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Non-isothermal melt-crystallization kinetics of poly (ethylene terephthalate-co-sodium-5-sulfo-*iso*-phthalate)

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ABSTRACT

The kinetic of non-isothermal crystallization of Poly (ethylene terephthalate-co-sodium-5-sulfo-*iso*-phthalate) (PETI) was investigated using differential scanning calorimetry (DSC). Various macrokinetic models namely the Avrami, Tobin, Ozawa, and Ziabicki were used to describe the non-isothermal crystallization process of PETI. Both of the Avrami crystallization rate constant and the Tobin crystallization rate constant were observed to increase with increasing cooling rate. The Avrami model is better than the Tobin model to describe the non-isothermal crystallization process of PETI. The Ozawa crystallization rate K_O was found to decrease with increasing cooling rate, while Ziabicki's kinetic crystallizability parameter G_Z was found to increase with increasing cooling rate. The effective energy barrier $\triangle E$ for non-isothermal crystallization process of PETI, analyzed based on the differential iso-conversional method of Friedman, was found to be an increasing function of the relative crystallinity.

1. Introduction

Poly(ethylene terephathalate-co-sodium-5-sulfo-*iso*-phthalate) (PETI) is a linear aromatic polyester which is always used to produce cationic dyeable fiber [1,2]. It is a typical ionomer. Most of the studies on ionomers to date have been limited to addition-type polymers, for example, polyethylene, polystyrene, and polyisobutylene, with only a few cases in which the ionic functionalities are introduced via a condensation process [3]. In this article we reported on the non-isothermal melt-crystallization kinetics of a polyester ionomer PETI derived from polyethylene terephthalate (PET) modified at 5 mol% content by a fully neutralized sodium-5-sulfo-*iso*-phthalate.

PETI was first synthesized by an American company named DU-PONT in 1959.At that time, it was not available commercially because of its high cost. In 1962, production of PETI for commercial uses was finished [4]. Its molecular structure is presented in Fig. 1. PETI is a semi-crystalline polymer when the content of third monomer is less than 9% [2]. Since both physical and mechanical properties of a semi-crystalline polymer is strongly dependent on the extent of crystallization and morphology developed during processin [4–6], studies related to crystallization kinetics are key information to gain an understanding on the relationship between the processing conditions, the structure developed and the properties observed in a final polymeric product [7,8].

Research on the polymer crystallization process can be carried out under isothermal or non-isothermal conditions [9,10]. Analysis of the overall crystallization rate under isothermal conditions is generally accomplished with the use of the so-called Avrami equation [11–13]. However, solidification during polymer processing is always dynamic. Therefore, several models for the non-isothermal crystallization have also been reported [14,15].

Study on the non-isothermal crystallization of PETI has not been reported in full detail. The present research aimed at studying the non-isothermal melt-crystallization kinetics of PETI in full detail. The experimental data were collected in a narrow cooling rate range of 2.5–20 °C $\min^{-1}$, with a small increment between adjacent cooling rates. The experimental data obtained from the differential scanning calorimetry (DSC) technique were thoroughly analyzed based on the Avrami, Tobin, Ozawa, and Ziabicki macrokinetic models. The effective energy barrier describing the non-isothermal melt crystallization process of PETI was estimated based on the differential iso-conversional method of Friedman.

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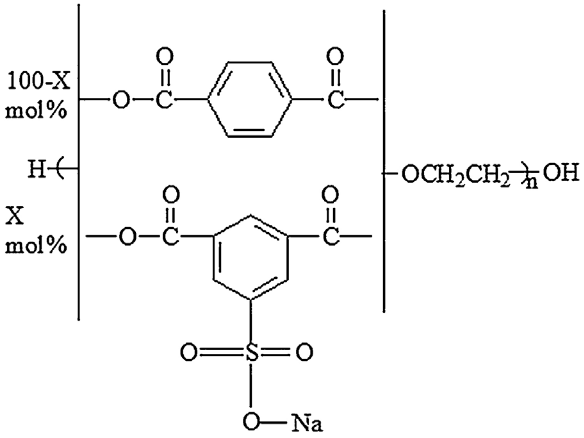

Fig. 1. Molecular structure of PETI.

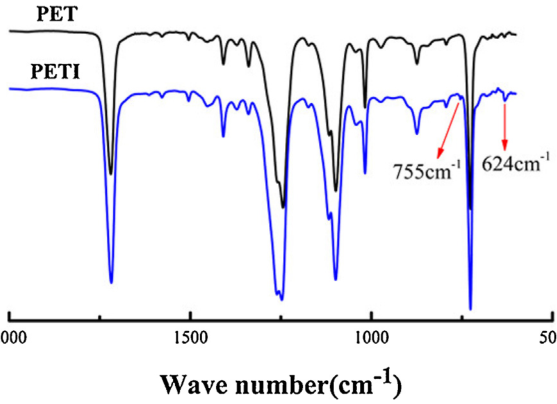

Fig. 2. FTIR spectrum of PETI and PET.

2. Experimental part

2.1. Materials

Terephthalic acid(TPA,purum99%), glycol(EG, purum99%),and sodium-5- sulfoisophthalic acid dimethyl ester(SIPM, purum 99%) used as reactants(analytical grade) were purchased from Aladdin Industrial Corporation. Trimethyl phosphate (TPP) used as heat stabilizer and antimony ethylene glycalate used as catalyst were also supplied by Aladdin Industrial Corporation. All other materials and solvents used for the analytical methods were of analytical grade.

2.2. Preparation of poly(ethylene terephathalate-co-sodium-5-sulfo-iso-phthalate)(PETI)

PETI was prepared by the two-stage melt polycondensation method (esterification and polycondensation) in a steel batch reactor. In brief, the proper amount of terephthalic acid, glycol(in a molar ratio of 1:1.4) and the catalyst (0.04 g catalyst per 100 g reagent) were charged into the reaction tube of the polyesterification apparatus. The reactor with the reagents was evacuated three times and filled with a nitrogen in order to completely remove any oxygen. The reaction mixture was heated at 230 °C under an atmosphere of nitrogen and stirred at a constant speed (50 rpm). This first step (esterification) was considered to be completed when the collection of the theoretical amount of H_2O, which was removed from the reaction mixture by distillation and collected in a graduated cylinder.

In the second step of the polycondensation, TPP was added(0.01gTPP per 100 g reagent), in order to prevent side reactions such as etherification and thermal decomposition. At the same time, SIPM was added(0.05 mol SIPM per mol PTA). A vacuum (40 Pa) was applied slowly over a period of about 50 min, to avoid excessive foaming and to minimize oligomer sublimation, which is a potential problem during the melt polycondensation. After the polycondensation reaction was completed, the polyester was easily removed, milled, and washed with methanol. Detailed presentation of the synthesis of the samples can be found in a paper [3]. The intrinsic viscosity of PETI homopolymer pellets was 0.69 dL/g measured in a phenol/tetrachloroethane solution (50/50, w/w) at 25 °C.

2.3. Characterization

Fourier transform infrared spectroscopy (FTIR) measurements were carried out on a Nicolet-Nexus 670 Fourier transform infrared spectrometer in the range of 500–4500 cm^{-1} with an accuracy of 4 cm^{-1}. A differential scanning calorimetry (DSC 200 F3) produced by NETZSCH-Gerätebau GmbH was used to study on non-isothermal melt-crystallization kinetics of PETI. Temperature calibration was carried out using an indium standard. The non-isothermal crystallization behaviors of PETI was performed as following: the sample was heated to 280 °C in nitrogen at heating rate of 50 °C/min, held for 5 min and then cooled to room temperature, at constant cooling rates of 5, 7.5,10,12.5, 15, and 20 °C/min, respectively. Also of importance is the fact that each sample was used only once and its weight is around 8 ± 0.5 mg. The exothermic curves of heat flow as a function of temperature were recorded and investigated. The subsequent melting behavior of each sample was recorded immediately after each cooling scan at heating rate of 10 °C/min.

3. Results and discussion

3.1. Chemical characterization of synthesized PETI

Fig. 2 displays FTIR spectra of PET (black line) and the synthesized PETI (blue line). Both PET and PETI are aromatic polyester. As a result, the FTIR spectrum of PETI is quite similar to that of PET. Band at round 873 cm^{-1}(C—H stretching) corresponds to motions associated with methylene groups. While bands at round 1724 cm^{-1},1267 cm^{-1} (O=C stretching), 1199 cm^{-1}(C—O stretching) and 1099 cm^{-1}(C—O stretching)are attributed to the ester groups. On the other hand, the absorption bands at round 1593 cm^{-1}, 1577 cm^{-1}, 1504 cm^{-1}, 793 cm^{-1} and round 725 cm^{-1} (C—H stretching) are attributed to the benzene. However, the characteristic bands of PETI at around 755 cm^{-1} and 624 cm^{-1} are observed, which are considered to be associated with the motions of the sulfonated benzene originating from copolymerization of SIPM with TPA and EG.

3.2. Non-isothermal melt-crystallization and subsequent melting behavior

The crystallization exotherms during cooling of PETI at six different cooling rates ranging from 5 °C min^{-1} to 20 °C min^{-1} are presented in Fig. 3. The relative crystallinity function(θ(T)) of temperature can be obtained by using Eq. (1).

$$\theta(T) = \frac{\int_{To}^{T} (\frac{dHc}{dT}) dT}{\Delta Hc} \quad (1)$$

where To and T represent the onset and an arbitrary crystallization temperature, respectively. dHc is the enthalpy of crystallization released during an infinitesimal temperature range dT, and △Hc