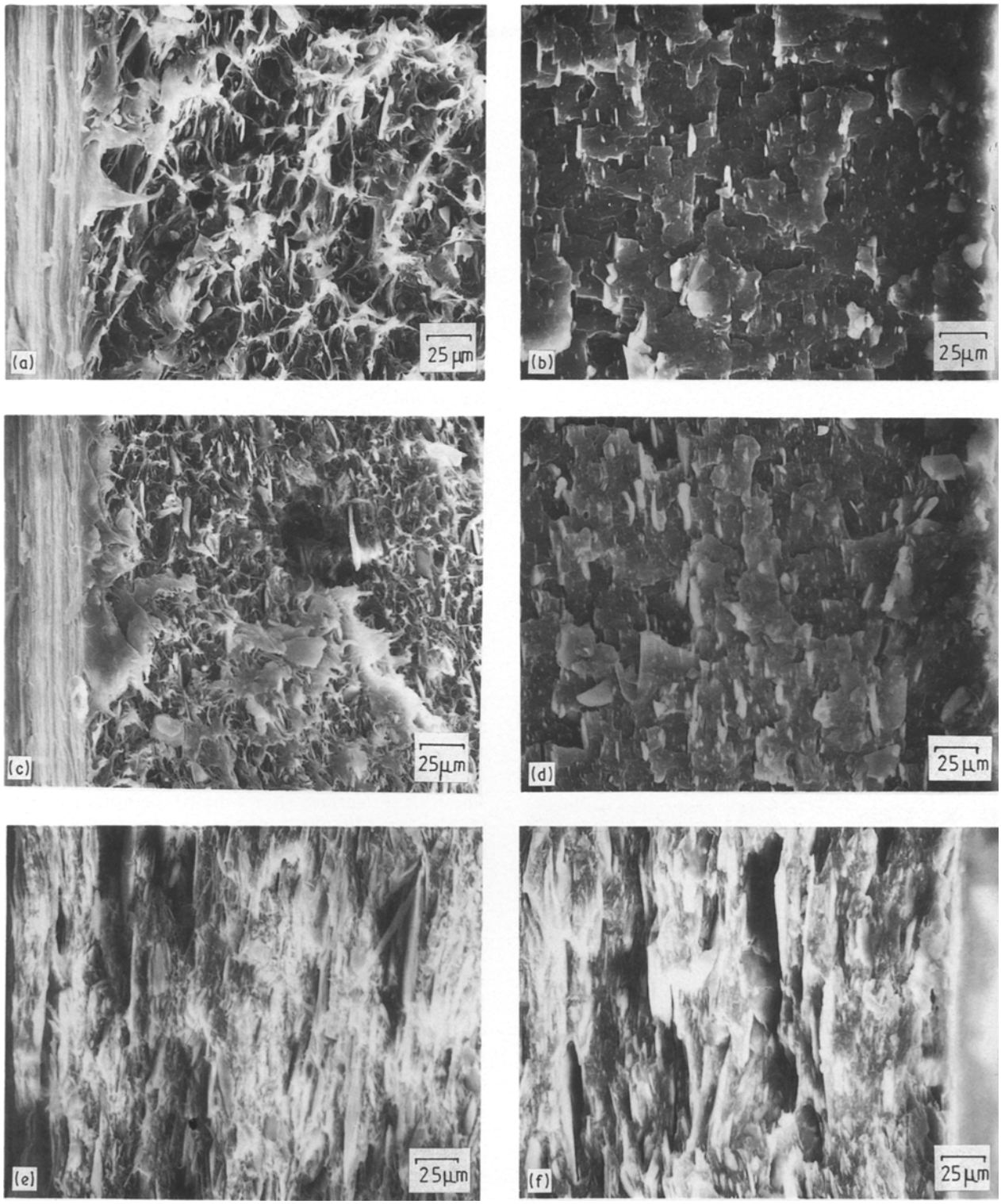


Figure 8 Scanning electron micrographs of the fracture surfaces obtained after fracture at −30° C: (a), (c) and (e) are taken close to the notch for PP composites with 20%, 40% and 60% mica, respectively; (b), (d) and (f) are taken near the edge opposite the notch for PP composites with 20%, 40% and 60% mica, respectively.

fracture process. It is probable that coalescence of microcracks has produced fracture here before the arrival of the main crack-front. A similar phenomenon has been observed by Lhymn and Schultz in glass fibre-reinforced PET composites [16] and is referred to as the "far-field effect".

In the case of a composite with 40% mica (Figs 8c and d), similar observations can be made. However, in the vicinity of the notch, the size of the dimples is reduced remarkably as the mica concentration is raised to 40%. The reason for this could be as follows: as the mica content is increased, the volume fraction and the size of PP domains is reduced correspondingly. The more constrained, smaller matrix domains must fail at relatively smaller levels of deformation, because their local strain level must be very high. However, the fracture surface far from the notch looks quite brittle, just as in the case of the composite with 20% mica. In the case of the 60% mica composite (Figs 8e and f) there is only marginal matrix deformation in the vicinity of the notch. And one can observe the flake pull-out and even the breaking of the flake at the initial stages

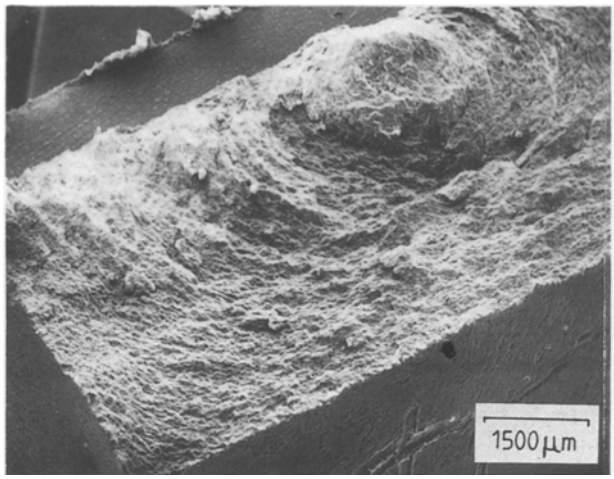


Figure 9 General view of PP/mica, 60%, composite fractured at −30° C.

of crack propagation. As the fracture reaches the opposite side of the notch, again the matrix appears to have undergone a brittle fracture, with flake pull-out as the dominant mechanism.

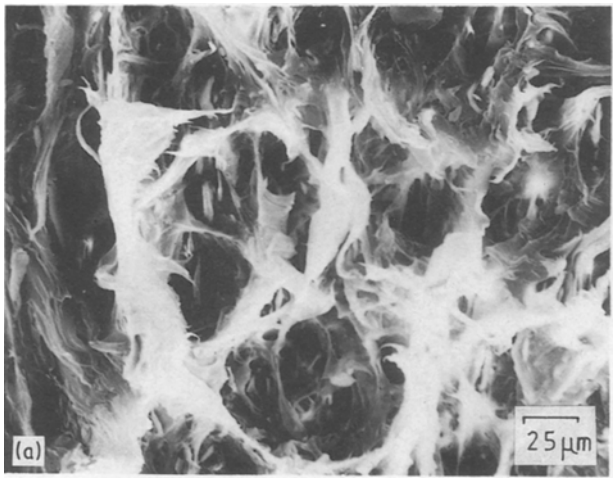
The fracture surfaces are influenced not only by the mica concentration, but also by the mica flake orientation [17]. The influence of mica flake orientation on the fracture surface morphology is clear in the case of the 60% mica composite (Fig. 9). The core regions appear rough, with hills and valleys ellipsoidally curved towards the core. This gives an indication of the mica flake orientation frozen-in during the injection-moulding process. However, the edges or skins are relatively smooth, as the mica flakes are mostly oriented parallel to the mould surface in these regions.

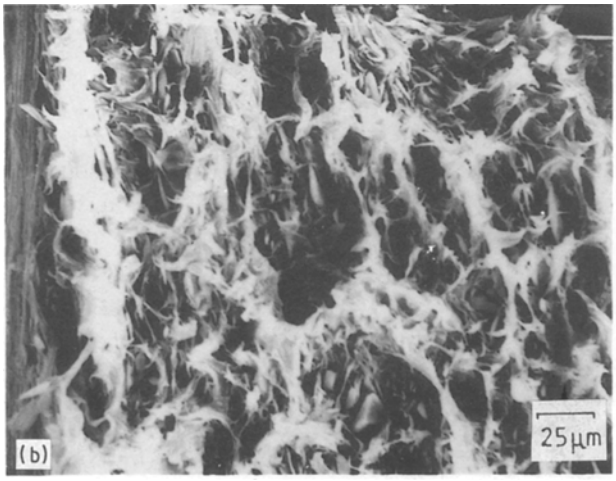
Failure surfaces of the composites fractured at room temperature are presented in Fig. 10. These micrographs were taken in the vicinity of the notches. It is evident that at +25° C the plastic deformation in the PP matrix, associated with the stable crack propagation, is large, compared with the same composites tested at −30° C. The characteristic dimple fracture, is nevertheless retained. However, the size of the dimples and the size of the dimple-lips gradually decrease with increasing mica concentrations (Figs 10a, b and c).

When the composites are tested at 80° C, increased local viscous deformation is observed. The degree of the matrix deformation is dependent on the mica concentration in the composite. In the case of a composite with 20% mica content, fracture does not take place, but massive matrix deformation, leading to blunting of the crack, was observed. In addition, voids, which enlarge under the flexural loading conditions (near the notch), and debonding of the flakes are observed (Fig. 11a). The heat disortion temperatures of these composites were studied and reported in an earlier publication [13]. A composite with 40% mica also revealed similar features [17], as does the composite with 20% mica. However, in a composite with 60% mica, the fracture propagated through the specimen. The fracture surface shows matrix deformation and the elongated PP fibrils further reveal microvoids present in them (Fig. 11c).

4. Conclusions

Mica concentration influences fracture propagation in the composites under study. Microstructural studies revealed that mica concentration influences the mica flake orientation and thereby affects the relative skin–core zone thicknesses, and these in turn affect the mechanical performance of the composites. At





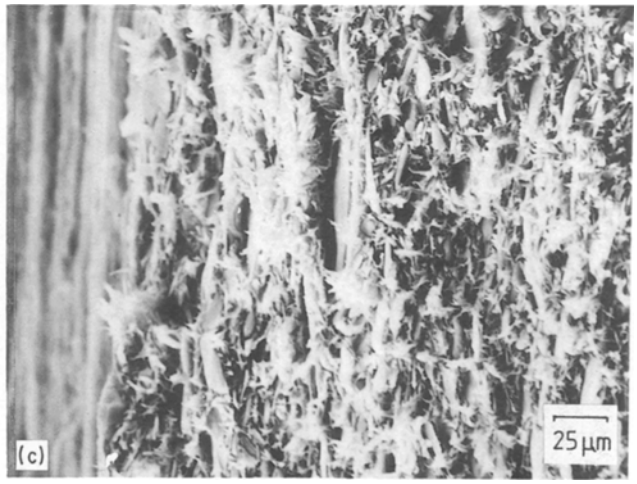


Figure 10 Scanning electron micrographs of the fracture surfaces observed close to the notch, after Instron testing at room temperature, for (a) PP/mica, 20%, (b) PP/mica, 40% and (c) PP/mica, 60%.

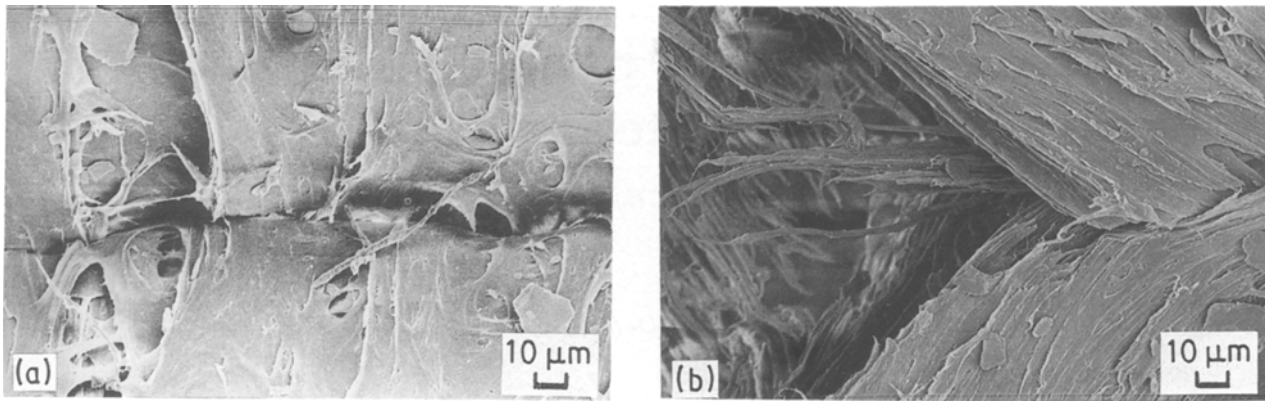


Figure 11 Scanning electron micrographs of the fracture surfaces observed close to the notch, after Instron testing at 80° C, for (a) PP/mica, 20%, (b) PP/mica, 40% and (c) PP/mica, 60%.

– 30° C, PP and its composites with 20% or more mica undergo unstable crack growth. At 25° C, while PP suffers from catastrophic failure, incorporation of mica up to 60% obviates unstable crack growth.

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