

# Nonisothermal crystallization behaviors of a polyolefin terpolymer and its foam

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**ABSTRACT:** Nonisothermal crystallization analysis of a terpolymer and its foam provides some important information about the crystalline structures of these materials. In the present work, a modified version of the Ozawa's method proposed by us was successfully applied to the DSC data for a polypropylene containing terpolymer and its foam at various low cooling rates. The Avrami exponent of the pristine terpolymer was 3.1, which is close to that of iPP, indicating that the crystallites had a spherulite structure. On the other hand, high Avrami exponent values (*ca* 5.6) were obtained for the foamed terpolymer, indicating that the crystallites had structures resembling a three dimensional solid sheaf. This difference between the pristine and foamed terpolymer samples is attributed to the appearance of the  $\gamma$ -form in the foamed terpolymer. The observed behavior can be attributed to a large number of nuclei being produced during the foaming process by FIC.

**Key words:** Nonisothermal crystallization analysis, a terpolymer and its foam,  $\gamma$ -phase.

## 1 INTRODUCTION

Polymer crystallization occurs via a nucleation and growth. 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  $\alpha$ ,  $\beta$  and  $\gamma$ .<sup>1-3</sup> The most common form of iPP is the  $\alpha$ -form which has been well characterized by many researchers. The crystal cell of the  $\alpha$ -iPP is monoclinic with

parameters  $a = 0.6657\text{nm}$ ,  $b = 2.096\text{ nm}$ ,  $c = 0.65\text{ nm}$ . The  $\gamma$ -form has a face-centered orthorhombic unit cell with parameters  $a = 0.85\text{ nm}$ ,  $b = 0.993\text{nm}$  and  $c = 4.241\text{ nm}$  containing no chiral helices.<sup>1</sup> The  $\gamma$ -form has a unique cell structure in that the chain axes in adjacent crystal layers are not parallel, rather the angle between the chains is about  $80^\circ$ . The higher the defect concentration, the higher the maximum amount of the  $\gamma$ -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.<sup>2,6</sup> 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  $\gamma$ -form. Since the  $\gamma$  phase is characterized by high molecular alignment and good mechanical properties, its presence is quite important to the final product performance.<sup>7</sup> 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.<sup>8</sup> Because Ozawa's approach compares the degrees of conversion at a fixed temperature for various cooling rates, it can lead to deviations from the predicted linear behavior. 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.<sup>8</sup> In the Ozawa equation, the Avrami equation is expressed using a cooling rate  $\ln[-\ln(1-x_v(T)_U)] = \ln K(T) - n \ln U$  (1) where  $x_v(T)$  is the volume fraction of the polymer transformed at a temperature  $T$  and the 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,  $x_w(T)$ , to volume fraction of the polymer,  $x_v(T)$ , is needed. 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 equation (1) with this condition, a linear relation between  $T_{\max}$  and  $\ln U$  can be obtained, i.e.,  $n \ln U = aT_{\max} + b - \ln[-\ln(1-x_v(T_{\max})_U)]$ . Therefore, Eq.(1) can be rewritten as  $\ln[-\ln(1-x_v(T)_U)] = a(T - T_{\max}) + \ln[-\ln(1-x_v(T_{\max})_U)]$  (2)

Hence the value of the parameter  $a$  can be estimated from the slope of a plot of  $\ln[-\ln(1-x_v(T)_U)]$  against  $T - T_{\max}$ . Also, plotting  $T_{\max}$  versus  $\ln U$  gives a straight line whose slope is  $n/a$  and intercept is  $(\ln[-\ln(1-x_v(T_{\max})_U)] - b)/a$ ; thus, all the parameter values can be determined without resorting to any numerical process.<sup>8</sup>

## 3. EXPERIMENTAL

The terpolymer (poly(propylene-co-ethylene-co-1-butene), with a composition of 94.5wt% of polypropylene unit, 3wt% of ethylene unit, and 2.5wt% 1-butene unit, was obtained from Honam Petrochemicals Co. (Korea). Its number and weight molar masses were 42000 and 230000 g/mole, 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 80°C in a vacuum oven for 24 hours. About 45mg 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 10°C/min, and then cooled at different cooling rates. A polarized optical microscope (Olympic BH-2) equipped with a Mettler FP82 HT hot stage and a CCD camera was used to measure the growth rate 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 K radiation from a rotating anode X-ray goniometer operating at 40 kV and 100 mA equipped with an automatic monochromator.

## 4. RESULTS AND DISCUSSION

Figure 1 displays a linear variation of the maximum temperature of the terpolymer crystallization isotherm,  $T_{\max}$ , with the logarithm of the cooling rates ( $\ln U$ ). The predicted behavior is observed provided the cooling rate is low ( $<7^\circ\text{C}/\text{min}$ ).  $T_{\max}$  decreases with increasing cooling rate because less time is available for crystallization at higher cooling rates. These findings show that our modified version of the Ozawa's theory is quite satisfactory.

The plot of  $\ln[-\ln(1-x_v(T)_U)]$  versus  $(T - T_{\max})$ , as shown in Figure 2, gives a straight line with a slope of  $n/a$ . The calculated values of the Avrami exponent,  $n$ , are between 2.6 and 3.7, with an average value of 3.1. This value is close to the characteristic value for spherulitic development arising from athermal instantaneous nucleation.<sup>14</sup> Figure 3 shows the variation of  $T_{\max}$  as a function of

$\ln U$  for the foamed terpolymer. This system also shows a good linear relationship between  $T_{\max}$  and  $\ln U$  at low cooling rates.  $T_{\max}$  of the foamed terpolymer is higher than that of the pristine terpolymer at the same cooling rate, indicating a faster crystallization for the foamed terpolymer. The observation of faster crystallization for the foamed terpolymer can be attributed to the existence of a greater density of nuclei in the foamed terpolymer than in the pristine terpolymer.

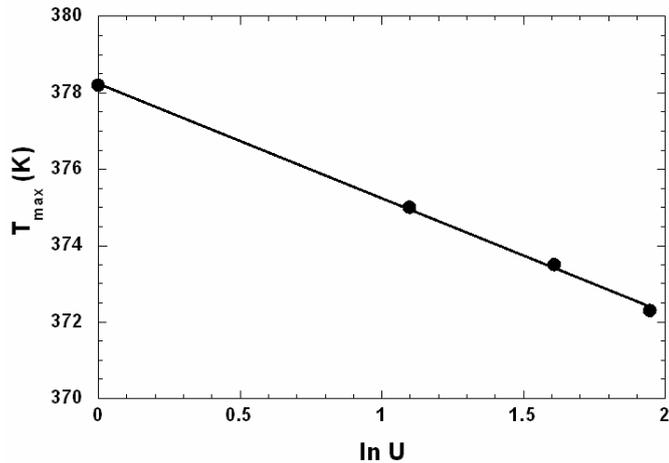


Figure 1. Evolution of  $T_{\max}$  of virgin terpolymer as a function of  $\ln U$  ( $U$  is the cooling rate). The slope of the solid line is  $-3.0$  which is the value of  $n/a$ .

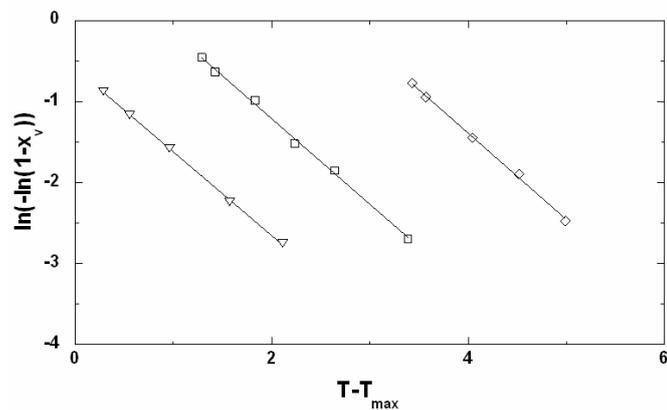


Figure 2. Plot of  $\ln[-\ln(1-x_v(t)_U)]$  versus  $T-T_{\max}$  for nonisothermal crystallization of virgin terpolymer ( $\nabla$ ) 1 K/min, ( $\square$ ) 3 K/min, ( $\diamond$ ) 5 K/min.

The foaming process is a mixed process of elongational flow with shear deformation. The difference between the effects of elongational flow and shear flow on the nucleation rate is more remarkable for highly elastic fluids. Specifically, forcing the molecular chains to flow past one another causes them to be in a more ordered state

thereby creating more nuclei for crystallization. This process is referred to as flow induced crystallization

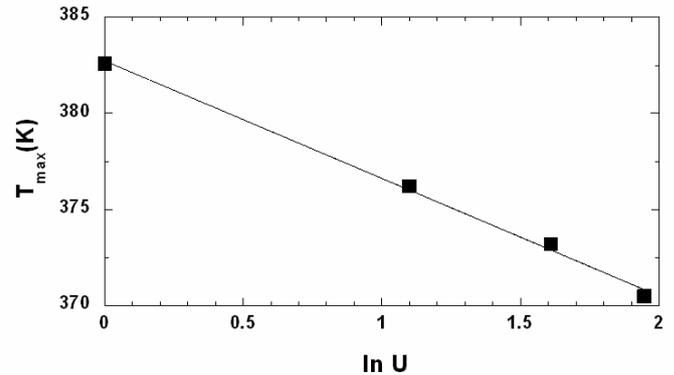


Figure 3. Evolution of  $T_{\max}$  of foamed terpolymer as a function of  $\ln U$  ( $U$  is the cooling rate). The slope of the solid line is  $-6.1$  which is the value of  $n/a$ .

(FIC). The ordering of macromolecules occurs more easily under elongational deformation than under shear flow because elongational flow is a strong deformation.<sup>1</sup> Our calculation results showed that for crystallization temperatures of  $100^{\circ}\text{C}$  to  $107^{\circ}\text{C}$ , the foamed resin contained about 3 times more nuclei than the pristine terpolymer and that the difference in nucleation density between the foamed and the pristine samples increased rapidly with decreasing crystallization temperature.

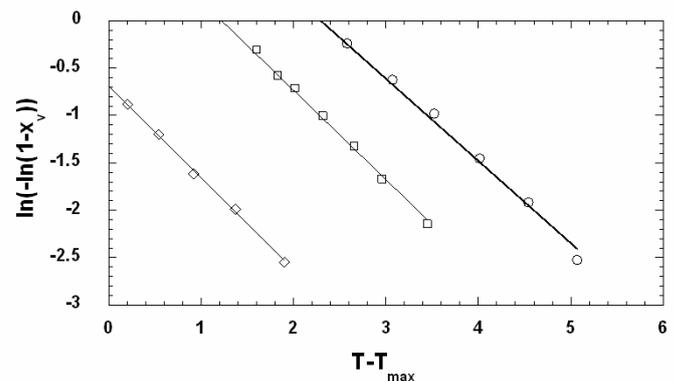


Figure 4. Plot of  $\ln[-\ln(1-x_v(t)_U)]$  versus  $T-T_{\max}$  for nonisothermal crystallization of foamed terpolymer. ( $\nabla$ ) 1 K/min, ( $\square$ ) 3 K/min, ( $\diamond$ ) 5 K/min

The faster crystallization of the foamed terpolymer due to its large number of nuclei leads to a greater number of defects in the crystallized terpolymer. These defects would contribute to the formation of the  $\gamma$ -form. The data published so far indicate that when the fully isotactic sequences are very short, iPP crystallizes in the  $\gamma$ -form whereas the very long regular isotactic sequences generally crystallizes

exclusively in the  $\alpha$ -form.<sup>1-3, 6</sup> As a result of this bias in the defect distribution, iPP produced using a ZN-catalyst crystallized into the  $\gamma$  phase to a much lesser extent than did in iPP sample synthesized using a metallocene catalyst with the same overall concentration of defects. Therefore, the  $\gamma$  phase could be expected to be formed more easily in the foamed terpolymer than in the pristine terpolymer. The calculated average value of Avrami exponent,  $n$ , from Figure 4 is *ca* 5.6 for the foamed terpolymer. This large exponent implies a solid sheaf morphology.<sup>23</sup>

The morphologies of the foamed one and pristine one are shown in Figure 5. They are completely different from each other. The pristine terpolymer (Figure 5(a)) shows a well developed spherulite, later limited by several adjacent ones, typical crystalline structure of the iPP. On the other hand, the foamed terpolymer (Figure 5(b)) shows elongated entities, that later develop as more bundle-like entities. This is a typical morphology of the  $\gamma$ -phase.<sup>1,2</sup> Some small spherulites were subsequently formed between the extended entities during the cooling process.

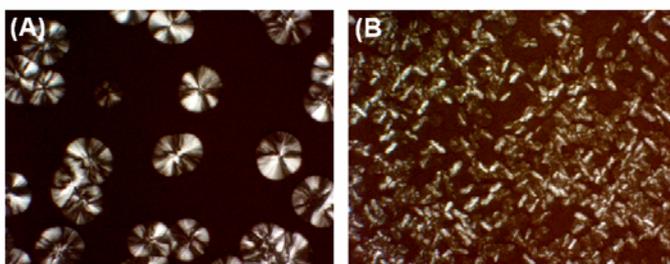


Figure 5. Polarized optical micrographs taken after nonisothermal crystallization of (a) a virgin terpolymer (poly(propylene-co-ethylene-co-1-butene)) (b) Foamed terpolymer

Formation of the  $\gamma$ -form could be confirmed by checking WAXD analysis of the samples. Figure 6 shows the WAXD traces of the as-prepared pristine terpolymer and the foamed one. The  $\alpha$  and  $\gamma$ -form give rise to very similar x-ray diffraction profiles, with the main difference being the position of the third strong diffraction peak, which occurs at  $2\theta = 18.6$  ( $(130)_\alpha$  reflection) for the  $\alpha$ -form and at  $2\theta = 20.1$  ( $(117)_\gamma$  reflection) for the  $\gamma$ -form.<sup>2</sup> The 117 peak of the  $\gamma$  phase appears weakly in the pristine

terpolymer sample but strongly for the foamed terpolymer. For the foamed terpolymer sample, the 130 peak of the  $\alpha$  phase appears weakly compared to that of the 117 peak.

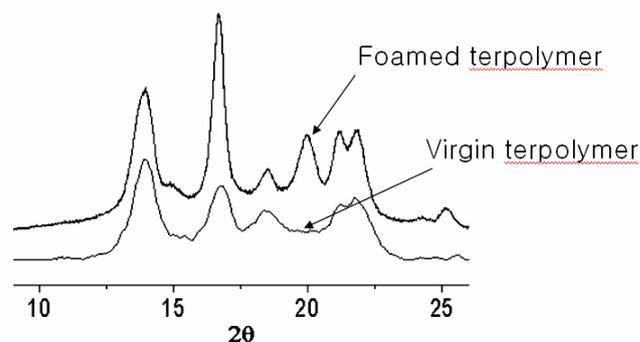


Figure 6. WAXD traces of samples as prepared. Expansion ratio of the foamed sample was 75 times.

#### ACKNOWLEDGEMENT

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