



In situ polymerization of poly(styrene-*alt*-maleic anhydride)/organic montmorillonite nanocomposites and their ionomers as crystallization nucleating agents for poly(ethylene terephthalate)



Shili Xing, Rui Li, Jingjing Si^{*}, Ping Tang^{*}

State Key Laboratory of Molecular Engineering of Polymers, Collaborative Innovation Center of Polymers and Polymer Composite Materials, Department of Macromolecular Science, Fudan University, Shanghai 200433, China

ARTICLE INFO

Article history:

Received 4 January 2016
Received in revised form 24 March 2016
Accepted 26 April 2016
Available online 2 May 2016

Keywords:

Crystallization
Nucleating agent
Ionomer
Poly(ethylene terephthalate)
Organic montmorillonite

ABSTRACT

The poly(styrene-*alt*-maleic anhydride)/organic montmorillonite (SMA/OMMT) nanocomposites are obtained through in situ polymerization of styrene and maleic anhydride. The OMMT is exfoliated into small platelets and dispersed well in SMA copolymers, which is thus easily made into ionomers/OMMT (IM) nanocomposites. The IMs are employed as nucleating agents for poly(ethylene terephthalate) (PET) and the crystallization behavior is investigated by DSC isothermally and non-isothermally, respectively. The crystallization rate of PET is significantly accelerated and melt-crystallization temperature is increased with the addition of IMs which acted as heterogeneous nucleating agent due to good miscibility between anhydride and PET, and large interfaces provided by exfoliated OMMT.

© 2016 The Korean Society of Industrial and Engineering Chemistry. Published by Elsevier B.V. All rights reserved.

Introduction

Poly(ethylene terephthalate) (PET) is one of the most important polyesters with wide applications ranging from functional fibers to automotive parts due to its excellent mechanical properties and thermal stability [1–3]. The final properties of most semicrystalline polymers depend on the microstructures, which are mainly affected by the crystallization behavior. As a result, the crystallization behaviors of PET have been extensively studied in order to improve the crystallization rate and especially increase the crystallization temperature. Introducing a foreign substrate of high affinity can reduce the nucleation energy barrier for polymer crystallization by providing heterogeneous nucleation sites, which is an important way to enhance the flux of crystal nucleation [4,5]. The small molecular organic compounds are commonly used as nucleating agents for PET crystallization [6]. Due to high processing temperature of PET, the small organic compounds in the PET melt will be melted, volatilized, or pyrolyzed, and thus the nucleation effect is quite limited. The inorganic compounds are

also used as nucleating agents, which need to solve the dispersal problem in the PET matrix [7].

According to the crystallization theory, the following requirements are necessary for designing effective nucleating agents. The nucleating agents should have good compatibility with polymer matrix when melt blending [8], high thermal stability and keep solid phase at the crystallization temperature of polymers, as well as large interface for crystal growth [9,10]. In this regard, the ionomers can server in this role and reduce the supercooling degree of polymers by increasing the onset of crystallization temperature. Recently, ionomers have been extensively used to accelerate the crystallization of PET because they can react with PET molecular chain end [5]. The ionomers, such as Surlyn which is a sodium salt of a copolymer of ethylene and methacrylic acid [11], Aclyn which is a sodium neutralized ethylene/acrylic acid copolymer [5,12], and poly(styrene-*block*-acrylate-potassium) copolymers (P(St-*b*-AK)) [13], etc. have been used as nucleating agents to accelerate the crystallization rate of PET (Fig. 1a–c). Our recent work revealed that poly(styrene-*alt*-maleic anhydride) (SMA) ionomers (SMA-Na, Fig. 1d) can act as nucleating agent to improve the crystallization behaviors of PET [14,15]. However, the ionomers as nucleating agents cannot provide more and larger interfaces for crystal growth compared with that of inorganic compounds.

Many literatures reported that the organic montmorillonite (OMMT) platelets within PET matrix can act as effective nucleating

^{*} Corresponding authors.

E-mail addresses: sijingjing@fudan.edu.cn (J. Si), pingtang@fudan.edu.cn (P. Tang).

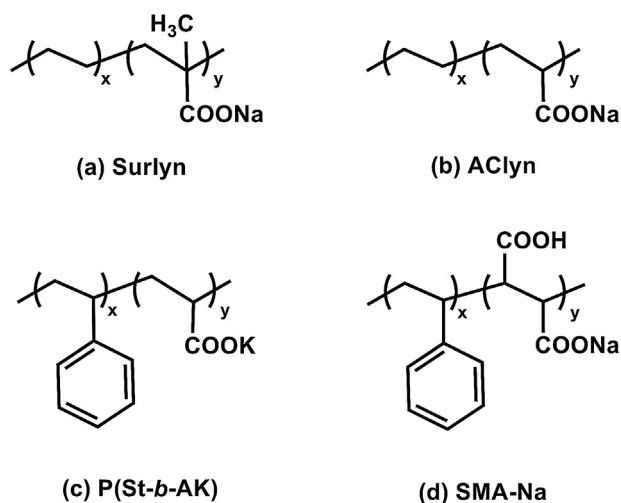


Fig. 1. Molecular structures of several ionomers: (a) Surlyn [Ref. 11], (b) AClyn [Ref. 12], (c) P(St-b-AK) [Ref. 13], and (d) SMA-Na [Ref. 14].

agent through in situ polymerization [16] or melt blending [17–19]. Qi et al. [16] reported that the crystallization rate of PET-clay nanocomposites prepared by intercalation, followed by in situ polymerization was three times greater than that of pure PET. They also mentioned that the nucleation effect of the exfoliated clay particles did not demonstrate to be the greatest degree because of the low content of clay and the relatively weak interaction between the clay particles and PET matrix. Bikiaris et al. [19] compared the nucleation activity of several types of OMMT (organo-modified Kunipia, Laponite, Nanomer 1.30E, and Cloisite 10A), found that the organo-modified Nanomer 1.30E was more effective nucleating agent for PET due to its better dispersion and exfoliation in PET matrix, compared with the other types of OMMT. Therefore, simultaneously improving the interaction between the OMMT and PET, and the dispersion and exfoliation of OMMT in PET matrix, are big challenges for increasing the nucleation effect.

In this paper, the SMA/OMMT nanocomposite (SMN) and its ionomer (IM) were prepared, and the IM effectively modified the crystallization behaviors of PET. As is shown in Fig. 2, SMN was obtained and the OMMT was exfoliated through in situ polymerization of styrene and MA with OMMT. The SMN was then salinized to prepare IM which was used as nucleating agent for PET crystallization.

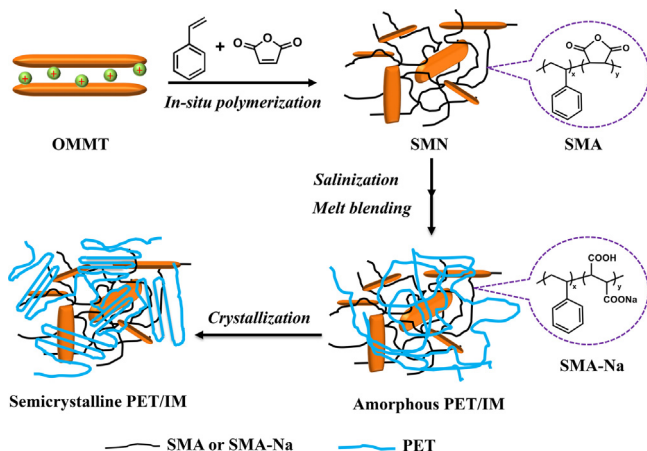


Fig. 2. Illustration of the preparation process of PET/IM.

Experimental

Materials

PET with intrinsic viscosity of 0.9 dL g^{-1} was kindly supplied by Sinopec Yizheng Chemical Fiber Co., Ltd. (China). MA and benzoyl peroxide (BPO) were purchased from Alfa Aesar, recrystallized three times from the chloroform. Styrene and cyclohexanone were purchased from Sinopharm Chemical Reagent Co., Ltd. (China), redistilled to remove water and inhibitor. The OMMT modified by octadecyltrimethylammonium (OTA) bromide was purchased from Nanocor Inc. Other chemicals which were analytical pure were purchased from the Sinopharm Chemical Reagent Co., Ltd., used as received.

Preparation of SMN

The SMN was prepared by in situ free radical solution polymerization with feed mole ratio of BPO, styrene and MA of 1:100:120. The additive amount of OMMT was 2, 5, 10 wt%, of MA and styrene, respectively. All of these materials were dissolved in cyclohexanone and sonicated for 0.5 h to make OMMT well dispersed in the mixture. The solution was heated at 80°C under nitrogen (N_2) atmosphere for 2 h, and then was added dropwise into methanol to precipitate and concentrate the product. The precipitate was dissolved in THF and then added into methanol, which was repeated at least three cycles to obtain purified SMN. The mass fraction of OMMT in the SMNs was calculated based on the feeding amount of OMMT and the final weight of nanocomposites. The SMNs with different weight fraction of OMMT of 2.22, 8.12, 21.10 wt% were denoted as SMN1, SMN2 and SMN3, respectively.

Preparation of IM and PET/IM

The SMN was salinized by sodium hydroxide to prepared IM. The methanol solution of sodium hydroxide was added dropwise into SMN solution of dioxane (0.1 g mL^{-1}) at room temperature until the solution reached alkalescence ($\text{pH} = 7$) to ensure the anhydride was completely changed to carboxylate, and the IM was precipitated from the solution. The final product was obtained through filtration and was dried at 60°C in the vacuum oven for 24 h. The IMs prepared from SMN1, SMN2 and SMN3 were denoted as IM1, IM2 and IM3, respectively.

The PET/IM composite was prepared through melt blending. The PET was dried at 110°C for at least 24 h in the vacuum oven, and then mixed with 1 wt% of IMs and Surlyn resin, respectively, in the torque rheometer (Kechuang XSS-300) at 280°C with twin-screw speed of 80 rpm for 5 min in an internal batch mixer for further study. All the samples were quenched in iced water after taken from the rheometer.

Characterization

The X-ray diffraction (XRD) measurements were performed over the 2θ range of $1\text{--}10^\circ$ at 3°C min^{-1} , using the XPert PRO model (PANalytical B.V., Netherlands) X-ray diffractometer with a Cu anode ($\lambda = 0.154 \text{ nm}$). In order to observe the morphology of OMMT in PET matrix, ultra-thin sections were prepared by cryogenic-sectioning using a Leica system (UCT/EMFCS) in combination with a Diatome 45° diamond knife. The images were taken by transmission electron microscope (TEM) Tecnai operated 120 kV. The thermogravimetric analysis (TGA) was carried out by TA thermogravimetric analyzer Q5000 instrument at the heating rate of $20^\circ\text{C min}^{-1}$ from room temperature to 600°C in N_2 atmosphere.

Download English Version:

<https://daneshyari.com/en/article/227200>

Download Persian Version:

<https://daneshyari.com/article/227200>

[Daneshyari.com](https://daneshyari.com)