Morphological investigations of polyethylene fibre reinforced polyethylene

F. v. Lacroix[a], J. Loos[b], K. Schulte[a],*

[a]Polymer and Composites Section, Technical University Hamburg-Harburg, D-21073 Hamburg, Germany
[b]Dutch Polymer Institute (DPI), Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

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.

Keywords: Polyethylene; Epitaxial crystallisation; Polymer composite

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 transcrystallisation 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 transcrystalline 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 transcrystalline 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. The

* Corresponding author.

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.
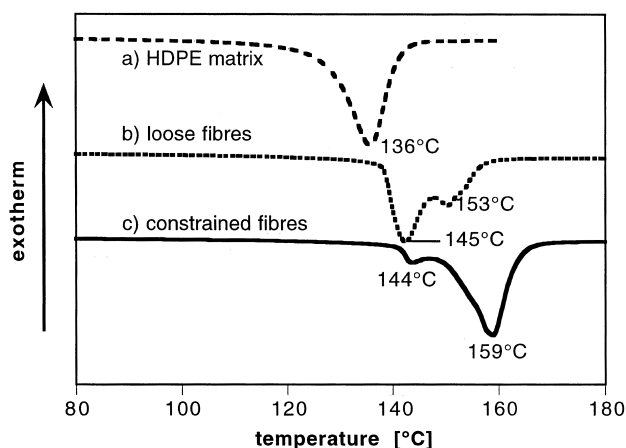

Fig. 1. D.s.c. scans of: (a) HDPE matrix; (b) UHMW PE fibre lying loose in the pan; (c) UHMW PE fibre fixed in the pan.
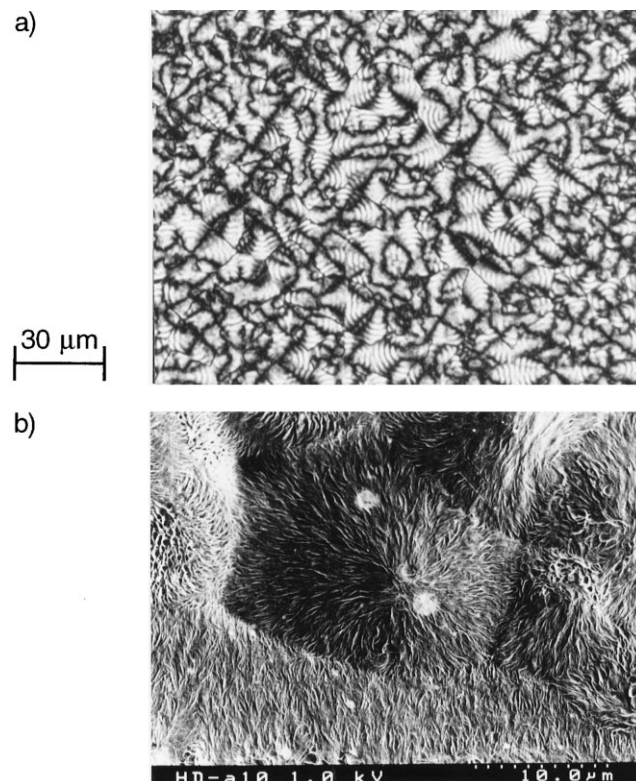

Fig. 2. HDPE matrix air-cooled crystallised from the melt: (a) light microscopy image with banded spherulites; (b) LVSEM image with lamellar resolution.

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

a)

30 μm

b)

HD-i19 1.0 kV 10.0 μm
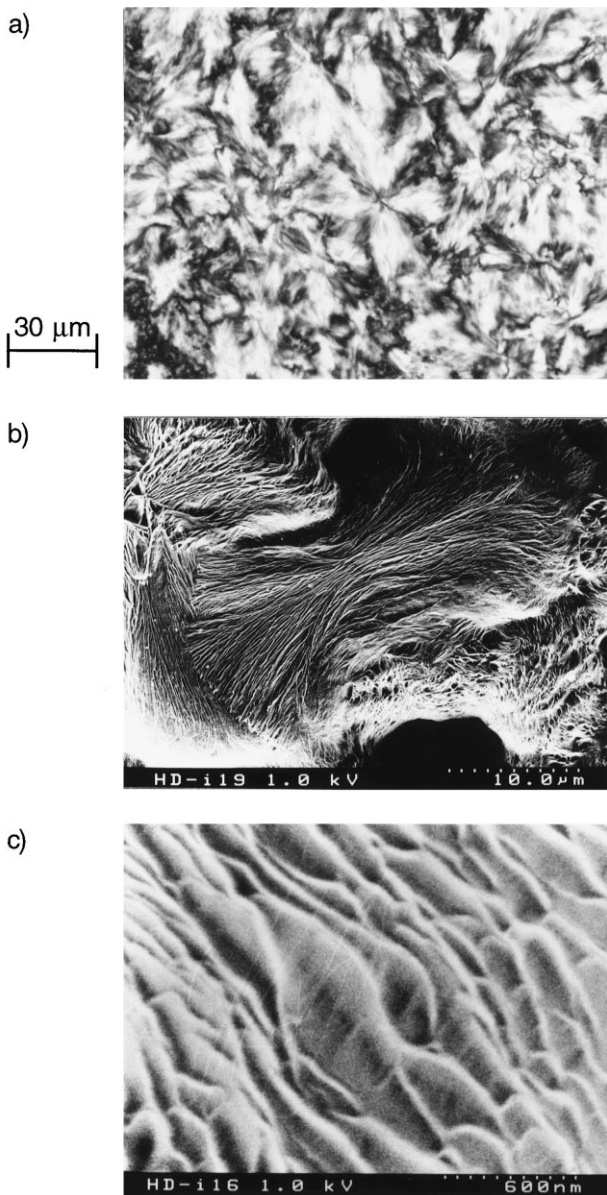
c)

HD-i16 1.0 kV 600nm

Fig. 3. HDPE matrix isothermally crystallised from the melt at 124°C for 24 h: (a) light microscopy image with sheaf-like superstructures; (b) LVSEM image with lamellar resolution; (c) single plate-like lamellar crystals of a sheaf-like superstructure with branches.

of the superstructure, which results in the sheaf-like appearance. Fig. 3(c) shows more details of the crystal topography. Looking at one single lamellae 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 transcrystalline 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 transcrystalline layer having an average thickness of approximately 10 mm 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 transcrystalline 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 transcrystalline 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 transcrystalline 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 transcrystalline 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
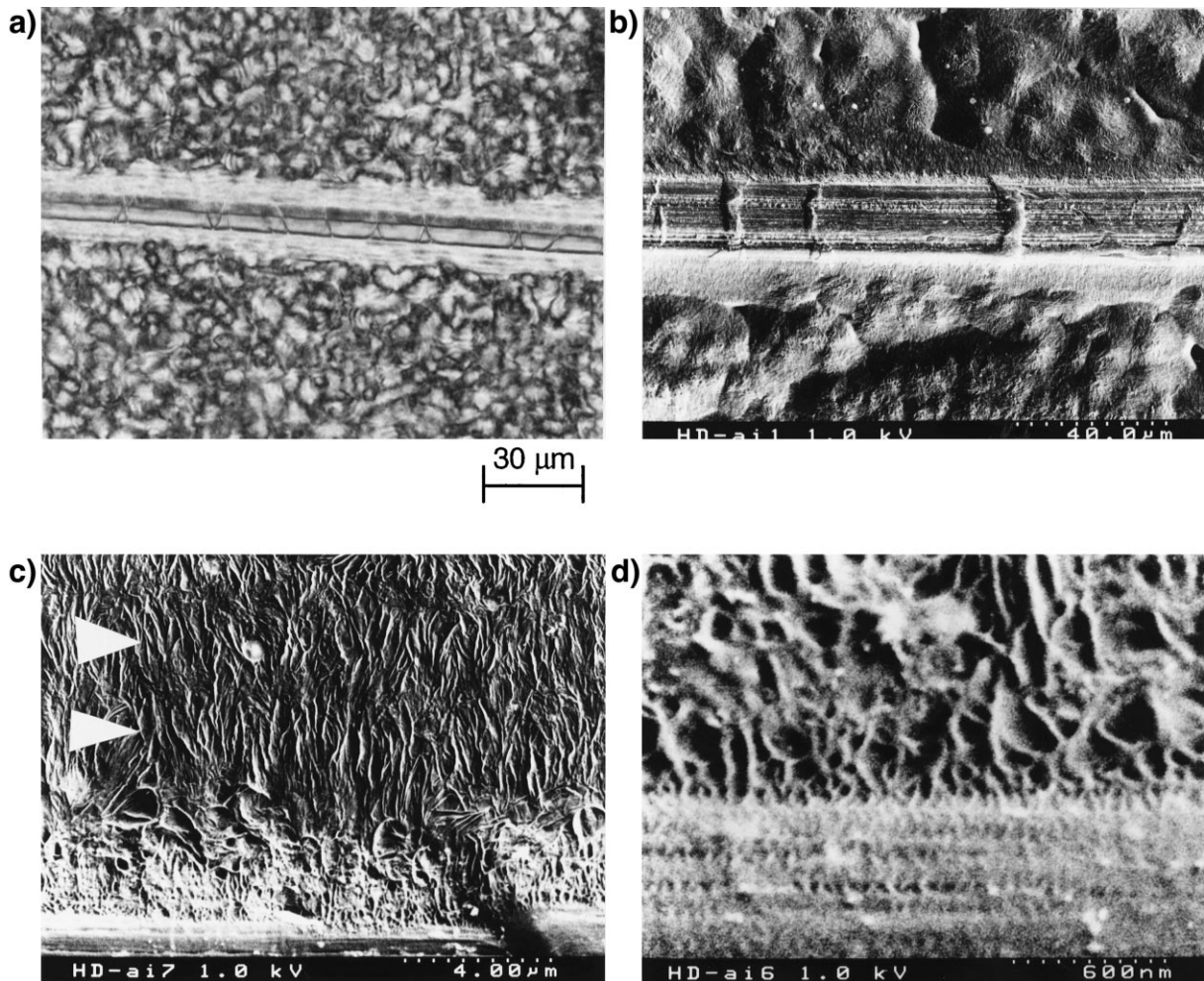
Fig. 4. Fibre/matrix composite, HDPE is air-cooled crystallised from the melt: (a) light microscopy image with a banded transcrystalline layer; (b) LVSEM image of the composite; (c) transcrystalline layer with lamellae twisting (the periodic changes of the surface morphology parallel to the fibre axis are indicated by arrows); (d) high resolution LVSEM image of the fibre/matrix interface.

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.

University of Jerusalem, Israel) for remarks and fruitful discussions.
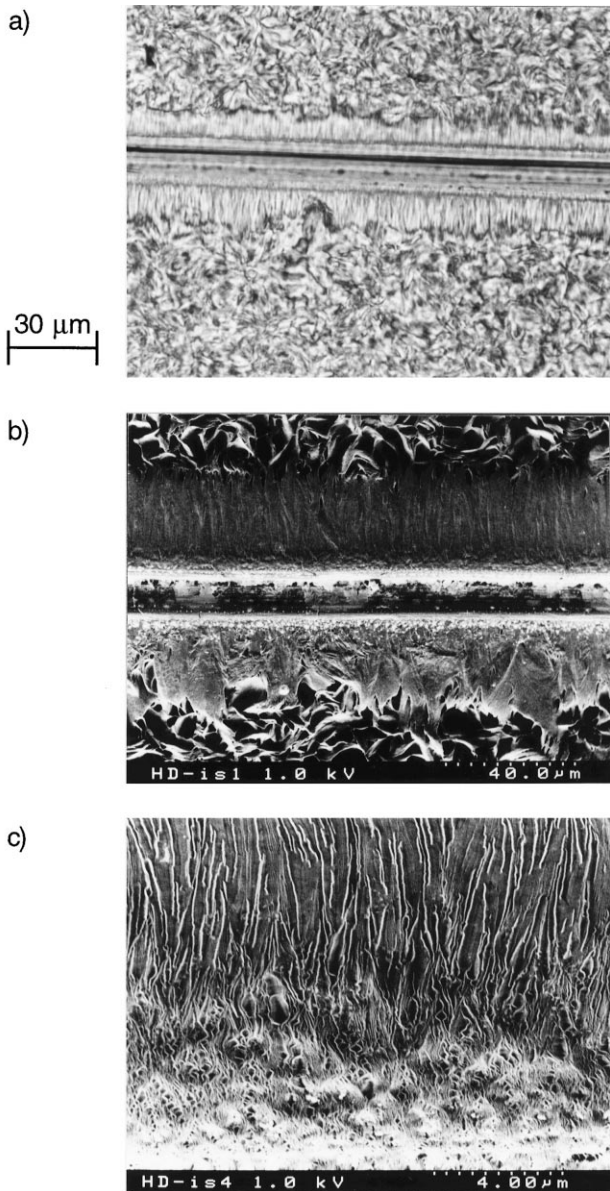
a)

30 µm

b)

c)

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.

References

[1] v. Lacroix F, Werwer M, Schulte K. Solution impregnation of PE-fibre/PE-matrix composites. Composites 1998;29A:371–376.

[2] Capiati NJ, Porter RS. The concept of one polymer composites modelled with high density polyethylene. Journal of Materials Science 1975;10:1671–1677.

[3] Ishida H, Bussi P. Surface-induced crystallisation in ultra-high-modulus polyethylene fibre reinforced polyethylene composites. Macromolecules 1991;24:3569–3577.

[4] Stern T, Wachtel E, Marom G. Epitaxy and lamellar twisting in transcrystalline polyethylene. Journal of Polymer Science, Polym Phys Ed. 1997;35:2429–2433.

[5] Stern T, Marom G, Wachtel E. Origin, morphology and crystallography of transcrystallinity in polyethylene-based single-polymer composites. Composites A 1997;28:437–444.

[6] Burke EA. Secondary emission from polymers. IEEE Trans Nucl Sci NS-27 1980;6:1760–1764.

[7] Butler JH, Joy DC, Bradley GF, Krause SJ. Low-voltage scanning electron microscopy of polymers. Polymer 1995;36:1781–1790.

[8] van Mele B, Verdonck E. Physico-chemical characterisation of the fibre/matrix interaction in polyethylene fibre epoxy matrix composites, Part 1 Characterisation with DSC. Composites Interfaces 1995;3:83–100.

[9] Keller A. Investigations on banded spherulites. J Polym Sci 1959;39:151–173.

[10] Fujiwara Y. The superstructure of melt-crystallised polyethylene. I. Screwlike orientation of unit cell in polyethylene spherulites with periodic extinction rings. J Appl Polym Sci 1960;4:10–15.

[11] Lustiger A, Lotz B, Duff TS. The morphology of the spherulitic surface in polyethylene. J Polym Sci, B, Polym Phys 1989;27:561–579.

[12] Wasiak A, Sajkiewicz P. Orientation distributions and melting behaviour of extended and folded-chain crystals in gel-drawn, ultra-high-molecular-weight polyethylene. J Mater Sci 1993;28:6409–6417.

[13] Kabeel MA, Bassett DC, Olley RH, Hine PJ, Ward IM. Compaction of high-modulus melt-spun polyethylene fibres at temperatures above and below the optimum. J Mater Sci 1994;29:4696–4699.

[14] Bassett DC, Olley RH, Hine PJ, Ward IM. Morphology of compacted polyethylene fibres. J Mater Sci 1993;28:1107–1112.

[15] Martinez-Salazar J, Garcia Ramos JV, Petermann J. On the fine structure of shish-kebabs in injection moulded polyethylene. Int J Polym Mater 1993;21:111–121.

[16] Loos J, Katzenberg F, Petermann J. Epitaxial crystallisation of linear low-density polyethylene on high-density polyethylene. J Mater Sci 1997;32:1551–1554.