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Effect of highly filled ferrites on non-isothermal crystallization behavior of polyamide 6 bonded ferrites

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ABSTRACT

The aim of this study is to characterize the non-isothermal crystallization of polyamide 6 bonded highly filled ferrites which were prepared by the melt extrusion. Especially, the effect of ferrite concentration and its surface property on the non-isothermal crystallization were investigated by means of differential scanning calorimetry. The highly filled ferrite particles acting as obstacles could severely hinder the motion of surrounding chain segments, which were irrespective of surface nature. The ferrite could be modified by silane and obtain a visually enhanced interaction with polymer matrix which evoked the heterogeneous nucleation. Increasing this enhanced interfacial area between polymer–particle can promote the heterogeneous nucleation. However, a strong interaction can slow the motion of surrounding chain segments of particles, thereby producing a competitive effect on the crystallization rate and crystallinity. The plot of crystallization activation energy against concentration also can evaluate dispersion performance of hydrophilic fillers within hydrophobic polymer.

1. Introduction

Polymer bonded magnets (PBMs) as one of the more important developments in magnetic materials in recent years, have opened a new world of application opportunities. PBMs composed of polymeric matrices and magnetic fillers (e.g. ferrites, NdFeB, SmCo) can be produced by conventional polymer processing methods, and offer significant advantages, in terms of processing and cost, as compared with their metallic counterparts [1–20]. However, the introduction of a small quantity of semicrystalline engineering plastics as binders dilutes the concentration of magnetic powders, resulting in low magnetic performance. Moreover, the applications of PBMs were limited because highly filled magnetic fillers can severely increase the apparent viscosity of polymer flow and further make the processing difficult. In addition, highly filled fillers not only evoked damage of polymer continuous matrix, but also impacted the crystallization behavior of semicrystalline polymer, (e.g. polyamide, poly(*p*-phenylene sulfide), etc.), suggesting a macroscopic influence of mechanical properties. Furthermore, the crystallization behaviors of semicrystalline polymer composites as a function of processing conditions are of great importance in polymer processing, particularly for the analysis and design of processing operations [21]. Hence, it is important to understand the effect of highly filled particles on the crystallization of semicrystalline polymer matrix.

So far, there were only a minority of existing works focusing on the crystallization of the highly filled fillers/semicrystalline polymer systems. Otaigbe et al. [11] investigated isothermal crystallization of PPS/NdFeB composites and disclosed that NdFeB particles modified by silane acted as the nucleation agent and accelerated the crystallization of polymer. Furthermore, particle size distribution did not affect the crystallinity of the composite significantly. On the contrary, according to Khalil and co-author's report [22], the highly filled rice hull ash within polypropylene

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matrix did not play a role as the nucleation agent but hindered the crystallization, due to the fact that highly filled particles confined the motion of polymer chain. However, for highly filled organically modified montmorillonite (MMT)/maleic anhydride grafted polyethylene nanocomposites, the MMT had no significant effect on the total non-isothermal crystallization due to neutralizing effect [23]. There were also some studies on the crystallization of highly filled systems such as PMMA-layered silicate nanocomposites [23,24], organic matter/PP composites [25], Chlorinated polyethylene/layered silicate nanocomposites [26], etc. In spite of the extensive theoretical and experimental effect in the past decade, the effect of highly filled fillers on the crystallization of semicrystalline matrix is still unclear. The role of highly filled fillers within polymer matrix upon crystallization process still remains an open question.

In this paper, a method of non-isothermal crystallization which is closely related to manufacture process was adopted to study the crystallization behavior of polyamide 6 (PA6) bonded highly filled ferrites. For magnetic material, ferrites have inferior magnetic performance and be geared to the needs of low-end fields. The ferrites as inorganic particles can be modified by silane [11,27] and titanate [28]. On the other hand, PA6 is a typical polyamide with several attractive advantages such as high strength, good toughness and abrasion resistance, which is regarded as the appropriate polymeric matrices for PBMs. The ferrites/PA6 composites are considered as model systems to explore the intrinsic non-isothermal crystallization behavior and kinetic of highly filled systems. The non-isothermal melting process together with cooling process was involved to study the substantive characteristics of the interaction between polymer and particles.

2. Experimental

2.1. Materials

Polyamide 6 powder used were obtained commercially from Nanjing Hongrui Plastic Products Co., Ltd. (China). The density, melting point, heat distortion temperature and molecular weight of PA6 were 1.13 g/cm^2, 216 °C, 201 °C and 27,500, respectively. The magnetic powder: ferrites with density of 5.1 g/cm^2 and hydrophilic surface, manufactured by BGRIMM Magnetic Materials & Technology Co., Ltd. (China), consisted of a $6Fe_2O_3 \cdot SrO$ alloy ($SrFe_{12}O_{19}$) with various particle sizes being produced in block form (see inset of Fig. 1). The particle size distribution utilized ranged from 0.1 to 4 μm is determined by randomly measuring 100 ferrite particle from the inset of Fig. 1, as shown in Fig. 1. *N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane (CAS: 1760-24-3) produced by Nanjing Xiangfei Chemical Research Institute (China) was utilized as the coupling agent.

2.2. Sample preparation

The polymers and magnetic fillers were dried at 80 °C in a vacuum oven for 24 h before use. Before melt extrusion, quantitative PA6, ferrites and silane (1 wt% of ferrites, if there was) were mixed under strenuous stirring, and then the mixture was extruded with a Brabender two-screw extruder (ZKS-25, Krupp Werner & Pfleiderer GmbH, Stuttgart, Germany). The temperature of the extruder was maintained at 190, 220, 230, 240 and 250 °C from hopper to die, respectively. The rotation speed of the twin screw was 80 rpm. The neat PA6 was also extruded under the same condition. In the paper afterward the PA6 bonded ferrites with rough ferrite volume concentration of *j*% was referred to as PA6-j and the subscribed 'S' was added for silane modified sample. For example, PA6-46 used for PA6/ferrites with volume ratio of 54/46, $PA6_S$-46 used for PA6/ferrite/silane with volume ratio of 51.76/46/2.23, calculated based on their density.

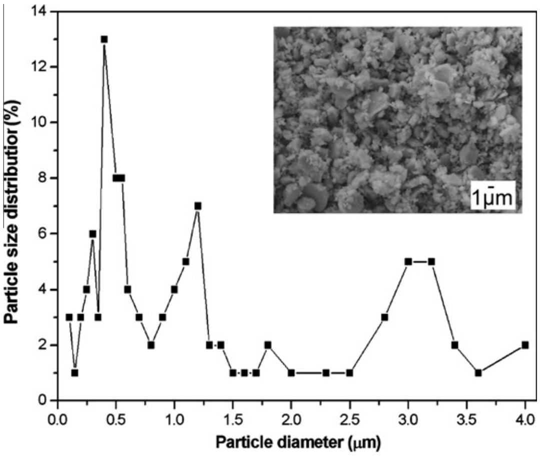

Fig. 1. The particle size distribution of ferrites is determined by randomly measuring 100 ferrite particles from the inset SEM photograph of ferrites.

2.3. Scanning electron microscope (SEM)

The morphologies of ferrites and PA6/ferrite composites were examined with a JEOL JSM-6700F for SEM experiment. The specimens were fractured by tensile testing with the drawing speed of 10 cm/s. The tensile fracture surfaces were coated with a thin layer of gold by JFC-1600 Auto Fine Coater and then examined by SEM.

2.4. Differential scanning calorimetry (DSC)

PerkinElmer DSC-7 calorimeter was used to characterize the cooling and melting process. The samples were dried under vacuum at 80 °C for 24 h to remove any remaining water. About 5 mg of the polymer samples was weighed accurately in the aluminum pan and placed in the DSC cell. All DSC analyses were performed under nitrogen atmosphere. The non-isothermal crystallization of PA6 and its composites were performed as follows: the sample was heated from 20 to 245 °C, at a heating rate of 40 °C/min. The sample was kept for 10 min at 245 °C to eliminate the thermal history. Then the sample was cooled to 100 °C at a heating rate of 40 °C/min. The non-isothermal crystallization behaviors were investigated by cooling samples from 245 to 100 °C at a constant cooling rate of