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Polypropylene reinforced with silicon carbide whiskers

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Thermal, crystallization and mechanical behaviour of isotactic polypropylene (iPP) reinforced with advanced silicon carbide whiskers (SiC_w) has been investigated. It is well established that the existence of chemical and physical interactions between the matrix and the reinforcement enhances the cohesive strength at the interphase thus improving the mechanical performance of the composite. In order to improve chemico-physical interactions between the components of the inorganic–organic composite system, their affinity has been enhanced in two ways: by coating the whiskers with a thin layer of acrylate-grafted polydivinylbenzene and by using as matrix a chemically modified polypropylene. The mechanical properties of the resulting composite materials have been compared and related to the dispersion grade of the whiskers within the matrices and the morphology of the samples.

1. Introduction

Silicon carbide whiskers are very attractive materials as a component of composites, because they combine high stiffness (silicon carbide is the hardest substance after diamond) and perfection grade. Owing to their small diameter, whiskers are almost devoid of defects and consequently present a resistance very close to the maximum theoretical value expected from the elasticity theory [1]. Whiskers have been used especially in ceramic–ceramic composites [2–6] but only a few attempts have been made to combine them with thermoplastic matrices. These latter present the advantage of lightness with respect to ceramic or metallic matrices. Thus a balance of properties could be reached by inorganic–organic composite systems provided that a good adhesion between the components exist. In order to improve mechanical resistance, a homogeneous dispersion of the reinforcement within the matrix must be achieved. Otherwise, clusters of whiskers act as failure regions reducing the mechanical behaviour of the materials.

The aim of this study was to prepare and characterize some thermoplastic-based composites reinforced with SiC_w where the tendency of the solid additive to aggregate is low. This object was pursued favouring the chemico-physical interactions in the following ways:

1. by taking advantage of chemical modifications of the polymeric matrix;
2. by varying the chemical nature of the whisker surface by coating with a layer of acrylate-grafted polydivinylbenzene.

Mechanical tests, and thermal and electron microscopic analyses, allowed a correlation to be made between the macroscopic behaviour of the composites and their microscopic and molecular characteristics.

2. Experimental procedure

2.1. Materials

Whiskers of β-silicon carbide, 5–50 μm in length having an average diameter of 3 μm (SiC_{w1} type whiskers), were provided by Advanced Refractory Technologies, Inc., Buffalo, New York. Whiskers named SiC_{w2} are silicon carbide whiskers coated with 21 wt % poly(divinylbenzene) and then 5 wt % grafted poly(methylmethacrylate). The procedure for coating the whiskers involved: (1) dispersing 12.5 g SiC_w in a solution composed of 440 ml mineral spirits, 0.5 ml 4-vinylpyridine, 5.0 ml divinylbenzene and 0.5 g benzoyl peroxide; (2) heating the stirred slurry at 100 °C for 18 h; (3) cooling the reaction mixture to 50 °C and adding dropwise 0.8 ml methyl methacrylate plus 0.5 g benzoyl peroxide; (4) heating the mixture at 90 °C for 4 h; and (5) filtering the cooled product mixture using 0.2 μm polycarbonate membrane and drying the solid at 50 °C/20 torr (1 torr = 133.322 Pa) for 5 h. The yield was 16.6 g. TGA analysis showed the solid to

TABLE I Codes of the materials examined

iPP	Isotactic polypropylene
iPPMa	Isotactic modified maleic anhydride polypropylene
SiC_{w1}	Uncoated silicon carbide whiskers
SiC_{w2}	Silicon carbide whiskers coated with polydivinylbenzene grafted polymethylmethacrylate

contain 21.7 and 26.2 wt % polymer after steps (2) and (5), respectively.

Unmodified isotactic polypropylene ($M_n = 17\,900$, $M_w = 172\,000$, $M_w/M_n = 9.6$) and modified maleic anhydride polypropylene ($M_v = 98\,900$) were provided by Himont. The weight percentage of the grafted anhydride was 1.6%. The examined materials and their codes are reported in Table I. Samples containing 10% and 20% by weight of whiskers were prepared.

2.2. Sample preparation

Powdered polypropylene was mixed under room conditions of temperature and pressure with silicon carbide whiskers. The resulting composite powder was first rigorously stirred and then compression moulded under the following conditions of temperature and pressure: $T = 180\,^{\circ}C$, $p = p$(room) for 3 min; $T = 180\,^{\circ}C$, $p = 100$ bar for 1 min. The molten sheet was then solidified in a mould by water-cooling according to the curve reported in Fig. 1. Sheets having thickness of 1 mm were cut to obtain dumb-bell shaped specimens for tensile tests. Samples for impact tests having dimensions 6.0 mm × 60 mm were cut by a mill from 3.5 mm thick sheets. The specimens were notched at the middle of their length as follows: first a blunt notch was made with a V-shaped machine tool and then a sharp notch 0.2 mm deep was produced by a razor blade fixed on a micrometric apparatus. After fracturing the sample, the final notch depth value was measured using an optical microscope.

2.3. Techniques

A Mettler TA-3000 differential scanning calorimeter (DSC) equipped with a control and programming unit and a calorimetric cell operating under a nitrogen atmosphere, were used in this study. Scanning electron microscopy (SEM) was performed using a Philips 501 equipment after vacuum metallization of the samples by means of a Polaron sputtering apparatus with Au–Pd alloy. Thermogravimetric analysis (TGA) was carried out by using a Mettler TG50 Thermobalance. An Instron machine was used to perform room-temperature tensile tests according to ASTM standard methods. The adopted crosshead speed was 1 mm min^{-1}.

The impact tests were carried out at room temperature and impact speed of 1 m s^{-1} by using an Instrumented Pendulum (Ceast Autographic Pendulum MK2). The tests were conducted according to ASTM-D256 standard methods.

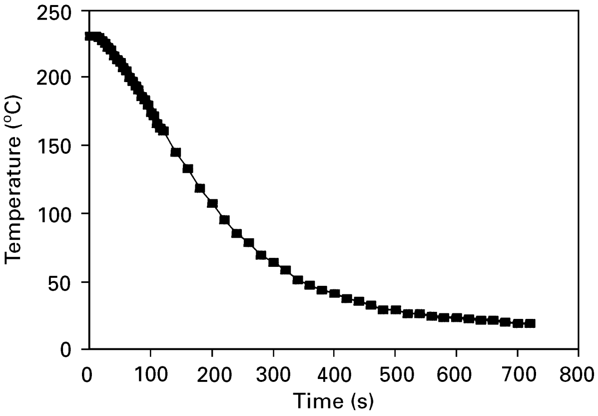

Figure 1 Temperature–time curve describing the cooling pattern followed by compression-moulded samples.

2.4. Procedures

Small amounts (about 15 mg) of the samples for calorimetric analysis were submitted to the following thermal treatment: first, heating from 30 °C to 230 °C at a rate of 20 °C min^{-1} (I RUN) and holding at the final temperature for 2 min. Then the temperature was diminished to $-100\,^{\circ}C$ at a cooling rate of 10 °C min^{-1} (II RUN). Finally, the material was reheated to 230 °C at a rate of 10 °C min^{-1} (III RUN).

SEM analysis was carried out on samples crystallized from the melt (230 °C) in a calorimetric cell with a cooling rate of 10 °C min^{-1}.

Thermogravimetric curves were obtained following the weight loss of the samples heated up to 500 °C at a rate of 5 °C min^{-1}. The analysis was performed using nitrogen as purge gas.

3. Results and discussion

3.1. Thermal and morphological investigations

Thermogravimetric analysis showed that the presence of whiskers does not considerably change the thermal properties of the polymeric matrices. As an example, in Fig. 2 the thermogravimetric curves of iPPMa and iPPMa/SiC_{w2} 10% are shown. They exactly overlap up to the temperature at which the polymer is completely degraded, while silicon carbide is still thermally stable. A slight diminution (about 14 °C) of the temperature at which the weight loss is 50% was observed for unmodified polypropylene in the presence of SiC_{w2}, as shown in Fig. 3. This finding indicates that dipolar interaction exists between ester groups of poly(methylmethacrylate) in the whisker coating and anhydride groups in the modified polypropylene backbones. Thus, the presence of polar groups, both on the whisker surfaces and in the polymer matrix, make the composite as stable as the unreinforced matrix, while the lack of interactions at the whisker/matrix interface can cause a slight reduction of thermal stability.

Table II reports the data obtained using DSC. The apparent fusion enthalpy, ΔH_c, and melting and crystallization temperatures, T_m and T_c, were determined in correspondence with the peak maxima and

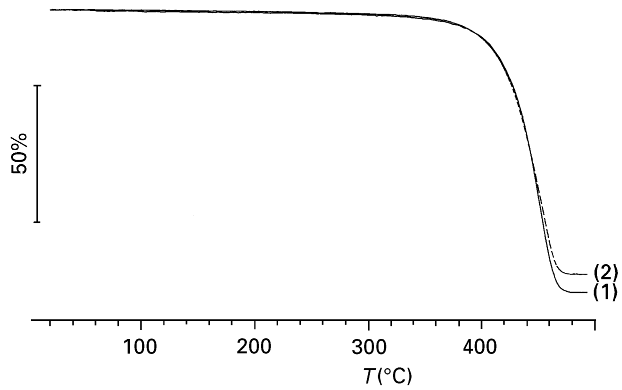

Figure 2 Thermogravimetric curves of (1) iPPMa and (2) iPPMa/SiC$_{w2}$ 10% performed under nitrogen purge gas at a scan rate of 5 °C min^{-1}.

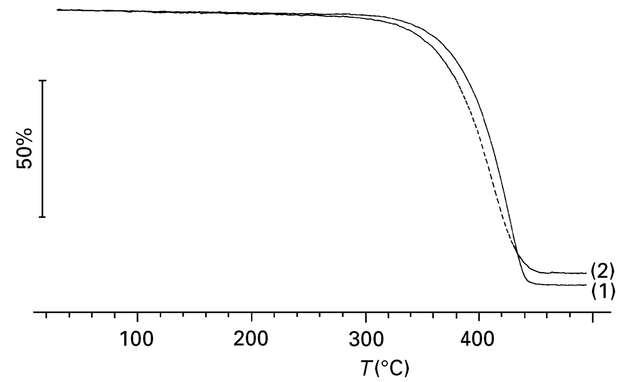

Figure 3 Non-oxidative degradation curves of (1) iPP and (2) iPP/SiC$_{w2}$ 10% carried out under nitrogen as purge gas at a scan rate of 5 °C min^{-1}.

crystallinity content, X_c. This latter number was calculated by using a literature value of fusion enthalpy of hypothetical 100% crystalline polypropylene equal to 209 J g^{-1} [7].

The samples underwent the three thermal runs described in Section 2. The data reveal that the presence of whiskers influences the melting temperatures of the polymer in the composites but does not affect the enthalpy of the first-order transitions. The shift of the melting temperature is negligible for iPP-based composites, whereas it becomes noteworthy in the case of iPPMa-based composites. The decrease of T_m in the system iPPMa/whiskers can be attributed to a lesser degree of perfection in lamellar crystals of the polymer grown in the presence of whiskers [8] and/or to different crystal morphology [9]. The main difference between the neat matrix and the composites is in the crystallization behaviour (II RUN). Indeed the value of T_c of the polymeric component is increased in the composite materials, especially for modified polypropylene.

According to the crystallization theory, the process of crystallization takes place in two stages: nucleation of individual crystals and their subsequent growth. Each stage occurs at a characteristic rate and both the processes contribute to the overall rate of crystallization, considered as the mass of the crystalline material formed from the melt in unit time. The rate of the nucleation stage determines the number of nuclei which arise per unit mass per unit time, while the rate at which the crystal growth front progresses in units of velocity, accounts for growth. The faster the nucleation process, the higher will be the nucleation density and hence the average diameter of spherulites will become smaller. The rate of nucleation is assumed to be proportional to $\exp(-\Delta\phi^*/kT)$, where k is the Boltzmann constant, T the absolute temperature and $\Delta\phi^*$ is the work to form a nucleus of critical dimension. A critical nucleus is large enough to prevent its disruption due to the micro-Brownian fluctuations in the melt. Nuclei smaller than the critical nucleus are continuously formed and disrupted in the melt, whereas those of critical dimensions are able to grow.

Depending on the chemical composition of the nuclei, the nucleation may be homogeneous or heterogeneous. In the first case, the atoms which aggregate to form a nucleus arise from the polymer chains themselves, while an extraneous nucleating particle (like impurities, catalyst residues, chain end groups, etc.) act as a nucleus in the heterogeneous nucleation type. In order that foreign particles are able to act as nucleating agents, the interfacial energy between their surface and the polymer crystal must be very low, so that a diminution of the work $\Delta\phi^*$ needed to form a critical nucleus is reached.

Whiskers may exhibit nucleating ability, as demonstrated by the comparison of the DSC crystallization curves of iPPMa and iPPMa/SiC$_{w2}$ 10%, shown in Fig. 4. It can be seen that the composite material crystallizes at lower undercooling, that is, at higher temperature, than the neat polymer. Unmodified polypropylene is much less sensitive to the presence of whiskers, as shown in the DSC thermogram (Fig. 5).

The morphological consequence of the perturbation of the whiskers on the crystallization of the thermoplastic matrices has been evinced by SEM analysis.

TABLE II Melting and crystallization apparent enthalpies, ΔH, melting, T_m, and crystallization, T_c, temperature, and crystallinity content, X_c, for each examined sample

	I RUN			II RUN		III RUN		
	ΔH_m (J g^{-1})	T_m (°C)	X_c (%)	ΔH_c (J g^{-1})	T_c (°C)	ΔH_m (J g^{-1})	T_m (°C)	X_c (%)
iPP neat	99	167	47	101	118	109	161	52
iPP/SiC$_{w2}$ 10%	99	169	47	98	120	104	162	50
iPPMa neat	86	163	41	88	110	91	160	43
iPPMa/SiC$_{w1}$ 10%	90	158	43	90	118	92	158	44
iPPMa/SiC$_{w2}$ 10%	83	159	40	88	117	95	157	45

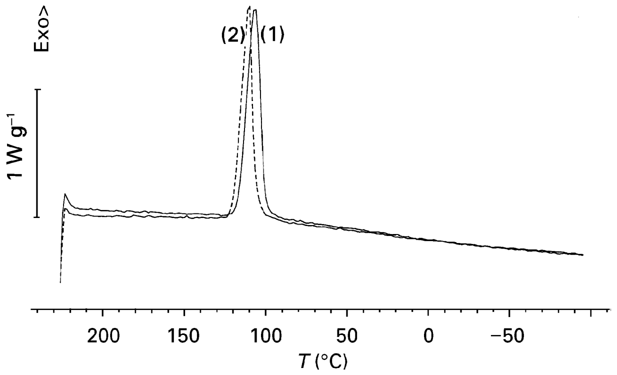

Figure 4 DSC crystallization curves of (1) iPPMa and (2) iPPMa/SiC$_{w2}$ 10%. The samples were crystallized from the melt by cooling at 10 °C min^{-1}.

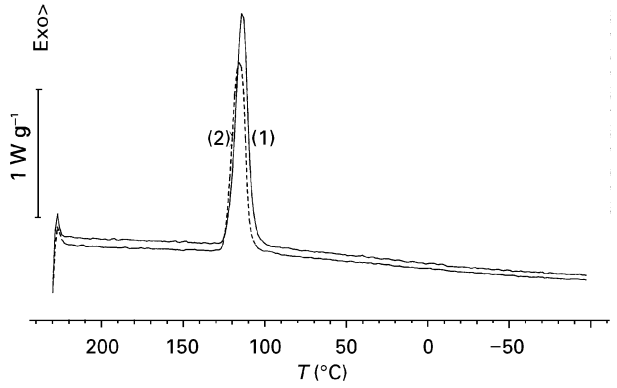

Figure 5 DSC exothermic peaks of (1) neat iPP and (2) iPP/SiC$_{w2}$ 10% crystallized from melt.

Fig. 6 shows the scanning electron micrographs of iPPMa neat (a) and iPPMa/SiC$_{w2}$ 10% (b), crystallized from the melt under the same conditions. By comparing the dimensions of the spherulites, it is evident that the presence of whiskers causes a reduction of their size and hence a finer spherulitic texture of the matrix. The same effect has been found for the system of unmodified polypropylene – silicon carbide whiskers as demonstrated in Fig. 7 where (a) shows neat iPP and (b) the iPP/SiC$_{w2}$ 10%.

3.2. Mechanical behaviour

3.2.1. Tensile properties and impact resistance

Table III reports the Young's modulus, *E*, the stress to break, σ_B, and the elongation to break, ε_B, of the composite systems. Samples of iPP/SiC$_{w1}$ 20% had no mechanical consistence and thus could not be tested. In almost all cases the addition of uncoated whiskers causes an enhancement of the modulus, *E*, and a diminution of both σ_B and ε_B. On the other hand, the addition of coated whiskers to modified polypropylene causes no or only a small decrease of these latter parameters. Indeed, the value of σ_B for iPPMa/SiC$_{w2}$ increases with increasing weight percentage of whiskers. The SEM analysis of the fractured surfaces of the samples shows that a better dispersion of whiskers in the matrix is achieved in the case of the composite iPPMa/SiC$_{w2}$. In Figs 8, 9 and 10, the

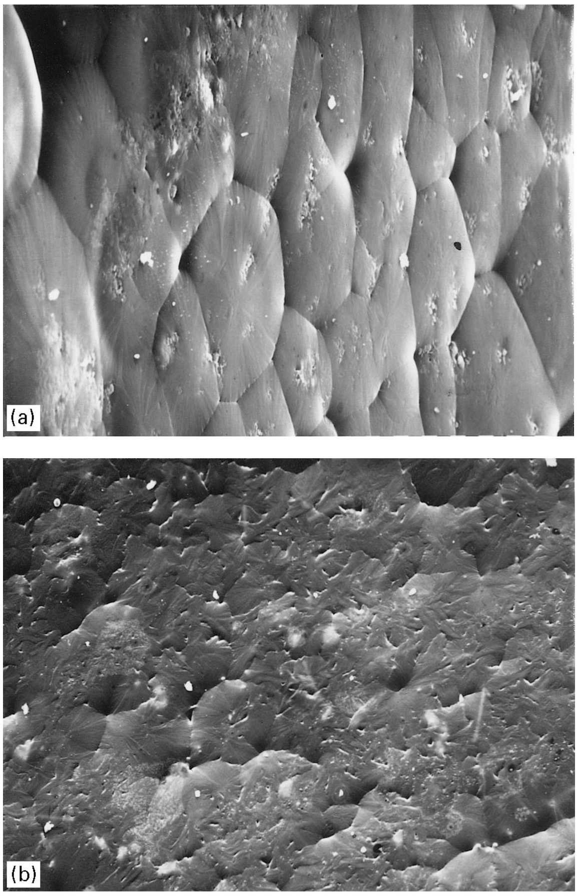

Figure 6 Scanning electron micrographs of (a) iPPMa and (b) iPPMa/SiC$_{w2}$ 10%. The samples were crystallized dynamically from 230 °C in a DSC calorimetric cell ×200.

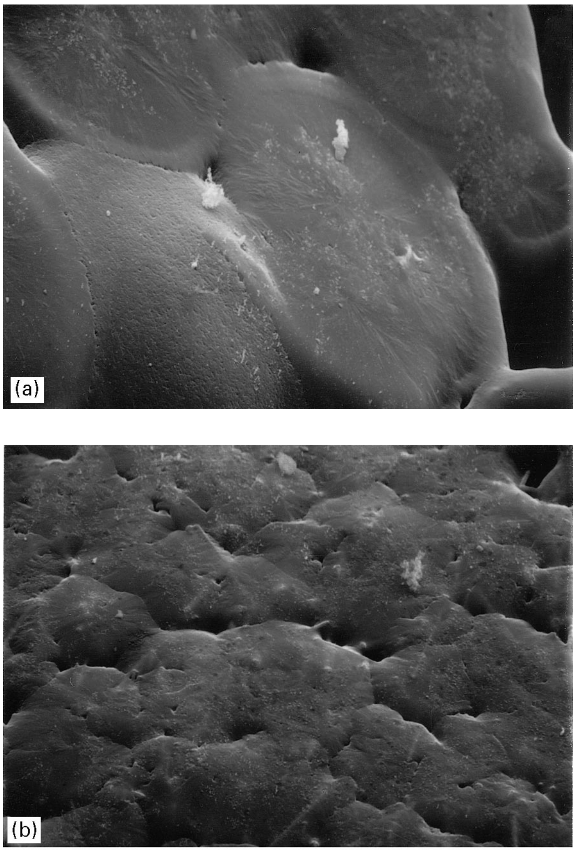

Figure 7 Scanning electron micrographs of DSC crystallized samples: (a) iPP and (b) iPP/SiC$_{w2}$ 10%. ×375.

TABLE III Tensile parameters of polypropylene/silicon carbide whiskers

		E (GPa)	σ_B (MPa)	ε_B (%)
iPP neat		1.4	30	4.0
iPP/SiC$_{w1}$	10%	1.6	23	2.2
iPPMa neat		1.2	28	4.4
iPPMa/SiC$_{w1}$	10%	1.4	26	2.7
iPPMa/SiC$_{w1}$	20%	1.8	17	1.1
iPPMa/SiC$_{w2}$	10%	1.2	22	3.3
iPPMa/SiC$_{w2}$	20%	1.8	28	2.3

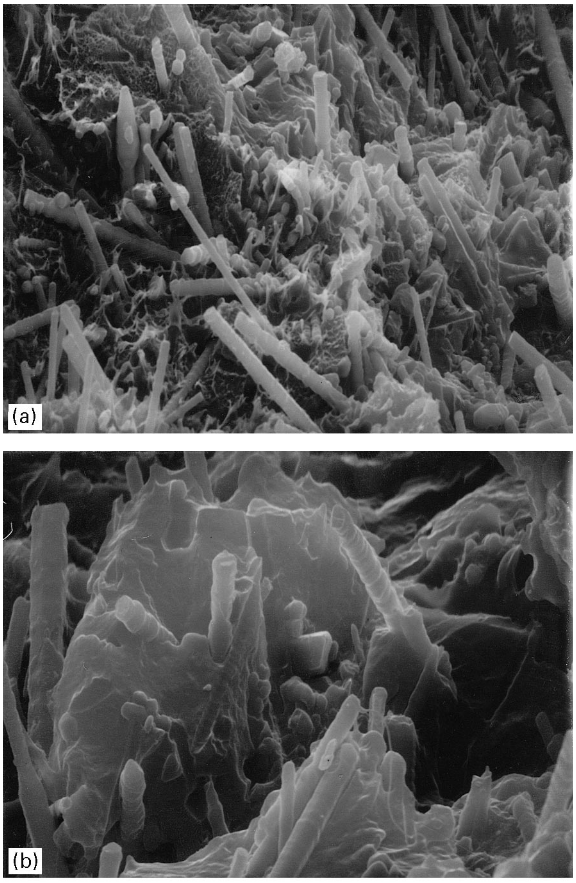

Figure 8 Fractured surface of iPP/SiC$_{w2}$ 10% samples submitted to tensile test: (a) × 750; (b) × 1500.

fractured surface of iPP/SiC$_{w2}$ 10%, iPPMa/SiC$_{w1}$ 10% and iPPMa/SiC$_{w2}$ 10% are shown respectively. From the observation of the lower magnification photos (× 1250) the composite iPPMa/SiC$_{w2}$ seems to present a better dispersion of whiskers in the matrix. In fact, the presence of whisker clusters can be seen in the case of iPPMa/SiC$_{w1}$ and iPP/SiC$_{w2}$ systems. Moreover, by observing the micrographs obtained at higher magnification (× 2500) a good fibre–matrix interfacial adhesion can be observed for both the composites iPP/SiC$_{w2}$ (Fig. 8b) and iPPMa/SiC$_{w2}$ (Fig. 10b), while a massive agglomeration of whiskers separated from the iPPMa matrix is noted for iPPMa/SiC$_{w1}$ (Fig. 9b).

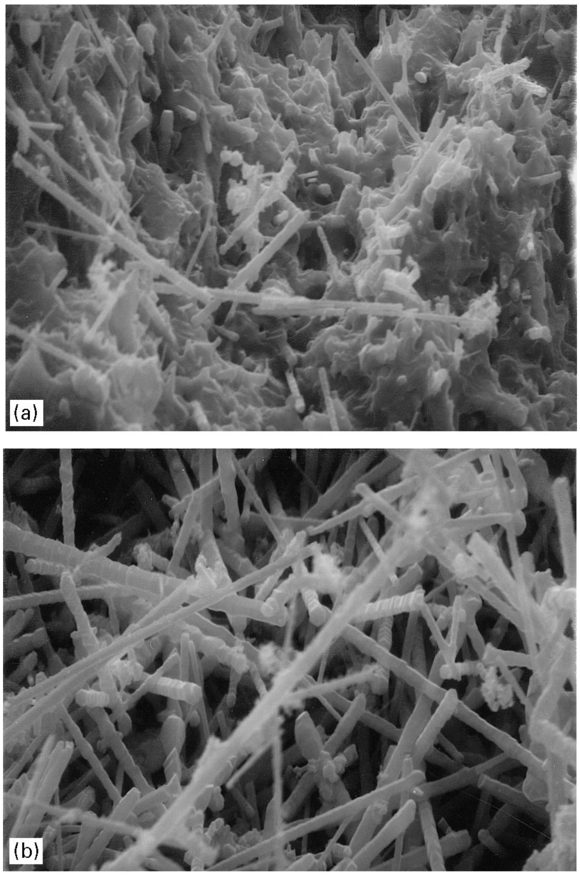

Figure 9 Scanning electron micrographs of iPPMa/SiC$_{w1}$ 10% fractured by applying tensile stress. (a) × 750; (b) × 1500.

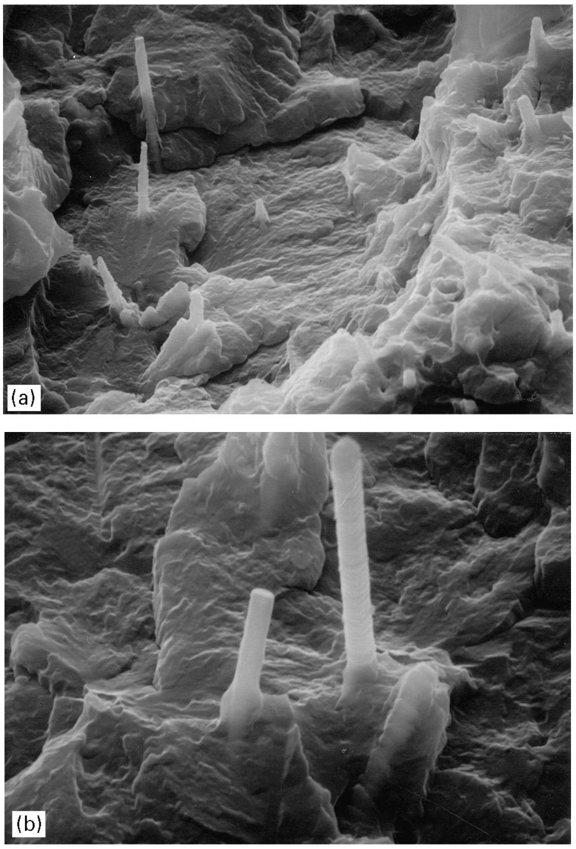

Figure 10 Fractured surface of iPPMa/SiC$_{w2}$ 10%. (a) × 750; (b) × 1500.

Table IV reports the critical stress intensity factor, K_c, and the critical strain energy release rate, G_c, calculated according to the linear elastic fracture mechanics (LEFM) theory. The higher values of G_c and K_c are obtained for iPPMa/SiC$_{w2}$ 20% and iPPMa/SiC$_{w1}$ 20%, which are more resistant than

TABLE IV Impact parameters of polypropylene/silicon carbide whiskers

		G_c (kJ m^{-2})	K_c (MN m$^{-3/2}$)
iPP neat		0.60	1.48
iPP/SiC$_{w1}$	10%	0.51	1.24
iPPMa neat		0.69	1.53
iPPMa/SiC$_{w1}$	10%	0.62	1.31
iPPMa/SiC$_{w1}$	20%	0.79	1.59
iPPMa/SiC$_{w2}$	10%	0.78	1.43
iPPMa/SiC$_{w2}$	20%	0.97	1.74

the pure iPPMa matrix. This indicates a better dispersion of whiskers having polar groups on the coating surfaces in a less hydrophobic matrix, such as iPPMa. Indeed, the better the distribution of the filler, the more uniform is the stress distribution within the matrix.

4. Conclusion

Fractographic analysis has demonstrated that improvements of the impact resistance of a whisker/polymeric matrix can be reached provided that a good dispersion of the filler within the matrix exists. Thermal, morphological and mechanical investigations concordantly indicate that the best dispersion of the whiskers has been obtained in the iPPMa/SiC$_{w2}$ composite material, which also exhibits the best mechanical resistance among all the studied composite systems. This finding can be explained in terms of "chemical resemblance" between the surface of the coated whiskers, and the polymer matrix.

Uncoated silicon carbide whiskers, owing to their inorganic nature, show little tendency to be dispersed within an organic matrix, even a non-polar one like polypropylene. Whiskers coated with a polymeric substance, like polystyrene, exhibit only a slightly greater tendency to be uniformly dispersed in a thermoplastic matrix. An optimum of distribution can be reached when the filler and the matrix share a double hydrophobic–hydrophilic nature, as in the case of SiC$_{w2}$/iPPMa composite. Such a system seems to be characterized by the stronger interphase interactions between the whisker coating and the matrix, the driving force for the dispersion process. Dipolar interactions between pendant succinic anhydride units (placed on the polypropylenic chains) and ester groups (belonging to the polymeric counterpart of the coated whisker surface) account for the observed experimental results. In view of this, it is likely that the selection of coatings more resembling the matrix would render a tougher composite. Further work is necessary to demonstrate this hypothesis. Another way to improve the interfacial adhesion between filler and matrix is to exploit chemical reactions between functional groups of the whisker coatings and matrices, respectively. As an example, covalent bonds can be obtained by reaction of succinic groups of iPPMa and polymeric coatings having aminic end groups. With this object in view, the preparation of tailored polymeric coatings for whiskers is in progress. Coated whiskers will be coupled to appropriate modified and/or grafted polymeric matrices in order to enhance dipolar interactions which favour the dispersion between the components.

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