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Studies on Crystal Transition of Polyamide 11 Nanocomposites by Variable-temperature X-Ray Diffraction*

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Abstract Polyamide 11 (PA11) and its nanocomposites with different organoclay loadings were prepared by melt-compounding and subsequent pelletizing. The crystal phase transitions of PA11 and its clay nanocomposites were investigated by variable-temperature X-ray diffraction. It was found that the Brill transition of the nanocomposite was 20 K higher than that of the neat PA11 for both heating and cooling processes. The PA11 *d*-spacings of the nanocomposites were observed to be smaller than those of the neat PA11 for melt crystallization. The constraints imposed by the addition of layered clay, restricting the thermal expansion of the polymer chains, are probably responsible for such a reduction of the *d*-spacing.

Keywords: Polyamide 11; Clay; Nanocomposites; Crystal transition; Variable-temperature X-ray diffraction.

INTRODUCTION

In the past decades layered silicates, such as montmorillonite, have been widely investigated in the polymer nanocomposite field for their unique chemical and physical properties. Nanocomposites with uniform silicate dispersion usually show significant enhancement in mechanical properties and other synergism effects such as reduced flammability and low gas/moisture permeability^[1–10]. However, the addition of layered silicates into thermoplastics sometimes changes the chain conformation, crystal structure and morphology of the polymeric matrices, as observed in nylon/clay nanocomposites^[11–15]. The structural and morphological changes of the matrices resulting from clay addition usually have significant effects on the mechanical and other physical properties of the polymer nanocomposites.

Polyamide 11 (PA11) is an important commercial semicrystalline polymer, which displays polymorphism and has been found to possess at least five kinds of crystal structures: triclinic α -form, monoclinic β -form and three pseudo-hexagonal forms (γ , δ , δ') with different crystal lattices^[13–21]. The α -form crystals are stable at temperatures below 95 °C, while the δ form exists above 95 °C. The δ' crystal form can be obtained by

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quenching the melt in ice/water bath as quenching suppresses the formation of hydrogen bonding and ordered alignment of these bonds in the thermodynamically stable state^[12, 13]. The δ' crystals of PA11 exhibit similar X-ray reflections as the δ -form crystals with a d -spacing of 0.42 nm and a broad profile^[19–21]. A crystal transition from the α -form to the pseudo-hexagonal forms can be observed by increasing temperature. This crystal-crystal transition is known as the Brill transition and is a common and unique phenomenon in most polyamide systems^[1–5, 22–29]. The temperature at which the crystal transition occurs is the so-called Brill transition temperature. Most studies of the Brill transition focus on nylon 66 and nylon 6, where the triclinic or monoclinic α -phase structures transform into the pseudo-hexagonal structure at elevated temperatures^[22, 23, 28, 29]. For instance, the Brill transition of nylon 66 is clearly illustrated by X-ray diffraction patterns, as two strong reflection peaks ($d_{\alpha 010} = 0.38$ nm and $d_{\alpha 100} = 0.44$ nm) merge into a single one ($d_{\gamma 100} = 0.42$ nm). However, the nature of this thermal treatment induced crystal-crystal transition has not yet been fully understood^[19].

The preparation, characterization and mechanical properties by the nanoindentation technique of PA11/clay nanocomposites were reported previously^[2, 13, 15]. The aim of this work was to investigate the effect of clay addition on the crystallization behavior of PA11 at various temperatures. Usually, the Brill transition is studied by X-ray diffraction with pre-crystallized samples during heating from room temperature to melting. In this paper, we report the crystal-crystal transition behavior of PA11 and its clay nanocomposites by means of high-temperature X-ray diffraction. Both neat PA11 and the nanocomposite samples were heated from the quenched amorphous state to the melt (*i.e.*, cold crystallization) and then cooled from the melt to room temperature (*i.e.*, melt crystallization); and the crystal transformation during heating/cooling processes was recorded by high-temperature X-ray diffraction.

EXPERIMENTAL

Polyamide 11 was purchased from Atofina (Rilsan Besno TL[®], melt flow index: 52 g/10 min), its glass transition temperature was 46 °C and melting temperature was 189 °C. The organically modified clay (Nanomer I.30TC) was supplied by Nanocor Inc. All the samples were dried in a vacuum oven at 80 °C for 24 h before mixing. PA11 was blended with 5 wt% organoclay *via* melt-compounding by using a Brabender twin-screw extruder at 220 °C with a screw speed of 150 r/min, followed by pelletizing^[13]. The obtained pellets were hot pressed into sheets (with thickness of about 0.5 mm) at 200 °C for 5 min, and then quenched in ice/water bath.

The variable-temperature X-ray diffraction (XRD) measurements were performed on a Rigaku D/Max 3C diffractometer with CuK α radiation ($\lambda = 0.15406$ nm) with a heating attachment. The samples were heated or cooled at a rate of 10 K/min between room temperature and the melt one (220 °C). To avoid thermal degradation, all the samples were kept in vacuum during conducting the experiments. The diffractometer was operated at 40 kV and 100 mA. The XRD patterns were recorded from $2\theta = 10^\circ$ to 30° at a scanning rate of 1 °/min and the step interval was 0.02°.

RESULTS AND DISCUSSION

Heating Process

Figures 1(a) and 1(b) show the temperature-dependent XRD patterns during heating from room temperature to melt (220 °C) for PA11 and its nanocomposite (with 5 wt% clay), respectively. As shown in Fig. 1(a), at room temperature (25 °C) the XRD pattern of the quenched neat PA11 had an amorphous halo with two crystalline reflection peaks corresponding to α_{100} and γ_{100} planes at $2\theta = 20.4^\circ$ and 21.6° , respectively^[15]. As the temperature reached 60 °C, the two reflection peaks (α_{100} and γ_{100}) were merging into a single reflection peak of γ_{100} . When further increasing the temperature, the reflection peak of γ_{100} slightly shifted toward lower 2θ angles, probably due to the thermal expansion of hydrogen bonding thus resulting in larger lattice spacing. It can be seen that the overall peak area was gradually reduced with increasing temperature, implying a decrease in the degree of crystallinity, which is probably due to the partial melting of imperfect crystals. When the temperature was increased to above 180 °C, only a typical amorphous halo can be observed.

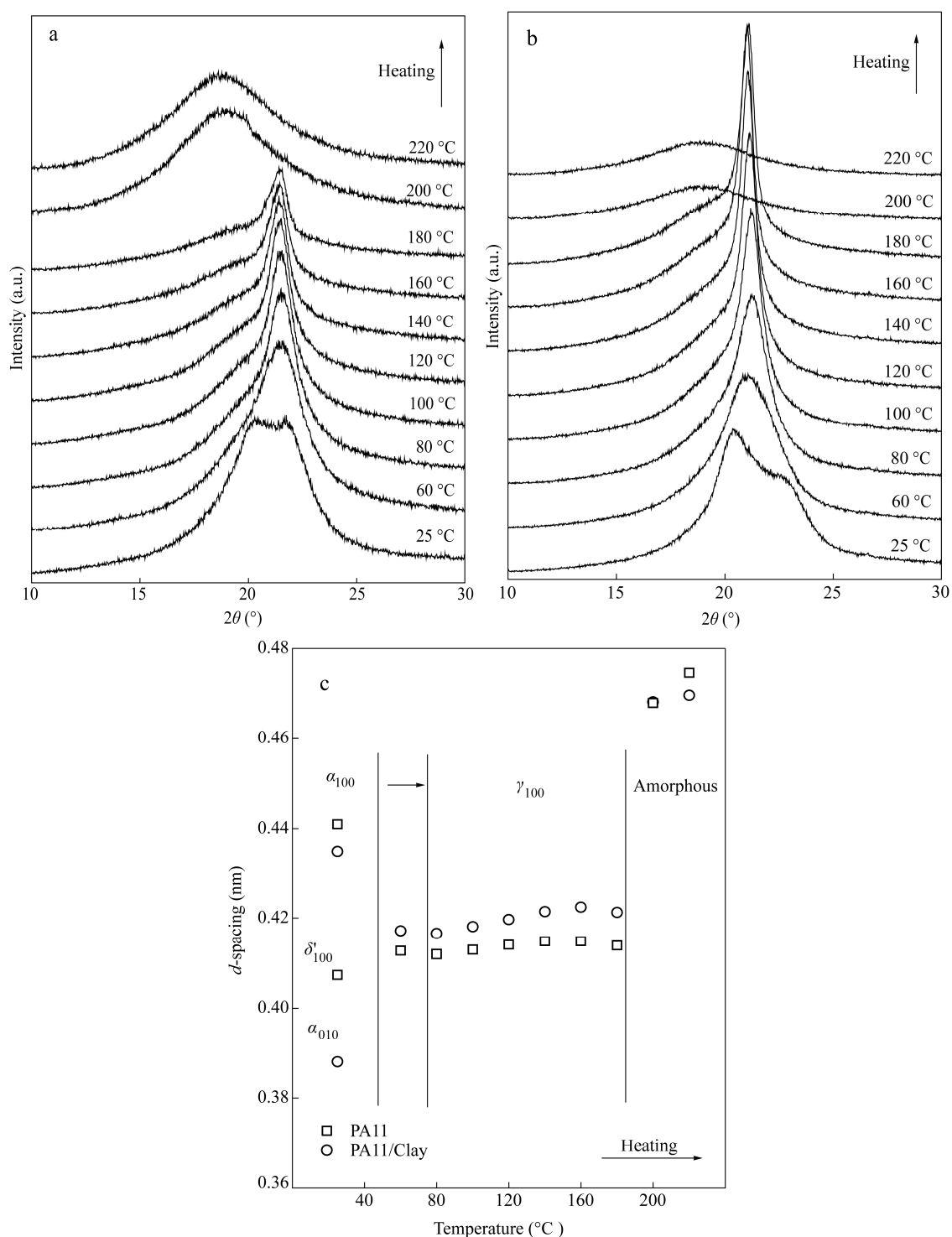


Fig. 1 Temperature-variable XRD patterns during heating process for neat PA11 (a) and its nanocomposite with 5 wt% clay (b) and the variation of d -spacings as a function of temperature (c)

The XRD patterns of PA11/clay nanocomposite sample during heating showed different temperature dependences, as presented in Fig. 1(b). The XRD reflections at $2\theta = 20.4^\circ$ and 22.9° correspond to the (100) and (010) planes of triclinic α -crystals, respectively. This is quite different from the case of neat PA11. The presence

of only α -form crystals is closely related to the addition of clay, which is always found to increase the crystallization rate by acting as heterogeneous nucleation sites. The two triclinic reflections (α_{100} and α_{010}) merged into a single broadened peak (γ_{100}) at 60 °C and only the crystalline peak of γ_{100} was observed when further increasing the temperature. The reflection peak γ_{100} became narrow and sharp as the temperature increased. There was no significant reduction in the intensity or area of the reflection peak at high temperatures, which is different from that in neat PA11, implying that the crystal size or perfection of PA11/clay nanocomposite was higher than that of neat PA11. This indicates that PA11/clay nanocomposite possessed better thermal stability than PA11, resulting from the layered structure of clay. The decrease in crystalline portion for neat PA11 is attributed to the melting of the lamellar surfaces and secondary and imperfect lamellae within the primary lamellar stacks^[16, 21]. However, the layered silicates in the nanocomposites acted as layers of inorganic insulation that may delay the lamellar melting (at high heating rate). In addition, the lamellae confined between the silicate layers have higher thermal stability due to chain confinement effect, especially for the intercalated nanocomposites^[13], and as a result, a more complicated melting behavior in polymer/clay nanocomposites can be observed. Zhang *et al.*^[15] studied PA11 and its nanocomposites by variable-temperature infrared spectroscopy, they showed that the hydrogen bonds in the nanocomposites were weakened, compared with those in neat PA11, because of the addition of montmorillonite. This probably indicates that the hydrogen bonds in the nanocomposites have less molecular vibration and thus the chain segments have lower mobility due to the constraints imposed by the layered silicates.

Figure 1(c) shows the temperature dependence of d -spacings for PA11 and its nanocomposite. The d -spacing values were calculated by the Bragg equation. As shown in Fig. 1(c), the d -spacings of PA11 (fill square) and PA11/clay nanocomposite (open circle) increased with the increase of temperature. And clearly, the nanocomposite experienced more expansion of the γ unit cell from thermal stimulation than neat PA11 when the samples were heated from 60 °C to melt.

Cooling Process

Figures 2(a) and 2(b) show the XRD scans at 10 K/min for neat PA11 and its nanocomposite at various temperatures during the cooling process. The X-ray diffraction patterns changed remarkably as the samples are cooled from the melt to room temperature. The amorphous background scattering, only remains visible at 180 °C and a crystalline reflection at $2\theta = 21.4^\circ$ (γ_{100}) appears at 160 °C for both neat PA11 and the nanocomposite samples. Both samples show similar XRD patterns with a single reflection of pseudo-hexagonal γ_{100} upon cooling to 120 °C. In addition, the reflection peak of γ_{100} steadily shifts toward higher diffraction angles with decreasing temperature due to the crystal lattice contraction. The γ_{100} reflection peak broadened at 100 °C and split into two reflection peaks at 80 °C, and further diverged with decreasing temperature down to 25 °C. These two reflection peaks at $2\theta = 20.4^\circ$ and 22.8° belong to α_{100} and α_{010} , respectively^[14, 15]. Therefore, for both neat PA11 and the nanocomposite samples, the Brill transition from pseudo-hexagonal γ -form crystals to triclinic α -form crystals occurred during the cooling process, as well as during heating from α -form to γ -form crystals.

Figure 2(c) shows the variation of d -spacing with temperature for neat PA11 and the nanocomposite cooled from the melt to room temperature. During the cooling process, the d -spacings of both neat PA11 and its nanocomposite decreased with the decrease of temperature due to thermal contraction. The d -spacings of the nanocomposite were smaller than those of neat PA11 because the nano-sized clay platelets created wall-like constraints that restricted the regular packing of the lattice during crystallization. The Brill transition temperatures for PA11 and its nanocomposite were determined to be 80 °C and 120 °C, respectively.

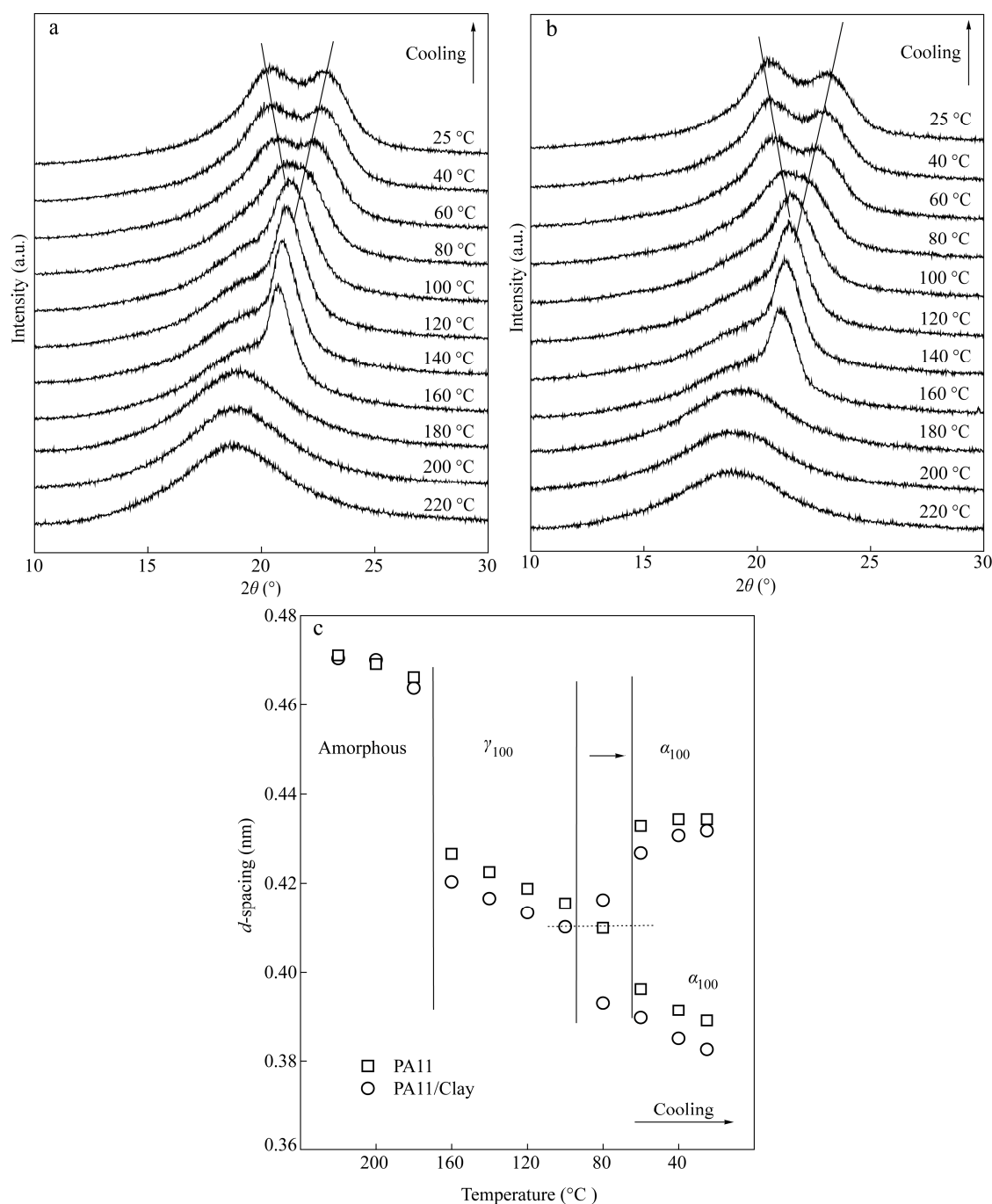


Fig. 2 Temperature-variable XRD patterns during cooling process for neat PA11 (a) and its nanocomposite with 5 wt% clay (b) and the variation of d -spacings as a function of temperature (c)

Discussion

The main finding in this work is that the γ -phase in melt-crystallized PA11 and its nanocomposite transformed to the α -phase upon cooling to room temperature from melt. This indicates that the pseudo-hexagonal γ -phase crystals undergo a phase transition into the triclinic α -phase when cooling through the Brill transition temperature. The Brill transition of PA11 is completely reversible for both heating and cooling cycles. Major conformation changes (such as *trans-gauche* transition) along the chain axis and melting of hydrogen bonding

sheets are not involved for this phase transition^[18, 21]. The unit cell of α -form for PA11 consists of a polymer chain lying parallel to the c -axis (molecular chain direction), with van der Waals bonds and strong hydrogen bonded sheets in the plane formed between the chain segments^[17–20]. Hydrogen bonds are perpendicular to the polymer chain direction. The phase transition in PA11 involves the anisotropic thermal expansions as the lattice responds to the thermal stimulation, and the lateral shifting of adjacent hydrogen bonded sheets caused by the increased mobility as the temperature increases^[21]. Previous studies by Mathias *et al.*^[18] showed that as the temperature increased, the methylene group segments in crystalline domains underwent rapid segmental rotations. The lateral motion expands the intersheet distance (α_{010}) from the triclinic to the pseudo-hexagonal structure (γ_{100})^[1, 2]. Model studies of nylon 1010 showed that the hydrogen bonding becomes weaker and the methylene segments show remarkable disordering in the conformation during heating^[30, 31]. During the crystal transition, the overall energy and stress in the final structure are reduced to minimum. The hydrogen bonding and van der Waals interactions must reach a minimum value in order to achieve optimum packing. The final crystal structure must be balanced between thermal motion and molecular packing tendency within the crystals. The disruption of hydrogen bonds occurs only at the melting point and this strong intermolecular interaction is preserved over all the temperature ranges. This model is successful in interpreting the crystal transition in other polyamide systems such as nylon 6, nylon 66 and nylon 1010^[15, 18, 21, 27–32].

However, the crystallization behavior of polymer nanocomposites becomes more complicated when the nanofillers are added. The exploration of polymer crystallization under pre-existing nucleation agents, such as silicate layers in nanocomposites, is technically important for better understanding of the structure-property relationship of the final products. As shown in Fig. 1(a), the changes of d -spacings provided some insight to molecular chain responses to the constraints from the clay. The confinement effect from silicate layers resulted in excessive lattice expansion in the nanocomposite, as evidenced by larger lattice size in the nanocomposite than in neat PA11. The clay platelets with size in the nanometer range are considered as nano-channels for the polymer chains in the intercalated nanocomposites. For those polymer chains tethered to the nanoplatelet surfaces, the motion along the chain direction was restricted (or less mobile) due to the constraints from the rigid silicate layers. The original three-dimensional chain mobility in PA11 crystals is confined to two-dimensional interlayer space in the nanocomposites by the incorporation of clay nano-platelets, thus leading to anisotropic thermal expansion in crystal lattice. Therefore, this enlarged response results in larger crystal lattice for PA11/clay nanocomposites than for neat PA11 when the samples are subjected to initial heating from room temperature. However, this confinement effect from silicate layers will lead to certain degree of crystal distortion during packing upon cooling for melt crystallization. On the contrary, PA11/clay nanocomposites showed smaller values of d -spacings than neat resin during cooling from the molten state. This is probably because the addition of clay platelets constrains the molecular packing and confines the chains in smaller dimensions. As shown in Fig. 1(c), the nanocomposite possessed smaller lattice size at room temperature compared to neat resin, further confirming the presence of the constraints on the polymer chains resulted from clay nanoplatelets. This confinement effect resulted in smaller crystal size in the nanocomposites during crystallization. The linear coefficients of thermal expansion (CTE) of γ_{100} can be calculated from Fig. 1(c) to be 1.15×10^{-4} /K and 1.95×10^{-4} /K for PA11 and PA11/clay nanocomposite, respectively. For the cooling process from Fig. 2(c), the CTE values of γ_{100} are 4.32×10^{-4} /K and 4.03×10^{-4} /K for neat PA11 and the nanocomposite, respectively. The higher CTE in the nanocomposites than neat resin agrees with the constraint effect from the silicate layers and higher anisotropic thermal expansion in crystal lattice. The difference in CTE between heating and cooling processes was probably due to different chain mobility. For both neat PA11 and the nanocomposite, the chain mobility is higher during cooling from the molten state and the CTE is almost doubled, compared with those calculated from heating process from the quenched state. During the cooling process, polymer chains have inherently higher mobility and higher CTE values, thus the packing or arrangement of polymer chains during melt crystallization was hindered by the presence of layered silicates, as indicated by 10% lower CTE values for the nanocomposites than those for neat PA11 during cooling.

Another notable observation is the change of the Brill transition temperature for neat PA11 and PA11/clay nanocomposites at 80 °C and 100 °C, respectively, as shown in Fig. 2(c). As is known, Brill transition is the critical balancing point between the packing tendency and thermal motion of polymer chains^[29–31]. In the PA11/clay nanocomposites, smaller size of crystal lattice leads to earlier onset of this transition during cooling. The horizontal dot line shown in Fig. 2(c) indicates that PA11/clay nanocomposite reached a *d*-spacing of 0.41 nm at 100 °C instead of at 80 °C for neat PA11. However, during the heating process, the excessive thermal expansion in *a*-axis direction for the nanocomposite may cause the lattice to reach this critical value faster or earlier than neat resin, and thus the Brill transition might occur at lower temperature in the nanocomposites. Similar phenomenon has been observed in nylon 66/clay nanocomposites^[33].

CONCLUSIONS

Both cold-crystallization and melt-crystallization of PA11 and PA11/clay nanocomposites were studied by *in situ* high-temperature XRD. The XRD results showed that the *d*-spacings of the nanocomposites are larger than that of the neat resin during the heating process. It was proposed that the external constraints imposed by the layered silicates restricted the thermal expansion in *c*-axis and thus resulted in excessive thermal expansion in *a*-axis when subjected to heating and cooling processes. The Brill transition of PA11/clay nanocomposites was found to be about 20 K higher than that of neat PA11. This phenomenon is probably originated from the lag of heat transfer in the nanocomposites because of the thermal barrier effect from the silicate layers. Therefore, the addition of nanoclay platelets in PA11 matrix not only acted as external constraints which restricted the expansion of the chain axis but also influenced the thermal distribution in the systems.

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