ELSEVIER

Thermochimica Acta 396 (2003) 75–78

thermochimica acta

www.elsevier.com/locate/tca

X-ray and DSC studies on the melt-recrystallization process of poly(butylene naphthalate)

Munehisa Yasuniwa [a,*], Shinsuke Tsubakihara [a], Takashi Fujioka [b]

[a] *Department of Applied Physics, Faculty of Science, Fukuoka University, Nanakuma 8-19-1, Jonan-ku, Fukuoka 814-0180, Japan*
[b] *Starlite Co. Ltd., Ohmiya 4-23-7, Asahi-ku, Osaka 535-0002, Japan*

Received 31 December 2001; received in revised form 27 July 2002; accepted 2 October 2002

Abstract

Melt-recrystallization in the heating process of poly(butylene naphthalate) (PBN) was studied with X-ray analysis and differential scanning calorimetry (DSC). DSC melting curve of an isothermally crystallized sample showed double endothermic peaks. With increasing the temperature, wide-angle X-ray diffraction (WAXD) patterns of the sample were obtained successively. Crystal structure did not change during the double melting process. The X-ray diffraction intensity decreased gradually in the temperature region up to about 200 °C, and then increased distinctly before steep decrease due to the final melting. This increase is interpreted as a proof of recrystallization. The temperature derivative curve of the diffraction intensity was similar to the DSC melting curve.

Keywords: Poly(butylene naphthalate); PBN; DSC; X-ray; Melting; Recrystallization

---

1. Introduction

When a poly(butylene naphthalate) (PBN) sample is studied with differential scanning calorimetry (DSC), double melting peaks are often observed [1]. Double melting peaks were also reported for numerous semi-crystalline polymers, and various interpretations were proposed to the origin of this double melting behavior [2]. Many authors have explained the double melting behavior by the melt-recrystallization model [3,4]. This model suggests that the low-temperature and high-temperature peaks in the DSC melting curve are attributed to the melting of some amount of original crystals and to the melting of crystals formed through the melt-recrystallization process during a heating scan, respectively. Then the exothermic dip between the two endothermic peaks is attributed to recrystallization. That is, the melting proceeds through the process of the melting of original crystals, recrystallization and melting of recrystallized and perfected crystals.

Wide-angle X-ray diffraction (WAXD) measurements give direct information on the crystal structure and crystallinity. Recently, we studied the double melting behavior of poly(butylene terephthalate) (PBT) with DSC and WAXD measurements [5]. Diffraction patterns of PBT in the heating process were obtained successively at a rate of 1 pattern min^{-1} with an X-ray measurement system equipped with a position-sensitive proportional-counter (PSPC). Recrystallization during the melting process of PBT was confirmed as an increase in X-ray diffraction intensity.

---

[*] Corresponding author.
E-mail addresses: yasuniwa@fukuoka-u.ac.jp (M. Yasuniwa), tfujioka@starlite.co.jp (T. Fujioka).

0040-6031/02/$ – see front matter © 2002 Elsevier Science B.V. All rights reserved.
PII: S0040-6031(02)00531-2

It was concluded that the double melting behavior of PBT originates from the increase in crystallinity (recrystallization), and that the crystal structure does not change in the heating process.

PBN gives comparatively evident reflection lines in its X-ray diffraction pattern, therefore PBN is a suitable polymer for the X-ray analysis of the melting behavior. Though most researchers have studied the double melting behavior of PBN with thermal analysis, the WAXD study on the crystal structure and crystallinity in the heating process of PBN has not been performed. In this investigation, to clarify the melt-recrystallization process of PBN, we studied crystallinity and crystal structure during heating with X-ray analysis and DSC.

2. Experimental

Additive free PBN pellets were supplied from Teijin Co. Ltd. (Teijin PBN TQB-KT77, $[\eta] = 0.767$). A PBN sample of about 5 mg was sealed in an aluminum sample pan for DSC. The sample was cooled to predetermined crystallization temperature (T_c) at a cooling rate of $100\,\mathrm{K\,min^{-1}}$ after holding in the molten state (300 °C) for 10 min. Isothermal crystallization was performed at T_c for 1 h, then the isothermally crystallized samples were used for the DSC and X-ray measurements. Thermal analysis was carried out with a Perkin-Elmer Pyris-1 DSC and a TA instruments TMDSC 2920 instrument. WAXD measurements were carried out using a heating cell and our X-ray measurement system reported in a previous paper [5].

3. Results and discussion

Fig. 1 shows DSC melting curves for the isothermally crystallized samples at a heating rate of $10\,\mathrm{K\,min^{-1}}$. Four endothermic peaks appeared in the DSC curve, and these peaks are assigned as A, L, H, and β as shown in the figure. Crystal structure of PBN has been reported by many authors, and α and β crystal modifications have been suggested [6,7]. The β-form develops under tension or at high-temperature. Contrary to this, the α-form appears under normal conditions. A small shoulder peak (β) corresponds to the melting of crystallites having β-form crystal structure. The double melting peaks in this work correspond to peaks L and H. With increasing T_c, the peak melting temperature and the peak area of L increased, whereas those of the high-temperature peaks decreased gradually. The low- and high-temperature peaks at T_c of 230 °C result in a single peak by shifting of peak L to a higher temperature. A small shoulder peak β splits from peak H. The appearance of the β-peak is an interesting problem. However, the β-peak was not studied in the present article because this work is focused on the double melting peaks.

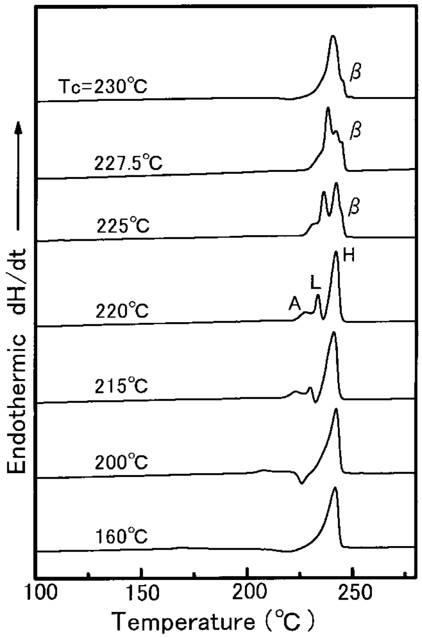

Fig. 1. DSC curves for the samples isothermally crystallized at T_c's which are indicated in the figure. Heating rate of the DSC scans was $10\,\mathrm{K\,min^{-1}}$.

The melt-recrystallization model suggests that small and/or imperfect crystals change successively to more stable crystals through melt-recrystallization process. That is, melting and recrystallization are competitive in the heating process. The low-temperature and high-temperature endothermic peaks appear when the rate of melting overwhelms that of the recrystallization. In contrast, the exothermic peak appears when the rate of recrystallization overwhelms that of the melting. Accordingly, the recrystallization behavior, especially increase in crystallinity, is considered to have an important role on the appearance of the double

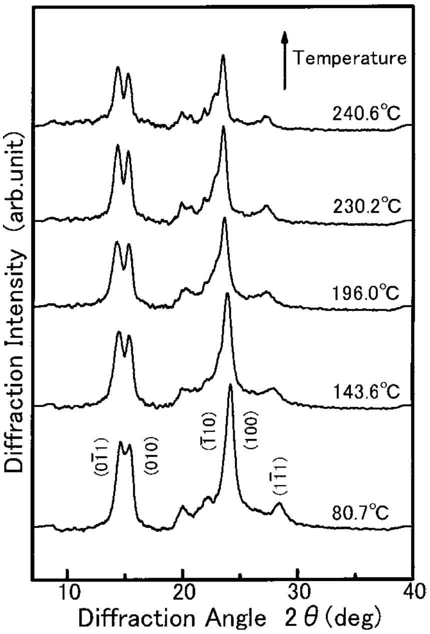

Fig. 2. X-ray diffraction patterns in the heating process for the samples isothermally crystallized at 160 °C. Heating rate was 1 K min^{-1}.

melting peaks. Contrary to this, the peak melting temperatures of L and H do not have a very important meaning for the interpretation of the melting process.

Fig. 2 shows X-ray diffraction patterns in the heating process for a sample isothermally crystallized at 160 °C. Heating rate was 1 K min^{-1}. To obtain an analyzable diffraction pattern, the accumulation time of the PSPC for obtaining one pattern was set to 1 min, i.e. 1 pattern min^{-1} and 1 pattern K^{-1}. Scattering X-ray from the amorphous part overlapped on the diffraction intensity from the crystalline part, so that these diffraction patterns were obtained after the subtraction of an X-ray scattering pattern of the molten state. As shown in the figure, peak height of the reflection lines decreases with temperature, and peak positions shift to lower angle due to the thermal expansion.

The diffraction pattern in Fig. 2 corresponds to that of triclinic crystal structure which has been assigned as α-form modification [6,7]. Miller indices are shown on the five dominant peaks, $(1\,0\,0)$, $(\bar{1}\,1\,0)$, $(0\,\bar{1}\,1)$, $(0\,1\,0)$, and $(1\,\bar{1}\,1)$ reflections, in the diffraction pattern. The peak of $(\bar{1}\,1\,0)$ reflection separates from $(1\,0\,0)$ reflection, and the separation increases with temperature. Except for this change, fundamental profile of the diffraction pattern did not change over the whole temperature range. This fact indicates that crystal structure of the PBN sample does not change during the double melting process.

Assuming the width of a diffraction peak does not change much in the heating process of the sample, we use peak heights for the individual reflection lines to estimate the quantity of crystallites in the sample, that is, crystallinity, in this article. The peak heights, that is, diffraction intensities of $(1\,0\,0)$, $(0\,\bar{1}\,1)$, $(0\,1\,0)$, and $(1\,\bar{1}\,1)$ reflections were obtained as a function of temperature from the diffraction patterns. The diffraction intensities of $(0\,\bar{1}\,1)$, $(0\,1\,0)$, and $(1\,\bar{1}\,1)$ reflections showed similar temperature dependence with one another, however the temperature dependence of $(1\,0\,0)$ reflection was different from the others because of the separation of $(\bar{1}\,1\,0)$ reflection. In the subsequent analysis, $(0\,\bar{1}\,1)$ reflection was used. Temperature dependence of the diffraction intensity of $(0\,\bar{1}\,1)$ reflection is shown in Fig. 3 (●).

A change in the X-ray diffraction intensity $\Delta I(T)$ from T_0 to T is approximately proportional to the crystallinity change in the temperature range from T_0 to T. Exothermic heat flow $\mathrm{d}H/\mathrm{d}t$ of a sample can be

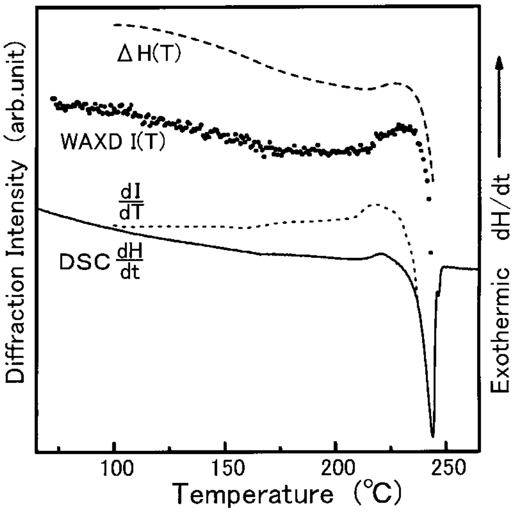

Fig. 3. Diffraction intensity $I(T)$ of $(0\,\bar{1}\,1)$ reflection, its temperature derivative curve $\mathrm{d}I/\mathrm{d}T$ (dotted line), DSC curve $\mathrm{d}H/\mathrm{d}t$ (solid line), and $\Delta H(T)$ (broken line) in the heating process for the samples isothermally crystallized at 160 °C. Heating rate of both experiments was 1 K min^{-1}.

obtained from a DSC melting curve, so that exothermic enthalpy change from T_0 to T with a constant heating rate R (=dT/dt) results in

$$\Delta H(T) = \int_{t_0}^{t} \left(\frac{\mathrm{d}H}{\mathrm{d}t}\right) \mathrm{d}t = \int_{T_0}^{T} \left(\frac{\mathrm{d}H}{\mathrm{d}t}\right) \frac{\mathrm{d}t}{\mathrm{d}T}\mathrm{d}T = \frac{1}{R}\int_{T_0}^{T} \left(\frac{\mathrm{d}H}{\mathrm{d}t}\right) \mathrm{d}T$$

where t_0 and t correspond to the times at sample temperatures T_0 and T, respectively. The exothermic enthalpy change $\Delta H(T)$ takes negative value for the melting and is proportional to the change of crystallinity from T_0 to T. Therefore, $\Delta I(T)$ is approximately proportional to $\Delta H(T)$. In addition, temperature derivative curve of the diffraction intensity is also proportional to the heat flow curve, i.e. $\mathrm{d}I/\mathrm{d}T \propto \mathrm{d}H/\mathrm{d}t$. This relation leads to an idea that profile of the DSC curve can be obtained from the temperature derivative curve of the diffraction intensity. As well known, the heat flow signal of DSC includes two components, enthalpy changes that arise from the latent heat and heat capacity. Therefore, deviation from the above proportional relations occurs when contribution due to the heat capacity increases.

Temperature derivative curve dI/dT obtained from the diffraction intensities of $I(T)$ is shown in Fig. 3 by dotted line. For the comparison of the data obtained with WAXD measurements and DSC, the DSC melting curve at a heating rate of 1 K min^{-1} is shown in the same figure on the same temperature scale. According to the above consideration, the exothermic enthalpy change $\Delta H(T)$ was obtained from the DSC curve by the integration of the heat flow. DSC curve and $\Delta H(T)$ are also shown in Fig. 3 by solid line and broken line, respectively. The exothermic enthalpy change and the exothermic heat flow are expressed as a positive direction of the ordinate axis in this figure.

As shown in Fig. 3, the exothermic enthalpy change $\Delta H(T)$ and the temperature derivative curve dI/dT were similar to the diffraction intensity $I(T) = \Delta I(T) + I(T_0)$ and the DSC curve dH/dt, respectively. The small difference between these correspondences maybe caused from the contribution due to the heat capacity. It is noteworthy that DSC melting curve could be reproduced by a temperature derivative curve of the diffraction intensity.

The appearance of the positive peak of the diffraction intensity before final melting indicates an increase in crystallinity during the melting process. Accordingly this peak is interpreted to be a solid proof of the recrystallization, and the exothermic peak in the DSC curve can be conclusively attributed to the recrystallization. In addition, the double melting behavior of PBN is concluded to originate from the increase in crystallinity through the recrystallization. The increase in crystallinity during the double melting process was also confirmed as an increase in X-ray diffraction intensity for a PBT sample, and the above conclusion agrees with that suggested in the previous paper [5].

4. Conclusions

The double endothermic peaks and the exothermic peak located between them appeared evidently in the DSC melting curve for a PBN sample. In the heating process, crystal structure does not change during the double melting process. The diffraction intensity decreased gradually and showed a peak before final melting. The peak is interpreted as a solid proof of recrystallization. $I(T)$ and dI/dT approximately coincided with $\Delta H(T)$ and dH/dt, respectively. DSC curve could be reproduced by a temperature derivative curve of the diffraction intensity. The double melting behavior of PBN originates from the increase in crystallinity through the melt-recrystallization.

Acknowledgements

The authors would like to thank Dr. Shuji Irie of Teijin Kasei Co., Ltd. for providing PBN resins.

References

[1] K.H. Yoon, S.C. Lee, O.O. Park, Polym. J. 26 (1994) 816.
[2] B. Wunderlich, Macromolecular Physics, Crystal Melting, vol. III, Academic Press, New York, 1980.
[3] M. Todoki, T. Kawaguchi, J. Polym. Sci. Polym. Phys. Ed. 15 (1977) 1067.
[4] S.Z.D. Cheng, R. Pan, B. Wunderlich, Makromol. Chem. 189 (1988) 2443.
[5] M. Yasuniwa, S. Tsubakihara, K. Ohoshita, S. Tokudome, J. Polym. Sci. Polym. Phys. Ed. 39 (2001) 2005.
[6] H. Watanabe, Kobunshi Ronbunshu 33 (1979) 229.
[7] H. Koyano, Y. Yamamoto, Y. Saito, T. Yamanobe, T. Komoto, Polymer 39 (1998) 4385.