Direct evidence of row-nucleated cylindritic crystallization in glass fiber-reinforced polypropylene composites*

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ABSTRACT

The development and nature of the transcystalline-like superstructure produced by pulling the glass fiber (GF) from the isothermal crystallizing ($T_c \approx 135$ °C) isotactic polypropylene (PP) melt was studied thermooptically. In the vicinity of the pulled GF α row-nuclei form which induce selective β-nucleation resulting in β-cylindrites.The presence of α row-nuclei was evidenced by selective melting of the β-phase having lower melting temperature than the α. Because of the above change in the crystal modification this phenomenon can not be termed by transcrystallinity. The thermal stability and β-nucleation ability of the primary α row-nuclei depend both on the applied shear stress (i.e. molecular orientation) and pulling temperature (T_{pull}) under the testing conditions: $T_{\alpha\beta} < T_c < T_{\beta\alpha}$ and $T_{\alpha\beta} < T_{pull} <> T_{\beta\alpha}$, where $T_{\alpha\beta}$ and $T_{\beta\alpha}$ are the lower and upper threshold temperature of the β-formation, respectively. It was suggested that the observed αβ-bifurcation may be related with epitaxial growth.

INTRODUCTION

Nowadays lots of scientific works are devoted to the question, whether a transcrystalline layer around the reinforcing fibers in composites with semicrystalline thermoplastic matrices may improve the mechanical property profile or not. In the literature controversal results are published in this respect. In addition, the attributes and controling parameters of transcrystallinity are not well understood yet in polymeric composites. (e.g.[1])

Recent works performed on the "transcrystallization" of glass fiber (GF) reinforced polypropylene (PP) [2-5] showed that this superstructure around the GF appears only when shear stresses are accomodated, e.g. by pulling the GF from the crystallizing melt. It is recognised that shear-induced crystallization during processing of PP gives rise the formation

of cylindrites [6]. The fact that the evolution of the "transcrystalline" morphology is linked to melt shearing suggests that instead of transcrystallization cylindritic crystallization occurs. What is the difference betwen these two modes of crystallization? Transcrystallinity is caused by heterogeneous nucleation: closely-spaced nuclei on a substrate originate one-dimensional growth of the spherulites by hindering their lateral extension. During this process no change in the crystalline structure takes place. Cylindritic crystallization, on the other hand, is induced by self-nucleation of the PP, which is different from both homogeneous and heterogeneous one [7]. The aim of this contribution was to clarify the nature of the columnar supermolecular structure in a GF/PP composite developed by shearing the PP melt crystallizing isothermally. Our working hypothesis considered the fact that PP is polymorph (e.g.[7]) and its selected crystalline form (α,β or γ) can be produced preferentially under given crystallization conditions. If it can be demonstrated that during crystallization the crystalline form of the PP alters, the cylindritic crystallization is unambigously verified. Self-nucleation may be generated by row-nuclei of high thermal stability that have been "survived" the fusion conditions. During cooling they generate "self-seeding" crystallization [7]. Obviously, the self-seeding activity of these row-nuclei depends on the conditions of their generation (shear stress and temperature). Therefore our further goal was to elucidate which parameters affect the stability and nucleation ability of these nuclei.

EXPERIMENTAL
In this study a commingled yarn (Toyobo Co.,Japan) composed of PP and unsized GF was used. The crystallization and melting behavior of the GF/PP composite was studied in a Leitz polarizing optical microscope equipped with a hot stage. PP fiber sections taken from the yarn were pressed into a film between two microscope slides at T=200 ^{o}C. After cooling down and removing the cover slide temporarily, one or more GF were placed onto this film and positioned by the cover glass before melting at T=200 ^{o}C. Crystallization was performed isothermally at T_c=134-136 ^{o}C, i.e. T_c was selected between the upper ($T_{\beta\alpha}$; [6,8] and lower threshold temperature ($T_{\alpha\beta}$;[9]) of the formation of the β-PP. Transcrystalline-like morphology along the GF was generated by pulling the GF manually either above or at T_c (T_{pull}). The effects of T_{pull} on the development of this supermolecular structure were investigated, too. In this thermooptical study the crystallized PP was heated from T_c up to a fusion temperatute (T_f) being set higher than the melting temperature of the PP ($T_m\approx$ 166 ^{o}C). In such a way the β-phase melts separately without any $\beta-\alpha$ recrystallization (the latter occurs only when the crystallized sample is cooled down below a critical temperature of about 100 ^{o}C). This peculiar feature of the β-PP was first reported by Varga [10]. The remelting process was followed by a second crystallization with the aim to assess the structural memory of the sample by means of self-seeding nucleation.

RESULTS AND DISCUSSION
Effects of crystallization temperature and molecular orientation

The set of pictures in Figure 1 shows the supermolecular structures formed under isothermal condition at $T_{\alpha\beta}<T_c<T_{\beta\alpha}$, as well as their changes due to remelting and recrystallization processes. Figure 1a shows the initial sample cooled down from T=200 °C to T_c=135 °C. Three GF were embedded into the PP; one of them was fully pulled-out (A), the second GF was pulled gently on a short distance (B), whereas the third GF was untouched (C). Figure 1a demonstrates that from the pulled and pulled-out GF (A and B) transcrystalline-like fronts of strong birefringence were grown. They seem to be composed only of β-PP. In contrary, the undisturbed GF (C) did not influence the crystallization. Based on the morphology at the pulled-out GF (A), one can conclude that the rise of the β-transcrystalline zone is due to the shear deformation of the melt and not due to the presence of the GF.

When the temperature of the partially crystallized sample is increased from T_c to T=166 °C, the β-phase melts separately (Figure 1b) and along the fibers A and B an α-layer of about 15 μm thickness can be evidenced. Obviously the shear stress field along the fibers during pulling generates α row-nuclei which further induce β-cylindritic crystallization [11]. Since $T_{\alpha\beta} < T_c <$ $T_{\beta\alpha}$, the growth rate of the β-phase is higher than α, so that the α-phase will be overgrown and occluded by the β-phase. The observation that the transcrystalline-like superstructure is generated on α row-nuclei is supported by Figures 1c and 1d, taken from the recrystallized sample. The sample was heated up to T_f=178 °C (>T_m) followed by a second isothermal crystallization at T_c=136 °C (Figure 1d). The α row-nuclei originated by shear deformation possess a rather high thermal stability, even above T_m of the PP. Figure 1c taken during the cooling regime to T_c at T=143 °C clearly displays that the α row-nuclei at the pulled-out fiber (A) appear again in close analogy to a photographic developing process, i.e. self-seeded crystallization takes place. In the second isothermal crystallization at T_c=136 °C only α-cylindrites form (Figure 1d). It means that the α row-nuclei have lost their β-crystallization ability due to the thermal treatment at T_f=178 °C. It is a reasonable assumption therefore,that the β-overgrowth onto the α row-nuclei is controled by the extension, stretching of the macromolecular chains in the shearing process. Lower stretching grade and thus easy molecular disorientation by thermal treatment results in spherulitic instead of cylindritic growth (cf. B in Figure 1d). This is a clear evidence that the formation of the transcrystalline-like superstructure along the pulled GF is linked to the molecular orientation, first proposed by Campbell and White [12]. When the above sample is heated up to T_f=185 °C before a third crystallization at T_c=136 °C, the row-nuclei disappear, i.e. their primary structure is fully destroyed and thus memory of the PP has been erased ("blank" melt, no self-seeding effect). In this case the sample crystallizes in spherulites (Figure 1e).
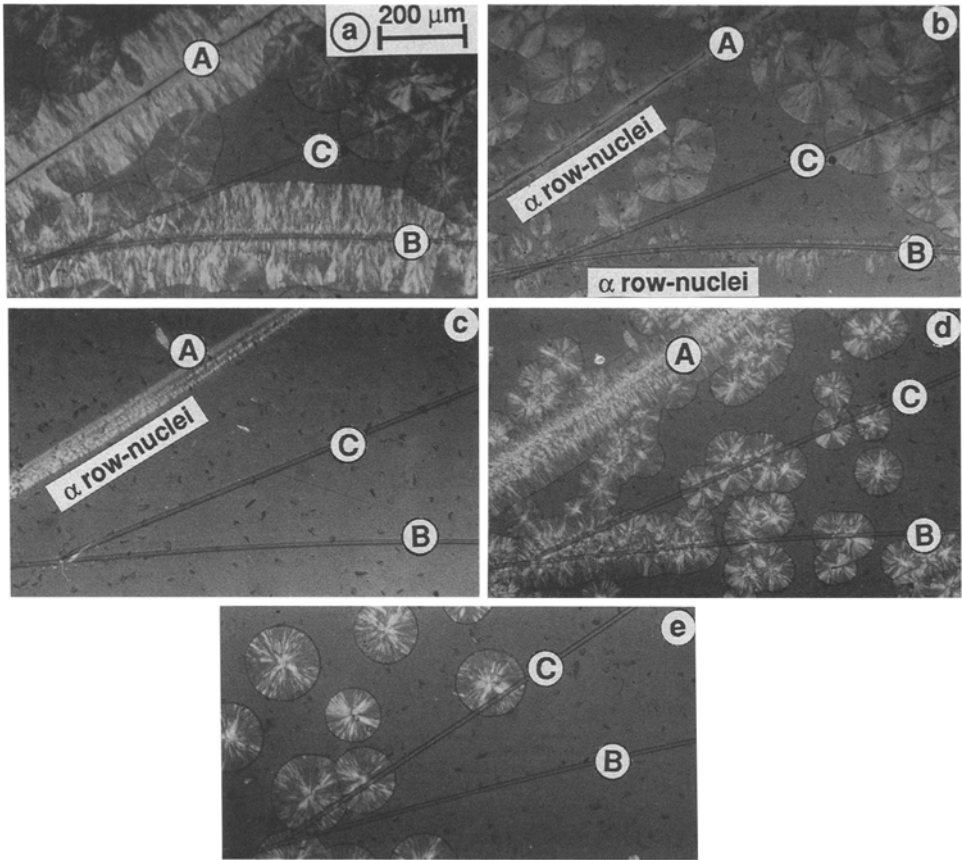
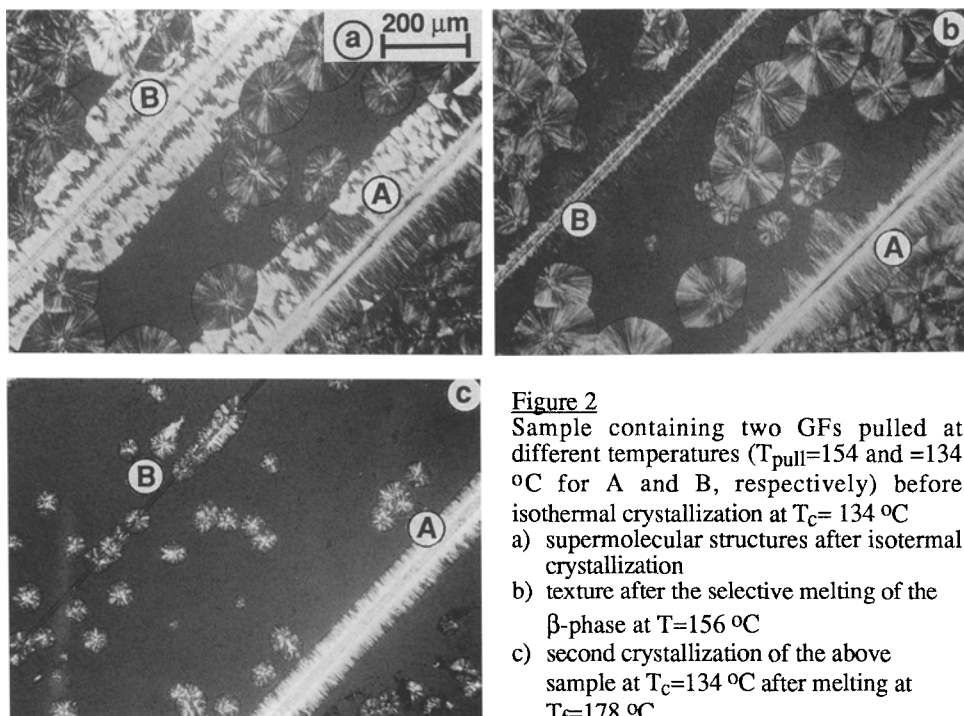Figure 1

a) sample crystallized under isothermal conditions (T_c=135 °C) showing β-supermolecular structures along the GF fully pulled-out (A) and gently pulled (B) from the melt at T_{pull}=T_c

b) the above sample after separate melting of the β-phase at T=166 °C

c) the above sample during cooling to T_c (=135 °C) at T=143 °C after melting at T_f=178 °C
   Note: the α row-nuclei of higher thermal stability at A appear,wheras those at B disappear

d) second cyrstallization of the above sample at T_c=135 °C showing an α-cylindrite at A and onset of spherulitic growth at the intersection of B and C.

e) third crystallization of the above sample at T_c=135 °C after melting at T_f=185 °C.

The peculiar feature of the in-situ formed (by pulling generated) α row-nuclei is related with their ability to nucleate the β-modification selectively. In injection molded, extruded or welded PP items optically bright bands of β-PP were often resolved, as reviewed recently by Varga [6]. These bands in the morphologic texture possess the highest molecular orientation and act as row-nuclei inducing cylindritic crystallization. It should be noted here that this cylindritic structure is often termed uncorrectly as "transcrystalline" in the literature.

Effects of the pulling temperature and thermal stability of the row-nuclei

It was underlined before that the molecular orientation affects the thermal stability of the row-nuclei (cf. Figure 1). Figure 2 demonstrates that this is not the only parameter determining the thermal stability of the row-nuclei produced by pulling the GF in the crystallizing PP melt. In Figure 2a two cylindritic structures can be seen, one of them (A) was produced at T_{pull}=154 °C ($>T_{\beta\alpha}$), while the other (B) at T_{pull}=134 °C ($<T_{\beta\alpha}$) before isothermal crystallization at T_c=134 °C. The crystalline structure of A is a mixed, polymorphic one ($\alpha+\beta$), whereas B shows a banded β-cylindritic structure (Figure 2a). After selective melting the β-phase at T=156 °C, the α row-nuclei at B are clearly discernible (Figure 2b). This sample was molten at T_f=178 °C ($>T_m$) and cooled down to T_c=134 °C for a second crystallization. It can be stated that this thermal treatment efficiently distroyed the α row-nuclei at B, since only their fragments remained (Figure 2c). Surprisingly row-nucleation was "revitalized" at A, although it was not expected. If the thermal stability of the α row-nuclei depends solely on the extension of the macromolecular chains, lower thermal stability could be predicted for A than for B (the viscosity of the melt at higher T_{pull} is reduced so that the molecular orientation that can be achieved by shearing should be also lower).

Figure 2
Sample containing two GFs pulled at different temperatures (T_{pull}=154 and =134 °C for A and B, respectively) before isothermal crystallization at T_c= 134 °C
a) supermolecular structures after isotermal crystallization
b) texture after the selective melting of the β-phase at T=156 °C
c) second crystallization of the above sample at T_c=134 °C after melting at T_f=178 °C

The explanation for this latent controversy is that α row-nuclei produced at higher temperature have also a higher melting point. Therefore their "memory can be erased" only at higher T_f. Obviously the fusion temperature chosen in this case (T=178 °C) was not sufficient to "erase the memory" of the α row-nuclei produced at T_{pull}= 154 °C. Thus the thermal stability of the primary α row-nuclei depends both on the pulling temperature and orientation of the molecular chains caused by shear and/or elongational flow.

CONCLUSIONS

It was demonstrated that in the sheared melt of PP under isothermal crystallization at T_c=134-136 °C β-transcrystalline-like superstructure appears. This structure consists of two layers. In the vicinity of the pulled glass fiber (GF) α row-nuclei develop due to melt shearing. These α-nuclei possess a selective β-nucleation ability which turns out in the growth of β-cylindrites. Since the growth of the β-form is higher than the α in the T_c range set ($T_{\alpha\beta}<T_c<T_{\beta\alpha}$), the resulting β-cylindrite looks like a β-transcrystalline layer because the α-phase occluded can hardly be resolved optically. The presence of the α row-nuclei was evidenced by selective melting of the β-phase being thermally less stable than α. The onset of this $\alpha\beta$-bifurcation is the major reason why the resulted structure is cylindritic instead of transcrystalline. It was also shown that both the thermal stability and the β-nucleation ability of the α row-nuclei strongly depend on the accomodated shear stress and temperature. The facts that β-crystallization is induced by α row-nuclei originated in-situ by pulling the GF and that they are loosing their selective β-nucleation ability by heat treatment, suggest that this feature may be related with epitaxial growth, probably with the autoepitaxy in PP [13].

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