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Nonisothermal crystallization behaviors of a polyolefin terpolymer and its foam

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Abstract

The nonisothermal crystallization kinetics of a polyolefin terpolymer (poly(propylene-*co*-ethylene-*co*-1-butene) and its expanded foam was investigated by differential scanning calorimetry. A kinetic equation for nonisothermal crystallization was employed to analyze the crystallization characteristics of the terpolymer and its foam. The Avrami exponent, *n*, can be reasonably well determined from the nonisothermal crystallization exotherm. The polarized optical microscopy showed that pristine terpolymer had a well-developed spherulite morphology whereas the foamed terpolymer consisted of elongated entities that subsequently developed as more bundle-like entities. The latter morphology is typical one of the γ phase. The difference in crystallization behavior observed for the pristine and foamed terpolymer samples is attributed to the formation of different morphologies during the foam expansion process.

Keywords: Nonisothermal crystallization; Terpolymer; Nucleation

1. Introduction

Polymer crystallization occurs via a nucleation and growth. In this process, the thermodynamic driving force provided by the supercooling of the amorphous melt causes the entangled polymer chains to rearrange into the ordered structures. Since the crystallization conditions decide the morphology, it is essential to understand the exact relationship between the structure and the stage of crystallization in processing. This is especially important for foamed structures, in which the crystallization simultaneously occurs. Despite a vast amount of research on crystallization, the nature of the crystallization process during foam formation remains unknown.

From the viewpoint of crystallization kinetics, the crystallization of isotactic polypropylene (iPP) is particularly interesting on account of this material's ability to form three distinct crystalline structures (i.e., polymorphism). Specifically, iPP crystallizes exclusively into a 3_1-helix structure as this conformation corresponds to an energy minimum, but with three forms, designated α, β, and γ [1–4]. The most common form of iPP is the α-form which has been well characterized by many researchers. The crystal cell of the α-iPP is monoclinic with parameters $a = 0.6657$ nm, $b = 2.096$ nm, $c = 0.65$ nm and $\beta = 99°80'$ consisting of alternating right- and left-handed helices [1]. The β-form iPP, by contrast, has a trigonal cell with parameters $a = b = 1.101$ nm and $c = 0.65$ nm containing three isochiral helices. Finally, the γ-form has a face-centered orthorhombic unit cell with parameters $a = 0.85$ nm, $b = 0.993$ nm and $c = 4.241$ nm containing no chiral helices [5–7]. The γ-form has a unique cell structure in which the chain axes in adjacent crystal layers are not parallel, rather the angle between the chains is about 80°. According to an extensive study by Alamo et al. [8], the stability of the γ-form, and hence its generation, depends on the total amount of stereo regulating

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defects, mainly 2.1 and 3.1 insertions. The higher the defect concentration, the higher the maximum amount of the γ-form. Hence, addition of very short isotactic sequences induces a random distribution of stereo defects and/or regio defects in iPP samples synthesized using metallocene catalysts [2,6]. The terpolymer used in the present study consists mainly of an iPP structure with the addition of small amounts of ethylene and 1-butene units, which favors the formation of the γ-form. Since the γ phase is characterized by high molecular alignment and good mechanical properties, its presence is quite important to the final product performance [7]. The content of the γ-form in iPP can be increased in several ways [1] including (1) the presence of very short isotactic sequences due to the random distribution of stereo defects and/or regio defects in iPP samples synthesized by metallocene catalysts, (2) application of high pressure during the crystallization process, (3) using random copolymers of propene with other 1-olefins, and (4) crystallization in shear fields. Addition of other 1-olefins into the PP chain induces constitutional defects in the polymer chains. The content of the γ-form in an iPP sample depends on the amount and the type of comonomers. We have been interested in the generation of γ phase in iPP phase and its crystallization behavior.

Isothermal crystallization kinetics is normally analyzed using Avrami's equation. In an isothermal crystallization experiment, however, it is difficult to maintain the melt sample in an amorphous state while cooling it to the crystallization temperature. Moreover the crystallization processes encountered in nature tend to be nonisothermal. Nonisothermal crystallization kinetics has been theoretically explored by Ozawa [9,10], who extended the mathematical derivation first proposed by Evans [11]. However, Ozawa's theory has some limits [12,13]. Most of all, because this approach compares the degrees of conversion at a fixed temperature for various cooling rates, it can lead to deviations from the predicted linear behavior. We recently devised an analysis scheme in order to avoid the problem of the Ozawa analysis [14,15]. Since accounting for nonisothermal crystallization kinetics when analyzing crystallization can provide supplementary information about the crystal structure, it may give additional insight into the crystallite structures produced during foam formation. Hence, the objective of the present study was to apply our previously proposed nonisothermal analysis method to the crystallization behavior of a pristine terpolymer and its expanded (foamed) form with a focus on the morphological changes that occur during the foaming process.

2. Description of the theoretical model

Here, we briefly present the basic equations from our earlier report [14]. In the Ozawa equation, the Avrami equation is expressed using a cooling rate

$$\ln\left[-\ln\left(1-x_{\mathrm{v}}(T)_{U}\right)\right]=\ln K(T)-n\ln U \tag{1}$$

where $x_{\mathrm{v}}(T)$ is the volume fraction of the polymer transformed at a temperature T and cooling rate U, and $K(T)$ is the so-called cooling function, which only varies as a function of the temperature. Since the Ozawa equation is based on the volume fraction of the crystallites, conversion of the weight fraction of the polymer, $x_{\mathrm{w}}(T)$, to volume fraction of the polymer, $x_{\mathrm{v}}(T)$, is needed. This can be easily done by using the density of the amorphous phase and the density of the crystallized phase [9,15]. As suggested by the theory, a linear dependence between $\ln K(T)$ and the temperature T is assumed, $\ln K(T)=aT+b$. When the temperature reaches the peak of the exothermal curve, $T_{\max}$, for a given cooling rate, the first and the second derivatives of the curve with respect to the temperature should be zero. Using Eq. (1) with this condition, a linear relationship between $T_{\max}$ and $\ln U$ can be obtained, i.e., $n\ \ln U=aT_{\max}+b-\ln[-\ln(1-x_{\mathrm{v}}(T_{\max})_{U})]$. Therefore, Eq. (1) can be rewritten as

$$\ln\left[-\ln\left(1-x_{\mathrm{v}}(T)_{U}\right)\right]=a(T-T_{\max})+\ln\left[-\ln\left(1-x_{\mathrm{v}}(T_{\max})_{U}\right)\right] \tag{2}$$

Hence the value of the parameter a can be estimated from the slope of a plot of $\ln[-\ln(1-x_{\mathrm{v}}(T)_{U})]$ against $T-T_{\max}$. Also, plotting $T_{\max}$ versus $\ln U$ gives a straight line whose slope is n/a and intercept is $(\ln[-\ln(1-x_{\mathrm{v}}(T_{\max})_{U})]-b)/a$; thus, all the parameter values can be determined without resorting to any numerical process [15].

3. Experimental

The terpolymer (poly(propylene-*co*-ethylene-*co*-1-butene), with a composition of 94.5 wt% of polypropylene unit, 3 wt% of ethylene unit, and 2.5 wt% of 1-butene unit, was obtained from Honam Petrochemicals Co. (Korea). Its number and weight molar masses were 42,000 and 230,000 g/mol, respectively. Foamed terpolymer was prepared by injecting out the blowing agent (butane gas) submerged terpolymer particle in an autoclave through a nozzle. The expansion ratio (expanded pellet volume/pristine polymer volume) was 75. The thermal properties of the terpolymer samples were analyzed using differential scanning calorimetry (DSC), performed on a Mettler DSC 30. Prior to analysis, samples were dried at 100 °C in a vacuum oven for 24 h. About 45 mg of the dried terpolymer was used in each run. To examine nonisothermal crystallization, samples were heated from 25 °C to 200 °C at a heating rate of 100 °C/min, and then cooled at different cooling rates. Relative crystallinity was determined from the crystallization curve by DSC. The area under the curve from the crystallization starting temperature to each temperature was integrated. After divided by the total area, it was taken as the relative crystallinity.

A polarized optical microscope (Olympic BH-2) equipped with a Mettler FP82 HT hot stage and a CCD camera was used to record the growth of the crystallites. Crystal structure analysis was performed using an X-ray diffractometer (XRD) of Rigaku Denki D/Max 2000. X-ray diffraction patterns were recorded using Cu Kα radiation from a rotating anode X-ray goniometer operating at 40 kV and 100 mA equipped with an automatic monochromator.