

# The Morphology of Fracture Surfaces and Mechanical Properties of Composites of Polypropylene with Glass Fibers Having Different Interface Adhesion

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## Synopsis

For composites polypropylene–short glass fibers having different interface adhesion, correlation has been proved to exist between the morphology of fracture surfaces, the temperature dependence of impact strength, and the deformational and fracture behavior in tensile loading. The results are interpreted in terms of the mechanism of distortion plasticity for unfilled PP and for filled PP having weak interface adhesion, and on the basis of dilatation plasticity for filled polypropylene with a higher interface adhesion. The transition from the distortion to the dilatation mechanism can be seen in fracture surfaces after tensile destruction in composites possessing a higher interface adhesion.

## INTRODUCTION

An addition of short fibers to thermoplasts has a favorable effect, especially on the elasticity modulus and strength.<sup>1-4</sup> The effect of fibers on toughness has not yet been satisfactorily explained.<sup>1</sup> In tough matrices, toughness usually decreases,<sup>5</sup> while the addition of short fibers to brittle matrices has an opposite effect.<sup>6-9</sup> For composites polyethersulfone/short fibers it was observed<sup>10</sup> that the higher toughness was due to the occurrence of specific additional mechanisms of energy consumption accompanied by an increase in the matrix toughness (initiation of crazes at the fiber ends and shear deformation of the matrix between the fibers) caused by the added fibers.

Toughness is determined by interactions between all processes of energy consumption taking place in the given composite. In addition to the properties of the fibers and matrix, the occurrence of such processes depends on the composition and structure of the composite and on interactions between the phases, especially on the fiber content, aspect ratio (length-to-diameter ratio of the fibers), and orientation of the fibers, and on the adhesion between matrix and fibers. The last factor in particular has an important effect on the mechanism of energy consumption.<sup>11,12</sup>

For poly(ethylene terephthalate) with short glass fibers it was found that an increase in the interface adhesion leads to a higher toughness of the composite which rises with increasing fiber content.<sup>13</sup> The decisive factor for the toughness of a composite with a low fiber content is the matrix toughness: with

TABLE I  
Materials

Denoted	Firm name	Nominal content of glass fibers (mass %)	Bond between matrix and fibers
V-0	Vestolen P5202, Hüls, FRG	—	—
V-20	Vestolen P5232G, Hüls, FRG	20	Weak—without coupling agent
P-20	Propathene HW60GR20, ICI, U.K.	20	Strong—special chemical coupling agent
P-30	Propathene HW60GR30, ICI, U.K.	30	Strong—special chemical coupling agent

increasing fiber content the effect of the interface boundary also becomes more pronounced. On the contrary, in the case of epoxy resins with short glass E-fibers an addition of the coupling agent had a negative effect on toughness.<sup>12</sup>

In this study we try to demonstrate the effect of interface adhesion on the impact strength of polypropylene with short glass fibers. Using a fractographic analysis of fracture surfaces, models have been suggested of the predominant mechanisms of energy consumption in the impact and tensile loading.

## EXPERIMENTAL

### Materials

Composites of isotactic polypropylene with short glass fibers were used in the investigation (Table I). The materials were chosen so as to evaluate the effect of various fiber contents and of bonds between fibers and matrix on the morphology of fracture surfaces and on the mechanical properties. The chemical nature of the coupling agent was not conveyed by the manufacturer—only its presence in P-20/P-30 and absence in V-20 was indicated. The effect of the fiber content is characterized for a pair of samples V-0 and V-20 (the same matrix, weak bond) and for a pair P-20 and P-30 (the same matrix, strong bond); the number characterizes the nominal content of glass fibers (in mass %). The effect of the bond between fibers and matrix is compared for a pair V-20 and P-20 (the same fiber content).

Test bodies for tensile tests (Czechoslovak standard 64 0605 Model II) and for impact tests, 74 × 10 × 4 mm in size, were prepared in a one-screw extruder from composite granulates at the temperature of the melt 230°C, and of the mold, 60°C.

### Testing Procedures

The mechanical properties were determined in the impact with a Charpy tester type PSW 0.4 at the impact energy of the hammer 1 J or 4 J and at the hammer rate 2.9 m/s at various temperatures, and also in the tensile stress at

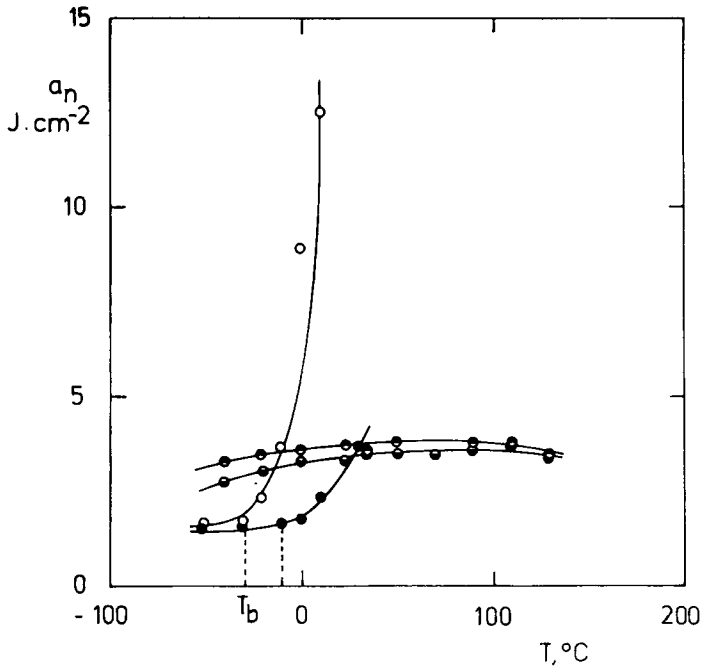


Fig. 1. Temperature dependences of impact strength of composites polypropylene/short glass fibers:  $\circ$  V-0 unfilled polypropylene;  $\bullet$  V-20 polypropylene/20 mass % of fibers with weak interface adhesion;  $\ominus$  P-20 polypropylene/20 mass % fibers with strong interface adhesion;  $\bullet$  P-30 polypropylene/30 mass % fibers with strong interface adhesion.

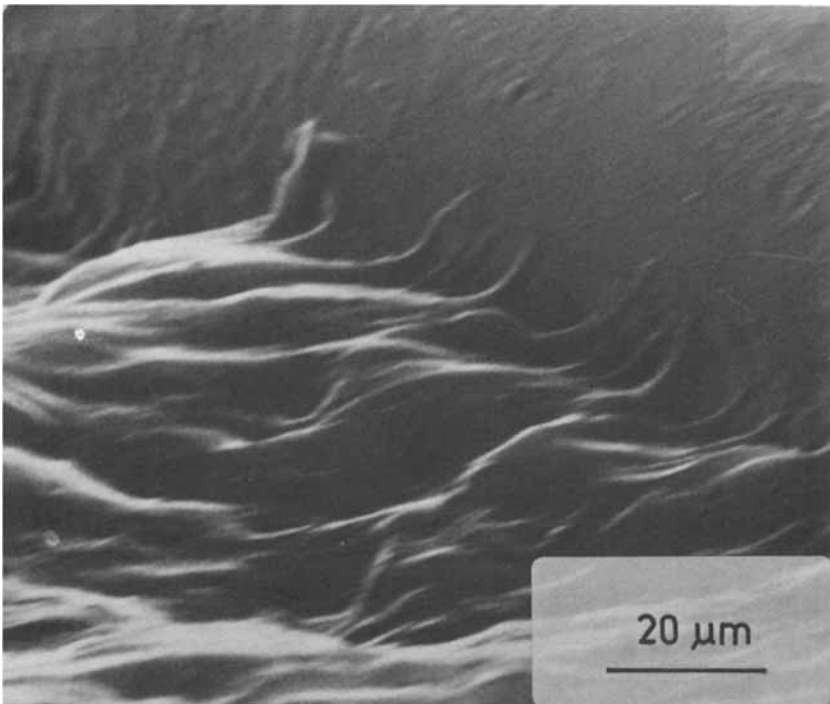


Fig. 2. Fibers initiate dilatation plastic deformations of matrix. SEM micrograph of fracture surface of composite P-30 (impact,  $0^{\circ}\text{C}$ ).

23°C at a constant rate of the crosshead 0.5 mm min<sup>-1</sup> using the Instron tensile tester. The test bodies were thermostated in advance to the required temperature (bath ethanol–solid CO<sub>2</sub> for temperatures below 23°C, hot-air drying box for temperatures above 23°C) for 20 min, after that they were removed from the bath and immediately broken.

The morphological evaluation of the fracture surfaces was carried out in a scanning electron microscope JSM 35 after vacuum deposition of a gold layer in order to remove the surface charge.

## RESULTS

For composites with the polypropylene matrix filled with short glass fibers (from 0 to 30% by mass) and having different interface adhesion (weak samples V, strong samples P), the temperature dependences of the bending impact strength (Charpy), and the deformational behavior at tensile loading were determined. The results were correlated with a fractographic investigation of broken bodies in a scanning electron microscope.

The results of the impact strength of materials as a function of temperature are presented in Figure 1. For materials V-20 and V-0 the curves have the usual form with a steep rise at the temperatures of the so-called brittle–ductile transition,  $T_b$ ; for V-20, this temperature is higher by ca. 20 K (–30°C for V-0 and –10°C for V-20). A different dependence is observed for samples P-20 and

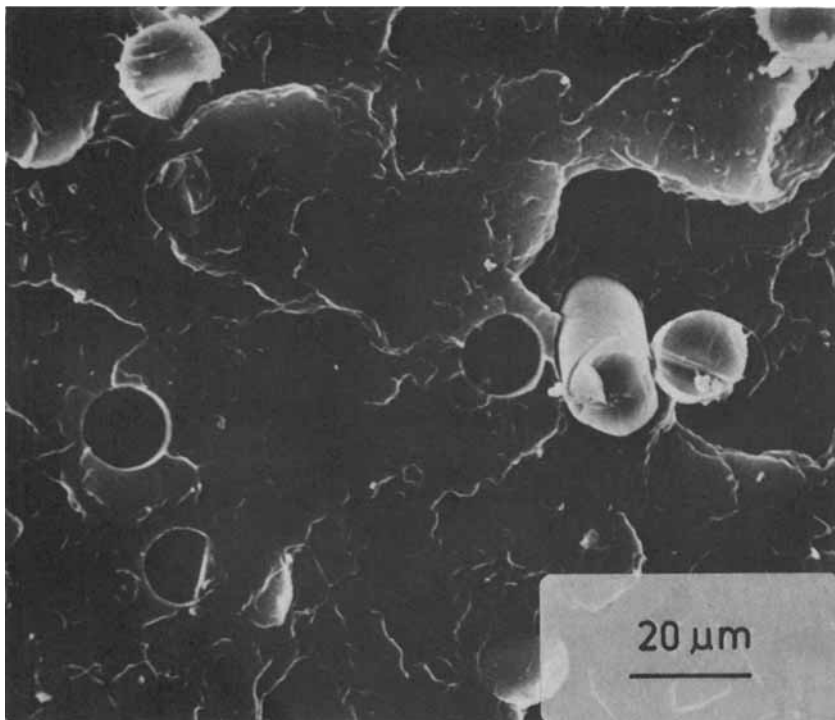


Fig. 3. Brittle morphology of fracture surface of material V-20 (impact, –50°C).

P-30. With increasing temperature the rise in impact strength is slowed down to a plateau at higher temperatures. Thus, samples P at low temperatures have a higher impact strength than samples V, while at higher temperatures it is the other way round.

In SEM micrographs of fracture surfaces of materials P, plastic deformations can be seen also at lower temperatures (below 0°C). Plastic deformations take place predominantly in the vicinity of glass fibers; they consist of a system of polymer fibers and cavities (Fig. 2). The structure of these domains resembles that of crazes; therefore, according to Argon et al., this way of plastic deformation can be regarded as the dilatation plasticity, in contrast to the shear (distortion) plasticity which proceeds without a change in volume and formation of cavities, and in micrographs appears as a continuously drawn material in microvolume. With V-20, no crazes were observed below 0°C; the fracture surface has a brittle morphology (Fig. 3). At higher temperatures, above 30°C, where the temperature dependences for V-20 and P-20 intersect each other, the fracture surfaces of materials P show predominantly crazes (Fig. 4), while in V-20 the main feature of the morphology of fracture surfaces are shear (distortion) plastic deformations reflected in the fracture surfaces by the formation of long fibers with a higher energy consumption (Fig. 5).

The effect of interface adhesion can be distinctly seen also in the tensile loading at a constant rate of deformation measured with the tensile tester. For

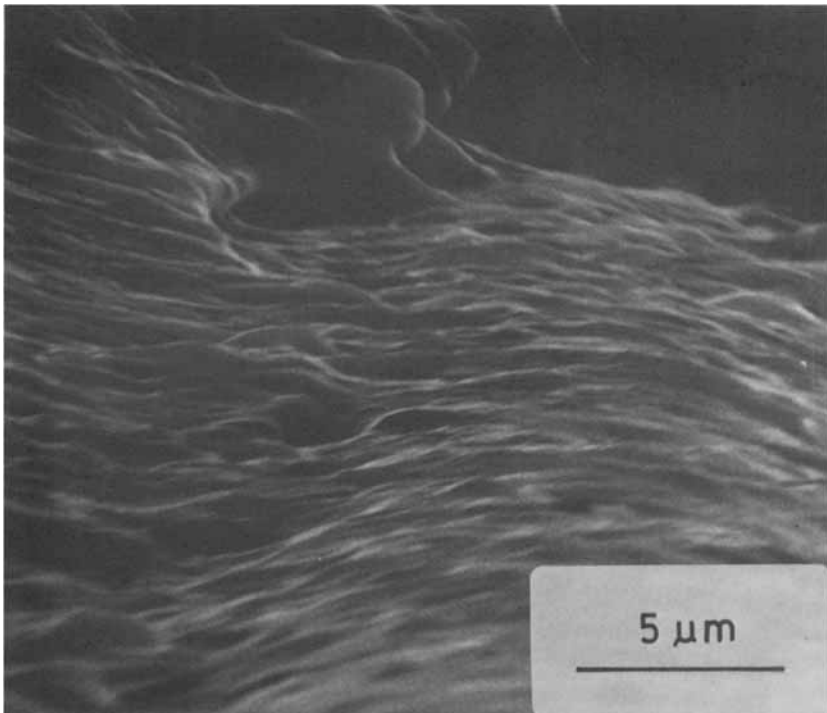


Fig. 4. Dilatation plastic deformation in materials P at higher temperatures (P-20, impact, 90°C).

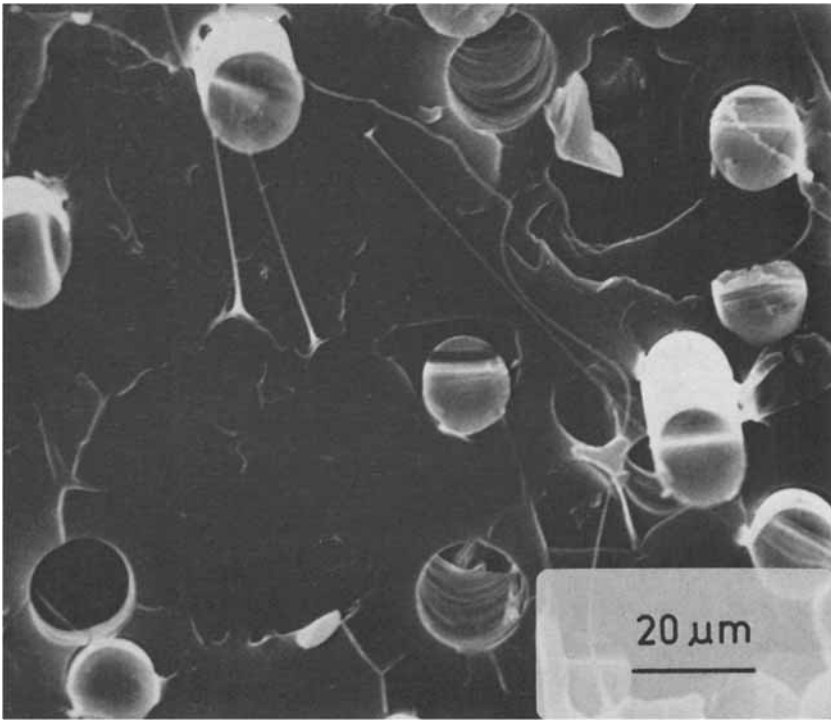


Fig. 5. Distortion plastic deformations (drawn material in microvolume) in material V-20 (impact, 30°C).

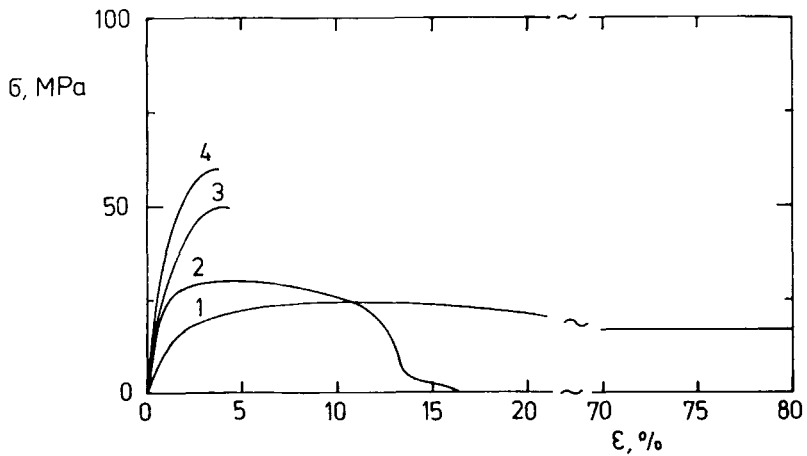
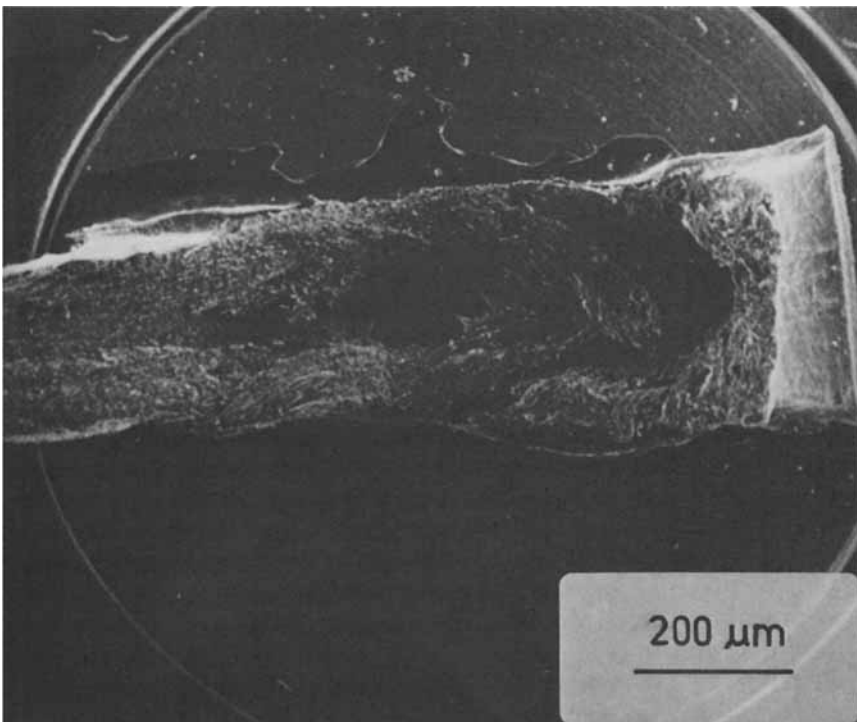


Fig. 6. Stress-strain curves of composites polypropylene/short glass fibers in tensile deformation at crosshead speed 0.5 mm/min at 23°C: (1) V-0; (2) V-20; (3) P-20; (4) P-30.

materials with the same fiber content (V-20 and P-20), this can be seen in Figure 6. An increase in the interface adhesion leads to a pronounced change in the shape of the stress-strain dependence. These dependences predominantly differ in the yield point value (which is higher for P-20) and in the shape of the dependence beyond this limit. The sample P-20 undergoes brittle fracture closely beyond the yield point, while the sample V-20 is drawn until eventually it undergoes ductile fracture.

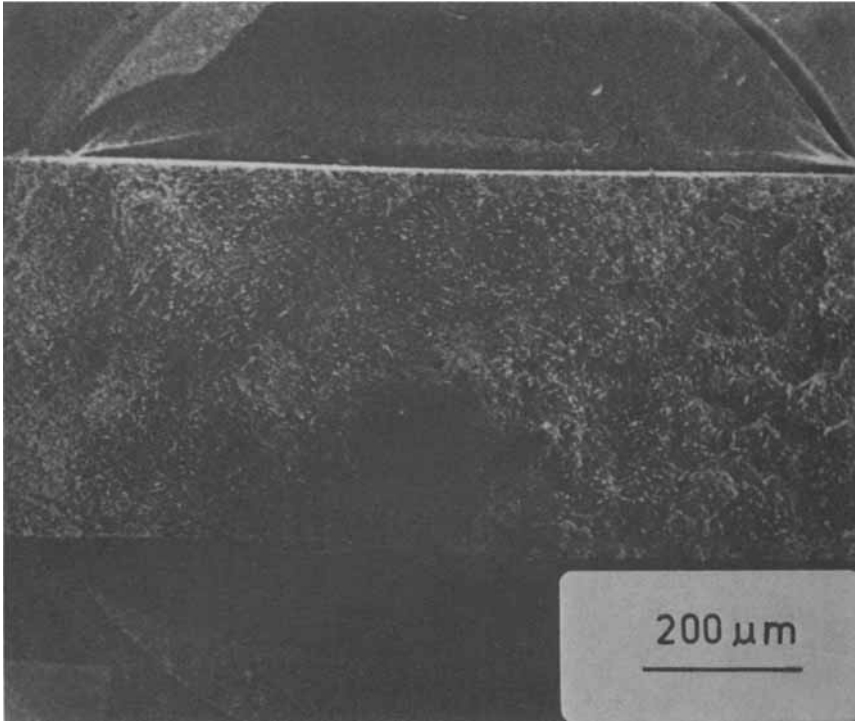
These changes can also be seen in the morphology of fracture surfaces. The material V-20 possessing only weak adhesion has a ductile morphology of the fracture surface with pronounced features of distortion plasticity [Fig. 7(a)] while the macroappearance of the fracture surface of materials P is brittle [Figs. 7(b), (c)]. A more detailed investigation reveals two areas in the fracture surface, namely, a ductile and a brittle one, which pass continuously one into another. The ductile area is characterized by interfibrillar microvolumes of the matrix transformed by plastic distortion, and also by pulled-out fibers, which are smooth [Figs. 8(a), (b)]. The brittle area is characterized by broken fibers [Fig. 8(c)], by pulled-out fibers, which, however, are covered by the matrix [Fig. 8(d)], and by the absence of distortion plastic deformations of matrix.

The position of the transition boundary between the two areas appeared to be of importance, in connection with the content of glass fibers. A comparison



(a)

Fig. 7. Morphology of fracture surfaces of composites PP/glass fibers after tensile test (0.5 mm/min, 23°C); (a) V-20; (b) P-20; (c) P-30.



(b)

Fig. 7. (Continued from the previous page.)

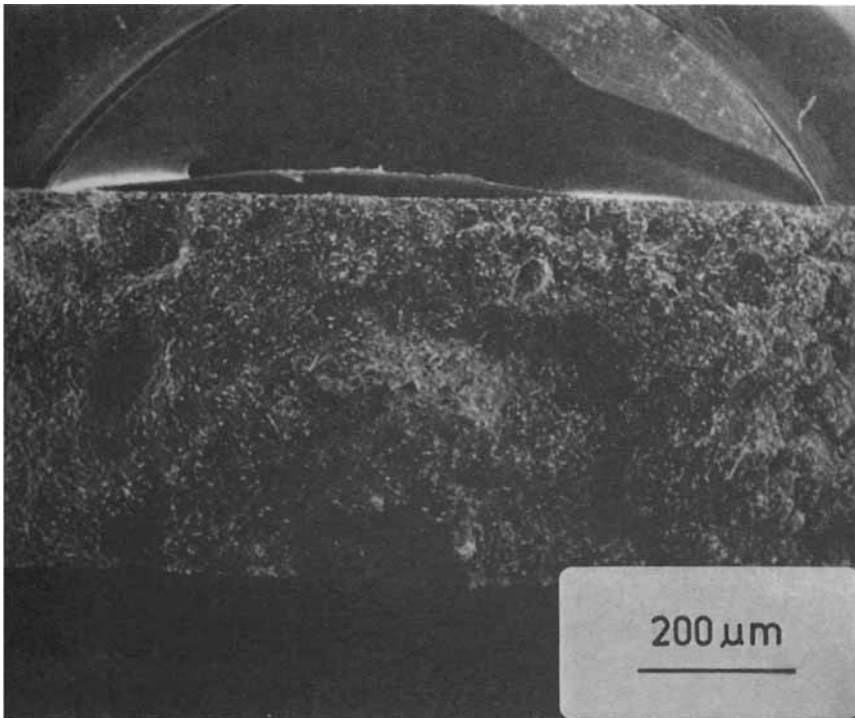
between the materials P-20 and P-30 shows that a rise in the degree of filling causes a decrease in the ductile area at the expense of the brittle one. The boundary between the ductile and brittle area is shifted to the place of fracture initiation. This finding has been expressed quantitatively by the dependence of sizes of holes around the fibers on the distance from the onset of fracture (Fig. 9).

For materials V having weak interface adhesion, the increase in fiber content is reflected in a rise in  $T_b$  (Fig. 1) and thus in a drop in the impact strength. In the morphology of fracture surfaces this is reflected in limited distortion plastic deformations [Fig. 10(b) compared with Fig. 10(a)].

In the stress-strain dependence measured with the tensile tester Instron, irrespectively of the degree of interface adhesion, the increase in the fiber content is reflected in an increase in the slope of the initial stage of the dependence (elasticity modulus), in an increase in the yield point (strength), and in a decrease in the strain-at-break (Fig. 6).

The effect on the morphology of the fracture surface is also pronounced. While at the rate of deformation used unfilled polypropylene (V-0) forms a neck, an addition of glass leads to the suppression of necking also in materials with weak phase adhesion.





(c)

Fig. 7. (Continued from the previous page.)

## DISCUSSION

Deformation processes which take place in both the tensile and impact bending loading are based on common principles. Argon<sup>14</sup> et al. discern two types of plasticity, viz., distortion (shear) and dilatation (crazes) plasticity. The crazes are usual in the tensile loading of brittle polymers [polystyrene, poly(methyl methacrylate)]. In tough polymers (polycarbonate), shear bands appear under the same conditions.<sup>15,16</sup> The distortion plasticity leads to a high consumption of energy, and polymers in which this plasticity prevails possess exceptional toughness.<sup>15</sup>

### Impact Bending Loading

According to Nielsen,<sup>1</sup>  $T_g$  of polypropylene is  $-10^\circ\text{C}$ . In unfilled polypropylene, deformation below this temperature leads to crazing (Fig. 11). With increasing temperature, and particularly on passing  $T_g$ , shear processes begin to predominate in the deformation [Fig. 10(a)], which raises impact toughness. If polypropylene is filled with glass fibers, the latter suppress shear plasticity and favor dilatation plasticity. Transition to shear plasticity calls for a higher temperature (Fig. 5). The impact strength of V-20 is then smaller than that of V-0 at all temperatures, especially above  $T_g$ .

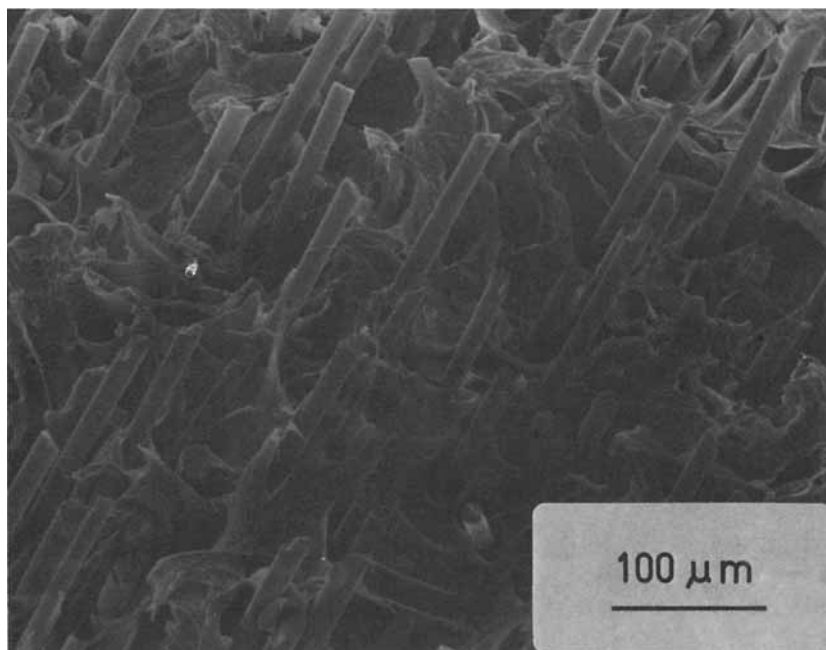
An improved adhesion of the matrix to the fibers raises the dilatation plasticity (crazing) so much that the impact strength of P-20 and P-30 below  $T_g$  is higher than that observed for polypropylene alone.

A rise in temperature leads to the transition to distortion plasticity, first for V-0, and—after a further rise—also for V-20. The common effect of two factors, i.e., of the presence of fibers and of their good adhesion to the matrix, is so important that it prevents the transition from dilatation plasticity to distortion plasticity in both P-20 and P-30. On the contrary, at elevated temperatures the impact strength decreases due to additional crystallization.

The effect of interface adhesion and temperature on the mechanisms of plastic deformation can be seen in Table II.

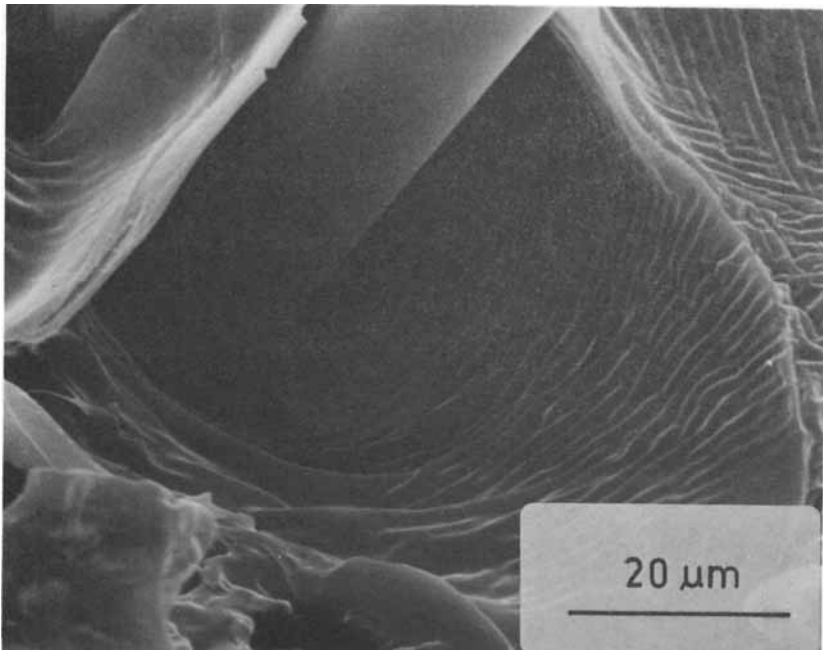
### Tensile Loading

Tensile tests carried out at 23°C lie above  $T_g$  of the amorphous fraction. During tensile loading of unfilled V-0 pronounced shear deformation (drawing) takes place. In filled V-20 which possesses a low interface adhesion, shear deformations also become operative, but unlike V-0 their development is suppressed by glass fibers [Fig. 7(a)]. The fibers act in the same way as in the impact bending loading. The strong bond between matrix and fibers in P-20 and P-30 restricts the shear plasticity still more. Fracture surfaces are pronouncedly brittle [Figs. 7(b), (c)]. In these materials we can observe transition from the distortion to the dilatation plasticity in the course of crack formation and propagation. This is reflected in the test body where one part of the

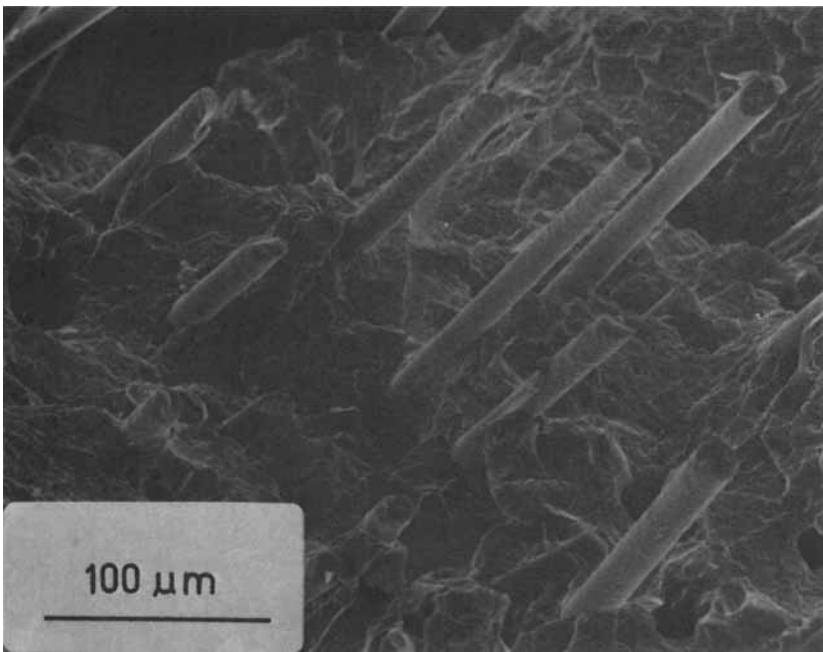


(a)

Fig. 8. Morphology of fracture surface of composite P-20 after tensile test (0.5 mm/min, 23°C); (a) distortion plasticity in ductile region; (b) detail of uncoated fiber; (c) dilatation plasticity in brittle region; (d) detail of coated fiber.

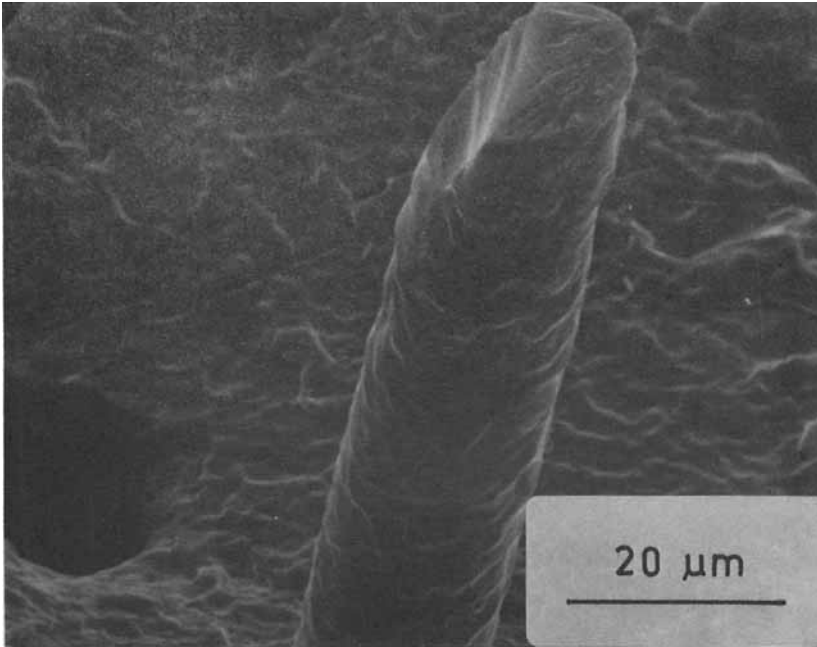


(b)



(c)

Fig. 8. (Continued from the previous page.)



(d)

Fig. 8. (Continued from the previous page.)

fracture surface shows shear deformation, while the other shows dilatation plasticity (Fig. 8). In Figures 8(a) and (b) we can see shear plastic deformations; in Figures 8(c) and (d) there are dilatation deformations.

The basic two mechanisms of crack propagation (distortion and dilatation) are schematically shown in Figure 12. In the case of the distortion mechanism the crack propagates with a larger transformation of the matrix, and, due to this, also with a higher energy consumption than in the more brittle dilatation

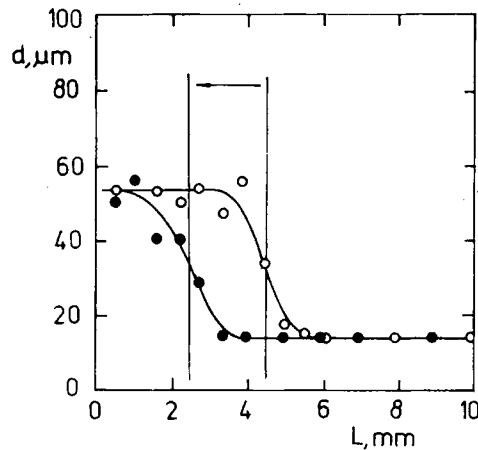
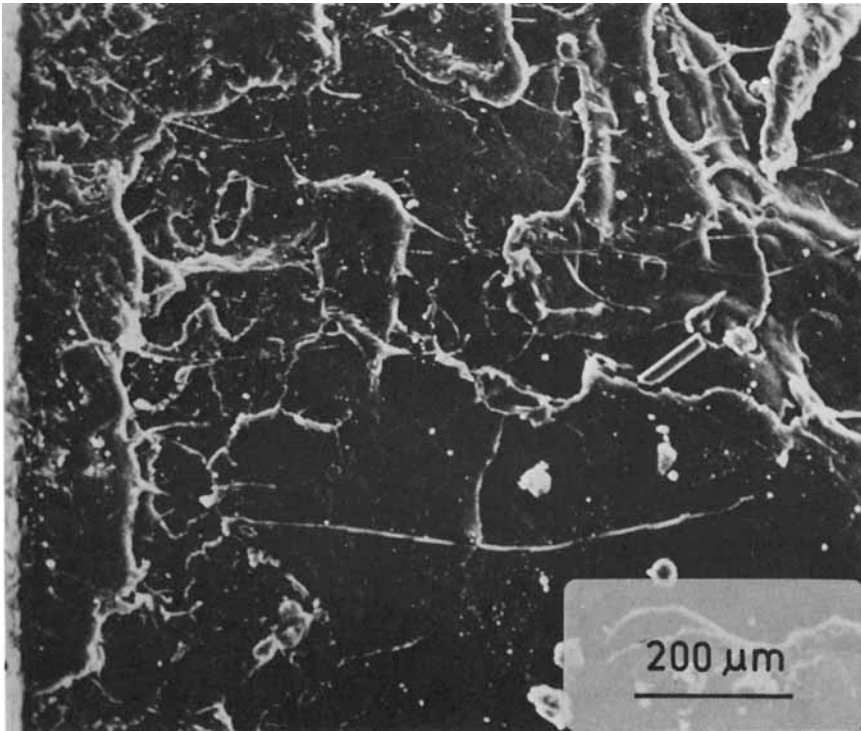


Fig. 9. Dependence of sizes around fibers,  $d$ , on the distance from the beginning of crack,  $L$ , on fracture surfaces of composites in tensile test: (○) P-20; (●) P-30.



(a)

Fig. 10. Restriction of distortion plastic deformations (i.e., of continuously drawn material in microvolume) by addition of fibers (impact, 0°C); (a) unfilled polypropylene V-0; (b) filled with 20% of glass fibers V-20.

process. The fracture surfaces differ in the lower adhesion between matrix and fibers in the former case (fibers uncoated with polymer, higher frequency of pulled-out unbroken fibers) as compared with the higher adhesion in the latter case (fibers wrapped in the polymer, broken fibers, smaller frequency of drawn unbroken fibers). The individual phases of crack propagation may be characterized as follows:

Distortion mechanism [Fig. 12(a)]:

Zone A—separation of matrix from fiber ends;

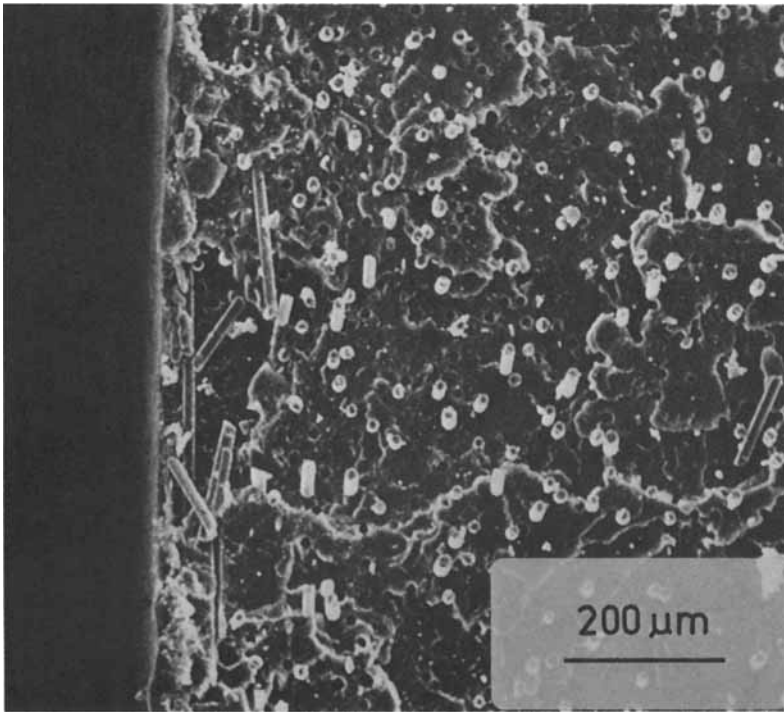
Zone B—crack formation and increase at fiber ends;

Zone C—shear deformations of “bridges” between fibers, leading to joining of cracks;

Zone D—highly plastic to viscous cracking of matrix between fibers accompanied by formation of ductile morphology of fracture surface [cf. Figs. 8(a), (b)].

Dilatation mechanism [Fig. 12(b)]:

Zone A—processes occurring in front of the crack tip: cracking of fibers and formation of microcracks at fiber ends;



(b)

Fig. 10. (Continued from the previous page.)

Zone B—joining of microcracks at fiber ends, crack propagation in the matrix, restriction of frequency of protruding fibers compared with distortion mechanism;

Zone C—local change in the direction of crack propagation, matrix is torn off from the interphase firmly bound to the fiber (Fig. 13); the rest of the matrix thus adheres to the fibers, the crack propagates through the broken fiber;

Zone D—the crack circumvents the fibers, cavities and drawn coated fibers are formed, and brittle morphology of the fracture surface is formed [cf. Figs. 8(c), (d)].

Similarly to the bending impact loading, the addition of glass fibers raises the ability of materials P to pass to dilatation plasticity also in the tensile loading. The higher fiber content in the composite P-30 compared with P-20 brings about earlier transition from the distortion to the dilatation plasticity, which is reflected in a decrease in the ductile domain on the fracture surface of the material P-30 (cf. Fig. 9).

### CONCLUSIONS

Correlation was made between the shape of the temperature dependences of impact strength, on the one hand, and the morphology of fracture surfaces of unfilled polypropylene and composites with short glass fibers having different

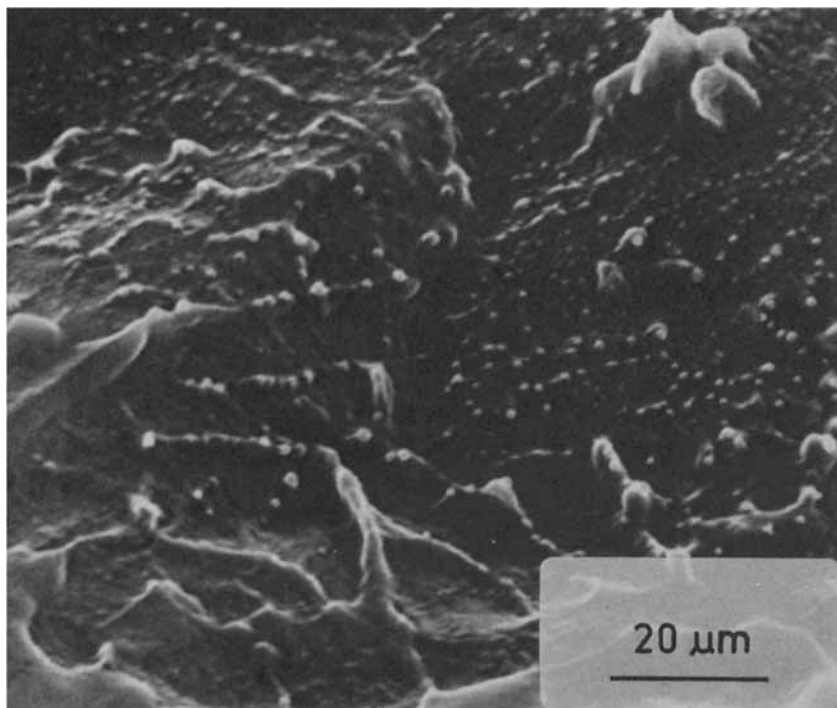
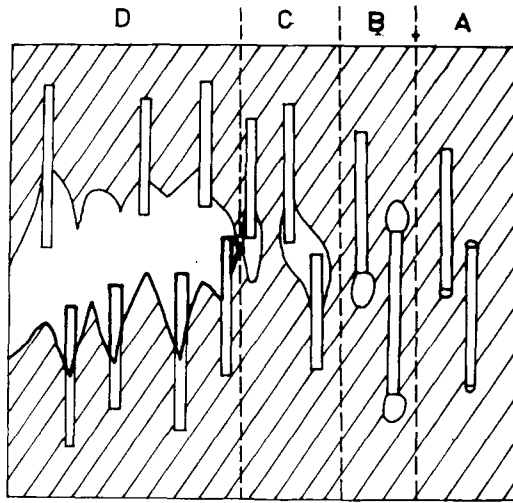


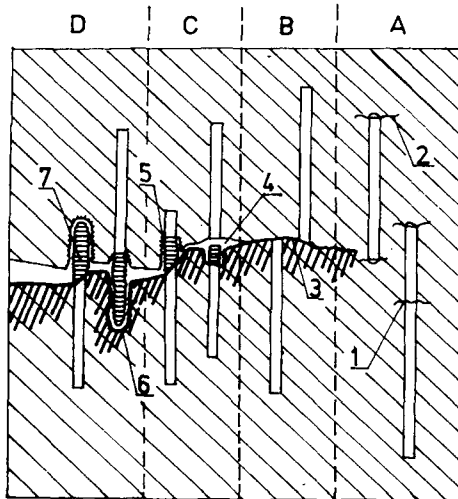
Fig. 11. Broken fibrillar structure of crazes in unfilled PP (V-0, impact, -50°C).

TABLE II  
Mechanisms of Plastic Deformation of Composites  
Polypropylene/Short Glass Fibers

Below $T_b$		Above $T_b$	
Unfilled PP	Filled PP	Unfilled PP	Filled PP
Crazes	Crazes	Shear deformations	Crazes transformed into shear deformations
Addition of coupling agent: causes an increase in the craze field; therefore, P-20 and P-30 possess higher impact strength		Addition of coupling agent: restricts transition crazes—shear deformations—so that at $T > 30^\circ\text{C}$ V-20 has a higher impact strength than P-20 and P-30, because in the latter the energy consumption is controlled by constant crazes, while in V-20 the decisive role is already played by shear deformations	



(a)



(b)

Fig. 12. Scheme of crack propagation by mechanism of distortion (shear) (a) and dilatation (b) plasticity. Fracture surface traced in bold line (cf. micrographs of fracture surfaces of both mechanisms, Fig. 8). Phases of crack development described in the text: (1) fiber fracture; (2) microcracks creation; (3) microcracks joining, matrix fracture; (4) crack propagates through broken fiber; (5) debonding of matrix from interface strongly bonded to fiber; (6) microvoids formation; (7) pulled-out coated fiber.

interface adhesion on the other. The higher impact strength of samples V (weak interface adhesion) compared with samples P (good interface adhesion) above the temperature of brittle-ductile transition ( $T_b$ ) is explained by the distortion (shear) plasticity. An opposite order observed at low temperatures is attributed to the mechanism of crazing in samples P. SEM micrographs of fracture surfaces show that an addition of glass fibers, and particularly an



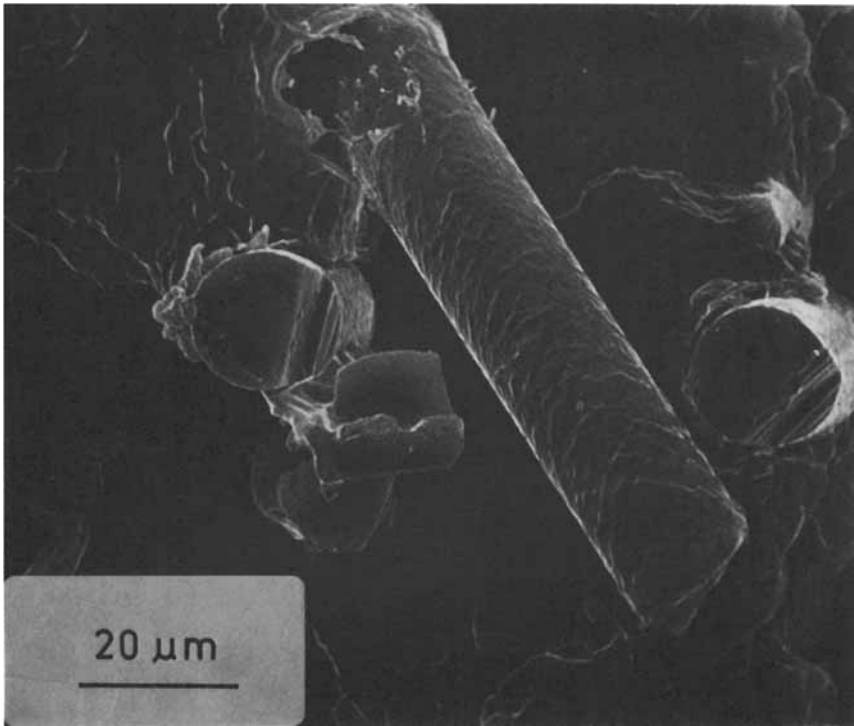


Fig. 13. Debonding of matrix from the interface region strongly bound to fiber in the region of dilatation plasticity of fracture surface of composite P-20 (tensile loading, 23°C, 0.5 mm/min).

increase in interface adhesion, suppress the shear plasticity while favoring the dilatation plastic deformation, i.e., crazing. In samples V at low temperatures cracks are formed in the weak interphase (cavities around the fibers), and only with increasing temperature is there an exponential increase in the shear plastic deformation. In samples P, where the toughness is conditioned by the formation and destruction of crazes, no pronounced temperature dependences were observed, because at increased interface adhesion the shear deformation cannot become operative.

The interpretation of differences in the temperature dependence of impact strength observed with samples having different interface strength and outlined above is also corroborated by their different behavior in the tensile deformation. The stress-strain curves at 23°C recorded for samples V show necking, high ductility, and low strength, while a characteristic property of samples P is low ductility without necking, and with increased strength.

The SEM microscopic investigation of fracture surfaces of bodies broken by tension confirms the interpretation of toughness and deformational behavior given above. Samples V undergo a markedly higher plastic deformation than samples P. In samples V cavities arise around the fibers throughout the fracture surface, while in samples P they are formed only in a small intercept at the very beginning, where the fracture develops slowly and in a plastic way. An increase in the fiber content from 20% to 30% by mass in samples P reduces the initial plastic region of fracture. In the plastic region at the

beginning the fibers are smooth, while in the brittle region of fracture they are coated by the polymer of the matrix. An increase in the interface adhesion raises the tendency of the composite towards deformation by dilatation. This is why in samples P the crack which propagates at the beginning in the stable phase by distortion, after transition to the unstable phase changes the mechanism of propagation to the dilatation one.

Hence, it was found that for the composite PP/short glass fibers the following parameters contribute to the transition from the distortion (shear) to the dilatation plasticity: decrease in temperature below  $T_b$ ; addition of glass fibers; improved adhesion of matrix to fibers and transition from stable to unstable crack propagation.

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