Abstract

The crystallisation behaviour and morphology of polyethylene-based single polymer composites has been investigated by light microscopy and low voltage scanning electron microscopy techniques. The surface crystals on ultra high molecular weight polyethylene fibres act as nucleation centres for the high density polyethylene matrix, which may result from epitaxial crystallisation. After crystallisation from the melt and independent of air-cooled or isothermal crystallisation conditions, a transcrystalline layer was found having lamellar crystals grown perpendicular to the fibre axis. © 1998 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Reinforcing a common polyethylene with polyethylene fibres leads to a strong and stiff single polymer composite [1]. Capiati and Porter first published work on such a self-reinforced high density polyethylene (HDPE) [2]. As reinforcement they used highly oriented polyethylene film strips, which are the predecessors of today’s commercially available ultra high molecular weight polyethylene (UHMW PE) fibres. Because of their different morphologies, a difference in the melting temperatures of the film strips and the unoriented matrix was found and used to manufacture the single polymer composites by hot pressing. Microscopic investigations of these samples showed a third, transcrystalline, morphology between the film strips and the matrix. Crystalline lamellae in this region had grown perpendicular to the fibre direction. The interfacial shear strength of the polyethylene composites, evaluated by pull out tests, falls between the strength for glass fibre reinforced polyester and epoxy resins, and this relatively high shear strength and the morphology of self-reinforced polyethylene are reasons for further investigations.

Using commercial gel-spun UHMW PE fibres as reinforcement for HDPE, transcrystalline morphologies also were found [3–5]. Possible reasons for the transcristallisation are heterogeneous and homogeneous nucleation on fibre surfaces. Because of the good lattice match between fibre and matrix and the highly favourable energetics a homogeneous, epitaxial nucleation seems to be the more probable alternative [3,4]. The morphologies of transcrystalline layers vary with the temperature cycle used to manufacture the composites; Stern et al. observed four different transcristalline morphologies with the same fibre matrix combination [5]. Three of these were obtained by cooling samples at different cooling rates from a temperature between the melting temperatures of fibre and matrix. The composite with the fourth morphology was crystallised under isothermal conditions at a temperature only a few degrees below the melting temperature of the matrix.

The present work on polyethylene-based single polymer composites concentrates on investigating the lamellar structure of two different transcrystalline morphologies. One is obtained by cooling from a temperature above melting temperature of the matrix to room temperature and the other one by isothermal treatment. The different transcristalline morphologies and the corresponding morphologies of the matrix obtained using light microscopic and low voltage scanning electron microscopic (LVSEM) investigations are described.

2. Experimental

The UHMW PE fibres used in this work were Dyneema SK 65 and kindly supplied by DSM, The Netherlands.
HDPE was Lupolen 6031M from BASF AG Ludwigshafen, Germany. Differential scanning calorimetry (d.s.c.) was performed using a Seiko Instruments SSC 5200 thermal analyser. The UHMW PE fibres and the HDPE matrix were measured individually at a heating rate of 10 K/min. The UHMW PE fibres were either placed free in the d.s.c. pan or fixed so as to prevent shrinkage.

For producing the microcomposites both ends of four UHMW PE fibres were fixed on a glass slide, so that the fibres could not relax during the heat treatment. HDPE pallets, as delivered, were hot pressed at 160°C for 10 min. The resulting 20 mm thick films were placed on the same glass slides as the fibres. These stacked samples were then annealed in a hot stage at 138°C for 5 min, melting only the HDPE film and not the UHMW PE fibres. Afterwards the samples were either air-cooled or isothermally crystallised at 124°C for 24 h.

The morphologies of these samples were investigated using a Leica transmission light microscope with crossed polarisers, and without additional surface treatment or coating of the samples with a S4500 Hitachi LVSEM using an accelerating voltage of 1 kV and a working distance of 7 mm. A survey of LVSEM applications on polymers is given in Refs. [6,7].

3. Results and discussions

D.s.c. scans of the HDPE matrix show a single melting peak with a peak maximum temperature at 136°C (Fig. 1(a)). For d.s.c. scans of UHMW PE fibres lying loose in the pan a triple peak due to melting of a part of the orthorhombic phase, a lattice transition from orthorhombic to hexagonal and melting of the hexagonal phase can be seen (Fig. 1(b)) [8]. If shrinkage of the fibres during heating is prevented, the first peak, and with this the melting of the orthorhombic phase, is reduced (Fig. 1(c)). Therefore the temperature window for processing the microcomposites is enlarged by fixing the UHMW PE fibres on the glass slide.

The morphology of the HDPE matrix has varied significantly with the crystallisation conditions. Fig. 2(a) shows the light microscope morphology of a sample air-cooled from the melt. Relatively large spherulites, with the characteristic Maltese cross extinction of banded spherulites when viewed through crossed polarisers [9–11], can be clearly seen. The LVSEM image of the same sample shows more details of the lamellar crystalline arrangement (Fig. 2(b)). For polyethylene 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 HDPE and a high yield of secondary electrons. Consequently, all presented LVSEM images show the surface topography of the investigated samples. The growth direction of the crystals may be seen from the centre to the edges of the imaged spherulite. Because the size of the spherulite is of the same order as the film thickness (20 mm) it exhibits three-dimensional rather than two-dimensional spherulite growth.

The morphology of isothermally crystallised HDPE differs from the above described air-cooled sample. It appears to be non-spherulitic; by the end of the isothermal crystallisation most of the space was filled with closely packed sheaf-like superstructures (Fig. 3(a)). Once more the corresponding LVSEM image clearly shows the sheaf-like arranged crystals of HDPE (Fig. 3(b)). The crystals have grown with branches from the bound centre.
of the superstructure, which results in the sheaf-like appearance. Fig. 3(c) shows more details of the crystal topography. Looking at one single lamella the plate-like shape of the crystals and some branches may be seen. Due to the higher secondary electron output at edges, the appearance of the raised sides of the lamellae, defined elsewhere as the thickness of the crystal, is clear, showing that the average thickness of the crystals to be approximately 40 nm.

Figs 4 and 5 show the transcristalline layer obtained under air-cooled and isothermally crystallised conditions. The morphology of the HDPE interaction with the fibres is, for both cases, almost comparable to the matrix morphology described above. The morphology, seen with light microscopy, of a composite air-cooled from the melt is shown in Fig. 4(a). Simultaneously with the banded spherulites in the matrix, a banded transcristalline layer having an average thickness of approximately 10 nm is obtained. Along the fibre many kinkbands with angles of about 45° to the fibre axis can be seen. These kinkbands indicate that the fibre buckled under the compressive stresses caused by shrinkage of the matrix during cooling and crystallisation. Again the LVSEM image of the same sample shows more details of the lamellar crystalline arrangement of the transcristalline layer at the fibre/matrix interface (Fig. 4(b–d)).

At low magnification the same morphology as described for the light microscope image is visible (Fig. 4(b)). The kinkbands seem to appear with an angle of 90° relative to the fibre axis, but this depends on the investigation technique used, the surface sensitive LVSEM instead of the transmission mode of the light microscope. Only in transmission mode, and independent of the orientation of the fibre relative to the view direction, does the projection of a kinkband plane always result in an angle of 45° to the fibre axis.

Fig. 4(c) shows the transcristalline layer at higher magnification. The appearance of the banded morphology observed by light microscopy can be confirmed by LVSEM. The periodic changes in the surface morphology of the HDPE layer parallel to the fibre axis (indicated by arrows) is an indication for the twisting of the lamellar crystals [11], which results in the banded spherulitic morphology visible in light microscopy. The density of lamellae of the HDPE material increases from the fibre/matrix interface to the non-interface region of the transcristalline layer. Near the interface the arrangement of the crystals is less perpendicular to the fibre axis as compared with the arrangement at the non-interface region of the layer, and some voids in the layer are visible. This indicates a low nucleation density of HDPE on the surface of the UHMW PE fibre at the interface, followed by crystal growth with branching resulting in an increasing number of lamellae. Also, due to the spatial constraints of the crystal growth at the non-interface region of the transcristalline layer, lamellae grown almost perpendicular to the fibre axis are visible.

More details of the low nucleation density at the interface are seen in Fig. 4(d). It is known that UHMW PE fibres are formed as extended crystals, but during the heat treatment the fibre surfaces melt and form lamellae after crystallisation [12–14]. The lamellar crystals of an UHMW PE fibre are recognisable in the lower part of Fig. 4(d), and some of them act as a nucleation surface for the HDPE matrix. The same nucleation behaviour of PE on a PE substrate is described for melted and crystallised skin of hot compacted melt spun PE fibres [13,14], for the shish kebab crystallisation in injection moulded PE [15], and for the epitaxial crystallisation of linear low density PE on high density PE [16]. From these results [12–16] the epitaxial nucleation of
the HDPE on the UHMW PE fibre is the probable explanation for the initial growth of the transcrystalline layer.

The appearance of the UHMW PE fibre and the morphology of the transcrystalline layer of isothermal crystallised HDPE differs from that described for the air-cooled sample. Because of the low axial compressive stress during the isothermal treatment and long time of crystallisation of the transcrystalline layer, the fibre has no kinkbands (Fig. 5(a) and (b)). The transcrystalline layer is formed by sheaf-like superstructures as described above and their growth direction is perpendicular to the fibre axis. At higher magnification the less ordered interface region again can be distinguished from the non-interface region of the layer by its higher lamellae density (Fig. 5(c)). The nucleation of the HDPE on the fibre surface seems to be of the same epitaxial nature as that for non-isothermal crystallisation.

4. Conclusions

The comparison of the results observed by light microscopy or by low voltage scanning electron microscopy yield to new insights on the interface morphology of polyethylene-based single polymer composites and the architecture of the transcrystalline layer. The transcrystalline layers only reflect the morphology of the matrix crystallised under certain conditions and without interaction with the fibre. The surface crystals of the fibres act as nucleation centres for the matrix, and may result from epitaxial crystallisation.

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References


Fig. 5. Fibre/matrix composite, HDPE is isothermal crystallised from the melt at 124°C for 24 h: (a) light microscopy image with a sheaf-like HDPE morphology; (b) LVSEM image of the composite; (c) transcrystalline HDPE layer.

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