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Nonisothermal crystallization kinetics and melting behavior of poly (butylene terephthalate) and calcium carbonate nanocomposites

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ABSTRACT

Nonisothermal crystallization kinetics of poly(butylene terephthalate) (PBT)/nano calcium carbonate ($CaCO_3$) composites were investigated by differential scanning calorimetry and polarized optical microscopy. PBT/nano $CaCO_3$ composites containing different wt.% of nano $CaCO_3$ were prepared by melt blending. Analysis of the melt crystallization data by various macrokinetic models like modified Avarami and Liu and Mo models revealed the dependence of crystallization rate on nano $CaCO_3$ content. Nano $CaCO_3$ addition upto 5 wt.% greatly accelerated the crystallization rate. However, higher loadings of the filler retarded the crystallization rate. These results were further supported by the effective activation energy calculations by isoconversional method of Friedman. Polarized optical microscopy showed a decrease in spherulites size with increase in filler content. The study showed that small amount of nano $CaCO_3$ acts as additional nucleating agent and is effective in accelerating the crystallization rate whereas higher loadings increase the nucleation density but restrict the mobility of polymer chains and retard the growth process.

1. Introduction

During the last decade polymer nanocomposites have attracted the attention of academic and industrial research and evolved as a new class of materials. The transition from conventional microcomposites to nanocomposites has brought about a radical change in the mechanical and thermal properties of polymers. The factor that has contributed to the exploitation of nanoparticles is their large surface area to volume ratio which enables to improve the mechanical and thermal properties of polymer at rather low filler loading [1–4]. The large interfacial area in polymer nanocomposites is also expected to have a marked effect on the crystallization behavior of polymer which in turn significantly influences its physical and mechanical properties. In this respect, understanding the crystallization kinetics of polymer nanocomposites is of practical importance. The processing of polymer generally involves nonisothermal crystallization conditions, therefore nonisothermal crystallization study is crucial from scientific prospective.

Precipitated calcium carbonate ($CaCO_3$), one of the most commonly employed nanofiller is known to influence not only the mechanical, but also the thermal properties of polymer. Investigations by researchers on the effects of nano $CaCO_3$ in polymer composites have shown an enhancement in mechanical properties like viscosity, modulus [5], ductility [6] and impact strength [7–9]. Besides this, the nonisothermal crystallization kinetics of nano $CaCO_3$ based polymer composites has also been the subject of large number of studies [10–16]. Avella et al. [10] analyzed the influence of different shape $CaCO_3$ nanoparticles on the thermal properties of polypropylene. They found an increase in the glass transition and crystallization temperature and attributed the diverse effects of particle shape on crystallization of polypropylene to be surface specific. In addition, a study on the effect of surface modification of nano $CaCO_3$ on the crystallization of isotactic polypropylene (iPP) by Avella et al. [11] revealed that the coating agent largely affects the nucleating ability of $CaCO_3$ towards formation of polymer crystals but exhibits a limited influence on crystal growth rate. Run et al. [12] investigated the effect of nano $CaCO_3$ filler content on the nonisothermal crystallization kinetics and crystal morphology of poly(trimethylene terephthalate) and found that the nucleation activity of nanoparticles accelerates the nanocomposites crystallization rate by decreasing the activation energy. The results of this study also indicated that optimum filler content is essential for maximum improvement in crystallinity and crystallization rate. Apart from this, nonisothermal crystallization kinetics studies on various polymer based $CaCO_3$ nanocomposites like polypropylene [13,14],

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polyethylene [15] and poly(ethylene terephthalate) [16] have demonstrated that nano $CaCO_3$ exhibits a pronounced effect as a heterogeneous nucleating agent and enhances the crystallization rate of polymer.

Poly(butylene terephthalate) (PBT), a semicrystalline thermoplastic polyester has excellent dimensional stability, high strength, chemical resistance and fast rate of crystallization. The versatile combination of mechanical, thermal and chemical properties makes PBT an ideal candidate for many engineering applications. To extend the applications of PBT, compounding with nanofillers like montmorillonite [17–19], oxidized single wall carbon nanotubes [20], nano SiO_2 [21] has been reported to be an effective method for improving the mechanical and thermal properties of PBT. These nanocomposites of PBT have also been investigated for their nonisothermal crystallization kinetics [22–24]. Zhang et al. [25] investigated the nonisothermal crystallization of PBT nucleated with elastomer-modified nano-SiO_2, a commercial nucleating agent (P250) and talc and concluded that these fillers lower the crystallization time by changing the nucleation mechanism and crystal growth in PBT. Mulla et al. [26] investigated the non isothermal crystallization kinetics of PBT/nano carbon fiber and PBT/nanoclay composites based on various macro kinetic models. They reported that addition of small amount of carbon nanofiber and nanoclay (2 wt.%) lowered the activation energy for crystallization and improved the crystallization rates whereas, higher filler loadings reduced the crystallization rate.

Incorporation of nano $CaCO_3$ in PBT matrix is known to improve its friction coefficient [27] which has also been demonstrated in one of our previous study [28]. However, to the author's knowledge research on the nonisothermal crystallization kinetics of PBT/$CaCO_3$ nanocomposites has not yet been reported in the literature. Therefore, the main objective of the present investigation is to analyze the influence of nano $CaCO_3$ on the crystallization behavior of PBT. The effect of nano $CaCO_3$ content on the nonisothermal crystallization kinetics of PBT has been analyzed using Avrami, Ozawa, Mo and co-workers macro-kinetic models respectively. The effective activation energies are also estimated by Friedman equation.

2. Experimental

PBT used in this study was of commercial grade procured from BASF under trade name Ultradur B 2550 with melt flow index and density of 18 g/10 min and 1.30 g/cm^3 respectively. Nano $CaCO_3$ having particle size of 100 nm was supplied by Specialty Minerals. PBT nanocomposites containing 2, 5 and 10 wt.% of nano $CaCO_3$ were prepared by melt blending method using single screw extruder. Corresponding to the wt.% of nano $CaCO_3$ the composites were designated as PBT (0 wt.%), NC1 (2 wt.%), NC2 (5 wt.%) and NC3 (10 wt.%) respectively. Prior to the compounding of composites, PBT and $CaCO_3$ were dried at 110 °C in oven for 6 h before use in order to remove the moisture. During compounding in single screw extruder, the temperatures of the four heating zones were set to 220, 230, 240, and 250 °C, and the screw speed was fixed at 30 rpm. The extruded strands were cooled in the water bath, then cut into pellets using a pelletizer and dried in oven to minimize the effects of moisture.

The nonisothermal crystallization behavior of PBT nanocomposites was analyzed using Mettler Toledo differential scanning calorimeter (DSC 821) equipped with an intracooler. High purity indium and zinc standards were used for instrument calibration. For recording nonisothermal crystallization exotherms, samples weighing around 10 mg were first heated from 30 °C to 250 °C at a heating rate of 10 °C/min and held at this temperature for 5 min in order to erase their thermal history. The samples were then cooled down from 250 °C to 30 °C at four different cooling rates (Φ) of 2.5 °C/min, 5 °C/min, 10 °C/min and 20 °C/min, respectively. The recorded nonisothermal crystallization exotherms were analyzed using different kinetic models. The nonisothermally crystallized samples were subsequently subjected to second melting by heating from 30 °C to 250 °C at a heating rate of 10 °C/min in order to study the melting behavior. All the experiments were carried out in nitrogen environment.

The dispersion of nano $CaCO_3$ in the PBT matrix was examined by JEOL JSM 6380A scanning eelctron microscope. The spherulitic morphology of neat PBT and the three composites were observed using Carl Ziss AXIOSkOP 2 MAT polarized optical microscope. Extruded samples were sandwiched between two microscopic slides and melted in an oven at 250 °C. They were then held at this temperature for 5 min in order to ensure complete melting and finally cooled to room temperature at cooling rate of 20 °C/min.

3. Results and discussion

3.1. Nonisothermal crystallization behavior

Dispersion of nanoparticles in the polymer matrix influences the crystallization rate and crystallinity of polymer. The scanning electron micrograph of the 5 wt.% PBT nanocomposites is shown in Fig. 1. The figure exhibits discrete particles of nano $CaCO_3$ welded in PBT matrix. This indicates that $CaCO_3$ nanoparticles are uniformly dispersed in PBT matrix. The nonisothermal crystallization exotherms of PBT and the three composites at various cooling rates are illustrated in Fig. 2. The onset crystallization temperature (T_o) and the peak crystallization temperature (T_p) evaluated from these thermograms are summarized in Table 1. From the thermograms and Table 1 it is clearly evident that an increase in cooling rate shifts the crystallization process towards lower temperature and broadens the crystallization peak. This indicates that the slower the cooling rate, the higher the temperature at which crystallization begins. At slow cooling rates there is sufficient time for polymer chains to overcome nucleation energy barrier and hence crystallization is initiated at higher temperature. Whereas, when the samples are cooled rapidly, the polymer molecules cannot lose their kinetic energy at the same rate. Hence, more undercooling is required for the nuclei to become active and initiate crystallization at high cooling rates [29–30].

Comparison of T_p for neat PBT and the composites at a given cooling rate in general reveals an increase in crystallization temperature on $CaCO_3$ addition. However, the T_ps for the three composites did not increase monotonically with the $CaCO_3$

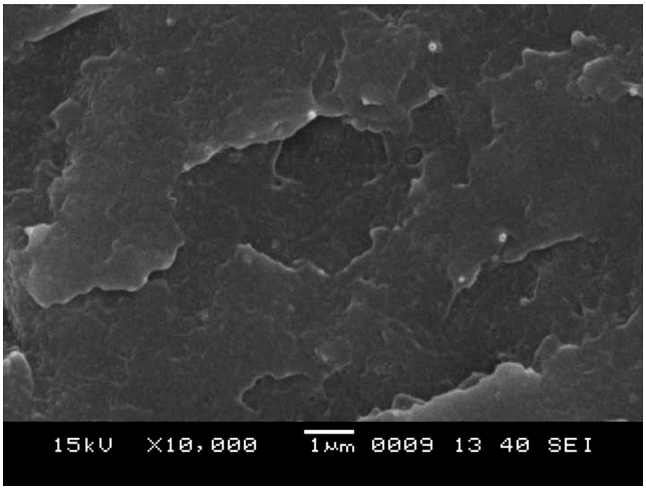

Fig. 1. Scanning electron micrograph of 5 wt.% PBT/nano $CaCO_3$ composite.