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High-temperature X-ray diffraction studies on polyamide6/clay nanocomposites upon annealing

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Summary

The influence of nanodispersed clay on the α crystalline structure of polyamide 6 (PA6) was examined in-situ with X-ray diffraction (XRD) between room temperature and melting. In pure PA6 upon annealing the α crystalline phase was substituted by an unstable pseudohexagonal phase at 150°C, then it transformed into a new stable crystalline structure - high temperature α′ phase above the transition temperature. However, in PA6/clay nanocomposite (PA6CN), the α phase did not present crystalline phase transition on heating. The increase in the annealing temperature only led to continuous intensity variation. The different behaviors were caused by the confined spaces formed by silicate layers, which constrained the mobility of the polymer chains in-between.

Introduction

In recent years, for the unexpected hybrid properties synergistically derived from the two components, polymer/clay nanocomposites (PCN) have attracted great interest from researchers. The majority of recent work on PCN has focused on synthesis and characterization of physical properties. Although the improved properties were achieved, such as improved tensile strength and modulus, decreased thermal expansion coefficient, decreased gas permeability and reduced flammability, the fundamental mechanisms for property enhancements in the nanocomposites are not well understood. It is complicated to establish the structure-property relationship since there may exist lots of morphological and processing factors, which has influence on both the inorganic filler and polymer, for example the orientation of the silicate layers and the influence of silicate layers on polymer conformation and morphology [1,2].

For the PCN with semi-crystalline polymer matrix, this problem turns more complicated because the addition of silicate layers impacts not only the conformation and morphology of polymer chains, but also the crystalline structure. As a typical example, polyamide 6/clay nanocomposites (PA6CN) which is perhaps the most successful system so far demonstrating dramatic improvement in properties, is a three phase nanoscale system, comprised of layered silicate, amorphous polymer regions and crystalline polymer regions [1]. The evidence has been found that the layers affect the formation of the lamellae, the crystallization rate, the crystalline form and so on [1-9]. Kojima et al reported that the presence of silicate layers induced the γ crystalline phase in PA6CN injected molded plates [6]. They noted that the degree of crystallinity in the nanocomposite was slightly lower than that in PA6, and it was independent of the amount of clay. Adopting high pressure DSC, they also observed a phase with higher melting temperature at 240ºC [7]. Mathias used solid-state ^{15}N NMR to observe that the addition of clay favored the formation of the γ crystalline phase in the same system [8]. While Akkapeddi reported an greatly increased degree of crystallinity, mostly γ phase, near the surface of the molded parts in their lab-made PA6CN [9].

An important feature of polyamide is that the structure undergoes a crystalline transition when subjected to heating. The crystalline transition in polyamide 66 was first investigated and is well known as Brill transition [10]. The Brill transition in polyamide 66 is clearly displayed in X-ray diffraction study, as two prime strong reflections at ~20º (200) and ~24º (002+202) merge into a single reflection at the transition temperature, indicating the room temperature triclinic structure transforms into a different triclinic structure. The crystal-to-crystal phase transition prior to melting in PA6 was also well observed and studied by some researchers using FT-IR, NMR and XRD. However, some different transition results were observed for a given crystalline phase by using different preparation methods or thermal routes. For example, Murthy et al observed a α→ α′ phase transition in the sample only containing α crystalline phase at room temperature by casting PA6-formic acid solution into thin film specimen [11,12]. Ramesh et al found that the α phase could transform into α′ phase or a pseudohexagonal phase depending on the cooling route [13]. While other authors also found that PA6 experienced a transition from the α phase into a pseudohexagonal unit cell between 80 and 170ºC [14,15].

In the present study, we focus on investigating the influence of silicate layers on the crystalline phase transition of PA6 prior to melting. A detailed study has been reported by vaia et al regarding the crystalline morphology of γ-dominant PA6CN in comparison with α-PA6 at elevated temperature [3]. Since the above-mentioned references have indicated the impact of different preparation method or thermal routes, in the present work, the α-dominant PA6 and PA6CN were prepared as starting materials by slow cooling bath without any other treatment, in order to compare their behavior in the same environment.

Experimental

In the present study, PA6CN was prepared by using a co-intercalation organophilic montmorillonite via the melt-compounding route. The detailed description of preparation, characterization, morphology and mechanical properties can be found elsewhere [16,17]. The nanocomposite containing 5wt% clay was used in the present work.

In order to eliminate the influence of specimen thickness on XRD data, ca. 100μm films of PA6 and PA6CN are prepared as follows: The powdered granules are put between two glass slides, then heated in oil-bath up to 250°C. After melting, they were kept at this temperature for 10 min, then a load is applied on the surfaces of the slides in order to press the molten materials into thin films. The films were cooled in oil-bath from 250°C to 20°C by natural convection with calculated cooling rate at 1-2°C/min.

In-situ XRD observations were performed using a Rigaku D/max 3C diffractormeter with curved graphite crystal filtered Cu Kα_1 radiation (λ= 0.15406nm). The observed film specimen was fixed on a rotating sample stage of the goniometer in order to eliminate the anisotropic effect, so a suitable average of the diffracted intensity in reciprocal space can be obtained. The system consists of a heating attachment to perform the annealing conditions. The sample was heated at the rate of 20°C/min, and when the sample temperature reached within 10°C of the required set temperature, the heating rate was automatically reduced to 2°C/min to minimize the overshooting effect. The temperature was maintained within 1°C of the set temperature thereafter. To avoid degradation, the sample was kept in nitrogen atmosphere during experiment. The diffractometer was operated at 40KV and 100mA. The XRD patterns were collected from 2θ=10-30° in a fixed time mode with a step interval of 0.02°.

Results and discussion

The structure and morphology of PA6 have been extensively studied. In the present study, as suggested by Ramesh [13], we designate all the structures that exhibit two distinct peaks having d-spacings at 0.37 and 0.44nm as α crystalline phase. The structures that present two peaks but having different d-spacings other than 0.37 and 0.44nm are designated as α′ phase. The stable structure having one sharp peak with a d-spacing at ca. 0.42nm is designated as γ phase. The structure that exhibits a d-spacing similar to the γ phase but transforms into other crystalline phases is designated as pseudohexagonal phase.

The slow cooling condition was used in this study to obtain the α phase dominant PA6 and PA6CN instead of chemical or other thermal-irrelevant methods. For better monitoring the conformational and phase variation during annealing, the α-only samples are the ideal starting materials. However, it is difficult to obtain the α-only sample in PA6CN by purely thermal method because of the γ phase favoring environment [18]. Therefore the α dominant PA6CN was prepared instead.

PA6 sample crystallizes into α crystalline phase as evidenced by XRD spectrum at 30°C in Fig 1(a). Fig 1 (a) presents the XRD patterns of the α phase in PA6 upon annealing at various temperatures. The two peaks in the spectrum at 30°C, one at 2θ=20.3° (α1) and another at 2θ=23.9° (α2), are the distinctive feature of the α crystalline phase of PA6. With increasing annealing temperature, the two peaks move towards each other, and the intensity of the α2 peak decreases more than that of the α1 peak. A substantial change in structure occurs at 150°C. A new diffraction peak at ca. 2θ=21° contributed by a pseudohexagonal phase of PA6 substitutes the α peaks. Only the pseudohexagonal phase is observed at and above 150°C in Fig 1(a), its intensity remains high and constant over the temperature range 150-190°C, and it disappears at 210°C in the molten polymer. The above results indicate that the α crystalline phase of PA6 transforms into a pseudohexagonal phase at 150°C upon annealing.

The changes in the d-spacing of the α crystalline phase in PA6 annealed at various temperatures are plotted in Fig 1 (b). The d-spacing due to the α1 peak at 20.3° is 0.44nm and the d-spacing due to the α2 peak at 23.9° is 0.37nm. With increasing annealing temperature, the d-spacing due to the α1 decreases while that of the α2 increases. The increase in the d-spacing of the α2 peak at higher temperature could be due to the thermal expansion of the lattice, while the decrease in the d-spacing of the α1 peak is caused by respective lattice distortion. Upon annealing over 150°C (the phase transition point), the d-spacing due to the pseudohexagonal peak decreases with temperature.

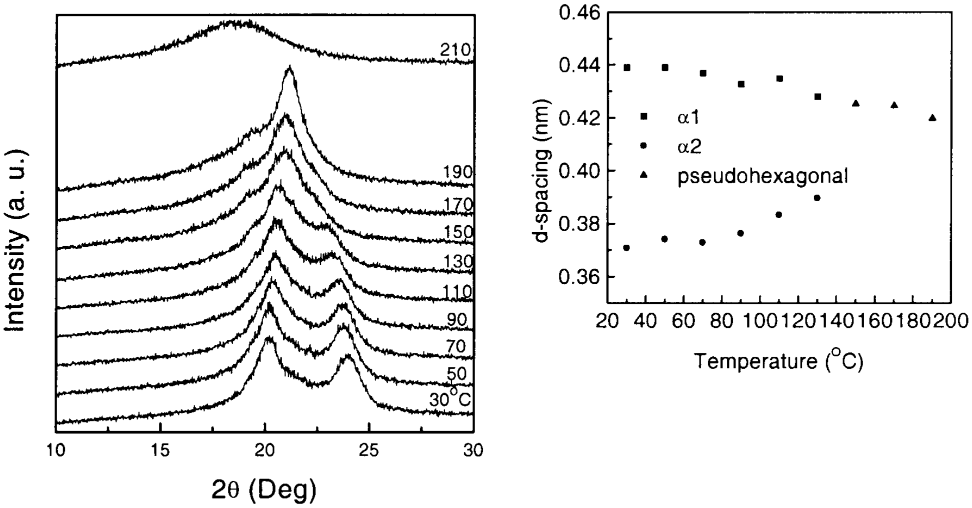

Figure 1. Behavior of (a) XRD patterns and (b) d-spacing of PA6 on annealing

The PA6 sample is annealed at 170°C, and the corresponding XRD patterns at various annealing period are presented in Fig 2. Before annealing (0 min), the sample is in the pseudohexagonal structure. However, the spectrum annealed for 1h shows a different character. The two distinct peaks, at 20.8° (strong) and 22.3° (weak), shows that the sample transforms into a new crystalline structure again, high temperature α′ phase. With increasing annealing time, the new appeared phase still maintains its existence. It is a stable crystalline structure at this temperature. Based on the two peaks character, it belongs to the α type structure [13].

The result indicates that the pseudohexagonal phase transformed from the stable α phase at room temperature upon annealing is not stable, it will transform into another stable crystalline structure above transition temperature given enough time.

Fig 3 (a) presents the XRD patterns of the slowly cooled PA6CN between room temperature and melting. Generally, PA6 would only crystalline into α phase at the slow cooling condition like that in Fig 1. However, PA6CN crystallized into a mixture of α- and γ-phase in this case, because silicate layers provide a γ-phase favoring environment in the nanocomposites and such behavior has been observed by many authors [3,6,9,17]. It is suggested that the proximity of silicate layer surface results in similar conformational changes that limits the formation of hydrogen bonded sheets [3]. As a consequence, the γ phase is induced and the α phase is distorted.

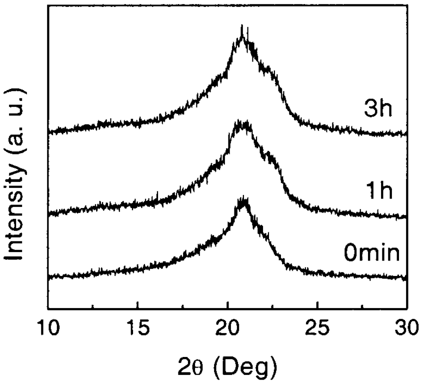

Figure 2. XRD patterns of PA6 annealed at 170°C up to 3h

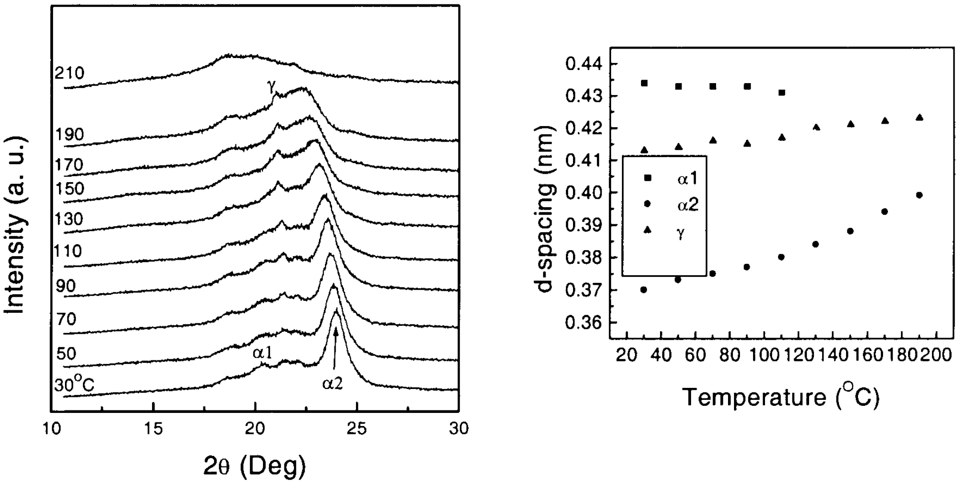

Figure 3. Behavior of (a) XRD patterns and (b) d-spacing of PA6CN on annealing

The addition of silicate layers significantly disturbs the formation of hydrogen bond in PA6CN, which has been confirmed by FT-IR in our previous investigation [17]. While the intensities of the two α peaks in Fig 3 (a) at 30°C is another evidence. In sharp contrast to PA6, in PA6CN, the α2 peak is dominant and the α1 peak is nearly disappeared. The α1 peak of PA6 in XRD pattern arises from the distance between hydrogen-bonded chains in sheets that is the reflection of hydrogen bonded sheets, and the α2 peak arises from the separation of the hydrogen bond sheets [12]. The obviously lower intensity of the α1 peak in the nanocomposites indicates that the addition of silicate layers disturbs the perfect arrangement of hydrogen bonded sheets of the α phase as Vaia suggested [3].

With increasing annealing temperature, the two peaks of the α phase move towards each other. During the annealing the α1 peak disappears completely above 120°C. The intensity of the α2 peak also decreases, but this peak always exists until melting though it shifts to lower angle. The intensity of the γ phase keeps growing in the whole process. For the α-dominant PA6CN sample, in contrast to PA6, no phase transition is observed. The room temperature α phase in PA6CN does not transform into any pseudohexagonal phase or high temperature α′ phase. Only continuous intensity change has been observed in PA6CN. Similar to PA6, as plotted in Fig 3 (b), the d-spacing due to α1 peak decreases while that of α2 peak increases with the annealing temperature in PA6CN. Upon annealing, the d-spacing due to the γ phase increases with temperature.

We have also investigated the behavior of PA6CN annealed at 170°C for 3h (data not shown). However, only intensity variations of diffraction peaks could be observed. Neither the α- nor the γ-phase presented phase transition. In PA6CN there appear a new reflection peak around 2θ=18° as presented in Fig 3 (a). The attribution of this peak is unknown yet and needs further investigation.

As suggested by Atkins [19,20], upon heating the α phase of PA6, the alkane segments within the polyamide chains become increasingly mobile. At a given temperature, the alkane segments have attained the same mobility in the inter-sheet direction as they posses within the sheets. This increased torsional flexibility of the alkane segments exerts a torsional force on the amide groups, a proportion of which then flip out to and thus the pseudohexagonal structure is formed. As an unstable phase formed in dynamically increasing temperature situation, with increasing annealing time, it cannot maintain its structure for long time. Then it transforms into a high temperature stable phase- α′ phase.

Based on the TEM observation [16], the mean distance between silicate layers is 35 - 45nm in our PA6CN and the average length and width of the layers is ca. 200nm. Therefore the molecular chains can be considered as being squeezed within 'nanoscale boxes' with a dimension of approx. 160nm×160nm×40nm. In such small spaces, the chain mobility of PA6 matrix is lowered. In consequence the phase transition cannot take place until melting, while the same transition is fulfilled at 150°C for neat PA6.

Besides, we also prepared the γ-dominant PA6 and PA6CN according to the method described in ref. [13] and [17]. The γ phase, either in PA6 or in PA6CN, does not present any crystalline phase transition during annealing. It does not respond to the temperature except for thermal expansion, which is in accordance with the results of Ramesh. Herein, the explanation suggested by Ramesh is cited as follows: The stability of the γ phase is caused by its crystalline structure. In this structure, the intersheet hydrogen bonds pin the polyamide chains onto the optimum packing lattice sites, and prevent the chains moving further apart until melting [13].

Conclusions

The influence of nanodispersed clay on the crystalline structure of polyamide 6 (PA6) was examined in-situ with XRD between room temperature and melting. The α phase in pure PA6 transformed into a pseudohexagonal phase at 150°C. Since the pseudohexagonal structure was unstable, with increasing annealing time above the phase transition point, it was substituted by a new stable crystalline structure - high temperature α′ phase. However, in the strongly confined spaces formed by silicate layers, the mobility of polymer chains has been constrained so that some different behaviors was observed in PA6CN. The α phase in PA6CN did not show crystalline phase transition on heating. The increase in the annealing temperature only leads to continuous intensity variation. The γ phase in PA6 or PA6CN was a stable crystalline phase that did not present any crystalline phase transition prior to melting.

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