Transcrystallisation with reorientation of polypropylene in drawn PET/PP and PA66/PP blends. Part 1. Study with WAXS of synchrotron radiation[*]

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Abstract

Transcrystallisation induced by annealing in the polypropylene (PP) component of nanostructured polymer-polymer composites (NPC) was studied for two different polymeric fillers. In contrast to the typical narrow columnar transcrystalline regions around filler fibres in common glass-fibre reinforced PP, volume-filling transcrystallisation was observed for both of the polymer fillers, thus resulting in reorientation of the PP matrix crystals instead of an expected isotropisation.

Two cold-drawn blends of PP with poly(ethylene terephthalate) (PET) or polyamide 66 (PA66), respectively, namely PET/PP and PA66/PP both in a ratio of 50/50 wt.% were investigated by means of wide-angle X-ray scattering (WAXS) of synchrotron radiation during heating, melting of only the low-melting component (PP) at 200°C yielding an isotropic melt, and subsequent crystallisation upon cooling. A strong epitaxial effect of the persistent embedded microfibrillar component (PET or PA66) on the non-isothermal crystallisation behaviour of PP during its cooling to room temperature was found. The composites obtained after such thermal treatment represented anisotropic semi-crystalline nanocomposites, in which the PP crystallites were reoriented. The ultimate structure for the PET/PP blend exhibited crystals with their molecular axis tilted at approx. 49° with respect to their initial orientation (parallel to the fibre axis). In the PA66/PP blends the ultimate structure returned to the initial orientation of the PP chains parallel to the fibre axis, but with a broadened orientation distribution. Results of

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

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similar studies on other blends are reviewed. **Keywords** Transcrystallisation, Blends, PET/PP, PA66/PP, Reorientation, Synchrotron radiation

1 Introduction

Classical transcrystallisation and polypropylene composites. It is well known [1] that polypropylene (PP) is distinguished by its strong ability to form transcrystalline layers in its short-glass fibre reinforced composites. These transcrystalline layers represent columnar structures, grown in radial direction away from the central core fibre. Their radial extension is about several tenths of a micron. They can easily be observed in a polarised light microscope on thin cuts in longitudinal direction. It is noteworthy that at larger distance from the glass fibres the PP matrix crystallises completely isotropic. Outside the columnar transcrystalline structures there is no macroscopic preferred orientation of the polymer chains.

Conditions precedent to transcrystallisation. In general, transcrystallisation takes place if heterogeneous nucleation occurs with sufficiently high density along the fibre surface and the resulting crystal growth is restricted to the lateral direction. The transcrystallisation is a function of nucleating activity of the fibre surface and crystallisation kinetics of the resin matrix. A literature survey [2] states that the fibre surface tends to induce nucleation of matrix material under at least one of the following conditions: (i) a topographical match between the fibre and the matrix; (ii) a thermal conductivity mismatch between the fibre and the matrix; (iii) an extensional flow field developed by processing conditions, or (iv) a high surface free energy on the fibre.

Structures found in transcrystalline regions. Depending on the interaction mechanism between the reinforcing microfibrils and the surrounding matrix, literature reports various arrangements of structure. For instance, in cellulose/PP composites, the PP chains of the matrix are found to be parallel to the fibre axis [3]. The same arrangement dominates in some advanced polymer composites based on polyetherketoneketone and polyetheretherketone reinforced by carbon, Kevlar, or glass fibres [2].

In a detailed study on the interfacial interaction between Kevlar filaments and a polyamide 6 (PA6) matrix crystallised from the melt, two kinds of transcrystalline zones have been observed around the filament surface [4]. It has been confirmed by polarising light microscopy, microbeam X-ray diffraction, and transmission electron microscopy that the PA6 chains crystallise epitaxially. In this case the a* and a axes of PA6 are directed along the radius of the Kevlar filament in the interfacial and intermediate zones, respectively. The b* axis (molecular axis) and the c axis rotate around the a* or a axis [4].

In a more recent study [5] on aramid and carbon fibre reinforced PA66 composites, atomic force microscopy reveals radial regularity in the transcrystalline layer, relative to the fibre, and X-ray diffraction investigations of the isolated layer suggest that the polymer chain is oriented predominantly perpendicular to the fibre axis.

Moreover, Seth and Kempster [6] study blends of polyamide 11 (PA11) and PP. Different orientations of PP crystallites are reported in dependence on the PA11 content in the blend. The c-oriented unit cells predominate in the range 5-40% PA11, but a second mode of crystallisation with unit cell a-directions parallel to the FA occurs alongside the c-oriented mode. The third mode, with unit cell [101]-directions parallel to the FA appears to be present to some extent throughout the series, but only becomes significant in the blends with more than 40% PA11. The proportion of the third mode then increases with the amount of PA11 present [6]. It is suggested that the third orientation of PP crystallites is the result of epitaxy on portions of the PA11 fold surface at the interface between the two components [6]. The orientation of PP crystallites in the as obtained thread is found to depend on the amount of PA11 present, and no reorientation due to recrystallisation is reported in this paper [6].

New focus on transcrystallisation studies. The nucleation of a transcrystallised region on the reinforcing fibre is thought to be central to the improvement of some composite properties [7]. The contribution of these transcrystalline layers to the improvement of the adhesion between the matrix and the reinforcing component as well as their effect on the entire mechanical behaviour of PP-based glass-fibre reinforced composites is extensively studied [1]. Unfortunately, this is neither the case for the orientation of PP macromolecules with respect to the axis of the reinforcing fibres in the transcrystalline layers, nor for the effect of a variation of the substrate material (in the most common cases it consists of glass fibres) on this orientation.

Advanced tools for the study of transcrystallisation. The reason might be that the most common technique for determination of molecular orientation, the classical X-ray diffraction, is not applicable to a bulk PP composite that is organised as it is described above, because the scattering from the relatively thin transcrystalline layers is masked by the scattering from the relatively huge amount of the isotropically crystallised PP matrix.

An advanced X-ray study of thin longitudinal slices, on the other hand, requires a high spatial resolution, i.e. the use of microbeam X-ray diffraction as is reported on investigation of various polymorphic modifications of PP after deformation [8]. A different approach for examining the same problem is a time-resolved synchrotron radiation X-ray diffraction study starting from samples in which PP is in molten state, whereas the fibrous substrate is solid. Studying such samples during cooling by application of a technique that is able to register chain orientation in real time with short exposure and short cycle time between successive snapshots, should yield results concerning the evolution of epitaxial chain orientation during the very first stage of the crystallisation process, i.e., when the major fraction of the crystallised PP is found close to the oriented substrate where the interaction is strong.

Transcrystallisation with reorientation. In fact, this approach was explored some time ago on the system poly(ethylene terephthalate) (PET) melt-blended with polyamide 12 (PA12) and cold drawn [9]. After selective melting of the PA12 component at 220°C, when the WAXS pattern indicated a completely isotropic amorphous halo and the PET reflections remained highly oriented, the subsequent cooling to room temperature lead to the quite unexpected result that the PA12 did not undergo isotropisation. During the cooling stage the major fraction of PA12 crystallised anisotropically, but did not preserve its original orientation, i.e., with the direction of the chains parallel to the drawing direction (i.e. the fibre axis, FA). Instead, the chains in the crystals turned perpendicular to FA. A process of transcrystallisation with reorientation [9] had been observed for the first time. A respective reorientation phenomenon upon temperature treatment was recently reported by Schmidt et. al. [10] resulting from analogous processing of a polyethylene/PP blend. It appears important to remind that the reported transcrystallisation with reorientation takes place on a highly crystalline polymeric microfibrillar substrate (PET or PP, respectively), as has been documented by means of scanning electron microscopy [11].

NPC Polymer-polymer composites. As a matter of fact, both the last-mentioned systems PET/PA12 and polyethylene/PP belong to the class of nanostructured polymer composites (NPC) [11–15], in which the polymer matrix is reinforced by polymer nanostructures of microfibrillar type [11]. In contrast to the common glass-fibre reinforced composites where the polymer is melt-blended with fibres, the NPCs are prepared by melt-blending of two polymer components (distinguished by different melting temperatures), followed by cold drawing of the blend, aiming at a high degree of orientation. An essential step of the NPC manufacturing is the thermal treatment of the oriented blend at temperatures between the melting temperatures of the two blend components. This treatment results in melting of the lower melting component. Upon subsequent cooling we frequently have observed isotropisation, i.e. the melted component recrystallises, but not again in oriented state as proved by WAXS tests [12, 15]. In this way only preserving the microfibrillar nanostructure and orientation of the higher melting component, the NPC is produced.

Variation of the substrate. Taking into account two facts, namely the strong ability of PP to form transcrystalline layers in the fibre reinforced composites [1, 8] and the emerging technical possibility to study the very early crystallisation stages by means of two-dimensional X-ray scattering from synchrotron source in order to determine the chain orientation [9] it appears challenging to, as well, study the crystallisation behaviour of PP on a substrate representing highly oriented polymeric microfibrils. For this purpose two melt-blended, extruded, and cold-drawn materials were prepared, namely PET/PP and PA66/PP, where PA66 stands for polyamide 6.6.

2 Experimental

Commercial, engineering grade PET (Yambolen, Bulgaria), PA66 (Ultramid, BASF, Germany) and PP (Burgas, Bulgaria) were dried at 100°C for 24 h. The blends PET/PP and PA66/PP were prepared in a ratio of 50/50 wt.% by extrusion in a Brabender single screw (30 mm diameter) extruder with a length-to-diameter ratio of 25 at 30-35 rpm. The temperature zones starting from the feed to the die were set to 210, 240, 270, 280, and 240°C. The extrudate from the 2 mm capillary die was immediately quenched in a water bath at 15-18°C. The threads were moved trough the bath by means of two rubber cylinders (60 mm diameter) rotating at a rate of about 90 rpm.

In the next step the blends were drawn in a tensile testing machine Zwick 1464 at room temperature and a strain rate of 80 mm/min to a draw ratio ($\lambda = 3.6 - 4.0$, which resulted in a final diameter of about 1 mm, followed by annealing at 140°C for 6 h with fixed ends in a vacuum oven.

WAXS patterns of these samples were obtained using synchrotron radiation from

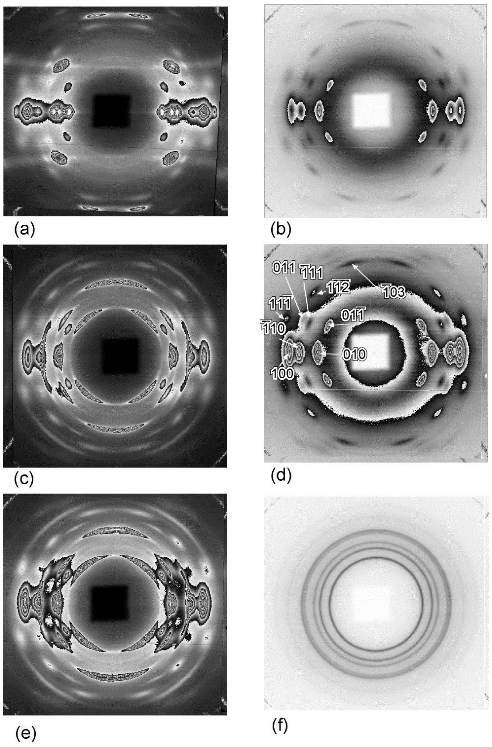

Figure 1: Wide-angle X-ray scattering patterns of PET/PP blend: a) initial sample, pattern taken at room temperature, b) after 1 hour at 200°C, pattern taken at 200°C, c) after 1 hour at 200°C, pattern taken at 30°C, d) after 2 hours at 200°C, pattern taken at 200°C (Miller indices of PET indicated), e) after 2 hours at 200°C, pattern taken at 30°C and f) after 5 min at 280°C, pattern taken at 30°C. The fibre axis (FA) is vertical

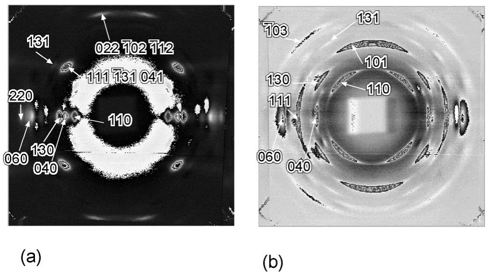

Figure 2: Scattering patterns of PET/PP blend obtained by: a) subtraction of the scattering pattern taken at 200°C (Figure 1b) from the scattering pattern taken at room temperature (Figure 1a); (b) subtraction of the scattering pattern taken at 200°C (Figure 1b) from the scattering pattern taken at room temperature after melting at 200°C (Figure 1c). Miller indices of α-PP are presented. The fibre axis (FA) is vertical

beamline A2 of HASYLAB in Hamburg, Germany. The sample-to-detector distance was set to approx. 150 mm. Diffraction patterns were registered on image plate. The exposure time was between 10 and 30 s. Scattering angle calibration was carried out by means of a PET standard. The observed reflections were identified with the aid of crystallographical data and scattering patterns from neat PP, PET, and PA66 samples [16–18].

In order to characterise the orientation of the PP crystallites before and after the recrystallisation, the azimuthal angle α_{hkl} of each reflection (hkl) on the respective pattern was measured. Bearing in mind that, before the recrystallisation, the PP-crystallites are oriented with the c–axis coinciding with FA, the indices of the plane perpendicular to the [001] direction were found after resorting to reference literature [19]. In order to find the orientation of the PP crystallites after the recrystallisation, the angles ρ_{hkl} between (hkl) and the plane normal to FA, characterising the new orientation, were calculated from the measured angles α_{hkl} and the Bragg's angle θ_{hkl} according to Cullity [20])

$$\cos\rho_{hkl} = \cos\theta_{hkl}\,\cos\alpha_{hkl}. \qquad (1)$$

Searching for low-index planes to be perpendicular to the FA, theoretical values for α_{hkl} were calculated on the basis of the alpha-PP unit cell parameters (a = 6.65 Å, b = 20.96 Å, c = 6.5 Å; β = 99.33° [21]) by varying the corresponding indices until a satisfactory match between the measured and calculated values of α_{hkl} was found.

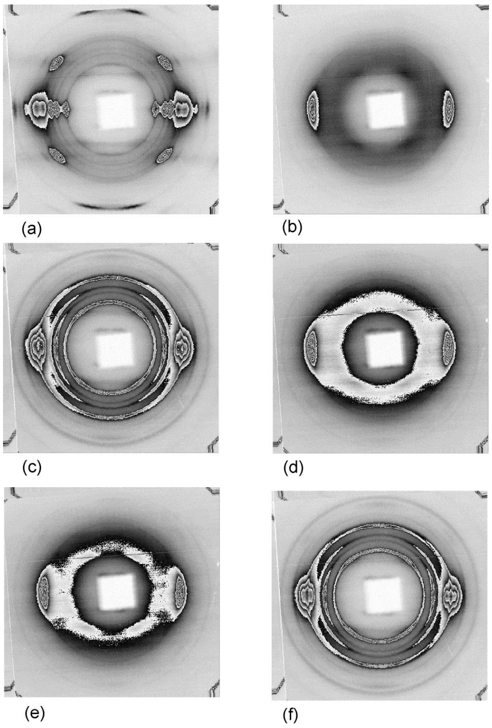

Figure 3: Wide-angle X-ray scattering patterns of PA66/PP blend: a) initial sample, pattern taken at room temperature, b) after 1 min at 200°C, pattern taken at 200°C, c) after 1 min at 200°C, pattern taken at 30°C, d) after 10 min at 200°C, pattern taken at 200°C, Miller index of PA66 is presented, e) after 1 hour at 200°C, pattern taken at 200°C and f) after 1 hour at 200°C, pattern taken at 30°C. The fibre axis (FA) is vertical

3 Results and discussion

Results are displayed in Figures 1 and 2 for the system PET/PP and in Figure 3 for the system PA66/PP. For both blends WAXS patterns were taken during equivalent stages of the thermal processing. First, such patterns were recorded at room temperature (Figures 1a and 3a), followed by patterns taken at 200°C (Figures 1b and 3b), i.e., well above the melting temperature of PP (171°C). After cooling down to room temperature new patterns were taken (Figures 1c and 3c). Then a similar cycle was started, in which the PP was kept in the molten state for a longer period of time.

Figure 1a exhibits a very well expressed fibre texture for both components of the PET/PP blend in accordance with the expectation for a highly drawn and annealed blend of semicrystalline polymers. Several PP reflections are well distinguished. From the position and the number of reflections it is concluded that PP exists only in α-modification with its c-axis parallel to the FA. The same chain axis orientation is found for the PET component. Nevertheless, in Figure 1a the WAXS reflections arising from both components, PET and PP, overlap to a great extent. In Figure 1b, on the other hand, the PP is molten and only the PET reflections are observed. Thus, before studying the PP reflections in detail, we separated the two contributions to Figure 1a by a weighted subtraction of Figure 1b from Figure 1a after proper scaling. For this purpose we used the commercial scientific image processing tool *pv-wave* [22]. The result of this separation is shown in Figure 2a. Figure 2b was obtained in a similar way by subtracting the scattering pattern taken at 200°C (Figure 1b) from the scattering pattern taken at room temperature after melting and recrystallisation (Figure 1c). Thus the separated patterns from Figure 2 exhibit the changes in the PP phase due to the applied melting/recrystallisation cycle.

Only in the subtracted pattern (Figure 2a) the position of the α-PP $[10\bar{6}]$ reflection is detectable. Its position on the meridian is an independent direct support of the mentioned c-axis orientation of the PP crystallites, as deduced from the analysis of several strong reflections and the α-PP unit cell parameters [21].

In Figure 1b taken at 200°C after melt annealing for 1 hour, one observes the fibre texture of only PET. The PP component forms an isotropic amorphous halo, i.e., the melt of PP is in perfect isotropic state.

After melting of PP at 200°C and recrystallisation (Figure 1c) the PP reflections in the WAXS pattern taken at room temperature are quite different from those in the patterns already discussed. Taking into account that PP before cooling is in the molten state and does not show any orientation (Figure 1b) we expected formation of a more or less isotropic crystalline phase as a result of non-isothermal crystallisation during the cooling. Surprisingly, the distribution of PP reflections is rearranged (better seen in comparison between Figures 2a and 2b). Similar to two earlier reports on polymer-polymer composites [9, 10], again a transcrystallisation with reorientation with respect to the original orientation is observed.

By application of the fitting procedure described in the experimental section a satisfactory match between measured and calculated azimuthal angles, α_{hkl}, was found for a preferred crystallite orientation in which the (101) plane is oriented perpendicular to the FA. Using the crystallographic data of the planes (10$\bar{6}$), (101) and the indices of the zone axis [010] (according to [20]), an angle of 49° between FA and the chain direction of the recrystallised PP was computed. Compared to the first study of a blend (PET/PA12 [9]) in which reorientation was observed, we thus observe a different reorientation angle with the PET/PP blend.

This finding is manifested by the result of the next experiment during which the same sample was annealed for a longer time of 2 hours (Figure 1d), followed, again, by non-isothermal crystallisation during cooling to room temperature (Figure 1e). The scattering pattern shows the same features as that of Figure 1c, and the effects already described are even more pronounced.

It is worth mentioning that the majority of the two-component blends which are used for manufacturing of NPC behave in a different way if subjected to melting and crystallisation of the low-melting component. Generally, the latter crystallises without a macroscopic preferrential orientation. Based on WAXS patterns showing only Debye-Scherrer rings, this isotropisation process is well documented for the blends PET/PA6 [12], PET/PBT, [12] and PET/PBT/PA6 [12,14], where PBT stands for poly(butylene terephthalate). However, it should be noted that from these observations one can hardly draw the conclusion that in the last-mentioned systems [12, 14] transcrystallisation with reorientation is completely excluded, because for these blends the WAXS patterns were taken after very long melt annealing times (between 6 and 24 h). Moreover, the patterns were taken by means of a conventional X-ray source that does not allow real-time in-situ experiments. Obviously, in these cases the high crystallinity of the samples [11–15] may have a masking effect on the transcrystallisation with possible reorientation as already observed for the blend PET/PA12 [9].

The difference between both the classical fibre-reinforced materials [2, 4, 7] as well as the common NPCs [12, 14] on the one hand, and the reoriented transcrystalline materials both from earlier work [9, 10] as well as from the present study is notable. The results of the in-situ measurements indicate that in the second case the oriented crystallisation emanating from the PET microfibrils is propagating through almost the complete matrix volume before the usual spherulitic crystallisation is activated. There may be several reasons for the dominance of the orienting crystallisation process. The crystallisation emanating from the fibrillar inclusions may (i) start earlier (at lower undercooling) than the spherulitic growth, (ii) may propagate faster than the spherulite, (iii) may propagate at a constant high speed, if the common transcrystallisation were slowed down during its propagation (e.g. due to accumulation of defects). In order to investigate this competition of two crystallisation mechanisms, in-situ studies with novel two-dimensional detectors are required.

The assumption about the crucial role of oriented PET microfibrils for the crystallisation and orientation of the low-melting blend component can easily be checked by extinguishing them. For this purpose the blend was heated up to a temperature well above the melting temperature of PET. In Figure 1f the WAXS pattern taken at 30°C is shown; after having kept the PET/PP blend at 280°C for 5 min and having cooled the sample. One observes isointensity circles which are characteristic for the crystallites of the two homopolymers and demonstrate that both the components crystallise in isotropic state during cooling.

The results from the PA66/PP blend are somewhat different. The WAXS patterns are taken in the same way as in the previous case and are shown in Figure 3. In the patterns taken at 200°C, where PP is molten, one observes an isotropic amorphous halo and crystalline reflections of only the semicrystalline PA66 oriented parallel to FA (Figures 3b, 3d and 3e). Thus up to this stage the evolution of the PA66/PP material is the same as that of PET/PP (Figure 1).

After the finalising non-isothermal crystallisation step, on the other hand, there are considerable differences. As compared to the data of the PET/PP material, the arc-shaped PP reflections in Figures 3c and 3f are much wider than the almost point-shaped reflections of the PET/PP material. Thus although we observe the return of an oriented PP matrix (reorientation) as well, the orientation distribution of the corresponding crystals is much wider for PA66/PP than in the case of PET/PP. This finding allows one to conclude that the orienting effect of PA66 fibrillar nanostructures on the crystallisation of PP from the melt is much weaker in comparison with PET.

Moreover, the positions of the returned PP reflections have not changed as compared to the initial cold-drawn thread (Figure 3a). Thus the PA66 induces oriented crystallisation of the isotropic PP melt with the chain axes, again, parallel to the chain axes of the PA66 filler fibrils.

4 Conclusions

The WAXS method utilised with synchrotron radiation offers the possibility to observe the initial stage of crystallisation and to draw important conclusions on this process as well as to gather detailed crystallographic information. Similarly to the previously studied cold drawn PET/PA12 blend [9] one observes in the present case a strong epitaxial effect of the nanostructures of microfibrillar type (PET) on the non-isothermal crystallisation behaviour of PP during its cooling from 200°C to room temperature. Thus, the cold drawn and annealed blends of PET/PP and PA66/PP represent highly anisotropic crystalline structures. Finally, the observed orientation effect due to transcrystallisation with reorientation is more uniform in the system PET/PP in comparison to the PA66/PP system, which indicates a stronger epitaxial effect of the microfibrillar nanostructures of PET than that arising from the PA66 microfibrils.

Reviewing the results concerning the crystallisation in an isotropic polymer melt containing oriented embedded core filaments (different polymer microfibrils, class fibres etc.) we have found competition between the isotropic crystallisation (spherulitic, three-dimensional, spreading from points in space) and the anisotropic transcrystallisation emanating from straight lines in space, namely the core filaments represented by the filler particles. Moreover, as the result of transcrystallisation we have found several variants of anisotropy. In order to understand both the process of competition and the mechanisms that control the formation of the different anisotropic structures the essential steps of NPC preparation should be studied in-situ in time-resolved studies. For such in-depth studies by means of synchrotron radiation modern two-dimensional CCD detectors are presently becoming available. Studies with a cycle time of 30 s should then be possible at almost every synchrotron source and yield WAXS patterns with sufficient accuracy even to carry out quantitative analyses of crystallite orientation distributions, ultimately using theoretical approaches devised in several papers of Ruland, e.g. [23–25]. If the results of corresponding studies would show that a continuous recording of structure evolution were necessary, high-brilliance synchrotron radiation sources are required. As a result of such studies one should finally become able to control the nanostructure formation during the physical NPC formation steps in order to manufacture advanced polymer materials. The wide spectrum of possibilities concerning the structure of NPCs can already be anticipated both based on the reviewed and the newly reported results.

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References

[1] Varga J (1995) In: Karger-Kocsis J (ed.), *Polypropylene: Structure, blends and composites*, chap. 3, pp. 51–106, Chapman & Hall, London

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

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

[4] Kumamaru F, Oono T, Kajiyama T, Takayanagi M (1983) Polym Compos 4:141

[5] Klein N, Marom G, Wachtel E (1996) Polymer 37:5493

[6] Seth KK, Kempster CJE (1977) J Polym Sci Polym Symp 58:297

[7] Peacock JA, Hill B, Niel E, Barlow CY (1996) In: Ishida H, Koenig JL (eds.), *Composite Interfaces. Proceedings of the ICCI-I*, North-Holland, New York

[8] Riekel C, Karger-Kocsis J (1999) Polymer 40:541

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

[10] Schmidt P, Baldrian J, Ščudla J, Dybal J, Raab M, Eichhorn KJ (2001) Polymer 41:5321

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

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

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

[14] Fakirov S, Evstatiev M, Petrovich S (1993) Macromolecules 26:5219

[15] Fakirov S, Evstatiev M, Friedrich K (2002) In: Fakirov S (ed.), *Handbook of Thermoplastic Polyesters*, vol. 1, chap. 23, pp. 1093–1132, Wiley-VCH, Weinheim

[16] Brandrup J, Immergut EH (eds.) (1999) Polymer Handbook. 4th edn., Wiley Interscience, New York, Chicester, Brisbane, Toronto, Singapore

[17] Liu J, Geil PH (1997) J Macromol Sci Phys B36:61

[18] Radusch HJ, Stolp M, Androsch R (1994) Polymer 35:3568

[19] Henry NFM (ed.) (1969) International Tables for X-ray Crystallography, vol. 1. Symmetry Groups. 3rd edn., The Kynoch Press, Birmingham

[20] Cullity BD (1978) Elements of X-ray Diffraction. 2nd edn., Addison-Wesley, Reading, Mass.

[21] Clark ES (1996) In: Mark JE (ed.), *Physical Properties of Polymers Handbook*, vol. 67, AIP Press, Woodbury, New York

[22] pv-wave, version 7.5 (2001), Visual Numerics Inc., Boulder, Colorado

[23] Ruland W, Tompa H (1968) Acta Cryst A24:93

[24] Ruland W (1977) Colloid Polym Sci 255:833

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