



Effect of graphene nanoplatelets diameter on non-isothermal crystallization kinetics and melting behavior of high density polyethylene nanocomposites



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ABSTRACT

In the present study the effect of different size of graphene nanoparticles 5, 15 and 25 μm in diameter, on melting behavior and crystallization kinetics of high density polyethylene (HDPE) was investigated. Crystallization of HDPE and its graphene nanocomposites in non-isothermal conditions was studied at several constant cooling rates from 1 to 20 K/min by means of differential scanning calorimetry. The results showed that the Avrami analysis modified by Jeziorny and a method developed by Mo could describe the non-isothermal crystallization of nanocomposites very well. Kinetics data analysis showed that the overall crystallization rate, the activation energy and the fold surface-free energy of the HDPE polymer were apparently changed due to the addition of graphene filler in different diameter size. Particularly, the incorporation of all graphene nanoparticles resulted in a greater crystallization temperature of HDPE, but graphene nanoparticles M5 with the smaller diameter increase more the number of heterogeneous crystallization nuclei and this resulted in a higher crystallization rate.

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1. Introduction

In the last decade, extensive research on nanocomposites in which the filler particles are plate-like with dimensions in the nanometer range has been carried out [1]. High aspect ratio fillers, such as graphene nanoparticles (GNPs), were used widely in order to enhance the properties of polymers due to the strong interaction between nanoparticles and polymer chains. Even the addition of small concentrations of nanoparticles has the potential to change the polymer matrix properties.

Graphene is a material with outstanding properties that make it an excellent candidate for the synthesis of polymer nanocomposites. It is a promising material suitable for thermally stable polymer nanocomposites [2]. HDPE is the most widely used polyolefin with numerous industrial applications based on its attractive properties. This is because of its regular chain structure, high melting point, good thermal and electrical resistance, excellent mechanical properties and the combination of low cost and energy demand

for processing [3]. Melt mixing process is a typical method for the preparation of thermoplastic polymer nanocomposites. It is a practical, environmentally friendly, cheap and suitable method for mass production in industrial applications.

A sound knowledge and understanding of crystallization mechanisms are necessary for designing materials with the required properties, because the crystallization process influences polymer properties through the crystal structure and morphology established during processing. The crystallization behavior of HDPE in the presence of various filler substrates has been extensively studied under isothermal conditions because problems related to the cooling rates and thermal gradients within samples can be minimized [4–6]. From the practical view, the non-isothermal crystallization seems to be much more realistic, since it can better simulate the actual industrial process of composite materials. According to literature, Avrami and Ozawa equation, along with the method proposed by Mo are applied in order to determine crystallization kinetics under non-isothermal conditions [7]. Shehzad et al. [8] used these methods for the non-isothermal crystallization kinetics of HDPE/graphene nanocomposites, prepared by in situ polymerization, at cooling rates of 5, 10, 15 and 20 K/min and three different graphene compositions without reference to the graphene shape.

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The aim of this work focuses to study the effect of different size of graphene nanoparticles on HDPE crystallization in non-isothermal conditions at cooling rates of 1, 2, 5, 10 and 20 K/min prepared by melt mixing. For this reason, graphene platelets with three different diameter size were used. A complete study with Avrami and Ozawa equations, along with the method proposed by Mo was applied to obtain the non-isothermal crystallization kinetics of HDPE and its graphene nanocomposites. The nucleation activity of the nanoparticles on the matrix was explored. Moreover, the effective crystallization activation energy was also calculated as a function of the relative degree of crystallinity using the differential isoconversional approach of Friedman, and for the first time for these materials the results were used by Vyazovkin's method for evaluating the Hoffman-Lauritzen parameters from overall rates of non-isothermal crystallization.

2. Experimental section

2.1. Materials

HDPE under the trade name Luminece mPE M5510 EP was supplied by Total Petrochemicals (Feluy, Belgium). It has a melt flow index of 0.28 g/10 min and 0.955 g/cm³ density. The GNP fillers with an average thickness of 10 nm were supplied by XG Sciences Inc., USA having three different average diameter sizes: GNP with an average platelet diameter of 5 μm (GNP M5), 15 μm (GNP M15) and 25 μm (GNP M25). This translates into an average particle surface area ranging from 120 to 150 m²/g. The bulk density of all three GNP fillers is reported to be 2.2 g/cm³.

2.2. Nanocomposites preparation

HDPE/GNP composites containing 5 wt% of GNPs were prepared by melt-mixing in a Haake–Buchler Reomixer (model 600) with roller blades and a mixing head with a volumetric capacity of 69 cm³. During the mixing period, the melt temperature and torque were continuously recorded. For this case, a 5 min mixing at 473 K with a torque speed of 35 rpm was used. The components were physically premixed before being fed into the reomixer. In order to achieve a better dispersion of the nanoparticles in HDPE matrix, a RETSCH centrifugal ball mill model S100 was used for solid-state mixing. The HDPE flakes along with the proper amount of GNPs were fed into a “C” type stainless steel grinding jar with a capacity of 50 mL. Five steel spheres of 10 mm diameter were also added as a grinding medium. The milling was set at 500 rpm for a period of 1 h. The prepared materials were coded as HDPE/M5, HDPE/M15 and HDPE/M25.

2.3. Characterization method

A differential scanning calorimeter (DSC) Pyris Diamond from Perkin-Elmer, calibrated with indium and zinc standards, was used for determination and measurement of the calorimetric behavior of HDPE and its nanocomposites. To promote optimal thermal contact between the sample and the sample container, a 15 μm thick, rectangular aluminum foil of approximately 0.5 × 1 cm is normally used to wrap the sample, instead of using a pan as sample container. On the reference holder an aluminum foil of the same dimensions and wrapped in the same way is placed.

As to the non-isothermal crystallization kinetics, the thermal history of the samples was erased by heating from room temperature up to 453 K and staying at this temperature for 2 min. Then, cooling scans were performed at rates of 1, 2, 5, 10 and 20 K/min. Subsequent melting after non-isothermal crystallization was measured at the heating rate of 20 K/min. The crystallinity of

the samples was calculated with the help of the ratio of the measured enthalpy with respect to the value for 100% crystalline HDPE material, which is assumed to be 293 J/g [9].

3. Results and discussion

3.1. Crystallization behavior of HDPE and HDPE/GNP composites

Neat HDPE and prepared HDPE nanocomposites of different graphene diameter size containing 5 wt%, have been characterized by DSC. To investigate the effect of each GNP on the crystallization behavior of the prepared nanocomposites, cooling rates from 1 to 20 K/min have been used. The sample mass was chosen to be 17.50 ± 0.1 mg, because the sample should be large enough at low cooling rates in order to have a good signal to noise ratio and a high sensitivity and resolution for the measurable signal [10].

The cooling curves of some selected samples, neat HDPE and HDPE/M5, are shown in Fig. 1. As it is obvious, all curves in both samples present only one well-defined exothermic peak. The lowest cooling rates, 1, 2, 5 K/min, induce a rather narrow crystallization peak, while the highest cooling rates, 10 and 20 K/min, provoke broad crystallization curves. As expected, the curves, and by that the peak temperatures, shift towards lower temperatures with increasing cooling rates as there is no sufficient time to activate nuclei at higher temperature. The molecular chains present less flexibility and there is shorter time in order to diffuse into the crystallite lattice and organize the chain configurations into more perfect crystallites. Particularly, with increased, controlled cooling rates, the crystallization peak temperatures of the HDPE and its nanocomposites show a significantly decrease of the crystallization temperature of about 9 K and 12 K respectively, as a result of cooling at 20 K/min as compared to 1 K/min.

As can be also seen from Fig. 1, the crystallization temperature for a given cooling rate, T_c , of prepared nanocomposites (HDPE/M5, HDPE/M15 and HDPE/M25) is slightly higher than that of the neat HDPE, indicating a clear nucleating effect of graphene filler over polymer matrix. Specifically, as can be seen from Table 1, GNP M5 that has the lower diameter size shifts the crystallization peak to higher temperatures than GNP M15 and M25. This should be reflected on the structure and the size of crystalline units. Because the crystallization process in these nanocomposites involves the segregation of the GNPs, the observed decrease in crystallization temperature with the increasing graphene diameter can be considered to be due to the rejection from the crystalline phase of these units, which makes the regular packing of the HDPE polymer chains more difficult [11]. Furthermore, due to the higher size diameter of GNP M15 and M25, the ability of HDPE macromolecules to be fold in order to create the lamellas may be hindered. However, even in these nanocomposites the crystallization temperatures are slightly higher than neat HDPE, especially in lower cooling rates, which indicate the nucleating effect of GNP on HDPE crystallization.

Since the crystallization process is time dependent, lower cooling rates provide more fluidity and diffusivity for the molecules because of the lower viscosity and more time for the perfection of crystallization. As a result, the enthalpy of crystallization increases with decreasing cooling rate, thus inducing much higher values. Results shown in Table 1 also indicate that the enthalpy of crystallization markedly increases with loading GNPs in composites.

3.2. Melting behavior following the non-isothermal crystallization

As there is no reference available for the melting following the non-isothermal crystallization of these materials, it is interest to study this behavior. So, DSC heating curves of the neat HDPE and

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