



Nucleation efficiency of fillers in polymer crystallization studied by fast scanning calorimetry: Carbon nanotubes in polypropylene



Jürgen E.K. Schawe^{a,*}, Petra Pötschke^b, Ingo Alig^c

^a Mettler-Toledo GmbH, Analytical, Sonnenbergstrasse 74, Schwerzenbach, CH 8603, Switzerland

^b Leibniz Institute of Polymer Research Dresden, Hohe Strasse 6, D-01069 Dresden, Germany

^c Fraunhofer Institute for Structural Durability and System Reliability LBF, Division Plastics, Schlossgartenstrasse 6, D-64289 Darmstadt, Germany

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ABSTRACT

The influence of multi-walled carbon nanotubes (0–5 wt%) on the crystallization process in isotactic polypropylene has been investigated by DSC and fast scanning calorimetry. In the non-isothermal experiments the crystallization temperature shifts to higher temperatures with increasing nanotube content, α_{CNT} , whereas the polymer crystallinity was not significantly influenced. The critical cooling rate, β_c , at which the PP does not crystallize, increases with increasing of α_{CNT} . From β_c and α_{CNT} a nucleation efficiency parameter was derived, which is independent of crystallization temperature and filler content. Isothermal crystallization experiments allow differentiating between α -phase and mesophase crystallization. Nanotubes accelerate only the α -phase formation. To describe the efficiency of a nucleation agent an acceleration factor, ϵ , was introduced, which is the ratio of the characteristic crystallization time of unfilled and filled polymer. For the α -phase formation the acceleration factor ϵ is related to the number of nuclei per nanotube and the specific effect of the filler on the growth rate.

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1. Introduction

Polypropylene (PP) is a widely used semi-crystalline polymer which forms different metastable crystalline polymorphs [1,2]. Without a nucleation agent [3,4] and in the absence of large mechanical stress or pressure [5,6] polypropylene can exist in two crystalline forms. At low supercooling the monoclinic α -phase is formed, which is considered to be the most stable phase. Whereas at high supercooling the configurationally disordered (condis) phase is formed. This phase is usually denoted as mesophase [7,8]. This phase occurs in nodular domains with a size of 5–20 nm [9–11].

The influence of the reinforcement of carbon nanotubes on the material properties of polymers has been extensively studied in the last decades [12–14]. For polypropylene reinforced with multi-walled carbon nanotubes (MWCNT) it is well established that the crystallization is accelerated and the nanotubes act as a nucleating agent for the α -phase [15–17]. In order to be an effective nucleating agent, a good dispersion of the nanoparticles in the polymer matrix is required and the particles must exceed of certain size. For

polypropylene, the desirable size is between 20 and 40 nm [3].

The arrangement of carbon nanotubes in the semicrystalline polymer matrix and the mechanism of nucleation are still unclear. Based on mechanical and fracture measurements [15] and supported by model calculations [18] a model has been proposed, assuming that the nanotubes are wrapped by PP helices which are adsorbed on the nanotube surface [15]. In this model the nanotube does not interact appreciably with crystalline domains [15]. Macromolecules which are partially wrapped around the nanotubes are assumed to act as nuclei for folding crystals [19], with macromolecules oriented parallel to the nanotubes. In this case crystals and nanotubes form hybrid shish-kebab structures [20–23]. Three dimensional crystal growth can be explained by secondary nucleation on the kebab structure [24].

The influence of carbon nanotubes (CNT) on crystallization is mostly studied at low supercooling [16,17,25,26]. Fast scanning calorimetry (FSC) is an effective technique to study crystallization processes of polymers at large supercooling [27–30] and the influence of nucleating agents [31–34]. Recently this technique was also used to study the nucleation kinetics of polymer-MWCNT composites [35].

In this investigation we focus on the influence of MWCNT on the crystallization behavior of polypropylene (PP) in a large supercooling range measured by non-isothermal and isothermal

* Corresponding author.

E-mail address: juergen.schawe@mt.com (J.E.K. Schawe).

crystallization experiments combining conventional differential scanning calorimetry (DSC) and FSC. Frequently [36–38] the nucleation efficiency of filler and nucleation agents is characterized by the nucleation activity parameter introduced by Dobrevá and Gutzow [39,40]. As a consequence of a critical discussion of this approach we introduced empirical models to characterize the nucleation efficiency for non-isothermal and for isothermal measurements. In both approaches the nucleation efficiency is a parameter independent on the content of the nucleation agent. For non-isothermal measurements the evaluation of nucleation efficiency is based on the critical cooling rate. The nucleation effect of MWCNT in a PP matrix - measured by isothermal measurements - is analyzed using a semi-empirical model to derive additional information on (i) the effective number of nuclei per nanotube and (ii) the influence of the nanotubes on the growth rate.

In isothermal measurements on a composite containing 5 wt.-% nanotubes, we have found a sharp thermal transition at which the nucleation efficiency of the MWCNT switches from a high activity to inactivity in a temperature range of 2 K. This switching effect will be discussed in terms of different nucleation activity and crystallization kinetics of the α - and meso phases.

2. Experimental

2.1. Sample preparation

Novolen 1106H from Lyondell Basell Industries was used as the polypropylene matrix of the composite (MFI = 2.1 g/10 min with 2.16 kg at 230 °C, density: 0.903 g/cm³, M_w = 462 kg/mol, M_n = 85 kg/mol). This grade of polypropylene was chosen, since it is expected that it does not contain nucleating agents. It is predominantly isotactic with a tacticity of 94.1%. The granular material was milled in liquid nitrogen to powder with a size of about 0.5–1 mm.

The multi-walled carbon nanotubes are Nanocyl™ NC7000 (Nanocyl S.A. Belgium) with an average diameter of 9.5 nm and an average length of 1.5 μ m (acc. to supplier data). The nanotubes were dried in vacuum at 120 °C for 1 h. PP and MWCNT were premixed mechanically at room temperature. For the final mixing process a DACA MicroCompounder with a conical co-rotating twin-screw and having a capacity of 4.5 g was used. Firstly the parameters of the mixing process were optimized in order to achieve the best micro-dispersion. The optimal conditions were found to be 15 min mixing time at 200 °C and 150 rpm. With this mixing procedure composites with 0, 0.2, 0.5, 1, 2 and 5 wt% MWCNT concentration, α_{CNT} , were prepared. The dispersion of the nanotubes in the polymer matrix using such preparation procedure was tested by transmission electron microscopy for similar PP-MWCNT systems. These previous investigations have been shown that the nanotubes are quite well dispersed even if areas with higher and lower nanotube concentrations may be observed [41].

The composite strands were cut in small pieces and compression molded to plates (60 mm diameter, 0.5 mm thickness) using a Weber press at a molding temperature of 200 °C with 50 kN applied pressure for 2.5 min.

2.2. Optical microscopy

An overview of the dispersion of the CNT was obtained using light microscopy. Thin sections of the extruded composite strands (5 μ m thickness) were cut using a Microtome Leica 2265 and then analyzed by light microscopy in transmission using an BH2 microscope combined with a DP71 camera (Olympus, Germany) (Fig. 1). The micrographs show an excellent nanotube micro-dispersion as MWCNT agglomerates are virtually zero, even for the higher CNT loadings.

2.3. Differential scanning calorimetry

The thermal characterization of the composites was performed by conventional differential scanning calorimetry (DSC) by a DSC3+ from METTLER TOLEDO with IntraCooler and purged with nitrogen. Heating – cooling – heating cycles with scanning rates of 10 K/min were recorded. The typical sample size was 4 mg. The cooling and second heating curves for different CNT content are shown in Fig. 2. The crystallinity was determined from the melting curves using a straight baseline between 50 and 150 °C. The crystallinity was calculated by using

$$\alpha_c = \frac{\Delta h}{\Delta h_f(1 - \alpha_{\text{CNT}})}, \quad (1)$$

where Δh is the measured total specific melting enthalpy, α_{CNT} is the mass content of MWCNT and $\Delta h_f = 206.7$ J/g is the equilibrium specific melting enthalpy of the α -phase [42].

2.4. Fast scanning calorimetry

The fast scanning calorimetry measurements were performed using a METTLER TOLEDO Flash DSC 1 fitted with the sensor UFS 1. The sample support temperature was set to –80 °C. To reach cooling rates up to 10000 K/s in the temperature range between 190 °C and 20 °C, a gas mixture of 90% helium and 10% nitrogen was used. The gas mixture was generated using two gas flow meters with a needle valve. The typical sample size was between 20 and 50 ng. More details about the use of the instrument and sample preparation are given in Ref. [43].

3. Results and discussion

3.1. Crystallinity and nucleation activity

As it is shown in the insert of Fig. 2, the crystallinity is about 54% and does not vary significantly with the MWCNT content. This result agrees with data derived from similar systems [15,26].

In a first step we analyze our DSC and FSC data using the approach proposed by Dobrevá and Gutzow [40]. These authors suggested a method based on semi empirical models for the determination of the nucleation activity, ϕ , of foreign substrates (here: fillers or nucleation agents) in the polymer melt from DSC measurements. This method is frequently used to characterize the activity of nucleation agents and filler in polymers [36–38]. For low supercooling, the cooling rate dependence of the maximum temperature of the crystallization peak, T_c , is described by

$$\log \beta = A - \frac{B}{(T_f^0 - T_c)^2}, \quad (2)$$

where β is the cooling rate, A and B are constants and T_f^0 is the equilibrium melting temperature. We take for PP $T_f^0 = 187.6$ °C [42].

In the Dobrevá-Gutzow approach the so-called nucleation activity parameter is defined by the ratio between the slopes in eq. (2) for the unfilled material, B_0 , and the composites with different filler content, B :

$$\phi = \frac{B}{B_0}. \quad (3)$$

In the case of a heterogeneous nucleation is $1 > \phi > 0$. The higher the nucleation ability of a foreign surface or particle, the lower ϕ becomes.

For the determination of ϕ the samples were measured by DSC

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