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Interfacial morphologies in carbon fibre-reinforced polypropylene microcomposites[*]

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Formation and build-up of interfacial morphologies along a high-modulus carbon fibre (HMCF), produced by isothermal crystallization in quiescent and sheared melts of isotactic polypropylene (PP), were studied by thermo-optical methods. It was established that in the quiescent melt, the HMCF generates α-transcrystallization due to its strong α-nucleation ability. In the isothermally crystallized sheared melt, achieved by pulling the HMCF slightly above the crystallization temperature, a transcrystalline-like supermolecular structure developed. It was evidenced that this shear-induced supermolecular structure is composed of two crystalline phases: α and β. The α-layer, generated by melt-shearing along the CF surface (α-row nuclei), triggered the growth of the β-modification of PP under the crystallization conditions selected. This shear-induced polymorphous interfacial morphology should be correctly termed 'cylindrite'. The basic difference between transcrystallization and cylindritic crystallization is related to the fact that transcrystallization is induced by heterogeneous nucleation, whereas cylindritic growth is induced by self (homogeneous) nucleation.

(Keywords: carbon fibre; cylindrite; polypropylene; transcrystallinity)

Introduction

Numerous research projects are presently devoted to the question of whether or not interfacial supermolecular structures around the reinforcing carbon and glass fibres (CF and GF, respectively) in semicrystalline thermoplastic matrix composites improve the mechanical properties of these composites. There are comprehensive reviews in this field[1–4], also demonstrating how controversial the published results are[2–4].

The interfacial morphology development of CF reinforced single fibre polypropylene (PP) composites was recently studied by Thomason and van Rooyen[5,6] and Greso and Phillips[2]. They showed that the high-modulus polyacrylonitrile-based CF (HMCF) is an effective nucleant and thus causes transcrystallization in quiescent PP melt under isothermal crystallization. Their results corroborated the pioneering work of Hobbs[7].

Transcrystalline-like interfacial morphologies were also produced by pulling the CF in the crystallizing PP melt[5,6]. The present authors showed for GF/PP[8,9] and poly(ethylene terephthalate)/PP[10] combinations that the supermolecular structure caused by melt-shearing is not transcrystalline but cylindritic. In the cited works, the difference between the crystallization and melting behaviour of the α- and β-modifications of PP was used in order to evidence the polymorphous build-up in the shear-induced cylindritic structures formed. It was shown that cylindritic growth along the pulled fibre was generated by row-nucleation, which is a variant of self-nucleation. No such evidence was given, however, for HMCF/PP composites until now.

The aim of this work was therefore to study the isothermal interfacial crystallization behaviour of single fibre microcomposites of HMCF/PP in quiescent and sheared melts, respectively.

Experimental

A ribbon-like mesophase pitch-based HMCF, produced at Clemson University (Clemson, SC, USA) by Professor D. D. Edie, was used as reinforcement. The isotactic PP used in this study was a general-purpose injection-moulding grade (Tipplen H-523, Tisza Chemical Works Ltd, Hungary; $M_w = 5.2 \times 10^5$ and $M_n = 3.1 \times 10^4\,\mathrm{g\,mol^{-1}}$, respectively; MFI $= 4\,\mathrm{dg\,min^{-1}}$ at 230°C and 21.2 N load).

The crystallization and melting behaviours of the CF/PP model composites were studied in a Leitz Dialux 20 polarizing optical microscope, equipped with a Mettler FP82 hot stage. A single HMCF was sandwiched between PP films, hot pressed at 220°C for 5 min, followed by a rapid cooling ($\sim 8^\circ\mathrm{C\,min^{-1}}$) to the isothermal crystallization temperature (T_c). The CF was manually pulled slightly above T_c, but was always kept below $T = 140^\circ\mathrm{C}$. The crystallized sample was then remelted (starting from T_c) at a heating rate of $2^\circ\mathrm{C\,min^{-1}}$

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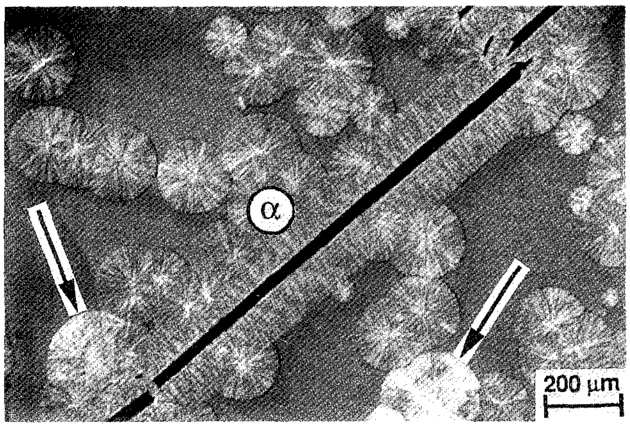

Figure 1 Isothermal crystallization (T_c = 129°C) of PP in quiescent melt in the presence of an HMCF inducing α-transcrystallization. The birefringence pattern of the 'control' spherulites evidences α-transcrystallization

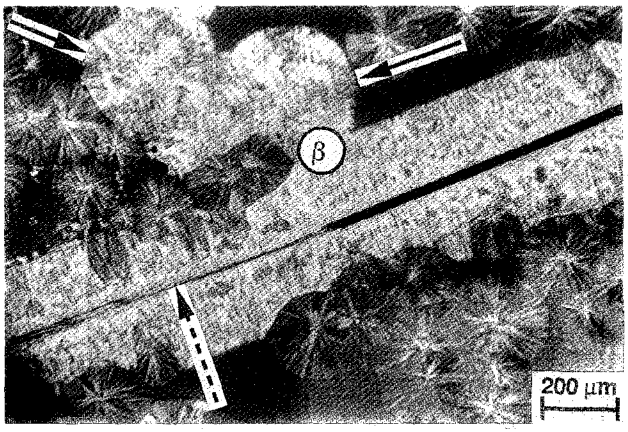

Figure 2 Shear-induced (achieved by CF pulling) β-columnar structure (cylindrite) produced under the conditions: T_{pull} = 138 °C, T_c = 129°C. No difference in the morphology can be revealed along the CF between the pulled CF and the pulled-out CF (indicated by the arrow with broken line)

in order to study the eventual presence of polymorphism in the interfacial morphology. Further experimental details can be found in our previous works[8,9].

Results and discussion

Interfacial morphology in quiescent melt. *Figure 1* envisages the effect of HMCF on the isothermal crystallization (T_c = 129 °C) of PP in its quiescent melt. The interfacial morphology along a broken segment of the HMCF in *Figure 1* clearly demonstrates that α-transcrystallization occurred in the quiescent melt. Well-developed α-spherulites ('control' spherulites) present in the partially crystallized PP melt indicate that the transcrystalline layer is composed of the α-form. α-transcrystallization becomes even more obvious if one views the bright appearance of the β-spherulites (due to

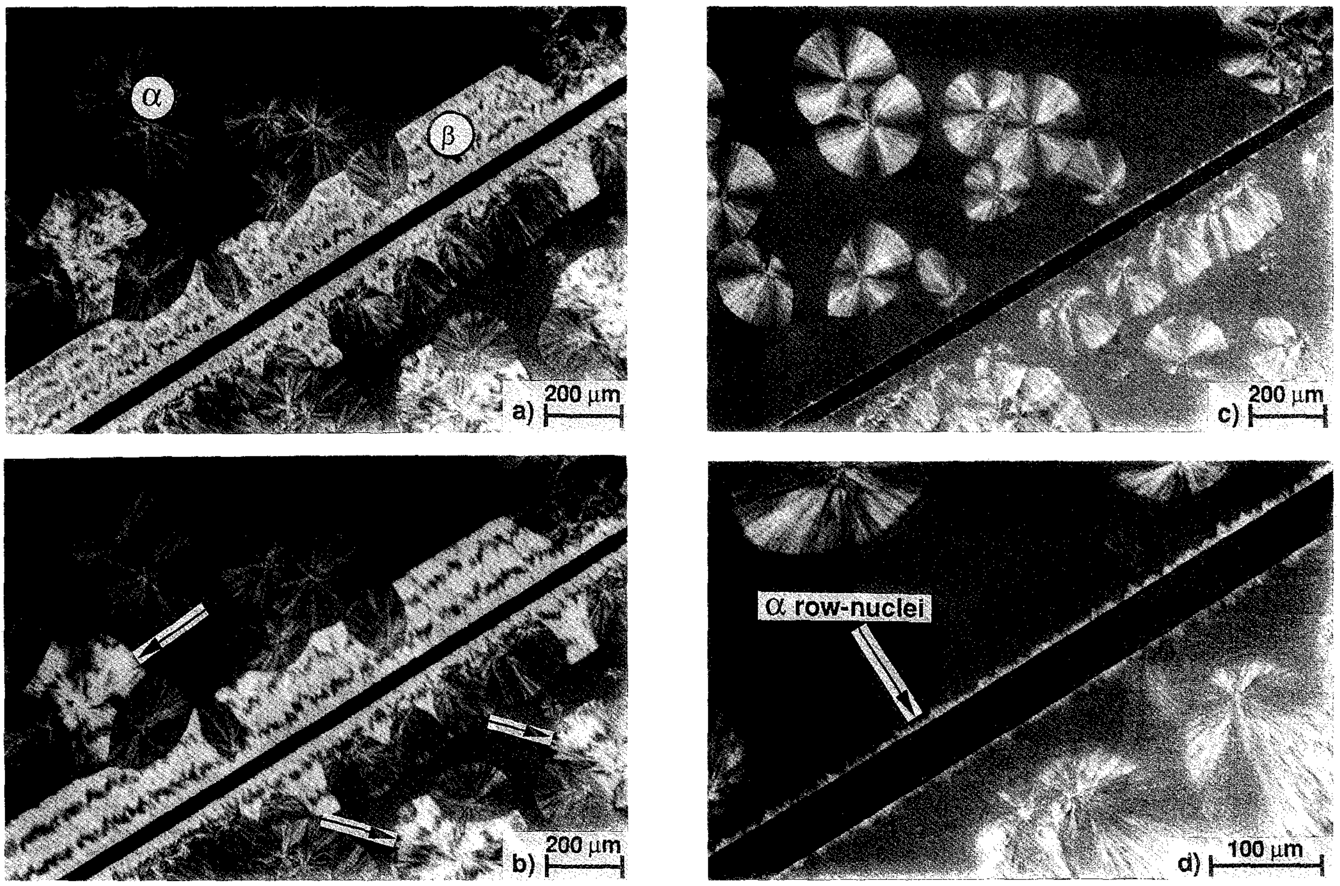

Figure 3 Evidence of β-cylindrite formation on α-row nuclei along an HMCF due to pulling the CF in the crystallizing PP melt. (a) Interfacial morphology under isothermal conditions (T_c = 129°C) after pulling the CF at T_{pull} = 138°C; (b) interfacial morphology at T = 148°C in the remelting phase; (c) structure after separate melting of the β-phase at T = 158°C; (d) higher magnification of (c) showing the α-phase (α-row nuclei) formed along the pulled CF

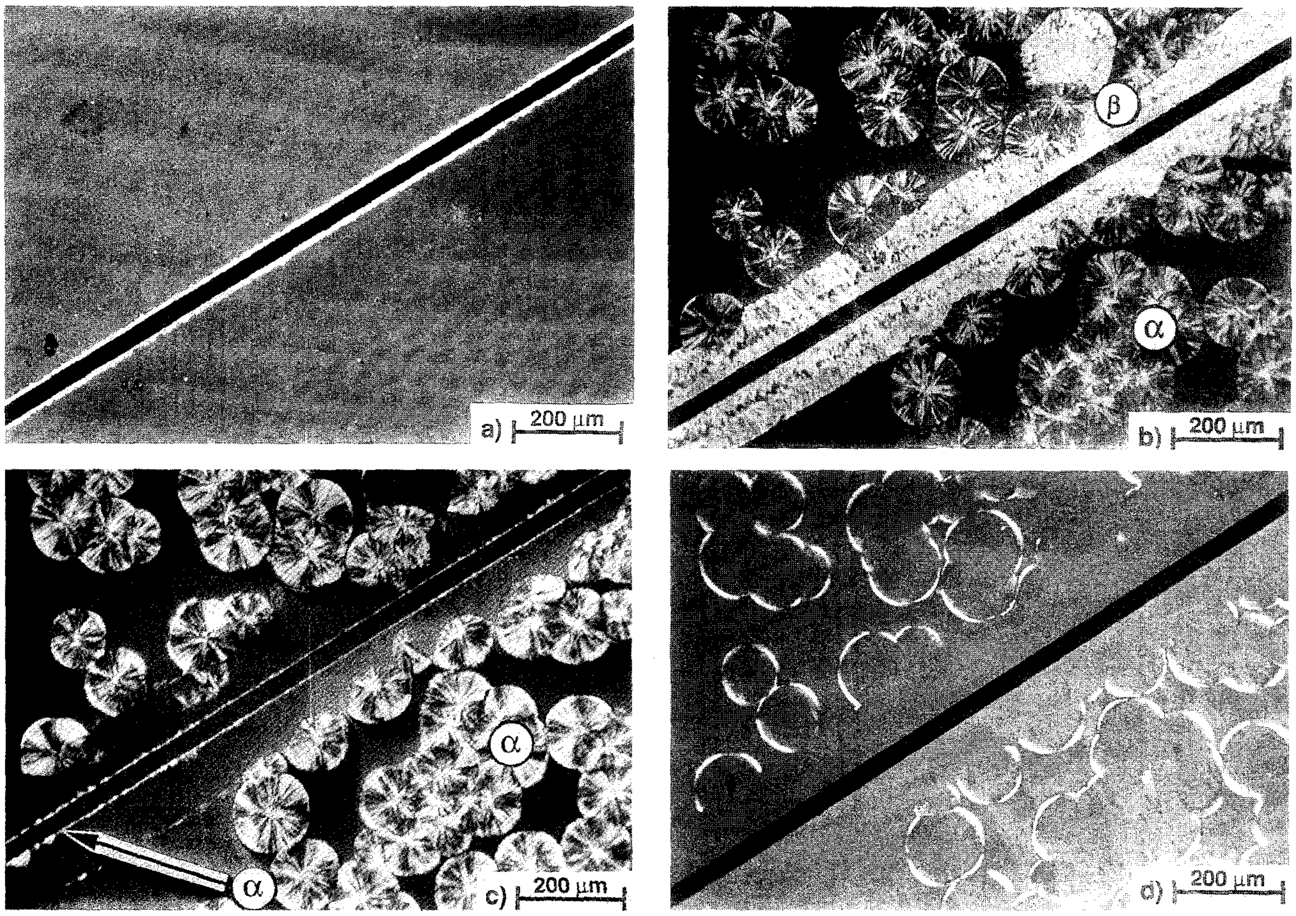

Figure 4 Evidence of β-cylindrite formation on α-row nuclei along an HMCF pulled in the crystallizing PP melt. Crystallization conditions: $T_{\alpha\beta} < T_c (= 130°C) < T_{pull} (= 135°C) < T_{\beta\alpha}$. (a) Initial crystallization at $T_c = 130°C$; (b) β-cylindrite formation (cf. control spherulites), the front of which was marked by an α-layer crystallized at $T_{c'} = 142°C$ (> $T_{\beta\alpha}$); (c) structure after separate melting of the β-phase at $T = 154°C$; (d) remaining structure after melting of the α-phase (α-row nuclei) crystallized at $T_c = 130°C$. The thermally more stable α-phase formed at $T_{c'}$ is clearly discernible in form of 'gloriae'

their strong birefringence; indicated by arrows in *Figure 1*) sporadically present in the field of view.

Note that the transcrystalline layer, produced in PP, always consists of the α-phase, irrespective of the nature of the nucleating agents used.

Interfacial morphology in sheared melt. When HMCF was pulled at $T_{pull} = 135°C$, before isothermal crystallization at $T_c = 129°C$, a β-transcrystalline-like columnar structure appeared (*Figure 2*). This supermolecular structure contains the β-phase of PP. This can be evidenced again by considering the 'control' β-spherulites in the field of view of the microscope (indicated by arrows in *Figure 2*). One can notice further that the supermolecular structures, both along the pulled and pulled-out area of the CF, are the same. It should be emphasized here, that the above interfacial morphology emerged when the following experimental conditions were set: $T_{\alpha\beta} < T_c, T_{pull} < T_{\beta\alpha}$; where $T_{\alpha\beta}$ (~ 100–110°C) and $T_{\beta\alpha}$ (~ 140°C) are threshold temperatures indicating where the onset of α to β and β to α bifurcation of growth can be observed, respectively[4,11]. In the temperature range between $T_{\alpha\beta}$ and $T_{\beta\alpha}$, the PP may crystallize in its β-form[4].

Since it is quite unlikely that, due to melt shearing, the HMCF lost its α-nucleation ability (cf. *Figure 1*) and became a strong β-nucleant, our further investigations were devoted to the analysis of the build-up of this shear-induced, β-columnar structure.

Figure 3 shows a set of photographs evidencing that melt-shearing results in cylindritic crystallization. *Figure 3a* portrays the interfacial morphology in the crystallizing melt ($T_c = 129°C$) after pulling the HMCF gently at $T_{pull} = 138°C$ (recall that in this case both T_c and T_{pull} are below $T_{\beta\alpha}$). The strongly birefringent, banded β-columnar structure reflects the twisting of the crystalline lamellae ribbons. Their arrangement changes slightly in the remelting stage at $T = 148°C$, as seen by comparing the pictures in *Figures 3a* and *3b*. After separate melting of the β-'constituent' of this supermolecular formation at $T = 158°C$ (i.e. slightly above the melting temperature of the β-PP) an α-layer, attached to the pulled CF, can be observed (*Figures 3c* and *3d*). This layer along the pulled HMCF consists of α-PP, according to a direct comparison with unmelted α-spherulites in the field of view. One can therefore conclude that melt-shearing resulted in aligned PP molecules that act as α-row nuclei. This scenario corroborates the suggestion of Campbell and White[12], who suggested a possible self-nucleation of aligned macromolecular chains. Interestingly, the surface of this α-layer (α-row nuclei) should be covered by a high concentration of β-nuclei which trigger the crystallization of the β-form (this peculiar feature of the α-row nuclei may be related to epitaxial phenomena). Therefore, under the conditions $T_{\alpha\beta} < T_c$ and $T_{pull} < T_{\beta\alpha}$, melt-shearing by pulling of the CF is associated with the formation of a complex polymorphous structure consisting both of the α- (row nuclei

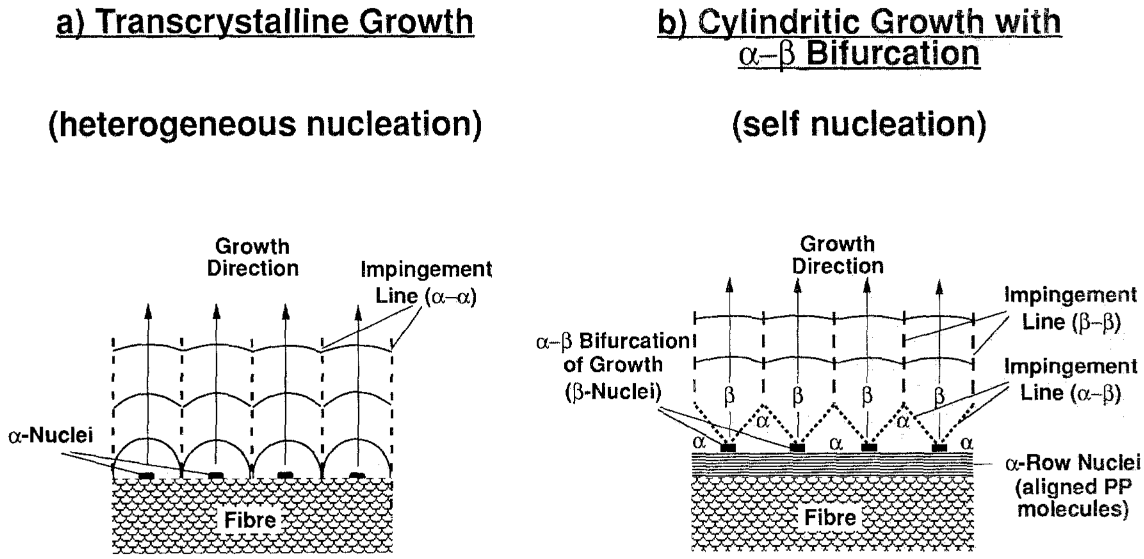

Figure 5 Schematic diagram of the difference between transcrystallization and cylindritic crystallization

along the CF) and β-forms of PP (grown onto the α-layer, the surface of which is 'covered' by β-nuclei). This β-overgrowth 'hides' the α-layer developed along the pulled fibre surface. The latter can be resolved on an optical level only after partial melting of the β-phase[4,8–11]. During the growth of this shear-induced columnar structure, an α–β bifurcation of growth, i.e. a change in the crystalline modification, took place. This fact excludes *per definitionem* the transcrystallization. Therefore, the columnar structure along a pulled HMCF (i.e. in a sheared melt) after isothermal crystallization should be termed cylindrite[13].

It is noteworthy that cylindritic structures of the β-form can be often found in injection or extrusion moulded items, where high shear stresses are accommodated during processing[11,14].

Figure 4 shows a further set of photographs demonstrating not only β-cylindritic growth on α-row nuclei, but also evidencing that the melting behaviour of the PP depends on its crystallization temperature (the most well-known use of this is the determination of the equilibrium melting temperature by the Hoffman–Weeks plot, discussed, for example, in reference 4). *Figure 4a* shows the initial crystallization at $T_c = 130°C$ after pulling the HMCF at $T_{pull} = 135°C$. The β-rich columnar structure and spherulites in the vicinity were 'marked' by α-overgrowth, achieved at $T_{c'} = 142°C$ (recall that this $T_{c'}$ lies higher than $T_{\beta\alpha}$, so that α-crystallization takes place; see *Figure 4b*). The remaining structure after separate melting of the β-phase at $T = 154°C$ is envisaged in *Figure 4c*. In this figure, both the growth front of the previous β-cylindrite ('marked' by temperature elevation from T_c to $T_{c'}$) and the α-row nuclei along the CF (indicated by the arrow in *Figure 4c*) are clearly discernible. Upon further heating of the sample up to 165°C (melting temperature of the α-PP), only the 'α-markings' in the form of gloriae remained. This is due to the fact that their crystallization took place at a higher crystallization temperature than the bulk material ($T_{c'} > T_c$, see above), thus they also possess a higher melting temperature.

Conclusions

Results showed that different interfacial supermolecular structures can be produced along carbon fibres (CFs), acting as heterogeneous nucleants, as a function of the crystallization conditions.

In the quiescent PP melt, the α-nucleating CF induced transcrystallization via heterogeneous nucleation. In the sheared PP melt, however, shear-induced or row-nucleated cylindritic crystallization occurred via self-nucleation. A common feature of both above structures is that the lateral growth of the spherulites is hindered because the nucleation sites are located very close to each other. This triggers unidirectional spherulitic growth and results in a columnar structure. The basic difference between the transcrystalline and cylindritic growth with α–β bifurcation is summarized schematically in *Figure 5*. *Figure 5* makes it obvious that a clear distinction should be made between transcrystallization 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)[15].

Considering the fact that cylindritic morphology is induced by self-nucleation, no enhancement in the fibre/matrix interfacial shear strength (τ_i) can be expected from its presence, when compared to spherulitic structures. Indeed, recent works investigating the effects of various spherulitic and cylindritic morphologies on the interfacial shear strength in GF/PP microcomposites supported this presumption[16,17]. On the other hand, the fibre–matrix adhesion, and thus τ_i, may eventually be enhanced by transcrystallization. In this situation, open questions relating to the nucleation behaviour (epitaxial or non-epitaxial in nature[2]), and especially to the stress transfer through the transcrystalline interfacial morphology, arise. The authors are sure that the application of atomic force microscopy and laser Raman microscopy for single carbon fibre-reinforced composites will contribute to a deeper understanding of this matter in the very near future.

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