

Fracture propagation in particulate-filled polypropylene composites

Part 3 *Influence of mica surface treatments*

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Composites of isotactic polypropylene and fixed weight (40%) of mica without and with different surface treatments (isopropyl triisostearoyl titanate (TTS) and 3-aminopropyl triethoxy silane) were prepared by injection moulding. The influence of surface treatment on the microstructure and fracture propagation in the composites was investigated. Microstructural investigations revealed that the surface treatments influenced the mica flake orientation, which in turn resulted in the changing of the skin-core zone thickness. The influence of the mica surface treatment was found to be insignificant at -30°C whereas at 25 and 80°C the surface treatments considerably influenced the fracture propagation. The normalized modulus and the fracture toughness (K_{IC}) of the composites were found to vary with mica surface treatments. Interfacial bonding was also found to vary with surface treatment. Schematic models for crack propagation in PP-mica composites are proposed.

1. Introduction

Polymers, being organic materials, exhibit little tendency to wet and cover the surface of inorganic filler particles during compounding [1]. Optimum properties in composites usually cannot be realized with fillers in the agglomerated form. One approach to surmount this problem is to improve the polymer-filler compatibility through the use of wetting agents or coupling agents. Wetting and coupling agents are significantly different from each other [2]. A wetting agent modifies the surface tension of the filler in such a way that the polymer will wet the filler particles, allowing then to separate and distribute in a better manner than obtained by shear mixing only. A coupling agent [3-5], on the other hand, is a bifunctional molecule having an organic end and an inorganic end. The inorganic end is designed to bond to the filler, the organic end to the polymer, resulting in a chemical bond between filler particles and polymer.

It has frequently been stated [3, 6], that the interphase between the reinforcement and the polymer matrix is crucial in determining the properties of polymer composites. It is well known that polypropylene can develop a transcrystalline interphase with untreated mica [4], mica treated with triisostearoyl isopropyl titanate (TTS) [7] or with silane coupling agent [4, 8]. But the transcrystalline interphase cannot be examined in isolation [5]. An attempt, however, is made here to explore the effects of the interphase on the skin-

core relative thicknesses, fracture propagation and fractography of PP-mica composites with different surface treatments to the mica flakes.

Parts 1 and 2 [9, 10] of this work dealt with the influence of filler nature and mica concentration on fracture propagation in PP composites. This part is devoted to the study of the effects of mica surface treatment with TTS, which is known [11] to provide a plasticizing effect, and also with 3-aminopropyl triethoxy silane, which is likely to improve the adhesion between mica and the matrix.

2. Experimental procedure

The preparation of the composites with different surface treatments to the mica and the methods followed in studying the fracture propagation are given in detail in Part 1 [9].

3. Results and discussion

3.1. Microstructure

The variation in mica flake orientation angle ($|\theta^{\circ}|$) with depth below the surface of the injection-moulded bars was measured (Fig. 1) after taking scanning electron micrographs in sequence, as described in Part 1 [9]. Confining discussion to the same definition of the skin-core regions presented elsewhere [9], it is evident that different surface treatments to mica have resulted in significantly different skin-core thicknesses. The titanate coupling agent has reduced the

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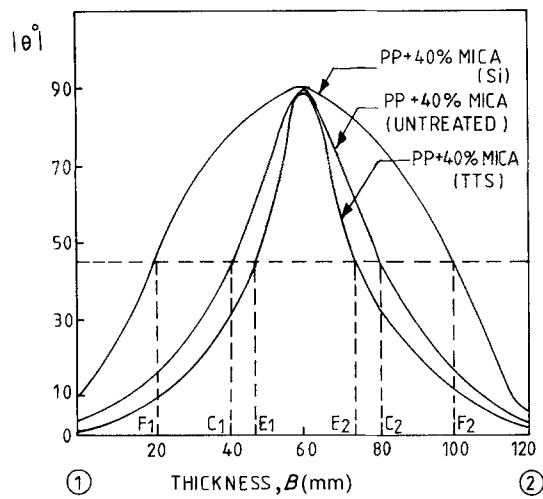


Figure 1 Variation of mica flake orientation ($\langle \theta^2 \rangle$) as a function of the thickness of the sample for PP composites with untreated, TTS-treated and silane-treated mica.

core thickness somewhat, while the silane coupling agent (3-aminopropyl triethoxy silane) has enhanced the core thickness enormously. The extent to which the coupling agents act through matrix plasticization or through the actual coupling of filler to matrix during flow is not known precisely. However, it is likely that coupling itself is important, because when the silane coupling agent (a very effective coupler) is used, the flake orientation increases, resulting in enhanced core thickness. In fact, the core thickness has increased to approximately three times that of the composite with TTS-treated mica.

3.2. Fracture properties

The flexural stress-strain curves of the PP composites with untreated mica and mica treated separately with

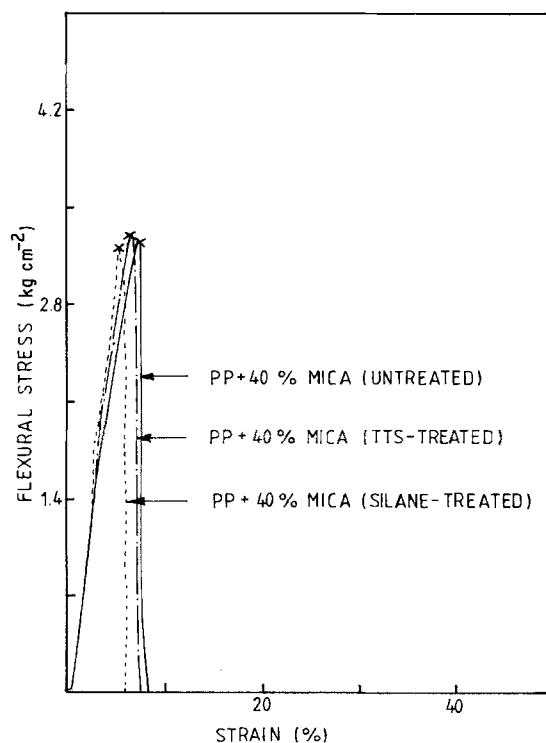


Figure 2 Flexural stress-strain curves of PP composites with 40% of untreated, TTS-treated and silane-treated mica. These curves were obtained at -30°C .

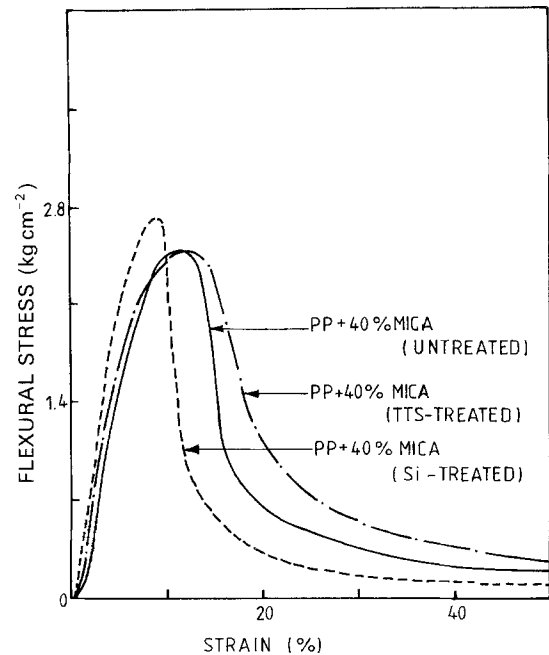


Figure 3 Flexural stress-strain curves of PP composites with 40% of untreated, TTS-treated and silane-treated mica, obtained at $+25^\circ\text{C}$.

a titanate coupling agent and a silane coupling agent are presented in Fig. 2. All these composites show brittle fracture at -30°C . The surface treatment to mica, either with titanate or silane, seems to have negligible effect on the fracture properties of the composites, *vis-à-vis* untreated mica. In other words, the nature of the interphase is such that its influence at -30°C is not significant enough to distinguish its effect on fracture propagation, although the interphase may differ from one composite to the other. In addition, even the variations in the mica flake orientations and also the skin-core thicknesses do not play a significant role in influencing the fracture properties at -30°C . However, at 25°C (Fig. 3), the composites with different surface treatments to mica show considerable difference in the fracture behaviour, in comparison to the one with untreated mica. The tensile/flexural strength is high, in the case of silane-treated mica, but the ultimate elongation is reduced. In the case of titanate-treated mica, the yield strength does not differ from what it is with untreated mica. However, the elongation is increased. Nevertheless, all three composites exhibit stable crack propagation at 25°C . When tested at 80°C (Fig. 4), the composite with no mica treatment and the one with TTS-treated mica show no apparent neck formation and exhibit gross yielding of the matrix. With silane treatment, one can observe gradual necking and reduction in elongation, however, with stable crack growth. It is evident from the fracture propagation studies (below) that the different surface treatments to mica affect the interphase differently, and the effects of these modified interphases are different at different temperatures. In other words, the material testing conditions somewhat mask the interphase effects.

The moduli of the composites were calculated as explained in Part I [9]. The variation of normalized flexural moduli (E^*) of the composites with

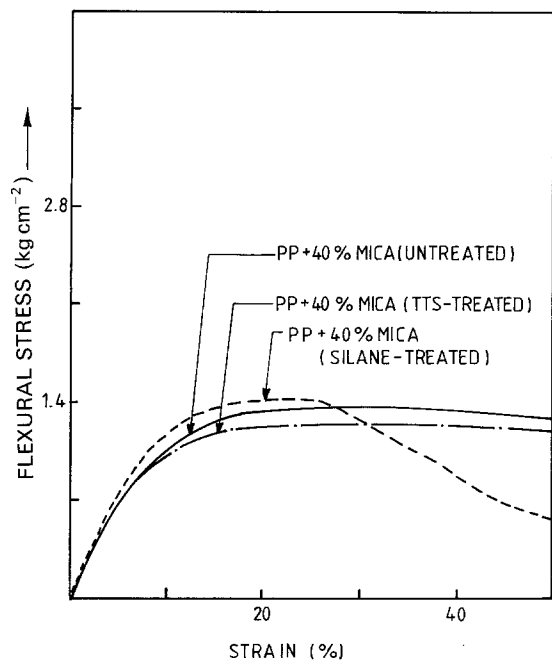


Figure 4 Flexural stress-strain curves of PP composites with 40% of untreated, TTS-treated and silane-treated mica, obtained at 80°C.

temperature is shown in Fig. 5. At all testing temperatures the material with silane-treated mica exhibits the highest modulus, and the modulus of the composite with untreated mica exhibits the lowest value of E^* at all the testing temperatures. The effect of titanate coupling agent is such that the modulus increase at low temperature (-30°C) is quite good; but with increasing temperature it falls close to that of untreated mica composite at 25°C and gradually merges with it at 80°C . The relative differences in the moduli of the composites approach each other at 80°C , confirming the fact that the matrix material plays a dominant role, no matter what surface treatment is employed.

The fracture toughness K_c was calculated for all the composites using the analytical procedure described in Part 1 [9]. The values of K_c at -30 and 25°C are presented in Table I. The silane treatment to mica has enhanced K_c both at -30 as well as at 25°C , in comparison to the untreated mica-filled composite. The titanate treatment to mica, on the other hand, has resulted in raising K_c at -30°C only, while at 25°C it went below that of the untreated mica composite. The effects of surface treatments on the PP-mica interphase are not known with certainty. However, one can speculate that the different surface treatments to mica result in different kinds of interphases, which would respond differently in modifying the plastic zone in front of the crack, eventually affecting the value of K_c .

3.3. Fractography

The fracture surfaces of the composites with TTS-

TABLE I

Sample	Surface treatment	K_c	
		-30°C	25°C
PP + 40% Mica	Untreated	3.95	3.5
PP + 40% Mica	TTS	4.13	3.34
PP + 40% Mica	Silane	4.19	3.66

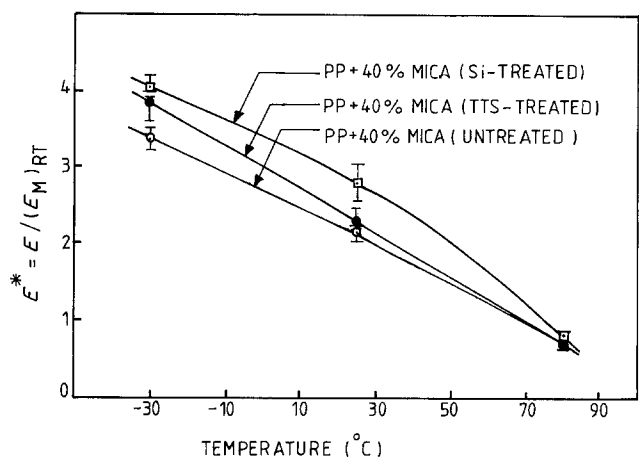


Figure 5 Variation of the specific modulus (E^*) with temperature for PP composites with mica having different surface treatments.

treated mica and silane-treated mica, obtained by fracturing the composites at -30°C , were studied. Micrographs taken near the notch of the respective samples do not indicate significant differences which can be attributed to the changes in mica treatment. Micrographs of the portion of the fracture surface opposite the notch indicate that the "far-field effect" [12] is prevalent in both cases. Our earlier fractographic studies [13] revealed that the interfacial adhesion between TTS-treated mica and PP is poor, although the former had developed a transcristalline interphase [7] with PP. However, the micrographs presented in Fig. 6, taken from specimens fractured at 25°C , give an indication that interfacial adhesion between silane-coated mica and PP exists, at least at the flake edges (Fig. 6b). One can observe PP in the form of elongated fibrils adhering at the mica edges, an indication that the adhesive strength here is apparently greater than the cohesive strength of PP. This small improvement in the interfacial adhesion is probably sufficient to cause the observed changes in the microstructure and also an increase in the yield strength and the modulus of the composite. It could also be responsible for altering the plastic zone in front of the crack, causing the fracture toughness to lie above those of other composites. For the other composites (other than silane-treated mica ones) no such adhesion of the material was observed [7, 13].

The composites flexed at 80°C did not undergo clear-cut breakage. However, the fracture propagated to some extent, with gross yielding of the matrix material (Fig. 7). This is observed in all three composites under study. Under close examination, the fracture surfaces reveal debonding of the flakes, voids and excessive matrix deformation. The composite with silane-treated mica (Fig. 7c) gives an indication that the matrix material still adheres to the pulled-out flakes.

4. Models of crack propagation in PP-mica composites

From a summary of the microscopic observations discussed so far, some models can be hypothesized to describe the crack propagation characteristics in PP-mica composites [14]. These models, however, need

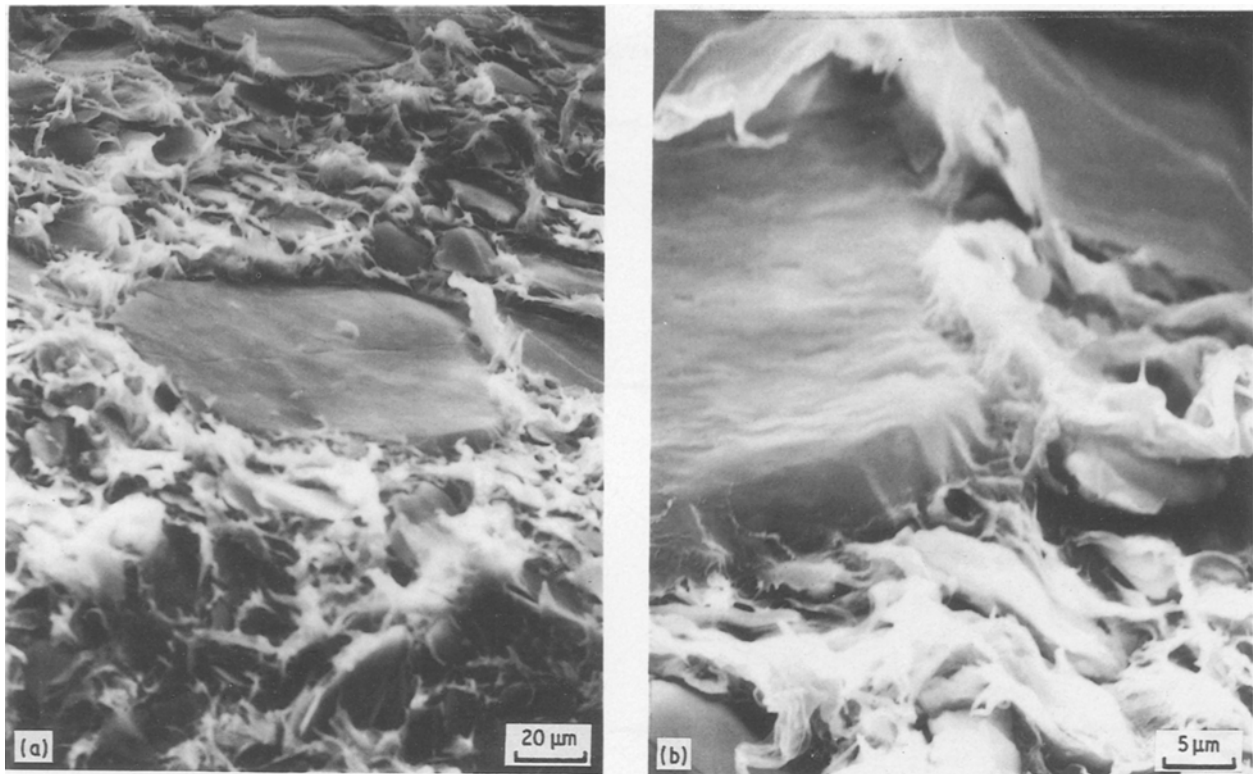


Figure 6 (a) SEM fractograph of composite with silane-treated mica, fractured at +25°C; (b) small portion of (a) magnified to resolve the PP-mica (silane-treated) interface.

not necessarily be confined to PP-mica composites alone; but can also be extended to any other semi-crystalline thermoplastic-mica composites.

Fig. 8 (case 1A) represents the case in which the mica flake's planar surface is parallel to the direction of crack propagation. The crack may deviate from its

direction temporarily by following the mica-matrix interphase. It may again come back to its original direction of propagation in order to minimize the energy involved. However, if the interfacial adhesion is strong, then the crack may propagate through the cleavage surfaces of the mica flake and thus cause flake delamination to take place (case 1B). In situations where mica flakes are inclined to the crack growth direction by an angle θ , again the crack may pass through the interphase or the cleaved surfaces of the mica flakes when $0^\circ < \theta \ll 90^\circ$ and also when $90^\circ \ll \theta < 180^\circ$ (case 2, A and B). When the mica flake is approximately perpendicular to the crack propagation direction ($\theta = 90^\circ$), in order to maintain the optimum propagation direction, the crack will follow the interphase, where the bonding is normally

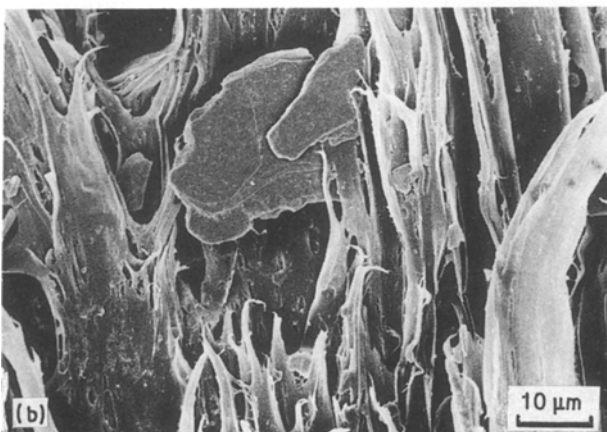
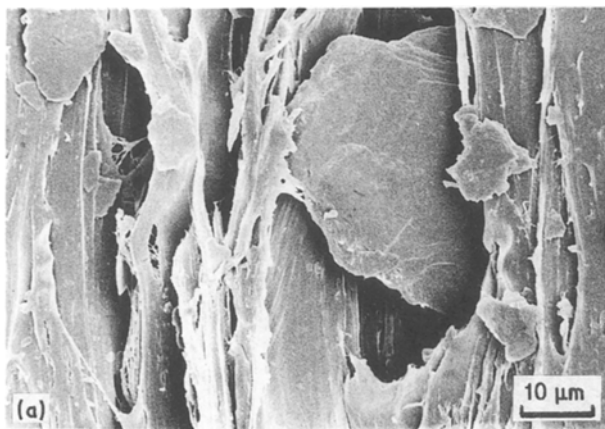
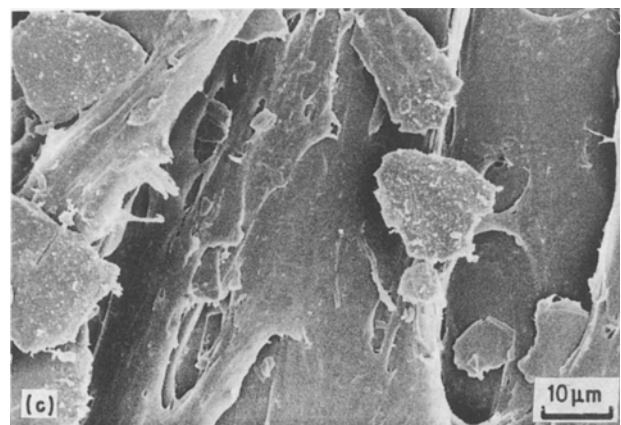


Figure 7 Scanning electron micrographs of the fracture surfaces of (a) PP-mica (untreated), (b) PP-mica (TTS-treated) and (c) PP-mica (silane-treated) and composites, obtained after testing to failure at 80°C.



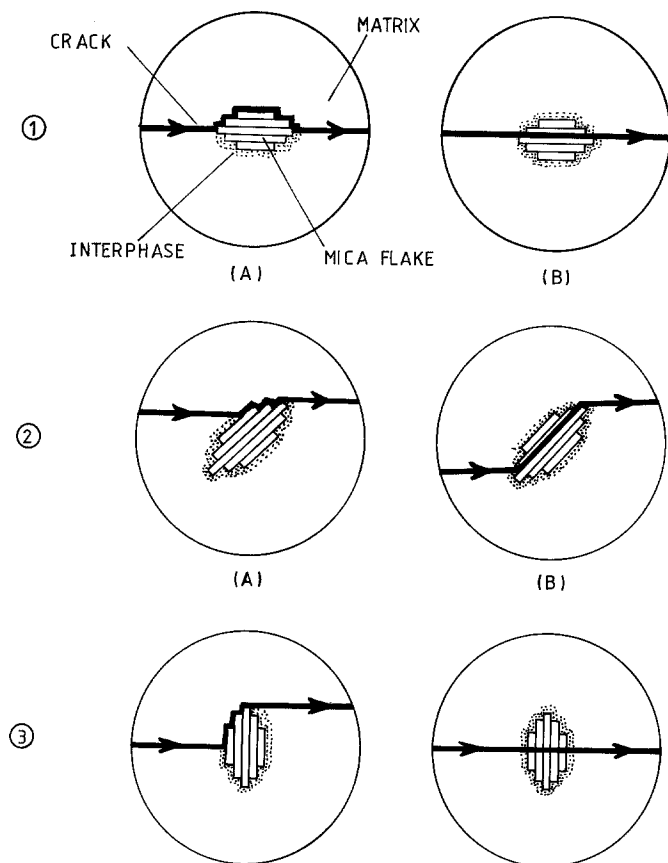


Figure 8 Possible modes of fracture propagation in mica-reinforced thermoplastic composites.

not strong (case 3A), or it will fracture the flake itself if the interfacial bonding is strong (case 3B). The cracks, in general, are found to grow in a flake avoidance mode. Favourable sites for the crack propagation are the mica-matrix interphase, voids, etc.

The crucial parameter, in all these cases, is the mica-matrix bond quality. If the adhesion between mica and matrix is good, high shear stresses are necessary to induce microvoiding across the interphase, which weakens the composite and gives rise to microcrack formation at the interfaces. These microcracks, in turn, can initiate crazing and yielding of the surrounding matrix material until the crazes coalesce. This mode allows the crack to adopt the path of least resistance.

Poor interfacial adhesion, on the other hand, lets the flakes debond easily from the matrix, providing sites of flake pull-out along the propagating crack. The possible basic mechanisms involved in the crack propagation are: (1) flake breakage, (2) flake pull-out, (3) flake delamination, (4) mica-matrix debonding, (5) plastic deformation and matrix failure.

5. Conclusions

Part 3 of this study of the effect of particulate fillers in PP has revealed that varying the surface treatment of mica, at constant mica content, alters the skin-core thicknesses of the injection-moulded samples. Improved interfacial adhesion was observed in the case of a silane-treated mica composite and could be responsible for changes in mica flake orientation, causing the core thickness to increase. For the same composite, fracture toughness and normalized flexural moduli were found to be high. The surface treatments used here were insufficient to avoid cata-

strophic failure of the samples at -30°C , although they modify to a significant extent the stress-strain curves at 25 and 80°C . Fracture surfaces obtained at 80°C reveal preferential adhesion of matrix material in the case of silane-treated mica. Schematic models for crack propagation in mica-thermoplastic composites are proposed.

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