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Transcrystallization in syndiotactic polypropylene induced by high-modulus carbon fibers

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SUMMARY

It was first shown that transcrystallization can be induced in syndiotactic polypropylene (sPP) when a carbon fiber (CF) of high-modulus (HM) is embedded in the melt of sPP crystallizing under quiescent conditions. High-tenacity carbon fiber (HTCF), on the other hand, did not cause transcrystalline growth. Coating of HMCF by silicon carbide (SiC) stopped the transcrystallization of sPP. The difference in the morphology of the transcrystalline layer between isotactic PP (iPP) and sPP was revealed by phase contrast light (PCLM), scanning electron (SEM) and atomic force microscopy (AFM) taken from the etched surface of single fiber microcomposite specimens.

1. INTRODUCTION

Transcrystallization caused by heterogeneous nucleating agents in semicrystalline polymers is a well-known phenomenon. Essential prerequisite of transcrystallization is the presence of active nuclei on the surface of the substrates (e.g., fillers, reinforcements) in high density. The closely spaced nuclei hinder the lateral extension of spherulites which are then forced to grow in one direction, namely perpendicular to the substrates' surface. Since the density of the nuclei on the substrates' surface is higher than in the bulk polymer a columnar morphology, termed to transcrystallinity, appears. Transcrystallization was first reported in 1952 [1] and became topic of numerous studies up to now. This phenomenon is reviewed for isotactic polypropyene (iPP) in refs. [2-5]. Nevertheless, it is not yet fully understood which are the controlling factors of transcrystallinity (why given fibers induce transcrystallization and other not). The still ongoing interest on this phenomenon is fueled by the belief that the resulting interphase morphology may promote the stress transfer from the matrix toward the reinforcement and thus polymeric composites of improved mechanical performance can be produced. It should be underlined here that transcrystallinity develops only in quiescent melt. In

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sheared melt no transcrystallization but cylindritic growth (induced by α-phase row nuclei [5]) occurs. Cylindritic crystallization is a special variant of self nucleation.

According to the authors' knowledge no report was published on the transcrystallization in sPP. What is the reason behind? This is likely an effect of the present commercial sPP grades manufactured by metallocene catalysts. They possess moderate tacticity, stereo- and regioregularity and thus the usual substrates are unable to generate their transcrystallization. Keeping in mind that the most straightforward explanation of transcrystallization is the epitaxial overgrowth on suitable crystalline substrates [6-7], as long as sPP of high tacticity is not available the right policy is to focus on the substrates. The hypothesis of this work was that carbon fibers (CF) with the highest crystallinity and most perfect crystalline structure may trigger transcrystallization in sPP.

2. EXPERIMENTALS

The sPP used was provided by Fina Research (Feluy, Belgium) and showed the following characteristics: tacticity (rrrr by nuclear magnetic resonance, NMR)=0.68, M_w=128 kg/mol, M_w/M_n=1.65, melting and crystallization temperatures (by differential scanning calorimetry, DSC) 124 °C and 63 °C, respectively. For comparison purpose an isotactic PP (iPP) homopolymer (Novolen® 100N, BASF, Ludwigshafen, Germany) was used in film form (thickness:50 µm).

Polyacrylonitrile-based high-tenacity (HTCF, Idemitsu Kosan Co., Chiba, Japan) and mesophase pitch-based high-modulus carbon fibers (HMCF, produced at the Clemson University, Clemson, SC, USA) were used as heterogeneous nucleants. The latter was available in ribbon and c-shape forms, respectively (Figure 1). None of the CFs contained any sizing or surface finish. Some HMCFs, on the other hand, were coated by silicon carbide (SiC) via a chemical vacuum deposition (CVD) process.

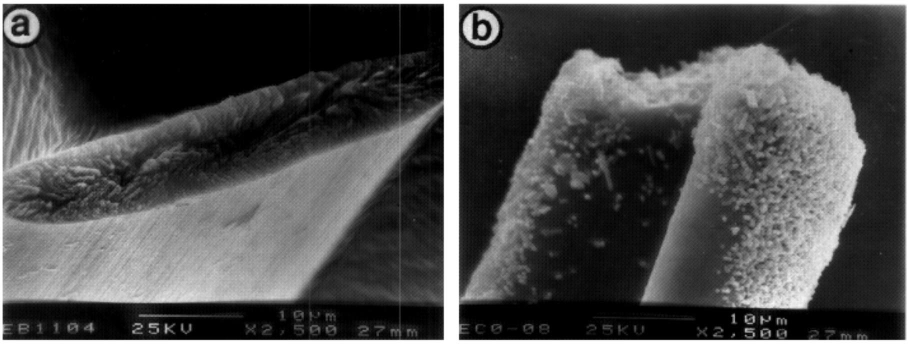

Figure 1
Scanning electron microscopic pictures on the HMCFs of ribbon (a) and c-shape (b, covered partially by SiC)

Single fiber microcomposites were produced by “sandwiching” the CF between two films of iPP and sPP (produced previously) which was heated to erase the melt memory (T_f) prior to cooling to the isothermal crystallization temperature (T_c). The following conditions were set for sPP and iPP, respectively:

T_f=180 [8-9] and 200 °C [5],holding time: 5 min

T_c=110 and 133 °C, holding time: ca. 1 h.

The above T_f values along with the holding time were definitely sufficient to destroy all nuclei and produce a melt of “blank memory”.

The crystallization of the quiescent melt was observed in a hot stage (THM S600 of Linkam, Waterfield, UK) under crossed polars. Single fiber microcomposites were also produced by placing one fiber on the PP melt surface prior to cooling to T_c. These specimens were later etched chemically according to the procedure of Olley and Bassett [10] in order to study the interphase morphology by phase contrast light microscopy (PCLM; Leitz, Wetzlar, Germany), scanning electron microscopy (SEM,; Jeol 5400, Tokyo, Japan) and atomic force microscopy (AFM; NanoScope, Digital Instruments, Santa Barbara, CA, USA). The topography of the etched samples was scanned (ca. 1 Hz) in tapping mode of the AFM.

3. RESULTS AND DISCUSSIONS

Transcrystallization

Figure 2 depicts how efficient α-phase nucleant the HMCF in iPP is. This is conform with our previous results [5,11].

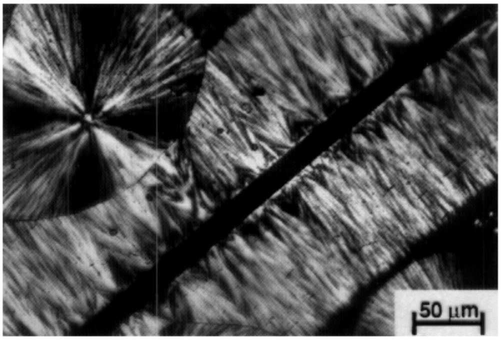

Figure 2
HMCF-induced transcrystallization in iPP (Note: the α-phase spherulitic crystallization is obvious)

HMCF does induce transcrystallization in sPP (Figure 3a) whereas HTCF not (Figure 3b).

The thickness of the transcrystalline layer in both sPP (Figure 3a) and iPP (Figure 2) is matched with the size of the spherulites, as expected.

The nucleation efficiency of HMCF diminishes after SiC coating (Figure 4a). In case of poor SiC-coating the non-coated (“bare”) sites still preserve their nucleation ability (Figure 4b). Considering the fact that HMCFs exhibit the highest crystallinity and most perfect crystalline lattice structure, one can conclude that transcrystallinity in sPP depends also on crystallinity parameters of the substrate, viz. HMCF. This assumption should be checked, however, by assessing the crystallinity parameters of HMCF. Further investigations are also needed to clarify the mechanisms of transcrystalline overgrowth (whether or not of epitaxial origin [6-7]) . Remember that SiC is crystalline, as well. The lack of transcrystallinity with SiC-coated HMCF hints that the requirements of epitaxy (lattice match in the crystalline structure between the substrate and polymer, polymer deposition onto the substrate etc.) are no more met. Therefore, providing the HMCF with various crystalline coatings would be a very useful strategy to check the control parameters and mechanisms of epitaxial growth.

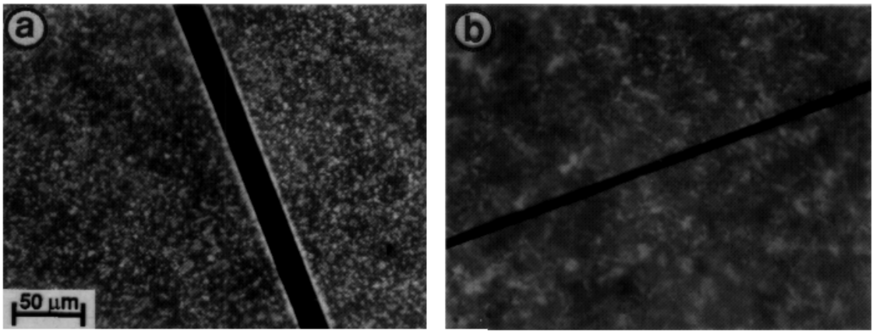

Figure 3
Interfacial morphology of isothermally crystallized sPP in the presence of HMCF (a) and HTCF (b)
Note: the specimen thickness was of about 60 (a) and 300 µm (b), respectively

It is worth emphasizing the difference in the spherulitic morphology between iPP (Figure 2) and sPP (Figures 3 and 4). In iPP well-developed spherulites are present whereas in sPP a disordered fine spherulitic texture can be revealed.

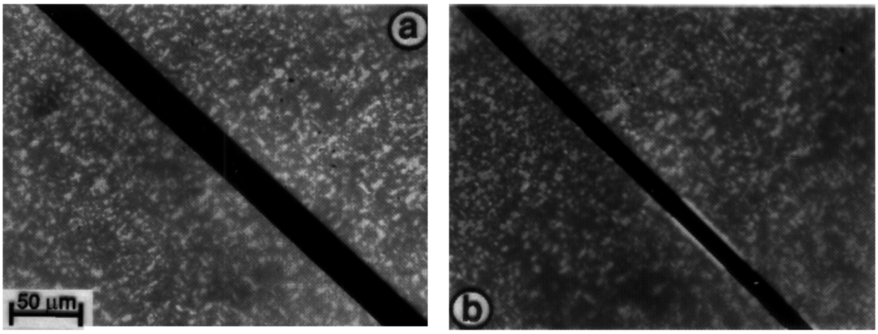

Figure 4
Interfacial morphology in isothermally crystallized sPP/HMCF microcomposites. Designations: ribbon HMCF of complete (a) and c-shape HMCF of partial SiC coating (b), respectively

Built-Up of the Transcrystalline Layer

The difference in the transcrystalline morphology between sPP and iPP becomes pertinent when viewed by PCLM after etching. Figure 5 compares the PCLM pictures in iPP (Figure 5a) and sPP (Figure 5b), respectively. Furthermore, the fine structure, viz. lamellar arrangement, within the transcrystalline layer is also different between iPP and sPP which is the outcome of differences in the crystalline structure and crystallization behaviour between iPP and sPP.

In iPP both nucleation sites and impingement lines between the “unidirectionally” growing spherulites can well be observed. Figure 5a shows also the lamellar lay-up and its orientation. By contrast, the fine structure of the transcrystalline layer in sPP is much less resolved. The lamellar lay-up of the sPP (disordered bundles or fibrils) in the vicinity of HMCF seems to be very similar what was observed in some sites of the bulk (see Figure 7a) which are likely aggregates of large single crystals [12].

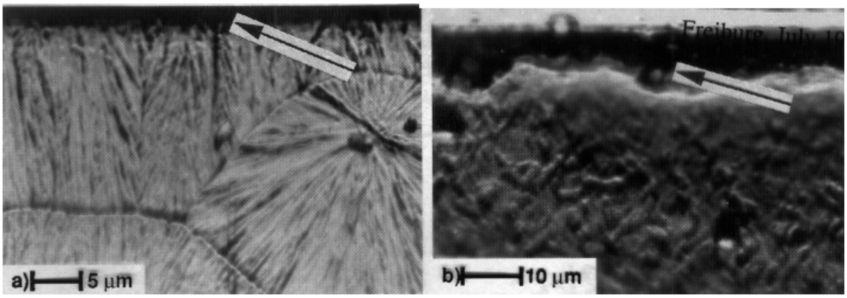

Figure 5
Interfacial morphology after chemical etching in iPP/HMCF (a) and sPP/HMCF (b) microcomposites revealed by PCLM
Note:arrow indicates the position of the HMCF removed during etching

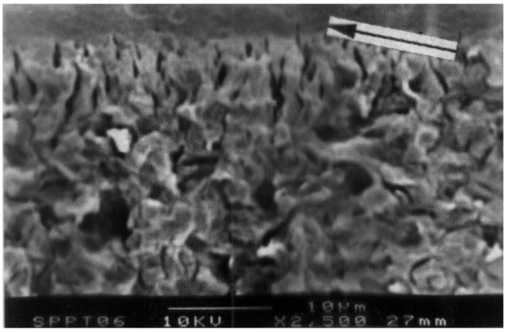

Figure 6
SEM picture on the interfacial morphology after chemical etching in the sPP/HMCF microcomposite
For note cf. Figure 5

The SEM picture taken from the interfacial region of the sPP/HMCF microcomposite shows that the thickness of the transcrystalline layer is ca. 10 µm (Figure 6). Figure 6 suggests that the orientation of the lamellae in the transcrystalline layer differs from that of the bulk. This becomes obvious in the AFM pictures (cf. Figures 7 and 8). The AFM scans taken by amplitude oscillation reveal the main difference between the transcrystalline region and the bulk. In the interfacial transcrystalline region the sPP lamellae seem to be larger and/or aligned differently from that of the bulk. A flat-on type overgrowth [13] of the sPP on the HMCF substrate can be supposed based on Figure 8. The microbeam X-ray scattering technique is trusted to shed light on the lamellar arrangement in the interfacial region.

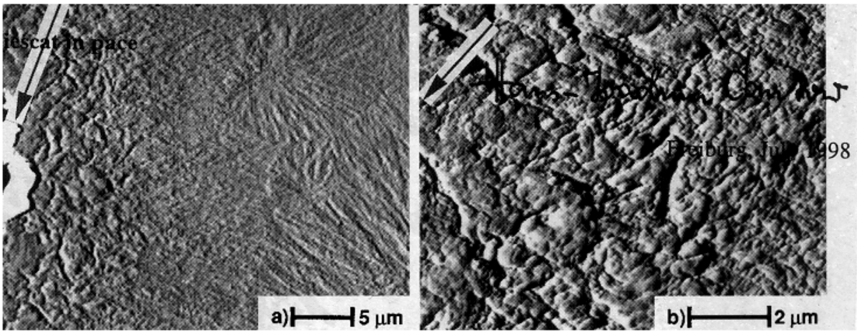

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Figure 7
Amplitude-modulated AFM scans at various magnifications from the transcrystalline region and bulk of the etched sPP
Notes: arrow indicates for the bed of the HMCF, picture b is taken from the interfacial (transcrystalline) region

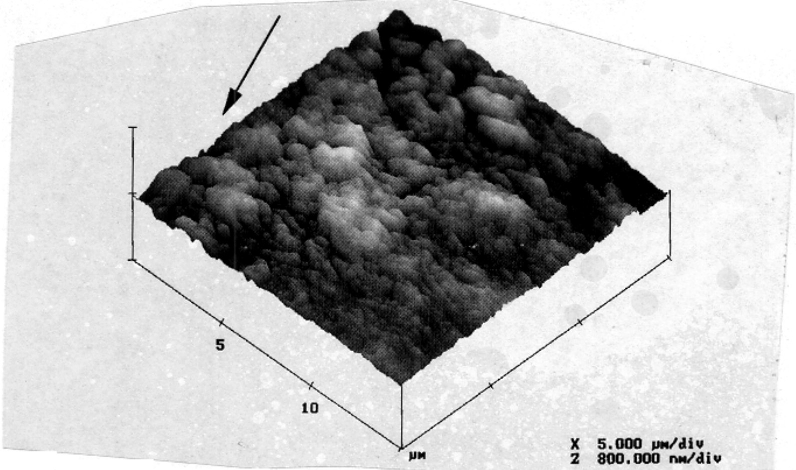

Figure 8
AFM image in tapping mode from the etched transcrystalline layer in an sPP/HMCF microcomposite

4. CONCLUSIONS

Based on this study performed on carbon fiber (CF)-induced transcrystallization in syndiotactic polypropylene (sPP) the following conclusions may be drawn:

i- transcrystallization of sPP can be triggered by high-modulus CF (HMCF) showing the highest crystallinity and most perfect crystalline structure. Sheathing the surface of HMCF by SiC stops the growth of transcrystallization. This fact may be treated as an indirect evidence for the epitaxial origin of transcrystallization.

ii- according to optical, scanning electron and atomic force microscopic inspections the lamellar arrangement in the transcrystalline layer differs from that of bulk in sPP. Further investigation by using microfocus X-ray scattering are now in progress in order to clarify the characteristics of the lamellar growth.

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