On transcrystallinity in semi-crystalline polymer composites

Article *in* Composites Science and Technology · June 2005

Impact Factor: 3.57 · DOI: 10.1016/j.compscitech.2004.11.015

Ganji Zhong
Sichuan University
172 PUBLICATIONS **4,813** CITATIONS

Rui Huang
University of Cincinnati Medical Center
142 PUBLICATIONS **1,778** CITATIONS

Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

Composites Science and Technology 65 (2005) 999–1021

COMPOSITES SCIENCE AND TECHNOLOGY

www.elsevier.com/locate/compscitech

Review

On transcrystallinity in semi-crystalline polymer composites

Hui Quan, Zhong-Ming Li *, Ming-Bo Yang, Rui Huang

College of Polymer Science and Engineering, The State Key Laboratory of Polymer Materials Engineering, Sichuan University, Chengdu 610065, PR China

Received 27 May 2004; received in revised form 29 November 2004; accepted 29 November 2004
Available online 19 January 2005

Abstract

In semi-crystalline polymer composites, when heterogeneous nucleation occurs with sufficiently high density along the interphase region, the resulting crystal growth is restricted to the lateral direction, so that a columnar layer develops around the fiber, known as transcrystallinity (TC) or transcrystalline layers (TCL). Since Jenckel et al. [Kolloid-Z 129 (1952) 19–24] described TC for the first time in 1952, many researchers have done the investigation of TC to reveal its formation mechanism, aggregate state, and influences on the performance of the materials in the semi-crystalline polymer composites containing various matrixes and fibers under different crystallization conditions. Several aspects of TC in some fiber reinforced semi-crystalline polymer composites were reviewed in the present paper, including the formation and growth mechanisms, factors that affect TC layers, and the influences of TC on the interfaces of fiber/polymer and the properties of composites.

Keywords: Transcrystallinity; A. Fibres

Contents

---

* Corresponding author. Tel./fax: +86 28 8540 5324.
E-mail address: zm_li@263.net.cn (Z.-M. Li).

0266-3538/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.compscitech.2004.11.015

1. Introduction

Semi-crystalline polymers are usually reinforced with various types of organic or inorganic reinforcements like fibers to form composites with improved mechanical properties. It is well known that these reinforcements can result in changes in morphology and crystallinity of the interphase regions. Some of the substrates, especially fibers, may act as heterogeneous nucleating agents and nucleate crystallization along the interface with sufficiently high density of nuclei. These nuclei will hinder the lateral extension and force growth in one direction, namely perpendicularly to the fiber surfaces and result in a columnar crystalline layer, known as transcrystallinity (TC) or transcrystalline layers (TCL), with limited thickness [1–9]. Fig. 1 shows a typical TC layer in dew retted flax fiber reinforced isotactic polypropylene (iPP) composites [10]. It is clear that the growth of the TC proceeds perpendicularly to the fiber until the growing front impinges with spherulites nucleated in the bulk.

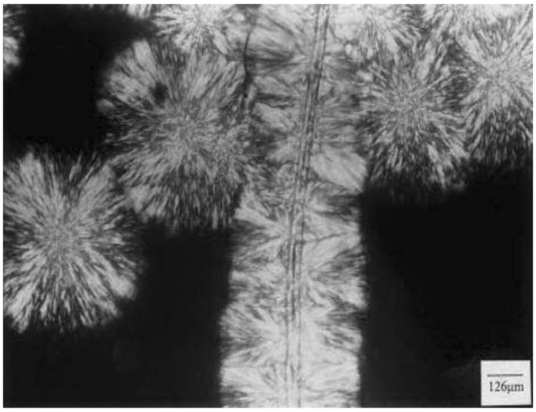

Fig. 1. Micrograph showing isothermal crystallisation of dew retted flax/iPP at 145 °C (120 min) (200×) [10].

Single fiber-polymer composites are often used for the research of TC, that is, a single or several fibers were embedded between two thin polymer films to prepare a model composite, which usually called "sandwiched". Its schematic representation is shown in Fig. 2 [11]. The samples are heated so that the matrix melts but fibers do not, then samples are cooled to crystallization temperature for isothermal or nonisothermal crystallization. There are also some researchers who studied TC of composites prepared by other process, such as injection molding. Besides, TC of in-situ microfibrillar reinforced composites (MFCs) may form under certain crystallization conditions.

TC has been reported to occur in several semi-crystalline polymers such as iPP, polyethylene (PE), poly (ether ether ketone) (PEEK), poly (phenylene sulfide) (PPS) and polyamide (PA), etc. in contact with carbon fibers (CF), glass fibers (GF), aramid fibers, natural fibers (NF), and so on. Due to its anisotropy, the formation of TC has significant influence on the performances of fiber/polymer interfaces, and hence affects greatly the mechanical properties of composites. Although TC has

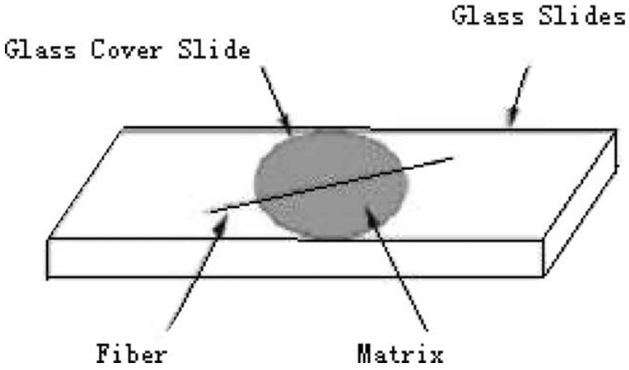

Fig. 2. schematic representation for the single fiber-polymer composite [11].

been reported to improve the properties of some fiber/polymer interfaces and composites, the mechanism by which TC layers occur is not fully understood and there are no rules to predict the appearance of TC in a particular fiber/matrix system, the effects of TC on the interfaces and properties of composites remains in dispute. Several authors have reported that TC can improve shear transfer at the interface, and, consequently, the mechanical properties of composites, whereas others claimed that it has no, or even a negative, effect on these properties. Many factors, such as the fiber material type, and its topology and surface coating, the matrix type, and thermal history, have all been reported to affect TC in these composites to some extent.

Since Jenckel et al. [1] described TC for the first time in 1952, more and more researchers have joined in the investigation of TC. Many efforts have been made to study TC in the composites containing various matrixes and fibers under different crystallization conditions. However, TC has not yet been fully understood; the formation and growth mechanisms of TC are still unclear and its effect on the properties of composites and their interfaces remains controversial. Besides, lots of factors, such as crystallization temperature, cooling rate, fiber topography, etc., will give a distinctive influence on TC. Hence, deeper and more detailed studies of the specific role of TC interfaces must be performed before general conclusions can be drawn. In this paper, several aspects of the study of TC layers in some fiber reinforced semi-crystalline polymer composites are reviewed, including the formation and growth mechanisms, factors that affect TC layers, and the influences of TC on the interfaces of fiber/polymer and the properties of composites.

2. Formation and growth mechanisms of transcrystallinity

The studies of TC have been carried on for more than half a century; however, the universal mechanism for the origin of TC is still ambiguous. There are a lot of factors that will influence the formation and growth of TC. But for different matrices and fibers, they will give different affections, which have always been the focus.

2.1. Conditions of transcrystallinity formation

Many factors like fiber topography, surface coating of the fiber and processing conditions of the composites have been reported to influence TC. The phenomenon of TC is highly specific to the fiber–matrix combination.

As observed from different experiments, TC depends on [12]: epitaxy between the fiber and the matrix [13,14]; topography of the fiber [14–16]; mismatch of thermal coefficients between the fiber and the matrix [17]; thermal conductivity of the fiber [18]; chemical composition of the fiber surface [19], and surface energy of the fiber [20,21]; crystallinity of substrate; processing conditions, such as cooling rate, temperature, flow field [17].

2.1.1. Fiber parameters

2.1.1.1. Nature of fiber [12]. The presence of nucleating sites on the surface of the fiber affects nucleation. Natural cellulosic fibers like cotton, bleached ramie, rayon and a variety of wood fibers having abundant nucleation sites on the surface induce TC in iPP [15]. Gray had identified the growth of a TC layer under isothermal crystallization at 136 °C with purified wood cellulose fibers, cotton, and ramie. When fibers containing larger amount of lignin and hemicelluloses apart from cellulose (pressure-refined aspen, unbleached softwood Kraft, and softwood sulfite fibers) were used TC, the nucleation sites were much further apart than on the more highly purified fibers. Gray attributed this to the presence of lignin and hemicelluloses (amorphous materials). At longer times significant nucleation did take place on the less purified wood fibers as well. Gray reported that regenerated cellulose (rayon) did not develop a TC layer at all. He showed that mercerization prevented the formation of a TC layer.

The modulus and strength of the fiber plays an important role in determining TC. Hobbs [22] using two kinds of fibers – one of high modulus and the other of high strength observed a major difference in their nucleating ability. He postulated that higher modulus polyacrylonitrile fibers possess an exposed basal planar surface structure (without presenting plane ends) which might support the epitaxial nucleation of iPP on the wider basal planes of such fibers. The high strength fibers proved to be poor nucleants and hence there was no TC. On this type of fiber, spherulites nucleated and grew in the bulk polymer with the same frequency of the fiber surface. A very well developed and evenly distributed TC occurred with the high modulus fiber at ~128 °C. Hobbs thus demonstrated the importance of the topography of the fiber and ascribed the difference in observation due to epitaxial growth of the PP onto the exposed graphite planes. Thomason et al. [3] also found that aramid fibers and high-modulus carbon fibers (HMCF) did induce TC, whereas high-strength carbon fiber and GF did not.

The effect of substrate surface energy on TC growth at the interface of a semi-crystalline polymer and its effect on interfacial adhesion were investigated for substrates treated with various silane coupling agents by Cho et al. [21]. A thin film of iPP crystallized on a high surface energy substrate (treated with γ-(aminopropyltriethoxysilane) (γ-APS)) was composed entirely of TC. On the other hand, when the iPP film was crystallized on a low surface energy substrate (treated with perfluorodecyltrichlorosilane (FDS)), the interface was dominated by spherulites, and only a very thin TC region (thickness ~1 μm) was observed. The substrate surface energy was found to exert a significant influence on the crystallinity, density of nuclei, crystal microstructure (e.g., lamellar thickness and crystal orientation), and thickness of the TC region near the interface. The adhesion energy measured by the asymmetric double cantilever beam (ADCB) test increased strongly (from 1 to 100 J/m^2) with surface energy.

Wang and Chen [23] studied the surface-induced crystallization of syndiotactic polystyrene (sPS) on HMCF, and found no difference in the crystal growth rate of sPS in either spherulites in the bulk or TC layers at the interface. The thickness of the TC layers increased with crystallization temperatures, from 5 to 13 μm in the temperature range of 247–259 °C. The efficiency of HMCF to induce the TC layer was better in sPS matrix than that in iPP matrix based on the surface energies of the constituents.

2.1.1.2. Surface roughness of fiber. Surface roughness of fibers is another important factor related to the TC formation. TC of PP on various fibers (Kevlar, poly (ethylene terephthalate) (PET), carbon, and polytetrafluoroethylene (PTFE) fibers) was extensively investigated by Wang and Liu [24]. They observed an inverse proportion between induction time and nucleation rate for PTFE and carbon fiber systems, but not applicable to Kevlar and PET fiber systems. This was attributed to the different types of nucleation sites resulting from the nonuniformity of surface roughness of Kevlar and PET fibers. It had been suggested by the authors that the presence of small scale grooves at the fiber surfaces cause thermal stress concentration and enhance the nucleating process.

Lin et al. [9] investigated various textures of copper surfaces prepared by sandpaper polishing and electrochemical anodizing utilizing to induce interfacial nucleation of iPP upon supercooling. Copper surface with higher surface roughness induced more nuclei of iPP and led to a thicker TC layer in the interfacial region upon supercooling over the temperature range $128 < T_c < 134$ °C. This result was consistent with their previous investigation on PTFE, polyimide (PI), and aluminum surfaces [25–27], which showed that the surface roughness, instead of chemical factors or surface energy, playing an important role in heterogeneous nucleating, consequently determining whether a TC could be formed at the interface or not.

2.1.1.3. Thermal conductivity of the fiber. Some researchers suppose that thermal conductivity of fiber to be an origin for the formation of TC. As observed by Cai et al. [18] thermal conductivity mismatch between fibers and matrix for CF and PP matrix was thought to be the principal reason behind TC observed in such composite. Thus high-tenacity CF having poor thermal conductivity (24 Wm^{-10} C^{-1}) did not transcrystallize the matrix as compared to ultra high modulus Carbon fibers (UHMCF) (360 Wm^{-10} C^{-1}). As explained by the authors, the high interface temperature gradient due to the conductivity difference was the principal cause for TC. Burton and Folkes [28] found that highly conductive carbon fibers create temperature gradients close to their surfaces, well into the interior of the specimen. Thus the TC varies along the surface. For polyester, having much lower thermal conductivity, the TC was much more uniform.

2.1.1.4. Fiber treatment. Treatment is an important method to have the surface properties of fibers changed, thus the ability of fibers to induce TC will be changed as well. Jin et al. [29] studied the TC effects caused by various fibers, which were untreated, or treated with sodium hydroxide and cellulase. Three kinds of specimens were prepared (i) cellulose treated with 20% NaOH solution, (ii) cellulose treated with cellulase and (iii) cellulose treated with cellulase after pretreating with NaOH. It was known that treating cellulose treated with cellulase hardly affects crystalline regions of cellulose. It was observed that the untreated and treated cellulose fibers all had a nucleating ability to transcrystallize at PP matrix, especially for the cellulose fibers treated with sodium hydroxide. Therefore the enhancement of TC, as assumed by the authors, was caused by the enlargement of the effective surface areas and roughness in the cellulose surface due to cellulase treatments.

Quillin et al. [4] showed that untreated cellulose fibers produced a TC layer, while fibers surface-treated with alkyl ketene dimer (AKD) or alkenyl anhydride (ASA) did not, due to the hydrocarbon chains.

2.1.2. Processing parameters of the composite

It is known that crystallization temperature and cooling rate are always significant to the crystallization of polymer. Crystalline morphology and crystallization kinetics will be changed under different temperature and cooling conditions. These influences will be similar as far as TC is concerned. In addition, interfacial properties will also play an important role.

2.1.2.1. Effect of cooling rate and methods. Huson and McGill [30] reported that rapid cooling from 215 °C to the crystallization temperature of 138 °C facilitated the growth of TC. Fast cooling to 170 °C followed by slow cooling to 135 °C over a period of 20 min retarded the TC growth.

Yue and Cheung [31] investigated GF with and without silane coat reinforced iPP composites and found that TC only developed in the water quenched specimens, but specimens quenched with air-cooled and cooled in an oven preheated to 50 °C had no TC. The size of TC was similar to the average spherulite size in the water quenched matrix and was 60 μm.

The two major phases of PP generally coexist as observed by Devaux and Chabert [32]. They found that when a shear stress was applied at a glass–PP interphase, the shear temperature needs to be higher for a higher cooling rate so as to allow β-TC. At a cooling rate of 0.2 °C/min, the β phase dominates above 145 °C.

2.1.2.2. Effect of crystallization temperature. The effect of crystallization temperature has been observed by several researchers [3,33]. Thomason [3] observed that for all the fibers used in the iPP matrix, TC regions were identical below 138 °C and no TC had been observed beyond 138 °C.

Avella et al. [34] concluded that the crystallization temperature intensively affected formation of TC. Increasing crystallization temperature resulted in a change of morphology from TC to spherulitic. The influence of annealing temperature in the melt also affected interphase properties.

2.1.2.3. Stress field around the fibers. Shear flow at the fiber–matrix interphase affects TC as observed by different researchers though the findings have been contradictory. Lagasse et al. [35] showed that the rate of nucleation was increased by flow and TC growth got hampered due to its competition with spherulitic growths. In Monasse's study [36], an α-phase nucleation process took place at the GF surface after shearing at 210 °C, while a strong nucleation process in β-phase appeared at 170 °C. The nucleation increased with shear but did not appear in static state. On the other hand, Gray [37] observed that when GF were pulled in molten PP, TC growth was observed while the stationary fiber did not induce any TC. Thomason et al. [17] also proposed that the origin of TC was actually stress-induced nucleation, due to the stress at the interface caused by cooling two materials with a large difference in thermal expansion coefficient. Similar observations were made by other researchers [2,32] which strongly suggested that shear induced flow facilitates TC growth. Work by Sengupta et al. [38] tended to suggest that localized melt flow was responsible for TC. TC developed when the fibers were pulled through the melt at the crystallization temperature (129 ± 1) °C.

2.1.2.4. Effect of a compatibilizer. A compatibilizer can enhance the interfacial adhension between fibers and matrix. Thermal, morphological, and dynamic mechanical properties of PP and cellulose fiber composites were investigated by Amash et al. [39] where two types of cellulose fiber and a compatibilizer (maleic anhydride modified polypropylene (MAPP)) were used. The nucleating effects of the fiber surfaces resulted in the formation of TC regions. There was an increase in the stiffness and a reduction in the damping values with increasing cellulose fiber content. The results were consistent with morphological observations, which verify an improved interfacial adhesion between fiber and matrix. For the composites investigated by the authors, the occurrence of chemical bonding during compounding was assumed since the functional group of the anhydride ring of MAPP was able to react chemically with the (OH) groups of cellulose at the fiber surfaces. In addition to the physical interactions, the resulting covalent and hydrogen bonds enhanced the interfacial adhesion and the compatibilization between the hydrophilic cellulose and the hydrophobic PP and improved the dispersion of the fillers in the matrix.

Other factors, such as the molecular weight of the matrix can affect TC as well. Folkes and Hardwick [40] observed that the lowest molecular weight PP had the highest TC. With increasing molecular weight, the TC layers became less uniform, with some parts incapable of nucleating the polymer. As observed by Vaughan et al. [41] an increase in the molecular weight implies a lower level of stress to induce crystallization. Moon [42] found that the thickness of TC layers was significantly influenced by both the fiber diameter and molecular weight of the polymer. Also, as the interfiber spacing became smaller, the spherulites in the matrix polymer were not seen to be formed between the TC layers developed on the GF surface.

2.2. Nucleation and growth mechanisms of transcrystallinity

There have been many hypotheses proposed to account for the formation of the TC. Campbell and Qayyum [43] claimed that the adsorption of the highly active nucleating promoters on the substrate surface was responsible for the formation of TC. Thomason and Van Rooyen [17] reported that an application of stress at the interface between fiber and supercooled PP melt by using pulling apparatus resulted in the growth of a TC. Chen and Hsiao [19] reported that the chemical similarity between the crystallizing polymer and the substrate increased the possibility of TC. Huang and Petermann [44] think that steric hindrance was a key factor for the formation of TC.

Based on the available literature, the origins of TC layers can be:

(1) Fibers acting as heterogeneous nucleating agents and inducing matrix to nucleate on the fiber surface [3,4,33,45–51]. The HMCF could generate α-TC in the quiescent melt due to its strong α-nucleation ability [46]. In the absence of maleic anhydride (MA), the PET fibers in PP showed TC morphology and thus proved to be a strong nucleating agent for PP spherulites [48].

The morphology of interfacial TC developed between a reinforcing fiber and a polymer matrix differs significantly from that of polymer crystals in the bulk due to the high density of heterogeneous nucleation sites at the fiber surface. Though epitaxy is not a necessary condition for nucleation, as evidenced by the large variety of nucleating agents, it does occur often for TC on fiber substrates. Epitaxy involves the oriented overgrowth of one crystal on another and the parallelism of the two crystal lattice planes that have nearly identical arrangements of atoms. In the case of polyethylene/polyethylene composites epitaxy can occur due to the obviously favorable lattice match. Chen and Hsiao [19] studied the surface-induced TC in various fiber (CF, GF and aramid) reinforced PEEK, PPS and PEKK composites. They found that the poly (*p*-phenylene terephthalamide) (PPDT) aramid fibers and pitch-based CF induced a TC interphase in all three polymers because of an epitaxial effect. Under certain conditions, TC was also observed in polyacrylonitrile (PAN)-based CF and E-glass (E-GF), which might be partially attributed to the thermal conductivity mismatch between the fiber and the matrix. Plasma treatment on fiber surface showed a negligible effect on inducing TC, whereas solution-coating of PPDT on the fiber surface showed a positive effect.

Orthorhombic (γ) iPP transcrystallinity nucleated on aramid fibers under high pressure was investigated by synchrotron X-ray diffraction and by scanning electron microscopy (SEM) by Assouline et al. [52]. It was determined that the *c*-axes of the lamellae (the growth axes) were distributed radially about the fiber and that the lamellar *ab* face was randomly oriented on the fiber surface. This finding is consistent with the apparent absence of an epitaxial relationship between the crystal structure of the surface of the Kevlar aramid fiber and the lattice of γ iPP crystals.

The fibers that were found to induce TC layer formation of the semi-crystalline polymer matrix include iPP, PE, PA, PEEK, and so on. When the nucleating ability of the fibers is poor they can be coated with nucleating agents or modified to induce TC.

(2) Shear or strain induced crystallization. When the samples are prepared, there are stresses to appear on the substrate/polymer interface, which results in a drop of crystallization steric hindrance of polymer molecules, and the polymer nucleates on the substrate surfaces with high density, and then crystal begins to grow TC [2,16,17,24,36,42,53–58]. Bushman and McHugh [58] developed a continuum model, which is based on ideas from the theory of strain-induced crystallization coupled with an irreversible thermodynamic formalism based on the continuum Hamiltonian Poisson Brackets, to account for the flow-induced crystallization. Wang and Liu [24] considered that a simple mechanism, based on thermal residual stress-induced orientation and relaxation of polymer chains, was responsible for the nucleation of TC. Wu et al. [54] proposed the micro morphological features of sheared iPP melts could be explained by a modified model by combining the concept of metastability and the theory of stress-induced crystallization without assuming epitaxial growth. Varga and Karger-Kocsis [56] thought that melt-shearing, which caused by fiber pulling, was associated with the development of α-row-nuclei. The surface of the in situ formed α-row-nuclei might induce the growth of the β-modification of iPP resulting in a cylindrite of polymorphous composition. The β-nucleation ability of the α-row-nuclei was lost by melt-shearing at high temperature or remelting because of coverage of the β-nuclei by the α-phase. It was also demonstrated that the mechanism of shear-induced crystallization was unaffected when the crystallizing PP melt contained selective β-nucleants. Misra et al. [2] studied TC in injection molded iPP/GF composites and found that slight mechanical stress at the fiber polymer interface could give rise to surface nucleation and growth of TC. The TC in injection molded samples was attributed to the availability of sufficient inherent stresses. Moreover, an increase in fiber concentration was found to enhance TC.

(3) Impurities acting as nucleating agents. Impurities in the matrix which has the ability to induce nucleation, such as residual catalyzer, dust, etc., may transfer and absorb to fiber surfaces and then cause matrix polymer to nucleate at interface with high density, finally result in a TC [5,33,43,58–65]. Nagae et al. [59] found that TC could be induced by coating E-GF with acid-modified PP (AMPP) without application of stress at the surface and without nucleating agents to coat GF, some impurities such as metallic compounds in AMPP acted as nucleating agents. Oliveira and Cramez [60] found that during the rotational molding, the poor mixing ability of turbo-blending led to the pigment concentrating around the polymer particles and to the development of TC textures.

2.3. Formation kinetics of transcrystallinity

Several theories of crystallization kinetics have been proposed for semi-crystalline polymers. Using the example of PE [66,67], Hoffman defined three crystallization regimes. Each regime was characterized by the way the chains are deposited on the substrate and by the relation between the spherulite growth rate and the nucleation rate. Another approach to nucleation concerned induction time, which was the delay between the time zero (when the temperature has reached the chosen crystallization temperature) and the time of the onset of nucleation. According to Ishida [68], this parameter was connected to the nucleation rate and it enabled the calculation of thermodynamic parameters.

It is important to study the kinetics of TC as a function of both crystallization temperature and the reinforcing fiber [69]. Indeed, these two parameters play a crucial role in the kinetics and in the morphology of the TC layer. The theories and techniques developed for the crystallization of matrices have been used also for TC.

Assouline et al. [70] studied the kinetics of α and β TC in iPP based composites under isothermal and gradient cooling conditions. No difference was found between growth rates of bulk spherulites and TC layers, and Hoffman's theory led to the same results in both cases. Regarding a TC, a transition between regimes II and III occurred near 137 °C and the ratio of the slopes of the two regimes was close to the theoretical value of 2. Regarding β-TC, only regime II was exhibited in the temperature range studied. However, the induction time for TC was strongly influenced by the type of fiber, which in turn-based on Ishida's approach-resulted in variations in free energy differences at the fiber-crystallite interface for various fibers and bulk PP. The respective values were 1.3, 1.5 and 2.1×10^{-3} J m^{-2} for Kevlar 149 fibers, HMCF than in PP, showing that α crystallization was more likely to occur in Kevlar 149 fibers and HMCF than in bulk PP. Gradient-thermal measurements were performed for a TC which allowed estimation of the activation energy of TC for the different composites. Activation energies of TC promoted on Kevlar 149 and HMCF were found higher than the activation energy for bulk crystallization.

Peron et al. [55] found that a TC layer could only be produced if the alumina fiber was pulled through the supercooled PP matrix, and that the thickness and growth rate of this TC depended upon the isothermal crystallization temperature, but not on the cooling rate. Increasing the crystallization temperature would slower the growth rate. Both α-monoclinic and β-hexagonal crystal structures were identified in the TC, with the β crystal only being induced in areas which existing α crystals. The α region transformed into β crystals except for a small region at the fiber/matrix interface. The β crystals grew at a faster rate than α crystals and were found to melt at 157 °C, compared to 170 °C for the α crystals. For PTFE fibers with pulling, Wang and Liu [16] found that both the nucleation rate and the saturated nucleation density increased with increasing shear rates. However, the induction time was significantly reduced. Both the thickness and the crystal growth rate of TC layers were found to increase with the increasing rate of fiber pulling, especially at low crystallization temperatures. It was argued that the presence of fibrillar-type features at the fiber surface was the main factor responsible for the development of TC.

The TC of iPP was found in its blends with ethylene-propylene-diene terpolymer (EPDM), reinforced with different fibers [49]. The half time of crystallization, $t_{1/2}$, and the overall crystallization rate, K_n, increased in the presence of all the fibers analyzed, showed the aramidic ones the most effective. The TC phenomenon was hindered at high rubber percentages. As in the case of the rate of crystallization, the highest proportion of TC was observed in the presence of the aramidic fibers.

The study of isothermal crystallization behavior of PP on the surface of PET fibers revealed that the extensive nucleation on the fiber surface was followed by the development of a TC phase [71], while normal PP spherulites appear much later than the TC phase in regions far from the interface. The crystallization kinetics was followed by spot-intensity measurements at selected areas on the picture frame near the fibers, showing that the kinetics in the TC zone was quite different from that in the PP bulk. Furthermore, a preferential orientation of the *b*-axis and/or *bc*-planes of PP crystallites along the *c*-axis of PET fibers were found, suggesting that the crystal structure of the fiber material could also influence the development of this phase.

MAPP was very effective to promote a finer dispersion of the LCP phase in the PP matrix [72]. Consequently, the LCP domains or fibrils acted as potential sites for the spherulite nucleation. The $t_{1/2}$ of the MA-PP/LCP blends was relatively smaller than that of the maleated PP copolymer. The rate of crystallization was enhanced in maleated PP/LCP blends which exhibit TC. Moreover, both isothermal and non isothermal kinetics measurements reveal that the Ozawa exponents of the PP, MA-PP, and PP/LCP blends are identical to the Avrami exponents of these specimens.

The TC of poly (vinylidene fluoride) (PVDF) on several different types of substrate materials had been studied by Benkhati et al. [73]. Although only approximately applicable, an Avrami-Ozawa analysis of the latter yielded reliable exponents, which characterized the TC nucleation conditions, the related dimensionality of growth, and the resulting texture.

2.4. Structure of transcrystallinity

In Amitay-Sadovsky's study there are two options exist for the TC lamellar ordering [74]: (1) the *a–c* plane of the lamella was exposed, revealing the thickness (20 nm) of the "card deck"; or (2) the *a–b* plane of the lamella (thus the plane that contains the lamellar folds) was exposed, revealing the width of the "cards". Twisting arrays would involve severe steric effects between neighboring lamellae, and the rotation of neighboring parallelipipedic entities would necessarily cause a reorganization of the lamellar "edifice".

The properties of the TC layer, when compared with those of the matrix, reflect a higher degree of order, which would result from a more compact crystal packing and possibly from a preferred crystalline alignment. The crystalline alignment may be characterized by a particular distribution in the orientation of the *c*-axes of the crystallites [13,14,46,49,52,56,75–81]. On the molecular level, since the *c*-axis is parallel to the chain axis of the polymer, the physical and mechanical properties in this direction reflect the covalent nature of the polymer chain, while the properties in the perpendicular directions, along the *a*- and *b*-axes, reflect weaker intermolecular interactions (Van der Waals and hydrogen bonding). For that reason, it is expected that the orientation distribution of the polymer chains in the TC layer will determine the nature and extent of its effect on the properties of the composite material [82].

X-ray diffraction analysis performed on various PE and PA transcrystalline layers in microcomposites [75,76,83] revealed preferential orientations of the polymer chain with respect to the fiber axis, so that their *c*-axes were inclined at specific angles relative to the fiber axis. The specific orientation in each case was determined by a combination of the crystal growth mechanism, which resulted in an orientation distribution, and of geometrical factors, such as the thickness of the TC layer or the fiber volume fraction. In a study of aramid and carbon fiber-reinforced Nylon 66 it was concluded that in the nucleation and initial growth stages the first chain folds were oriented so that the chain axis was aligned in the fiber direction, and in the crystal growth that followed a typical sheaf structure was formed (described graphically in [84]), leading gradually to spherulite formation, as in bulk crystallization [83]. In a study of PE-fiber-reinforced HDPE matrix [75,76], PE based single-polymer microcomposites crystallized under different processing conditions, i.e., liquid nitrogen or ice-water quenching, air cooling and isothermal crystallization, a TC was grown on the fiber surface. A smooth and banded TC morphology developed under ice-water quenching and air cooling conditions, respectively, corresponding to smooth and banded spherulites in the matrix. Under isothermal crystallization, an apparent rod-like morphology was observed to develop in the matrix. Accordingly, the TC obtained under the same conditions exhibited a similar morphology. They considered that the TC growth most probably started epitaxially with the *a*-axis make an angle of approximately 39° with the fiber axis and the *b*-axis developed radially outwards from the fiber surface, and the *c*-axis of the orthorhombic unit cell aligned in the fiber axis direction. In the growth stage that followed, the lamellae twisted as the crystals grew outward from the fiber surface, exhibiting variable angles with respect to the fiber axis for different TC layer thicknesses.

Assouline et al. [52] investigated γ-iPP TC nucleated on aramid fibers under high pressure by synchrotron X-ray diffraction and by SEM. It was determined that the *c*-axes of the lamellae (the growth axes) were distributed radially about the fiber and that the lamellar *ab* face was randomly oriented on the fiber surface, which was consistent with the apparent absence of an epitaxial relationship between the crystal structure of the surface of the Kevlar aramid fiber and the lattice of γ-iPP crystals. They also studied the TC of different systems, and found that in the TC layers, the parent lamellae nucleated at the fiber surface with the crystallite *c*-axis paralleled to the fiber axis, twisted one quarter turn about the parent a^*-axis within an approximate distance of 25 μm, and then continued to grow without further twisting [78].

In the quiescent state, the iPP lamellae grew from the surface of talc and the TC region was formed at the interface between iPP melt and the talc [26]. The nucleation of iPP was very frequent on the cleavage plane of talc. The X-ray diffraction pattern of the transcrystal showed a^*-axis orientation to the crystal growing direction. In injection-molded samples of the talc-filled iPP, the morphology of lamella growing from talc appeared as same as that of the transcrystal. However, the crystalline orientation of injection-molded talc-filled iPP, in which the *b*-axis was oriented to the thickness direction and the a^* and the *c*-axis was oriented to the flow direction, was quite different from that of the transcrystal. This *b*-axis orientation resulted from the orientation of the plate plane of talc, which induced the nucleation and the crystallization under shear flow.

Loos et al. [13] studied details of the lamellar arrangement in the TC layer and of the PP fiber–PP matrix interface by using high-magnification low-voltage scanning electron microscope (LVSEM). There were dominant crosshatched morphology consisted of mother lamellae nucleated on the fiber surface and daughter lamellae epitaxially crystallized on them. The holes at the fiber–matrix interface resulted from the shrinkage of the iPP matrix during crystallization. The TC layer of samples isothermal crystallized at 145 °C showed only radial grown lamellae, which was similar to the spherilitic architecture.

Some researchers found that TC layers are often composed of two regions [77,85,86]. Kitayama et al. [77] studied TC in iPP fiber reinforced iPP composites and found that in one region close (<300 nm) to the fibers, lamellae exist very densely and the *c*-axes of the crystal lattices were oriented along the longitudinal direction of the fiber. In the other region, a little away (>300 nm) from the fiber, a cross-hatched structure composed of the parent lamellae (whose *c*-axes were parallel to the fiber surface) and the daughter lamellae (whose *c*-axes were perpendicular both to the fiber surface and the parent lamellae), was observed. A schematic illustration of the lamellae orientation near the fiber surface was shown in Fig. 3 [77].

He and Porter [85] also reported that the TC of uniaxial gel-spun high modulus PE fiber/HDPE was found to be consisted of an inner and an outer zone. The inner zone, 2–3 μm thick, was composed of HDPE crystals nucleated on the PE fiber surface. Photomicrographs showed a well-defined region of row-nucleated HDPE

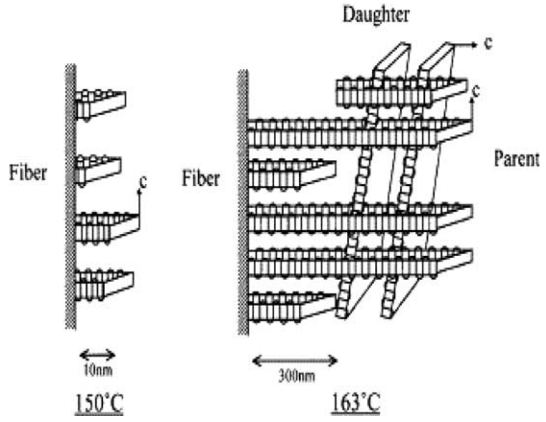

Fig. 3. Schematic illustration of lamellae orientation near the fiber surface [46].

on the surface of PE fiber, which meant that the fibrils of HDPE were found to grow out from the PE fiber axis and HDPE crystallites were oriented in planes perpendicular to the PE fiber surface axis.

Feldman et al. [86] studied the structural details of nylon-66 TC induced by aramid (Kevlar 29, 49 and 149) and carbon (pitch based) fibers, as determined by high spatial resolution X-ray diffraction. Using stepwise scanning, the orientation of the lamellae in the TC layer was measured as a function of distance from the fiber. The main observation was that the orientation was distinct for each system and almost independent of distance from the fiber. Of particular interest was the bi-layered TC formed on a surface treated Kevlar 49 fiber, in which the lamellar *a**-axis was nearly perpendicular and at an angle of ~12° to the fiber in the outer and inner layer, respectively. The crystallographic analysis generated grids of oriented lamellae with respect to the fiber axis.

3. Transcrystallinity in several semi-crystalline polymer composites

3.1. Transcrystallinity in iPP

iPP is a semi-crystalline thermoplastic polymer which is capable of crystallizing in four polymorphic forms, such as monocline (α), hexangular (β), triclinic (γ) and smectic form, under different conditions. Many types of fibers can induce TC of iPP to form on their surface, and configurations of TC may result in α, β or γ as well if crystallization conditions are controlled. So iPP is widely used for the research of TC.

HMCF is an effective nucleating agent for iPP, and can induce TC on its surface [46,87–92]. Studies by Varga and Karger-Kocsis [46] showed the interfacial morphologies of HMCF/iPP produced by isothermal crystallization in quiescent and sheared melts of iPP. In the quiescent melt, the HMCF generated α-TC due to it's strong α-nucleation ability. But in the sheared melt, achieved by pulling the HMCF slightly above the crystallization temperature, a transcrystalline-like supermolecular structure developed. TC formed under different crystallization temperature were also studied [90], based on the theory of heterogeneous nucleation, the interface free energy difference function $\Delta\sigma$ of PP on CF was determined and compared to that in the bulk matrix. From a thermodynamic point of view, TC was likely to take place on CF due to a lower value of $\Delta\sigma$, 1.14 erg cm^{-2}, when compared with that in the bulk, 1.23 erg cm^{-2}.

Whether GF could induce TC or not is debated to date. Some authors reported that GF could not induce the formation of TC [93,94], but when GF surface was modified by nucleating agents or coupling agents [45,59,95,96], or GF was pulled from the matrix to generate a shear field around the fiber during crystallization [2,31,32,57,97,98], TC might develop around GF. It was found that when GF was coated with an aminosilane coupling agent and then coated with AMPP, it would induce TC. Some impurities such as metallic compounds in AMPP acted as nucleating agents, and TC could occur even at a low cooling rate [59]. Wagner et al. [45] also demonstrated that TC could form at the surface of E-GF if appropriate nucleating agents (a 1% solution of the sodium salt of methylene bis (2,4-di-*t*-butyl phenol) acid phosphate in methanol, or a 1% solution of quinacridone pigment in dimethylformamide), were used to coat the fibers, and these agents could nucleate either the α or β crystal forms of PP. Zheng et al. [95] found that TC were generated at the interface of γ-APS treated GF-reinforced iPP when it was blended with MAPP, but fiber without treatment and or treated with γ-methacryloxypropyltrimethoxysilane (γ-MPS) did not lead to the formation of TC. These results are accordant with those achieved by Ishida and his colleagues [99,100]. The application of a mechanical stress at the GF/iPP interface during cooling of matrix might give rise to different crystalline superstructures (α or β-TC) [57], depending on the stress intensity and temperature. A typical bulk α spherulite was obtained in the vicinity of a single GF, where β-TC was initiated by a shear stress applied at 140 °C with the cooling rate of 0.2 °C min^{-1}, but when the sample was submitted to a shear stress during cooling at two temperatures (155 and 130 °C), another superstructure of α-TC with β bulk spherulites was developed. Misra et al. [2] found that slight mechanical stress at the fiber-polymer interface could give rise to surface nucleation and growth of TC layers. TC could be also formed when PP and chopped GF compounded in a single screw extruder at about 230 °C, due to the internal stresses developed during the injection molding, and internal stresses increased with increasing fiber population, so TC layers were enhanced. However, some other researchers thought that the superstructures induced by fiber through pulling it were not TC, but tanscrystalline-like structure, might be called "columnar crystal" [46,56,101,102]. They said that TC occurred *via* heterogeneous nucleation, whereas the later *via* self-nucleation. The basic difference between TC and cylindritic growth with α β bifurcation was summarized schematically in Fig. 4 [46]. Fig. 4 makes it obvious that a clear distinction should be made between TC and shear-induced or row-nucleated cylindritic crystallization, since the former is caused by heterogeneous nucleation, and the latter is caused by self-nucleation (a form of homogeneous nucleation).

Natural fibers are attractive as reinforcement in synthetic polymers because of their low price and density, high stiffness, biodegrability and recoverable resources. Gray [15] firstly reported the TC induced by NF (cellulose) in 1974. Various NF, such as sisal [20], jute [53,103], cellulose [4,15,29,39,50,104,105], flax [10], kenaf [106], bamboo [107] fiber, and so on, can be used for the formation of TC. Joseph et al. [53] found that when chemical modifications were made to sisal fiber using a urethane derivative of polypropylene glycol (PPG/TDI), MA-PP, and $KMnO_4$ in order to improve the interfacial adhesion between the fiber and matrix, a TC layer occurred at the interface. The thickness of the TC layer formed depended on crystallization temperature and time. The TC growth rate was slow in the quiescent state, on the other hand, upon the application of stress, TC developed quickly. Fiber surface modification by PPG/TDI increased the nucleating ability of sisal fiber to a very small extent. In the study of Mildner and Bledzki [103] of jute fiber (untreated and alkali treated)/iPP and jute fiber/MA-PP, it was found that the thickness of the TC layer varied with the cooling rate, with the system jute/MA-PP having the thickest TC layer at the lowest crystallization temperature (115 °C). Gray [15] pointed out that many of the effective nucleating agents contained carbonyl groups, and such groups might be well represented on the cellulose surface as ketone, aldehyde, or carboxylic acids residues. Further, no TC was induced on regenerated cellulose fibers, whereas the fibers which exposed a clean natural cellulose surface induced TC rapidly, the presence of lignin or hemi-cellulose on the fiber's surface inhibited TC. When PP was allowed to crystallize isothermally at different temperatures (125–133 °C) [104], a TC layer was created around the cotton fibers. The thickness reached 80–120 μm when crystallized for 15 min at 131 °C. The TC layers of different thicknesses were created by interrupting the isothermal crystallization at certain intervals and quenching the melt. Zafeiropoulos et al. [10] examined isothermal crystallization (ranges of 137–155 °C) from the melt of two different iPP in the presence of flax (Linum usitatissinum) fibers with four different types (green flax, dew retted flax, duralinw treated flax and stearic acid sized flax). They found that the fiber surface micro-roughness seemed to be an important factor affecting the morphology of the TC and the ability of the fiber to induce it. Stearic acid treated flax fibers inducing a TC layer was a new finding and the cooling rate from the melt to the crystallization temperature was found not to affect the morphology of the TC layer. If MAPP coupling agent was used to improve the stress-transfer efficiency in the kenaf fiber–PP composites [106], TC was observed for both uncoupled and coupled composites, although the growth rate of the coupled composites was higher than that of the uncoupled ones.

Recently, there is an increasing interest in the field of self-reinforced homogeneity polymer composites due to both their ideal recyclability and expected improvement of interfacial bonding. Li et al. [108] reported that TC layers in the iPP homogeneous composite through introducing the iPP fibers into their supercooled homogeneity matrices was a function of introduction temperature, and it was triggered by strong heterogeneous nucleation rather than the shear stress produced by fiber introduction. The interfacial TC layers of iPP which composed of purely α-form if the fibers were introduced at 138 °C. With increase of fiber introduction temperature, an increasing content of β-iPP surrounding the iPP fibers was observed. A TC layer of mainly β-modification iPP could be obtained when the fiber introduction temperature was set at 173 °C. The formation of rich α-iPP TC layer at an even higher fiber introduction temperature, e.g., 178 °C, was observed. Further study demonstrated that the melting state of the iPP fibers played

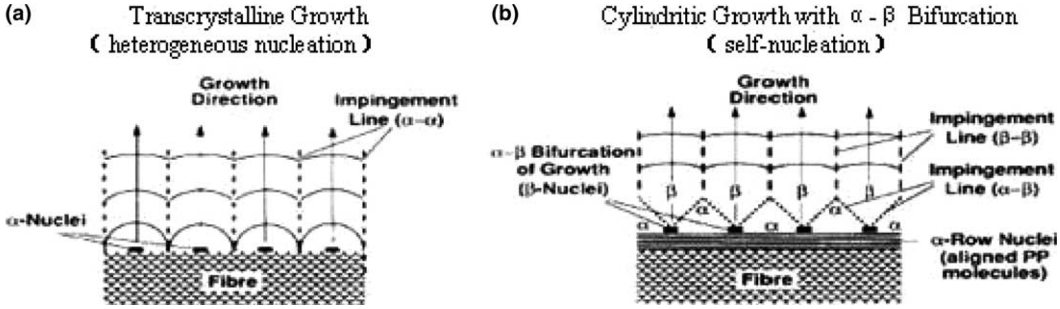

Fig. 4. Schematic diagram of the difference between TC layer and cylindritic crystallization [77].

an important role in generating the β-iPP. They [109] also reported that through vacuum evaporating a thin carbon film partially on the surface of iPP fiber, the nucleation ability of the molten iPP matrix in the course of recooling could be enhanced tremendously. The early formation and high density of the iPP row nuclei formed along the partially carbon-coated iPP fibers led to the formation of an apparent iPP TC zone in the vicinity of its precoated fiber.

Besides, other fibers, such as PTFE fiber [16,51,88,110,111], aramid fiber [52,112–116], PET fiber [48,71,117,118], PI fiber [14,88,119] and cupper [9,61], aluminum [25,61], talc [26], have been reported to induce TC of iPP. Dean and Register [116] obtained a mixture of α and γ TC by inserting a high weight fraction of HMCF or Kevlar 49 aramid fibers in iPP at atmospheric pressure, The proportion of the γ form depended on the fiber concentration, wherein 90% of fibers were required to obtain a significant proportion of γ, which decreased rapidly as the fiber concentration decreased. Li et al. [117,118,120–123] studied the crystal morphology of PET/iPP in-situ MFC, prepared by a slit extrusion-hot stretching-quenching progress, and found that TC was formed around the PET in-situ microfibers, and a shish-kebab structure could be observed as well. Three nucleation origins were proposed in the microfibrillar composite under a flow field: (a) the classical row-nuclei model; (b) fiber nuclei; (c) nuclei induced by fiber assistant alignment, and the last model provided a natural explanation for the case that TC only occurred in some fiber-reinforced composites under flow rather than without an external field. The TC of iPP was reported to be induced by PI fiber with different nucleation ability [14]. The TC layer had a composed structure, with a characteristic layer adjacent to the fiber surface. The layer was about 1 μm thick and had a crosshatched lamellar morphology. At the interface between iPP and the PI fiber which could induce TC, the nuclei from which the TC zone grew were observed. The nuclei consisted of sheaves of closely packed parallel needle-shaped lamellae of uniform thickness. The TC could be explained by the epitaxial crystallization of iPP matrix on the surface fragments (domains) formed by extended chains of PI fibers. The TC layer of iPP could only be produced if the alumina fiber was pulled through the supercooled matrix [55], both α-monoclinic and β-hexagonal crystal structures were identified in the TC, with the β crystal only being induced in areas which existing α crystals. The α region transformed into β crystals except for a small region at the fiber/matrix interface. The β crystals grew at a faster rate than α crystals and were found to melt at 157 °C, compared to 170 °C for the α crystals.

Some researchers have compared the nucleation ability of different fibers [3,18,24,47,70,88,113,119,124]. Manchado et al. [124] studied the effects of the incorporation of different types of fibers, such as PET, aramid fiber, GF and sisal fiber, on the crystallization kinetics and thermodynamics of iPP. The crystallization kinetics of composites was successfully described by the Avrami model. The fibers behaved as effective nucleating agents and TC took place in all kind of fibers studied, but aramid fibers were the most effective in promoting TC. Ton-That and Jungnickel [119] found that TC developed between all polymeric substrates PI, PTFE, and PET. Metallic substrates like steel, copper, and aluminum yielded, in no case, TC, and GF did not promote TC either. The thicknesses of the TC layers increased severely with decreasing cooling rate if they did develop. By suitable choice of the cooling rate, the structure could then be controlled between purely spherulitic and completely TC. Cai et al. [18] studied the TC of iPP on different fibers (CF, GF, and aramid fiber) conducted in a temperature gradient. The UHMCF, the HMCF, and the aramid fiber showed sufficient nucleation ability to form TC of iPP in certain temperature ranges. Among them, the UHMCF showed the best nucleation ability. On the contrary, the intermediate-module CF, the high-tenacity CF, and the E-GF showed too low nucleation ability to form TC. One efficient way to induce TC on these fibers was proved by pulling the fibers in supercooled iPP melts. The interface shear and temperature gradient between fiber and supercooled matrix melt on crystallization were considered to be two important factors for the formation of TC. Thomason and Van Rooyen [3] found that the occurrence of TC depended on the type of fiber used and the crystallization temperature. The aramid fibers and HMCF do induce TC, whereas high-strength CF and GF did not. However, the ability of aramid fibers and HMCF to induce TC in PP was dependant on the crystallization temperature, and no TC was observed in quiescently crystallized PP above 138 °C.

3.2. Transcrystallinity in PE

Reinforcing a common polyethylene with PE fibers leads to a strong and stiff single polymer composite [125]. HDPE [68,85,126–129] is often used as the matrix for the studies of TC, while the fiber reinforcements are usually its homogeneity fiber [68,85,127–133], namely PE fibers.

Von Lacroix et al. [127] studied the TC of ultra-high-molecular-weigh polyethylene (UHMWPE) fibers/HDPE composites, and found that the surface crystals on UHMWPE fibers acted as nucleation centers for the high density PE matrix, which might result from epitaxial crystallization. After crystallization from the melt, a TC layer was found having lamellar crystals grown perpendicular to the fiber axis which was independent of air-cooled or isothermal crystallization conditions. Vaisman et al. [128] reported that the UHMWPE fibers treated by photochemical bromination, through offering a higher concentration of crystallization nuclei, generated a denser TC layer with higher specific radial orientation with respect to the fiber axis – compared with the untreated fiber. He and Porter [85] reported that aided by the similarity between the HDPE matrix and uniaxial gel-spun high modulus PE fiber, TC of HDPE melt on the PE fiber surface was generated without nucleating agents employed. The TC growth was found to be consisted of an inner and an outer zone. A higher PE fiber fraction in the composites increased the nucleation density and produced more TC at a higher temperature. The isothermal crystallization of a single PE composite with 50 wt% fiber fraction showed dual-step crystallization, corresponding, respectively, to the TC of HDPE on the PE fiber and the crystallization in the bulk of HDPE. The gel-spun ultrahigh-modulus PE fiber exhibited very good nucleation ability toward linear high-density polyethylene (LHDPE) as seen from a uniform TC zone [68]. A new approach based on induction time was used to obtain an estimate of $\Delta\sigma$, which was calculated to be 0.3 erg cm^{-2}, indicating that TC was energetically favored.

MFCs [134], for example, PET microfibrillars reinforced LDPE, were processed under industrially relevant conditions *via* injection molding in a weight ratio of PET/LDPE = 50/50, and dog bone samples with MFC structure were obtained. By means of TEM on stained ultrathin slices one could observe the formation of TC layers of LDPE matrix on the surface of the PET microfibrillars. In these layers the crystalline lamellas were aligned parallel to each other and were placed perpendicularly to the fibril surfaces. This was in contrast to the bulk matrix where the lamellae were quasi-randomly arranged. NdFeB magnetic powder had a remarkable heterogeneous nucleation effect on HDPE matrix [126], and led to the formation of TC in the interface region and made the DSC melting peak split into multiple peaks and moved to higher temperature. NdFeB filler also restricted the spherulites' propagation, resulting in more defective crystals. But the crystal type was unchanged. When the recycled short GF [135], remained by LDPE residual matrix, were used with new PE matrix, the residual matrix could recrystallize to form a TC layer. The size of this layer seemed to depend on the amount of the residual matrix. Stern et al. [75,76] found a smooth and banded TC morphology in PE based single-polymer microcomposites which developed under ice-water quenching and air cooling conditions, respectively, corresponding to smooth and banded spherulites in the matrix. However, Teishev et al. [136,137] found that there was no TC occurred in single-polymer PE composites under rapid cooling conditions, even for chemical or plasma surface-treated fibers.

3.3. Transcrystallinity in PA

Polyamide is also one of the typical semi-crystalline polymers which can develop TC when reinforced by certain fibers [11,72,82,83,138–150]. The TC of the GF/PA6 composite interfaces were obtained by Cartledge and Baillie [11] which achieved in the slow cooling process, and disappeared with increasing cooling rate during thermal processing. The slow cooling led to thicker lamellae formed than that of fast cooling process. It was reported by Clark et al. [143,144] that TC occurred in the composites of E-GF or HMCF reinforced PA66 composites. Adding poly (vinyl pyrrolidone) PVP to the composites as either a matrix diluent or a fiber sizing had a dramatic influence on the morphology of PA66. The diluent removed the TC region when applied as a fiber sizing by reducing the nucleation density on the fiber surface. When PVP was added as a diluent only in trace amounts, the TC was allowed to grow substantially in size. If PVP was then also added as a sizing to these composites, the size of the interphase was reduced. Therefore, by means of this blending procedure, the interphase could be 'tailored' depending upon the concentration and location of the PVP. Single-filament composites of E-glass embedded in PA66 showed that, as the morphology was changed from TC to spherulitic by adding PVP as a fiber sizing, the average interfacial shear strength is decreased. Furthermore, when PVP was also added to the matrix, TC morphology returned in the composites, and no interfacial shear strength decrease was found. Fakirov et al. [140,142] prepared MFCs of PET/PA12 through heating to a temperature between the melting temperature of the two components, cold drawing, isothermal crystallization, and subsequent cooling. The authors found that PET microfibrillars were not only effective nuclei for TC of PA12 molecules, but also caused their reorientation by 90° with respect to their initial direction, i.e., it was perpendicular to the main chain direction of PET molecules in the microfibrillars. Such a TC with reorientation was reported for the first time. Yu et al. [147] found that Kevlar fibers (chemically treated), had an improved nucleation ability to induce TC of PA6 and PA11 compared to ones that washed. Chemical treatments performed on the fiber were found to affect the size of the TC zone and its crystal structure for PA11, but no change in the crystal structure was observed for PA6. At crystallization temperatures ranging from 100 to 220 °C [148], the TC interphase always occurred. The thickness of the TC layer was temperature dependent, but independent of the geometry characteristics of the reinforcement. Incardona et al. [149,150] studied the TC of CF/J-polymer (a kind of polyamide homopolymer produced by Du Pont), and found that the TC layer grew linearly with time and its growth rate reached a maximum at 240 °C. Both the spherulitic and TC growth rates increased sharply in the range 245–240 °C, while keeping almost constant at very low value for higher temperature (up to 275 °C).

3.4. Transcrystallinity in PEEK

CF is often applied to induce TC for PEEK matrix [19,62,69,151–156], and aramid fiber [157] can induce TC of PEEK as well. It was reported by Lee and Porter [62] that the repeated melting (at 396 °C) of the same PEEK sample resulted in a decrease of the number of nuclei for crystallization induced by CF. At equivalent thermal histories, PEEK with CF was found to have a higher nucleation density than PEEK itself. The surface of CF and nuclei in the PEEK matrix compete for crystallization growth. As the holding time in melt was increased, the number of matrix spherulites formed on cooling decreased; hence a more pronounced TC region was developed. Zhang et al. [153] found that the nucleation rate on the CF decreased greatly with increasing crystallization temperature and fell slightly when melting temperature was rather low. TC of PEEK appeared in a wide crystallization temperature range of 280–315 after PEEK was melted at rather high temperature. TC formation occurred only when the nucleation on the fiber was unaffected and a sufficient number of nuclei appeared on the fiber. Linear growth rates of TC at various temperatures were similar to those of the spherulites in the bulk, and the thickness depend on the crystallization and melting temperatures. Variation of the molecular weight of PEEK within a small range had no obvious influence on its nucleation rate on the fiber, but affected the TC growth rate. They also found that TC formed very easily at the interface of PEEK with phenolphthalein poly (ether ether sulphone) (PES-C) on CF, compared with CF/PEEK system [155]. The thickness of the TC in which PES-C was interfibrillarly incorporated varied linearly with time, and its growth rate depend on PES-C content and crystallization temperature. Korbakov et al. [157] studied dielectric spectroscopy of aramid fiber-reinforced PEEK for the first time, wherein the effect of the fiber on the dielectric response was examined for both amorphous and crystalline PEEK over wide temperature and frequency ranges. Whereas the temperature behavior of the dielectric losses of the materials exhibited the typical α and β processes of PEEK, the specific effect of the fibers in the crystalline PEEK was revealed in shifting the α process to a higher temperature. The unique effect of the fibers was expressed by a significantly higher activation energy and lower dielectric strength for the α relaxation, reflecting a higher constraint level that was imposed by the fiber. It was proposed that this additional constraint was associated with fiber generated TC.

3.5. Transcrystallinity in PPS

PPS represents a high temperature resistant, semi-crystalline thermoplastic polymer with improved mechanical properties that has been mainly used as matrix material for fiber-reinforced composites in recent years. Auer et al. [158], Desio and Rebenfeld [159,160] have reported their studies of the crystallization of CF, GF and aramid fiber reinforced PPS composites. In Auer and his coworkers' [158] study, they found that aramid fiber/PPS had a much shorter half-time of crystallization than CF/PPS and GF/PPS systems attributed to the high nucleation effect of aramid fiber surface to PPS. As a consequence of the high nuclei density a TC zone was built up around the aramid fiber. According to Desio and Rebenfeld' work [159,160], the authors reported that there was no TC occurred in GF/PPS system, and the degree of crystallization showed nonlinear crystallization temperature dependence for those systems that exhibited TC. Meretz et al. [161] also studied the TC of CF/PPS composites by single-fiber pull-out test. Two types of untreated and unsized CF were investigated, a high-modulus type with an active surface induced TC and a high-strength type with an inactive surface had no TC developed around its surface.

3.6. Transcrystallinity in other matrices

Tanscrystallinity developed in other polymer matrices, such as syndiotactic polypropylene (sPP) [7,91], PET [162,163], poly (ε-caprolactone) (PCL) [164,165], PBT [166], liquid crystalline polymers [44,72,167,168], polycarbonate (PC) [169], sPS [23,170], Mcl-PHAs/cellulose composites [171,172], Polychlorotrifluoroethylen (PCTFE) [173], and so on, have been reported in the available literature (or up to now).

Wu et al. [7,91] reported for the first time that TC induced in sPP when a HMCF was embedded in the melt of sPP crystallizing under quiescent conditions, high-tenacity CF, on the other hand, did not cause TC growth. Coating of HMCF by silicon carbide (SiC) stopped the TC of sPP.

Sajkiewicz et al. [163] studied the nonisothermal crystallization of PET during cooling with constant rates. The results were analyzed using the Ozawa model for nonisothermal crystallization. It was shown that this model described the nonisothermal process only at relatively low cooling rates. At rates exceeding 20 °C/min, crystallization progress became higher, indicating higher crystallization rates than those resulting from the Ozawa approach. Additional deviation from the Ozawa model observed at the very beginning and the end of crystallization could be attributed to spatial constraints of spherulitic growth. In the first case, the spherulitic growth was impeded by the dense instantaneous nucleation on the polymer surface (TC) and in the second one by impingements of bulk growing spherulites.

The surface induced crystallization of PCL on an UHMWPE fiber had been investigated by Ishida and Bussi [164]. They found that PE fibers exhibited a high nucleating ability toward the PCL melt as seen from a regular TC growth front and from a low value of the free energy difference function. The induction time approach had proved to be a valuable tool in the study of energetics of TC process, and the classical theory of heterogeneous nucleation was not applicable in this case. The interfacial morphology could be controlled when the temperature dependency of the induction time for the fiber and for the melt was known. In particular it was possible to grow large all TC composite films. They thought that epitaxy was believed to occur in PE/PCL composites because of a very good lattice matching between the fiber and the matrix.

Huang and Petermann [44] developed two technical methods, placing the cold fibers into the polymer matrix and drawing the fibers embedded in the matrix at the crystallization temperature to create perfect TC growth for both thermoplastics and liquid crystalline polymers. The formation of nuclei with high density along the fibers or on a two-dimensional unit and the suppression of the nucleation in the matrix were necessary for the formation of the TC growth. In compared with the formation of oriented spherulites of polymers in the thermal gradient, it was cleat that the steric hindrance was a key factor to create the TC growth in isothermal crystallization.

Although PC is considered to be an amorphous thermoplastic it can be crystallized to some degree by prolonged heating at elevated temperatures. Wood et al. [169] reported that an isothermal treatment at 190 °C for 64 h, the TC grown adjacent to the surface of a carbon fiber embedded in PC was observed, with a thickness of 9 μm. The growth of the layer was linear with time at the isothermal temperature without an apparent change in the amorphous nature of the bulk matrix. However, only after isothermal crystallizing for 106 h, was the bulk crystallization found.

Wang and Chen [23] studied the surface-induced crystallization of sPS on HMCF, and found no difference in the crystal growth rate of sPP in either spherulites in the bulk or TC layers at the interface. The efficiency of HMCF to induce the TC layer was better in sPS matrix than that in iPP matrix based on the surface energies of the constituents. In addition of HMCF, several other fibers, such as PTFE, Kevlar 49, acid-treated copper wire, and so on, are used for a preliminary study of the development of sPS TC layers [170].

4. Influences of transcrystalline layer on interfaces and mechanical properties of fiber/semi-crystalline polymer composites

The mechanical properties of fiber-reinforced polymer composites are primarily dependent upon the following three factors: (1) strength and modulus of the fiber, (2) strength and modulus of the matrix, and (3) effectiveness of the bond between fiber and matrix in transferring stress across the interface [174]. These factors are basically determined by the microstructural details of these materials which include TC of the interface, crystallinity and spherulite size of the matrix which are, in turn, controlled by thermal processing of these materials. The interfaces between the fibers and the matrix in the composite materials are widely regarded as the most important factor determining their mechanical properties. In addition, TC has a significant effect on various mechanical properties. The effect of TC on the mechanical properties will depend on its thickness and thereby on the fiber volume fraction. The largest mechanical effects are expected for high fiber contents where the *c*-axis of the epitaxially nucleated TC layer is mostly aligned in the fiber direction. However, as yet few measurements of such effects on bulk composite samples have been conducted, and it is still debatable as to whether TC increases or decreases the interfacial strength, consequently affecting the performance of thermoplastic composite materials. Moreover, the nature of the crystalline phase affecting the mechanical properties of these materials has never been systematically investigated [175]. These disputes are probably result from the difference of fiber/polymer systems and processing conditions, simultaneously, matrix morphology, the crystallization structure around the fibers, the shear strength of the matrix, and the interaction of the fiber/polymer have diversity as well. A number of mechanical tests have been developed to determine the effective adhesion and stress transfer from the matrix to the fiber in a composite. These include tests on single-fiber composites and those conducted on real composites. The most commonly used tests on single-fiber composites are single-fiber pull-out test [51,115,161,176], single-fiber fragmentation test [55,91,169], microorientation test and microdebond test [143,165].

4.1. Interfacial properties

Many researchers have found that the formation of TC can improve the interfacial properties [10,19,21,39,48,59,87,91,95,104,115,130,143,150,153,161,169,177–181]. Nagae et al. [59] studied the fragmentation test of GF (coated with AMPP) and iPP composites with TC. The results showed that the interfacial adhesion between GF and matrix PP was so good that fracture at the surface was transferred to PP matrix. The interfacial shear strength was drastically improved from

6 to 24 MPa. Both the flexural strength and notched lzod impact strength were significantly improved. The same conclusion was made by Heppenstall-Butler et al. [176] who had investigated the pull-out behavior of iPP/arimid fiber composites. Three matrix morphology types, two TC (fast-cooled and slow-crystallized) and one spherulitic (slow-crystallized) were compared. The debond shear stress was of the order of 10MPa for three morphologies. The mean interfacial frictional shear stress of the two TC samples was similar at ~2.2 MPa, higher than that of the spherulitic sample (~1.5 MPa).

Meretz et al. [161] investigated the single-fiber pull-out measurements performed with samples containing HMCF and high-strength fibers that had been subjected to different thermal treatments. They found that TC led to a prevailing brittle fracture process in the interface and to a higher value of the apparent shear strength. Samples with high-strength fibers and high crystallinity showed ductile fracture behavior at a high apparent shear strength lever.

Zhang et al. [153] found that the formation of TC in CF/PEEK composites improved the characteristic of the composites as tensile stiffness, strength and toughness, enhanced fiber/matrix adhesion, and reduced stress concentration and cavitation at the fiber ends. The predominant deformation mechanism of the composites was changed from cavitation to shear progress in the presence of TC, and moreover, significant local plastic deformation that absorbed more energy occurred, resulting in cohesive failure of the composites instead of adhesive failure happening to the composites without TC layers.

Salehi Mobarakeh et al. [182] studied chemical modifications of the surface of Kevlar fiber as a means of improving fiber–matrix adhesion. The fiber surface was used as a polymerization support for interfacial polycondensation. Nylon66 was successfully polymerized in this way. An increase of the TC layer thickness was observed through optical microscopy, indicating better fiber–matrix adhesion. Both plasma treated fibers having been submitted or not to chemical treatments were used as reinforcements for nylon-66 unidirectional composites. Improvement of the mechanical properties was related to better interfacial interactions due to grafted nylon chains.

The influence of thermal history on the interfacial load transfer efficiency and fiber failure in CF/PP microcomposites was studied by Nielsen and Pyrz [87]. The results indicated that the TC affected the load transfer efficiency by increasing the maximum interfacial shear stress. The load transfer mechanism was primarily frictional, as seen from the linear strain distribution, but a slight nonlinearity of the strain profiles, particularly for the TC samples might indicate other mechanisms than pure friction. This could be explained by the nucleation on the fiber. Furthermore, the anisotropy of the mechanical properties was offered as an explanation for the improved load transfer efficiency. The study of Felix and Gatenholm [104] on single-fiber fragmentation test of cellulose/PP composites also showed that the TC morphology at the fiber/matrix interface improved the shear transfer considerably when a tensile load was applied in the fiber direction. One mechanism proposed by the authors was slow cooling favors the kinetics of the approach of PP molecules, and hence interfacial adsorption, which yielded an ordered TC PP interphase having a high density of intermolecular secondary bonded with the cellulose surface.

In the study of Wu et al. [91], the interfacial adhesion was enhanced further by TC growth of sPP induced by a HMCF. However, a poor interfacial adhesion existed between iPP and HMCF even in the presence of TC. The interfacial shear strength was at about 80% of the yield strength of sPP which was considerably higher than the ‘reference’ iPP/CF system (where the interfacial shear strength was at 20% of the yield strength). Matrix yielding and interfacial debonding were the dominant failure mechanisms for the sPP/HMCF and iPP/HMCF microcomposites, respectively. The fraction and the location of the amorphous phase along with a peculiar lamellar orientation in the TC layer were suggested to be responsible for improved interfacial shear strength.

Jeng and Chen [151] studied the flexural failure mechanisms in injection molded CF/PEEK composites. The TC layer enhanced the fiber/matrix adhesion, improved the flexural deflection and strength of the composite, and changed the flexural damage approach of the composites. Multiple shallow and deep shear cracks were observed in the compression side of the damaged specimen. The appearance of the load/deflection curves and the fractography suggested that compressive cracks occurred first; the stress concentration under the loading nose and the shear stress maximum induced the upper shear cracks which blunted the propagation of the compressive crack. The tension crack then initiated from the tension side, met with the lower shear crack near the core region, and resulted in catastrophic failure.

Moon [97] introduced a new method to form resin droplets on fibers, and GF/PP single-fiber pull-out test samples were prepared using this method. The results showed that TC formed at the interface between the GF and PP resin improved the interfacial strength when no spherulites developed in the PP matrix. On the other hand, it had been found that when the spherulites were well developed in the PP matrix, the TC formed at the interface reduced the interfacial strength. Finally, rapid cooling had been shown to improve the interfacial strength.

4.2. Longitudinal properties

The existence of a TC layer in semi-crystalline thermoplastic unidirectional composites has been shown to improve the fiber-dominated longitudinal strength and modulus significantly [154]. From 'rule-of-mixtures' calculations, the contributions of the TC layer are approximately one order of magnitude greater than those of the bulk crystalline matrix. In general, a number of cases has been reported, where property enhancements have been recorded that could not have been attributed directly to improvements in the performance of the crystalline matrix. The suggested explanation, which is based on a series of studies aiming to link the mechanical performance to microstructure, attributes the effect of the TC layer to a preferred crystallite orientation relative to the fiber, thereby conferring on the matrix in the fiber direction higher strength and rigidity and reduced thermal expansion, which in turn improve directly the corresponding properties of the composite and reduce the residual thermal stresses [136,145,154,169,183,184].

A study relates to the influence of the degree of crystallinity on the static and dynamic mechanical properties of CF reinforced PEEK composites were carried out by Tregub et al. [154]. The authors reported that the flexural modulus and strength, as well as the fatigue life, are significantly higher for the maximum 35% crystallinity, compared with the 10% minimum, obtained by the longitudinal direction with respect to other loading angles was attributed to relieving of the residual thermal stresses by the TC.

Nuriel et al. [82] reported that the improvement in the longitudinal properties of unidirectional composites was inversely dependent on the thickness of the TC layer. Both the stiffness and strength increased as the thickness decreases. This result was taken as a valid proof of the assumption that an effective contribution of the TC layer was generated only when the *c*-axis (chain axis) of the polymer in the TC layer was parallel to the fiber. Moreover, this result corresponded to the experimental observation that the TC layer grows by a shearing mechanism [83] which determines the thickness dependent orientation of the *c*-axis.

Barber et al. [112] observed the longitudinal damage in a TC of Kevlar/iPP under the effect of a transverse notch, propagating in a direction perpendicular to the axis of a Kevlar fiber, and found that a Cook–Gordon-like damage mechanism was active. The damage growth rate in the TC layer, paralleled to the fiber axis, was larger in thinner layers. The damage induced in the TC layer by the stress emanating from the notch tip first appears as a transverse, dark, fine micro-cracking formation (termed "treeing"). The fine cracks rapidly merged into a full, dark region, which propagated parallel to the fiber length as the notch came closer to the fiber. This was not a classical Cook–Gordon mechanism as no physical separation of TC layer material from the fiber occurred. Rather, the TC layer as a whole was 'sensing' the enhanced stresses and local deformation – or partial damage – of the layer results, rather than physical separation. Therefore, they claimed that the damage mode involved in the thermoplastic-based composite was not a classical Cook–Gordon mechanism, but was termed a Cook–Gordon-like mechanism. The length of damage area of TC layer was linear to the stress applied.

The tensile behavior of PP/PP composites was studied by Kitayama et al. [77]. Polarized optical micrographs of the cross section around the single fiber before and after the tensile tests showed that the interface was not destroyed and the TC layer was stretched along the tensile direction. When the composites were stretched to break in the transverse direction, even after the tensile tests, the surface was as smooth as that of the original fiber in the sample molded at 150 °C, indicating that interfacial debonding occurred. Tensile tests which calculated from the law of mixture, in the 0° and 90° directions showed that: in the longitudinal direction, the coefficient α_0 was 0.79, which was lower than 1; on the hand, in the transverse direction, the coefficient α_{90} was 1.03, which was near about 1. This means that the TC layers improve the tensile properties of the PP/PP composites in the direction perpendicular to the fiber. Furthermore, these results agreed with the results reported by Teshev and Marom [136], which showed that with the occurrence and growth of TC of UHWPE/HDPE composites had a negligible effect on the composite mechanical properties in the longitudinal direction, where it resulted in a 50% decrease of the transverse tensile strength and strain to failure.

A scanning force microscope was fitted with an elongated, blade-like tip, with which nanoindentations were performed in the TC-iPP phase grown from the surface of HMCF by Amitay-Sadovsky et al. [88,185]. The anisotropic Young's modulus was evaluated by measuring the force-penetration curve of the indentation and the tip topography, as a function of the indentation depth. Anisotropy in the mechanical properties of a TC layer may be revealed only when long and narrow indenters such as Knoop tips (at the micrometer level), or Knoop-like tips (at the nanometer level) were used. At the nanometer scale the Young's modulus was 1.6 to 3 times higher in the direction perpendicular to the TC growth direction, as compared to the modulus within the growth direction. At the micrometer scale this ratio was only 1.2, which indicated a loss in anisotropic features at progressively larger scales.

4.3. Transverse properties

Cartledge and Baillie [175] found that cooling rate during thermal process had significantly affected the mechanical and interfacial properties of the GF/PA6 composites. Slow cooling resulted in a better interfacial bond between the GF and PA6 matrix than that of fast cooling. It led to a high maximum tensile stress and elastic modulus in the transverse flexural test. These results could be attributed to the high TC achieved in the slow cooled GF/PA6 samples. The high crystallinity and high content of the α phase in the slow cooled PA6 matrix contributed to the high tensile strength and elastic modulus in the transverse flexural test as well.

Karger-Kocsis et al. [115] prepared fully TC, fully spherulitic specimens, and single Kevlar fiber microcomposites for iPP with positive, negative, or mixed birefringence and annealed condition. It was showed that the optical birefringence change of iPP was related to the contribution of cross-hatch lamellae. The interfacial shear strength was determined by means of a modified single-fiber pull-out test. Specimens with positive birefringence (or dominantly cross-hatched lamellae) hinder the thermal expansion of radial lamellae and decrease the interfacial strength. The more radial lamellae increased the radial stiffness relative to the tangential one, and produced higher normal stresses on the fiber surface. This stiffness enhancement within the TC layer caused by the higher crystallinity and radial lamella's fraction could be the major reason which improves the normal compression stress. The results revealed that the optical birefringence in the TC layer significantly affected the interfacial shear strength, which was related to the mechanical friction, thermal mismatch and the crystallinity.

4.4. Other physical properties

Effects of CF surface modification on the crystalline structure and both electrical and mechanical properties of conductive CF/HDPE films were studied by Mironov et al. [186]. Three different types of surface-treated CF (epoxy-sized, unsized, and sized but thermally treated) were considered. It was found that the uniformity of the TC zone around CF and the overall crystallinity of the PE matrix decreased when epoxy-sized CF was used. Epoxy-sized CF caused a significant reduction not only in electrical resistivity and temperature coefficient of resistivity (TCR) but also tensile strength and coefficient of linear thermal expansion (CLTE) of composite films compared with that of unsized or sized CF that was thermally treated. The authors observed the systematic changes of TCR and CLTE values in accordance with CF surface modification and CF content in composite films. It was concluded that thermal expansion of the polymer matrix was the main reason for the positive TCR of CF/HDPE films. As the most probable reasons for decreased resistivity and strength of the CF/HDPE films with epoxy-sized CF, the diffusion of epoxy sizing agent into the polyethylene matrix and the formation of loosened semiconductive interphase structure in the film were considered.

Nielsen and Pyrz [8] studied the influence of a TC layer on the thermal residual stress distribution in composites and found that the TC layer resulted in high thermal residual shear stress. This was explained by anisotropy in the TC layer resulting in higher radial thermal expansion and thus higher radial stress. However, Marom [183] attributed the effects of the TC layer to the transcrystals having a preferred orientation relative to the fibers, thereby providing the surrounding matrix with a high rigidity and reduced thermal expansion in the fiber direction, which effectively lowered the residual thermal stresses.

Saujanya and Radhakrishnan [48] found that the mechanical properties *via* impact strength and tensile modulus showed enhancement for the PET fiber/PP composites with the TC as compared to pure PP. The results could be understood in terms of high aspect ratio for PET fibers, TC morphology, good fiber/matrix adhesion and nucleating ability of PET fibers in PP matrix.

Amash et al. [39] found that cellulose would trigger TC of PP and the interfacial adhesion would be improved. The dynamic mechanical spectra of the composites revealed an increase in the stiffness and a reduction in the damping values with increasing fiber content. Increasing draw ratio, the uniaxial elastic modulus was considerably enhanced.

Wendt [133] reported that the parallel and more perfect arrangement of the chain segments in TC of LDPE induced by HDPE resulted in a higher melting temperature, a difference in unit-cell spacing and a less ductile behavior during fracture than with spherulitic LDPE.

Folkes and Hardwick [187] reported that the modulus of the TC was higher than that of the bulk, and the strain to failure in a TC layer of PP was only 4% versus 300% for a spherulitic sample. Shanks [188] and Kwei et al. [189] both reported that the Young's modulus was higher compared to that in the spherulitic areas. Hata et al. [111] investigated the mechanical properties of TC layer. They prepared an all TC film of PP with more than 300 mm thickness between two sheets of PTFE. The TC film could be stretched up to 800% accompanied by the development of opacity and necking. However, the spherulite film could be stretched up to 30% at maximum, exhibiting brittle fracture. Klein et al. [183] studied the behavior of interfacial TC in aramid fiber/PA66 composites using a dynamic mechanical thermal analyzer. The strips of all-TC specimens were cut from the microcomposite samples using a microtome. For the TC layer, the damping energy was half reduced, and the dynamic modulus was double when compared to the respective properties of the crystallized matrix.

Wagner et al. [43] obtained both α and β TC of E-GF/PP composites by coating GF with appropriate nucleating agent. The occurrence of TC was found to allow a new damage mechanism to take place in microcomposite samples under tension, consisting of interlamellar separation in the TC region. The interlamellar fractures form preferentially at the interface well before any bulk matrix damage occurred. The density of this damage zone was higher in TC of the β crystal form than that of α form, although it was found that in the α form the damage could propagate into the matrix. The occurrence of this damage mechanism suggested that toughness may potentially be obtained by careful design of the interfacial TC region in E-GF/PP composites.

5. Conclusions

Transcrystallinity is a unique morphology of the fiber reinforced semi-crystalline polymer composites. Since it was discovered in 1952, it never fails to attract people's attention due to its mystery and interesting. A number of factors may influence the formation and growth of TC, the significant ones are as follows: polymer matrix (crystallinity of substrate, mismatch of thermal coefficients between the fiber and the matrix, epitaxy between the fiber and the matrix), fiber parameters (the nature, surface toughness, thermal conductivity, treatment of fiber, and so on), and processing conditions (cooling rate, temperature, interfacial stress, and so on). Kinds of fibers can trigger TC of various matrices under diversified conditions. However, the studies of TC are vast but the formation and growth mechanisms are not yet fully understood. The formation of TC is deemed to improve the interfacial strength mechanical properties by some people but it is reported to have no effect, or even a negative effect on the interfacial and mechanical properties. These disputes are probably result from the difference of fiber/polymer systems and processing conditions, simultaneously, matrix morphology, the crystallization structure around the fibers, the shear strength of the matrix, and the interaction of the fiber/polymer have diversity as well. All of these require further and deeper studies of TC.

Many approaches have been introduced to the investigation of transcrystallinity, however, the majority of the systems that were used to develop TC are usually the single-fiber/polymer composites, which are quite different from the industrially available fiber reinforced polymer composites. The effects of TC on the mechanical properties of composites are often measured by single-fiber pull-out test, single-fiber fragmentation test, microorientation test, microdebond test, etc. The results, got from these experimentations based on single-fiber/polymer composites, are microcosmic properties which can not reflect its actual influences. So improved or innovative methods should be developed and applied in the TC investigation.

Recently, several researchers started to investigate the TC in the samples/parts obtained by injection molding, extrusion and other processing approaches. MFCs, being the hotspot now, are also brought into the research of TC. Microfibrils can act as heterogeneous nucleating agents and induce TC around them under certain conditions. These microfibrils are quite different from macroscopical fibers, so TC triggered by them maybe extremely interesting and worth to be detailedly investigated. These all provide us some good ideas of studying TC.

Acknowledgements

The authors gratefully acknowledge the financial support from the National Natural Science Foundation of China (Grant No. 50103007, 29934070) and Sichuan Youth Science and Technology Foundation (China) (Grant No. 04ZQ026-037).

References

[1] Jenckel K, Tcege E, Hinrichs W. Kolloid-Z 1952;129:19–24.

[2] Misra A, Deofpura BL, Xavier SF, et al. Transcrystallinity in injection molded polypropylene glass–fiber composites. Angew Markomol Chem 1983;113(4):113–20.

[3] Thomason JL, Van Rooyen AA. Transcrystallized interphase in thermoplastic composites. 1. Influence of fiber type and crystallization temperature. J Mater Sci 1992;27(4):889–96.

[4] Quillin DT, Caulfield DF, Koutsky JA. Crystallinity in the polypropylene/cellulose system. 1. Nucleation and crystalline morphology. J Appl Polym Sci 1993;50(7):1187–94.

[5] Billon N, Magnet C, Haudin JM, et al. Transcrystallinity effects in thin polymer-films – experimental and theoretical approach. Colloid Polym Sci 1994;272(6):633–54.

[6] Billon N, Haudin JM. Influence of transcrystallinity on DSC analysis of polymers – experimental and theoretical aspects. J Therm Anal 1994;42(4):679–96.

[7] Wu CM, Chen M, Karger-Kocsis J. Transcrystallization in syndiotactic polypropylene induced by high-modulus carbon fibers. Polym Bull 1998;41(2):239–45.

[8] Nielsen AS, Pyrz R. A Raman study into the effect of transcrystallisation on thermal stresses in embedded single fibres. J Mater Sci 2003;38(3):597–601.

[9] Lin CW, Ding SY, Hwang YW. Interfacial crystallization of isotactic polypropylene molded against the copper surface with various surface roughnesses prepared by an electrochemical process. J Mater Sci 2001;36(20):4943–8.

[10] Zafeiropoulos NE, Baillie CA, Matthews FL. A study of transcrystallinity and its effect on the interface in flax fibre reinforced composite materials. Compos Part A-Appl S 2001;32(3–4):525–43.

[11] Cartledge HCY, Baillie CA. Studies of microstructural and mechanical properties of nylon/glass composite. Part I. The effect of thermal processing on crystallinity, transcrystallinity and crystal phases. J Mater Sci 1999;34(20):5099–111.

[12] Mukhopadhyay S, Deopura BL, Alagiruswamy R. Interface behavior in polypropylene composites. J Thermo-plastic Compos Mater 2003;16(6):479–95.

[13] Loos J, Schimanski T, Hofman J, et al. Morphological investigations of polypropylene single-fibre reinforced polypropylene model composites. Polymer 2001;42(8):3827–34.

[14] Sukhanova TE, Lednicky F, Urban J, et al. Morphology of melt crystallized polypropylene in the presence of polyimide fibers. J Mater Sci 1995;30(9):2201–14.

[15] Gray DG, Guillet JE. Open tubular columns for studies on polymer stationary phases by gas chromatography. J Polym Sci Polym Lett Ed 1974;12(4):231–5.

[16] Wang C, Liu CR. Transcrystallization of PTFE fiber PP composites. III. Effect of fiber pulling on the crystallization kinetics. J Polym Sci Pol Phys 1998;36(8):1361–70.

[17] Thomason JL, Van Rooyen AA. Transcrystallized interphase in thermoplastic composites. 2. Influence of interfacial stress, cooling rate, fiber properties and polymer molecular-weight. J Mater Sci 1992;27(4):897–907.

[18] Cai YQ, Petermann J, Wittich H. Transcrystallization in fiber-reinforced isotactic polypropylene composites in a temperature gradient. J Appl Polym Sci 1997;65(1):67–75.

[19] Chen EJH, Hsiao BS. The effects of transcrystalline interphase in advanced polymer composites. Polym Eng Sci 1992;32(4):280–6.

[20] Schonhorn H, Ryan FW. Effect of morphology in the surface region of polymers on adhesion and adhesive joint strength. J Polym Sci 1968;6:231–40.

[21] Cho K, Kim D, Yoon S. Effect of substrate surface energy on transcrystalline growth and its effect on interfacial adhesion of semicrystalline polymers. Macromolecules 2003;36(20):7652–60.

[22] Hobbs SY. Nature. Phys Sci Ed 1971;12:234.

[23] Wang C, Chen CC. Surface-induced crystallization of syndiotactic polystyrene on high modulus carbon fibers. Polym Bull 1999;43(4–5):433–40.

[24] Wang C, Liu CR. Transcrystallization of polypropylene composites: nucleating ability of fibres. Polymer 1999;40(2):289–98.

[25] Lin CW, Lai YC, Liu SS. Effect of the surface roughness of sulfuric acid-anodized aluminum mold on the interfacial crystallization behavior of isotactic polypropylene. J Ashes Sci Technol 2001;15(8):929–44.

[26] Naiki M, Fukui Y, Matsumura T, et al. The effect of talc on the crystallization of isotactic polypropylene. J Appl Polym Sci 2001;79(9):1693–703.

[27] Lin CW, Lai YC, Liu SS. In: Proceedings of the 21th ROC polymer symposium, Taiwan, 1998.

[28] Burton RH, Folkes MJ. Unpublished Work; 1984.

[29] Son SJ, Lee YM, Im SS. Transcrystalline morphology and mechanical properties in polypropylene composites containing cellulose treated with sodium hydroxide and cellulose. J Mater Sci 2000;35(22):5767–78.

[30] Huson MG, McGill WJ. Transcrystallinity in polypropylene. J Polym Sci Pol Chem 1984;22(11):3571–80.

[31] Yue CY, Cheung WL. Some observations on the role of transcrystalline interphase on the interfacial strength of thermoplastic composites. J Mater Sci Lett 1993;12(14):1092–4.

[32] Devaux E, Chabert B. Nature and origin of the transcrystalline interphase of polypropylene glass–fiber composites after a shear-stress. Polym Commun 1991;32(15):464–8.

[33] Chatterjee AM, Price FP. Heterogeneous nucleation of crystallization of high polymers from the melt. I. substrate-induced morphologies. J Polym Sci Polym Phys Ed 1975;13(12):2369–84.

[34] Avella M, Volpe GD, Martuscelli E, et al. Transcrystallinity phenomena in a polypropylene Kevlar fiber system. 1. Influence of crystallization conditions. Polym Eng Sci 1992;32(5):376–82.

[35] Lagasse RR, Maxwell B. Experimental-study of kinetics of polymer crystallization during shear-flow. Polym Eng Sci 1976;16(3):189–99.

[36] Monasse B. Polypropylene nucleation on a glass–fiber after melt shearing. J Mater Sci 1992;27(22):6047–52.

[37] Gray DG. J Polym Sci Polym Letts Ed 1974;12:645.

[38] Sengupta PK, Mukhopadhyay D, Xavier SF. Transcrystallinity in unidirectional carbon fiber reinforced composites. In: Proceedings of conference on interfacial phenomena in composite materials. Sheffield, 5–7 September 1989 Butterworth-Heinemann, Oxford. p. 111.

[39] Amash A, Zugenmaier P. Morphology and properties of isotropic and oriented samples of cellulose fibre-polypropylene composites. Polymer 2000;41(4):1589–96.

[40] Adolhpi K, Schulze G, Behrens H. Study of the formation of transcrystalline structures at polyethylene interfaces. 2. Determination of molecular mass, gravimetric, DSC, and small-angle x-ray measurements. Acta Polym 1989;40(9):555–8.

[41] Vaughan AS, Bassett DC. Early stages of spherulite growth in melt-crystallized polystyrene. Polymer 1988;29(8):1397–401.

[42] Moon CK. Effect of molecular weight and fiber diameter on the interfacial behavior in glass fiber/PP composites. J Appl Polym Sci 1998;67(7):1191–7.

[43] Campbell D, Qayyum MM. Melt crystallization of polypropylene: effect of contact with fiber substrates. J Polym Sci Polym Phys Ed 1980;18(1):83–93.

[44] Huang Y, Petermann J. Transcrystalline growth of thermoplastics and LCPs during isothermal crystallization. J Appl Polym Sci 1995;55(7):981–7.

[45] Wagner HD, Lustiger A, Marzinsky CN, et al. Interlamellar falure at transcrystalline interfaces in glass polypropylene composites. Compos Sci Technol 1993;48(1–4):181–4.

[46] Varga J, Karger-Kocsis J. Interfacial morphologies in carbon-fiber-reinforced polypropylene microcomposites. Polymer 1995;36(25):4877–81.

[47] Lopez-Manchado MA, Arroyo M. Crystallization kinetics of polypropylene – Part 4: Effect of unmodified and azide-modified PET and PA short fibres. Polymer 1999;40(2):487–95.

[48] Saujanya C, Radhakrishnan S. Structure development and properties of PET fibre filled PP composites. Polymer 2001;42(10):4537–48.

[49] Manchado MAL, Torre L, Kenny JM. Kinetic crystallization of polypropylene in ternary composites based on fiber-reinforced PP-EPDM blends. J Appl Polym Sci 2001;81(5):1063–74.

[50] Amash A, Zugenmaier P. Study on cellulose and xylan filled polypropylene composites. Polym Bull 1998;40(2–3):251–8.

[51] Wang C, Hwang LM. Transcrystallization of PTFE fiber/PP composites. 2. Effect of transcrystallinity on the interfacial strength. J Polym Sci Pol Phys 1996;34(8):1435–42.

[52] Assouline E, Wachtel E, Grigull S, et al. Lamellar orientation in transcrystalline gamma isotactic polypropylene nucleated on aramid fibers. Macromolecules 2002;35(2):403–9.

[53] Joseph PV, Joseph K, Thomas S, et al. The thermal and crystallisation studies of short sisal fibre reinforced polypropylene composites. Compos Part A-Appl S 2003;34(3):253–66.

[54] Wu CM, Chen M, Karger-Kocsis J. The role of metastability in the micromorphologic features of sheared isotactic polypropylene melts. Polymer 1999;40(15):4195–203.

[55] Peron B, Lowe A, Baillie C. The effect of transcrystallinity on the interfacial characteristics of polypropylene/alumina single fibre composites. Compos Part A-Appl S 1996;27(9):839–45.

[56] Varga J, Karger-Kocsis J. Rules of supermolecular structure formation in sheared isotactic polypropylene melts. J Polym Sci Pol Phys 1996;34(4):657–70.

[57] Devaux E, Gerard JF, Bourgin P, et al. 2-dimensional simulation of crystalline growth fronts in a polypropylene glass–fiber composite depending on processing conditions. Compos Sci Technol 1993;48(1–4):199–203.

[58] Bushman AC, McHugh AJ. Continuum model for the dynamics of flow-induced crystallization. J Polym Sci Part B: Polym Phys 1996;34(14):2393–407.

[59] Nagae S, Otsuka Y, Nishid AM, et al. Transcrystallization at glass–fiber polypropylene interface and its effect on the improvement of mechanical-properties of the composites. J Mater Sci Lett 1995;14(17):1234–6.

[60] Oliveira MJ, Cramez MC. Rotational molding of polyolefins: processing, morphology, and properties. J Macromol Sci Phys 2001;B40(3–4):457–71.

[61] Fitchmun DR, Newman S. Surface crystallization of polypropylene. J Polym Sci Part A-2: Polym Phys 1970;8(9):1545–64.

[62] Lee YC, Porter RS. Crystallization of poly (ether ether ketone) (PEEK) in carbon fiber composites. Polym Eng Sci 1986;26(9):633–9.

[63] Chatterjee AM, Price FP. Heterogeneous nucleation of crystallization of high polymers from the melt. II. Aspects of transcrystallinity and nucleation density. J Polym Sci Polym Phys Ed 1975;13(12):2391–400.

[64] Fraser GV, Keller A, Odell JA. Of nucleation density and cooling rate on crystallization of polyethylene from the melt. J Appl Polym Sci 1978;22(10):2979–89.

[65] Kalam MR, Chu E. Isothermal and nonisothermal crystallization of polyethylene. Polym Eng Sci 1983;23(1):27–31.

[66] Hoffman JD, Miller RL. Kinetics of crystallization from the melt and chain folding in polyethylene fractions revisited: theory and experiment. Polymer 1997;38(13):3151–212.

[67] Hoffman JD. Regime-III crystallization in melt-crystallized polymers-the variable cluster model of chain folding. Polymer 1983;24(1):3–26.

[68] Ishida H, Bussi P. Surface-induced crystallization in ultrahigh-modulus polyethylene fiber reinforced polyethylene composites. Macromolecules 1991;24(12):3569–77.

[69] Zhang ZY, Zeng HM. Nucleation and crystal-growth of PEEK on carbon-fiber. J Appl Polym Sci 1993;48(11):1987–95.

[70] Assouline E, Pohl S, Fulchiron R, et al. The kinetics of alpha and beta transcrystallization in fibre-reinforced polypropylene. Polymer 2000;41(21):7843–54.

[71] Saujanya C, Radhakrishnan S. Macromol. Development of a transcrystalline phase in poly (propylene) at the PET interface. Macromol Mater Eng 2001;286(1):1–4.

[72] Tjong SC, Chen SX, Li RKY. Crystallization kinetics of compatibilized blends of a liquid crystalline polymer with polypropylene. J Appl Polym Sci 1997;64(4):707–15.

[73] Benkhati H, Tan TTM, Jungnickel BJ. Transcrystallization kinetics of poly (vinylidene fluoride). J Polym Sci Pol Phys 2001;39(17):2130–9.

[74] Amitay-Sadovsky E, Cohen SR, Wagner HD. Nanoscale shear and indentation measurements in transcrystalline alpha-isotactic polypropylene. Macromolecules 2001;34(5):1252–7.

[75] Stern T, Wachtel E, Marom G. Epitaxy and lamellar twisting in transcrystalline polyethylene. J Polym Sci Pol Phys 1997;35(15):2429–33.

[76] Stern T, Marom G, Wachtel E. Origin, morphology and crystallography of transcrystallinity in polyethylene-based single-polymer composites. Compos Part A-Appl S 1997;28(5):437–44.

[77] Kitayama T, Utsumi S, Hamada H, et al. Interfacial properties of PP/PP composites. J Appl Polym Sci 2003;88(13):2875–83.

[78] Assouline E, Grigull S, Marom G, et al. Morphology of alpha-transcrystalline isotactic polypropylene under tensile stress studied with synchrotron microbeam X-ray diffraction. J Polym Sci Pol Phys 2001;39(17):2016–21.

[79] Yan S, Petermann J. Nucleation and overgrowth of PE on PTFE/iPP interfaces. J Polym Sci Pol Phys 2000;38(1):80–3.

[80] Dean DM, Rebenfeld L, Register RA, et al. Matrix molecular orientation in fiber-reinforced polypropylene composites. J Mater Sci 1998;33(19):4797–812.

[81] Lovinger AJ. Microstructure and unit-cell orientation in alpha-polypropylene. J Polym Sci Part B: Polym Phys 1983;21(1):97–110.

[82] Nuriel H, Klein N, Marom G. The effect of the transcrystalline layer on the mechanical properties of composite materials in the fibre direction. Compos Sci Technol 1999;59(11):1685–90.

[83] Klein N, Marom G, Wachtel E. Microstructure of nylon 66 transcrystalline layers in carbon and aramid fibre reinforced composites. Polymer 1996;37(24):5493–8.

[84] Harel H, Marom G. On crystalline interfaces in composite materials. Acta Polymerica 1998;49(10–11):583–7.

[85] He TB, Porter RS. Melt transcrystallization of polyethylene on high modulus polyethylene fibers. J Appl Polymer Sci 1988;35(7):1945–53.

[86] Feldman AY, Gonzaleza MF, Wachtel E, et al. Transcrystallinity in aramid and carbon fiber reinforced nylon66: determining the lamellar orientation by synchrotron X-ray micro diffraction. Polymer 2004;45(21):7239–45.

[87] Nielsen AS, Pyrz R. Study of the influence of thermal history on the load transfer efficiency and fibre failure in carbon/polypropylene microcomposites using Raman spectroscopy. Compos Interface 1999;6(5):467–82.

[88] Amitay-Sadovsky E, Cohen SR, Wagner HD. Anisotropic nanoindentation of transcrystalline polypropylene by scanning force microscope using blade-like tips. Appl Phys Lett 1999;74(20):2966–8.

[89] Vancso GJ, Liu G, Karger-Kocsis J, et al. AFM imaging of interfacial morphologies in carbon fiber reinforced isotactic polypropylene. Colloid Polym Sci 1997;275(2):181–6.

[90] Wang C, Liu CR. Transcrystallization of polypropylene on carbon fibres. Polymer 1997;38(18):4715–8.

[91] Wu CM, Chen M, Karger-Kocsis J. Interfacial shear strength and failure modes in sPP/CF and iPP/CF microcomposites by fragmentation. Polymer 2001;42(1):129–35.

[92] Burton RH, Day TM, Folkes MJ. Localized flow-induced morphological features in fiber reinforced thermoplastics. Polym Commun 1984;25(12):361–2.

[93] Avalos F, Lopez-Manchado MA, Arroyo M. Crystallization kinetics of polypropylene III. Ternary composites based on polypropylene low density polyethylene blend matrices and short glass fibres. Polymer 1998;39(24):6173–8.

[94] Arroyo N, Lopez-Manchado MA, Avalos F. Crystallization kinetics of polypropylene. 2. Effect of the addition of short glass fibres. Polymer 1997;38(22):5587–93.

[95] Zheng A, Wang HG, Zhu XS, et al. Crystallization kinetics of polypropylene. 2. Effect of the addition of short glass fibres. Compos Interface 2002;9(4):319–33.

[96] Yue CY, Cheung WL. The morphology, character and strength of the interface in glass–fiber polypropylene composites. J Mater Sci 1991;26(4):870–80.

[97] Moon CK. The effect of interfacial microstructure on the interfacial strength of glass–fiber polypropylene resin composites. J Appl Polym Sci 1994;54(1):73–82.

[98] Pegoretti A, Fidanza M, Migliaresi C, et al. Toughness of the fiber/matrix interface in nylon-6/glass fiber composites. Composites Pt A 1998;29(3):283–91.

[99] Scott C, Ishida H, Maurer FHJ. In: Ishida H, editor. Composite interface. New York: Elsevier; 1986. p. 177.

[100] Scott C, Ishida H, Maurer FHJ. Infrared analysis and izod impact testing of multicomponent polymer composites: polyethylene/EPDM/filler systems. J Mater Sci 1987;22(11):3963–73.

[101] Varga J, Karger-Kocsis J. The occurrence of transcrystallization or row-nucleated cylindritic crystallization as a result of shearing in a glass fiber-reinforced polypropylene. Compos Sci Technol 1993;48(1–4):191–8.

[102] Varga J, Karger-Kocsis J. Direct evidence of row-nucleated cylindritic crystallization in glass fiber-reinforced polypropylene composites. Polym Bull 1993;30(1):105–10.

[103] Mildner I, Bledzki AK. In: Proceedings of the Second International, Wood Nat Fiber Comp Symposium, Kassel, Germany, 1999, p. 17.

[104] Felix JM, Gatenholm P. Effect of transcrystalline morphology on interfacial adhesion in cellulose polypropylene composites. J Mater Sci 1994;29(11):3043–9.

[105] Quillin DT, Yin MP, Koutsky JA, et al. Crystallinity in the polypropylene cellulose system. 2. Crystallization kinetics. J Appl Polym Sci 1994;52(5):605–15.

[106] Sanadi AR, Caulfield DF. Transcrystalline interphases in natural fiber–PP composites: effect of coupling agent. Compos Interface 2000;7(1):31–43.

[107] Mi YL, Chen XY, Guo QP. Bamboo fiber-reinforced polypropylene composites: crystallization and interfacial morphology. J Appl Polym Sci 1997;64(7):1267–73.

[108] Li HH, Jiang SD, Wang JJ, et al. Optical microscopic study on the morphologies of isotactic polypropylene induced by its homogeneity fibers. Macromolecules 2003;36(8):2802–7.

[109] Liu JC, Li HH, Duan YX, et al. Morphologies of iPP induced by its partially carbon-coated homogeneity fibers. Polymer 2003;44(18):5423–8.

[110] Wang C, Hwang LM. Transcrystallization of PTFE fiber PP composites. 1. Crystallization kinetics and morphology. J Polym Sci Pol Phys 1996;34(1):47–56.

[111] Hata T, Ohsaka K, Yamasa T, et al. Transcrystalline region of polypropylene-its formation, structure and mechanical-properties. J Adhesion 1994;45(1–4):125–35.

[112] Barber AH, Wiesel E, Wagner HD. Crack deflection at a transcrystalline junction. Compos Sci Technol 2002;62(15):1957–64.

[113] Arroyo M, Zitzumbo R, Avalos F. Composites based on PP/EPDM blends and aramid short fibres. Morphology/behaviour relationship. Polymer 2000;41(16):6351–9.

[114] Assouline E, Fulchiron R, Gerard JF, et al. Gamma-transcrystallization in isotactic polypropylene-based composites promoted by aramid fibers. J Polym Sci Pol Phys 1999;37(17):2534–8.

[115] Wu CM, Chen M, Karger-Kocsis J. Effect of micromorphologic features on the interfacial strength of iPP/Kevlar fiber microcomposites. Polymer 2001;42(1):199–208.

[116] Dean DM, Register RA. Oriented γ-isotactic polypropylene crystallized at atmospheric pressure. J Polym Sci Part B: Polym Phys 1998;36(15):2821–7.

[117] Li ZM, Yang W, Li LB, et al. Morphology and nonisothermal crystallization of in situ microfibrillar poly (ethylene terephthalate)/polypropylene blend fabricated through slit-extrusion, hot-stretch quenching. J Polym Sci Part B: Polym Phys 2004;42(3):374–85.

[118] Li ZM, Li LB, Shen KZ, et al. Transcrystalline morphology of an in situ microfibillar poly (ethylene terephthalate)/poly (propylene) blend fabricated through a slit extrusion-hot stretching-quenching process. Macromol Rapid Commun 2004;25(4):553–8.

[119] Ton-That TM, Jungnickel BJ. Water diffusion into transcrystalline layers on polypropylene. J Appl Polym Sci 1999;74(13):3275–85.

[120] Li ZM, Yang MB, Xie BH, et al. In-situ microfiber reinforced composite based on PET and PE via slit die extrusion and hot stretching: influences of hot stretching ratio on morphology and tensile properties at a fixed composition. Polym Eng Sci 2003;43(3):615–28.

[121] Li ZM, Yang MB, Lu A, et al. Tensile properties of poly (ethylene terephthalate) and polyethylene in-situ microfiber reinforced composite formed via slit die extrudion and hot-stretching. Mater Lett 2002;56(5):756–62.

[122] Li ZM, Yang MB, Feng JM, et al. Morphology of in-situ poly (ethylene terephthalate)/polyethylene microfiber reinforced composite formed via slit die extrusion and hot-stretching. Mater Res Bull 2002;37(13):2185–98.

[123] Li ZM, Yang MB, Huang R, et al. Poly (ethylene terephthalate)/polyethylene composite based on in-situ microfiber formation. Polym-Plast Eng Technol 2002;41(1):19–32.

[124] Manchado MAL, Biagiotti J, Torre L, et al. Effects of reinforcing fibers on the crystallization of polypropylene. Polym Eng Sci 2000;40(10):2194–204.

[125] Von Lacroix F, Werwer M, Schulte K. Solution impregnation of polyethylene fibre/polyethylene matrix composites. Composites A 1998;29(4):371–6.

[126] Zheng Q, Peng M, Yi XS. Crystallization of high density polyethylene: effect of contact with NdFeB magnetic powder substrates. Mater Lett 1999;40(2):91–5.

[127] Von Lacroix F, Loos J, Schulte K. Morphological investigations of polyethylene fibre reinforced polyethylene. Polymer 1999;40(4):843–7.

[128] Vaisman L, Gonzalez MF, Marom G. Transcrystallinity in brominated UHMWPE fiber reinforced HDPE composites: morphology and dielectric properties. Polymer 2003;44(4):1229–35.

[129] Pegoretti A, Ashkar M, Migliaresi C, et al. Relaxation processes in polyethylene fibre-reinforced polyethylene composites. Compos Sci Technol 2000;60(8):1181–9.

[130] Flores A, Poeppel A, Riekel C, et al. Evidence of a transcrystalline interphase in fiber PE homocomposites as revealed by microdiffraction experiments using synchrotron radiation. J Macromol Sci Phys 2001;B40(5):749–61.

[131] Stern T, Teishev A, Marom G. Composites of polyethylene reinforced with chopped polyethylene fibers: effect of transcrystalline interphase. Compos Sci Technol 1997;57(8):1009–15.

[132] Ajji A, Aitkadi A, Rochette A. Polyethylene ultra high modulus polyethylene short fibers composites. J Compos Mater 1992;26(1):121–31.

[133] Wendt U. Thermooptic, DSC and microfractographic investigation of PE–PE mixtures. J Mater Sci 1991;26(12):3154–8.

[134] Friedrich K, Ueda E, Kamo H, et al. Direct electron microscopic observation of transcrystalline layers in microfibrillar reinforced polymer–polymer composites. J Mater Sci 2002;37(20):4299–305.

[135] Zafeiropoulos NE, Varelidis PC, Papaspyrides CD, et al. Characterisation of LDPE residual matrix deposited on glass fibres by a dissolution reprecipitation recycling process. Compos Part A-Appl S 1999;30(7):831–8.

[136] Teishev A, Marom G. The effect of transcrystallinity on the transverse mechanical-properties of single-polymer polyethylene composites. J Appl Polym Sci 1995;56(8):959–66.

[137] Teishev A, Incardona S, Migliaresi C, et al. Polyethylene fibers polyethylene matrix composites – preparation and physical-properties. J Appl Polym Sci 1993;50(3):503–12.

[138] Ryabov YE, Nuriel H, Marom G, et al. Relaxation peak broadening and polymer chain dynamics in aramid-fiber-reinforced nylon-66 microcomposites. J Polym Sci Pol Phys 2003;41(3):217–23.

[139] Cartledge HCY, Baillie CA. Effects of crystallinity, transcrystallinity and crystal phases of GF/PA on friction and wear mechanisms. J Mater Sci 2002;37(14):3005–22.

[140] Fakirov S, Stribeck N, Apostolov AA, et al. Crystallization in partially molten oriented blends of polycondensates as revealed by X-ray studies. J Macromol Sci Phys 2001;B40(5):935–57.

[141] Nuriel H, Kozlovich N, Feldman Y, et al. The dielectric properties of nylon66/aramid fibre microcomposites in the presence of transcrystallinity. Compos Part A-Appl S 2000;31(1):69–78.

[142] Sapoundjieva D, Denchev Z, Fakirov S, et al. Transcrystallization with reorientation in drawn PET/PA12 blend as revealed by WAXS from synchrotron radiation. J Mater Sci 1999;34(13):3063–6.

[143] Clark RL, Kander RG, Sauer BB. Nylon 66/poly (vinyl pyrrolidone) reinforced composites: 1. Interphase microstructure and evaluation of fiber–matrix adhesion. Compos Part A-Appl S 1999;30(1):27–36.

[144] Clark RL, Craven MD, Kander RG. Nylon 66/poly (vinyl pyrrolidone) reinforced composites: 2 bulk mechanical properties and moisture effects. Compos Part A-Appl S 1999;30(1):37–48.

[145] Klein N, Marom G. Adv. Thermal-expansion of transcrystalline strips. Compos Lett 1995;4(1):9–11.

[146] Shiao ML, Nair SV, Garrett PD, et al. Effect of glass–fiber reinforcement and annealing on microstructure and mechanical-behavior of nylon 66. 1. Microstructure and morphology. J Mater Sci 1994;29(7):1973–81.

[147] Yu Z, Aitkadi A, Brisson J. Nylon Kevlar composites. 2. Investigation of interfaces. Polym Eng Sci 1991;31(16):1228–32.

[148] He CC, Dong X, Zhang XQ, et al. Morphology investigation of transcrystallinity at polyamide 66/aramid fiber interface. J Appl Polym Sci 2004;91(5):2980–3.

[149] Incardona SD, Dimaggio R, Fambri L, et al. Crystallization in j-1 polymer carbon-fiber composites-bulk and interface processes. J Mater Sci 1993;28(18):4983–7.

[150] Incardona S, Migliaresi C, Wagner HD, et al. The mechanical role of the fiber matrix transcrystalline interphase in carbon-fiber reinforced J-polymer microcomposites. Compos Sci Technol 1993;47(1):43–50.

[151] Jeng CC, Chen M. Flexural failure mechanisms in injection-moulded carbon fibre/PEEK composites. Compos Sci Technol 2000;60(9):1863–72.

[152] Li TQ, Zhang MQ, Zeng HM. A preliminary proof of the quasi-epitaxial growth of a semicrystalline polymer in its short carbon fiber composites. J Mater Sci Lett 1999;18(22):1861–4.

[153] Zhang MQ, Xu JR, Zhang ZY, et al. Effect of transcrystallinity on tensile behaviour of discontinuous carbon fibre reinforced semicrystalline thermoplastic composites. Polymer 1996;37(23):5151–8.

[154] Tregub A, Harel H, Marom G, et al. The influence of thermal history on the mechanical-properties of poly (ether ether ketone) matrix composite-materials. Compos Sci Technol 1993;48(1–):185–90.

[155] Zhang ZY, Zeng HM. Interfacial crystallization of PEEK pes-c blends on carbon-fiber. Eur Polym J 1993;29(12):1647–50.

[156] Wang W, Qi ZN, Jeronimidis G. Studies on interface structure and crystal texture of poly (ether ether ketone) carbon-fiber composite. J Mater Sci 1991;26(21):5915–20.

[157] Korbakov N, Harel H, Feldman Y, et al. Dielectric-response of aramid fiber-reinforced PEEK. Macromol Chem Phys 2002;203(16):2267–72.

[158] Auer C, Kalinka G, Krause T, et al. Crystallization kinetics of pure and fiber-reinforced poly (phenylene sulfide). J Appl Polym Sci 1994;51(3):407–13.

[159] Desio GP, Rebenfeld L. Crystallization of fiber-reinforced poly (phenylene sulfide) composites. 2. Modeling the crystallization kinetics. J Appl Polym Sci 1992;45(11):2005–20.

[160] Desio GP, Rebenfeld L. Crystallization of fiber-reinforced poly (phenylene sulfide) composites. 1. Experimental studies of crystallization rates and morphology. J Appl Polym Sci 1992;44(11):1989–2001.

[161] Meretz S, Auersch W, Marotzke C, et al. Investigation of morphology-dependent fracture-behavior with the single-fiber pull-out test. Compos Sci Technol 1993;48(1–4):285–90.

[162] Reinsch VE, Rebenfeld L. Crystallization of poly (ethylene terephthalate) polycarbonate blends. 2. The effects of fiber reinforcement. J Appl Polym Sci 1996;59(12):1929–36.

[163] Sajkiewicz P, Carpaneto L, Wasiak A. Application of the Ozawa model to non-isothermal crystallization of poly (ethylene terephthalate). Polymer 2001;42(12):5365–70.

[164] Ishida H, Bussi P. Induction time approach to surface induced crystallization in polyethylene poly (epsilon-caprolactone) melt. J Mater Sci 1991;26(23):6373–82.

[165] Gati A, Wagner HD. Stress transfer efficiency in semicrystalline-based composites comprising transcrystalline interlayers. Macromolecules 1997;30(13):3933–5.

[166] Vendramini J, Mele P, Merle G, et al. Mechanical modeling of the transcrystalline interphase behavior in commingled PBT/Glass fiber composites. J Appl Polym Sci 2000;77(11):2513–24.

[167] Huang Y, Petermann J. Interface layers of fiber reinforced composites with transcrystalline morphology. Polym Bull 1996;36(4):517–24.

[168] Kenneth E, Evans Andrew Alderson. Blends of polypropylene resins with a liquid crystalline polymer. I. Isothermal crystallization. Adv Mater 2000;12(9):617–28.

[169] Wood JR, Wagner HD, Marom G. Transcrystallinity in polycarbonate-carbon fiber microcomposites-the key to the mechanical role of the interphase. J Mater Sci Lett 1995;14(22):1613–5.

[170] Huang J, Marand H. Kinetics of spherulitic growth of poly (pivalolactone) in blends with poly (vinylidene fluoride-co-tetrafluoroethylene): effect of specific interactions on the thermodynamic and kinetic secondary nucleation parameters. Macromolecules 1997;30(4):1069–73.

[171] Dufresne A, Kellerhals MB, Witholt B. Transcrystallization in Mcl-PHAs/cellulose whiskers composites. Macromolecules 1999;32(22):7396–401.

[172] Angles MN, Dufresne A. Plasticized starch/tunicin whiskers nanocomposites. 1. Structural analysis. Macromolcules 2000;33(22):8344–53.

[173] Love BJ, Cherry K, Longhenry JL, et al. Transcrystallinity at interior boundaries in multilayer crystalline PCTFE films. J Mater Sci Lett 1998;17(19):1681–3.

[174] Saiello S, Kenny J, Nicolais L. Interface morphology of carbon fiber/PEEK composites. J Mater Sci 1990;25(8):3493–6.

[175] Cartledge HCY, Baillie CA. Studies of microstructural and mechanical properties of nylon/glass composite – Part II – The effect of microstructures on mechanical and interfacial properties. J Mater Sci 1999;34(20):5113–26.

[176] Heppenstall-Butler M, Bannister DJ, Young RJ. A study of transcrystalline polypropylene/single-aramid-fibre pull-out behaviour using Raman spectroscopy. Compos Part A-Appl S 1996;27(9):833–8.

[177] Lee SG, Kang TJ. Preparation and crystallization behavior of UHMWPE/LLDPE composites. Polym Bull 1998;40(1):95–102.

[178] Lustiger A. Polym. Morphological aspects of the interface in the PEEK-carbon fiber system. Composite 1992;13(5):408–12.

[179] Mader E, Pisanova E. Interfacial design in fiber reinforced polymers. Macromol Symp 2001;163:189–212.

[180] Jay F, Haudin JM, Monasse B. Shear-induced crystallization of polypropylenes: effect of molecular weight. J Mater Sci 1999;34(9):2089–102.

[181] Hsiao BS, Chen EJ. In: Ishida H, editor. Controlled interphases in composite materials. New York: Elsevier Sci.; 1990. p. 613.

[182] SalehiMobarakeh H, AitKadi A, Brisson J. Improvement of mechanical properties of composites through polyamide grafting onto Kevlar fibers. Polym Eng Sci 1996;36(6):778–85.

[183] Klein N, Marom G, Pegoretti A, et al. Determining the role of interfacial transcrystallinity in composite materials by dynamic-mechanical thermal-analysis. Composites 1995;26(10):707–12.

[184] Klein N, Selivansky D, Marom G. The effects of a nucleating-agent and of fibers on the crystallization of nylon66 matrices. Polym Compos 1995;16(3):189–97.

[185] Amitay-Sadovsky E, Wagner HD. Hardness and Young's modulus of transcrystalline polypropylene by Vickers and Knoop microindentation. J Polym Sci Pol Phys 1999;37(6):523–30.

[186] Mironov VS, Park M, Choe C, et al. Influence of carbon fiber surface treatments on the structure and properties of conductive

carbon fiber/polyethylene films. J Appl Polym Sci 2002;84(11):2040–8.

[187] Folkes MJ, Hardwick ST. Direct study of the structure and properties of transcrystalline layers. J Mater Sci Lett 1987;6(6):656–8.

[188] Shanks RA. Nucleation of impact modified filled polypropylene. Polym Polym Compos 1997;5(8):541–7.

[189] Matsuoka S, Daane JH, Bair HE, et al. A further study of the properties of transcrystalline regions in polyethylene. J Polym Sci Polym Lett Ed 1968;6:87–91.