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Direct electron microscopic observation of transcrystalline layers in microfibrillar reinforced polymer-polymer composites

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Microfibrillar reinforced composites (MFC) comprising an isotropic matrix from a lower melting polymer, i.e., low density polyethylene (LDPE), reinforced by microfibrils of a higher melting polymer, recycled from bottles, i.e., poly(ethylene terephthalate) (PET), were processed under industrially relevant conditions via injection molding in a weight ratio of PET/LDPE = 50/50. Dog bone samples with MFC structure were characterized by means of scanning (SEM) and transmission (TEM) electron microscopy. SEM observations on cryogenic fracture surfaces show an isotropic LDPE matrix reinforced by more or less randomly distributed PET microfibrils. By means of TEM on stained ultrathin slices one observes the formation of transcrystalline layers of LDPE matrix on the surface of the PET microfibrils. In these layers the crystalline lamellae are aligned parallel to each other and are placed perpendicularly to the fibril surfaces. This is in contrast to the bulk matrix where the lamellae are quasi-randomly arranged. © *2002 Kluwer Academic Publishers*

1. Introduction

A special case of crystallization in glass or carbon fiber-reinforced polymer composites is the transcrystallization [1]. It is a function of the nucleating effect of the fiber surface and of the crystallization kinetics of the thermoplastic matrix. The phenomenon is also observed in composites of which the reinforcement is based on polymeric fibers (Cellulose [2], Kevlar [3] and others). Transcrystallization takes place when heterogeneous nucleation occurs with sufficiently high density along the fiber surface. In this way, the resulting crystal growth is restricted to the lateral direction, so that a columnar layer develops around the fiber. The formation of a transcrystallized region around the reinforcing fiber is thought to be in some cases central to the improvement of some composite properties [4]. But the issue is more complicated, because in other cases transcristalline regions can also be detrimental for the material properties. If, for example, the crystalline lamellae are perpendicular to the reinforcing fibrils, the transcrystalline layers are highly anisotropic and probably very weak in tension or shear parallel to the fibers. An anisotropic layer might also have undesirable residual strains and premature failure. In fact, Marom and others [5–7] have extensively studied transcrystalline regions around various types of fibers. Through direct observations of the crystal orientation relative to the fibers and by measuring the mechanical properties of those regions, the authors demonstrated very clearly (i) the rather complex interaction between the molecular orientation in the interphase, (ii) the local properties, and (iii) performance of the bulk material.

Microfibrillar reinforced composites (MFC) were recently [8–10] developed on the basis of polymer blends comprising components with different melting temperatures. Unlike classical macrocomposites (e.g., short glass fiber reinforced ones) or molecular composites, the MFC are reinforced by polymeric microfibrils. The latter are created during MFC manufacturing by drawing (*fibrillization step*), followed by melting of the lower-melting component during processing (*isotropization step*), with preservation of the microfibrils of the higher-melting component. In addition to isotropization during the thermal treatment, chemical reactions (additional condensation and transreactions) in the melt and in the solid state can take place at the interface of condensation polymers, resulting in the formation of a copolymeric interface, thus

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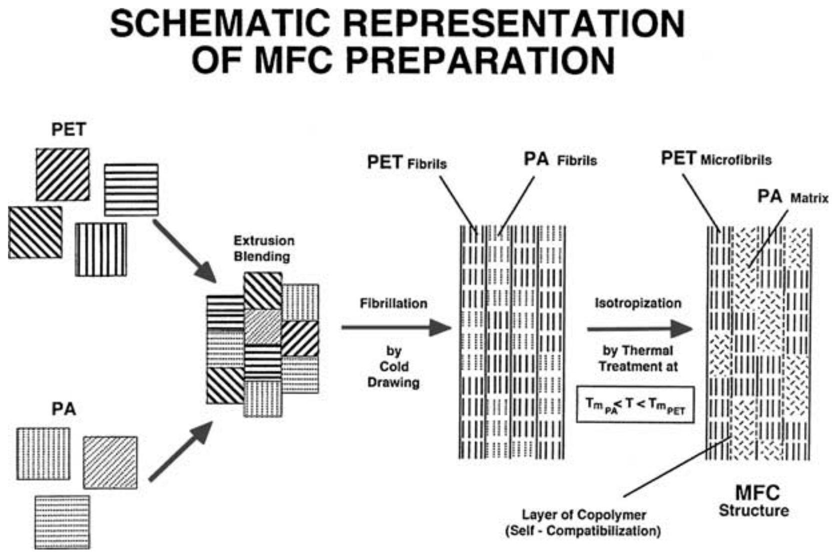


Figure 1 Schematic illustration of MFC manufacturing procedure.

playing the role of a *self-compatibilizer* [10] (Fig. 1). Moreover, in the microfibrillar reinforced composites an epitaxial effect of the microfibrils on the crystallization of the matrix after melting of the drawn blend was also observed. By means of X-ray radiation from a synchrotron source and because of its extremely high intensity it was possible to follow the structural changes in real time during the very first stages of crystallization, i.e., the transcrystallization, and in this way it was possible to avoid the masking effect of the bulk matrix crystallization.

For the system poly(ethylene terephthalate)/ polyamide 12 (PET/PA12) [11] and PET/polypropylene (PET/PP) [12] it was demonstrated that the well documented [13] PET microfibrils do not only promote the crystallization. They also affect strongly the orientation of the matrix chains during transcrystallization at some angle to the chain direction of PET as well as to their own orientation (i.e., fibril axis, FA) direction before melting. Quite similar effects of transcrystallization with partial reorientation was observed again by means of wide angle X-ray scattering (WAXS) in the system PET/polyethylene (PET/PE) [14].

The main goal of the present study is the attempt to check and visualize the formation of transcrystalline layers on the surface of the reinforcing microfibrils during the crystallization from melt of the matrix by means of transmission electron microscopy.

2. Experimental

2.1. Materials and their processing

Recycled material from PET bottles (as reinforcing component) and low density polyethylene (LDPE) (matrix) in a 50/50 wt ratio after drying were melt blended and extruded in a Leistritz LSM 30.34 co-rotating twin-screw extruder. The extrudates were continuously drawn (through neck formation) by means of a take-up device, peletized and processed to dog bone test samples using a "Kloeckner Feromatik - FM 20" injection molding machine.

2.2. Scanning electron microscopy (SEM)

A JEOL LSM 5400 SEM with an acceleration voltage of 20 kV was used for studying the injection molded samples after cooling in liquid nitrogen and subsequent fracturing. The fracture surface was coated with a thin gold layer prior to SEM analysis.

2.3. Transmission electron microscopy (TEM)

For the TEM observations by the use of a TEM-2010 (NIHONDENSHI), ultrathin sections (100 nm) were prepared at −60°C by means of an ultramicrotome Ultracut S (Reichert-nissei), equipped with a Cryo apparatus FC S (Reichert-nissei). In the case of the lower magnification micrographs the ultrathin section was stained by vapour of RuO_4 for 10 min, while for higher magnification the bulk sample was stained overnight, and thereafter it was cut by the ultramicrotome.

The preparation procedure is based on finding by Kanig [15], and it was also systematically described in [16].

3. Results and discussion

Fig. 2 shows three SEM micrographs of cryogenic fracture surfaces of a PET/LDPE sample of different MFC production stages. Fig. 2a represents the situation right after the blend extrusion, showing PET spheres in the LDPE matrix. Rather well shaped microfibrils can be observed, on the other hand, in Fig. 2b. The latter are created during the cold drawing stage of MFC manufacturing. WAXS patterns taken from the as drawn PET/LDPE blend indicate a highly oriented semicrystalline structure with the chain axis of both components arranged in the draw direction [17]. This implies that also the PET-fibrils must be aligned in the draw direction which actually has been observed by various microscopic methods.

A different situation is found after injection molding of the drawn blend (Fig. 2c). Taking into account the fact that this second processing step of the drawn blend took place at a temperature far below the melting of PET, one can conclude that the PET-microfibrils shown in Fig. 2c are the same that are created during the cold drawing [17]. The substantial difference between the two cases is, however, that after injection molding the microfibrils of PET are oriented within the LDPE matrix in a more complex manner, leading

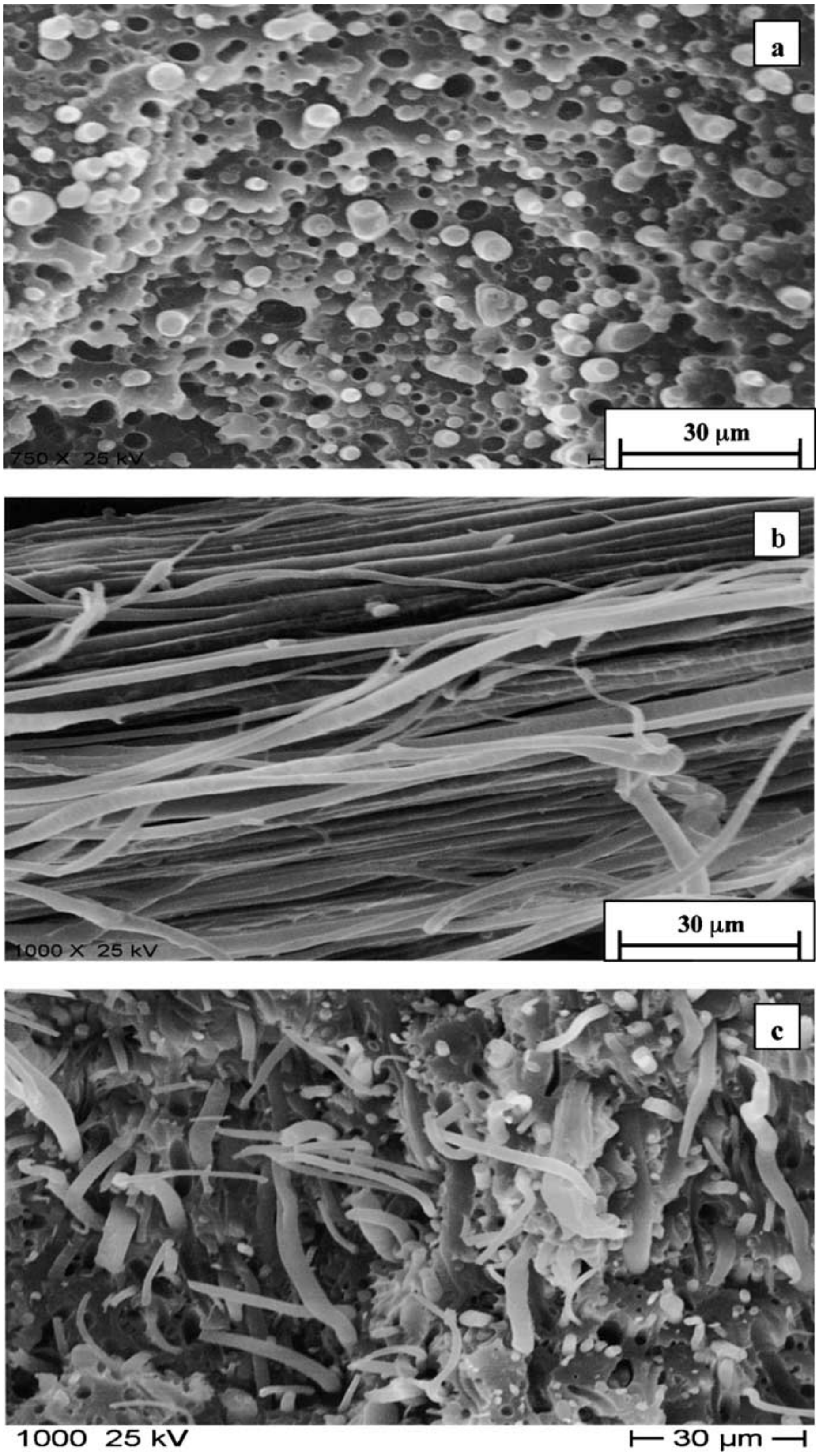


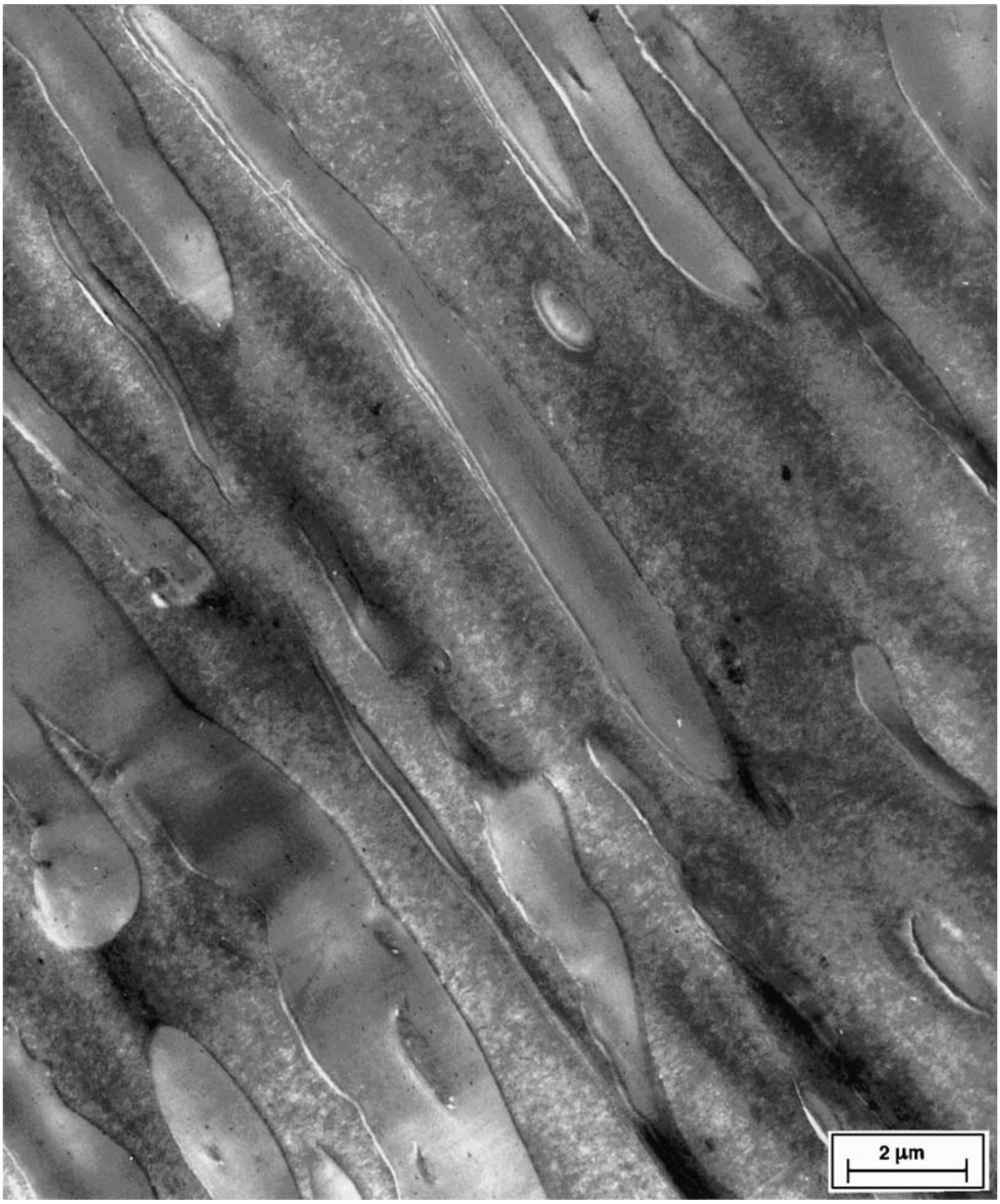
Figure 2 SEM micrographs of the cryogenic fracture surfaces of a PET/LDPE (50/50 by wt) sample, taken at different stages of the MFC production and processing: (a) extruded blend, (b) cold drawn blend, and (c) after injection molding of the drawn blend at a temperature between the two melting temperatures of the two blend components.

macroscopically to a quasi-isotropic behavior, when compared to the highly anisotropic case right after the drawing step. Such a change in the arrangement of the PET-microfibrils is related to the isotropization of the molten LDPE and its shear and fountain flow conditions during processing. The fact of an isotropization of the LDPE-matrix is evidenced by the WAXS analysis of the injection molded dog bone test samples where isointensity Debye rings of LDPE reflections can be observed [17].

Surprisingly, almost the same isotropic distribution of the PET crystallites can be seen on the same WAXS pattern [17], although the PET chains should still be aligned strongly parallel to the fibrils axis (FA). It seems, therefore, that the isotropic arrangement of the PET crystals, as documented by WAXS analysis, is due to the quasi-randomly distributed microfibrils after injection molding. It should be noted here that a systematic study is needed for constructing the microfibrils orientation distribution pattern in the injection molded sample's cross section. So far this orientation is affected mostly by the melt-flow conditions one can expect a similar pattern as known for short glass fibers reinforced injection molded thermoplastics.

The crystallization of LDPE-matrix starts after injection molding during cooling of the melt down to room temperature. As manifold documented, during this process the reinforcing elements (fibers [1–7] or microfibrils, as in the present case [11, 12, 14] play an essential role as nucleating agents, sometimes also associated with a strong epitaxial effect. For the system PET/PE this situation was verified by means of WAXS from synchrotron radiation during the formation of MFC [14]. The fact that in the very first portion of crystallites arising during cooling of the molten matrix on the surface of PET-microfibrils there are some chains displaced in a direction different from that of the PET chains (and also different from their own direction before melting) leads to the conclusion that one deals actually with *transcrystalline* layers.

It seemed reasonable to expect the formation of similar transcrystalline layers also in the system PET/LDPE. The result of the attempt to check this assumption one can see on Fig. 3, showing a series of TEM micrographs taken from a thin section of an injection molded dog bone sample which possessed the



(a)

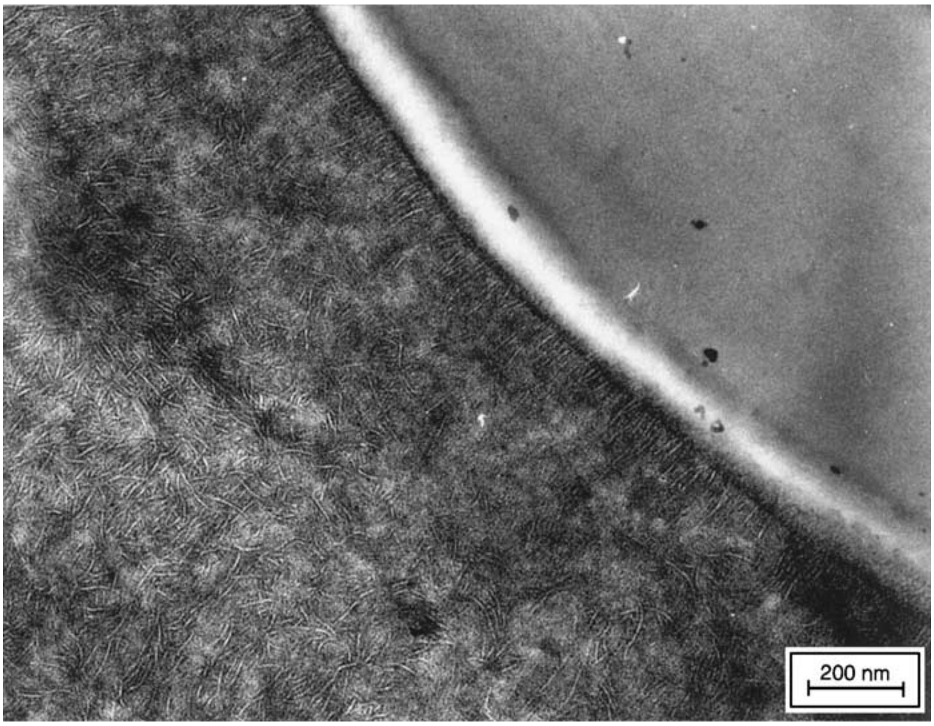
Figure 3 TEM micrographs of an ultrathin, stained section of an injection molded dog bone sample of PET/LDPE (50/50 by wt) with an MFC structure: (a) overview,(b) and (c) details of the lamellar structure in the LDPE matrix. (*Continued.*)

(b)

Figure 3 (*Continued*).

same MFC structure as shown in Fig. 2c. The lower magnification TEM-micrograph (Fig. 3a) gives an idea of the degree of alignment of the PET-fibrils and their average diameter. In the regions, where the thin section was taken from, the alignment of the fibrils of about 2 μm in diameter, was almost perfect. A five times higher magnification (Fig. 3b) allows to view not only the arrangement of the PET-fibrils in the LDPE-matrix, but also the organization of the LDPE-lamellae in direct vicinity of the microfibrils and in a distance further away from them.

The upper right part of Fig. 3c, i.e., one third of the TEM-micrograph, represent a section through one of the PET fibrils. The lighter and darker grey areas are supposed to be a result of the cutting procedure and probably not due to any structural differences within the PET-fibril itself. More interesting is the left part of the figure starting from the borderline between the surface of the fibril and the LDPE-matrix. Of particular importance is the observation that due to the staining technique used one can clearly see the individual crystalline lamellae of LDPE. Their thickness is about 6–7 nm, and the long period amounts to ca 14 nm. Moreover, the lamellae are differently organized depending on how close they are to the surface of the PET-microfibril. In the bulk material, i.e., far away from the microfibril, the LDPE lamellae are dispersed quasi-homogeneously, showing no preferred orientation direction. This situation contrasts drastically to the organization of the crystalline lamellae closest to the PET-microfibril. Here, they are placed strongly parallel to each other and perpendicular to the surface of the microfibril. There is no doubt that this thin, around 150 nm wide LDPE-layer, composed of uniformly organized



(c)

Figure 3 (*Continued*).

lamellae, is nothing else as a transcrystalline layer on the surface of the PET-fibril. The TEM micrograph demonstrates therefore very nicely the basic difference between the crystalline mass in the bulk of the matrix and the transcrystalline layers around the fibrils. In addition, it can be assumed that an important role of transcrystalline layers on the adhesion between the reinforcing elements and the matrix exists. If this effect is positive for the properties of the composite can not be jugded from these observations, but according to the conclusions of Marom and his coworkers [5–7] it may probably be the opposite. Starting from the superior mechanical properties profile of the samples under investigation [17] at least in this particular case one can assume a positive effect of the transcrystalline layers.

It also seems worth mentioning that the width of the transcrystalline layers in this particular case is much smaller than that of the well studied transcrystalline layers in fiberreinforced PP and other polymer matrix composites [5–7, 18].

4. Conclusions

Summarizing, one can conclude that by means of TEM on stained ultrathin slices of injection molded PET/LDPE samples with an MFC structure one can observe quite well the formation of transcrystalline layers of the LDPE-matrix on the surface of the PET-microfibrils. In these layers the crystalline lamellae are aligned parallel to each other and placed perpendicularly to the fibril surfaces in contrast to the bulk matrix where they are quasi-chaotically arranged.

Acknowledgments

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