

The Effects of Annealing (Solid and Melt) on the Time Evolution of the Polymorphic Structure of Polyamide 6

Xiong-Yan Zhao,¹ Bing-Zhu Zhang²

¹College of Material Science and Engineering, Hebei University of Science and Technology, Shijiazhuang 050018, People's Republic of China

²School of Chemical Engineering and Technology, Hebei University of Technology, Tianjin 300130, People's Republic of China

Received 29 November 2008; accepted 25 July 2009

DOI 10.1002/app.31190

Published online 7 October 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: To understand whether and how the thermal history, especially the melting annealing, affects the polymorphism and thermal property of polyamide 6 (PA6), the temperature-modulated differential scanning calorimetry technology was used to investigate the effects of thermal histories, including annealing temperature, annealing time, and cooling rate, on the polymorphic behavior and thermal property of PA6. It was found that longer annealing time and faster cooling rate favored the formation of α crystal when PA6 samples were annealed in the solid-state at 175°C. As the annealing temperature was elevated to 195°C, faster cooling rate also favored the formation of α crystal, whereas longer annealing time was

more favorable for the formation of γ -form crystals. When PA6 samples were annealed in the melt-state (245°C), however, although the α crystal was dominating crystalline phase, the formation of γ crystal was greatly enhanced with increasing annealing time and cooling rate. Moreover, a small endothermic peak was observed in the low-temperature region in PA6 samples annealed at 175°C and 195°C, which might be related to the melting of microcrystals formed in the amorphous regions during annealing. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 1688–1694, 2010

Key words: polyamide 6; polymorphic structure; polymorphism; annealing

INTRODUCTION

Polyamide 6 (PA6) is a semicrystalline polymer that exhibits excellent chemical stability and mechanical strength properties and is also competitively priced in comparison to other PAs.¹ Exceptional value and performance in many products are thus making PA6 become one of the best choices for a number of consumer goods and industrial applications. PA6 exists in two major crystal forms: monoclinic (α -form) and pseudo hexagonal (γ -form).^{2,3} The essential difference between them is the molecular packing. For the α -form, hydrogen bonds are formed between anti-parallel chains of PA6. For the γ -form, however, the molecular chains have to twist away from the zigzag planes to form hydrogen bonds among the parallel chains giving rise to lesser interchain interactions compared with the α -form. One of the most remark-

able features of PA6 is that this semicrystalline polymer exhibits polymorphism depending on the thermal history, processing conditions, mechanical stress, crystallization conditions, and so on.⁴

Since the polymorphic form may have important effect on thermal properties such as heat distortion temperature, softening, dimensional stability and warpage, polymorphism, and polymorphic transformations of PA6 have drawn much considerable research interests. Studies on the formation of the α - versus γ -forms under different crystallization temperature and time were mainly carried out by three independent research groups,^{5–7} who reported that crystallization for extend periods of time below 130°C leads solely to the γ -crystallites whereas above 190°C only the α -form is produced. Temperatures in between these limits result in a mixture of the two forms, with higher fractions of α produced at higher temperatures. Kyotani and Mitsunashi⁷ found that annealing also affects the crystal structure. For example, annealing of quenched samples or those crystallized between 100 and 150°C, at 200°C for extended times leads to the conversion of the γ -form into α -form. Similar annealing results were demonstrated by Gurato et al.⁶ and Gogolewski et al.⁸ Murthy et al.^{9,10} reported that in PA6 fibers, both γ -form and α -form can coexist, and the content of the phases depends on the spinning and drawing

Correspondence to: X.-Y. Zhao (zhaoxy66@126.com) or B.-Z. Zhang (zhangbingzhu@hebust.edu.cn).

Contract grant sponsors: Scientific Research Key Foundation for Returned Overseas Chinese Scholars (Ministry of Personnel of the People's Republic of China); Research Fund of Hebei University of Science and Technology.

conditions, in which high-speed spinning is favorable for the formation of the γ -form. Okada et al.^{11–13} reported that higher crystallization temperatures or slow cooling leads to the α -form, whereas rapid cooling and low-temperature crystallization promotes the γ -form of PA6. Ramesh and Bhoje Gowd¹⁴ showed from their XRD results that PA6 crystallize directly into high-temperature α' -phase, if crystallized from the melt in a narrow temperature range between 200°C and melting temperature. This structure transforms into the room temperature α -phase on cooling, and the transition occurs over a temperature range. On heating, the room temperature α -phase transforms into the α' -phase at about 190°C and melts in that phase. If the sample is crystallized at temperatures below 190°C from the melt, then on subsequent heating the α -phase first transforms into a pseudohexagonal phase and then into the α' -phase at about 190°C before melting. Moreover, a third phase has also been reported by Stepaniak et al.,¹⁵ Sandeman and Keller,¹⁶ and Rolden and Kaufman,¹⁷ which can be converted into the α -form by annealing. Hu and Zhao¹⁸ observed from their MDSC results that annealing in the melt-state (230 and 250°C) has no significant effects on the structure of PA6, and the α crystal is still the most predominant phase independent of annealing time.

Although intensive research efforts have been devoted to this system, to our knowledge, most research mainly focus on the effect of solid-state annealing on crystallization behavior of PA6, the effect of melt annealing on thermal behavior of PA6 is still an interesting subject needed to be further investigated since some microstructural changes may occur at such high-annealing temperature, which would have a significant impact on properties of PA6 matrix. In this work, a comparative study of PA6 samples annealed at solid-state and melt-state, respectively, was carried out. In particular, we will focus our attention on the investigation of the effects of thermal histories, especially the melt histories, on the polymorphic transformation behavior of PA6, and to understand whether and how the thermal history affects the thermal property of PA6.

EXPERIMENTAL

Material

PA6 (SF 1018A) with a weight-average molecular weight of 18,000 was purchased from UBE Industries (Tokyo, Japan). The obtained samples were cut into small pieces and then dried under vacuum at 80°C for 24 h. The dried samples were melted in metal molder under N_2 at 260°C for about 8 min to eliminate the thermal history of samples. Finally, the

samples were cooled down to room temperature naturally.

To have a deep understanding of the effects of thermal histories on the thermal behavior and structures of PA6, two programs on thermal history were used in this research. (1) The samples were first heated to the appointed temperature at 40°C min⁻¹, then maintained at this temperature for 60 min, and then cooled to the room temperature at different cooling rate (0.5, 10, 20, 40, and 60°C min⁻¹, respectively). Finally the sample was heated from room temperature to the designated temperature at the rate of 5°C min⁻¹. (2) The sample was first heated to the annealing temperature at 40°C min⁻¹, maintained at this temperature for a given duration time (10, 60, 120, 240, and 720 min), and then cooled to the room temperature at the same rate. At last, the sample was heated from room temperature to the appointed temperature at the rate of 5°C min⁻¹. To better investigate the thermal and crystal morphological properties of PA6, three different annealing temperatures were chosen carefully in this study, i.e., 175°C and 195°C (below T_g , solid-state annealing), and 245°C (above T_g and T_m , melt-state annealing).

Measurements

Wide-angle X-ray diffraction patterns were taken on a Rigaku D/MAX2500PC X-ray diffractometer, CuK α radiation, 40.0 kV, 30.0 mA. Q-200 Modulated differential scanning calorimetry (MDSC) (TA Instrument) was used to analyze the thermal transition behaviors of the samples. MDSC is a relatively new technique, which subjects a sample to a linear heating ramp with a superimposed low-frequency temperature oscillation (modulation) resulting in a modulation in the heating profile. It could provide a better insight into the study of complicated transition in polymers; in addition, the ability to study transitions at very low heating rates gives very high resolution that permits the detection of weak transition. The MDSC was carefully calibrated for temperature and heat flow following the standard procedures. The thermal transitions are reported as maximum or minimum of the endothermic or exothermic peaks, respectively. To avoid any influence of earlier thermal history, every sample was used only once.

RESULTS AND DISCUSSION

Figure 1 illustrates the X-ray diffraction patterns of the received PA6 sample. It can be seen from Figure 1 that two reflections have been observed at $2\theta = 20.3^\circ$ and 24.1° corresponding to α_1 and α_2 respectively. α_1 originates from the distance between hydrogen-bonded chains, whereas α_2 comes from the

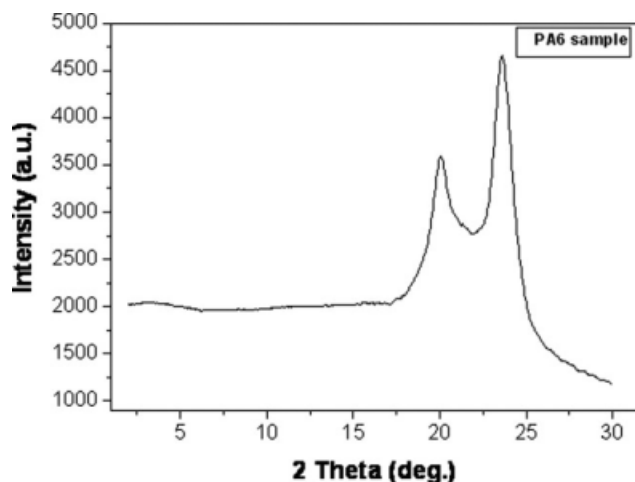


Figure 1 Wide-angle X-ray diffraction patterns of the received PA6 sample.

distance between hydrogen-bonded sheets. This indicates that the α -phase is the dominant crystalline phase for PA6 specimen.

Figure 2 shows the traces of MDSC thermograms of PA6 specimens, after annealing at 175°C for different times. It can be seen from Figure 2 that three different transitions appeared in PA6 MDSC thermograms. In addition to the presence of a sharp endothermic peak at 220°C assigned to the melting of α -form crystals of PA6,^{19–21} another two endotherms were also detected. There are a broad and less pronounced endothermic shoulder around 213°C and a broad but distinct endothermic peak centered around 180°C. The former is associated with the melting of γ -form crystals of PA6.⁵ A remarkable feature in Figure 2 is the appearance of a small low-temperature endothermic peak in all PA6 samples annealed at 175°C for different durations. It has been reported^{22–24} that the most plausible reason for

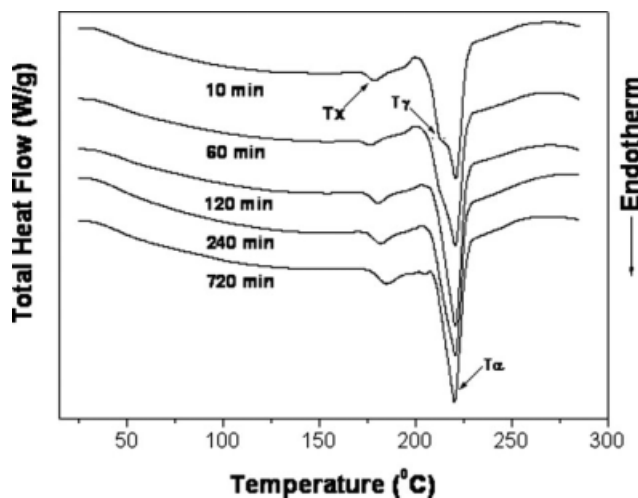


Figure 2 MDSC traces of PA6 annealed at 175°C for different durations.

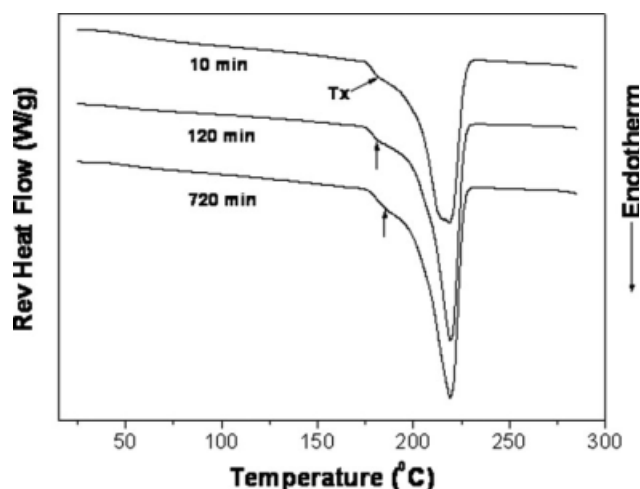


Figure 3 Reversing MDSC data of PA6 annealed at 175°C for different durations.

such behavior might be related to an enthalpy relaxation process of an interphase between the crystalline and amorphous phases, which can be induced by isothermal crystallization or annealing process. However, our results donot support this speculation, since this small endothermic peak (T_x) can also be detected in the reversing MDSC signal of PA6 samples (Fig. 3). So this endothermic behavior might be an indication of the melting of microcrystals formed in the amorphous regions during annealing. To distinguish the three endothermic peaks appeared in PA6 during heating run, their temperatures were defined as T_γ for the melting peak of γ -form crystals, T_α for the melting peak of α -form crystals, and T_x for the low-temperature melting peak, respectively. The corresponding heats of melting transition were named as ΔH_γ , ΔH_α , and ΔH_x , respectively.

It is also clear from Figure 2 that the α -form crystal is the most predominant phase, and melting peaks corresponding to α -form crystals are greatly enhanced with increasing annealing time, whereas the melting peaks corresponding to γ -form crystals are observed only as a less pronounced shoulder and finally disappeared as the annealing times exceeded 60 min. This is not surprising, since, in solid-state, polymer chains or segments are allowed to arrange themselves into a better organization when suitable conditions such as temperature and time are maintained to keep the system in a relatively lower energy. Furthermore, it can also be seen that the peak temperatures, T_α , remained fairly constant independent of annealing time, but T_x for the low-temperature endothermic peak shifts to higher temperature with increasing annealing time. Meanwhile, its enthalpy of transition, ΔH_x , increased steadily with increasing annealing time (Fig. 4). The increase in both T_x and ΔH_x appears to indicate that

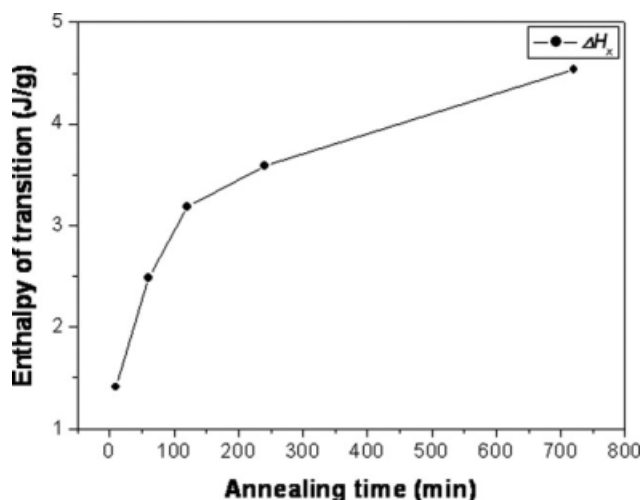


Figure 4 Changes in enthalpy of transition (ΔH_x) as a function of annealing time (annealed at 175°C).

this annealing temperature could lead to an increase in crystalline perfection of microcrystals with increasing annealing time, probably due to the fact that the longer annealing duration could provide more time to relieve the microcrystal defects.

Furthermore, it was also observed from Figure 2 that there is a small exothermic peak around 200°C in some of the PA6 MDSC scans. Li et al.²⁵ reported that this exothermic peak probably indicated that some uncrystallized materials may have undergone reorganization or recrystallization during the heating process.

The MDSC traces of PA6 samples, annealed at 175°C (solid-state annealing) for 60 min, and then cooled to the room temperature at different cooling rates, are shown in Figure 5. It can be seen from Figure 5 that peak temperature T_x and its associated enthalpy of transition, ΔH_x , of PA6 specimens

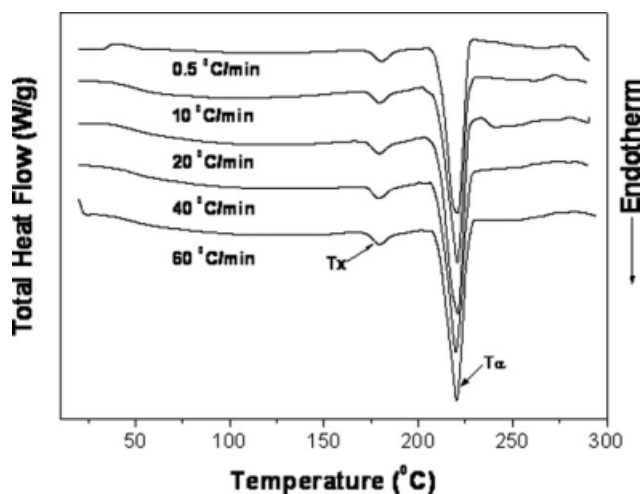


Figure 5 MDSC traces of PA6 annealed at 175°C for 60 min, and then cooling at different cooling rates.

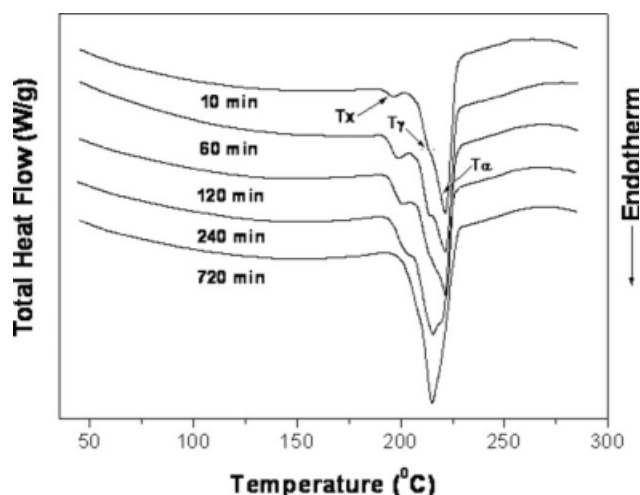


Figure 6 MDSC traces of PA6 annealed at 195°C for different durations.

showed no change for different cooling rates. Also, the peak temperatures of low-temperature endotherm, T_x , and its associated enthalpy of transition, ΔH_x , remain fairly constant regardless of the cooling rate employed. This means that cooling rate cannot affect the low-temperature melting peak and α -form crystal melting peak during solid-state annealing at 175°C.

The MDSC thermograms of PA6 specimens, annealed at 195°C for various durations, are shown in Figure 6. It is worthwhile to note from Figure 6 that the melting peaks of γ -form crystals are greatly enhanced with increasing the annealing time whereas the melting peaks corresponding to α -form crystals are reduced to only a much less pronounced shoulder as the annealing time was 240 min, and this melting peak finally disappeared as the annealing time reached to 720 min. It has been reported that annealing can relieve some of the residual stress accumulated during process,²⁶ and consequently, the dominant α -form crystals in PA6 are able to rearrange to an increasingly favored γ -phase conformation because of the thermal activation provided by annealing, and this phase conversion will become more prominent when enough annealing time is given. The dominant fractions of the γ -crystal in PA6 samples annealed at 195°C when compared with those annealed at 175°C suggest that γ -crystal forms more readily during a higher temperature solid-state annealing. Furthermore, it can also be seen from Figure 6 that the values of T_γ and T_α remained fairly stationary independent of the thermal history, but the low-temperature melting peak, T_x , was found to shift to higher temperature with increasing annealing time and finally overlapped with T_γ .

Figure 7 gives the traces of MDSC thermograms of PA6 specimens, after annealing at 195°C for 60 min,

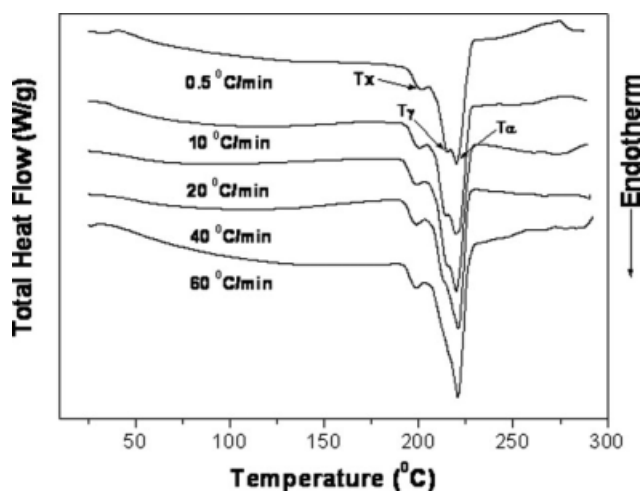


Figure 7 MDSC traces of PA6 annealed at 195°C for 60 min and then cooled at different cooling rates.

then cooling to the room temperature at different cooling rates. The following observations are worth noting in Figure 7. The melting peaks corresponding to α -form crystal is greatly enhanced with increasing cooling rate, whereas the melting peaks corresponding to γ -form crystal is much reduced with increasing cooling rate and observed only as a shoulder at last. On the other hand, the peak temperatures of low-temperature endotherm, T_x , and its associated enthalpy of transition, ΔH_x , remain fairly constant regardless of the cooling rate employed, which is quite different from that observed for PA6 annealed at the same temperature for different annealing times. Moreover, it is also clear from Figure 7 that the peak values of T_x show an obvious increase in comparison with those annealed at 175°C and then cooled at different cooling rates (Fig. 5), the maximum of the increase of more than 20°C ($\sim 199^\circ\text{C}$ versus $\sim 178^\circ\text{C}$) being observed.

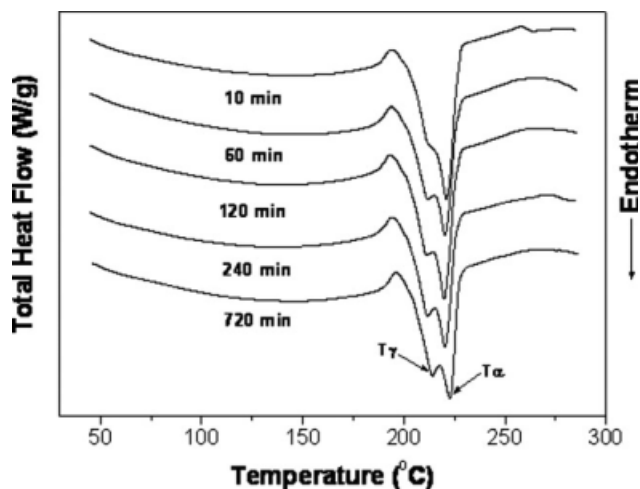


Figure 8 MDSC traces of PA6 annealed at 245°C for different durations.

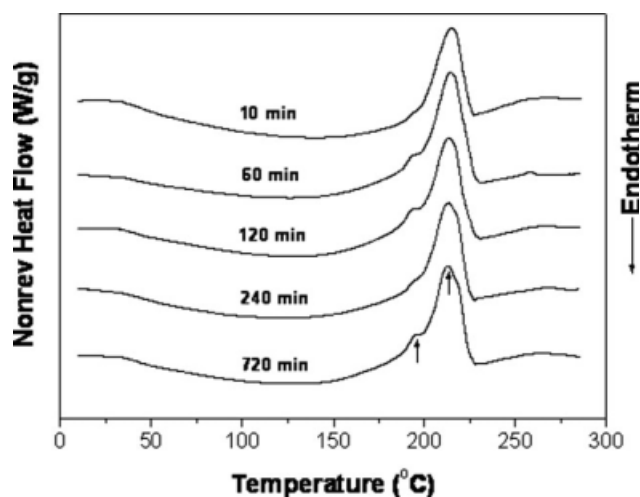


Figure 9 Nonreversing MDSC data of PA6 annealed at 245°C for different durations.

The MDSC thermograms of PA6, annealed at 245°C (melt-state annealing) for various durations, are shown in Figure 8. It can be seen that both α -crystals and γ -crystals were detected in all PA6 samples during annealing at 245°C for different durations. This phenomenon is illustrated more clearly in Figure 9, which shows the nonreversing MDSC signals of PA6 specimens annealed at 245°C for different durations. It is clear from Figure 9 that two nonreversible events were detected. There is a broad but distinct exotherm centered at 194°C, immediately followed by a strong exothermic peak at 213°C, indicating that both α -crystals and γ -crystals undergo a process of crystal perfection during the heating scan. Meanwhile, it is also clear from Figure 8 that the enthalpy of transition of γ -crystals, ΔH_γ , was found to increase with increasing annealing time and the ΔH_α showed a decrease after annealing. The relative ratios between ΔH_α and ΔH_γ in PA6 are

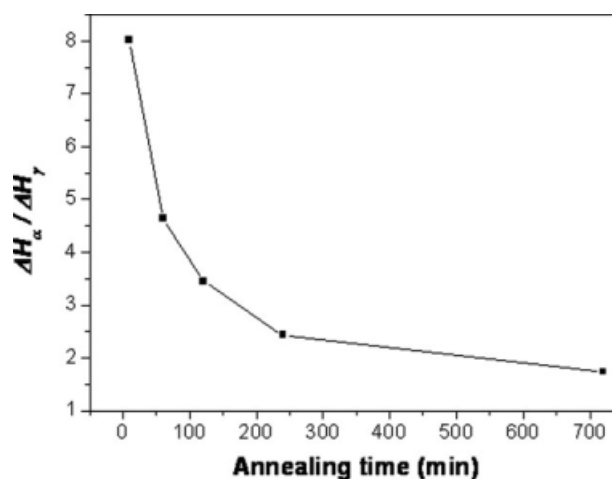


Figure 10 Changes in the content of γ -phase and α -phase as a function of annealing time (annealed at 245°C).

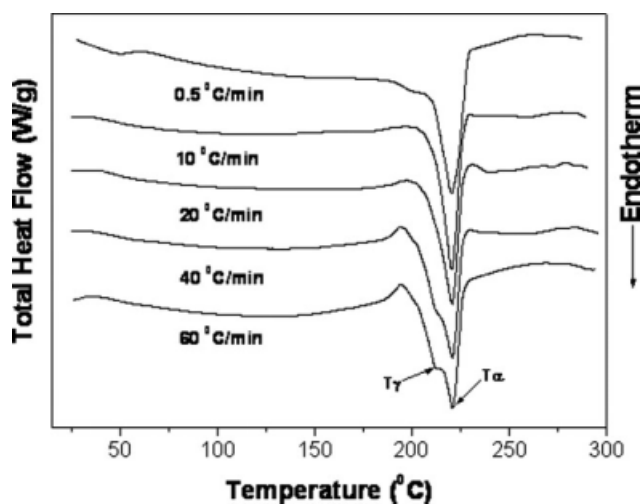


Figure 11 MDSC traces of PA6 annealed at 245°C for 60 min, and then cooling at different cooling rates.

illustrated clearly in Figure 10, which compares the changes in $\Delta H_\alpha/\Delta H_\gamma$ as a function of annealing time. There is a rapid initial drop of the $\Delta H_\alpha/\Delta H_\gamma$ value followed by a gradual decrease after about 240 min. This means the annealing at 245°C induces the formation of the γ -phase of PA6 samples. The real origin about "annealing at 245°C inducing the formation of the γ -phase" is not very clear at present, the possible explanation might be due to the fact that annealing at high-temperature can provide more space, by which the amide groups in adjacent sheets can shift to a position in which they are opposite to each other, resulting in a decrease in the total energy because of the offsetting charges between opposing amide groups in γ -crystals. In addition, the melting peak corresponding to T_x was not detected during melt-state annealing at 245°C, this

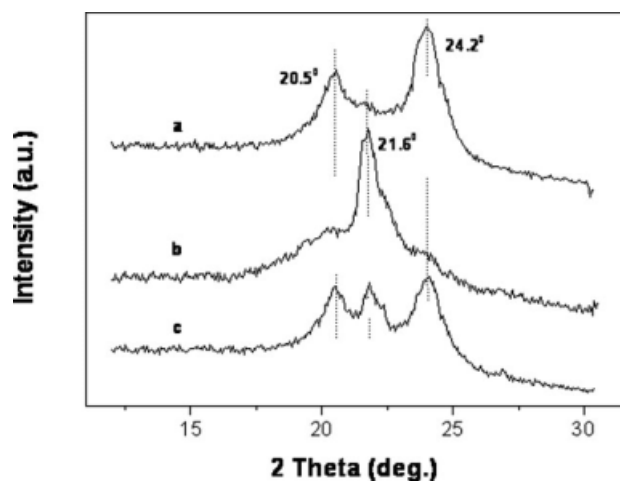


Figure 12 Wide-angle X-ray diffraction patterns of PA6 samples annealed at (a) 175°C, (b) 195°C, and (c) 245°C for 720 min.

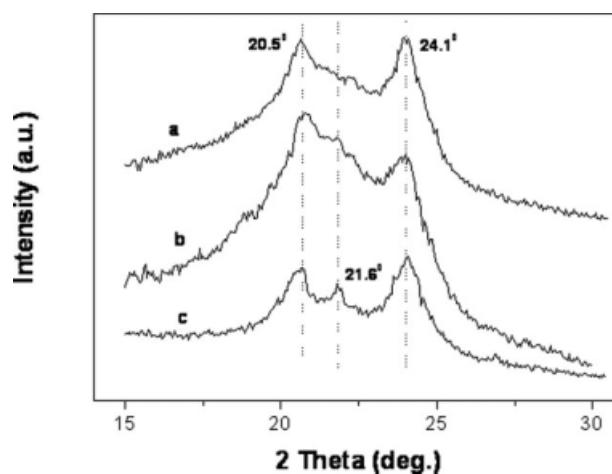


Figure 13 Wide-angle X-ray diffraction patterns of PA6 samples annealed at (a) 175°C, (b) 195°C, and (c) 245°C for 60 min, and then cooled at 60°C min⁻¹.

could be because the small endothermic peak is overshadowed by the melting of the γ -crystal and α -crystal. It is also possible that microcrystals do not form when annealing occurs in the melt-state.

The MDSC thermograms of PA6, annealed at 245°C for 60 min and then cooled down to room temperature at different cooling rates, are illustrated in Figure 11. It is observed that the α -form crystals were the absolutely dominant crystalline phase and the γ -crystals were detected as the cooling rate exceeded 20°C min⁻¹. This means that a relatively high cooling rate could lead to the formation of less stable γ phase.

To further confirm the MDSC results obtained, XRD analysis was carried out using the annealed samples which were prepared using the same procedures as for the MDSC measurements. Figure 12 illustrates wide-angle X-ray diffraction scans of the PA6 sample annealed for 720 min at 175, 195, and 245°C, respectively, and Figure 13 shows Wide-angle X-ray diffraction patterns of PA6 sample annealed for 60 min at 175, 195, and 245°C, and then cooled at 60°C min⁻¹. It is clear from both Figures 12 and 13 that the XRD results agree well with the MDSC observations.

CONCLUSIONS

The differences in polymorphism and thermal behavior of PA6 during annealing at different temperatures have been comparatively studied, and the effect of thermal history on the time evolution of the polymorphic structure of PA6 was also investigated. The polymorphic behavior and thermal property of PA6 were found to strongly depend on the thermal history of the specimen. Annealing in the solid-state at 175°C is more favorable for the formation of the

thermodynamically stable α -crystal. When the annealing temperature was elevated to 195°C, faster cooling rate also favored the formation of α crystal, whereas longer annealing time was more favorable for the formation of the γ -form crystal. On the other hand, annealing in the melt-state at 245°C has lead to the phase conversion from the α -phase to the γ -phase, which is subjected to the annealing time. Meanwhile, faster cooling rate is also favorable for the formation of γ crystal and this phenomenon would be amplified with increasing cooling rate. Furthermore, a small low-temperature endothermic peak has been detected during MDSC scans for PA6 samples annealed at 175°C and 195°C. This low-temperature endothermic peak was also found to depend on the thermal history. A longer annealing time and higher annealing temperature can lead to this endothermic peak moving to the high-temperature region.

References

- Hasan, M. M.; Zhou, Y. X.; Mahfuz, H.; Jeelani, S. *Mater Sci Eng A* 2006, 429, 181.
- Holes, D. R.; Bunn, C. W.; Smith, D. J. *J Polym Sci* 1955, 17, 159.
- Arimoto, H.; Ishibashi, M.; Chatani, Y. *J Polym Sci* 1965, 3A, 317.
- Fornes, T. D.; Paul, D. R. *Polymer* 2003, 44, 3945.
- Illers, K. H.; Haberkorn, H. *Makromol Chem* 1971, 142, 31.
- Gurato, G.; Fichera, A.; Grandi, F. Z.; Zannetti, R.; Canal, P. *Makromol Chem* 1974, 175, 953.
- Kyotani, M.; Mitsuhashi, S. *J Polym Sci Polym Phys Ed* 1972, 10, 1497.
- Gogolewski, S.; Gasiorek, M.; Czerniawska, K.; Pennings, A. *J Colloid Polym Sci* 1982, 260, 859.
- Murthy, N. S.; Aharoni, S. M.; Szollosi, A. B. *J Polym Sci Polym Phys Ed* 1985, 23, 2549.
- Murthy, N. S. *Polym Commun* 1991, 32, 301.
- Okada, A.; Kawasumi, M.; Tajima, I.; Kurauchi, T.; Kamigaito, O. *J Appl Polym Sci* 1989, 37, 1363.
- Campoy, I.; Gomez, M. A.; Marco, C. *Polymer* 1998, 39, 6279.
- Salem, D. R.; Moore, R. A. F.; Weigmann, H. D. *J Polym Sci Part B: Polym Phys* 1987, 25, 567.
- Ramesh, C.; Bhoje Gowd, E. *Macromolecules* 2001, 34, 3308.
- Stepaniak, R. F.; Garton, A.; Carlsson, D. J.; Wiles, D. M. *J Polym Sci Polym Phys Ed* 1979, 17, 987.
- Sandeman, I.; Keller, A. *J Polym Sci* 1956, 19, 401.
- Rolden, L. G.; Kaufman, H. S. *J Polym Sci Polym Lett Ed* 1963, 2, 603.
- Hu, X.; Zhao, X. Y. *Polymer* 2004, 45, 3819.
- Liu, L. M.; Qi, Z. N.; Zhu, X. G. *J Appl Polym Sci* 1999, 71, 1133.
- Wu, T. M.; Liao, C. S. *Macromol Chem Phys* 2000, 201, 2820.
- Cheng, L. P.; Lin, D. J.; Yang, K. C. *J Membr Sci* 2000, 172, 157.
- Bonnet, M.; Rogausch, K. D. *J Colloid Polym Sci* 1999, 277, 513.
- Liu, T. X.; Yan, S. K.; Bonnet, M.; Rogausch, J. *J Mater Sci* 2000, 35, 5047.
- Liu, T. X.; Petermann, J. *Polymer* 2001, 42, 6453.
- Li, T. C.; Ma, J. H.; Wang, M.; Tjiu, W. C.; Liu, T. X.; Huang, W. *J Appl Polym Sci* 2007, 103, 1191.
- Khannam, Y. P. *Macromolecules* 1992, 25, 3298.