JOURNAL OF MATERIALS SCIENCE 25 (1990) 2411–2420

Fracture propagation in particulate filled polypropylene composites

Part 1 *Influence of filler nature*

S. F. XAVIER*[1], J. M. SCHULTZ*, K. FRIEDRICH‡
**Centre for Composite Materials, University of Delaware, Newark, Delaware 19716, USA*
‡Polymer and Composites Group, Technische Universität Hamburg – Harburg,
2100 Hamburg 90, Federal Republic of Germany

Isotactic polypropylene (PP) composites with 40% (by weight) of different fillers, such as talc, $CaCO_3$ and mica (325 and 1000 mesh sizes) were prepared by injection moulding. In the case of PP–mica composites, scanning electron micrographs of the polished sections revealed that flakes are oriented in the skin areas parallel to the mould surface and in the interior there is a flake distribution more perpendicular to that. The notched specimens of PP and all its composites under study were fractured at −30, 25 and 80° C. Virgin PP exhibited brittle failure at −30 and 25° C with comparatively higher values of fracture toughness (K_C), and gross yielding leading to crack-blunting took place at 80° C. The fracture toughness of neat matrix and its composites were correlated with microstructural parameters. Incorporation of $CaCo_3$ avoided the catastrophic failure of PP at −30° C while any of the fillers could avoid brittle failure at 25° C. Failure mechanisms were observed by scanning electron microscopy of the fractured surfaces. The performance of PP was significantly affected by the incorporation of fillers.

1. Introduction

Incorporation of mica, $CaCO_3$ or talc as a reinforcement/filler in thermoplastics is a common practice in plastics technology [1, 2]. These fillers improve the physical properties of virgin polymers, help reduce the cost of moulded products and also aid in tailoring the material to suit requirements.

The characterization of a particulate composite system is a very difficult task because of the great number of parameters affecting its mechanical behaviour. Such parameters are the nature of the reinforcing particles, the filler volume/weight fraction [3], the adhesive bond between the filler and the matrix [4], the degree of dispersion and the amount of particle agglomeration [5]. Among these factors, the nature of the filler particle and its physico-chemical properties are of cardinal importance.

The filler fraction is also very important; this study leads to the concept of optimum concentration, which is regarded as the limit of saturation of the adsorption centres on the surface of the filler by the macromolecules [5]. For filler concentrations greater than this optimum value the continuity of the network structure is upset and this leads to a deterioration rather than to an improvement in the mechanical properties.

Moreover, the adhesion between polymer and filler is another factor affecting greatly the strength of a particulate composite [6]. For instance, a proper surface treatment of the filler particles can lead to a better adhesion between polymer and filler and, consequently to a change in the overall mechanical behaviour of the composite system.

It is well-known that in the region between matrix and filler, a third phase is developed, consisting of areas of imperfect adhesion, where stress concentrations, impurities and other defects develop. These micro-defects lead to localized stress concentrations, which are in excess of the average stress in the bulk of the material. If the localized stresses are sufficiently high, they may lead to a growth of the defect and subsequent failure of the material [7].

In the present work, which is divided into three parts, an attempt has been made to show how the fracture mechanical properties of polypropylene (PP) are affected by the addition of different fillers, such as $CaCO_3$, talc and mica flakes with different mesh sizes (in Part 1), different mica concentrations (in Part 2) and also with different surface treatments to mica (in Part 3). The fracture mechanical properties of the composites were studied at −30° C, ambient temperature and also at 80° C, in order to understand the behaviour of the composites in the whole workable temperature range. The filler dispersion, the flow-induced flake orientation, the fracture morphology and the interfacial adhesion of the composites were studied extensively in order to understand the fracture behaviour of the composites. And, finally, attempts are made to summarize the fracture behaviour of the PP–mica composites in terms of certain models. It is

---

[1] *Permanent address*: Research Centre, Indian Petrochemicals Corporation Ltd, Baroda 391 346, Gujarat, India.

0022-2461/90 $03.00 + .12

expected that this work would help in understanding the performance of PP composites, which, in turn, would help in finding new applications for these materials.

2. Experimental details

2.1. Materials

An injection grade polypropylene (produced by Indian Petrochemicals Corporation Ltd, with the trade name Koyalene) was used in the form of powder mixed with antioxidants, and having melt flow index 10 g per 10 min. Muscovite mica powder (supplied by Pneumatic Atomising Mills Pvt Ltd, India) of two different mesh sizes, 325 and 1000, and with the particle size distribution given in Table I; talcum powder of average particle size ~ 5 μm; and calcium carbonate of average particle size ~ 6 μm (both supplied by Kenrich Petrochemicals Inc., USA) were used. Two coupling agents, isopropyl triisostearoyl titanate (TTS) (supplied by Kenrich Petrochemicals Inc.) and 3-aminopropyl triethoxysilane (supplied by Fluka Inc.) were engaged in the present investigations.

2.2. Sample preparations

Polypropylene and a filler were dry-blended in a ribbon blender at room temperature after dehumidifying. In the case of composites consisting of treated mica, the mica was initially taken in a mixer. Calculated amounts of titanate/silane coupling agent, mixed with toluene (1 : 10), were added and then mixed thoroughly for 30 min. Then it was dry-blended with the polymer. The mechanical mixtures were separately extruded using a twin screw extruder (ZSK-30, Werner and Pfleiderer), keeping the melt temperature at 190° C, screw speed 70 r.p.m. and maintaining the temperature of the zones at 200, 210, 230 and 220° C. The strands of the extrudates were cooled in water and later dried by blowing air. They were chopped in a granulator to obtain granules of average size 5–7 mm. Using these granules, standard ASTM flexural bar specimens (listed in Table II) were moulded under identical conditions, using an injection moulding machine, maintaining an injection pressure of 1000 kg cm^{-2}, injection temperature 250° C, rate of injection 2 cm sec^{-1} and screw speed 80 r.p.m.

2.3. Microscopy

The microscopy work was done using mostly a scanning electron microscope (SEM). Specimens used to determine the orientation distribution of mica flakes were polished using the standard metallographic polishing technique. These specimens, as well as those used for fractographic analysis, were gold-coated in a sputtering chamber prior to SEM studies.

TABLE I Particle size distribution of mica

Mesh size		Particle size (μm)
325	1000	
18% finer than	26% finer than	2
30% finer than	38% finer than	5
68% finer than	77% finer than	10
92% finer than	96% finer than	20
100% finer than	100% finer than	44

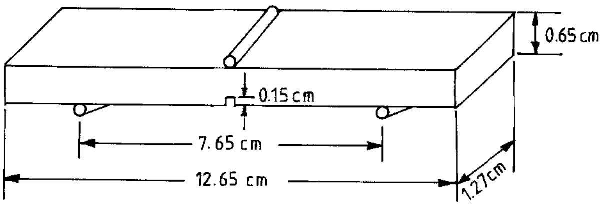


Figure 1 Geometry of the injection moulded flexural bar used.

2.4. Fracture toughness measurements

All standard flexural specimens were given a notch of depth 1.5 mm (Fig. 1) using a diamond cutter. The notched samples were used for studying the fracture mechanics using an Instron Universal Testing Machine, Model 1125, and a fixture for studying the flexural properties at different temperatures. The samples were fractured at −30, 25 and 80° C, keeping the chart speed at 20 in min^{-1}, the cross-head speed at 2 mm min^{-1} and the span length constant, in the three-point bending mode. At each temperature at least two specimens of each type were tested.

3. Results and discussion

3.1. Microstructure

Investigations on fibre-filled polyethylene terephthalate [8] and polyether ether ketone [9] revealed that the microstructure of a composite is extremely important in understanding its mechanical properties. The orientation of mica flakes in polymer composites has not been studied in detail. Recently, Malik and Prudhomme [10] used wide-angle X-ray diffraction for quantitative measurement of the orientation distribution function of mica flakes in compression-moulded polymer composites.

Fig. 2 illustrates the section (PQRS) of the sample that was subjected to the polishing and later on for sequential microscopic observations. A schematic illustration of the mica flakes in the polished surface and the area where the microscopic scanning was undertaken (mid-way between the centre and edge SP, represented by the dotted lines) are also shown in Fig. 2. The orientation of mica flakes (325 mesh size) in the *YZ* plane is clearly shown in Fig. 3. At the top, in Fig. 3a, the flakes are oriented parallel to the mould wall surface. As one goes downwards from the mould surface to the core of the sample, the orientation of the flakes (α°) gradually turns from 0 to 45°, and as one reaches the core it turns to 90°; later on it gradually turns to 0°, as one reaches the other surface of the mould wall. Fig. 4 clearly shows the angle of mica flake orientation (α°) as a function of the thickness of

TABLE II Composites of polypropylene studied

Filler	Particle size/mesh	Concentration (wt %)	Surface treatment	Studied in part
$CaCO_3$		40	Nil	I
Talc		40	Nil	I
Mica	325 mesh	40	Nil	I
Mica	1000 mesh	40	Nil	I, II and III
Mica	1000 mesh	20	Nil	II
Mica	1000 mesh	60	Nil	II
Mica	1000 mesh	40	TTS	III
Mica	1000 mesh	40	Silane	III

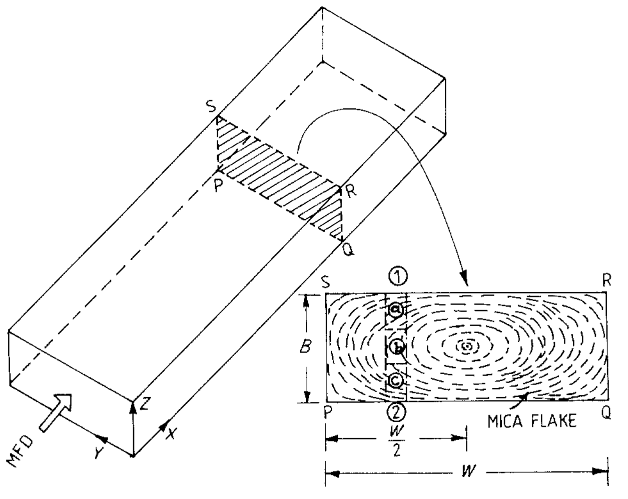


Figure 2 Injection moulded flexural bar with melt flow direction. PQRS is the polished cross-sectional area where the microstructure was examined under the scanning electron microscope, top side surface (1) to bottom side surface, (2) within the area indicated by the dotted lines and subdivided into (a), (b) and (c) sections.

the sample. The flake orientation is symmetric with respect to the centre of the sample. If we define the limits of the core region as having mica flake orientations of ±45°, then the central layer for the composite with mica 325 mesh (denoted by G_1, G_2) is larger in comparison to that of the composite with mica of 1000 mesh. This indicates that with bigger mica flakes, the thickness of the core is increased and simultaneously the skin thickness on either side is correspondingly reduced. These changes in flake orientation and the corresponding changes in skin–core thicknesses would affect the mechanical properties of the composites.

3.2. Fracture properties

The flexural stress–strain curves of the PP composites with various fillers such as $CaCO_3$, talc and mica of two different mesh sizes are shown in Figs 5 to 10. From these curves, the effect of filler nature on the mechanical behaviour of the particulate composites over the entire temperature range selected becomes clear. It is evident (from Figs 5 and 6) that, except for the PP–$CaCO_3$ composite, all other composites and virgin PP exhibit catastrophic failure at $-30°$C. Only the PP–$CaCO_3$ composite does not undergo brittle failure, but exhibits stable crack growth. Talc and mica fillers help only in improving the modulus of the composite, although they bring down the maximum stress level at which the composites undergo catastrophic failure. With an increase in mica flake size, there is a small reduction in the maximum stress level.

At room temperature, only the virgin PP exhibits catastrophic failure (Figs 7 and 8). This was also observed by Vu-Khanh *et al.* [11, 12]. On the other hand, all the composites show a gradual increase in stress value, going through a peak, indicating stable crack propagation in the composites. It is quite evident from these curves that the presence of any filler used here helps in overcoming the brittle failure exhibited by the virgin PP. It is also evident (from Figs 7 and 8) that the stress level at the yield point is highest in the case of PP, followed by PP–talc, PP–mica and then PP–$CaCO_3$. This will be examined further in the context of the fracture toughness of these materials.

At 80° C (Figs 9 and 10), all the materials, including virgin PP, show slow ductile tearing. During this process, there was considerable crack opening, sometimes with gross yielding. The same behaviour was observed by Scott and Philips [13] who tested the fracture energy of different glass sphere-filled Nylon 6 and Nylon 66 composites with edge-notched tensile specimens. At this temperature, the yield stress of PP increases with the addition of mica or talc (Fig. 9). Another factor affecting both the reinforcing action of fillers and the crack propagation mode is the ratio of the particle diameter to the diameter of the fracture zone developed at the crack tip. The smaller the particle diameter, when compared to the dimensions of the fracture zone, the smaller the particle effect on the path of the crack (Fig. 8). On the contrary, the possibility of crack-arrest taking place is greater as the particle size becomes bigger. This is exhibited in the PP–mica (325 mesh) composite by the reduction in the stress level after the peak is obtained.

In order to demonstrate relative changes, only the modulus values were calculated from the stress–strain curves obtained for the notched samples and were normalized to a standard, for which the flexural modulus of the matrix at room temperature was chosen. Fig. 11 shows the expected decrease of the normalized modulus (E^*) of PP with temperature and also shows that the addition of any filler also increases the normalized modulus of the composite in comparison with the matrix. Among the fillers studied, talc shows the greatest modulus increase relative to PP throughout the temperature range studied. And among the two varieties of mica used, mica of 325 mesh (the coarser variety) has been found to offer better modulus, in comparison with mica of 1000 mesh size. However, as the temperature is increased, the relative differences in E^* values of the composites gradually reduce and a coalescence of the moduli curves can be visualized around 95–100° C. The continuous fall of E^* of PP and all its composites with temperature is attributed to the increasing thermoplasticity of the matrix.

The criteria prescribed for the validity of K_{IC} or K_c (the material fracture toughness) in the standard ASTM E-399 [14] are not satisfied with respect to specimen size requirements in these fracture tests. Nevertheless, an apparent fracture toughness, computed according to Equation 1 [15, 16] can be used to follow the relative changes in the toughness of a material with microstructural variations

$$K_c = \frac{F_c S}{BW}(a_i)^{1/2} f\left(\frac{a_i}{W}\right) \quad (1)$$

where F_c is the maximum load in a loading cycle, S is the span between the two supporting points in the three-point bending mode, a_i is the crack length (determined with the help of an optical microscope), $f(a_i/W)$ is a polynomial which accounts for finite specimen width [15], B is the breadth and W is the width of the sample (see Fig. 1). The calculated values

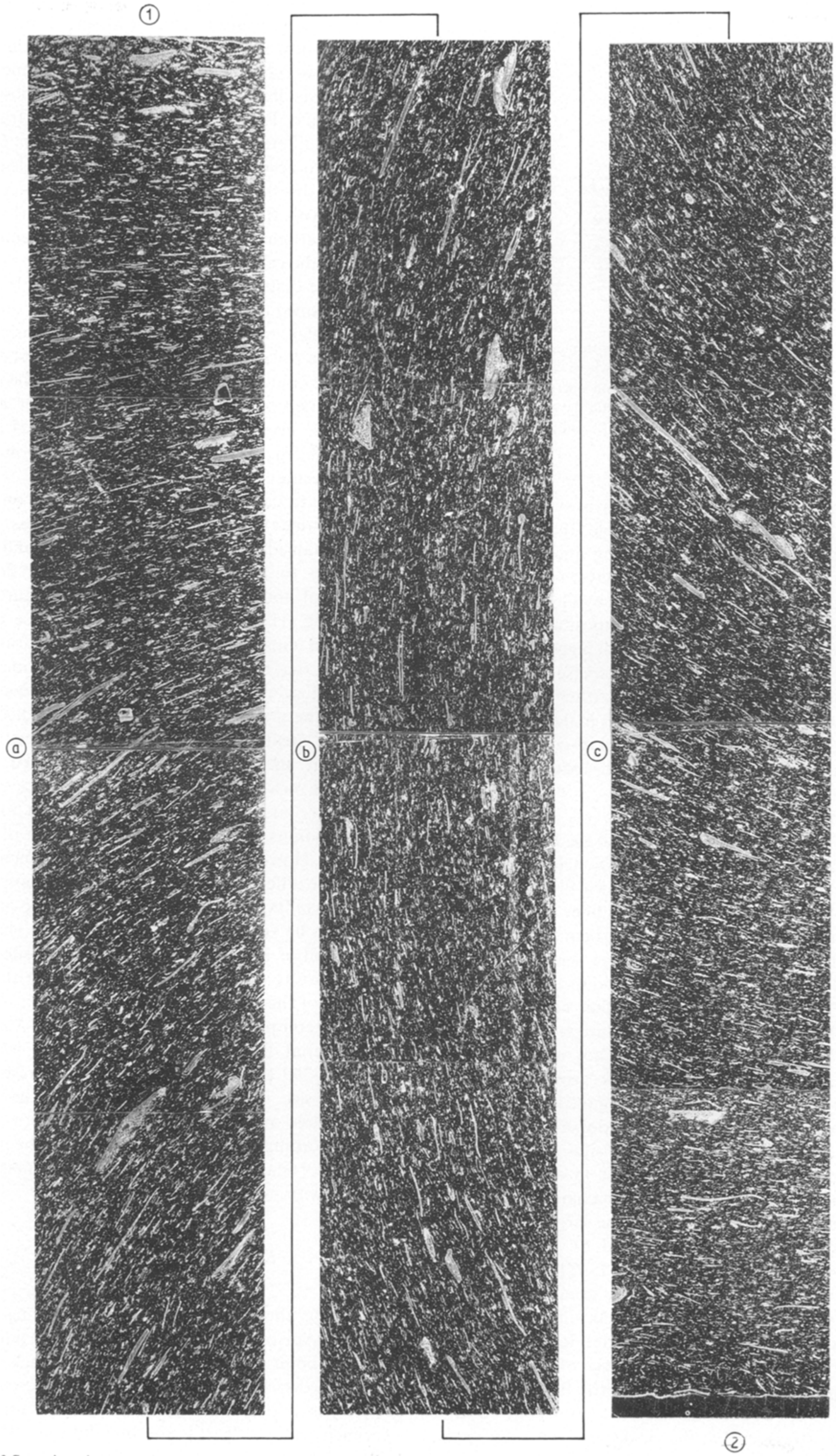


Figure 3 Scanning electron micrographs of mica flake (325 size) orientation from mould surface (1) to (2), subdivided as (a), (b) and (c).

TABLE III Calculated fracture toughness K_c (MN m$^{-3/2}$) of samples with heat distortion temperature

Sample	Testing temperature		Heat distortion temperature (° C) (ASTM 648)
	30° C	25° C	
Polypropylene	4.55	3.91	56
PP + 40% $CaCO_3$	3.87	3.10	62
PP + 40% Talc	3.89	3.52	91
PP + 40% Mica	3.95	3.49	85
PP + 40% Mica (325 mesh)	3.88	3.36	87

of the fracture toughness are listed in Table III. By lowering the temperature, K_c values of PP as well as all its composites under study have increased. This is in confirmation with the observations made by Savadori [17] on the homopolymer. The influence of the filler nature on K_c at − 30° C is only marginal. However, its influence is enhanced on increasing the testing temperature. The incorporation of any of the fillers has given rise to plastic deformation of the matrix and the degree of deformation is dependent on the nature as well as the size of the filler. Both at − 30° C as well as 25° C, the samples which have undergone brittle (or catastrophic) failure have exhibited higher K_c values. Further, by reducing the temperature, the plastic zone size is reduced, even with the introduction of the fillers. The relative influence of the fillers on the plastic zone is probably reduced by reducing the temperature; and hence the K_c values did not show much variation from filler to filler at − 30° C. In addition, in the case of samples (except PP–$CaCO_3$) which had exhibited unstable crack propagation at − 30° C a loud bang was observed (and shattering of the specimen also took place in the case of PP). According to Fernando and Williams [18] these phenomena provide clear evidence for excess strain energy being dissipated during unstable fracture propagation. It was also pointed out that in bending, the compression stress field eliminates the local toughening and does not call for severe notch sharpness requirements.

3.3. Fractography

The fracture surfaces of virgin PP obtained at − 30, 25 and 80° C are presented in Fig. 12. A close examination of the fracture surface of PP broken at − 30° C (Fig. 12a) reveals the nucleus of crack initiation which appears to be smooth and the feathery markings seem to converge to the crack initiation site. The general view of the fracture surface of virgin PP that had exhibited catastrophic failure at 25° C is presented in Fig. 12b. From this micrograph, it is evident that

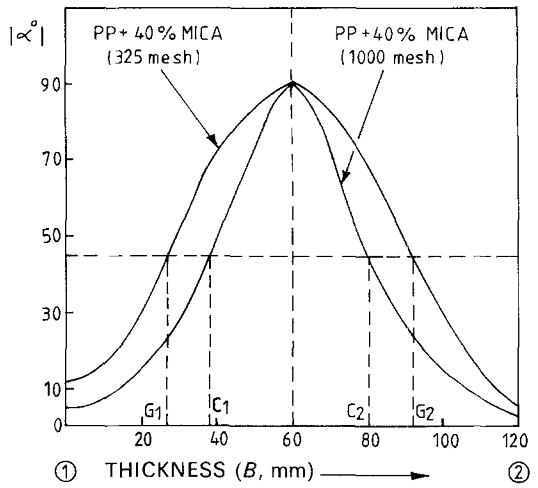


Figure 4 Variation of mica flake orientation (α°) as a function of the thickness of the sample for composites with mica of 325 and 1000 mesh sizes.

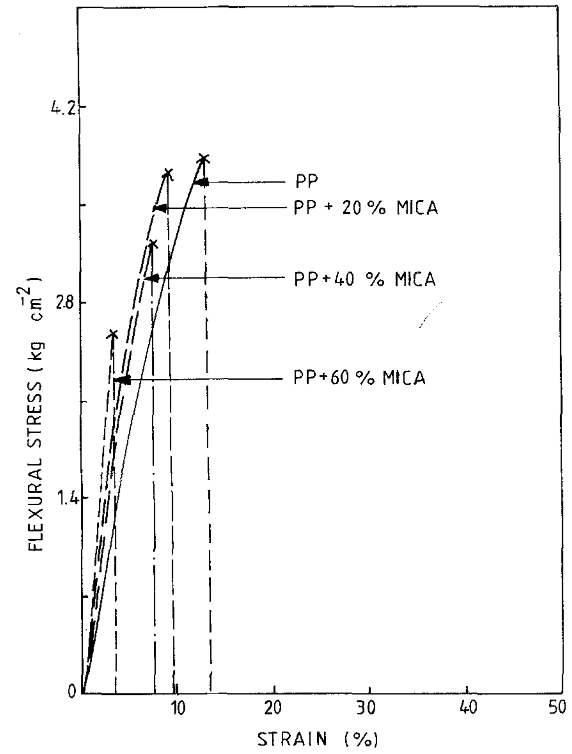


Figure 5 Flexural stress–strain curves of PP composites with various fillers ($CaCO_3$, talc and mica (1000 mesh)), obtained at − 30° C. (X indicates catastrophic failure.)

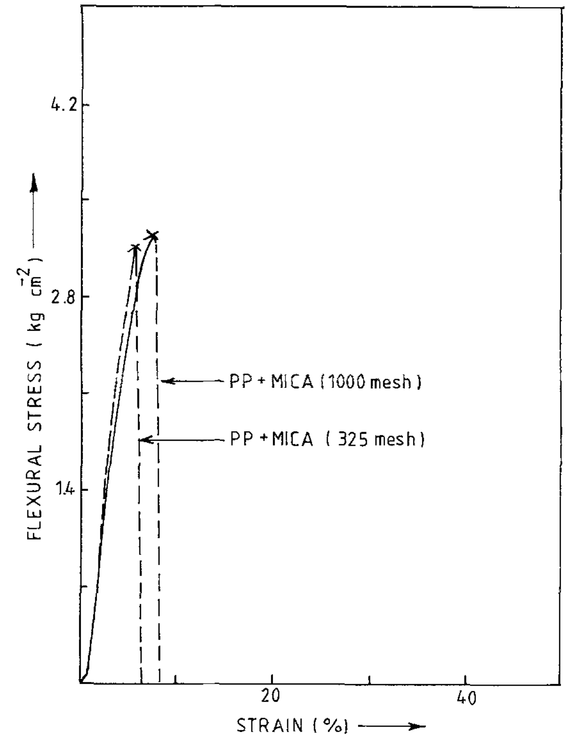


Figure 6 Flexural stress–strain curves of PP composites with two different mesh sizes of mica, obtained at − 30° C. (X indicates catastrophic failure.)

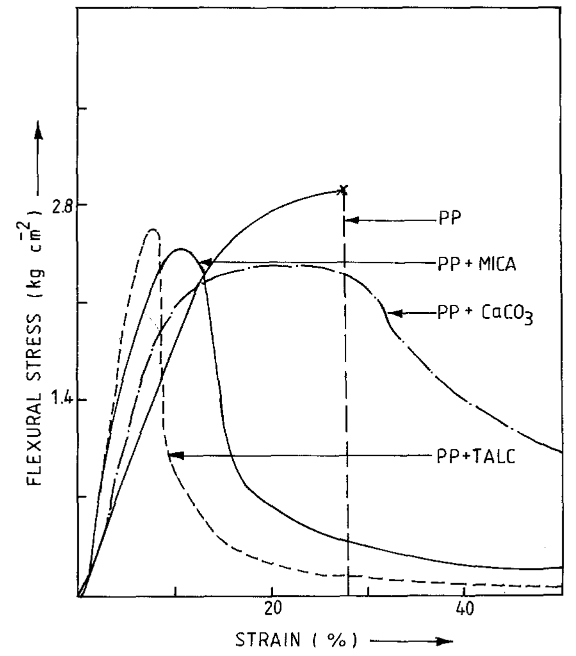


Figure 7 Flexural stress–strain curves of PP composites with various fillers ($CaCO_3$, talc and mica (1000 mesh)), obtained at 25° C. (X indicates catastrophic failure.)

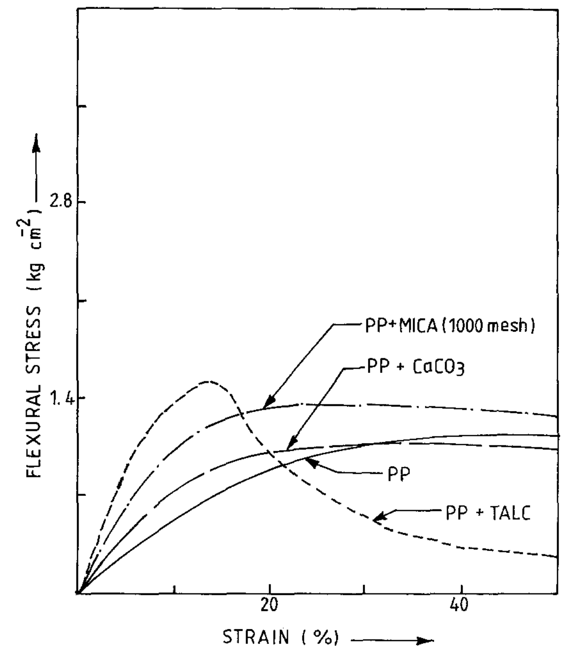


Figure 9 Flexural stress–strain curves of PP composites with various fillers, obtained at 80° C.

virgin PP exhibits quasi-cleavage fracture, which is a sort of cleavage fracture accompanied with some plastic deformation. A close examination of Fig. 12b revealed [7] even "Wallner Lines" (indicated by small arrows) which appear as a set of parallel cleavage steps perpendicular to the direction of radially propagating crack (indicated by big arrow). Also, a "twist boundary" and "tilt boundaries" can be seen. Fig. 12c shows the deformed surface of the virgin PP that has undergone excessive plastic deformation without actually allowing the crack to propagate. Because of the blunt notch that is given to the sample (see Fig. 1) and also because of the excessive plastic deformation of the polymer at 80° C, a single crack front could not develop and the strain energy is dissipated in creating the multiple shear-lips visible in Fig. 12c.

The process of crack propagation is characterized by the fracture zone developed at the crack tip. In the case of composite materials the size of this fracture zone, when compared to the particle size, is a factor affecting the mode of crack propagation. In particular, when the particle size is small compared to the dimensions of the fracture zone, according to Theocaris *et al.* [3], the presence of the particle at the vicinity of the propagating crack tip changes the rheological properties of the viscoelastic matrix while, at the same time, the particle size may not affect the path of the crack.

On the contrary, when the filler particles are big, as compared to the dimensions of the fracture zone, then the presence of filler particles may lead to a crack delay. The size of the fracture zone is greatly affected by the presence of dispersed particles. When the size of

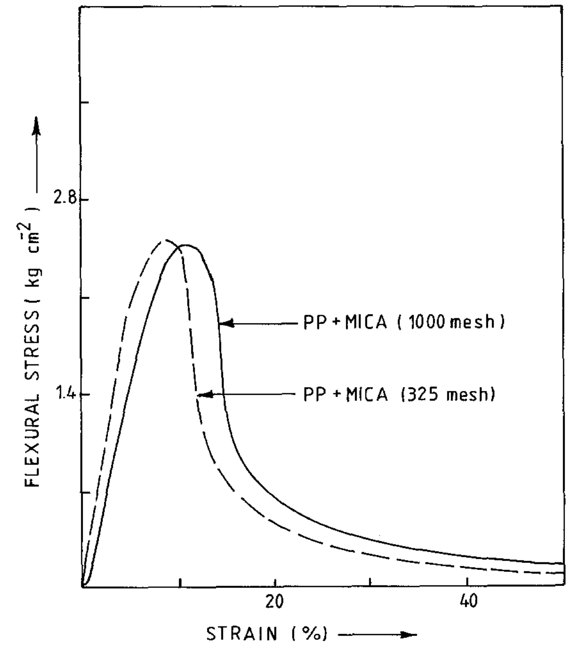


Figure 8 Flexural stress–strain curves of PP composites with two different sizes of mica, obtained at 25° C.

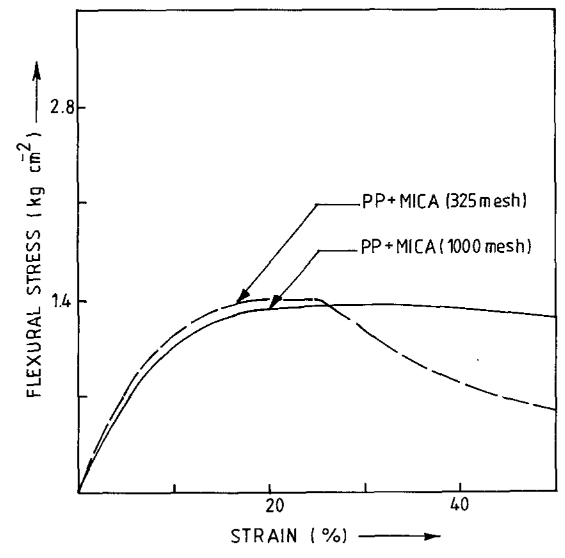


Figure 10 Flexural stress–strain curves of PP composites with two different mesh sizes of mica, obtained at 80° C.

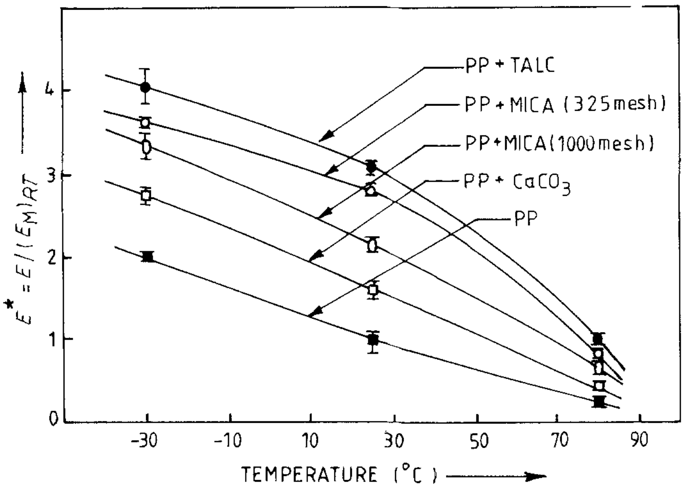


Figure 11 Variation of specific modulus (E^*) with temperature for PP composites with various fillers.

the fracture zone increases (with increase of temperature) then a microfracturing process takes place and this may lead to an increase in the overall fracture energy. It is generally recognized that crack pinning [19] is the dominant mechanism contributing to the fracture energy in polymers filled with rigid particles.

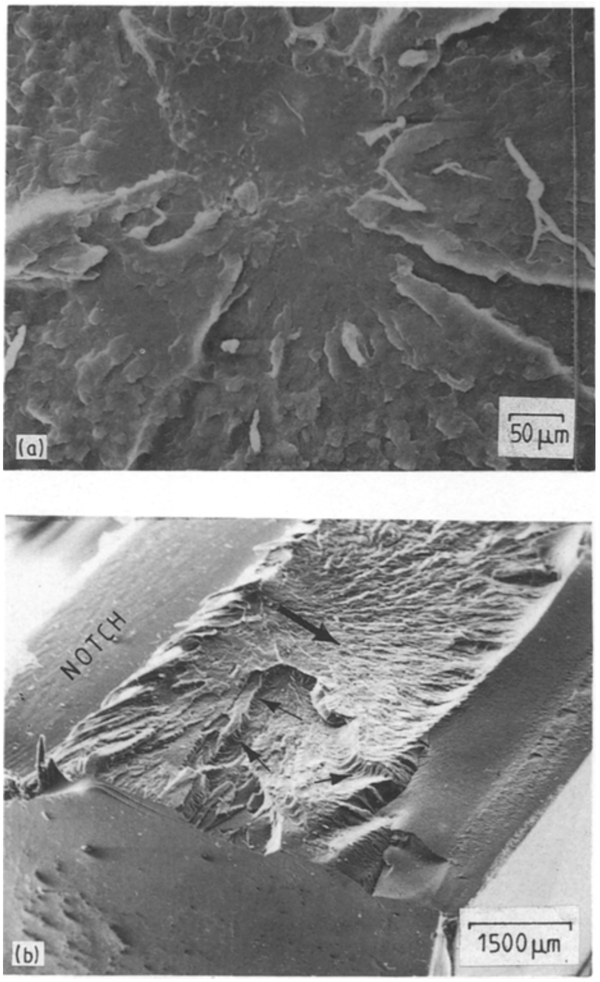
The crack front is temporarily pinned at the points where it meets the filler particles. It would bow forward between pinning points until it forms semicircular segments of diameters equal to the spacing between the points; then the segments will break off from the pinning points and the crack front will move further.

Fig. 13 shows the fracture surfaces (near the notch) of PP–$CaCO_3$ and PP–talc composites fractured at 25° C. In both these micrographs the notch is visible on the left side. The fracture surfaces reveal that the degree of plastic deformation of the matrix is very much dependent on the nature of the filler, for the same filler concentration. The degree of matrix deformation is greater in the case of the PP–$CaCO_3$ composite as compared to the PP–talc composite. Hence the energy absorption is also high during the fracture testing.

The fracture surfaces far from the notch of PP–$CaCO_3$ and PP–talc composites fractured at 25° C are presented in Figs 14a and b, respectively. The micrographs further confirm that the degree of plastic deformation in the PP–$CaCO_3$ composite is much more than that in the PP–talc composite. In the case of PP–mica composites (Figs 14c and d), the material with bigger flakes appears to undergo less plastic deformation than that with smaller flakes.

The greater fracture surface ductility observed in filled PP is at first glance surprising, since the same particulates also increase the elastic modulus of the material. It is likely that crack-pinning by the particulates is responsible for the enhanced crack-front ductility. While the crack is pinned, time-dependent viscous behaviour of the matrix is given the necessary time to occur and extensive local deformation occurs. This behaviour is general to the systems studied here.

When the notched samples were tested at 80° C,



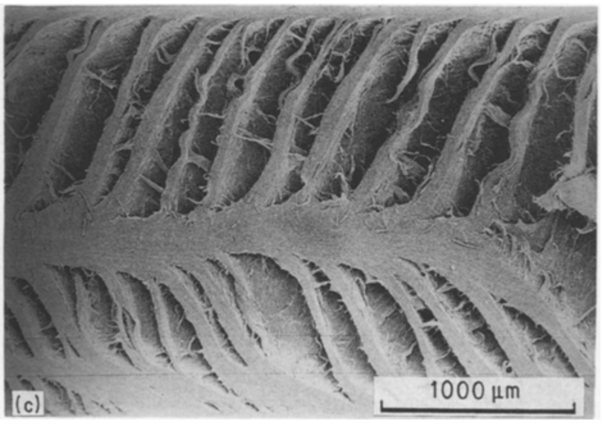


Figure 12 SEM micrographs of the fracture surfaces near the notch of polypropylene, obtained after Instron testing at (a) – 30° C, (b) 25° C and (c) 80° C.

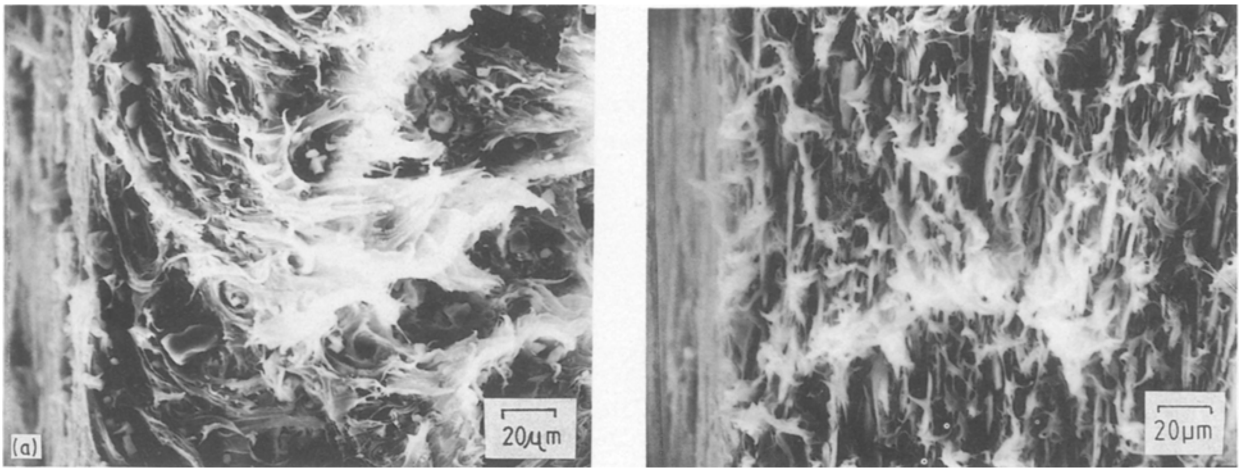


Figure 13 SEM micrographs of the fracture surfaces of (a) PP–$CaCO_3$ and (b) PP–talc composites obtained after Instron testing at room temperature and close to the notch.

besides lowering the yield strengths and moduli, increased viscous deformation was observed (Fig. 15) in all the composites. However, the degree of deformation depended on the nature of the filler and its size. In the case of the PP–$CaCO_3$ composite, the fracture did not take place; only blunting of the crack was observed. Under SEM examination, a large degree of matrix deformation, voids and debonding (Fig. 15a) are seen.

The heat distortion temperatures [20] of these composites are given in Table III. In the case of the PP–$CaCO_3$ composite, the deformation sets in at 62° C under static load, indicating clearly that beyond this temperature the composite cannot be rigid. In the case of the other composites, however, the testing temperature is below the heat distortion temperatures of the composites. The PP–talc composite showed limited crack propagation. The other two composites exhibited similar effects, with debonding and excessive matrix deformation.

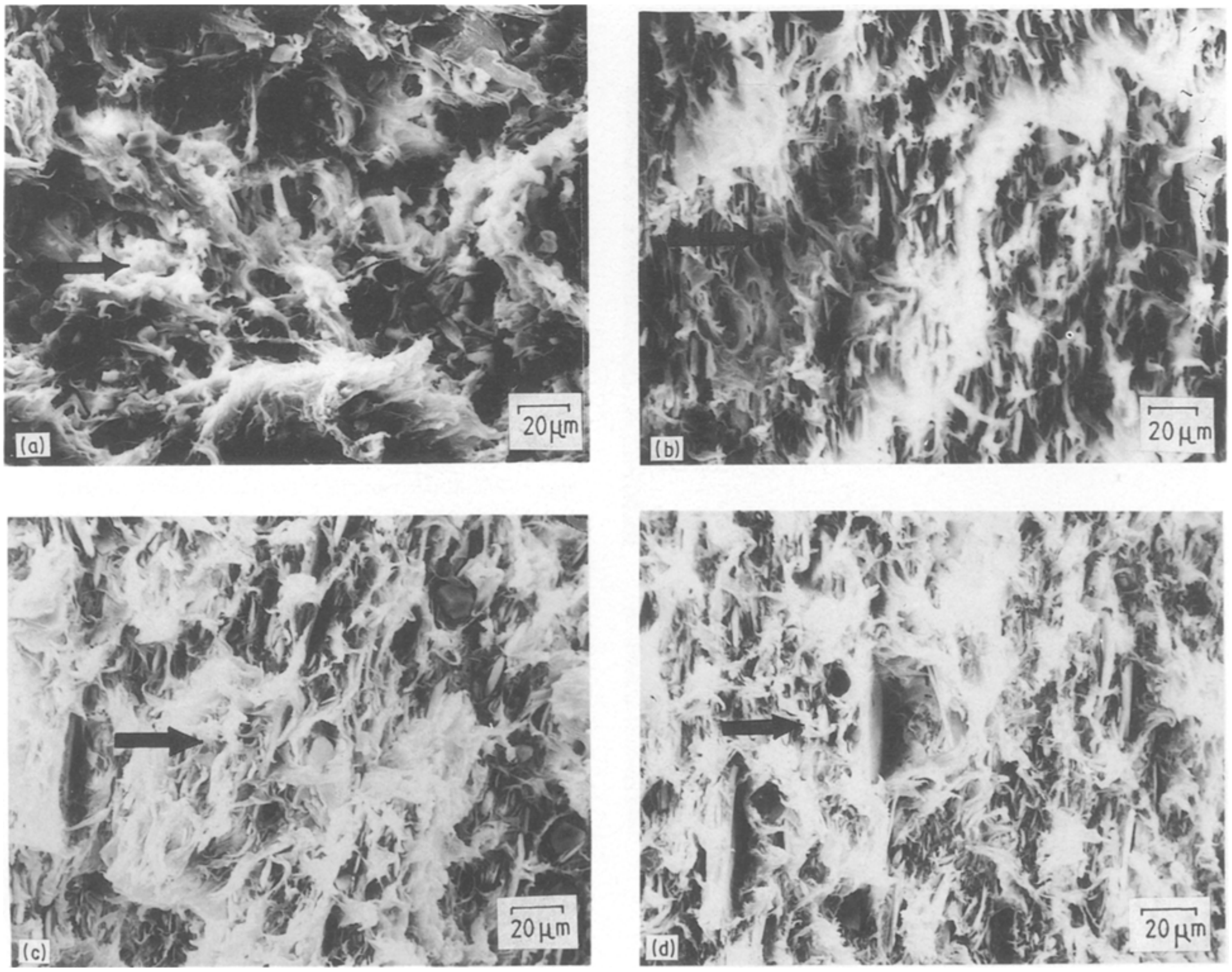


Figure 14 SEM micrographs of the fracture surfaces in the core regions of (a) PP–$CaCO_3$, (b) PP–talc, (c) PP–mica (1000 mesh) and (d) PP–mica (325 mesh), obtained after Instron testing at 25° C. (Arrow indicates fracture propagation direction.)

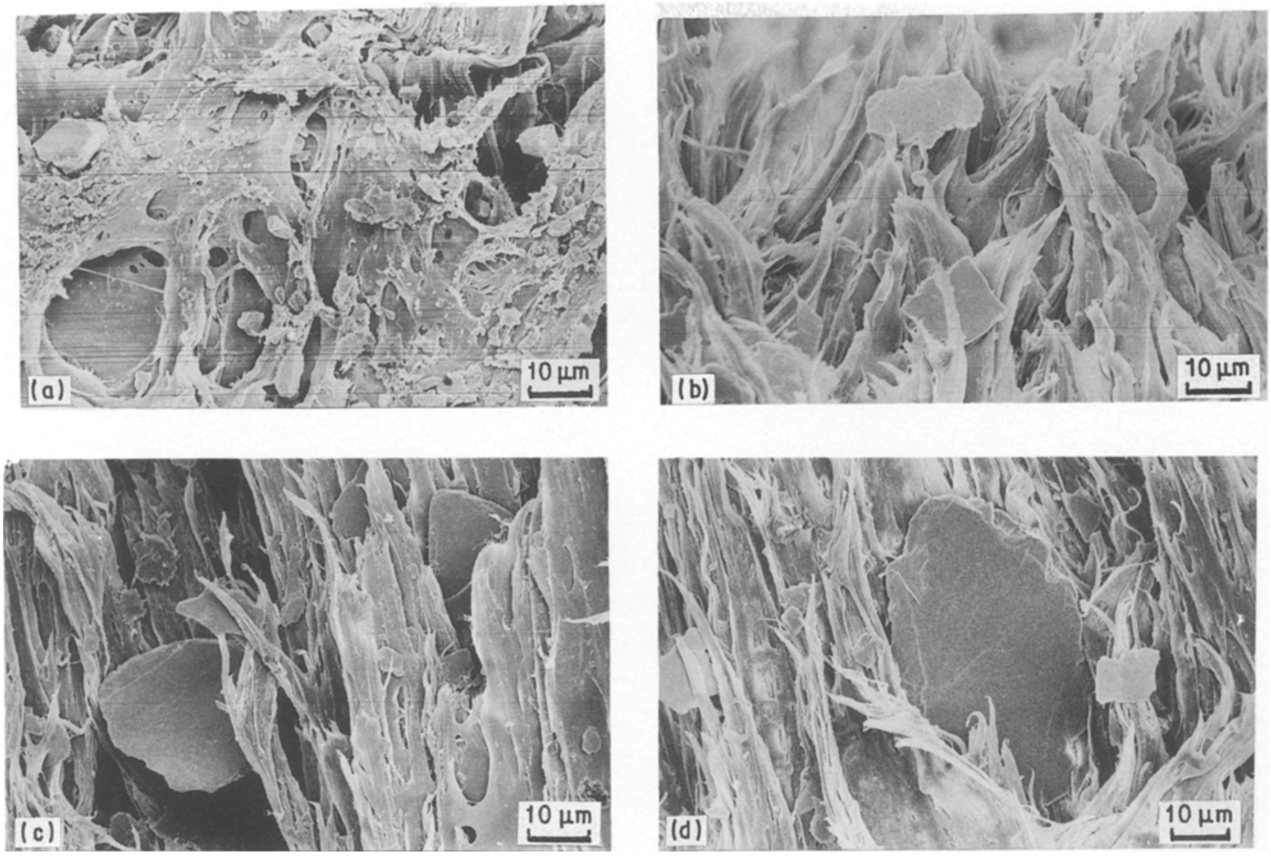


Figure 15 SEM micrographs of the fracture surfaces in the core regions of (a) PP–$CaCO_3$, (b) PP–talc, (c) PP–mica (1000 mesh) and (d) PP–mica (325 mesh) obtained after Instron testing at 80° C.

4. Conclusions

This work has revealed that the type of filler and its size (in the case of mica) considerably influence the fracture characteristics of polypropylene composites. The mica flake orientation varied in an ordered fashion from place to place in the injection moulded samples. This pattern also changed with a variation in mica flake size, affecting the thickness of skin and core zones. Mechanical tests show that at $-30°$ C only $CaCO_3$ is useful in avoiding the catastrophic failure in PP, while mica and talc could not. At room temperature, any one of the four fillers was good enough to overcome the brittle failure of virgin PP. Talc provided the highest normalized modulus in the whole temperature range studied, $CaCO_3$ offered the minimum increase, and mica took the intermediate position. Larger mica flakes provided a higher modulus, in comparison to the smaller flakes. SEM studies revealed that the incorporation of a filler enhanced the ductility of the matrix and thereby the composite was enabled to undergo stable crack propagation instead of a brittle failure. This behaviour is likely to be associated with the pinning of the crack front by the particles and the consequently longer times available for plastic deformation of the matrix near the crack front. When tested at 80° C the matrix material exhibited large-scale viscous deformation, leading to crack blunting, rendering the material unsuitable for the application of linear elastic fracture mechanics.

Acknowledgements

One of us (S.F.X.) wishes to express his gratitude to Dr Y. N. Sharma, Dr S. Sivaram, Dr J. S. Ananc and Dr K. V. Rao for their help and encouragement. He would like to acknowledge the financial assistance provided by UNDP and the Department of Science and Technology, Government of India, and the experimental help of Messrs Touey Thiravong (CCM, University of Delaware), H. N. Vaidya, A. R. Parikh and U. M. Shah.

References

1. R. T. WOODHAMS and M. XANTHOS, "Handbook of Fillers and Reinforcements for Plastics", edited by J. V. Milewski and H. S. Katz (Van Nostrand Reinhold, New York, 1978).
2. C. E. CHAFFEY, *Ann. Rev. Mater. Sci.* **13** (1983) 43.
3. P. S. THEOCARIS, G. C. PAPANICOLAOU and G. A. PAPADOPOULOS, *J. Compos. Mater.* **15** (1981) 41.
4. C. D. HAN, V. VAN DEN WEGHE, P. SHETE and J. R. HAW, *Polym. Eng. Sci.* **21** (1981) 196.
5. L. M. ALTHOUSE, D. M. BIGG and W. M. WONG, *Plast. Comp.* **6** (1983) 71.
6. C. D. HAN, C. SANDFORD and H. J. YOO, *Polym. Eng. Sci.* **18** (1978) 849.
7. S. F. XAVIER, "Fracture Mechanics in Particulate Filled Polypropylene Composites", UNDP/DST Report (1986).
8. K. FRIEDRICH, "Microstructure and Fracture of Fiber Reinforced Thermoplastic Polyethylene Terephthalate", Center for Composite Materials, University of Delaware, Report CCM-80-17 (1980).
9. K. FRIEDRICH, R. WALTER, H. VOSS and J. KARGER-KOCSIS, *Composites* **17** (1986) 205.
10. T. M. MALIK and R. E. PRUDHOMME, *Polym. Comp.* **7** (1986) 315.
11. T. VU-KHANH, B. SANSCHAGRIN and B. FISA, *ibid.* **6**(4) (1985) 249.
12. T. VU-KHANH and B. FISA, *ibid.* **7**(4) (1986) 219.

13. J. M. SCOTT and D. C. PHILLIPS, Report AERE-R 7798, Process Technology Division, AERE Harwell, UK (1974).
14. ASTM Standard E-399 Standard Test Method for Plane Strain Fracture Toughness of Metallic Materials, Annual Book of ASTM Standards (1983).
15. A. J. KINLOCH and R. J. YOUNG (eds) "Fracture Behaviour of Polymers" (Applied Science Publishers, Barking, Essex, 1983) p. 102.
16. K. FRIEDRICH, *Plastics Rubber Proc. Appl.* **3** (1983) 255.
17. A. SAVADORI, *Mater. Tech.* **4** (1985) 212.
18. P. L. FERNANDO and J. G. WILLIAMS, *Polym. Eng. Sci.* **20** (1980) 215.
19. G. M. NEWAZ, *J. Mater. Sci. Lett.* **5** (1986) 71.
20. S. F. XAVIER and Y. N. SHARMA, *Polym. Comp.* **7** (1986) 42.

Received 24 October 1988
and accepted 14 April 1989