

Polypropylene composite materials oriented by solid-state drawing: low-temperature impact behaviour

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Isotactic polypropylene samples, both neat and containing short glass fibres, with two different interfacial adhesions, were oriented by solid state drawing with typical neck propagation. A microscopic examination showed that the glass fibres turned to the orientation direction rather suddenly in the narrow region at the neck shoulder. Such extensive movement of fibres up to 1 mm long indicates high mobility of the polypropylene matrix in this region. Thus, these results seem to support the hypothesis of stress-induced melting of semicrystalline polymers in the propagating neck. The resulting oriented materials showed high resistance to crack propagation at cryogenic temperatures. Inspection of the crack surfaces after impact testing revealed that macroscopic failure was accompanied by multiple fractures and splitting of the specimens along the orientation direction. Such a mechanism effectively blunts the crack tip and dissipates mechanical energy even at very low temperatures.

1. Introduction

Isotactic polypropylene is a typical high-volume polymer with favourable application properties. However, its disadvantage is a relatively low toughness at low temperatures.

The toughness of any material is the expression of its ability to withstand the energy of an impact or to hinder crack propagation. Correspondingly, there are two approaches for the study and interpretation of toughness of polymeric materials: *G*-concept (see, for example, [1]) and *K*-concept (see, for example, [2]).

The first approach is focused on the explanation of toughness of polymeric materials by various mechanisms of energy dissipation [3]. In particular, incorporation of rubber particles into the polypropylene matrix stimulates local plasticity (crazing), which is macroscopically manifested by isotropical increase of toughness [4].

The second approach to toughness tries to identify mechanisms that prevent crack propagation, such as crack blunting, and crack branching, and the effect of barriers (crack-stoppers) [3, 5, 6]. In particular, the

toughness of fibrous polymer composites has been ascribed to several micromechanisms [7]. It has been suggested that the external impact energy is dissipated as interfacial surface energy, post-debond friction energy, the work of fibre pull-out, and the release of elastic strain energy from the fibres.

There is a specific mechanism of crack blunting that often dominates in highly anisotropic materials, referred to as the Cook–Gordon (CG) mechanism [8]. If a main crack propagates perpendicularly to the orientation direction it can be stopped and deflected at a plane of weakness [8, 9]. The CG mechanism comprises some of the energy dissipation modes mentioned above, by increasing the toughness anisotropically. Also, it is basically temperature independent and can therefore increase the toughness at very low temperatures.

The objective of this work was to investigate the preparation, structure and low-temperature fracture behaviour of special oriented polypropylene-based composite materials. These materials were prepared by solid-state drawing of neat polypropylene and

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polypropylene containing short glass fibres with different surface adhesion. The action of the CG mechanism was studied by macroscopic fracture behaviour and morphology of fracture surfaces. Moreover, analysis of neck morphology of materials containing short macroscopic fibres can contribute to the resolution of the mechanism of plasticity in semicrystalline polymers.

2. Experimental procedure

2.1. Materials

Four types of polypropylene-based materials have been used throughout this study: (1) neat polypropylene Vestolen P 5202 (Hüls, Germany), $\bar{M}_v = 219\,000$, (2) neat polypropylene Mosten 58.412 (Chemopetrol, Czechoslovakia), (3) polypropylene containing 19.4 wt % (8.3 vol %) short glass fibres, Vestolen P 5232 G1 (Hüls), and (4) polypropylene with 20.6 wt % (8.9 vol %) short glass fibres, Propathene HW 60 GR 20 (ICI, UK). The fibres of diameter of 13 μm and length between 50 and 1000 μm were routinely surface treated by the manufacturers; however, they differed in the surface adhesion. In the case of Material 3, no special adhesion promotor was present; in the case of Material 4 the fibres were treated by a special coupling agent providing better interfacial adhesion.

2.2. Preparation of oriented composites

The starting dumb-bell specimens were prepared by injection moulding. Their dimensions were thickness 4 mm, width 10 mm and gauge length 60 mm. The specimens were then drawn in the temperature cabinet of an Instron tensile tester. The drawing temperatures were 90, 100, 110, 120, 130, 140 and 150 $^{\circ}\text{C}$; the cross-head speed was typically 50 mm min^{-1} . The lengths of the drawn parts of the specimens were limited to approximately 30 cm by the dimensions of the temperature cabinet. The investigated samples are listed in Table I.

2.3. Impact testing

Specimens for Charpy impact bending tests of non-oriented samples were cut from the dumb-bell test pieces into rectangular bars with dimensions of 60 mm \times 10 mm \times 4 mm. Specimens of oriented samples were cut from the oriented strips in dimensions of 60 mm \times 4 mm \times 1.5 mm. The specimens were provided with sharp single-edge notches 2.9 mm deep cut with a razor blade.

For oriented Vestolen P 5232 G1, preliminary tensile impact tests were also performed at room temperature using a Zwick Real Test apparatus at a speed of 0.5 ms^{-1} . In this case, the specimens were provided with sharp double-edge notches of 1 mm deep again introduced with a razor blade. The tensile impact tests were used only for morphological inspections.

For quantitative data, the standard Charpy test was applied at two cryogenic temperatures, -75 and

TABLE I Notched impact strength (Charpy) data (kJm^{-2}) at two cryogenic temperatures together with standard deviation values of drawn materials under test

Material	Test temperature ($^{\circ}\text{C}$)	Drawing temperature		
		100 $^{\circ}\text{C}$	120 $^{\circ}\text{C}$	150 $^{\circ}\text{C}$
Mosten 58.412	-75	139 ± 3	143 ± 27	191 ± 8
Vestolen P 5202	-196	59 ± 17	—	—
Vestolen P 5232 G1	-75	159 ± 16	150 ± 11	180 ± 38
Propathene HW60GR20	-196	65 ± 14	—	—
Propathene HW60GR20	-75	—	59 ± 6^a	51 ± 15

^a Drawing temperature 110 $^{\circ}\text{C}$.

-196 $^{\circ}\text{C}$. At these temperatures, ethylalcohol with dry ice and liquid nitrogen were used as coolants, respectively. The specimens were kept immersed in the coolant for at least 15 min before each individual test, quickly removed and immediately broken. As oriented unnotched specimens could not be fully fractured, the quantitative results were evaluated and compared only for notched specimens. The specimens were exposed to edgewise impact and the resulting Charpy impact strength a_{cn} (kJ m^{-2}) was calculated according to

$$a_{\text{cn}} = \frac{W}{h b_n} 10^3 \quad (1)$$

where W is the energy absorbed by breaking the test specimen (J), h is the thickness of the test specimen (mm) and b_n is the remaining width of the notch base of the test specimen (mm).

2.4. Morphological inspections

To study the internal structure of the starting and oriented composite materials, polished surfaces of longitudinal and transverse sections of the specimens were prepared. Special attention was devoted to the neck shoulder. Optical microscopy in reflected light and scanning electron microscopy were used to reveal the structure and fibre alignments. The supermolecular structure of the polymeric matrix was observed on thin slices using optical polarization microscopy. Typical fracture modes of the specimens were documented by macrophotography.

3. Results and discussion

3.1. Drawing morphology

Orientation of polypropylene samples throughout this study was carried out at elevated temperatures, in most cases above the alpha crystallization temperature $T_{\alpha c}$, which is about 100 $^{\circ}\text{C}$ for isotactic polypropylene [10]. Under such conditions, both neat polypropylene and polypropylene containing short glass fibres showed heterogeneous drawing with a neck propagation (Fig. 1). The onset of neck propagation of Vestolen P 5232 G1, containing glass fibres,

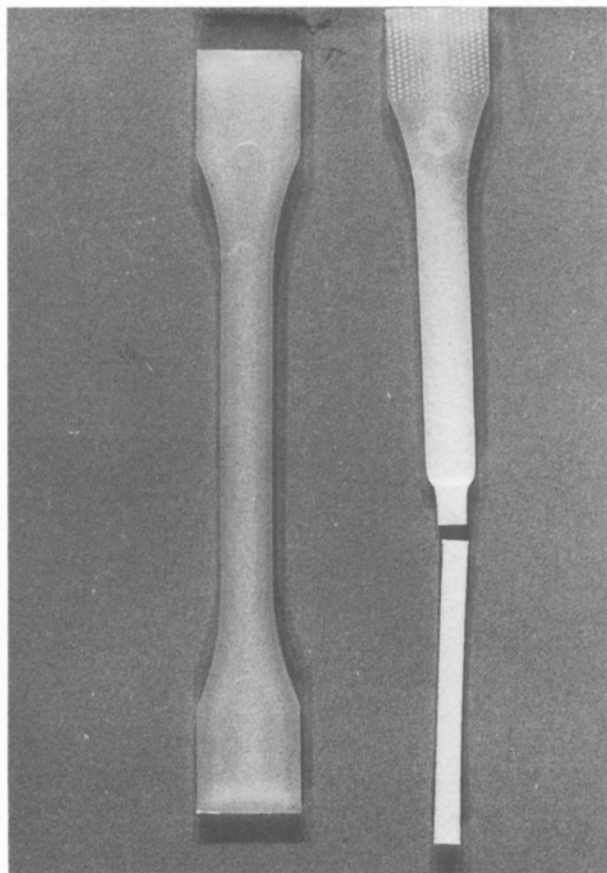


Figure 1 Original specimen of glass-reinforced isotactic polypropylene (left) and the same specimen after drawing at 100°C (right). A cut test piece for impact testing can be seen in the lower right corner.

occurred either at a sufficiently high temperature (but still in the solid state) and at a relatively high drawing rate, or at room temperature and an extremely slow drawing rate. For example, we observed neck propagation at 100°C and a crosshead speed of 500 mm min⁻¹ or at 23°C and 0.05 mm min⁻¹. On the other hand, Propathene HW 60 GR 20 with better fibre-matrix adhesion showed neck propagation only at 110°C and above. At lower temperatures, semi-brittle fracture occurred. (It appears that the conditions of the onset of neck propagation can serve for a qualitative evaluation of the interfacial adhesion.)

The opaque silver-like appearance of drawn specimens with glass fibres suggests the occurrence of microscopic inhomogeneities. Indeed, a microscopic inspection of sections taken both along and across the drawing direction revealed numerous voids in the vicinity of the glass fibres, and also in the matrix between the fibres, as shown in Fig. 2. Longitudinal voids are represented as open slits in scanning electron micrographs (Fig. 2a and b) or dark regions in light micrographs taken both along the drawing direction (Fig. 2c) and perpendicular to it (Fig. 2d). It is worth noting that the onset of voiding occurs rather abruptly at the boundary of the neck shoulder, as illustrated by Fig. 2c.

To visualize the solid-state transformation of an isotropic composite into an anisotropic one with unidirectionally oriented fibres, polished surfaces from the region of the neck shoulder were prepared. While

in the non-oriented portion of the specimen only a few elongated imprints can be seen showing little alignment, after passing the neck shoulder all fibres are aligned along the drawing direction. Fig. 3 shows clearly that the fibres turn to the orientation direction in a narrow region.

3.2. Structural transformation at the neck

It is well-known that during solid-state drawing, semicrystalline polymers undergo a marked transition from originally lamellar or spherulitic structure into fibrillar morphology with molecules oriented preferentially along the direction of draw. Typically, this transformation is concentrated in a "telescopic" neck. The detailed molecular mechanism of the transformation is, however, still an object of discussion and controversy.

The classical model developed by Peterlin [11] supposes that the transformation from lamellae to microfibrils merely demands a chain tilt and slip in limited regions but is not seriously affected by what happens at a distance. The tensile strength of microfibrils is mainly ascribed to tie molecules connecting individual crystalline regions.

More recently, an alternative concept has been proposed [12, 13] in which the onset of neck propagation is described as a collective process seizing simultaneously the whole cross-section of the body. The transformation from the lamellar to the fibrillar morphology is treated as a stress-assisted phase transition. The stored mechanical energy is supposed first to cause local "melting" of the semicrystalline polymer at the draw temperature. Then, in a second step, the action of mechanical stress causes a rapid extension and chain-induced recrystallization of the amorphous "melt". It is supposed that the resulting morphology of the cold-drawn polymer consists of "shish-kebabs" similar to those produced by crystallization from polymer solution in a flow field. The high strength and rigidity of the oriented polymer is then ascribed to covalent bonds in the extended chain core.

During solid-state drawing and neck propagation, not only individual molecules but also larger structural units, or even glass fibres, become oriented along the draw direction. Microscopic observations show clearly sudden and collective orientation of the glass fibres up to 1 mm long in the neck and uniaxial alignment of the fibres in the oriented portion of the specimen (see Figs 3 and 4). Obviously, macroscopic fibres could freely rotate in the neck shoulder thus suggesting high mobility of the polypropylene matrix. Inspection of supermolecular structure of the polypropylene matrix in polarized light reveals that the transition from the spherulitic to the fibrillar structure occurs just in the same region (Fig. 4). Thus, these observations seem to support the hypothesis of stress-induced melting of semicrystalline polymers in the propagating neck. Juska and co-workers [12, 13] suggested that the strain-energy input into the neck zone is sufficient to cause a complete local disintegration ("melting") of the lamellar structure and its further transformation into fibrillar morphology under

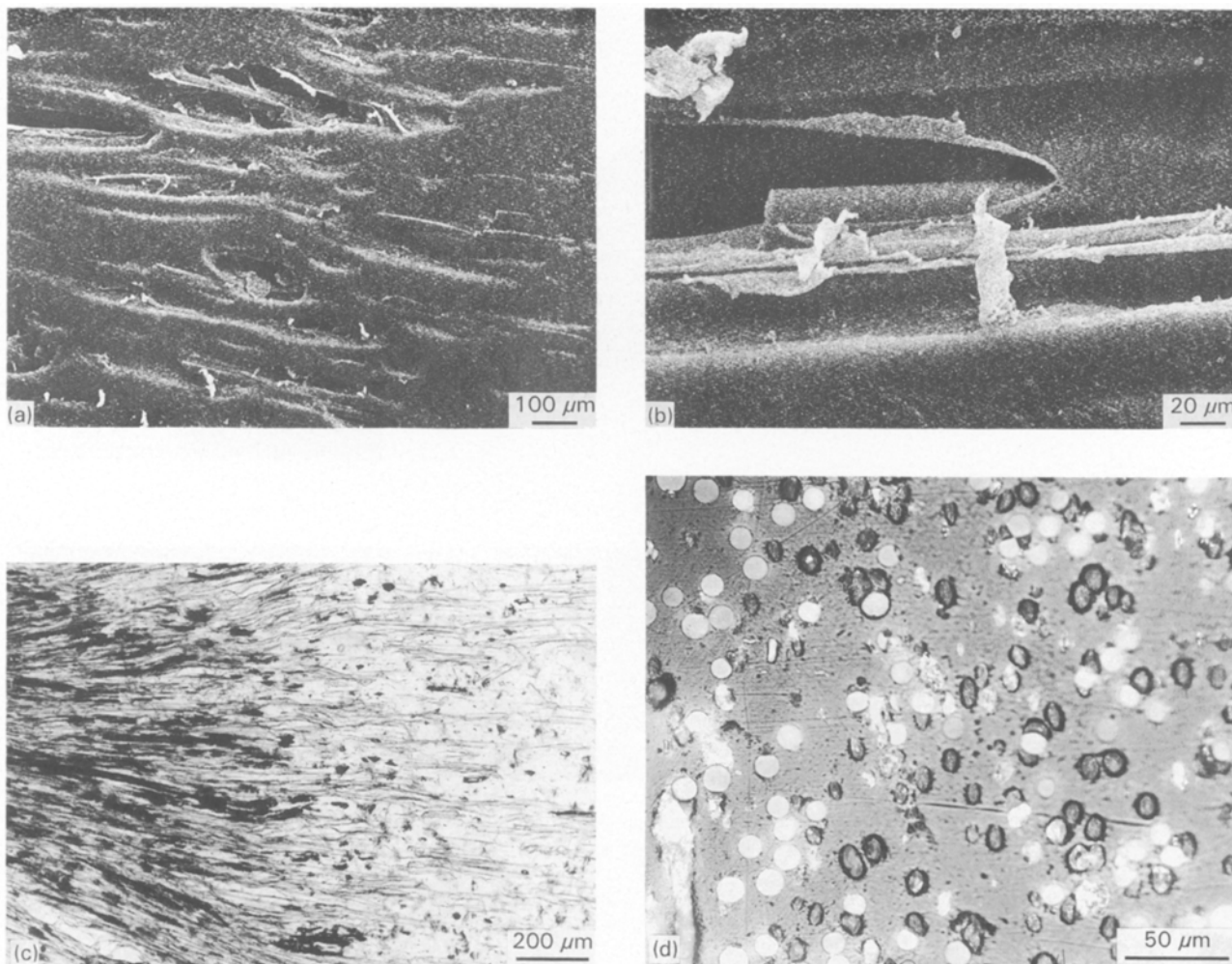


Figure 2 Micrographs showing numerous voids in the vicinity of the glass fibres and also between the glass fibres in the oriented composite material Vestolen P 5232 G1. (a, b) Scanning electron micrographs of polished surfaces taken along the drawing direction. (c) Transmitted light micrograph of a thin section taken along the drawing direction. (d) Reflected light micrograph of the polished surface taken perpendicular to the drawing direction.

the influence of shear stresses. It is important to note that, according to this concept, the local temperature does not necessarily reach the melting point of the polymer as proposed originally by Miller and Jäckel [14, 15]. However, the relatively high drawing temperature above the critical alpha crystallization temperature, $T_{\alpha c}$, certainly assists the transformation [10]. The softening of the matrix in the neck shoulder and an abrupt orientation of the embedded fibres, are shown diagrammatically in Fig. 5.

3.3. Toughening mechanisms

Non-oriented notched polypropylene specimens show typical brittle behaviour with relatively low values of Charpy impact strength (Table II). At -196°C also, the unnotched non-oriented polypropylene specimens showed brittle behaviour with impact strength values $19 \pm 1 \text{ kJ m}^{-2}$ for neat polypropylene Vestolen P 5202 and $14 \pm 1 \text{ kJ m}^{-2}$ for Vestolen P 5232 G1 containing glass fibres.

On the other hand, the most notable feature of the oriented polypropylene samples is their high (but anisotropic) toughness, even at very low temperatures down to liquid nitrogen temperature (-196°C). With oriented unnotched specimens, no fracture in the

conventional Charpy test could be reached at all experimental temperatures used. Therefore, only notched impact strength data could be compared. Table I shows the results obtained at two cryogenic temperatures for all oriented samples studied. The effect of the drawing temperature on the low-temperature notched impact strength is illustrated in Fig. 6. Several observations can be drawn from these results.

First, as shown in Table II, notched impact strength for non-oriented samples decreases with decreasing temperature. Vestolen P 5232 G1 containing glass fibres shows higher impact strength but the effect is not very pronounced.

Second, as shown in Fig. 6, the dependence of notched impact strength for oriented samples on the drawing temperature has a distinct minimum at about 130°C . This type of behaviour can be explained as a result of two competitive processes, namely improving homogeneity but decreasing orientation with increasing drawing temperature. Visual inspection of the drawn specimens reveals decreasing stress whitening with increasing temperature, cf. Fig. 7. As stress whitening reflects the presence of microdefects, one can expect increase of toughness with decreasing the stress whitening. On the other hand, WAXS data suggest [16] that the degree of orientation achieved

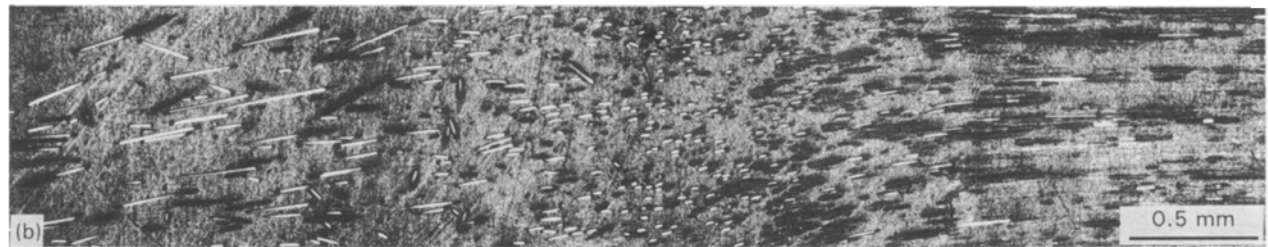
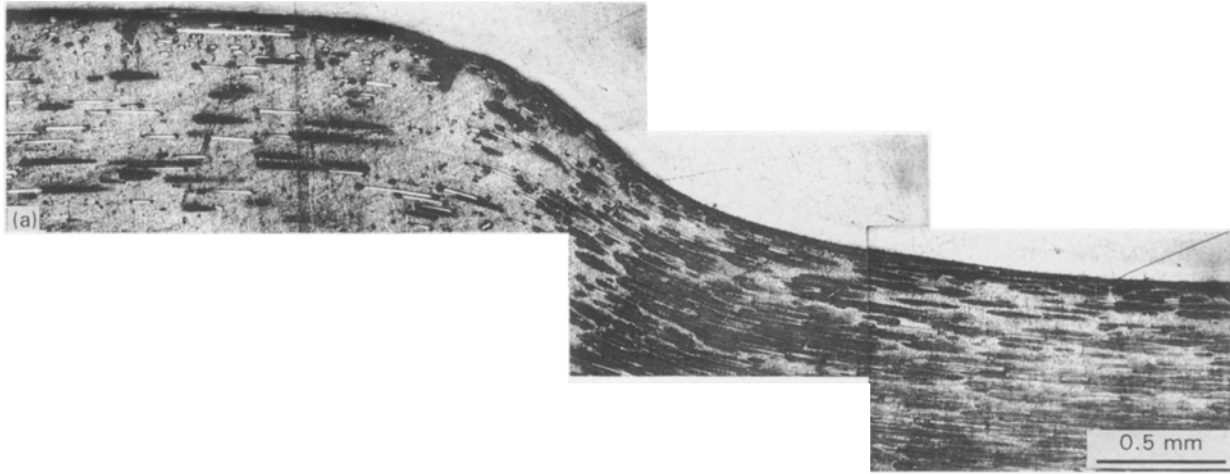


Figure 3 Reflected light micrographs of two mutually perpendicular polished sections of the neck region of a polypropylene composite Vestolen P 5232 G1. Sudden orientation of short glass fibres in the neck shoulder is demonstrated. (a) Edge region, (b) centre region; scale bars are parallel to specimen axis.

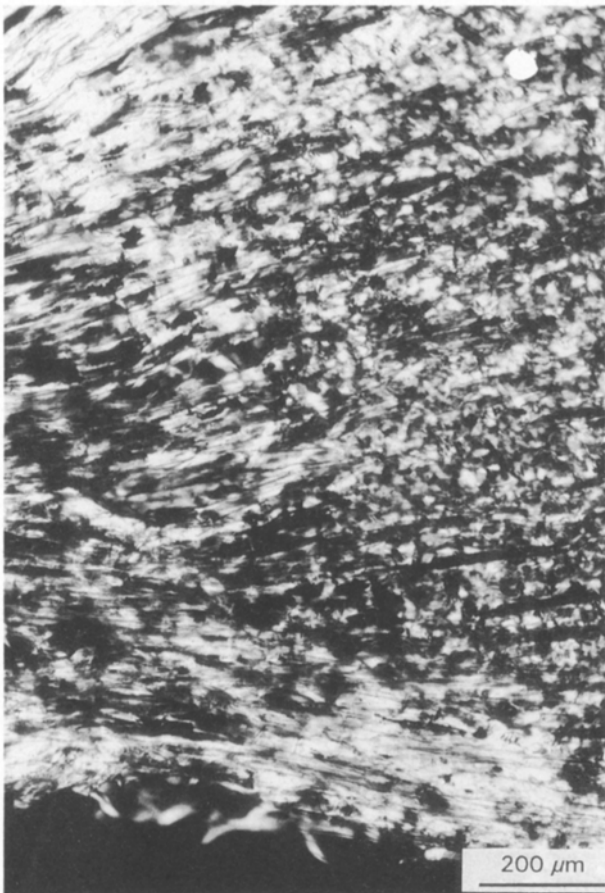


Figure 4 Optical micrograph in polarized light taken from the neck shoulder of oriented composite material Vestolen P 5232 G1. Transition from spherulitic to fibrillar structure is clearly seen in the central region.

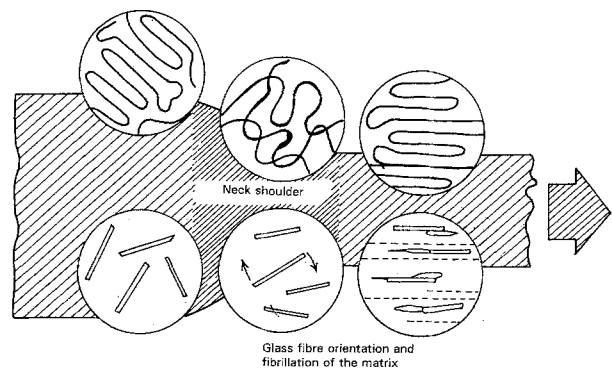


Figure 5 Schematic model showing two levels of structural transformation in the neck shoulder during solid-state drawing. The orientation of glass fibres and transition from lamellar to fibrillar morphology occur in the same region.

during solid-state drawing decreases with increasing draw temperature. As the efficiency of the CG mechanism depends on the orientation, one can expect a decrease of toughness with decreasing orientation. The superposition of both mechanisms can produce the observed temperature dependence of the toughness (Fig. 6).

Third, a comparison of notched impact strength data of the oriented polypropylene materials with and without glass fibres (Fig. 6) shows small but systematic increases of impact strength due to the presence of glass fibres. This suggests the positive action of multiple CG mechanisms at the fibre-matrix interface.

Fourth, specimens of oriented Propathene HW 60 GR 20 with higher interfacial adhesion in the original

TABLE II Notched impact strength Charpy data for non-oriented samples at two temperatures.

Material	Notched impact strength (kJ m^{-2})	
	23°C	-70°C
Mosten 58.412	4.4 ± 0.6	3.8 ± 0.4
Vestolen P 5232 G1	-	5.2 ± 0.5

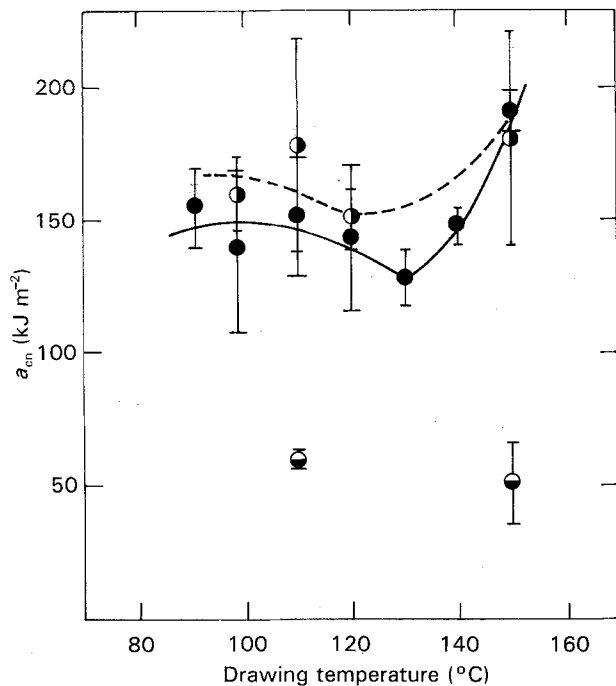


Figure 6 Notched impact strength (Charpy), a_{en} , for oriented polypropylene specimens as a function of drawing temperature. Test temperature -75°C. (●) Neat polypropylene MOSTEN 58.412 (○) Polypropylene VESTOLEN P 5232 G1 containing 20% of short glass fibres (●) Polypropylene PROPATHENE HW 60 GR 20 containing 20% of short glass fibres with enhanced interfacial adhesion.

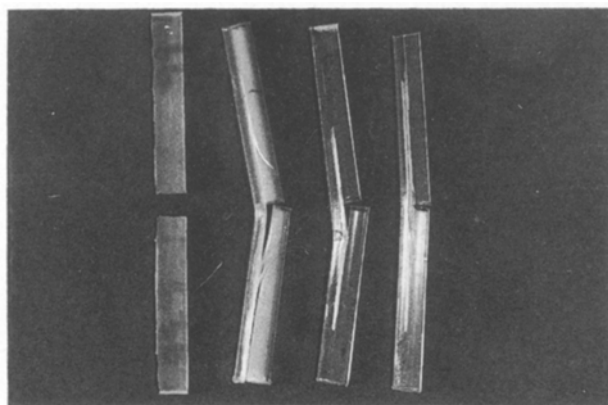


Figure 7 Notched specimens of neat polypropylene MOSTEN 58.412 broken at -75°C. From left to right: non-oriented specimen, specimens drawn at 90, 120 and 150°C, respectively. Note increased stress whitening in the specimen drawn at the lowest temperature (90°C).

material show substantially lower notched impact strength values than Vestolen P 5232 G1. In this case, the higher interfacial adhesion prevented the formation of well-developed neck and formation of regularly oriented and aligned structure (see Section 3.1).

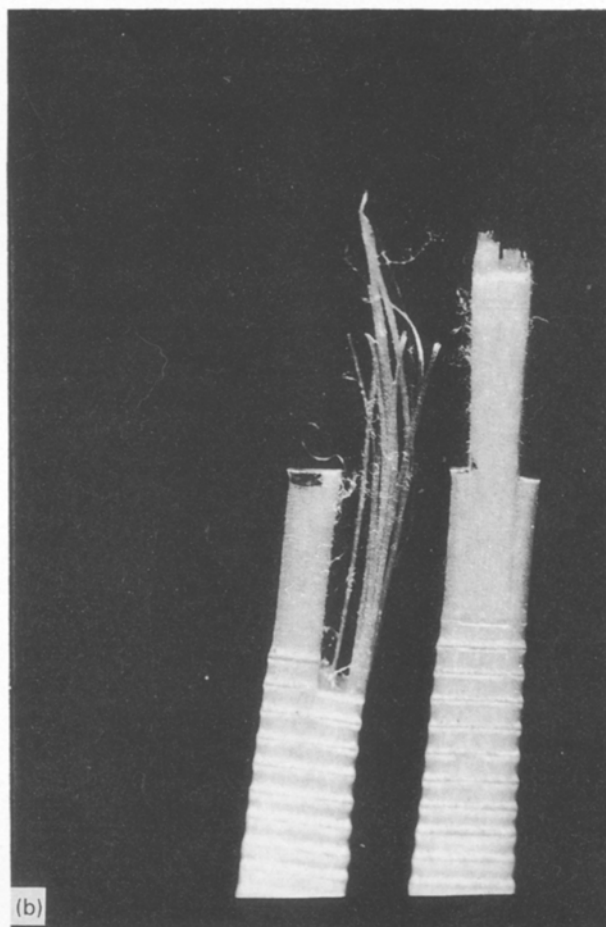
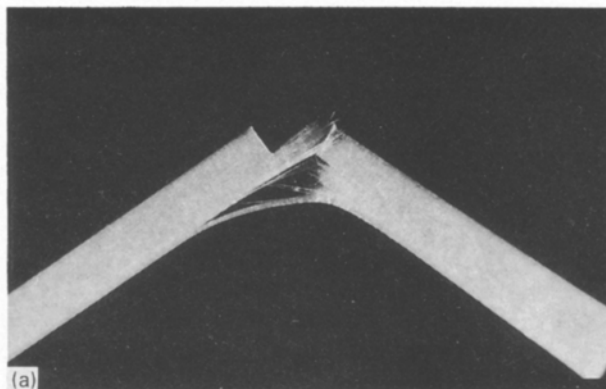


Figure 8 Close-up views of notched test pieces of the oriented composite material Vestolen P 5232 G1 fractured at the liquid nitrogen temperature. (a) Charpy bending mode, (b) tensile mode. Multiple blunting of crack propagation across the orientation direction is clearly demonstrated.

In the impact tests, the non-oriented specimens failed by a complete brittle break (C-type according to ISO standard 179) while oriented specimens showed a hinge break (H-type), i.e. an incomplete break such that both parts of the specimens were held together by a thin peripheral layer (Figs 7-9). The values of Charpy impact strength for non-oriented specimens could be somewhat influenced by the kinetic energy of fragments. However, this is not the case in the oriented specimens. Consequently, the real difference in the impact strength values between non-oriented and oriented samples would be even greater.

The mechanism of toughness of the oriented composites could be derived from the fracture surface

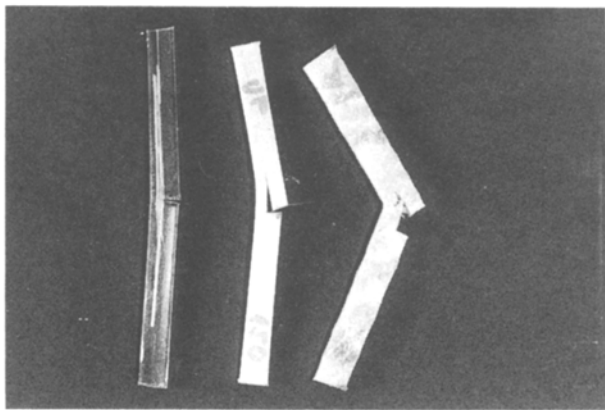


Figure 9 Comparison of the fracture mode of three polypropylene-based materials oriented at 150°C and broken at -75°C. From left to right: Mosten 58.412, Vestolen P 5232 G1 and Propathene HW 60 GR 20.

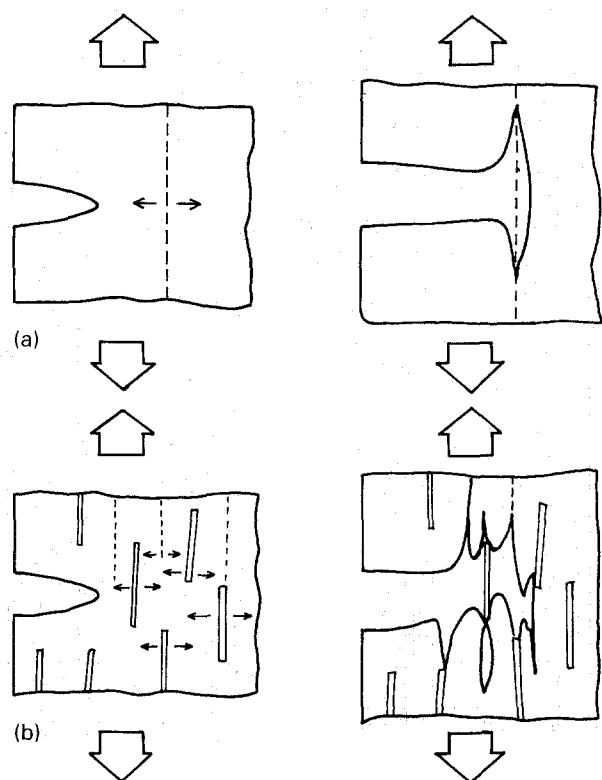


Figure 10 Diagrammatic representation of crack blunting in oriented materials. (a) Simple Cook-Gordon mechanism stopping the crack at a plane of weakness, (b) multiple crack branching at fibre-matrix interfaces. Large arrows indicate the action of main tensile stress; small arrows show the induced stress system opening secondary cracks at the planes of weakness.

morphology. The notched test pieces of oriented composites broken at the liquid nitrogen temperature are shown in Fig. 8, both for the Charpy bending (a) and tensile mode (b). A large damage zone could be seen in the vicinity of the starting notch, occupying a significant portion of the specimen. Splitting of the crack front and effective crack blunting in the case of the Charpy test and jumping of the fracture front by several millimetres along the specimen length in the case of tensile impact, is evident. Obviously, such bulk failure absorbs a lot of impact energy.

Stopping of a crack in oriented materials was originally analysed by Cook and Gordon [8, 9], who showed that in a uniaxially loaded plate with a crack, there are two systems of stresses acting around the crack tip. In addition to the main tensile stress perpendicular to the crack plane, secondary tensile stress is induced acting along the crack-propagation direction with a maximum located somewhat ahead of the crack tip. In the elastic case, this cross-stress maximum was found to be close to one-fifth of the maximum longitudinal stress. Consequently, at a plane of weakness perpendicular to the main crack propagation, a secondary crack could be opened, Fig. 10a. This would blunt and deflect the main growing crack. The CG mechanism enhances the toughness anisotropically, i.e. predominantly in one direction, and remains effective down to at least liquid nitrogen temperature depending on the material. This is unlike the toughening of a hard polymeric matrix by embedment of rubber particles in which the effect ceases below the glass transition temperature of the rubber.

While the classical CG model describes only an isolated plane of weakness ahead of a crack, in the case of oriented composite samples described here, multiple fractures occur simultaneously at many individual weak interfaces between the matrix and weakly bonded fibres (see Fig. 10b). Interestingly, a similar failure mode could be observed in some biological composites, such as beetle shells, timber or bones [17].

4. Conclusion

Unidirectional composite materials can be prepared from injection-moulded polypropylene samples containing short glass fibres via solid-state drawing.

Extensive movements of fibres, accompanied by the transformation of polypropylene crystalline structure, support the concept of strain-induced "melting" of the polymeric matrix in the neck shoulder.

Oriented polypropylene composite materials possess high toughness down to liquid nitrogen temperature, if the main crack propagates across the drawing direction. This effect arises from crack blunting by the Cook-Gordon mechanism and is enhanced in samples containing short glass fibres. The combined effect of stress whitening and orientation causes non-monotonic dependence of notched impact strength on the draw temperature with a minimum at 130°C. The highest value of impact strength was obtained with specimens drawn at 150°C.

The properties of the interesting class of polymeric composite materials prepared by solid-state drawing can be further optimized by varying interfacial adhesion, drawing conditions and subsequent treatment [18]. This is subject of further study.

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