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Synthesis, characterization and thermal history dependence of the polymorphic structure of nylon6/montmorillonite nanocomposites

Xiong-Yan Zhao · Ming-Zhu Wang

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Abstract Nylon6/clay nanocomposites with 5-wt% montmorillonite (NCN5) were prepared by a twin-screw extruder. The effects of thermal histories including annealing temperature (195 °C, solid-state annealing; 245 °C, melt-state annealing), annealing time and cooling rate on the polymorphic behavior and thermal property of NCN5 have been studied using Modulated Differential Scanning Calorimetry (MDSC) and wide angle X-ray diffraction. It was found that longer annealing time and faster cooling rate favored the formation of the γ crystal when NCN5 samples were annealed at 195 °C. As the annealing temperature was elevated to 245 °C, the α crystal became the absolutely dominating crystalline phase independent on the annealing durations and cooling rate. Moreover, a small endothermic peak was observed around 195 °C in NCN5 samples and this new transition peak was also found to be dependent on the thermal history.

Introduction

One of the exciting and promising developments in material science today is the design and synthesis of organic-inorganic nanocomposites that posses enhanced and novel properties, which are impossible in the individual organic and inorganic materials [1–3]. With the development of nylon6/clay nanocomposites by Tyoto Research Centre [4, 5], there have been increasing attentions to this system in the past decade [6–12]. As we know, one of the most remarkable features of nylon6 is that this semicrystalline polymer exhibits polymorphism depending on the thermal history, processing conditions, mechanical stress, crystallization conditions and so on. Since the polymorphic form may have important effect on thermal properties such as heat distortion temperature (HDT), softening, dimensional stability and warp, polymorphism and polymorphic transformations of nylon6 nanocomposites have drawn considerable research interests.

Studies on the crystal structure of nylon6 in nanocomposites were first carried by Kojima et al. [13], who reported that both α and γ crystals were present in nanocomposites. However, after annealing under elevated pressure, they found that the fraction of γ-phase decreased. The non-isothermal crystallization studies on polyamide/clay nanocomposites by Liu et al [14] showed that the addition of silicate layers favored the formation of the γ-crystalline form. Mathias et al. [7] reported that while both crystal forms were present in nanocomposites, annealing at 200 °C under vacuum produced only γ crystals. Paul et al [15] found that there were significant differences in crystal type within the core and skin regions of injection-molded nanocomposites. The skin region contains only the

X.-Y. Zhao (✉)
College of Material Science & Engineering, Hebei University of Science and Technology, Shijiazhuang 050054, P.R. China
e-mail: zhaoxy66@126.com

M.-Z. Wang
Hebei Province Analysis and Testing Research Centre, Hebei University of Science and Technology, Shijiazhuang 050018, P.R. China

γ-crystalline form; the core region, on the other hand, contains both α and γ-forms of nylon6. Okamoto et al [16] investigated the effect of crystallization temperature (T_c) on crystal structure of nylon6 and its nanocomposite. Their results show that at lower T_c, both α and γ crystal structures are formed in nylon6, with increasing T_c, the γ-from gradually disappeared. On the other hand, only the γ crystal is pronounced for the nylon6 nanocomposites throughout the whole T_c range studied. Although intensive research efforts have been devoted to this system, to the best of our knowledge, most research works mainly focus on the effect of clay and the annealing temperature on crystallization behaviors of nylon6 matrix [6–12, 17–19], the effect of thermal histories on thermal behavior of nylon6/clay nanocomposites is still an interesting subject needed to be further investigated since some microstructural changes may occur at different thermal histories, which would have a significant impact on properties of nylon6/clay nanocomposites.

In this paper, we will focus our attention on the investigation of the effects of thermal histories including annealing temperature annealing time and cooling rate on the polymorphic structure of nylon6 matrix in nylon6 nanocomposites and in order to understand whether and how the thermal history affects the thermal property of nanocomposites.

Experimental details

Materials

Nylon6 (SF 1018A) with a molecular weight of 18000 was purchased from UBE Industries Ltd. and its degree of crystallinity measured by XRD is 37.5%. Clay used in this research is montmorillonite mineral modified by Nanomer® I.30TC. Before extrusion, both nylon 6 and montmorillonite mineral were dried under vacuum at 100°C for 48 h. The nylon6 nanocomposite with 5-wt% clay (NCN5) was prepared by a Leistritz Mic 18/G1-30D twin-screw extruder. Each sample was extruded twice. 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 moulder under N_2 at 260 °C for about 8 min to eliminate the thermal history of samples. Finally, the samples were naturally cooled down to room temperature.

Characterization

Modulated Differential Scanning Calorimetry (MDSC) (2920 Modulated DSC, TA Instrument) was used to analyse 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 make the total heat flow to be separated into the heat capacity-related (reversible) and kinetic (nonreversible) components. Thus, the endothermic signals can be detected in both reversible and nonreversible scans, whereas the crystallization exotherms only contribute to the nonreversible signal. This makes MDSC a very powerful technique for the separation of exotherms (including crystallization and recrystallization) from reversible melting or other heat capacity-related events. All MDSC runs were made under a nitrogen atmosphere with heating and/or cooling rates of 5°C/min, and the thermal histories (namely, annealing temperature, annealing time and cooling rate) of the specimens were varied. The MDSC was carefully calibrated for temperature and heat flow following the standard procedures. The thermal transitions are reported as the maximum or minimum of the endothermic or exothermic peaks, respectively. In order to avoid any influence of previous thermal history, every sample was used only once. Wide-angle X-ray diffraction (WAXD) patterns were taken on a Rigaku RINT 2200 X-ray diffractometer.

Results and discussion

The total MDSC heat flow signals for neat nylon 6 and nylon6/montmorillonite nanocomposites (NCN5) are shown in Fig. 1. Upon heating from 25 °C to 280 °C, at a heating rate of 5°C/min, only one peak appeared in neat nylon6 MDSC thermograms with maximum at 220.8 °C which is associated with the α-form crystals of nylon6 [6, 8, 20, 21]. For NCN5, however, a quite different MDSC thermogram was observed as compared with that of neat nylon 6. It can be seen from Fig. 1 that three different transitions appeared in NCN5 total MDSC thermograms, in addition to the presence of a sharp endothermic peak at 220.3 °C related to the melting of α-form crystals of nylon6, another two endotherms were also detected. There are a broad less pronounced endothermic shoulder around 213 °C and a broad but distinct endothermic peak centered around 195 °C. The former is associated with the melting of γ-form crystals of nylon6 [22], which suggests that the presence of layered silicates in nylon6 is more inclined to promote the formation of γ-form crystals. This is because loading of silicates has a strong heterophase nucleation effect, which is favorable for the formation of γ-form crystals [8, 17, 19].

A remarkable feature in Fig. 1 was the appearance of a small low-temperature endothermic peak around 195 °C in all CNC5 MDSC scans. It has been reported [23–25] that the most plausible reason for 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 don't support this speculation since this endothermic peak can also be detected in the reversing MDSC signal (see Fig. 2). So this endothermic behavior might be an indication of the melting of microcrystals formed in the amorphous regions during annealing. In order to distinguish the three endothermic peaks appeared in NCN5 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.

X-ray diffraction data also confirm the difference in the structural features between neat nylon6 and NCN5. It can be seen from Fig. 3 that for neat nylon6, two reflections have been observed at $2\theta = 20.2°$ and 24.3° corresponding to α_1 and α_2 respectively, α_1 originates from the distance between hydrogen-bonded chains, while α_2 comes from the distance between hydrogen-bonded sheets. This indicates that the α-phase is the dominant crystalline phase for neat nylon6. For NCN5 samples, however, in addition to the two reflections as in neat nylon6, another reflection is also detected at $2\theta = 21.5°$, which is related to γ crystal planes of nylon6. Thus, the addition of silicates into neat nylon6 could favor the formation of γ-phase crystalline, which agrees well with the MDSC results. In addition, no diffraction peak is observed at low 2θ angle for the NCN5 nanocomposites. This indicates that a fully exfoliated morphology has been formed in this nanocomposite.

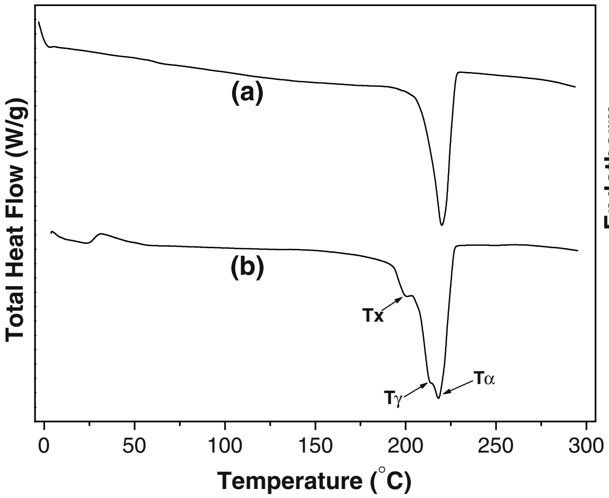

Fig. 1 MDSC thermograms (**a**) neat nylon6 and (**b**) NCN5

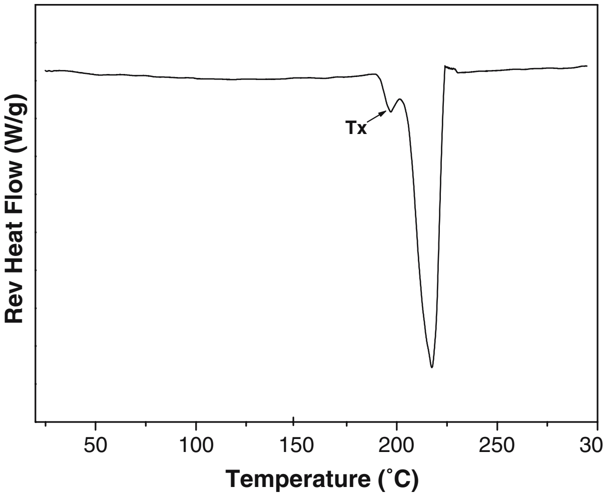

Fig. 2 Reversible MDSC data of nanocomposite NCN5

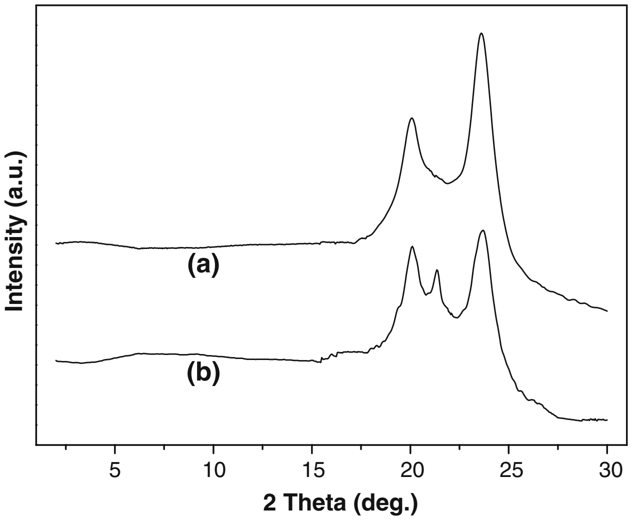

Fig. 3 Wide-angle X-ray diffraction patterns of (**a**) neat nylon6 and (**b**) NCN5

In order to have a deeper understanding of the effects of thermal histories on the thermal behavior and structures of nylon6/montmorillonite nanocomposites, two programs on thermal history were used in this research. (1) The samples were first heated to the annealing temperature at 40 °C/min, then maintained at this temperature for 30 min, and then cooled to the room temperature at different cooling rate (0.5, 2, 10, 20 and 40 °C/min, respectively). Finally the sample was heated from room temperature to the designated temperature at the rate of 5°/min. (2) The sample was first heated to the annealing temperature, maintained at this temperature for a given duration time, 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°/min. In order to better investigate the thermal and crystal morphological properties of NCN5 sample, two different annealing temperatures were chosen carefully in this study, i.e., 195°C (below T_γ, solid-state annealing), 245 °C (above T_γ and T_α, melt-state annealing).

The MDSC traces of NCN5, annealed at 195 °C for different durations of time, are shown in Fig. 4 and Fig. 5. It can be seen from both Figs that after being annealed at 195 °C for different durations, the γ-form crystal of NCN5 specimen becomes the absolutely dominant crystalline phase while the melting peak corresponding to α-form crystal is much reduced and observed only as a shoulder at last. 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 NCN5 are able to rearrange to an increasingly favored γ-phase conformation because of the thermal activation provided by annealing and this phase conversion will became more prominent when enough annealing time is given.

It is also worthwhile to note from Fig. 4 and Fig. 5 that the values of T_γ and T_α remain fairly stationary and appear unaffected by the annealing time. But the low-temperature melting peak, T_x, was found to shift to higher temperature with increasing annealing time. Meanwhile, when the annealing time is not more than 120 min, the enthalpy of transition, ΔH_x, was found to increase steadily with increasing annealing time (see Fig. 6). The increase in both T_x and ΔH_x appears to indicate that this annealing temperature could lead to an increase in crystalline perfection of microcrystals with increasing annealing duration, probably due to the fact that the longer annealing duration could provide more time to relieve the microcrystal defects. However, when the annealing time exceeds 120 min, the melting peak areas (ΔH_x) are greatly reduced and finally the melting peak corresponding to T_x becomes a much less pronounced shoulder. This can be ascribable to the fact that the longer annealing duration could provide more time to allow microcrystals to arrange

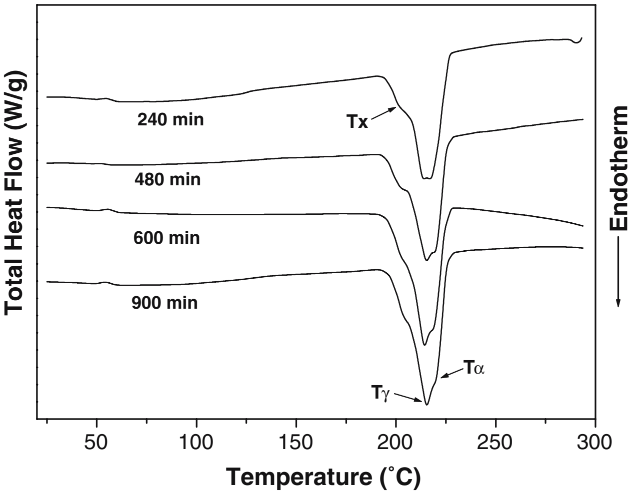

Fig. 5 MDSC traces of NCN5 annealed at 195 °C for (**a**) 240 min, (**b**) 480 min, (**c**) 600 min, (**d**) 900 min

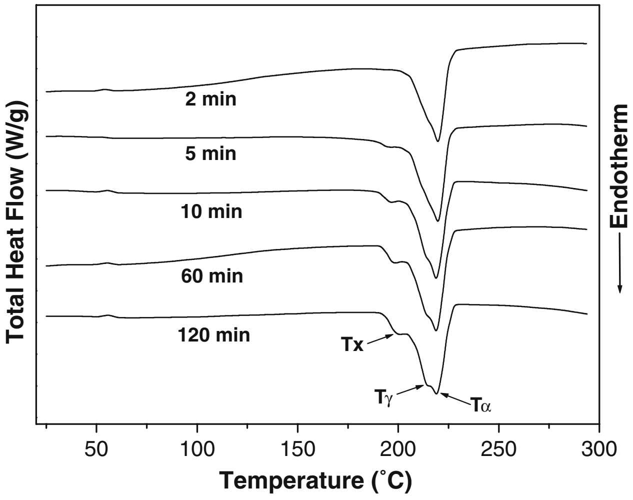

Fig. 4 MDSC traces of NCN5 annealed at 195°C for (**a**) 2 min, (**b**) 5 min, (**c**) 10 min, (**d**) 60 min and (**e**) 120 min

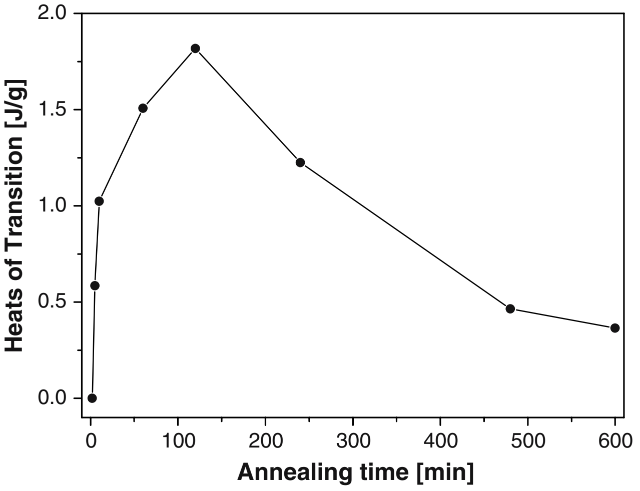

Fig. 6 Changes in enthalpy of transition (ΔH_x) as a function of annealing time (annealed at 195 °C)

themselves into a more perfect form, which results in a gradual increase in T_x value and overlapping with T_γ at last.

Figure 7 gives the traces of MDSC thermograms of NCN5 specimens, after annealing at 195 °C for 30 min, then cooling to the room temperature at different cooling rates. The following observations are worth noting in Fig. 7. The melting peak corresponding to γ-form crystals is enhanced with increasing the cooling rate although the α-crystal is still the most predominant phase. This is probably due to the presence of clay that induced the heterophase nucleation of γ phase as well as due to the high cooling rate both favoring the γ phase formation. It has been reported by Berglund et al. [27] that the relatively high cooling rate could lead to the formation of less stable γ phase. 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 NCN5 annealed at the same temperature for different annealing durations of time. This means that cooling rate cannot affect the low-temperature melting peak during solid-state annealing.

The MDSC thermograms of NCN5, annealed at 245 °C (melt-state annealing) for various durations, are shown in Fig. 8. It can be seen from Fig. 8 that only one endothermic peak was observed in NCN5 that corresponds to the α-form crystal and no γ phase was detected. This can be attributed to the fact that annealing in the melt state could provide more thermal activation to allow nylon6 molecules to arrange themselves into a more stable chain conformation, which results in the formation of the most favorable packing arrangement with lower energy crystal conformation. Hence, thermodynamically stable α-phase is expected as the predominant phase during the melt-state annealing. This phenomenon is illustrated more clearly in Fig. 9, which shows the non-reversing MDSC signals of NCN5 specimens annealed at 245°C for different durations. It is clear from Fig. 9 that only two non-reversible events were detected. There is a strong exotherm centred at 214 °C, immediately followed by a sharp endothermic peak at 222 °C, indicating that the α-phase crystals undergo a process of crystal perfection during the heating scan and subsequently these higher melting species melt at 222 °C. In addition, the melting peak corresponding to T_x was not detected during

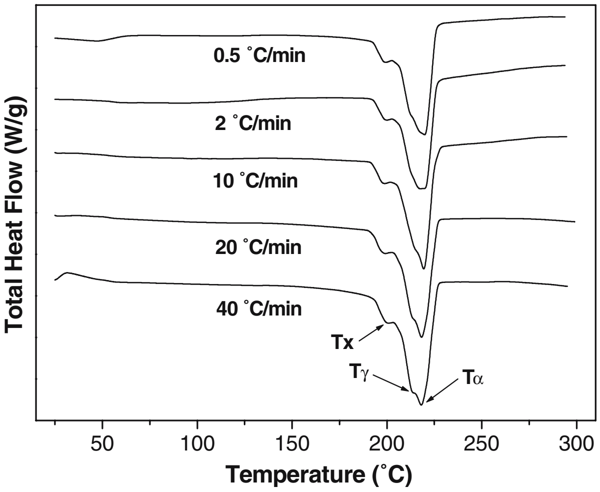

Fig. 7 MDSC traces of NCN5 annealed at 195 °C for 30 min, and then cooling at (**a**) 0.5 °C/min, (**b**) 2 °C/min, (**c**) 10 °C/min, (**d**) 20 °C/min and (e) 40 °C/min

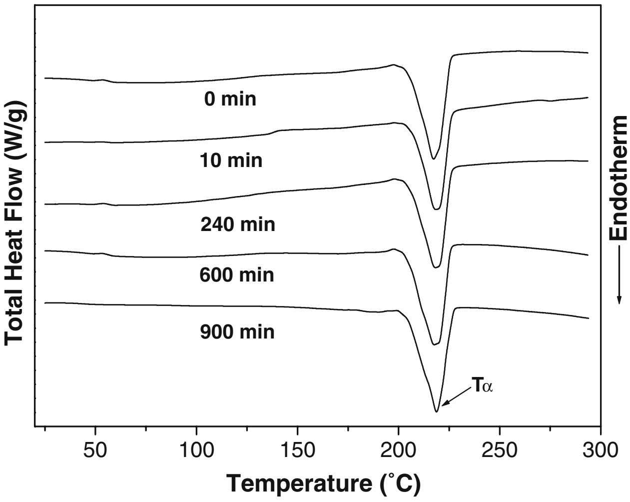

Fig. 8 MDSC traces of NCN5 annealed at 245 °C for different time durations

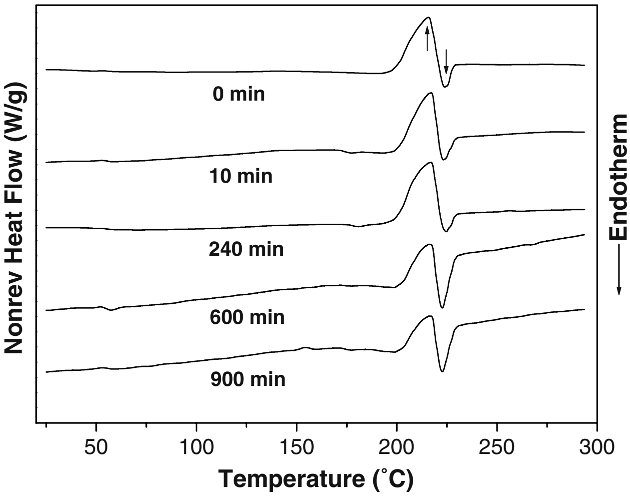

Fig. 9 Non-reversing MDSC data of NCN5 annealed at 245 °C for different time durations

melt-state annealing at 245 °C, this could be because the small endothermic peak is overshadowed by the melting of α-crystal.

The MDSC thermograms of NCN5, annealed at 245 °C for 30 min and then cooled down to room temperature at different cooling rates, are illustrated in Fig. 10. It is observed that the α-form crystal becomes the absolutely dominant crystalline phase and almost no γ-phase was detected. This suggests that melt-state annealing at 245 °C for 30 min has led to the formation of thermodynamically stable α-phase and the subsequent cooling rate cannot change the crystal structure of NCN5. But the enthalpy of melting transition for α-crystal was found to greatly decrease with increasing the cooling rate (see Fig. 11), probably due to the fact that some α-phase crystals could be formed during cooling at lower cooling rate. Since lower cooling rate could provide more time and thermal activation for nylon6 molecules to arrange themselves into a thermodynamically more stable α-phase.

Conclusion

In this paper, nylon6/montmorillonite nanocomposite with 5-wt% clay (NCN5) has been successfully synthesized. The polymorphism and thermal behavior of NCN5 and nylon6 have been comparatively characterized. The difference in polymorphism between neat nylon6 and NCN5 reflected the complexity of the melting behavior of NCN5 system. The polymorphic behavior and thermal property of nanocomposites NCN5 were found to depend on the thermal history of the specimen. Annealing in the solid state at 195°C is more favorable for the formation of the γ crystal subjected to the annealing time and cooling rate while annealing in the melt state at 245 °C favored the formation of thermodynamically stable α-crystal regardless of annealing time and cooling rate. Furthermore, a small low-temperature endothermic peak has been detected during MDSC scans for NCN5 samples, which might be related to the melting of microcrystals formed in the amorphous regions during annealing. This low-temperature endothermic peak was also found to depend on the thermal history. A longer annealing time can lead to this endothermic peak moving to the high-temperature region as NCN5 was annealed in the solid state at 195 °C.

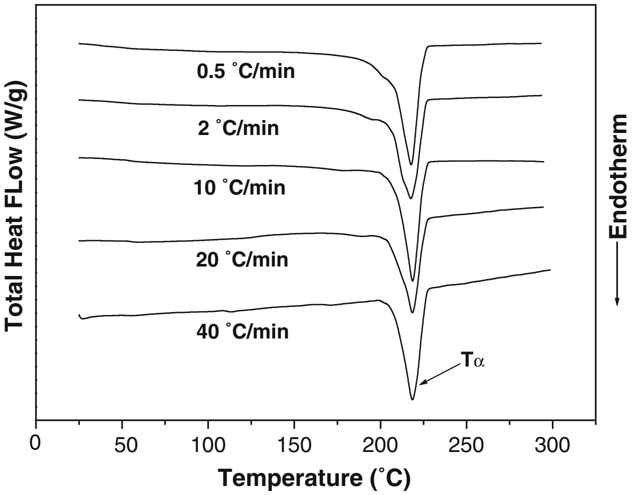

Fig. 10 MDSC traces of NCN5 annealed at 245 °C for 30 min, and then cooling at (**a**) 0.5 °C/min, (**b**) 2 °C/min, (**c**) 10 °C/min, (**d**) 20 °C/min and (**e**) 40 °C/min

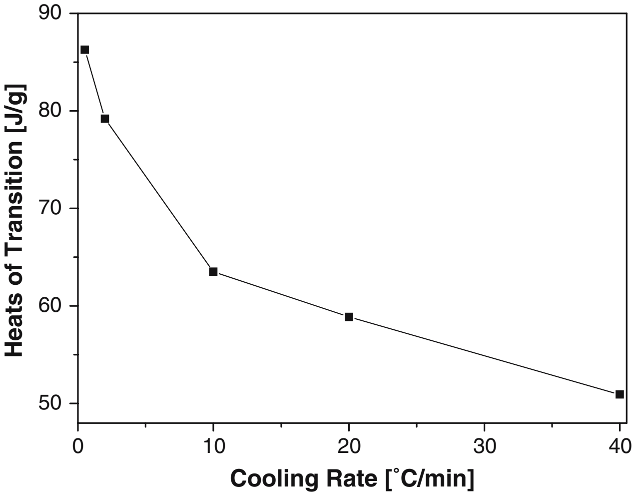

Fig. 11 Changes in enthalpy of transition (ΔH_{α}) as a function of cooling rate

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