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Material Behaviour

Effect of ionization of polyamide-66 on its heterogeneous nucleation of poly(ethylene terephthalate) crystallization: An efficient polyamide-66 ionene nucleator promoted by ion–dipole interactions

Jingjin Luo[1], Nian Ma[1], Sheng Zeng, Xinghou Gong, Biao Shi, Chunqing Li, Xipo Zhao, Tao Hu, Chonggang Wu*

Hubei Provincial Key Laboratory of Green Materials for Light Industry, Collaborative Innovation Center of Green Light-weight Materials and Processing, and School of Materials and Chemical Engineering, Hubei University of Technology, Wuhan, Hubei, 430068, PR China

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ABSTRACT

A polyamide (PA)-66 ionene successfully was prepared by ≤ 5.0 mol% of ionization of the amide groups of a PA-66 into ammonium cations via facile, room-temperature solution reaction of the PA-66 with a dilute aqueous HCl, which was confirmed by Fourier transform infrared (FTIR) and ^{1}H nuclear magnetic resonance (NMR) spectroscopies. A small amount (5.0 wt%) of the PA-66 added was found to effectively nucleate both the melt- and solution crystallizations of a poly(ethylene terephthalate) (PET) heterogeneously, as reflected from differential scanning calorimetry (DSC) melt crystallization temperature and -enthalpy increases, a wide-angle X-ray scattering (WAXS) degree of crystallinity (X_c) rise, polarized optical microscopy (POM) schlieren-texture densification and refinement, Mo's method nonisothermal crystallization kinetic a increase and -$F(T)$ decrease of the PET matrix. Compared with the PET/PA-66 (5.0 wt%) system, the same content of the PA-66 ionene incorporated further displayed significantly higher or, say, maximized heterogeneous nucleation efficiency for the PET melt- and solution crystallizations, as verified by similar DSC, WAXS, POM, and Mo's approach observations, to again remarkably expedite the crystallization, enhance the X_c, and refine the crystal size of the PET matrix. Such extraordinarily high efficiency of the PA-66 ionene nucleator arose typically from, at the interphase, the ion–dipole interactions (IDIs) formed between the amide-carbonyl affected ammonium-chloride ion pairs of the PA-66 ionene and the ester groups of the PET, which considerably were stronger in both covalent and ionic components than the hydrogen bonds present between the PA-66 amide groups and the PET ester groups. The IDIs constituted greatly enhanced interfacial adhesion of the PET/PA-66 ionene (5.0 wt%) to presumably improve its interfacial compatibility, hence refine the size and increase the number density of the PA-66 ionene crystal particles, all of which contributed collectively to the efficiency maximization of the PA-66 ionene heterogeneous nucleator for the PET crystallization. It seems that nucleator ionization offers an effective approach to the enhancement of heterogeneous crystalline nucleation of a polymer by another semicrystalline polymer nucleator.

1. Introduction

Owing to the presence of rigid phenylene groups spaced by short ethylene flexible moieties in its structural repeat units, poly(ethylene terephthalate) (PET) exhibits a slow rate of homogeneous nucleation that leads usually to a low degree of crystallinity in practical melt processing operations such as injection molding. This results in relatively weak mechanical strengths, low dimensional stability, and poor heat resistance of PET manufactures, which impede their engineering applications to automotive, electrical, constructive, etc. fields. To overcome the disadvantage, a large amount (25–45 wt%) of reinforcing glass fiber has commonly been added to produce commercial PET engineering resins [1]; however, the economy of this approach is questionable since the much loaded glass fiber significantly accelerates the mechanical wear and abrasion of both compounding and molding equipment. Blending and copolymerization with more rigid polymer and monomer, respectively, have been employed as well to modify PET [2,3], whereas the high inclusion level of the expensive modifier may

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* Corresponding author.
E-mail address: cgwu@mail.hbut.edu.cn (C. Wu).
[1] J. Luo and N. Ma contributed equally to this work.

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considerably raise the production cost and, more importantly, compromise the unique characteristics of blowability, spinnability, etc. of the PET itself.

Most prevalently, people have made extensive investigations on the crystalline modification of PET through incorporation of small amounts (0.1–5.0 wt%) of different types of heterogeneous nucleating agents, to enhance its nucleation rate of melt crystallization and consequently degree of crystallinity. These nucleators include ceramic fillers (e.g., clays [4–10], oxides [11–14] and hydroxides [15–17], inorganic salts [18–22], Si_3N_4 [23], carbon nanotubes and graphitics [24–31], etc.), small organic molecules (e.g., carboxylate salts [32–34], diamines [35], bisamides [36], modified sorbitols [37], etc.), organic polymers (e.g., crystalline polymers [38], liquid-crystalline polymers [39,40], block copolymers [41], ionomers [42–44], etc.), and composite nucleators, usually binary, based on the three basic types (e.g., clay/crystalline polymer [45], clay/ionomer [46], etc.). Of all the nucleators researched above, the organic polymers and the polymer-containing composite nucleators generally are found to be most efficient for the advancement of PET melt crystallization, both of which meantime do not incur notable degradation of the PET chains. Nevertheless, the PET crystallization facilitated by both the included polymer-based nucleators has been far from maximized towards its equilibrium level especially at fast melt-cooling rates (e.g., 40 °C/min), presumably due to a morphological impediment of large domain-size and low number-density of the dispersed nucleators.

In an effort to maximize the crystallization of a polyamide (PA)-66 nucleated PET, we have managed in this work to improve the PET–PA-66 interfacial compatibility through a slight degree of ionization of the PA-66 into an ionene (i.e., conversion of a small fraction of the interfacial adhesion from weak hydrogen bonding to stronger ion–dipole interactions [47]), thereby to refine the size and enhance the number density of the nucleating PA-66 dispersed phase. The crystallinity of the PA-66 ionene nucleated PET is probed against that of the PA-66 nucleated PET using differential scanning calorimetry (DSC), wide-angle X-ray scattering (WAXS), polarized optical microscopy (POM), and nonisothermal crystallization kinetic analysis. It turns out that, at a fast cooling rate of 40 °C/min, the PET crystallizability in the presence of the PA-66 nucleator becomes increased up to its intrinsic equilibrium level upon ionization of the PA-66, which suggests that ionization, i.e., introduction of ion–dipole interactions [47], may constitute an effective strategy for maximization of the heterogeneous nucleation rates of polymers by polymer or polymer-composite nucleators.

2. Experimental

2.1. Materials

A PET resin (commodity-grade base material, CB-609) was purchased from Far Eastern Industries (Shanghai) Ltd., China. A PA-66 resin (injection-grade, unmodified base material, 101 L) was supplied by DuPont USA. Formic acid, methanol, dichloromethane (DCM), all being analytical reagents of ≥99.5% purity, and trifluoroacetic acid (TFA) (chemically pure, ≥99.0%) were obtained from Sinopharm (Shanghai) Chemical Reagents Co., Ltd., China. A concentrated hydrochloric acid (aqueous HCl) (analytical reagent, 36–38 wt%) was purchased from Xinyang Chemical Reagents Factory, China. Distilled water was home made in our laboratory using a stainless steel water distiller.

2.2. Ionization of PA-66

First, a predetermined volume of the concentrated (36–38 wt% of) aqueous HCl was diluted with distilled water in a 1000-ml volumetric flask to prepare a 0.1 mol/L of aqueous HCl as the ionizing agent. Then, 2.0000 g of the well-dried, as-purchased PA-66 was stirred with and dissolved into 50 ml of formic acid at a speed of 200 r/min in a 250-ml stoppered, single-necked flask to form a clear solution. Subsequently, a stoichiometric amount (~8.9 ml) of the 0.1 mol/L of aqueous HCl, according to a 5.0 mol% of ionization of the amide groups into ammonium cations, was added dropwise to the stirred PA-66 solution using a 10-ml pipette. Upon standing stirred vigorously at 200 r/min in the stoppered flask for 2 h, the reaction solution was injected with a 25-ml syringe into a large amount (~1500 ml) of methanol agitated at 200 r/min in a 5000-ml beaker to precipitate a white fibrous product, which was next allowed to stand in a refrigerator overnight. The product was then Buchner filtrated followed by repeated washing with methanol, subsequently fume-hood drying, and finally vacuum drying at 60 °C for at least 24 h. Such a facile ionization process of PA-66 primarily was conducted at room temperature (RT), through which the PA-66 supposedly was converted into a PA-66 ionene that contains ≤5.0 mol% of ammonium cations to original amide groups in its backbone chains, as schematically shown in Fig. 2c vs. d below.

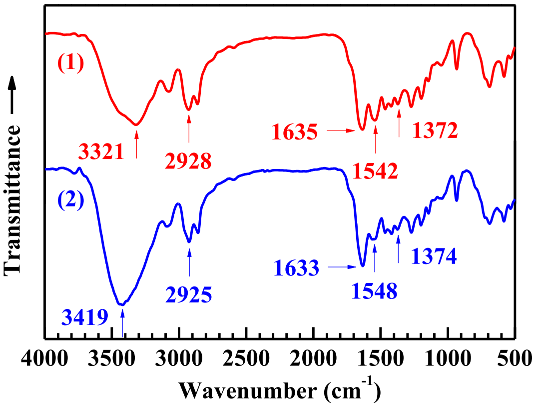

Fig. 1. Fourier transform infrared (FTIR) absorption spectra of (1) a polyamide (PA)-66 and (2) an HCl-modified PA-66, supposedly PA-66 ionene containing ≤5.0 mol% of ammonium cations to original amide groups in its backbone chains, that is formed from facile, room-temperature solution reaction of the PA-66 with a dilute aqueous HCl.

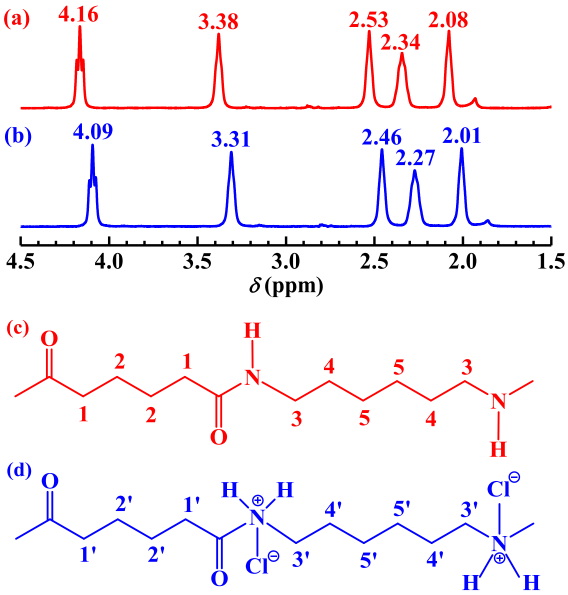

Fig. 2. ^{1}H nuclear magnetic resonance (NMR) spectra of (a) a polyamide (PA)-66 and (b) an HCl-modified PA-66, presumably PA-66 ionene having ≤5.0 mol% of ammonium cations to original amide groups in its backbone chains, that is prepared from facile, room-temperature solution reaction of the PA-66 with a dilute aqueous HCl, respectively, for H-atoms nos. 1–5 shown in (c) and 1′–5′ shown in (d). The assignments of (a) to (c) and (b) to (d) are given in Table 1.