Transcrystallisation with reorientation of polypropylene in drawn PET/PP and PA66/PP blends. Part 2. Electron microscopic observations on the PET/PP blend[*]

M. Krumova[1][†], G. H. Michler[1], M. Evstatiev[2], K. Friedrich[3],
N. Stribeck[4], S. Fakirov[5][‡]

[1]Martin-Luther-University, Halle-Wittenberg, D-06099 Halle (Saale), Germany
[2]University of Sofia, Laboratory on Polymers, BG-1164 Sofia, Bulgaria
[3]Institute for Composite Materials (IVW GmbH),
University of Kaiserslautern, D- 67663 Kaiserslautern, Germany
[4]Institute of Technical and Macromolecular Chemistry,
University of Hamburg, Bundesstr. 45,
D-20146 Hamburg, Germany
[5]Department of Mechanical Engineering and
Centre for Advanced Composites Materials of
The University of Auckland,
Private Bag 92019, Auckland, New Zealand

Progr. Colloid Polym. Sci. (2005), in print

Abstract

In the present second part of the study it is shown that polymer microfibrils are able to promote transcrystallisation of the surrounding polymer matrix in agreement with the results of an X–ray study reported in the first part. Polymer blends (microfibrillar-reinforced composites, MFC) containing microfibrils of poly(ethylene terephthalate) (PET) in a matrix phase consisting of polypropylene (PP) were studied by means of transmission electron microscopy (TEM), scanning electron microscopy (SEM) and environmental scanning electron microscopy (ESEM) after melting and crystallisation of only the matrix phase polymer in an injection moulding process. Collective preferred orientation of layers was observed in the PP matrix in transcrystalline zones grown epitaxially from the PET microfibrils. With respect to these microfibrils the lamellar stacks are oriented in perpendicular direction. The range of collective layer orientation along the longitudinal direction of a microfibril was found to be very long. ESEM exhibits layers which appear

---

[*] Dedicated to Prof. Dr. Wilhelm Ruland on the occasion of his 80th birthday

[†] Corresponding author. Phone: +49 3461 462558, FAX: +49 3461 462535, eMail: marina.krumova@iw.uni-halle.de

[‡] On leave from University of Sofia, Laboratory on Polymers, BG-1164 Sofia, Bulgaria

to be stacked, two-dimensional spherulites with a diameter of several microns. TEM micrographs show a transcrystalline zone around the PET microfibrils containing stacked crystalline PP layers. The lateral extension of these zones is restricted to a region narrower (100 - 200 nm) than that observed in respective MFC fibre materials (cf. Part 1) in which the matrix phase polymer was molten and crystallised more slowly and under quiescent conditions. The differing results of ESEM and TEM concerning the extension of the transcrystalline zone can be explained on the basis of a complex model by Bassett (dominant crystallites close to the nucleating microfibril and subsidiary crystallites farther out). The addition of a compatibiliser to the PET/PP blend completely inhibits the formation of transcrystalline layers in samples with MFC structure. Keywords: Transcrystallisation, Lamellae, Blends, PET/PP, Electron microscopy

1 Introduction

Whenever a polymeric material or a blend of several polymers is first partially molten and then recrystallised, the newly forming crystals may grow epitaxially from the conserved entities. This so-called transcrystallisation process has a considerable effect on the bonding between the afore molten matrix phase and the conserved entities, and therefore on materials properties [1]. In the first part of this study [2] the transcrystallisation phenomenon was discussed in detail. It was shown that it is an important characteristic feature of all polymer composites, particularly those reinforced with such kind of fibres that show a considerable nucleating power concerning the matrix crystallisation. In our studies the required fibres are prepared in a process starting from co-extrusion of two polymers with different melting temperature that finally results in microfibrillar reinforced composites (MFC). The MFC represent a new type of polymer-polymer composite where the isotropic matrix is reinforced with microfibrils of another polymer [3–7].

Fibres blended into a polymer matrix may nucleate matrix material crystallisation and thus induce peculiar crystalline morphologies in the surrounding zone, which are different from the morphology in the bulk [1]. Such a zone is called “transcrystalline layer”. An early electron microscopic study on polypropylene (PP) [8] evidenced columns of crystalline and amorphous layers around a “central linear thread” with long periods of 12 – 14 nm. This “shish-kebab” structure (in which two components of a polymer–polymer blend are discriminated not by their chemical structure but by extremely different molecular weight) is, in fact, nothing but a transcrystalline morphology. In a later paper [9] the same group studied the propagation of crystallisation from “linear instead of point-nuclei” emerging from high molecular weight polyethylene (PE) fibres immersed in linear low-density polyethylene. Concerning the diameter of the transcrystalline zone around the central fibre they proposed that “accumulation of rejected species ahead of the growth envelope” should lead to the breakdown of correlated crystal growth that is typical for the transcrystalline zone. The basic principle of this idea was already put forward in an early paper of Bassett and Patel [10] which states that during growth front propagation at first “dominant lamellae” are formed, which are followed by imperfect crystallites in “subsidiary lamellae”. An in-situ X-ray study of polymer crystallisation that supports such an idea of two crystallisation mechanisms can be found elsewhere in this special issue [11], and another paper [12] from this special issue is devoted to *in situ* X-ray studies of shish-kebab crystallisation in PE-blends similar to the ones used by Bassett [9]. The goal of all these efforts is the tailoring of the properties of thermoplastic materials after understanding their complicated issues of structure and processing. Detailed insight concerning these interrelationships is progressively achieved by means of newly developed advanced equipment (e.g. Environmental scanning electron microscopy (ESEM) or synchrotron radiation).

Transcrystallisation takes place in the matrix component whenever heterogeneous nucleation occurs with sufficiently high density along the fibre surface. In this way, the resulting crystal growth is restricted to the lateral direction, away from the microfibrillar core. Transcrystallisation is a function both of the nucleating activity of the fibre surface, and of the crystallisation kinetics of the matrix resin. The phenomenon is well known for the case of polymer composites that are either reinforced by carbon fibre or surface-treated glass fibre [13] and has also been observed in composites in which the reinforcement is based on polymeric fibres like cellulose [14], Kevlar [15] and others [16].

For such polymer-polymer composites complete melting of all blend components and subsequent crystallisation should lead to an isotropic material in which the crystallites of both components are oriented at random. This behaviour has been demonstrated in part 1 [2] by means of wide-angle X-ray scattering (WAXS) for the drawn blend poly(ethylene terephthalate) (PET) / PP (40/60 by wt.). It was found that after melting the blend at 280°C completely, the subsequent non-isothermal crystallisation during the cooling down to room temperature (RT) takes place in an isotropic manner, i.e. the initially very high uniaxial orientation of both the PET and the PP is totally lost. Quite different is the situation when an intermediate melting temperature (200°C) is chosen, and thus only the lower melting component (PP) of the blend is molten. According to the WAXS data, then its non-isothermal crystallisation takes place with a well-expressed preferential orientation of crystallites (under an average angle of 49°) with respect to the initial orientation direction (fibre axis, FA). Thus this phenomenon may be called a “transcrystallisation with reorientation”, as it has already been well documented for the system PET/polyamide 12 (PA12) [17].

For the last-mentioned drawn PET/PA12 blend it must be stressed that the WAXS patterns have been taken continuously during the cooling down, and the crystallisation has thus been followed in real-time. From the series of scattering patterns it has been concluded [17] that for this material the crystallisation with reorientation takes place only at the very first stages of crystallisation, i.e. during the period in which the predominant fraction of already crystallised PA12 material is found close to the unmolten PET microfibrils, whereas the later stages of crystallisation are proceeding in the bulk and are producing randomly oriented crystals, the Debye-Scherrer rings of which are increasingly masking the arc-shaped reflections from the minor volume fraction occupied by the transcrystalline material.

This situation was later confirmed on the system PET/low density polyethylene (LDPE). By means of transmission electron microscopy (TEM) on stained thin sections the transcrystalline morphology was resolved on a lamellar level [18]. The TEM observations demonstrated that close to the PET microfibrils the PE lamellae are not only parallel to each other, but also oriented perpendicular to the microfibrils surface in contrast to the bulk, where the lamellae are oriented at random [18, 19].

These observations were recently supported by those of Li et al. [20] who reported similar results for samples of PET / isotactic polypropylene (iPP) characterised also by a MFC-structure although obtained in a slightly different way (slit dye extrusion with hot drawing [21]).

Coming back to the results on PET/PP reported in Part 1 [2] it should be stressed that the WAXS patterns have been taken in a "*post mortem*" mode, i.e. after the completion of the crystallisation process. For this reason, starting from the reported results [2], it is hardly possible to derive reliable conclusions regarding the stage of the crystallisation process when this well-documented reorientation of crystallites takes place. Some useful information in this respect can be obtained from TEM analysis on stained thin sections, where the arrangement of the PP lamellae can be identified as a function of their distance from the PET microfibrils. In fact, this task is the goal of this second part of our systematic study on the transcrystallisation phenomenon in oriented polymer blends and systems distinguished by a MFC structure.

2 Experimental

2.1 Materials

Microfibrillar reinforced composites for this investigation were prepared from PET, iPP and a compatibiliser. The compatibiliser used was ethylene glycidyl methacrylate (E-GMA) (type Lotader AX 8840, a commercial product of Atochem, France). Recycled material from PET bottles (type FR 65, with a melting temperature (T_m) range of 236 - 252°C, supplied by Rethmann Plano GmbH, Germany) was used as the reinforcing component. The matrix-component iPP was provided by Basell, Germany (type Novolen with melt flow index 5). The blends PET/iPP were prepared in a 40/60 wt ratio. Compatibiliser content was varied between 0 and 9 wt.-%.

MFC manufacturing comprised melt blending of the two immiscible blend components at high temperature and extrusion in a co-rotating twin-screw extruder, followed by a fibrillation process achieved by cold drawing. The highly drawn filaments were chopped and, finally, converted to “dog bone” test specimens via injection moulding (Kloeckner Feromatik FM20) under industrially relevant conditions. During this stage the maximum processing temperature was 200°C.

2.2 Characterisation techniques

2.2.1 Scanning electron microscopy (SEM)

SEM observations were performed on a JEOL JSM 5400 SEM with an accelerating voltage of 20 kV. As-drawn samples were fractured in liquid nitrogen for observation of their surface. Part of these samples was treated with boiling xylene, a selective solvent for PP, in order to remove this component. All the samples were coated with a thin gold layer prior the SEM analysis.

2.2.2 Environmental scanning electron microscopy (ESEM)

A FEG XL30 Philips ESEM was used for morphological observation of the injection moulded samples. Flat surfaces were prepared by cutting the samples at -100°C along the injection moulding direction. A wet mode at 0.2 Torr water pressure and accelerating voltage of 15 kV was chosen for the observation. The signal was recorded using a detector for backscattered electrons.

2.2.3 Transmission electron microscopy (TEM)

For the TEM observations a JEM 2010 JEOL microscope at 200 kV accelerating voltage was used. Ultrathin sections of 80 nm thickness were cut by means of an ultramicrotome “Leica Ultracut UCT”

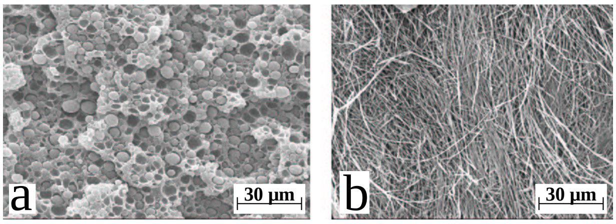

Figure 1: SEM micrographs of: a) - cryofracture of PET/PP blend (40/60 by wt.) after melt blending and extrusion, b) - PET microfibrils obtained via selective dissolution of PP from the same PET/PP blend

after staining the bulk sample in RuO_4 vapour overnight.

3 Results and discussion

3.1 MFC without compatibiliser

Figure 1 shows SEM micrographs reflecting the blend morphology after each of the first two essential stages of MFC manufacturing – the melt-blending in an extruder and the subsequent cold-drawing step imprinting orientation of the two blend components.

The picture on Figure 1a is obtained from the cryofracture of the as-extruded PET/PP blend. The typical morphology for a well homogenised blend of two immiscible polymers is observed, characterised by spherical particles with diameters of several microns (average around 5 μm).

Figure 1b shows PET microfibrils obtained via selective dissolution of PP (by boiling xylene) from a drawn PET/PP blend. One observes excellent microfibrils with diameters between 1 and 3 μm and a length of several hundreds of microns (almost no fibril ends are observed). Such microfibrillar morphology is well documented for various drawn polymer blends [3–7, 18–24] and injection [22] or compression [23, 24] moulded samples with MFC structure. In this new class of polymer-polymer composites [3–7, 18–24] they not only play the role of the reinforcement, but also express their ability to induce transcrystallisation of the respective matrix polymer (PA12 [17], LDPE [18, 19], iPP [20]).

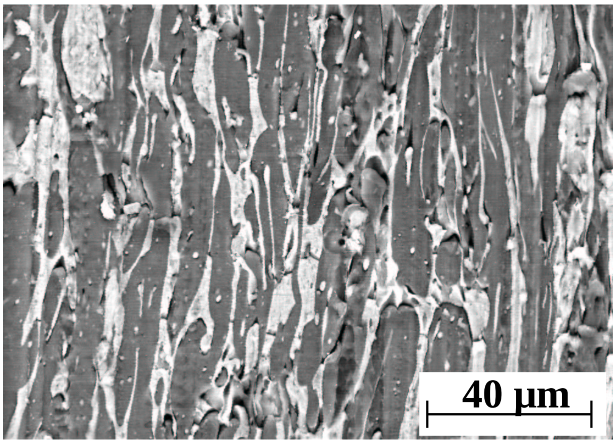

Figure 2: ESEM micrograph of injection moulded PET/PP blend (40/60 by wt.) sample with MFC structure. The observed surface is obtained via cryo-cutting along the injection moulding direction (vertical)

Figure 2 is an ESEM micrograph which shows the morphology of the MFC after the final processing step (injection moulding) at a similar magnification as Figure 1. The PET microfibrils appear bright in the surrounding PP matrix. As compared to Figure 1 however, their shape is altered as a result of this last processing step. Although the majority of the PET microfibrils are aligned in the direction of the melt flow during injection moulding (vertical), some of the microfibrils are not. Thus after cutting parallel to this direction and taking a micrograph they either appear as bright short lines or even as dots only.

It is known that exposure of semicrystalline polymers to electron beam provokes radiation-induced changes in the structure [25], e.g. mass loss, chain break or cross-linking in the amorphous phase. As a result, contrast enhancement is frequently observed in spherulites as a function of radiation dose, thus increasing the visibility of the lamellar morphology. The fact that the ESEM does not require the coverage of the sample with a thin metal layer offers the opportunity to *in situ* observe the varying contrast of the semicrystalline PP morphology as a function of radiation dose.

As shown in Figure 3, after a short irradiation in the electron beam, well-defined columns built from stacked “two-dimensional spherulites” (which are supposed to contain high amounts of lamellae of crystalline PP) with an average diameter of 1 – 4 μm can be distinguished around the PET fibrils. The formation of such structures can be attributed to collective oriented growth of PP crystallites away from the PET fibrils into the thermoplastic matrix, thus forming some kind of transcrystalline zone. For PP such morphology has early been evidenced by Monks et al. [8]. The growing crystalline PP layers, built up along the PET fibrils, impinge upon one another and cannot develop to larger dimensions. This situation is well-known and repeatedly documented by polarising light microscopy particularly for fibre reinforced PP [1, 13, 14, 16, 26].

A much higher magnification is possible, if ultra-thin stained sections are studied in a TEM instrument. The TEM micrograph in Figure 4 exhibits the organisation of the crystalline entities on a much finer level. Here the crystalline lamellae of the PP matrix are resolved. The bright regions in the micrograph represent cross-sections of PET microfibrils. In the PP matrix close to these regions the crystalline lamellae are extending more or less in radial direction away from the PET surface, whereas far from the microfibrils (in the bulk) the layer orientation appears to be no longer correlated to the surface normal of the microfibrils and resembles the typical morphology of α–iPP bulk material. The fact that the transcrystalline layers obviously are not covering the PET microfibrils completely on all sides may result from the irregular shape of the fibrils and from the cutting, which is not everywhere strictly perpendicular to the fibril axis.

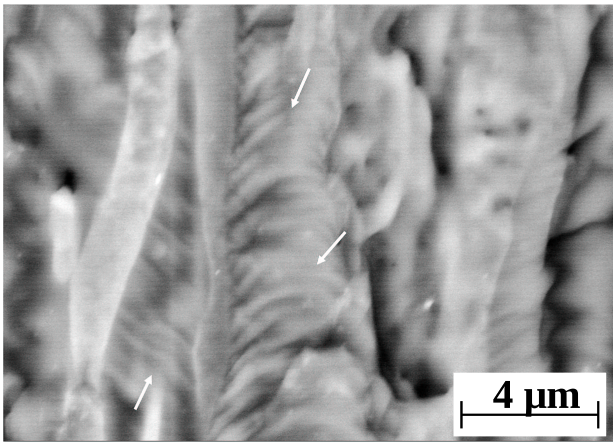

Figure 3: ESEM micrograph of the same sample according to Figure 2 after irradiation. Some of the column forming layers are marked by arrows

Figure 5 represents a detail of the transcrystalline structure as observed in the TEM at a higher magnification. One can clearly see that the individual PP crystalline lamellae closest to the PET microfibril are both oriented strongly parallel to each other and at the same time perpendicular to the microfibril surface. In cases when two microfibrils lie close to each other, the PP lamellae are again arranged parallel to each other and perpendicular to the both surfaces as observed in many cases (not shown in Figure 5). In all the cases the average thickness of the individual lamellae is about 8 - 10 nm and the width (thickness) of the transcrystalline layer is 100 - 200 nm.

Not only samples from the final MFC material were investigated by SEM and TEM, but also samples taken after different earlier stages of the MFC preparation process. Even immediately after the first stage (blend melt-extrusion) transcrystalline PP lay-

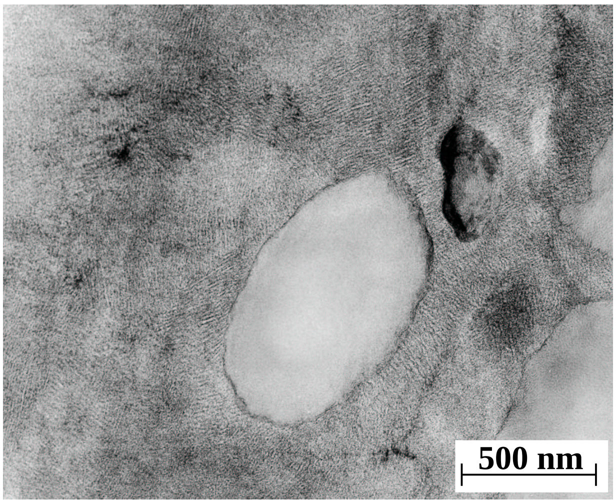

Figure 4: TEM micrograph of a stained ultra thin section (perpendicular to the orientation direction) of injection moulded PET/PP (40/60 by wt.) blend sample with a MFC structure

ers were found at the surface of some of the PET spheres. The latter look very similar to those presented on the TEM micrograph of Figures 4 and 5. Obviously, the conditions prevailing during cooling down to RT after the melt blending lead to formation of transcrystalline layers around the PET spheres. During cold drawing, i.e. the next step of MFC preparation, these transcrystalline formations on the PET-PP phase boundary are destroyed. As already discussed, transcrystallisation again takes place, when the blend is cooling down from the intermediate temperature after injection moulding (cf. Figures 4 and 5).

3.2 MFC with compatibiliser

Figure 6 shows the TEM micrograph of a PET/PP/E-GMA composite 40/54/6 containing 6 wt.-% of the compatibiliser E-GMA. A reduction of the average diameter of the PET fibrils to 1 μm is observed [27] and, what is more striking, in comparison to Figure 4, no transcrystalline zones with lamellae preferentially extending away from the microfibrils are found. Even in a magnified image (Fig. 7) the thin layer of oriented “dominant” lamellae [10] that are

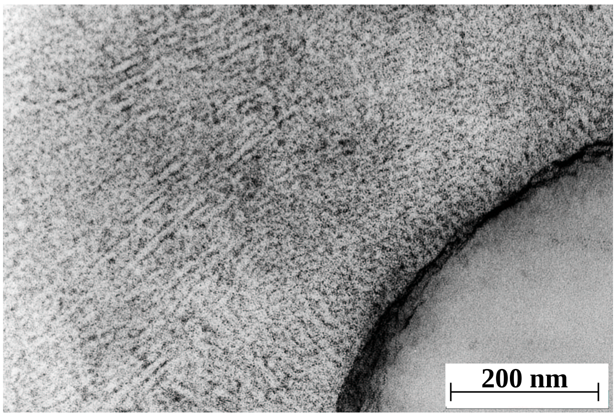

Figure 5: Detail of the lamellar structure in the PP matrix. TEM micrograph on ultrathin section

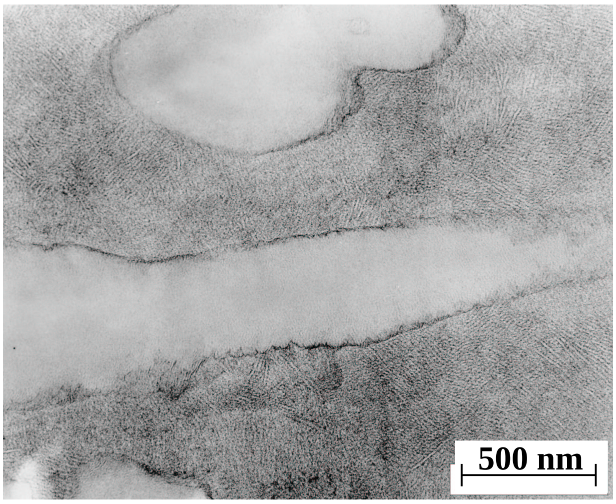

Figure 6: Injection moulded PET/PP/E-GMA (40/54/6 by wt.) material containing compatibiliser. TEM micrograph of a stained ultra thin section (perpendicular to the orientation direction) of blend sample with MFC structure

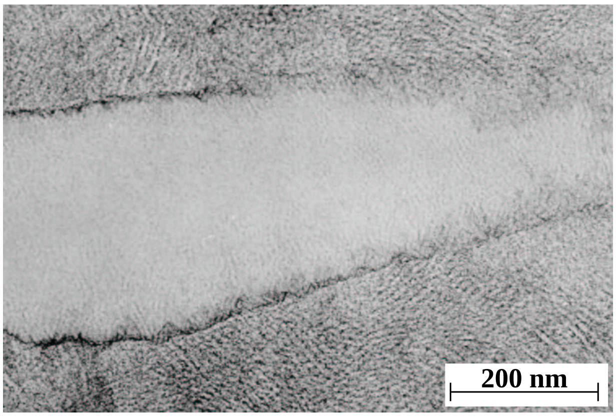

Figure 7: Injection moulded PET/PP/E-GMA (40/54/6 by wt.) material containing compatibiliser. Detail of the typical lamellar structure close to the PET microfibrils. TEM micrograph on ultrathin section

clearly visible in the material without compatibiliser (compare to Fig. 5) is not present on the microfibril surface if compatibiliser is present. A small–angle X–ray scattering (SAXS) study [28] during drawing (between 0 and 10 % relative deformation) of PET/PP drawn blends containing various amounts of compatibiliser demonstrates the effect of compatibiliser on the MFC nanostructure. An extended equatorial streak (void scattering) is typical for the PET/PP blends without compatibiliser. The PET/PP/E-GMA blends show equatorial scattering as well, but the reflection is much shorter, much higher, and by more than an order of magnitude less intense. Thus the few holes generated in the blend during cold drawing are needle-shaped for the material without compatibiliser, whereas they are shorter, wider and less pronounced for the material containing compatibiliser. This result supports the expected role of the compatibiliser, namely that it is enriched in the interphase between the two blend components where it changes the delamination behaviour of the components during cold drawing.

The suggested interpretation of these SAXS and electron microscopic data [27] assumes that the PET microfibrils (particularly after the isotropisation of the second blend component, the PP in the present case) are coated by a thin layer of the added compatibiliser. The latter prevents the direct contact between PET and PP and thus suppresses the epitaxial as well as the nucleating effect of the PET microfibrils on the PP crystallisation, i.e. transcrystalline layers can not be formed and the crystallisation of PP even in the very close proximity to the microfibrils surface is performed in the same way as in the PP matrix far from the microfibril surfaces.

3.3 Transcrystalline structure and materials processing

In Part 1 of this study the material, at the beginning of the last MFC processing step, is a fibre in which the PET microfibrils are excellently oriented. Then the quiescent PP matrix is molten, and during the following and relatively slow cooling stage the transcrystalline nanostructure is formed. Our WAXS results show that, obviously, under these conditions the epitaxial nucleation of the PP is very efficient, and as a result the transcrystalline PP crystallites are able to interfuse a considerable fraction of the matrix volume before the ordinary bulk crystallisation sets in.

The measured reorientation effect of the PP matrix crystallites in the MFC fibre material even requires a second prerequisite. Not only must the epitaxially nucleated crystallites be able to interfuse the matrix volume, but also must the PET microfibrils be well-oriented, so that the orientation of the crystallites with respect to their local microfibrils will lead to an observable global orientation in the PP phase. In general, such kind of macroscopic orientations of crystal lamellae or microfibrils cause peculiar materials properties, as e.g. in the well-established hard elastic materials [29, 30]. For a systematic study of orientation distributions in transcrystalline MFC materials as a function of the processing parameters appropriate methods have been developed by Ruland [31–33].

Concerning the materials investigated here in Part 2 of the study, the PP matrix is molten as well, but thereafter the material is injection moulded. Caused from the melt flow some preferential orientation of the embedded PET microfibrils is established, and during the quenching in the mould the observed transcrystalline nanostructure is formed. Its constricted transcrystalline zones can be explained, if it is assumed that the advantage of epitaxial nucleation with respect to nucleation in the bulk is decreased as a result of the considerable undercooling of the PP melt which is rapidly established in the moulding process. In this way the rather thin (around 100 nm) transcrystalline layers found by the TEM analysis on stained thin sections can be explained.

4 Conclusions

The obtained results show that polymer microfibrils of PET are able to promote transcrystallisation also in a polypropylene matrix. This is similar to the already reported cases of PET/PA12 [17] and PET/PE [18–20] blends. Using TEM on stained ultra thin sections one can observe the alignment of the crystalline lamellae in the proximity of the microfibril's surface. In addition, imaging with backscattered electrons in ESEM gives excellent possibilities for investigation of the "spherulitic" morphology at an intermediate scale – over the resolution limit of the light microscopy.

Thus each of the utilised structure investigation methods is recognising different aspects of the transcrystalline structure. The ESEM exhibits that an oriented growth front propagation away from the line nucleus may reach out into the matrix for several microns, even if (as shown in the TEM micrographs) the oriented and stacked "dominant" [10] crystalline lamellae are only found in a zone that is not wider than a few hundred nanometres. Moreover, in the WAXS patterns transcrystallisation is indirectly detected based on preferred orientation of the growing matrix crystals. A first study [11] indicates that the distorted "subsidiary" [10] crystals are oriented at random. Under this assumption WAXS data should be compared to the data from TEM rather than to the ESEM results.

Comparing the MFC fibres of Part 1 with the MFC injection-moulded parts investigated here, different characteristics of the transcrystalline nanostructure and its orientation with respect to the main axis of the specimen are found. The observed differences exhibit that the importance of the process control for the specificity of the transcrystalline structure should not be underestimated.

Acknowledgements. This study has partly been supported by the Bilateral Cooperation Program between the University of Hamburg, Germany, and the University of Sofia, Bulgaria, which is funded by the DAAD (German Academic Exchange Service). M.E, K.F. and S.F. express their appreciation to Alexander von Humboldt Foundation for the partial support of this study through the Institute Partnership Program (Project no. 4584). One of us (S.F.) would like to acknowledge the financial support of the Foundation for Research, Science and Technology of New Zealand making possible his stay at the Department of Mechanical Engineering and the Centre for Advanced Composite Materials of The University of Auckland, Auckland, New Zealand where this paper was finalised. The SEM observations were performed with an instrument donated by the

Alexander von Humboldt Foundation to the Faculty of Chemistry of the Sofia University, Sofia, Bulgaria.

References

[1] Folkes MJ (1995) In: Karger-Kocsis J (ed.), *Polypropylene: Structure, blends and composites*, chap. 10, pp. 340–370, Chapman & Hall, London

[2] Apostolov A, Samokovlijski O, Fakirov S, Stribeck N, Denchev Z, Evstatiev M, Friedrich K, Funari SS (2005) Progr Coll Polym Sci in press

[3] Evstatiev M, Fakirov S (1992) Polymer 33:877

[4] Fakirov S, Evstatiev M (1994) Adv Mater 6:395

[5] Fakirov S, Evstatiev M, Friedrich K (2000) In: Paul DR, Bucknall CD (eds.), *Polymer Blends*, vol. 2, chap. 33, p. 455, J. Wiley & Sons, New York

[6] Fakirov S, Evstatiev M, Friedrich K (2002) In: Fakirov S (ed.), *Handbook of Thermoplastic Polyesters*, vol. 2, chap. 23, pp. 1093–1132, Wiley-VCH, Weinheim

[7] Evstatiev M, Nicolov N, Fakirov S (1996) Polymer 37:4455

[8] Monks AW, White HM, Bassett DC (1996) Polymer 37:5933

[9] Janimak JJ, Bassett DC (1999) Polymer 40:459

[10] Bassett DC, Patel D (1994) Polymer 35:1855

[11] Stribeck N, Bösecke P, Bayer R, Almendarez Camarillo A (2004) Progr Coll Polym Sci in print

[12] Keum JK, Burger C, Hsiao BS, Somani R, Yang L, Kolb R, Chen H, Lue CT (2005) Progr Colloid Polym Sci in print

[13] Chen EJH, Hsiao BS (1992) Polym Eng Sci 32:280

[14] Verpoest L, Desaeger M, Keunings R (1990) In: Ishida H (ed.), *Proc. of ICCM-4: Controlled interphases in composite materials*, pp. 653–666, Elsevier, New York

[15] Felix JM, Gatenholm P (1994) J Mater Sci 29:3043

[16] Assouline E, Wachtel E, Grigull S, Lustiger A, Wagner HD, Marom G (2001) Polymer 42:6231

[17] Sapoundjieva D, Denchev Z, Evstatiev M, Stribeck N, Stamm M (1999) J Mater Sci 34:3063

[18] Friedrich K, Ueda E, Kamo H, Evstatiev M, Krasteva B, Fakirov S (2002) J Mater Sci 37:4299

[19] Fakirov S, Kamo H, Evstatiev M, Friedrich K (2004) J Macromol Sci Phys 43:775

[20] Li ZM, Li LB, Shen KZ, Yang W, Huang R, Yang MB (2004) Macromolecul Rapid Commun 25:553

[21] Li ZM, Yang MB, Lu A, Feng JM, Huang R (2002) Mater Lett 56:756

[22] Evstatiev M, Fakirov S, Krasteva B, Friedrich K, Covas JA, Cunha AM (2002) Polym Eng Sci 42:826

[23] Friedrich K, Evstatiev M, Fakirov S, Evstatiev O, Ishii M, Harass M (2004) Compos Sci Technol in press

[24] Evstatiev M, Fakirov S, Friedrich K (2004) In: Friedrich K, Fakirov S, Zhang Z (eds.), *Polymer Composites: From Nano- to Macroscale*, p. in press, Springer, Boston

[25] Grubb DT (1974) J Mater Sci 9:1715

[26] Felix JM, Gatenholm P (1994) J Mater Sci 29:3043

[27] Krumova M, Michler GH, Evstatiev M, Friedrich K, Fakirov S (2003) In: *Proc. of PC2003: Polymer Crystallization, Linz, Austria*

[28] Stribeck N, Evstatiev O, Boyanova M, Almendarez Camarillo A, Fakirov S, Friedrich K, Cunis S, Gehrke R (2003) Hasylab Ann Rep 1:953

[29] Noether HD (1979) Intern J Polymeric Mater 7:57

[30] Sprague BS (1973) J Macromol Sci Phys B8:157

[31] Ruland W (1969) J Polym Sci Part C 28:143

[32] Perret R, Ruland W (1969) J Appl Cryst 2:209

[33] Ruland W, Smarsly B (2002) J Appl Cryst 35:624