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Poly(ethylene 2,6-naphthalate)/layered silicate nanocomposites: fabrication, crystallization behavior and properties

Tzong-Ming Wu*, Chuh-Yi Liu

Department of Material Science and Engineering, National Chung Hsing University, 250 Kuo Kuang Road, Taichung 402, Taiwan, ROC

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Abstract

In this study, poly(ethylene 2,6-naphthalate) (PEN)/layered silicate nanocomposites (PLSNs) were successfully prepared by the intercalation of PEN polymer into organically-modified layered montmorillonite through the melt blending process. Both X-ray diffraction data and transmission electron microscopy images of PEN/layered silicate nanocomposites indicate most of the swellable silicate layers were exfoliated and randomly dispersed into the PEN matrix. Mechanical and barrier properties of the fabricated nanocomposites performed by dynamic mechanical analysis and permeability analysis show significant improvements in the storage modulus and water permeability when compared to neat PEN. Differential scanning calorimeter (DSC) was used to investigate the isothermal crystallization behavior and melting behavior of PLSNs. DSC isothermal results revealed that the crystal growth process of PEN and PLSNs are a three-dimensional spherulitic growth. The activation energy of PEN increases with increasing content of layered silicates. The result indicates that the addition of layered silicate into PEN reduces the transportation ability of polymer chains during crystallization processes.

Keywords: Poly(ethylene 2,6-naphthalate); Nanocomposite; Structural behavior

1. Introduction

Polymer layered silicate nanocomposites (PLSNs) have been the focus of academic and industrial attention in recent years because the final composites often exhibit a desired enhancement of physical and/or chemical properties relative to the neat polymer matrix [1–5]. The synthesis of PLSNs is done by the intercalation of monomers or polymers into swellable layered silicate hosts. In most cases, the synthesis involves either intercalation of a suitable monomer and then exfoliating the layered host into their nanoscale elements by subsequent polymerization or melt-direct polymer intercalation by using a conventional polymer extrusion process [6–8]. The high aspect ratio layered silicate affects the mechanical, physical and thermal properties of the synthesizing polymer nanocomposites.

Poly(ethylene 2,6-naphthalate) (PEN) has received considerable attention due to its superior strength, low permeability to gases and excellent thermal stability [9,10], which is a possible candidate used in flexible substrate display. Crystallization studies of PEN including crystalline structure [11–13], crystallization kinetics [13], liquid-induced crystallization [14], structural change/formation during uniaxial [15–18] or biaxial drawing [15], flow-induced crystallization [19], and crystal morphology [20–23] have recently been reported and revealed a complex polymorphic behavior. The various crystalline structures differ with respect to the chain conformation and the chain packing within a unit cell. Two major crystalline forms, α and β form, were determined by Mencik [11] and Zachmann et al. [12] as triclinic unit cells with $a=6.51$ Å, $b=5.75$ Å, $c=13.2$ Å, $\alpha=81.33°$, $\beta=144°$, $\gamma=100°$ and $a=9.26$ Å, $b=15.59$ Å, $c=12.73$ Å, $\alpha=121.6°$, $\beta=95.57°$, $\gamma=122.52°$, respectively. Various effects on polymeric behavior of PEN are dependent on the crystallization condition such as crystallization temperatures and pre-melting temperatures [11–15]. Nevertheless, no further work appears and a deep understanding of the formation of both crystalline forms is still lacking.

It is well known that the physical and mechanical

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* Corresponding author. Tel.: +886 4 22840500x806; fax: +886 4 22857017.

E-mail address: tmwu@dragon.nchu.edu.tw (T.-M. Wu).

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properties of crystalline polymers depend on the structure and the morphology of the polymer crystallites and on the degree of crystallization. It has been recently found that the crystallization behavior and crystalline morphology of polymer nanocomposites are strongly affected by the presence of the layered silicates, including of polyamide [24–26], polypropylene [27–29], poly(ε-caprolactone) [30,31] and syndiotactic polystyrene [32–34]. General effects included induced polymorphism [24–27,32–34], small and irregular crystallite [27], increased crystallization rate [31–33] and alteration of the crystal fraction [32]. The extent of these effects depends on process history and specific characteristics of the resin.

In this report, we have used organically-modified montmorillonite as the dispersed phase to prepare PEN/layered silicate nanocomposites by melt-direct intercalation of PEN into swellable layered hosts. Due to the presence of rigid naphthalene ring in its backbone, it was not thought that homogeneous dispersion of the silicate layers in PEN would be realized. Therefore, the montmorillonite has been modified by *n*-hexadecyl trimethyl-ammonium bromide (CTAB) cations and then polymerized by a mixture of styrene and methyl methacrylate monomer at a styrene/-methyl methacrylate ratio of 8/2 with potassium presulphate as a catalyst to provide the chemical similarity between polymer matrix and surface-modified clay, which may further improve their interaction. The PLSNs have been prepared through the direct insertion of PEN polymer chains from the melt into the surface-treated clay. A conceptual illustration of the preparation of PLSNs is shown in Fig. 1. X-ray diffraction data indicate most of the swellable silicate layers were exfoliated and randomly dispersed into the PEN matrix. To the best of our knowledge this is the first report of exfolicated silicate layers within a PEN matrix. The physical properties of prepared nanocomposites were measured by dynamic mechanical analysis (DMA) and permeability analysis. Since the final mechanical properties of PLSNs are directly related to the crystalline features and behaviors [35,36], it is necessary to characterize the microstructure of PLSNs during formation. In particular, the addition of small amount of nanoscale layered silicate into PEN affected their crystalline behaviors during sample formation. This work is focused on the isothermal melt-crystallization kinetics and melting behavior of PLSNs from DSC thermal analysis. The parameters of crystallization kinetics, such as the laternal-surface and fold-surface energy of isothermal crystallization as well as the activation energy of PEN and PLSNs can also be discussed.

2. Experimental

2.1. Preparation of PLSNs

The poly(ethylene 2,6-naphthalate) (PEN) with weight average molecular weight (M_w) of 60,000 was kindly supplied by Union Chemical Laboratory (Hsinchu, Taiwan). Natural sodium montmorillonite (MMT) with a cation exchange capacity (CEC) of 110 mequiv/100 g was used as the dispersed phase to reinforce the PEN. The surface of natural sodium MMT was modified by cationic exchange between Na^+ in MMT galleries and *n*-hexadecyl trimethyl-ammonium bromide (CTAB) cations in an aqueous solution at 60 °C for 2 h. The exchanged MMT was then polymerized with a mixture of styrene and methyl methacrylate monomer at a styrene/methyl methacrylate ratio of 8/2 with potassium presulphate (KPS) as a catalyst. The PLSNs were prepared by a melt-direct intercalation process using

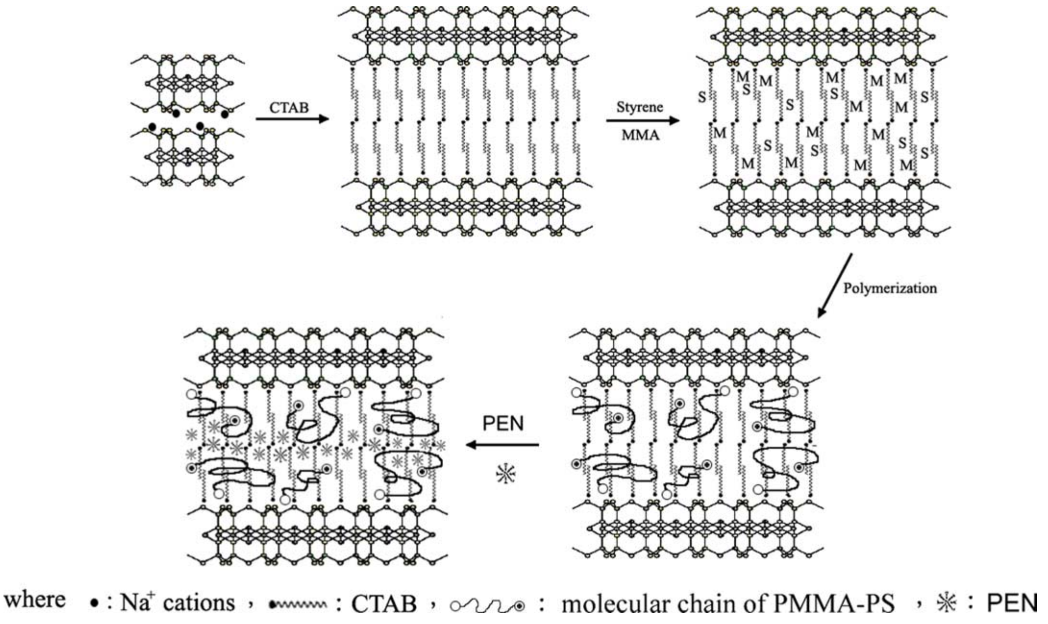

Fig. 1. Schematic representation of the preparation of PEN/organically-modified clay nanocomposites.