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Kinetics of nucleation and crystallization of poly(ϵ -caprolactone) – Multiwalled carbon nanotube compositesEvgeny Zhuravlev^{a,*}, Andreas Wurm^a, Petra Pötschke^b, René Androsch^c, Jörn W.P. Schmelzer^a, Christoph Schick^a^aUniversity of Rostock, Institute of Physics, Wismarsche Str. 43–45, 18051 Rostock, Germany^bLeibniz Institute of Polymer Research Dresden, Hohe Str. 6, 01069 Dresden, Germany^cMartin-Luther-University Halle-Wittenberg, Center for Engineering Sciences, 06099 Halle/S., Germany

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ABSTRACT

The nucleation efficiency of multiwall carbon nanotubes (MWCNT) in poly(ϵ -caprolactone) (PCL), as an example, was tested for a wide range of temperatures and cooling rates and compared to the efficiency of homogeneously formed nuclei. The temperature range below the maximum of crystallization rate is generally not accessible for non-isothermal cooling experiments because the sample becomes amorphous at the needed cooling rates. Isothermal experiments after fast quenches extend the temperature range down to and below the glass transition. The employed differential fast scanning calorimeter (DFSC) allows cooling at rates up to 100,000 K/s and precise adjustment and control of isothermal conditions in the time range from 10^{-4} to 10^4 s and longer. As shown in previous work, heterogeneous crystal nucleation dominates at low supercooling, revealing a significant dependence of crystallization rate on MWCNT concentration. Nevertheless, no saturation of the nucleation activity at a MWCNT loading of 0.2–0.5 wt% as seen in slow DSC experiments was observed at the much higher cooling rates employed here. At high supercooling, where homogeneous nucleation is prevalent, the addition of MWCNT neither enhances nor reduces the crystallization rate. At the temperature of maximum homogeneous nucleation rate, formation of homogeneous nuclei always dominates crystallization.

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1. Introduction

Nucleating additives are widely used to initiate crystallization during processing of polymers since a number of properties of the final product can be modified by tailoring crystallization. The direct influence of the degree of crystallinity on optical, mechanical and dielectric properties was investigated by several authors, e.g. [1–4]. In particular, it is known that the increase of the amount of nucleation sites may lead to the formation of a large number

of crystals which do not organize in a higher-order superstructure. Absence of spherulites in semicrystalline polymers has been shown to be beneficial to obtain highly transparent films, of high stiffness and simultaneously high ductility.

In any such attempt to initiate crystallization by heterogeneous nucleation sites, one has to appropriately account for the effect of homogeneous nucleation too. By homogeneous nucleation, under certain conditions, a very large number of nuclei can be formed [5–7] and therefore it is expected to compete with nuclei formation caused by nucleating additives. As one prerequisite, a large undercooling (temperature sufficiently below the melting temperature) has to be achieved, and therefore a certain high

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enough cooling rate has to be realized in order to avoid crystallization initiated by heterogeneities during cooling. Realizing experimentally such conditions, one can control the degree of crystallinity/semicrystalline morphology by allowing homogeneous nucleation for some given interval of time in addition to heterogeneous nucleation due to additives. However, these conditions are not so easy to achieve for relatively fast crystallizing polymers. Making homogeneous nucleation the dominant mechanism for polyethylene (PE) crystallization is expected for cooling rates larger than 2×10^6 K/s. Isotactic polypropylene (iPP), poly(butylene terephthalate) (PBT), polyamides (PA) and poly(ϵ -caprolactone) (PCL) can be solidified with dominant homogeneous nucleation at cooling rates of the order of 10^2 to 10^3 K/s. Cooling rates of this order of magnitude are of technological interest and can nowadays be mimicked in fast scanning calorimeters. At high enough cooling rates the formation of homogeneous nuclei may be significantly or totally suppressed [8–11]. Samples containing no or only a small number of homogeneously formed nuclei and a defined heterogeneous nucleation density provide an interesting model system for studying nucleation kinetics and nucleation efficiency of the different types of heterogeneous nucleation sites at technologically relevant cooling conditions. The analysis of this problem on the example of PCL as a model system is the main goal of the present paper.

Judging the nucleation efficiency is commonly done by comparing the crystallization peak temperature on cooling from the melt in differential scanning calorimeter (DSC) traces at cooling rates of the order of 10 K/min [12]. A higher crystallization temperature is considered to indicate higher nucleation efficiency. Fig. 1 shows data of pure and MWCNT nucleated PCL samples with different amounts of the nucleating agent. The increase of crystallization temperature by adding MWCNT to the PCL sample is well pronounced. From Fig. 1 one could conclude that already 0.2% MWCNT yield a saturation of the nucleation effect. Müller et al. [13] describe a similar behavior for different samples.

Going beyond the traditional methods of nucleation efficiency comparison, in the current work we suggest a comparison based on a quantitative measurement of isothermal crystallization rates. Furthermore, the influence of homogeneous nucleation on isothermal crystallization of pure and nucleated samples was investigated and compared with the nucleation efficiency of MWCNT.

2. Experimental

2.1. Materials

Poly(ϵ -caprolactone) (PCL), a linear aliphatic polylactone, having the desired thermal and mechanical stability, a relatively high crystallization rate, and the possibility to tune the nucleation intensity was previously chosen as a model polymer for studying solidification of semicrystalline polymers [6,8]. For this reason, PCL was used again as a model system to study the influence of multiwalled carbon nanotubes (MWCNT) on the kinetics of nucleation

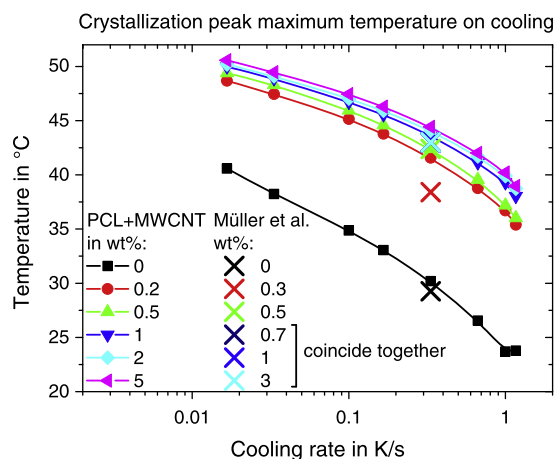


Fig. 1. Influence of multiwalled carbon nanotubes (MWCNT) on the crystallization peak temperature on cooling of poly(ϵ -caprolactone) (PCL), studied by conventional DSC (Perkin Elmer Pyris 1 DSC). Crosses are data from [13].

and crystallization. The different modes of crystallization initiated by or around MWCNTs are described by [14] and references therein. The PCL is a commercial material from Fluka with a molecular weight average $M_w = 20$ kg/mol and $M_w/M_n = 3$. The PCL/MWCNT nanocomposites, the same as used in [15], with 0.2, 0.5, 1, 2, and 5 wt% MWCNT were produced by melt mixing for 15 min at 65 °C and 150 rpm using a conical small-scale (4.2 g) DACA Microcompounder (DACA Instruments, Santa Barbara, USA). The multiwalled carbon nanotubes Nanocyl™ NC7000 were purchased from Nanocyl SA, Sambreville, Belgium. Their average diameter is 9.5 nm and the length is 1.5 μ m; the purity is about 90% [16].

For the investigation of polymer nucleation and growth in the form as desired by us and described in the introduction, conventional techniques, including DSC, are not suitable. Employing these methods, one cannot cool rapidly crystallizing polymers fast enough to prevent nucleation. These problems can be resolved by applying differential fast scanning chip calorimeter (DFSC). It was shown in previous work that employing DFSC one is able to perform heat flow measurements during controlled heating and cooling up to rates of 500,000 K/s. The power control circuit allows one to perform isothermal experiments for times shorter than 0.1 ms (with over- or undershoots <1 K). A PCL sample of about 20 ng can be quenched at cooling rates up to 70,000 K/s. This rate was proven to be sufficiently high to avoid homogeneous nucleation in pure PCL (>10,000 K/s), but it is just at the border of detection of the same effect in slightly nucleated materials (0.2 wt% MWCNT) (Fig. 7 in [8]). Therefore, it was decided to reduce, in comparison to [8], the size of the sample by a factor of 2 and to use a calorimeter chip with a smaller heated area (XI 269 instead of XI 320). Thus we extend the maximum possible cooling rate up to 70,000 K/s. The sample mass was determined independently from the heat capacity step at the glass transition, the heat capacity far below glass transition at 150 K and above the melting temperature at 380 K [17]. A qualitative upgrade of the calorimeter was

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