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Morphological investigations of polypropylene single-fibre reinforced polypropylene model composites

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Abstract

Melt-spun isotactic polypropylene (iPP) fibres have been prepared with moduli of about 12 GPa and strength of 730 MPa. Single-fibre model composites are prepared by embedding constrained high-modulus iPP fibres in thin films of a matrix material based on the same isotactic polypropylene grade. The morphology of these composites has been investigated by optical microscopy and low-voltage scanning electron microscopy techniques. After isothermal crystallisation from the melt a transcrystalline layer was found having lamellar crystals grown perpendicular to the fibre axis. The work illustrates that the processing of polypropylene fibre reinforced polypropylene composites as self-reinforced single-polymer composite systems is feasible and that these composites may fulfil the demands for fully recyclable engineering composites.

Keywords: Polypropylene fibres; Self-reinforced polypropylene composites; Morphology

1. Introduction

Isotactic polypropylene (iPP) is apparently the major polymeric construction material of the future in view of its impressive growth figures of the past years. However, iPP as such has to be reinforced to meet the high demands on stiffness and strength in engineering applications and glass fibres are the major reinforcing elements used in these materials. Unfortunately, in view of recyclability, glass fibres are components, which still cause environmental problems, both in mechanical recycling and thermal recycling (incineration). Polypropylenes reinforced with polypropylene fibres may have the opportunity to overcome these problems. Such self-reinforced single-polymer composites have specific economic and ecological advantages since, upon recycling, a polypropylene blend is obtained which can be re-used for PP-based applications. Essential for this concept is that the PP fibres and matrices are optimised in structure, properties and processing performance.

The tensile properties of iPP fibres are highly correlated with the molecular orientation in crystalline and amorphous regions. Fundamental studies on the melt spinning of iPP date back to the 1960s, when the polymer of commercial significance had just emerged [1–3]. Several investigations have shown the importance of processing conditions on filament structure development and the resulting mechanical properties of melt-spun filaments [4–9]. In particular, the influence of spinning speed, cold-drawing conditions and certain grade characteristics such as molecular weight and molecular weight distribution has been examined. The literature on the effect of cold-drawing and annealing on the tensile properties is sparse, but there are a number of articles that discuss structure development at these stages of the fibre production process [10–14]. Some relevant articles on tensile properties versus cold-drawing conditions can be found among the literature on polyethylene fibres [15–18]. In this study we have investigated the tensile properties of single-filament iPP fibres, which where prepared using lab-scale spinning apparatus. The research into fibre optimisation involved a systematic study of the influence of various melt-spinning and drawing conditions on the mechanical properties of the filaments in order to achieve a high value of the elastic modulus and strength.

Beside recyclability the interest in the concept of single-polymer composites is based upon the idea that interfacial bonding should improve if matrix and reinforcement are made from the same semi-crystalline polymer [19,20]. Next, other morphological features such as the so-called transcrystallisation of the matrix material onto fibre surfaces may be related to enhanced stress transfer capability along

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the fibre–matrix interface [21,22]. A possible reason for transcrystallisation is heterogeneous nucleation on fibre surfaces. Because of the good lattice match between iPP fibre and iPP matrix and the highly favourable energetics, an epitaxial nucleation seems to be favoured, as in the case of polyethylene fibre reinforced polyethylene composites [23,24], which initiates the formation of a transcrystalline layer.

It is believed that at least some of the questions about the role of transcrystallisation in fibre composites could be resolved if morphological observations of lamellar details are able to reach the interface. Quite recently, improved equipment for low voltage as well as environmental scanning electron microscopy (LVSEM, ESEM) has become available, which permits lamellar resolution to be obtained from polymer surfaces without the need for additional sample preparation techniques [25–28]. It is the purpose of the second part of this work to report on some preliminary LVSEM results on the formation of transcrystalline layers in a single-fibre reinforced polypropylene composite.

2. Experimental

The commercial iPP grade used in this study was X7284, kindly provided by DSM, The Netherlands, which has an average molecular weight of 280 kg/mol and a melt flow index of 13. The fibres were prepared using a home-built lab-scale melt-spinning device which consisted of a double walled storage cylinder which could accommodate about 10 g of material. The spinning temperature was 200°C, and the spinning device was equipped with a capillary of 1.3 mm diameter and a length of 8 mm. The fibres were wound on a drum at rates varying from 5 to 120 m/min. The next step in the fibre preparation procedure was cold-drawing of the filaments. Cold-drawing was performed using a home-built stretching unit, consisting of two small drums of 48.5 mm diameter separated by a 600-mm long ceramic oven. Absolute speed, speed ratio of the two drums and temperature are computer controlled. The fibres were cold-drawn at a temperature of 145°C with draw ratios (speed relation of the two wheels of the drawing unit) varying between 3 and 10.

All fibres were tested using a Zwick 1435 tensile tester equipped with a load-cell of 5 N and pneumatic fibre clamps. The sample length used was 100 mm and the fibres were tested at a rate of 50 mm/min.

The calorimetric measurements were performed using a Perkin–Elmer DSC-7 apparatus. The fibres were either placed unconstrained in the aluminium pans or wound on an aluminium rod to keep them constrained during heating. A heating rate of 10°C/min was used throughout this study.

For the production of single-fibre model composites, both ends of the high-modulus iPP fibres were fixed on glass slides in order to prevent them from relaxation during heating. iPP pellets of the same grade were hot-pressed at 180°C for 10 min. The resulting ~80 μm thin films were placed on the same glass slides as the fibres. These stacked samples were heated in a hot stage at 170°C for 5 min, melting only the iPP matrix material and not the constrained fibres. Afterwards the samples were air-cooled, isothermally crystallised at 140°C for 3 days or isothermally crystallised in a gradient hot-stage. This rather simple stage consisted of two individual heating blocks that were separated by a small gap of 8 mm width. Hot-stage temperatures were monitored by

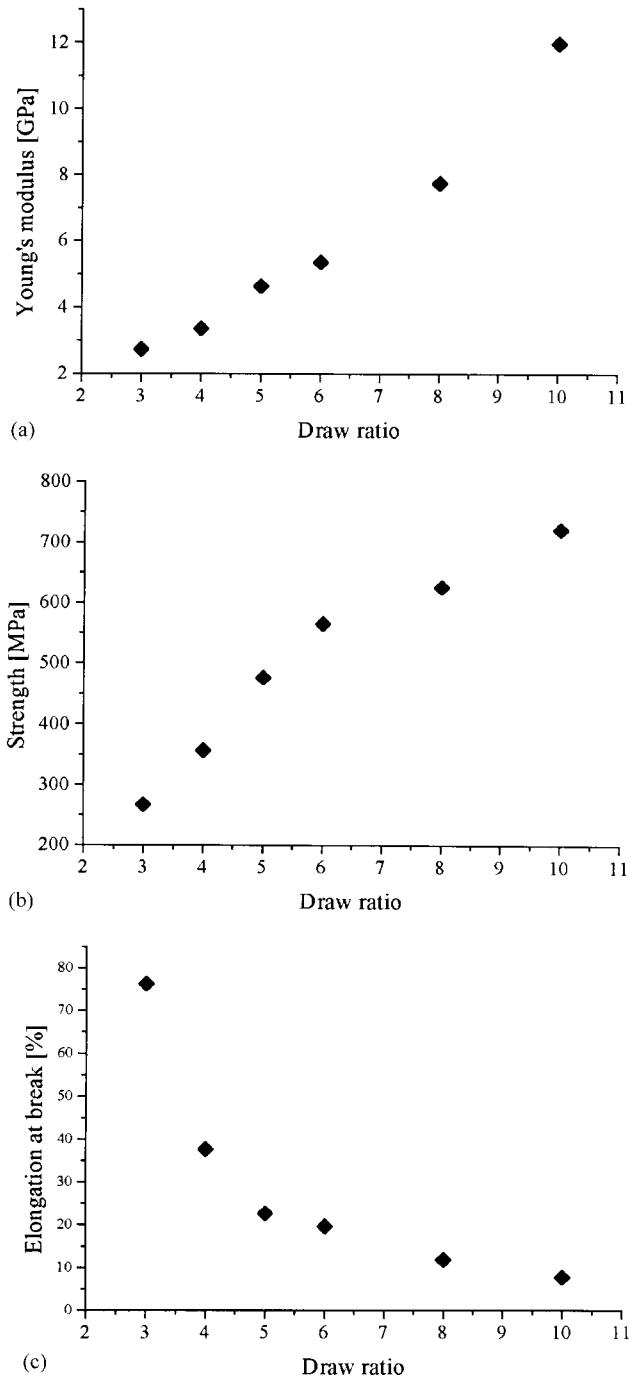

Fig. 1. Mechanical properties of cold-drawn iPP fibres: (a) Young's modulus; (b) tensile strength; and (c) elongation at break versus draw ratio.

thermocouples embedded into the heating blocks and were controlled within 0.5°C. Several commercial calibration powders (Phenacetin, Acetanilid, Bencil and Acobencol) with melting temperatures of 134.5, 114.5, 95 and 68°C, respectively, were used to calibrate the temperature gradient within the sample, which was established across the gap for any particular choice of block temperatures.

The investigation of the composite morphology was performed using a transmission light microscope (Zeiss Universal) equipped with crossed polarisers. Without additional surface treatment or coating of the samples the fibre–matrix interface morphologies were investigated using a Philips environmental scanning electron microscope (XL30 ESEM-FEG) in low-voltage mode (LVSEM).

3. Results and discussion

3.1. Fibre characterisation

The tensile properties of melt-spun iPP fibres are influenced by their physical structure, which is controlled by the fibre processing conditions. Common fibres produced by a commercial spin line have tensile moduli up to 3–5 GPa, tensile strengths up to 600 MPa and an elongation at break in the range of 50–600% [14]. Through optimised cold-drawing of single filaments a high overall draw ratio could be reached. Such highly cold-drawn iPP filaments have excellent mechanical properties. Fig. 1 shows plots of Young's modulus, tensile strength and elongation at break versus draw ratio of cold-drawn single iPP filaments, respectively. Young's modulus and tensile strength improves with increasing draw ratio and the highest values are observed for the highest draw ratio. Elongation at break, on the other hand, decreases with increasing draw ratio. Fibres cold-drawn at 145°C with a draw ratio of 10 have reached a Young's modulus in the order of 12 GPa and a strength of 730 MPa at an elongation at break of 8%.

Typical stress–strain curves of cold-drawn single-filament fibres are shown in Fig. 2. The as-spun fibres show after an initial linear portion a yield point, and up to break, a region of low slope, where large extensions are produced by small increases in stress. This behaviour indicates the development of a neck and large plastic deformations before the stress starts to rise again followed by fracture of the fibres. The cold-drawn fibres exhibit higher moduli, no apparent yield point and a considerably lowered elongation to break but increased tensile strength compared to the filaments from which they were drawn. These qualitative similarities exist in all drawn fibres.

Further investigations of the melting behaviour of optimised fibres were performed. Fig. 3 shows DSC heating traces of constrained and unconstrained iPP fibres of the highest draw ratio. Compared with isotropic iPP, after spinning and drawing a small shift of the melting temperature and an increased enthalpy of melting is observed. The higher melting temperature can be assigned to an increase of crystal size caused by the stress-induced recrystallisation during the cold-drawing process. Constraining the same fibre results in differences in the DSC trace. Again, the melting temperature shifts to higher values and the melting enthalpy increases further. Almost the complete melting area is localised above the original melting temperature of the isotrope, as delivered iPP, and the peak maximum of the melting temperature reaches a value of about 190°C. Therefore, the difference in melting temperature between constrained fibres and the isotrope, as delivered iPP, offers an enlarged temperature window for processing of iPP fibre reinforced iPP composites. The overheating behaviour of constrained fibres has been reported for gel-spun UHMW-PE [29] and gel-spun UHMW-iPP [30], and for melt-spun iPP fibres with a low (cold) draw-down [31] and drawn iPP films [32], but in the latter studies only melting temperature shifts of about 10°C are observed.

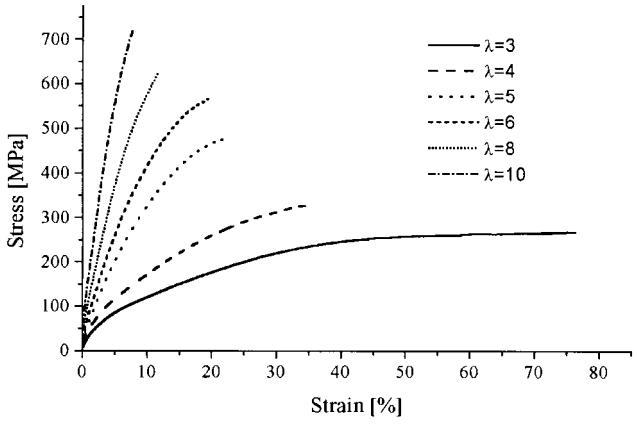

Fig. 2. Typical stress–strain curves of cold-drawn iPP single filaments. The draw ratio λ is indicated in the legend.

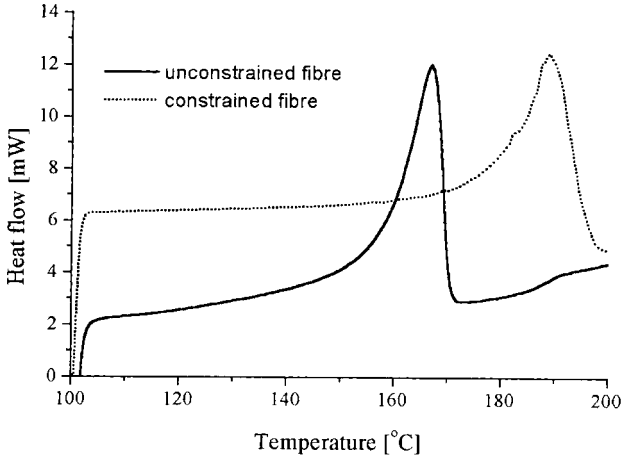

Fig. 3. DSC heating traces of constrained and unconstrained highly drawn iPP fibres.

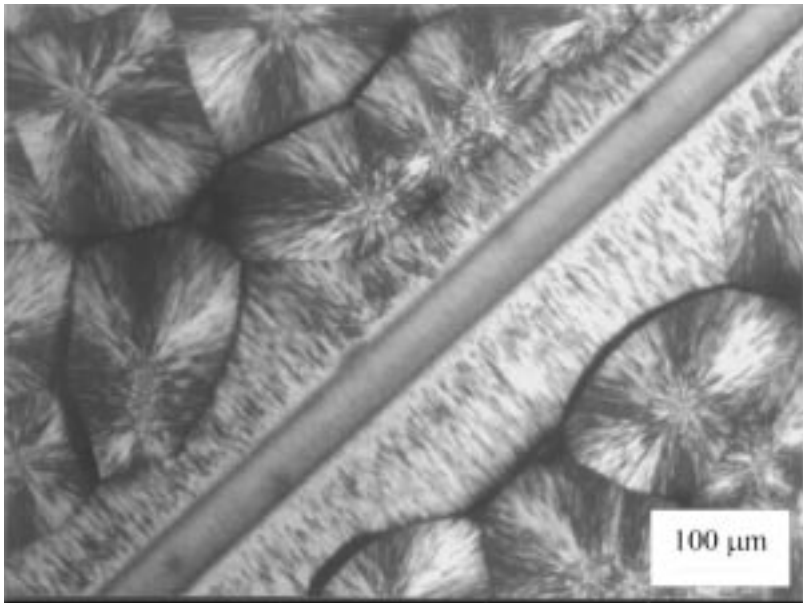

Fig. 4. Transmission optical micrograph showing the morphology of a polypropylene single-fibre model composite isothermally crystallised at 145°C for 3 days.

3.2. Polypropylene single-fibre model composites

Fig. 4 shows the morphology of a polypropylene single-fibre model composite isothermally crystallised at 145°C for 3 days using an optical microscope. The sample shows three different regions: the iPP fibre partially embedded in a transcrystalline layer surrounded by the iPP matrix material consisting of spherulitic superstructures. Birefringence measurements indicate an optical negative character of the matrix spherulites and the transcrystalline layer indicating the appearance of the crystalline α-phase of iPP, which is in accordance with previous observations [33,34]. The presented image proves that the preparation of polypropylene fibre reinforced polypropylene composites is possible using the introduced constrained fibre preparation method. Even fibres and matrix of the same grade can be combined utilising the overheating behaviour of constrained high-modulus polymer fibres.

The following section of the present study focuses on the morphological details of the matrix material, especially the

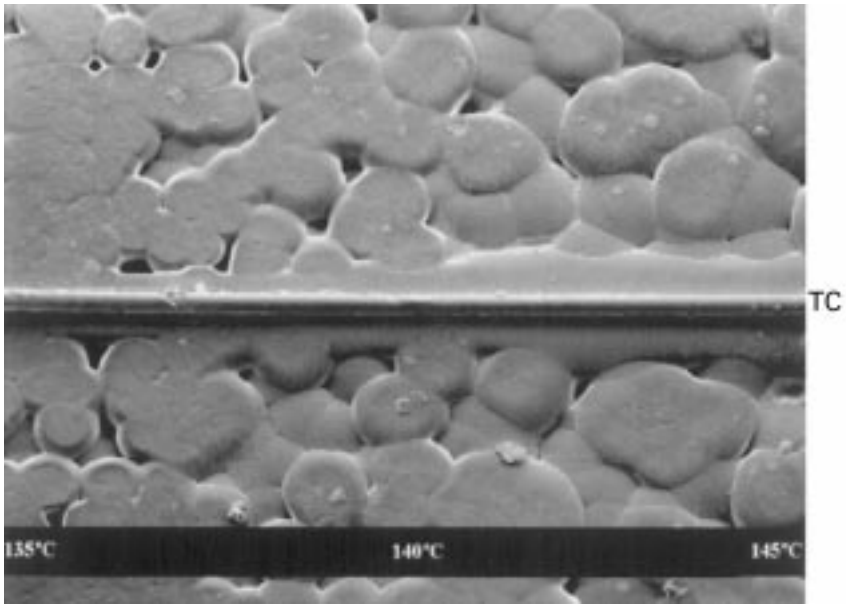

Fig. 5. Low-voltage scanning electron microscope image of a part of a single-fibre model composite which has been quasi-isothermally crystallised at a temperature gradient from 135°C (left) to 145°C(right). TC is indicating the transcrystalline layers.

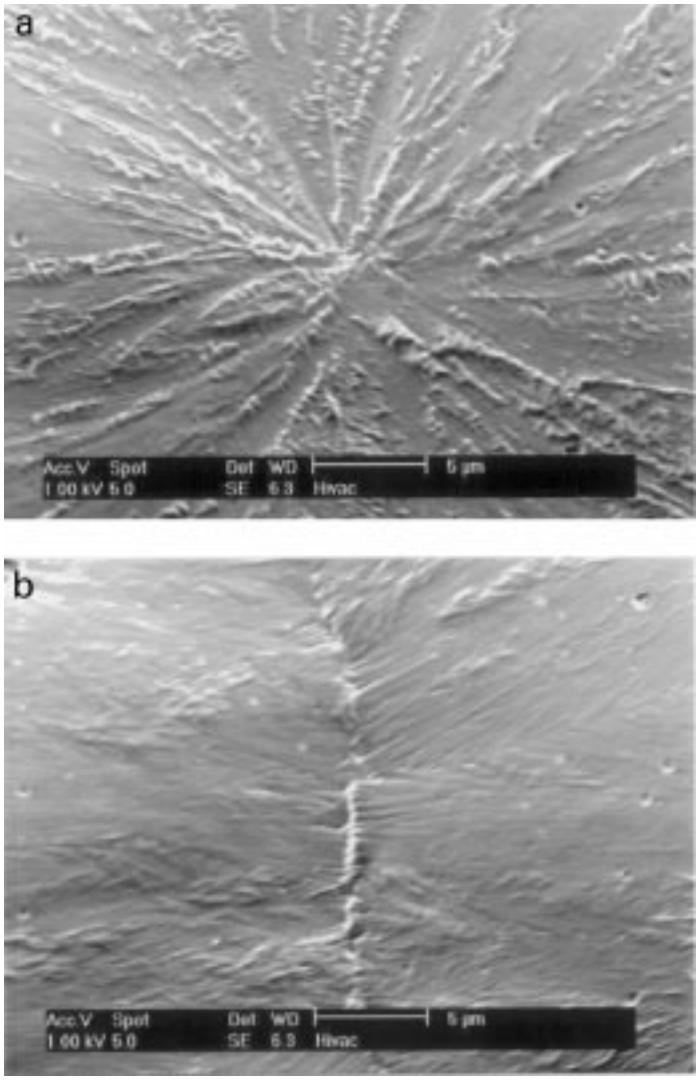

Fig. 6. Low-voltage scanning electron microscope image of the spherulitic morphologies of the iPP matrix after isothermal crystallisation at: (a) 135°C (centre of a spherulite) and (b) 145°C (boundary between two spherulits).

transcrystalline layer, and the fibre–matrix interface. Fig. 5 shows a LVSEM image of a part of a single-fibre model composite, consisting of a melt-spun fibre and a matrix material based on the same iPP grade, quasi-isothermally crystallised at a temperature gradient from 135 to 145°C. The highly drawn iPP fibre is partly embedded, only half of the fibre is in contact with the matrix. For polypropylene no charging problem occurs when using an accelerating voltage of 1 kV. This low accelerating voltage results in a low penetration depth ($<$50 nm) of the primary electron beam into the PP and a high yield of secondary electrons. Consequently, the presented LVSEM images show the surface topography of the investigated samples. A survey of LVSEM applications on polymers is given in Refs. [26,35].

The fibre surface is smooth and no kink bands are visible for the used crystallisation conditions. Along the length of the fibre a transcrystalline region is formed. The influence of temperature on the width of the transcrystalline layer and the spherulite size in the matrix is clearly shown. As with increasing supercooling, being the difference between the melting temperature of the matrix and the used isothermal crystallisation temperature, the thickness of the transcrystalline layer decreases, and at an isothermal crystallisation temperature of $\sim$135°C almost no transcrystalline layer seems present. At low degrees of supercooling holes between the spherulites in the matrix indicate that all material is used for crystallisation and the crystallisation time has been sufficient. The radius of the spherulites is approximately equal to the thickness of the transcrystalline layer indicating that the crystallisation at the fibre surface has started at almost the same time as the crystallisation in the melt. Thus, the nucleation at the fibre surface does not start at a lower supercooling. For the used material this behaviour is expected, because nucleation agents are present.

For a more detailed analysis of the observed

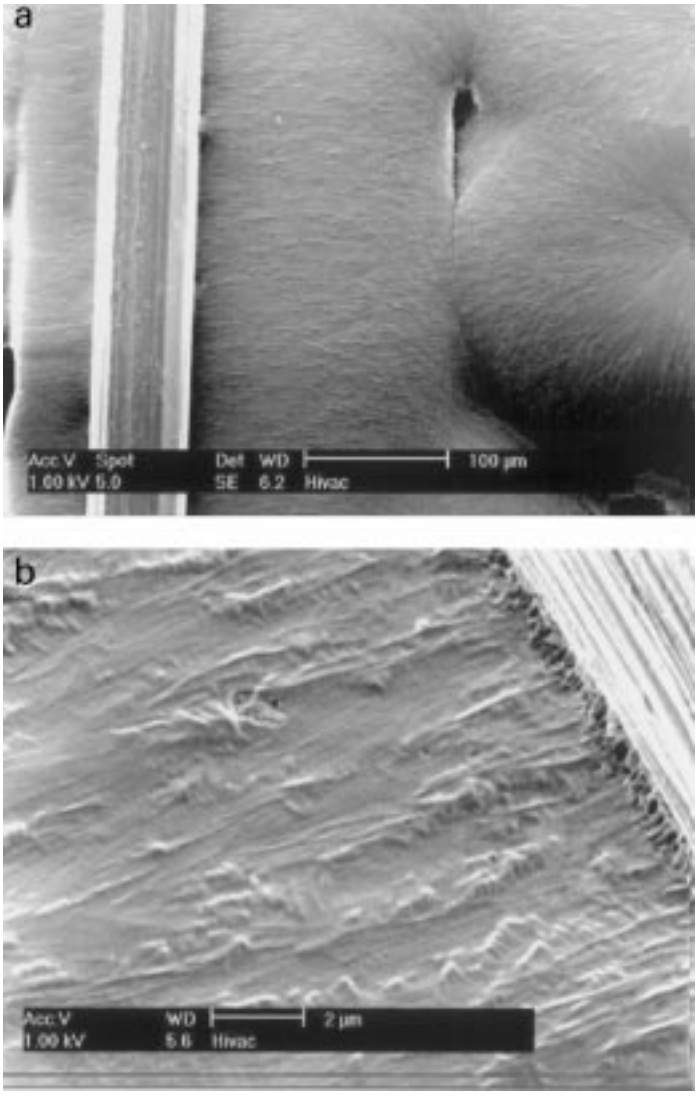

Fig. 7. Low-voltage scanning electron microscope image of the fibre/matrix interface of a single-fibre model composite isothermally crystallised at 135°C: (a) overview and (b) high magnification.

morphological features of the transcrystalline layers in polypropylene single-fibre reinforced polypropylene model composites we need to discuss first the morphological appearance of the matrix depending on the isothermal crystallisation temperature. Crystallisation of the iPP matrix at low supercoolings form pronounced sperulitic superstructures. More details of their lamellar architecture can be observed by using high-magnification LVSEM. Fig. 6a shows the centre of a spherulite crystallised at 135°C. The main growth direction of lamellar crystals is radial (mother lamellae), whereas additional tangentially crystallised lamellae (daughter lamellae) indicate the presence of the so-called crosshatched morphology [36,37]. It is consistent with the thin film observations of Padden and Keith [38], who state that the cross-hatching lamellae nucleate on the side surface of α-lithes and lie in a different plane. In contrast, samples crystallised at 145°C only consist of radial grown lamellae (Fig. 6b), which are especially pronounced at the boundaries of the spherulites. A detailed survey on the lamellar architecture of iPP spherulites depending on the crystallisation conditions can be found in Ref. [34].

LVSEM observations are carried out along the prominent, well-developed layer of transcrystallisation in polypropylene single-fibre model composites isothermally crystallised at low supercoolings. The transcrystalline layers show similar morphological features as described for the matrix spherulites. Fig. 7a presents the morphology of a sample crystallised at 135°C. The fibre is partly embedded in the matrix material. The nucleation density on the fibre surface is very high but low in the matrix. Therefore, the crystals can grow only in the direction perpendicular to the fibre surface forming the transcrystalline layer. The local thickness of the transcrystalline layer can be determined

and is around 130 μm. Details of the lamellar arrangement in the transcrystalline layer and of the fibre–matrix interface can be seen in the high-magnification LVSEM image (Fig. 7b). The dominant crosshatched morphology consists of mother lamellae nucleated on the fibre surface and daughter lamellae epitaxially crystallised on them. The holes at the fibre–matrix interface result from the shrinkage of the iPP matrix during crystallisation, whereas the remaining fibrils indicate good interfacial adhesion. The transcrystalline layers of samples isothermally crystallised at 145°C show only radial grown lamellae (figure not shown). This morphology is similar to the spherulitic architecture as discussed above.

The influence of a transcrystalline layer on interface adhesion and overall mechanical properties of the composite is studied for a large number of fibre–matrix systems, e.g. PE/PE [24,27,39,40], aramid or high-modulus carbon fibres embedded in iPP [41]. Transcrystallisation is usually studied using optical microscopy, which makes it often difficult to obtain information about its origin and its physical cause. Lamellar detail of transcrystalline layers has recently been studied by transmission electron microscopy after permanganic etching [42]. In that case, the preferred orientation of individual iPP lamellae (crosshatched morphology) within the transcrystalline regions is taken as proof for the occurrence of epitaxial nucleation of iPP on polyimide fibres. The same argument can be used in the present case because a preferred orientation of the very first iPP matrix lamellae, which have nucleated on the fibre surface, and the pronounced crosshatched morphology (for a crystallisation temperature of 135°C) can be seen very clearly.

4. Conclusions

The idea of embedding high-modulus/high-strength polymeric fibres in thermoplastic matrices to enhance mechanical properties of the resulting composite is not new. However, in the case of high-modulus iPP fibres and iPP matrix such composites may present some specific features for industrial applications. The specific modulus and strength of highly drawn iPP fibres embedded in an iPP matrix may well be able to compete with standard glass-fibre reinforced polypropylene grades, whereas environmental advantages favour single-polymer composites. In the present study it was shown that the preparation of such polypropylene single-fibre reinforced polypropylene model composites is possible using a melt impregnation method based on constrained fibres.

After optimisation of the cold-drawing process melt-spun fibres of iPP were prepared, possessing high mechanical properties, e.g. Young's moduli of 12 GPa and tensile strengths of around 730 MPa were obtained. Constraining of highly cold-drawn fibres results in overheating and a drastic increase of the melting temperature to about 190°C. Single-fibre model composites were prepared using constrained high-modulus fibres and a matrix material based on the same polypropylene grade.

Low-voltage scanning electron microscopy has been used to image the morphology of the spherulitic matrix and the transcrystalline layer formed in polypropylene single-fibre model composites under a large variety of crystallisation conditions. The transcrystalline layers only reflect the morphology of the matrix crystallised under certain conditions without interaction with the fibre. The surface of the fibres acts as a nucleation centre for the matrix and the nucleation may result from epitaxial crystallisation.

The presented results are promising and indicate a possible preparation route for polypropylene fibre reinforced polypropylene composites. Moreover, in the case of processing conditions, which result in epitaxial crystallisation, these composites may show improved interfacial adhesion properties. Further results on the influence of crystallisation conditions on the development of a transcrystalline layer at the fibre surface and its adhesion properties are planned and will be published in the near future.

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