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Non-isothermal crystallization behavior of low-density polyethylene/copper nanocomposites

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Abstract

The influences of copper nanoparticles content and cooling rate on non-isothermal crystallization behavior of low-density polyethylene/copper (LDPE/Cu) nanocomposites were investigated. Nanocomposites were prepared by extruding mixtures of pure LDPE and copper nanoparticles using melt-blending method in a single-screw extruder. Differential scanning calorimetry (DSC) was used to analyze their non-isothermal crystallization behavior. The results indicate that both the incorporation of copper nanoparticles and cooling rates influence the crystallization behaviors of the LDPE matrix significantly. Especially, the dependence of the effective activation energy on the relative extent of crystallization implies that the copper nanoparticles dispersed in the nanocomposites may act as a heterogeneous nucleation for the crystallization of the LDPE matrix, and that the presence of the copper nanoparticles may hinder the transport of the molecule chains at the same time, resulting in a decrease of the crystallization growth rate of the LDPE matrix.
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1. Introduction

Polymer-based metal nanocomposites are a very important branch of nanocomposites based on polymer matrix. They have combined the advantages of the matrix polymer with the unique characteristics of metal nanoparticles organically. The incorporation of metal nanoparticles makes the nanocomposites gain a series of unique properties, such as optical properties [1–3], electronic properties [4–6], magnetic properties [7], catalytic properties [8], sensitive properties [9], wear properties [10] and so on. Polymer-based metal nanocomposites have become a novel kind of functional materials that has great potential application in many fields.

The polyethylene (PE) is one of the most widely used thermoplastics resins. Considering the fact that the LDPE possesses excellent biocompatibility with human body and usually used as implantable material, LDPE/Cu nanocomposites have been developed as a new kind of intrauterine contraceptive devices (IUDs) materials by using their properties of controlled release in our research. As we know, the cupric ions released from copper-containing IUDs in uterine fluid can enhance their contraceptive effect [11–13], and the larger the release rate of cupric ions, the better the contraceptive effect is. But the release rate of cupric ions in uterine fluid is affected by the structure, i.e. the crystallinity degree, of this new IUDs material. Therefore, it is necessary to study the crystallization behavior of this new IUDs material.

In addition, compared with the investigation of the crystallization behavior of polymer-based non-metal nanocomposites, such as the PTT/clay nanocomposites [14], the PA/clay nanocomposites [15], the PP/P-g-MAH/Org-MMT nanocomposites [16], and so on, the investigation of the crystallization behavior of polymer-based metal nanocomposites is lagged behind relatively. Whether both of them have the similar crystallization behavior or not is not clear, this is an-

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other reason why it is necessary to study the crystallization behavior of LDPE/Cu nanocomposites.

Compared with the isothermal crystallization conditions, the non-isothermal crystallization conditions are much more closer to the real industrial processing conditions, and the results of investigation on non-isothermal crystallization can guide us to control the structure of this new IUDs material. Consequently, the non-isothermal crystallization behavior of LDPE/Cu nanocomposites was investigated in this paper.

The LDPE/Cu nanocomposites were analyzed using differential scanning calorimeter (DSC) to examine the influences of copper nanoparticles content and cooling rate on their non-isothermal crystallization behavior. Simultaneously, pure LDPE was analyzed in the same process for comparison.

2. Experimental

2.1. Materials

The LDPE (melt index at 463 K/2.16 kg is 1.8–3.2 g/10 min) was bought as pellets from Qilu Petrochemical Corporation of China. The copper nanoparticles were prepared via our own patent techniques, i.e. hybrid induction and laser heating (HILH) evaporation condensation method [17]. Their mean diameter is about 50 nm, and purity is over 99.9%.

2.2. Preparation of nanocomposites

The LDPE/Cu nanocomposites were formed by compounding the polymer with 2.0, 6.0, 7.5, and 11.0 wt.% of copper nanoparticles by using melt-blending process in a single-screw extruder (SJ20, made in Jiangshu, China) at a screw speed about 15–20 rpm, respectively. The temperature of the extruder was maintained at 145, 160, and 180 °C from hopper to die, respectively. The composites are referred to here as LC-2.0, LC-6.0, LC-7.5, and LC-11.0, respectively. For comparison, samples of pure polymer were processed in the same way. Table 1 shows the amount of copper nanoparticles in LDPE/Cu nanocomposites.

2.3. Differential scanning calorimetry (DSC) procedures

The non-isothermal crystallization behavior of the pure LDPE and its nanocomposites was analyzed using a Perkin-Elmer DSC 7 differential scanning calorimeter. The temperature scale of the DSC was calibrated from the melting point (156.60 °C) of high purity (99.999%) indium metal. The power response of the calorimeter was calibrated from the enthalpy of fusion of indium, taken to be 28.45 J/g. The specimens were excised from extruded strands. Each sample is less than 5 mg and was accurately weighed using analytical balance, and then placed in the DSC cell. All DSC analyses were performed under argon atmosphere.

Table 1
Amount of copper nanoparticles in LDPE/Cu nanocomposites

Samples	LC-2.0	LC-6.0	LC-7.5	LC-11.0
Copper nanoparticles (wt.%)	2.0	6.0	7.5	11.0

The samples were composed of two groups. The first group was used for evaluating the influence of copper nanoparticles content on the non-isothermal crystallization behavior of the nanocomposites. It contains five samples, of which copper nanoparticles content were 0, 2.0, 6.0, 7.5, and 11.0 wt.%, respectively. Each sample was analyzed using the same process, i.e. heated from 30 to 160 °C at a rate of 10 °C/min, held for 2 min at 160 °C to ensure melting, and then cooled to 30 °C at 10 °C/min. Both the exothermic and endothermic curves were recorded. The second group was used for evaluating the influence of cooling rate on the non-isothermal crystallization behavior of the pure LDPE and its nanocomposites. It includes two samples. One is pure LDPE and the other is its nanocomposites with 7.5 wt.% copper nanoparticles. Both of them were performed as follows: heated from 30 to 160 °C at a rate of 10 °C/min, kept for 2 min at 160 °C to eliminate the heat history before cooled at a specified cooling rate, then cooled to 30 °C at constant cooling rate of 5, 10, 15 and 20 °C/min, respectively. After kept at 30 °C for 2 min, samples were heated to 160 °C at a rate of 10 °C/min, then followed by the next cooling cycle. Both the exothermic and endothermic curves were recorded too.

Heating scans were analyzed for the initial melting temperature T_{fi}, the peak melting temperature T_{fp}, the final melting temperature T_{ff}, and the heat of fusion ΔH_f; while cooling scans were used to obtain the initial crystallization temperature T_{ci}, the peak crystallization temperature T_{cp}, the final crystallization temperature T_{cf}, and the heat of crystallization ΔH_c. The heat of fusion ΔH_f, which was determined by integrating the heat flow from 60 to 115 °C, was used to calculate the crystallinity degree of the pure LDPE and the matrix of the LDPE/Cu nanocomposites, X_c, defined by the ratio of $\Delta H_f/(1-x)$ (where x is the content of copper nanoparticles) to the heat of fusion of the purely crystalline form of PE, ΔH_f°, i.e. 289.9 J/g [18], as indicated in Table 2. The heats of crystallization ΔH_c, were determined by integrating cooling scans from 60 to 105 °C. Fig. 1 shows a representative example of a full heating and cooling cycle and the analytical technique used to calculate ΔH_f, ΔH_c, T_{fi}, T_{fp}, T_{ff}, T_{ci}, T_{cp} and T_{cf}.

3. Results and discussion

3.1. Influence of copper nanoparticles content on non-isothermal crystallization behavior

The non-isothermal crystallization exothermic and endothermic curves of the neat LDPE and its nanocomposites with various copper nanoparticles contents are illustrated in Figs. 2 and 3, respectively, and the values of ΔH_f, ΔH_c, T_{fi},

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