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Crystallization kinetics and nucleation activity of filler in polypropylene/surface-treated SiO₂ nanocomposites

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Abstract

Isothermal and non-isothermal crystallization kinetics of polypropylene (PP)/surface-treated SiO₂ nanocomposites were extensively studied. Analysis of the isothermal crystallization showed that the phenomenon is characterized by faster rates as the amount of silica is increased. In the case of non-isothermal crystallization, it was found that the Ozawa analysis was rather inapplicable for the nanocomposites. In contrast, the modified Avrami method, as well as the method proposed by Mo was applied giving satisfactory results. The effective energy barrier for non-isothermal crystallization was estimated as a function of the relative degree of crystallinity using the isoconversional analysis of calorimetric data. This was found to vary with the degree of conversion, as well as with the presence of filler. Finally, the nucleation activity of the silica nanoparticles on the polymer matrix was explored and it was proved that when the content of filler exceeds 7.5 wt.% the nucleation is not drastically improved.

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1. Introduction

The synthesis of new polymeric materials involves high cost therefore research is directed towards modifying current polymers to achieve inexpensive materials with tailored structures and suitable for targeted applications. The use of additives in polymer matrices is a common practice. It usually aims at material reinforcement, enhanced crystallization rates and plasticizing for easier processing. Recently, there has been much research on creating organic/inorganic composites by adding nanoparticles to the polymer matrix [1], resulting thus in materials having greatly improved mechanical and rheological properties [2].

Isotactic polypropylene (i-PP) has become the most interesting commodity thermoplastic, due to its higher isotacticity, enhanced mechanical properties, narrow molecular weight distribution and increased clarity. Therefore, its worldwide production grew up very fast during the last years and there is a tendency to replace some of the traditional polymers in many of their applications. Thermal and mechanical properties of this polymer can be significantly improved using fillers that will act as artificial nucleating agents [3]. Nanoparticles are new classes of fillers, which due to their higher surface area may enhance further the crystallization rate of semicrystalline polymers. SiO₂ nanoparticles are used for effective reinforcement of synthetic rubbers [4], as well as to enhance notch toughness and tensile performance improvement of polypropylene [5–7]. However, different and some times contradictory results have been mentioned about the effect of SiO₂ nanoparticles on crystallization rate of semicrystalline polymers. Rong et al. [6] reported that SiO₂ exhibits some nucleation effect on the crystallization rate of PP matrix though the addition of the nanoparticles does not greatly influence the whole crystalline features of PP. In polyamide 6, unmodified silica nanoparticles increase the crystallization rate of the matrix while modified ones degrase it [8]. In contrast, it was reported that pretreated SiO₂ nanoparticles slightly increased

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the non-isothermal crystallization rates of nylon 6 [9]. In case of larger SiO_2 particle size (5–25 μm) than the nanoscale, it was found that crystallization of polytetrafluoroethylene decreases slightly with the addition of different SiO_2 content [10].

Furthermore, the final polymeric material properties are dependent on the morphology generated during their processing. In this stage, the filler in polymeric-based composite materials may act as a nucleating agent and affect thus the crystallization behavior. So, the knowledge of the parameters affecting crystallization is crucial for the optimization of the processing conditions and the properties of the end product. Research on the polymer crystallization process can be carried out under isothermal or non-isothermal conditions [11]. Analysis of the overall crystallization rate under isothermal conditions is generally accomplished with the use of the so-called Avrami equation [12–17], which is valid at least for the early stages of the process. However, non-isothermal crystallization of polymers is quite difficult to be modelled. Some authors tried to model the non-isothermal process, assuming it can be approximated by a sequence of infinitesimally small isothermal stages, so that it can be described by models based on modifications of the Avrami equation [18–26]. Recently, the non-isothermal crystallization kinetics of several polymer nanocomposites have been studied [27–33]. In this context, although the crystallization kinetics of plain PP have been extensively examined [11], few works dealing with the crystallization kinetics of its nanocomposite have been published [27,33–35].

In this work, the crystallization kinetics of new i-PP nanocomposites containing fumed silica at various amounts, from 1 to 10 wt.%, was studied under both isothermal and non-isothermal conditions. For this purpose various PP/SiO_2 nanocomposites samples were prepared and the effect of SiO_2 content on the crystallization rate of PP was examined. The spherulitic growth rate was used to obtain data on the specific surface free energies for the plain PP and all nanocomposites. Moreover, the kinetic parameters of the Avrami and Ozawa equations were obtained, along with the combined Avrami–Ozawa method. The nucleation activity of the nanoparticles on the polymer matrix was explored. Finally, the effective energy barrier of non-isothermal crystallization was calculated as a function of the relative degree of crystallinity using an isoconversional approach.

2. Experimental

2.1. Materials

Isotactic polypropylene was supplied from BASELL polyolefines with a melt flow index (MFI) 12 g/10 min at 190 °C. The hydrophobic fumed silica (SiO_2) nanoparticles used were supplied from Degussa AG (Hanau, Germany) under the trade name AEROSIL® R974. It was produced by treating hydrophilic fumed silica nanoparticles with dimethyldichlorosi-

lane, and had a specific surface area 170 m^2/g and average primary particle size 12 nm.

2.2. Nanocomposites preparation

Nanocomposites containing 1, 2.5, 5, 7.5 and 10 wt.% SiO_2 nanoparticles were prepared by melt mixing on a Brabender (model DSC Φ25/32D) twin screw corotating extruder with L/D 32 (D25 mm). Along the screw there were different screw elements in order to induce polymer melting and nanoparticle fine dispersion in the polymer melt. Prior to the melt processing, silica nanoparticles were dried for 24 h at 105 °C. After compounding the material was extruded to produce cylindrical extrudates. These were immersed immediately in a cold-water bath (20 °C) and pelletized with an adjustable rotating knife, located after water bath, into 5 mm length.

2.3. Differential scanning calorimetry measurements

Crystallizations of the PP nanocomposites were performed in a Perkin-Elmer Pyris 1 differential scanning calorimeter (DSC). Samples of 5 ± 0.01 mg were used. Isothermal crystallization tests were performed at 125, 127.5, 130, and 132.5 °C. The samples were initially melted at 200 °C for 5 min in order to erase all previous thermal history. The temperature selected to begin the thermal treatment was quite higher than the measured melting point of all composites (around 162 °C), although not very high in order to avoid any possible thermal degradation of the polymer chains. Subsequently, the specimens were cooled at a rate of 200 °C/min to a temperature 20 °C above the crystallization temperature (T_c) and finally at a rate of 40 °C/min to T_c, so that equilibrium of the instrument was achieved. The samples were held at T_c until no change in the heat flow was recorded in the heat flow versus time plot. From the enthalpy evolved during crystallization the kinetics of crystallization was evaluated.

For non-isothermal crystallizations, samples were cooled at various cooling rates. Crystallizations were performed at cooling rates 2.5, 5, 10, and 20 °C/min. The crystallinity of the samples was determined from the heat of crystallization. Fast cooling lead to slightly lower crystallinity.

2.4. Morphological examination

Scanning electron microscopy (SEM) was carried out using a JEOL JMS-840A scanning microscope equipped with an energy-dispersive X-ray (EDX) Oxford ISIS 300 microanalytical system. For this purpose fractured surfaces as well as thin films were used. From these films the Si elemental composition of each nanocomposite sample was determined. The operating conditions were: accelerating voltage 20 kV, probe current 45 nA and counting time 60 s, with ZAF correction being provided on-line. All the studied surfaces were coated with carbon black to avoid charging under the electron beam.