JOURNAL OF MATERIALS SCIENCE 16 (1981) 2167–2175

Failure processes in particulate filled polypropylene

K. FRIEDRICH, U. A. KARSCH
Institut für Werkstoffe, Ruhr-Universität Bochum, 4630 Bochum, West Germany

In this paper the common degradation effect of silicon oxide filler on fracture strain and fracture toughness of isotactic polypropylene is investigated by analysing the failure processes in the composite material by microscopic methods. Experiments demonstrate that, although fracture of the polymer regions absorbs considerable energy by plastic deformation, void formation and cracking of the interface between the polymer and the filler usually requires very little energy. These weak interfaces do not resist cracking and are the cause of brittleness in particulate filled systems. The crucial parameters influencing the fracture data of the composite were found to be the volume fraction of the filler and the interfacial adhesion between polymer matrix and particles. As the interfacial fracture energy is usually much smaller than the polymer fracture energy, the composite toughness drops when filler is added. Using a model which describes the individual steps of crack formation and final fracture, an attempt is made to explain the decrease of crack resistance of the polymer matrix with increasing filler fraction and to calculate the fracture energy of the composite by introducing partial values of crack resistance of the matrix and the interface, respectively. In addition, it is discussed how a coarse spherulitic morphology of the matrix, as produced by isothermal crystallization from the melt, can modify this behaviour.

1. Introduction

Particulate fillers are added to plastics in commercial production primarily for reasons of economy and improvement in moulding characteristics. Nonetheless, there are also many circumstances under which the addition of fillers results in improved properties of the plastics.

The most prominent physical effect of fillers is the stiffening, or modulus increase, which they cause in thermoplastic matrix composites. In addition, hardness increases, creep diminishes and distortion at elevated temperatures is often reduced [1].

However, the fracture properties of a polymer may vary quite unpredictably when filler is incorporated. Addition of particulate fillers to tough thermoplastics tends almost always to reduce the toughness of the compound. The tough plastics are intrinsically capable of absorbing a great deal of energy during fracture, primarily through shear deformation processes or crazing. Thus, values of fracture energy of 10^3 to $10^4\,\mathrm{J\,m^{-2}}$ are exhibited by materials such as polyamides or polypropylene, for example. As the amount of tough material available is reduced by the filler, elongation at break is generally decreased.

On the other hand, when thermoplastic polymers orientate or crystallize with strain, they often exhibit remarkable tensile yield strength improvements with most fillers, at least at lower filler contents [2, 3]. They also exhibit poor bonding with fillers, and thus, are able to draw away from the particles to orientate and work harden, even when the final fracture stress decreases continuously with increasing filler fraction.

Due to these opposing tendencies it seems impossible to predict the course of fracture energy with increasing amount of filler, as measured in simple tear tests, in impact resistance testing or in fracture mechanics tests. In all these cases the measured resistance to crack propagation and fracture involves a combination of effects, which,

0022–2461/81/082167–09$02.90/0

in flexible composites, is the most predominant filler–matrix bonding. Most often the addition of fillers causes a more or less continuous and drastic reduction of the fracture properties, resulting in a brittle, weak product. In some special cases, however, the fracture energy can be improved when small amounts of filler are added and appropriate coupling agents are employed, although it falls again at higher volume loadings [4].

The object of this paper is to show how damage accumulation and fracture are affected by the addition of particulate mineral filler in highly ductile polypropylene. Analysing the individual steps of crack initiation, crack propagation and fracture by microscopic methods, a model is established which describes the mode of failure in detail for various filler fractions. Using this model, an attempt will be made to explain the fracture energy of the composite by introducing partial values of crack resistance for the individual components of microstructure in this particle-reinforced thermoplastic matrix composite.

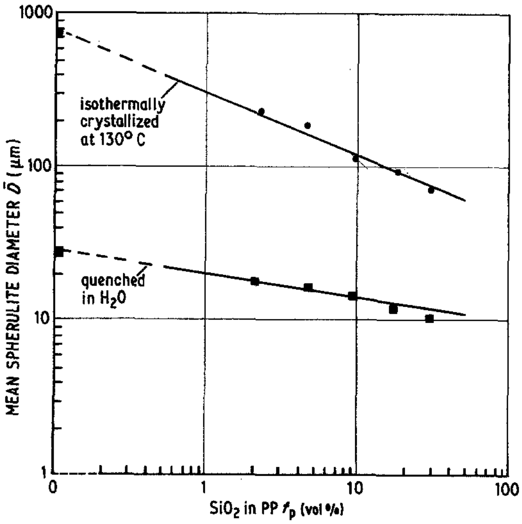

Figure 1 Variation of mean spherulite diameter $\bar{D}$ in polypropylene by thermal treatment and volume fraction of SiO_2 filler.

2. Experimental procedure

2.1. Material preparation

The polymer to be investigated was a semicrystalline polypropylene (Novolen® 1320L, BASF, Ludwigshafen, Germany). Its properties are described elsewhere [5]. The material was melted by heating on a twin-roll mill. Various weight fractions of mineral filler (silica gel, Syloid®, W. R. Grace & Co., Baltimore, Maryland, USA) were then mixed into the melt, to form a composite material.

Silica gel is a porous, particulate, amorphous silica (99.5% SiO_2, specific gravity $2.1\,g\,cm^{-3}$) formed as a result of the chemical reaction of sodium silicate and a mineral acid. The particle-size range is between 2.0 and 25.0 µm. The usual contributions of this filler in thermoplastics include plate-out prevention, antiblocking of films, viscosity control, processing aid and moisture removal [2]. The volume fraction of the filler, f_p, was computed from the known weights of polymer and filler in the mixture (sheets having 0, 5, 10, 20, 35, 50 wt % filler were used).

Before machining specimens for mechanical tests, 50 mm x 50 mm plaques of 3 mm thickness were remelted at 220° C and then either quenched to room temperature or isothermally crystallized at 130° C over a period of 3 h. During these processes initial internal stresses due to the production process of the larger sheets were removed and two different kinds of microstructure were obtained. The quenching treatment provided a fine spherulitic microstructure with homogeneous particle distribution, while by the slower cooling process coarse spherulitic morphologies were produced, in which the average spherulite diameter decreased with increasing particle content (Fig. 1). In addition to the nucleating character of the particles, a higher concentration of fine particle powder could be observed along the spherulite boundaries (Fig. 2).

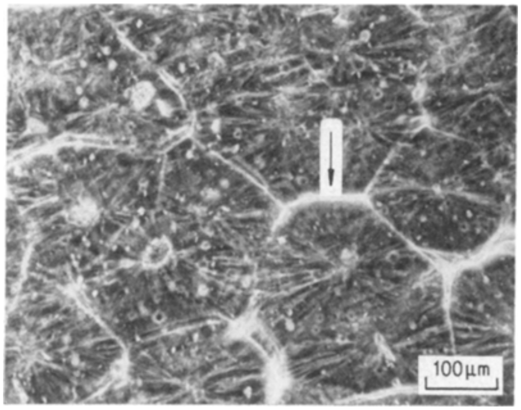

Figure 2 Coarse spherulitic morphology in particulate filled polypropylene. The white areas along the spherulite boundaries are due to the concentration of filler powder in these morphological regions (arrow).

2.2. Testing procedure

The strength properties of the specimens, especially the true fracture stress σ_F and the true strain-at-break ϵ_F were determined in a simple tensile test.

Fracture-toughness testing of the samples made use of a fracture mechanics test, using razor-notched compact tension (CT) specimens. Details of the testing method are described by Friedrich [6]. Both tests were performed at room temperature, using a cross-head speed of 5 mm min^{-1}. The elastic moduli E of the compositions were calculated from the shear moduli, as measured by torsion pendulum tests, assuming a nearly constant Poisson's ratio of 0.4 for all specimens.

3. Results and discussion

3.1. Particle induced fracture in a tough matrix composite

The quenched condition of the testing samples turned out to be the most appropriate one for determining the influence of particles on fracture separately. In this case the specimens had a quasi-homogeneous microstructure over their cross-sections, without distinct differences in spherulite diameter for various particle contents. Thus any influence of the microstructure of the tough matrix could be neglected.

Fig. 3, plotted in logarithmic scale, compares the true fracture stress, σ_F, with the true strain-at-break, ϵ_F, for various volume fractions of SiO_2–filler, f_p. σ_F declines steadily as the filler concentration increases while ϵ_F decreases at first slightly with increasing volume fraction of filler. In a range between 10 and 15%, however, both properties start to fall more drastically to a nearly constant minimum level for higher values of f_p.

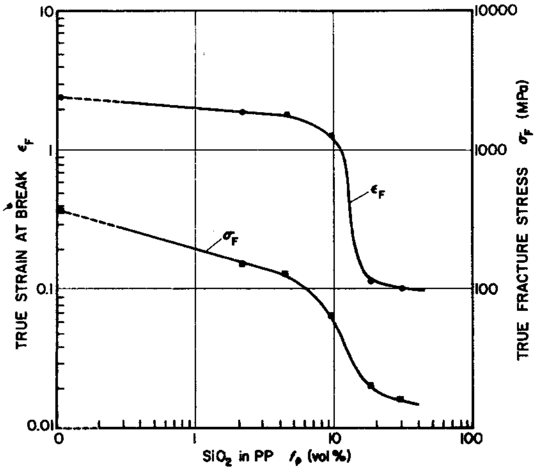

Figure 3 Diagram showing the true strain-to-fracture ϵ_F and the true fracture stress σ_F, respectively, as a function of volume fraction of SiO_2 particles in a polypropylene matrix.

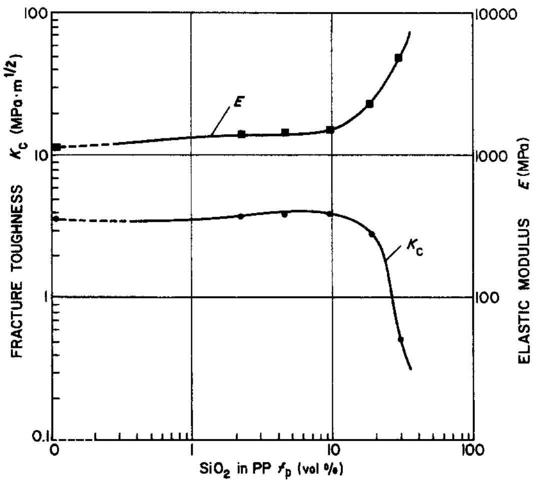

Figure 4 Diagram showing the fracture toughness K_c and the elastic modulus E, respectively, as a function of volume fraction of SiO_2 particles in a polypropylene matrix.

This drastic change in data is also found for the fracture toughness, K_c, as well as for the elastic modulus, E, as indicated in Fig. 4. For the lower filler fractions (below 10%), however, both properties are only slightly affected by the amount of filler in the composite. In this area, in turn, the K_c values do not represent real values of instability, because even at the maximum of the load–deflection curves, which was used together with the initial crack length for the calculation of K_c, no crack instability occurred. Rather, cracks propagated in a stable manner under futher increase of the plastic zone in front of the crack tip. Thus, these values are only K_c data for crack initiation, a term which is usually used for the description of this kind of crack behaviour [7–10].

The variety of mechanisms which occur during the plastic deformation inside the tensile specimens or in front of a propagating crack, and the resulting steps of crack propagation and final fracture can be investigated by the use of various microscopic methods. The basic mechanisms by which the failure processes in this kind of composite are induced are very similar to those observed in soft metallic alloys containing hard particles [11]. They are schematically represented in Fig. 5. Due to the very poor bonding between filler and matrix, the polymer detaches easily from the particles and creates a series of voids, on both sides of the particles, perpendicular to the applied

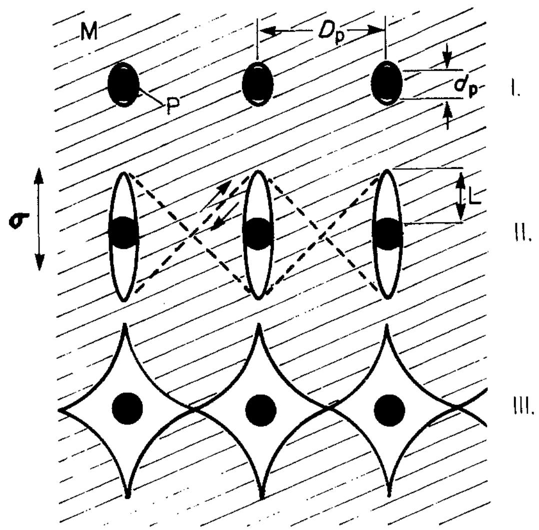

Figure 5 Steps in crack formation around hard particles P in a ductile matrix M: d_p = particle diamter, D_p = distance between particles, L = length of dimples around particles at the condition for the onset of local multiple necking.

stress. Only a small amount of plastic strain is needed for this first step of damage in the composite (Step I).

With further plastic strain the voids usually grow in the stress direction, forming dimple-like holes around the particles. Their individual length L corresponds to the diameter of the particles, d_p. L seems to be stabilized as soon as the local stress concentration around the particle is reduced (Step II). This state of deformation is shown in Fig. 6 for a composite with 5 wt % filler particles.

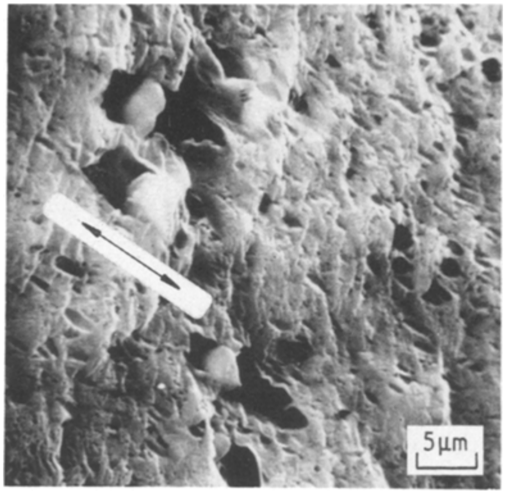

Figure 6 Scanning electron micrographs showing step II of void formation in a 5 wt % particle-filled PP composite. The arrow indicates the direction of the applied load.

After these processes a third amount of strain is needed to deform the rest of the matrix under shear stress conditions until the holes coalesce and provide failure of the composite (Step III).

The strain levels in Steps II and III are continuously reduced with increasing filler fraction. This will finally lead to a transition from a more ductile mode of failure to a macroscopically brittle fracture behaviour. In the ductile mode, the polymer matrix is not restricted in its ability to stretch and to support a load and therefore would be expected to provide greater strength. In the brittle mode, the coalescence of holes, which is the dominant mechanism of crack formation and fracture, will occur even before the ultimate dimple length L is reached. At a critical filler fraction, the particles of the composite are separated only by approximately the thickness of matrix sufficient to uniformly coat them. Under these conditions, the matrix volume is at a minimum, and acts only as individual segments or pockets to support a tensile load. When a tensile load is applied, these matrix segments stretch and pull away from the particles resulting in very low strength and elongations of the highly filled composites. The diagrams in Figs 3 and 4 indicate that this conditions seems to be reached above a filler fraction f_p of 15%.

Looking at the fracture surfaces of the CT-specimens (Fig. 7) two zones of different crack propagation mechanisms can be distinguished, their size being determined by the amount of filler in the composite (and by external parameters like testing time t or temperature T which were held constant in this investigation). Zone I, which follows the initial razor notch of length a_r, corresponds to the amount of stable crack growth after highly plastic deformation of the matrix. As mentioned above, this process is modified by the filler fraction in the composite resulting in a more ductile (Fig. 7b) or a more brittle mode of fracture (Fig. 7c). Finally, Zone I is followed by a completely brittle part of the fracture surface (Zone II), belonging to the crack instability, which occurs as soon as the energy release rate $G_I(a, t)$ is sufficient to account for the material resistance $R_m(a, t)$, i.e. for all modes of energy consumption related to the propagating crack of length, a. At low crack propagation rates, i.e. in Zone I, kinetic energy terms in R_m can be neglected. Then the material resistance will include the specific surface energy to overcome the cohesion of molecules

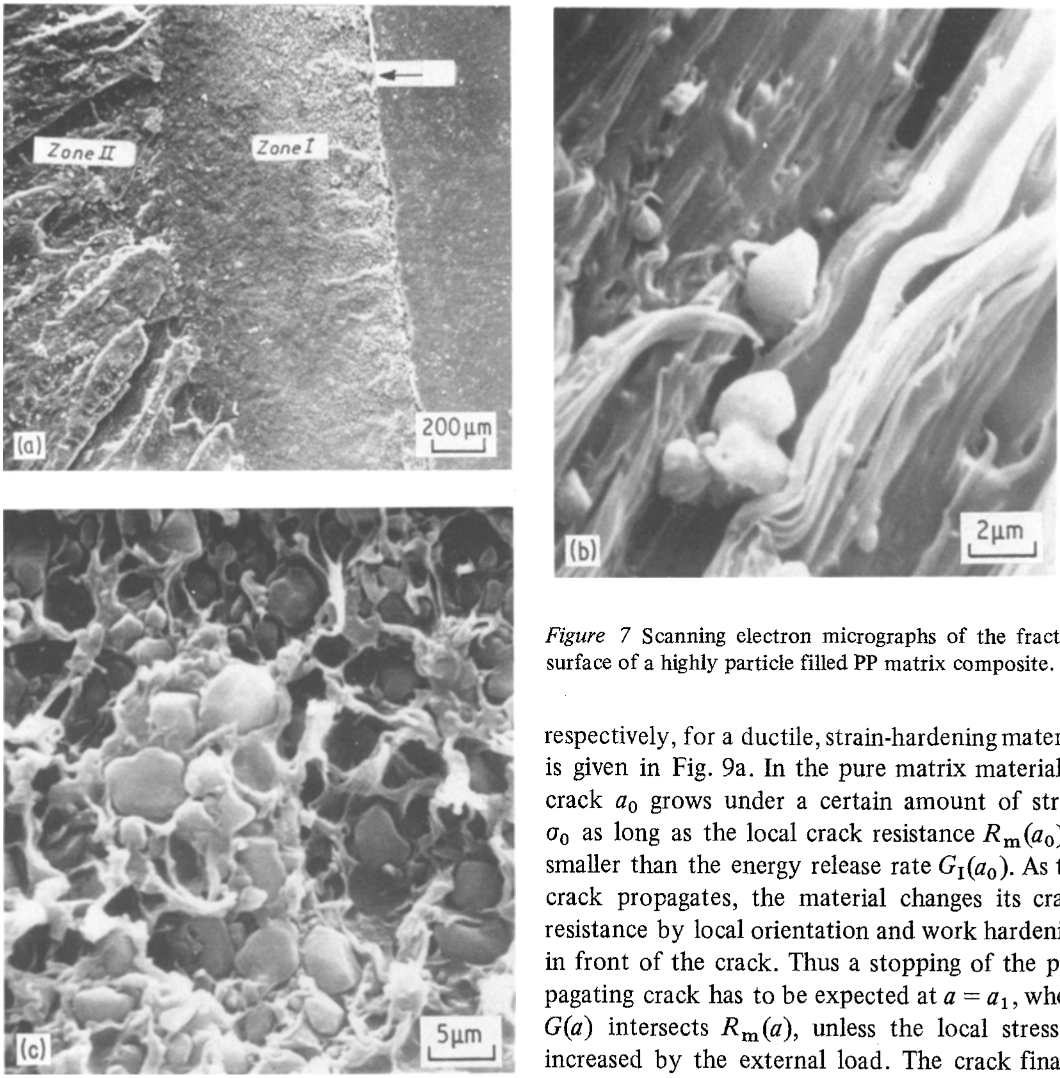

Figure 7 Scanning electron micrographs of the fracture surface of a highly particle filled PP matrix composite.

across the newly-formed fracture surface area and some other energy terms, of which the plastic deformation term V_{pl} is the most important energy absorbing part [12]. It can be several orders of magnitude larger than the specific surface energy term. However, in the case of particulate filled systems V_{pl} is strongly influenced by the amount of filler fraction. When f_{p} is low, all the mechanisms of void formation, dimple growth and plastic deformation of the matrix can become effective in front of a crack before it propagates (Fig. 8). Thus, a relatively large plastic zone r_{p} has to be expected. This large plastic zone can lead, in specimens with finite dimensions, to a completely stable kind of crack growth when r_{p} extends across the whole specimen width.

A schematic representation of $G(a)$ and $R_{\mathrm{m}}(a)$, respectively, for a ductile, strain-hardening material is given in Fig. 9a. In the pure matrix material, a crack a_0 grows under a certain amount of stress σ_0 as long as the local crack resistance $R_{\mathrm{m}}(a_0)$ is smaller than the energy release rate $G_{\mathrm{I}}(a_0)$. As the crack propagates, the material changes its crack resistance by local orientation and work hardening in front of the crack. Thus a stopping of the propagating crack has to be expected at $a = a_1$, where $G(a)$ intersects $R_{\mathrm{m}}(a)$, unless the local stress is increased by the external load. The crack finally continues to grow if the slope of the line $G_{\mathrm{I}}(a)$, i.e. $\partial G/\partial a$ is larger than the change of material resistance with crack length, $\partial R_{\mathrm{m}}/\partial a$. In this case the condition for crack instability, i.e. $G_{\mathrm{I}}(a) \geqslant G_{\mathrm{c_m}}$, the critical strain energy release rate of the matrix material, is reached.

It follows from Fig. 9a that $G_{\mathrm{c_m}}$ generally is the smaller when $R_{\mathrm{m}}(a > a_0)$ is smaller. In the case of higher filler fractions the matrix is not able to develop its full resistance to crack growth because the maximum amount of strain at break is reduced by the coalescence of holes around the filler particles. This leads to a reduction of $G_{\mathrm{c_m}}$ with f_{p} and a decrease of the plastic zone size r_{p} in which R_{m} can develop to its maximum value (Fig. 9b). The actual decline of the matrix resistance $R_{\mathrm{m}}(f_{\mathrm{p}})$ is not linear, but seems to follow a function in which for smaller filler fractions the decrease of R_{m} on the ductile brittle transition of fracture

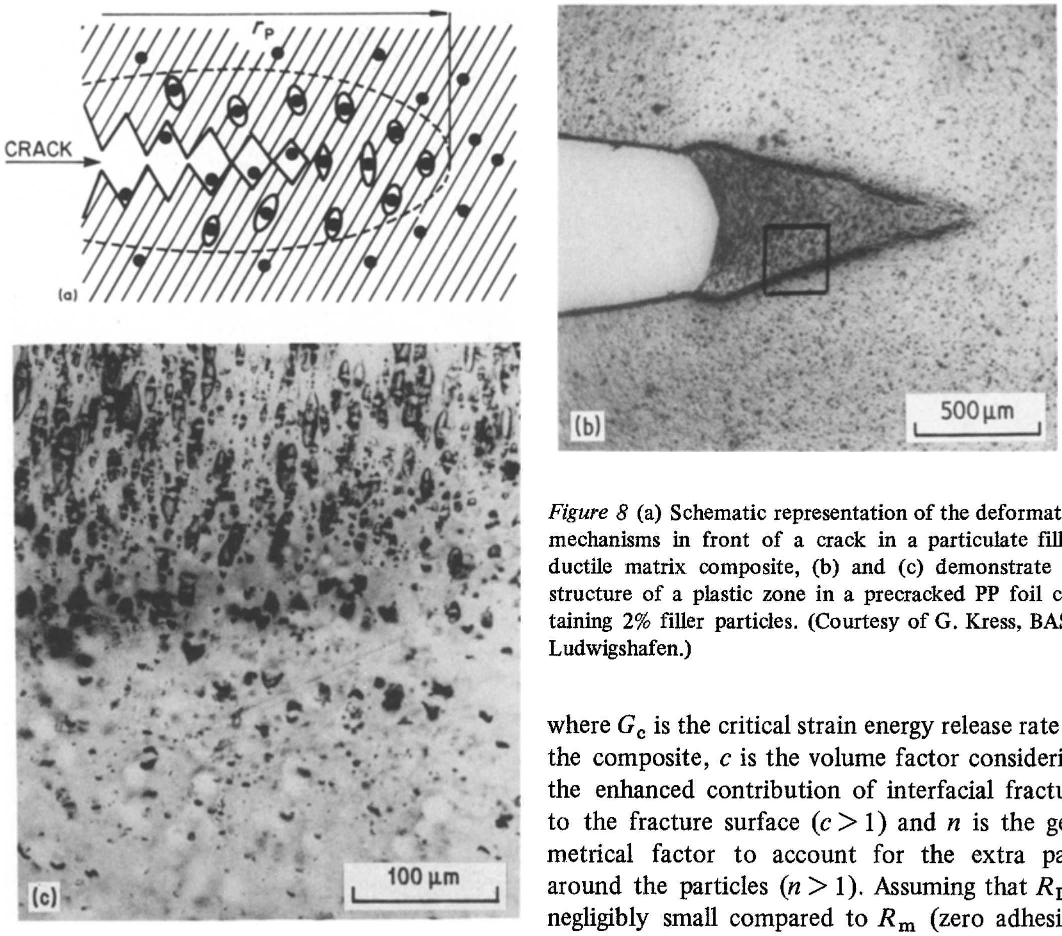

Figure 8 (a) Schematic representation of the deformation mechanisms in front of a crack in a particulate filled, ductile matrix composite, (b) and (c) demonstrate the structure of a plastic zone in a precracked PP foil containing 2% filler particles. (Courtesy of G. Kress, BASF, Ludwigshafen.)

is negligible. For higher filler fractions ($f_p > 10\%$), however, an increasing reduction of R_m leads to a condition, in which a transition from ductile to macroscopically brittle fracture behaviour becomes more and more likely (Fig. 9c).

The complete crack resistance is identical to the critical strain energy release rate G_c of the composite material. This quantity can be described by introducing partial crack resistances for the matrix (R_m) and the interface between matrix and particles (R_I), respectively. Similar models have been successfully used by various authors for the calculation of the fracture properties of coarse two-phase microstructures in metallic and polymer materials [13], as well as for particulate-filled thermoplastics [14].

Using a modified model of Kendall [14], the fracture energy of the composite is a function of two other fracture energies (R_m and R_I) and of the volume fraction of the filler particles:

$$G_c = R_m(f_p)\cdot(1 - c\cdot f_p) + R_I\cdot c\cdot f_p\cdot n, \quad (1)$$

where G_c is the critical strain energy release rate of the composite, c is the volume factor considering the enhanced contribution of interfacial fracture to the fracture surface ($c > 1$) and n is the geometrical factor to account for the extra path around the particles ($n > 1$). Assuming that R_I is negligibly small compared to R_m (zero adhesion theory) Equation 1 reduces to

$$G_c = R_m(f_p)\cdot(1 - c\cdot f_p). \quad (2)$$

Fig. 10, plotted on logarithmic scales, compares Equation 2 with the fracture energy G_c of the composite calculated from the measured fracture toughness values (K_c) and the elastic moduli (E), respectively, using the equation

$$G_c = K_c^2/E. \quad (3)$$

As the filler volume increases, the critical strain energy release rate G_c decreases in reasonable accord with theory. Here the constant c equals 3.3 and the $R_m(f_p)$ dependence of Fig. 10c is assumed.

It is expected that the measured data, as well as the calculated curve, will shift to higher values, especially in the range of higher filler concentration, when the bond between filler and matrix is improved (dotted line in Fig. 10). In this case the resistance of the filler–matrix interface is no longer negligible, but contributes markedly to the fracture energy of the composite material.

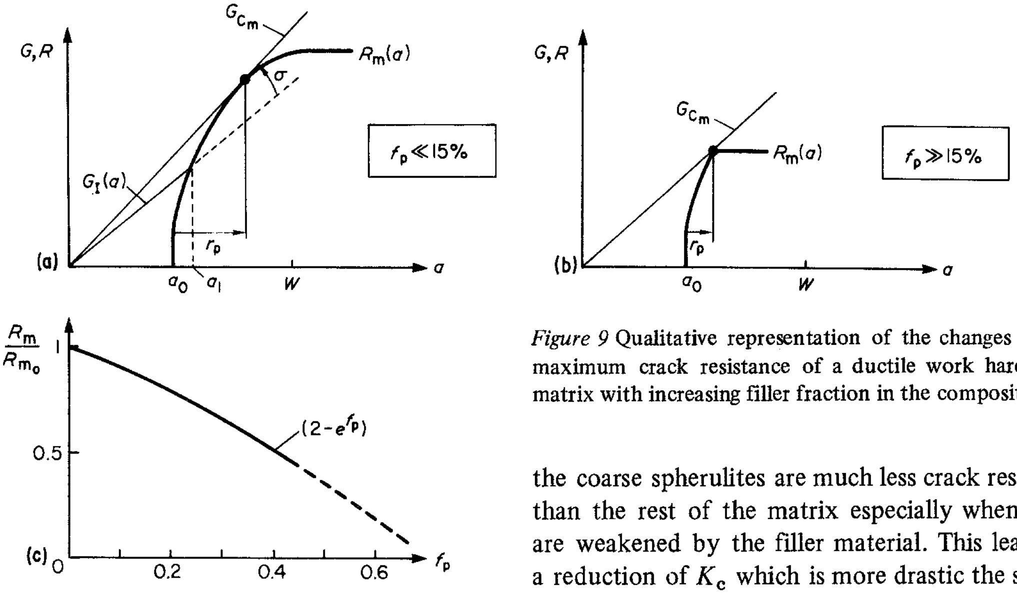

Figure 9 Qualitative representation of the changes in the maximum crack resistance of a ductile work hardening matrix with increasing filler fraction in the composite.

3.2. Influence of a coarse spherulitic matrix on fracture in particulate filled polypropylene

As shown in Figs 1 and 2 isothermal crystallization of the material leads to inhomogeneities in the matrix of the composite, mainly highly crystalline and therefore hard spherulites and impurity-rich weak spherulite boundaries. In addition, the diameter of the spherulites decreases markedly with increasing filler fraction. The general weakening effect caused by this kind of matrix modification is shown for the measured fracture toughness K_c in Fig. 11. In general, the boundaries of the coarse spherulites are much less crack resistant than the rest of the matrix especially when they are weakened by the filler material. This leads to a reduction of K_c which is more drastic the stiffer the interior of the spherulite. The dotted line in Fig. 11 indicates this effect for highly isotactic, and therefore highly crystalline, polypropylene (PP) (Novolen® 1120LX, BASF) compared with the higher atactic, more ductile type of PP usually used in this study. The corresponding fracture surfaces in the region of stable crack growth for both types of PP are shown in Fig. 12. In the highly crystalline PP (Fig. 12a) the weakening of the spherulite boundaries and the increase of stiffness in the spherulite interior during the slow crystallization process yield a completely interspherulitic fracture behaviour for this kind of material, even at a relatively low volume fractions

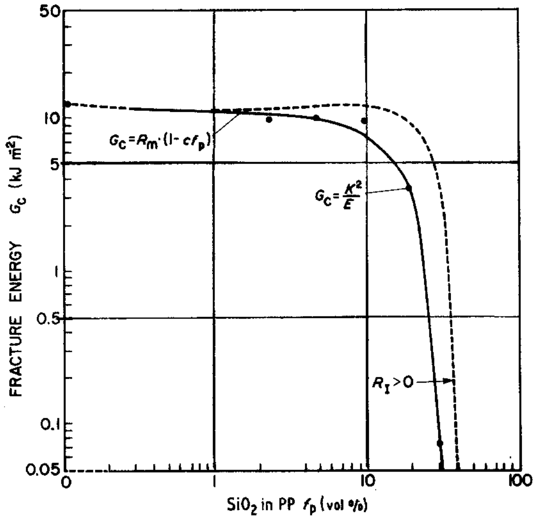

Figure 10 Variation of fracture energy G_c of the composite with filler fraction.

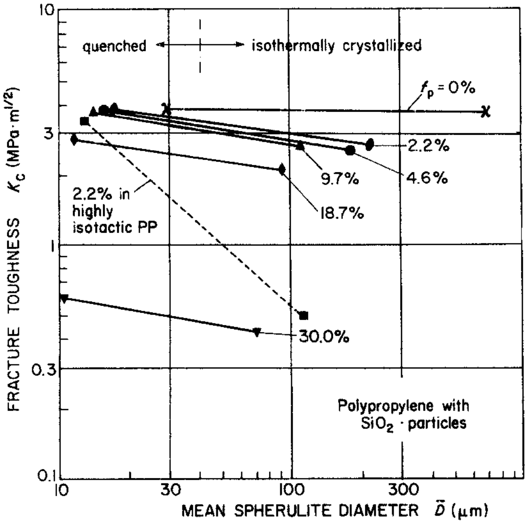

Figure 11 Diagram showing the fracture toughness K_c as a function of both, volume fraction of filler and morphology of the PP matrix.

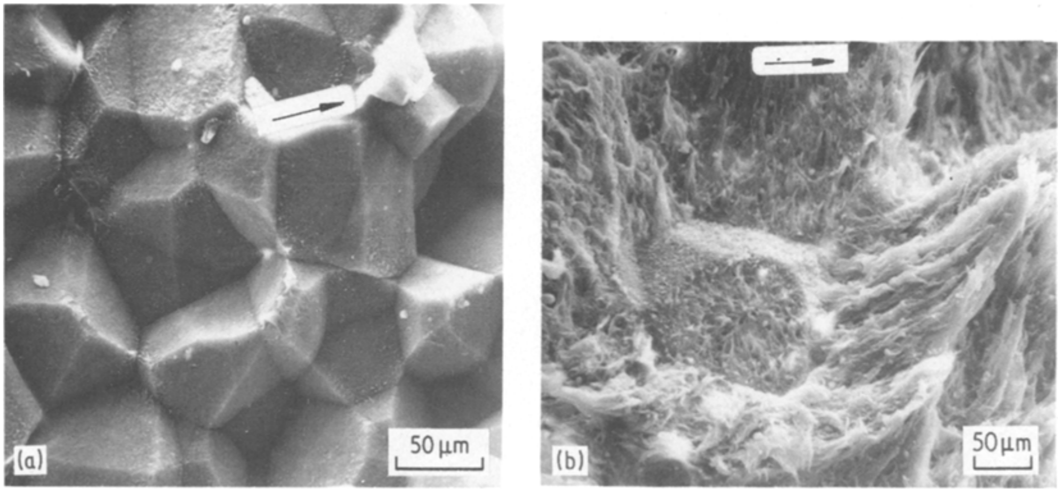

Figure 12 Various tendencies to interspherulitic fracture in coarse spherulitic morphologies of two different types of PP matrix material. The arrow indicates the crack propagation direction.

of particulate filler (2.2%). For this condition, the more ductile PP exhibits only some islands of spherulite boundary fracture, while the rest of the matrix is plastically deformed (as described in Section 3.1.) before the crack can propagate (Fig. 12b). For both cases, the general path of the crack through the microstructure can be depicted schematically as demonstrated in Fig. 13. Using this model, for the calculation, of the critical strain energy release rate of the composite, G_c, Equation 1 has to be modified by a term which considers the crack resistance of the spherulite boundaries. This value, R_s, as well as the crack resistance of the spherulite interior, R_m, depends on the filler fraction f_p and on the molecular parameters of the PP matrix in the composite.

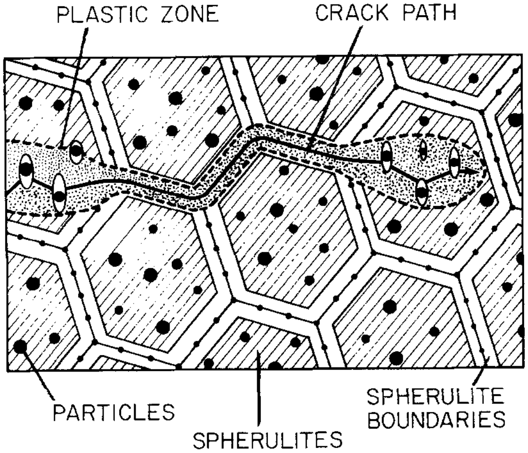

Figure 13 Schematic representation of the crack propagation mechanism in coarse spherulitic PP containing hard filler particles.

4. Summary and conclusion

Failure of polypropylene filled with silicon oxide particles is an accumulation of various deformation processes, their effectiveness depending on the volume fraction of the particles and the adhesion between particles and polymer matrix. In general, the addition of this kind of filler to PP provides a more or less continuous degradation of the fracture properties of the composite. Although the fracture of the polymer regions absorbs considerable energy by plastic deformation, void formation and cracking of the interfaces between polymer and filler usually require very little energy.

A theory has been proposed for understanding the rapid deterioration of the fracture energy of the composite in terms of changes in the partial properties of the matrix and the interface, respectively, with increasing filler content. The idea is that when the adhesion between particles and polymer is poor, the filler becomes detached from the polymer. Thus the composite fractures as a weak foam, in which the fracture energy of the matrix is additionally reduced with increasing filler fraction. Measurements of the true fracture strain and the fracture toughness of the composite support this view. An additional degradation effect caused by differences in the matrix property due to a coarse spherulitic morphology is also discussed.

Acknowledgements

The authors are grateful to the Deutsche Forschungsgemeinschaft for supporting this endeavour. K. Friedrich wishes to acknowledge the hospitality of the University of Delaware, USA, where this paper was prepared. His research stay was supported by the Alexander-von-Humboldt-Foundation (AvH), which is also gratefully acknowledged.

References

1. M. O. W. RICHARDSON, "Polymer Engineering Composites," (Applied Science Publishers, Ltd, London, 1977).
2. H. S. KATZ and J. V. MILEWSKI, "Handbook of Fillers and Reinforcements for Plastics," (Van Nostrand Reinhold, Wokingham, 1978).
3. M. ARINA, A. HONKANEN and V. TAMMELA, *Polymer Eng. Sci.* 19 (1979) 30.
4. S. J. MONTE, G. SUGERMAN and D. J. SEEMAN, "Titanate Coupling Agents-Current Applications," presented at a meeting of the Rubber Division American Chemical Society, Chicago, Illinois, May 1977. (Published in Bulletin No. KR-0577-6, Kenrich Petrochemicals, Inc., Bayonne, New Jersey).
5. K. FRIEDRICH, *Progr. Colloid Polymer Sci.* **66** (1979) 299.
6. *Idem, ibid.* **64** (1978) 103.
7. J. G. WILLIAMS, Imperial College, London, private communication, 1977.
8. K. V. GOTHAM, *Plastics Polymers* **12** (1973) 273.
9. M. PARVIN and J. G. WILLIAMS, *Int. J. Fract.* **11** (1975) 963.
10. H. G. SCHRADER, PhD Thesis, Institute of Materials Science, Ruhr-Universität Bochum, Germany, 1979.
11. L. M. BROWN and J. D. EMBURY, Proceedings of the 3rd International Conference on Strength of Metals and Alloys, Paper 33, Cambridge, UK 1973 (Institute for Metals and the Iron and Steel Institute, London) p. 164.
12. H. H. KAUSCH, "Polymer Fracture," (Springer Verlag, New York, 1978).
13. E. HORNBOGEN and K. FRIEDRICH, *J. Mater. Sci.* 9 (1980) 2175.
14. K. KENDALL, *Brit. Polymer J.* 10 (1978) 35.

Received 9 December 1980 and accepted 26 January 1981.