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Shear-induced crystallisation of molten isotactic polypropylene within the intertube channels of aligned multi-wall carbon nanotube arrays towards structurally controlled composites

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ABSTRACT

A melt processing route was successfully applied in the manufacturing of aligned multi-wall carbon nanotube/isotactic polypropylene (MWCNT-iPP) composites. As high as 25 wt% content of the catalytic Chemical Vapour Deposition (*c*-CVD) derived nanotube filler could be introduced into the iPP matrix. The composite was characterised by a practically retained nanotube alignment as well as an enhanced crystallisation of iPP. Analysis of the phase iPP composition in the composite using XRD and DSC revealed a dominating α-phase with polymer molecules uniaxially oriented in the same direction as the nanotube alignment. Furthermore, kinetic in situ Synchrotron XRD studies verified that the enhanced crystallisation was induced mainly by shear stress occurring in the initial stage of infiltration MWCNT arrays by flowing molten polymer and, to a lesser extent, by the template-based growth of iPP crystallites.

1. Introduction

MWCNTs comprise an extensively applied filler in the polymer matrix composites [1]. Polypropylene (PP) was one of the most widely studied matrix here due to well-balanced physical properties [2]. Anisotropic CNT composites display an enhanced mechanical, electrical and thermal performance [3]. Several techniques of manufacturing anisotropic CNT composites were employed in which nanotubes were oriented by growth as vertically/horizontally aligned films and post-treated or spun online as fibres [4]. Importantly, isotactic polypropylene (iPP) can be produced from a semi- to crystalline form [2]. Also, shear-induced crystallisation of iPP is a known phenomenon [5,6]. CNTs have been already found to nucleate crystallisation of iPP in composites of a random nanotube orientation as revealed by DSC – in the non-isothermal approach an expansion of crystalline phase with the increase of nanotube content was observed [7,8], whereas in isothermal experiments an acceleration of the crystal growth followed an Avrami-type behaviour [9,10]. However, up to date, iPP composites with MWCNTs only randomly oriented were analysed comprehensively.

A continuation of our recently developed melt processing route toward anisotropic MWCNT-iPP composites is presented [11]. The elaborated method preserves nanotube alignment from the initial *c*-CVD growth, prevents from the nanotube coalescence and enables an enhanced crystallisation of iPP matrix during its infusion into the MWCNT array. We laid a special emphasis on the understanding MWCNT-polymer interactions and a mechanism of iPP crystallites formation in the composites.

2. Materials and methods

Aligned MWCNT arrays were synthesised via *c*-CVD process using 6 wt% solution of ferrocene in toluene as feedstock, at 760 °C under argon atmosphere [12]. Based on TEM statistics the mean outer and inner diameters of MWCNTs were 60 ± 25 and 10 ± 2 nm, respectively. The number density was 5×10^6 nanotubes/mm^2, corresponding to an intertube separation of ca. 440 nm. According to the SEM measurements, thickness of the free-standing nanotube arrays grown directly on the tubular quartz furnace tube was 0.34 mm. A *hot plate* method [11] was explored to infiltrate MWCNTs with iPP film placed on the top of free-standing nanotubes array and heated to 250 °C using an electric heater (20 min), and then cooled to room temperature (rt). Various iPP films of thicknesses 0.10 ± 0.02, 0.15 ± 0.02,

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0.20 ± 0.03, 0.30 ± 0.03 and 0.90 ± 0.03 mm were prepared from commercially available iPP films (*Borealis Polymers*).

In the kinetic Synchrotron experiment, an optimally nanotube-filled composite was heated up to 250 °C (20 °C/min), maintained at this temperature until iPP melted down and cooled down (20 °C/min), while XRD patterns were acquired continuously.

3. Results and discussion

Morphology/composition: SEM images of the MWCNT arrays infiltrated with the particular films are shown in Fig. 1. Due to comparable Hildebrand solubility parameters of MWCNTs and iPP [13] and low viscosity of molten polymer, the latter perfectly wetted MWCNT arrays (Fig. 1D), and all of the iPP films completely infiltrated them leaving the nanotube alignment intact (Fig. 1B). In case of the 0.90 mm-thick film an excess of polymer was clearly visible on top of the arrays (Fig. 1A), whereas the optimal film thickness was 0.30 mm – the film completely and not excessively infiltrated the arrays (Fig. 1C). Based on weight and volumetric measurements, MWCNT content in this composite was 25 wt% [11] (SD).

Orientation of polymer molecules and MWCNTs in the composite: XRD was used to study relative orientation of MWCNTs and the matrix molecules in the optimally nanotube-filled composite. The incident beam was applied both perpendicularly and parallelly to the nanotube alignment. The level of MWCNTs misalignment at full width half maximum (FWHM) was equal to 34 ± 17° as determined from the arcing of the (002) reflection [3,11]. In the MWCNT-iPP composite the nanotube alignment was found identical as before infiltration. The wide-angle 2D XRD patterns of the MWCNT-iPP composites are presented in Fig. 2. A distinct orientation of polymer molecules in the composite is reflected in Fig. 2A in which the incident beam was perpendicular to the MWCNT alignment, whereas no preferential orientation of iPP molecules was observed in the parallel orientation (Fig. 2B).

Radially integrated 2D XRD patterns yielded the intensity vs. 2θ plot (Fig. 2C) where peaks at $2\theta = 14.1°$, $16.9°$, $18.5°$, $21.0°$, and $22.0°$ were identified and assigned to reflections of the lattice planes of α-iPP: (110), (040), (130), (111) and (041/-131), respectively [14] Based on Fig. 2A, the arcing of *hkl* reflections were used to quantify misalignment of the crystallites with *c*-axis parallel to the nanotubes (Table 1).

Misalignments were equal ± 15° and ± 17° for the crystallites in the *b*-axis (040) and nanotubes, respectively.

A relative crystallinity of iPP (X_c) in the composite was calculated by Eq. (1) [15] and found equal to 56%:

$$X_c = \frac{A_{total} - A_{amorphous}}{A_{total}} \quad (1)$$

where A_{total} is total area between 10° and 24° (on 2θ), and $A_{amorphous}$ is area of the amorphous halo.

In order to verify the origin of a higher content of iPP crystallites in the composite, a kinetic in situ Synchrotron experiment was performed (Fig. S1). Time-scans of 2D XRD patterns were acquired throughout the changing iPP crystallinity stages in the

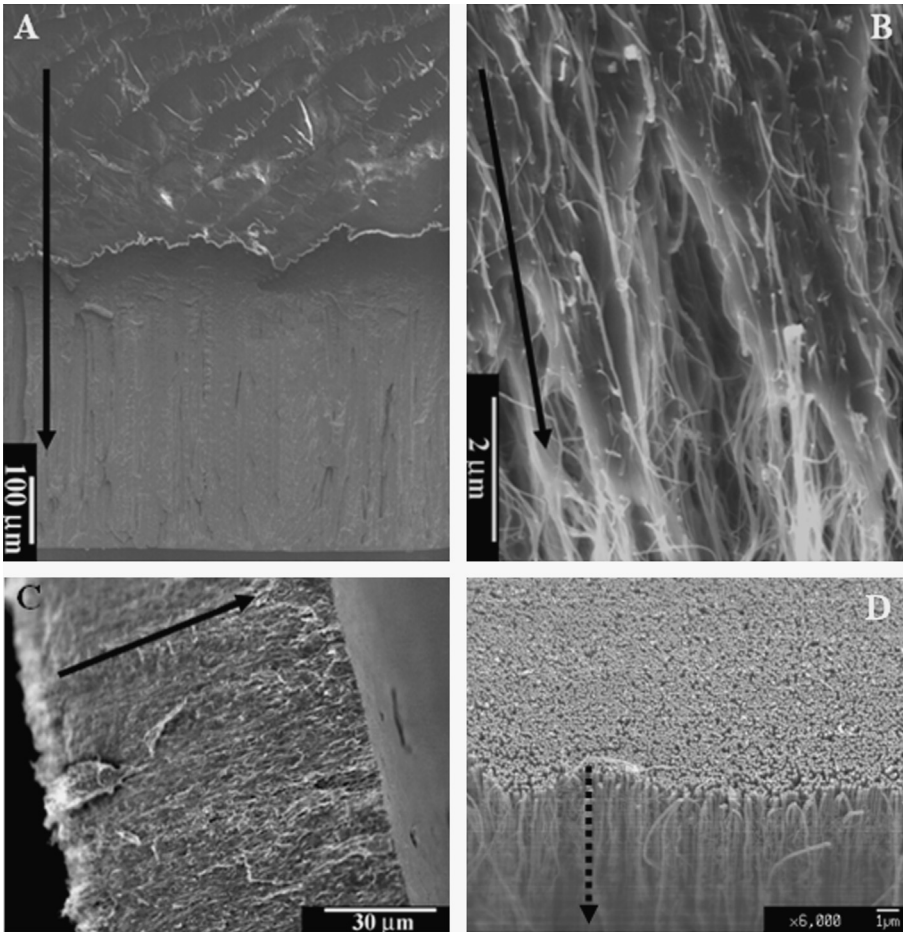

Fig. 1. SEM images of: (A) a side-view of fully and 'overinfiltrated' MWCNT arrays with a 0.90 mm-thick iPP film, (B) a magnified infiltrated part; (C) a side-view of the composite prepared from the *optimally* 0.30 mm-thick film; and (D) as-grown aligned MWCNT arrays. The arrows indicate direction of the nanotube alignment and of the polymer infiltration.