Thermochimica Acta 521 (2011) 161–169

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Nonisothermal melt-crystallization kinetics for in situ prepared poly(ethylene terephthalate)/monmorilonite (PET/OMMT)

G. Antoniadis[a], K.M. Paraskevopoulos[a], A.A. Vassiliou[b], G.Z. Papageorgiou[b], D. Bikiaris[b], K. Chrissafis[a,*]

[a] Solid State Physics Department, School of Physics, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece
[b] Laboratory of Polymer Chemistry and Technology, Department of Chemistry, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece

ARTICLE INFO

Article history:
Received 8 February 2011
Received in revised form 19 April 2011
Accepted 20 April 2011
Available online 30 April 2011

Keywords:
Poly(ethylene terephthalate)
Nanocomposites
Montmorillonite
Crystallization
Activation energy

ABSTRACT

Poly(ethylene terephthalate) (PET) montmorillonite nanocomposites were prepared by in situ polymerization containing 0.5, 1, 2 and 5 wt% of organically modified montmorillonite (OMMT). In order to prepare exfoliated nanocomposites a new thermally stable modifier for montmorillonite nanoparticles like chlorohexadecane triphenylphosphine (CHDTPP) was synthesized. The preparation of nanocomposites was carried out using the two-stage melt polycondensation method. As verified by TEM micrographs, the dispersion of OMMT nanoparticles into the PET matrix was homogeneous while these were dispersed in the exfoliated form, proving the effectiveness of the modifier. The influence of OMMT nanomaterials on the thermal behaviour of PET and its non-isothermal crystallization was studied. Furthermore, the crystallization kinetics of PET and its nanocomposites were investigated by DSC. The activation energy was calculated using the Friedman's method. The Avrami exponent was calculated and analyzed. The effect of OMMT nanoparticles on spherulite growth rate of PET in all nanocomposites was also evaluated using the modified Lauritzen–Hoffman equation. From all these results it was found that OMMT nanoparticles can act as nucleating agents enhancing the crystallization rate of PET. The dispersion of OMMT nanoparticles in exfoliate form plays also an important role.

1. Introduction

Poly(ethylene terephthalate) is a linear semi-crystalline thermoplastic polyester with excellent mechanical, physical, and chemical properties, including very good heat resistance, high stiffness and strength, and good dimensional stability. These properties make PET an attractive high performance polymer for engineering plastic applications in areas of electronics, transportation, construction and consumer products. However, PET application as an engineering plastic for injection moulding is rather limited, due to its slow crystallization rate and large cycle time [1]. In order to increase its performance and mainly the mechanical and thermal properties of PET, during the past years, nanocomposites were prepared and studied, especially that containing montmorillonites (MMT).

Among the properties of PET that were enhanced due to the addition of MMT is, also, the crystallization rate, which was significantly increased with such an addition [2]. Xiao et al. [3] has shown that, MMT nanoparticles increase the heat of melting of PET/MMT nanocomposites, which is generally resulting from the high orientation or higher crystallinity. Yin et al. [4] studied the crystallization behaviour of PET/MMT nanocomposites, using MMT pre-treated with polyvinylpyrrolidone (PVP). Their results indicated that MMT treated with less PVP would retain relatively higher nucleation efficiency while in MMT containing more PVP, the nucleation effect of MMT became weaker. This behaviour was attributed to the exfoliation of MMT layers, when higher PVP amounts were used, which would slow down the crystallization process of PET matrix. Crystallization behaviour of PET/clay nanocomposites has been investigated, also, by other researchers indicating the nucleating effect of organoclay and that the crystallization rate of PET/MMT nanocomposite depends mainly on the surface modification of MMT [5,6]. Ke et al. [7] have reported that the PET/clay nanocomposite had three times greater crystallization rate than that of pure PET. Finally, Wang et al. [8] described the nonisothermal melt crystallization process of PET and two PET/clay nanocomposites. The activation energy for nonisothermal crystallization of pristine PET and two PET/clay nanocomposites was evaluated, and it was concluded that the absolute value of activation energy for PET is lower than that of PET/clay nanocomposites.

High-melt-temperature engineering polymers, such as PET raise additional concerns when considering preparation of nanocomposites with MMT by melt extrusion or in situ polymerization: as most alkylammonium treatments for MMT have an onset of thermal decomposition at about 200 °C or below [9], and as the

* Corresponding author. Tel.: +30 2310 998188; fax: +30 2310 998188.
E-mail address: hrisafis@physics.auth.gr (K. Chrissafis).

0040-6031/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2011.04.019

melt processing temperature of PET is above this temperature (close to 300 °C), the byproducts formed from the breakdown of these organic surfactants might lead to degradation of the polymer during melt processing or polymerization [10]. Therefore, the prepared polymer has low molecular weight and insufficient mechanical properties. The processing stability of both the polymer and the organic-treated layered silicate has a significant influence in nanocomposite properties. For this reason new thermally stable modifiers for MMT should be prepared and used [11–13]. In the present study PET/OMMT nanocomposites were prepared by in situ polymerization method, the aim of this study being the preparation of exfoliated PET/MMT nanocomposites. However, in order to achieve this, since neat MMT cannot be sufficiently dispersed into the polymer matrix, a new thermally stable organic modifier for MMT like chlorohexadecane triphenylphosphine compound was synthesized. As far as we know, no literature on similar work has been reported with this modifier. Furthermore, in this work we have focused in the study of the effect of the modifier, the dispersion of OMMT into PET matrix, and in the influence of OMMT amount to the nonisothermal melt-crystallization behaviour of pristine PET and PET/OMMT nanocomposites. This was achieved using a differential scanning calorimeter (DSC). Emphasis has been given also, in the study of the effect of OMMT nanoparticles on the crystallization mechanism of PET.

2. Experimental

2.1. Materials

Dimethyl terephthalate (DMT) (99%), ethyleneglycol (EG) (99%), antimony trioxide (Sb_2O_3) (98%) and triphenylphosphate (TPP) (95%) were obtained from Fluka. Zinc acetate [$(CH_3CO_2)_2Zn$] (99.99%) was purchased from Sigma–Aldrich. Pristine montmorillonite [$Na_x(Al_{4-x}Mg_x)Si_8O_{20}(OH)_4$, $0.5 \geq x \geq 1.3$] under the trade name Cloisite Na^+ was obtained from Southern Clay Products Inc. (Gonzales, TX, US). It had a Cation Exchange Capacity (CEC) of 92 mequiv/100 g. Triphenylphosphine ($(C_6H_5)_3P$) (≥95.0%) and 1-chlorohexadecane ($CH_3(CH_2)_{15}Cl$) (≥97.0%) were supplied from Sigma–Aldrich. All other materials and solvents used for the analytical methods were of analytical grade.

2.2. Modification of montmorillonite

To prepare the chlorohexadecane triphenylphosphine organic modifier ($Ph_3P^+C_{16}Cl^-$) for montmorillonite, 1-chlorohexadecane and triphenylphosphine were added simultaneously in a round bottom flask at a molar ratio of 1:1. The mixture was heated in an inert atmosphere (argon) at 100 °C for 2 h under constant mechanical stirring. The final viscous product of $Ph_3P^+C_{16}Cl$ was extensively washed with petroleum ether and dried at 50 °C for 24 h.

For the modification of the neat montmorillonite 25 g of Cloisite-Na^+ were added in 1 L of distilled water and stirred for 24 h. The suspension was then cooled (0–5 °C) and 30 mmol of the aforementioned synthesized $Ph_3P^+C_{16}Cl^-$ organic modifier, which was dissolved in 100 mL of distilled water, were added drop-wise. After 3 h of stirring at 0–5 °C, the white precipitate was removed by filtration and washed with distilled water until no chloride ions were detectable from an aqueous solution of $AgNO_3$. Subsequently, the sample was left to dry at room temperature under vacuum for 24 h, and then it was suspended in petroleum ether under constant stirring for 3 h. The sample was removed by filtration and washed again with additional petroleum ether. Finally, the prepared organically modified montmorillonite with chlorohexadecane triphenylphosphine (MMT-$Ph_3P^+C_{16}Cl^-$, OMMT), was dried at 70 °C for 24 h.

2.3. In situ preparation of PET/OMMT nanocomposites

Nanocomposites of PET were prepared in situ by the two-stage melt polycondensation of DMT and EG in a glass batch reactor. The nanoparticles were dried in vacuum at 120 °C for 24 h. Appropriate amount of filler was dispersed in EG by ultrasonic vibration (50 W) and intense stirring with a magnetic stirrer (300 rpm) for 10 min prior to polymerization. Zinc acetate was added (1×10^{-3} mol/mol DMT) and DMT at a molar ratio of DMT/EG = 1/2.2. The mixture was de-aired and purged with argon three times. Subsequently, it was heated at 190 °C for 1 h, under constant mechanical stirring (500 rpm). The methanol produced by the transesterification reaction was removed from the mixture by distillation and collected in a graduated cylinder. The temperature was raised to 230 °C and the reaction was continued for a further 2 h, where the complete removal of the anticipated produced methanol took place.

During the second stage, under an argon atmosphere, the polycondensation catalyst (Sb_2O_3, 250 ppm) and TPP (0.03 wt% DMT) as thermal stabilizer, dispersed in a small amount of EG, were added in the mixture. TPP is known to prevent side reactions such as etherification and thermal decomposition. Afterwards, vacuum was applied (~5 Pa) slowly, over a period of 15 min, to avoid excessive foaming and to minimize oligomer sublimation, which is a potential problem during the melt polycondensation. The temperature was raised to 280 °C and the reaction continued for 2 h. When the polycondensation reaction was completed, the reaction tube was broken to remove the product out of the flask. All polyester samples, after the glass particles were removed with a grinder, were grounded in a mill, sieved, washed with methanol and dried at 110 °C for 12 h.

In order to prepare the PET/OMMT nanocomposites different amounts of OMMT such as 0.5, 1.0, 2.0 and 5.0 wt% were added at the beginning of the transesterification reaction. The procedure was the same as described above for neat polyester.

2.4. Viscosity and molecular weight measurements

Intrinsic viscosity [η] measurements on the isolated polymers were performed using an Ubbelohde viscometer cap. Ic at 25 °C in phenol/tetrachloroethane 60/40 (w/w) at a solution concentration of 1 wt%. The solutions were filtered through a disposable membrane filter 0.2 μm (Teflon) prior to the measurement.

The number-average molecular weight $\bar{M}_n$ of the samples was calculated from intrinsic viscosity [η] values, using the Berkowitz equation [14]:

$$\bar{M}_n = 3.29 \times 10^4 \times [\eta]^{1.54} \quad (1)$$

2.5. Transmission electron microscopy

Electron diffraction (ED) and transmission electron microscopy (TEM) observations were performed on ultra thin film samples of the various nanocomposites that were prepared by an ultramicrotome. These thin films were deposited on copper grids. ED patterns and TEM micrographs were obtained using a JEOL 120 CX microscope operating at 120 kV, and in order to avoid the destruction of the films after exposure to the electron irradiation, they were coated with carbon black.

2.6. Differential scanning calorimetry (DSC)

The differential scanning calorimetric (DSC) measurements were carried out with a Setaram DSC-141 calorimeter. Temperature and energy calibrations of the instrument were performed for different heating rates, using the well-known melting temperatures and melting enthalpies of high-purity Zinc (Zn), Tin (Sn) and