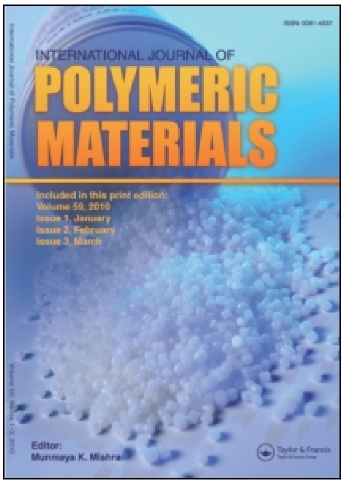

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Preparation and Characterization of Polyamide6/Montmorillonite Nanocomposites by Reactive Extrusion

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The polymerization of polymide6/montmorillonite (MMT) nanocomposites in a twin-screw reactive extruder is introduced in this article. Samples with different amount, of montmorillonite were measured and characterized by X-ray diffraction (XRD) and differential scanning calorimetry (DSC). The results indicate that the crystallization and thermal behaviour of PA6 are influenced by the addition of montmorillonite. A silicate-induced γ-form crystal formation was confirmed by XRD and DSC. The molecular weight and molecular weight distribution were measured by GPC and showed a tendency to increase and then decrease with increase, screw speed. Moreover, the obtained PA6/MMT was spun into fiber and fiber structure and properties were also analyzed and characterized.

Keywords: twin-screw extruder, nanocomposite, extrusion, polyamide-6, montmorillonite

INTRODUCTION

In recent years, polyamide-6/clay nanocomposites (PA6/CN) have been commercialized and used as engineering plastics in many applications. PA6/CN is a molecular composite in which the silicate monolayer is about 1 nm thick and 100 nm wide and uniformly dispersed in the polyamide-6 matrix [1–3]. PA6/CN can be processed in molten state by injection or extrusion molding [4–6]. The injection-molded

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and extruded articles have displayed better tensile strength, flexural strength, young's modulus [7], disortion temperature, and gas barrier properties than unfilled PA6.

Many studies on preparation of PA6/MMT are based on the method of melt-mixing PA6 with montmorillonite using a twin-screw extruder. However, during preparation of PA6/montmorillonite (MMT) by mechanical blending of polyamide-6 and montmorillonite it is difficult to obtain nano-scale and uniformly dispersed MMT particles and may cause a phase separation in a twin-screw extruder. Consequently, it is difficult to further improve PA6 properties.

Reactive twin-screw extrusion is a production technique used for monomer polymerization or polymer modification. The anionic polymerization of caprolactam in the presence of alkaline catalysts could produce high molecular weight polyamides in just a few minutes, by contrast to hydrolytic polymerization with reaction time of up to several hours [8–9]. With the progress of extrusion technology, people noticed and understood that the application of the extruder could be expanded and used in industry. However there are only a few studies on the synthesis of PA6/MMT by twin-screw reactive extrusion, especially the synthesis of fiber grade PA6/MMT chips.

In this article, a continuous polymerization by anionic mechanism and twin screw extruder as reactor were used to produce PA6/MMT and the resulted nanocomposites were melt spun into fibers. The objective of this study was to find out the optimized process conditions for fabricating fiber-grade chips by twin-screw reactive extrusion. Fiber structure and properties were also analyzed and characterized.

EXPERIMENTAL

Materials

The basic materials used in this study were required for the synthesis of PA6/MMT. These include industrial grade caprolactam purchased from BASF, Germany, self-made sodium caprolactam as catalyzer and N-acetyl caprolactam co-initiator as activator, purchased from Chemical Reagent Company of Shanghai. Montmorillonite (MMT) and its organic modifier cetyltrimethylammonium chloride (C-18) were supplied by Zhejiang Fenghong Clay Chemical Company.

Apparatus

The polymerization of PA6 was carried out in a intermeshing corotational twin-screw extruder (SJS-35 × 28) with 35 mm diameter screw, and the casting strip products were directly cut into chips by STJ cutter after quench bath.

Characterization of PA6/MMT

X-ray (WAXD)

Wide angle X-ray differaction measurements, were made using a Japan Rigaku D/MAX-R/b X-ray diffractometer (XRD) with voltage 40 kV, current 40 mA, and Cu K_α radiation with Ni filtration. The scan speed was 4°/min. Patterns were recorded by monitoring diffraction angle 2θ from 3.0° to 36°.

Differential Scanning Calorimetry (DSC)

The samples with a same weight of 15 mg were tested on a Perkin Elmer 7 Series DSC. The measurement was conducted with the temperature elevated quickly from 20°C to 250°C under nitrogen atmosphere. Each sample was kept for 10 min at 250°C to erase any thermal history, and then cooled to 20°C at a rate of 10°C/min. The samples were heated again to 250°C at a rate of 10°C/min.

Molecular Weight and Molecular Weight Distribution

The study of the molecular weight and molecular weight distribution was performed on a Waters 991 GPC, with m-cresol as solvent.

Mechanical Properties Test

Mechanical properties of the samples were measured on a Textechno Tensile Tester, Germany.

Sample Preparation

Modification of MMT

A mixture of MMT and water was heated to 80°C and stirred in a flask. Specific amount of organic modifier C-18 was then added into the mixture and allow the mixture to react at 80°C for 3 h. The mixture was kept overnight and then washed by deionized water three times to get rid of the halogen ions and was dried at 100°C in vacuum. A modified organic MMT was thus obtained.

Polymerization of PA6/MMT in the Extruder

A mixture of 30 kg ε-caprolactam and specific amount of sodium caprolactam was melted in a pretreatment vessel at 100°C with agitation and vacuum for about 2 h, to remove the water from the reaction system. A certain amount of MMT was then added into the system,

TABLE 1 Temperature Distribution of the Twin-Screw Extruder Barrel

Zone 1	Zone 2	Zone 3	Zone 4	Zone 5	Zone 6
170°C	190°C	190°C	195°C	210°C	210°C
Zone 7	Zone 8	Zone 9	Zone 10	Zone 11	Die
220°C	225°C	230°C	235°C	240°C	250°C

and the vessel was purged with nitrogen gas for another 2 h, and subsequently N-acetyl caprolactam was added into the system. The active mixture was then pumped into running twin-screw extruder. Temperature distribution of the twin-screw extruder barrel is shown in Table 1. Meanwhile, the polymerization progressed by initiation, chain propagation, and termination at different zones along the twin-screw. The removal of residual monomer was carried out at the end of the extruder. polymer was extruded through a die, cooled down in a running water bath, cut into chips by a pelleting machine and finally dried by hot air.

Fiber Spinning and Drawing

The dried polymide6 chips were fed into a spinning machine, and melt-spun with a take-up speed of 800 m/min. The spun fiber was relaxed at a conditioning temperature and moisture for about 3 h. After that the fiber was drawn with total draw-down ratio of 3.5.

RESULTS AND DISCUSSION

Extrusion

Anion ring-open polymerization was carried out in an intermeshing co-rotational twin-screw extruder to directly extrude the PA6/MMT. The twin-screw extruder as a reactor must satisfy the following requirements: The additives must be blended adequately with the caprolactam, the reaction zone of the screw must be long enough to meet the kinetic requirements, The screw form and temperature profile must be controlled correctly to adapt not only to the low-viscosity flow at the beginning of the reaction but also to the high-viscosity flow at the latter stage, effectively. Excessive shear, too high temperature and long residence time should be avoided to reduce the possible degradation to a minimum. The unreacted monomer and inactive catalyzer and activator should be eliminated as well. Because high molecular weight and conversion rate were required, the screw profile was decided according to the principle that the reactor must be coincident with the chemical reaction feature. The profile of the screw elements form were designed and are shown in Figure 1 and Table 2.

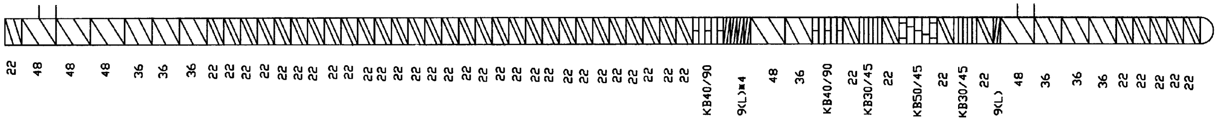

FIGURE 1 Screw configurations used in the study.

TABLE 2 Screw Form

Screw form	Screw length
22, 48 × 3, 36 × 3, 22 × 29, KB40/90°, 9 (L) × 4, 48, 36, KB40/90°, 22, KB30/45°, 22, KB50/45°, 22, KB30/45°, 22, 9 (L), 48, 36 × 2, 22 × 5	1557 mm

Note. In Table 1, 48 × 3 denoted the screw thread length was 48 mm and the number was 3. KB30/45° denoted the element length of the kneading disc was 30 mm and the stagger angle was 45°. 9(L) denoted the length of the reverse screw thread elements was 9 mm. Other figures had the same meaning.

Figures 2 and 3 show the effect of screw speed on molecular weight and molecular weight distribution for PA6/MMT and PA6, respectively, at the same extrusion conditions. Results were determined by GPC and expressed in trems of number average molecular weight (M_n). They clearly show that the effect of screw speed on the molecular weight and molecular weight distribution of PA6/MMT is almost the same as that for pure PA6. The molecular weight and its distribution were very small both at the lowest and highest screw speeds.

The increase of screw speed could reduce the residence time in the polymerization zone and accordingly had a positive effect on molecular weight and molecular weight distribution. Figures 2 and 3 show that the number molecular weight (M_n) was increased and then decreased with the increase of the screw speed, and the molecular weight distribution also varied with the speed. Some very long molecule chains

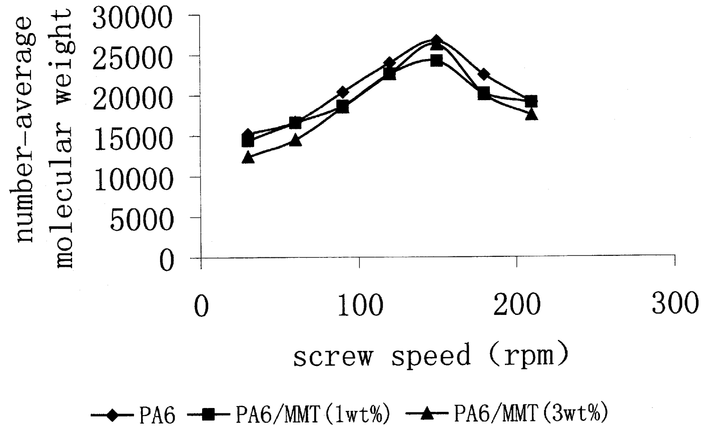

FIGURE 2 Effect of screw speed on number–average molecular weight.

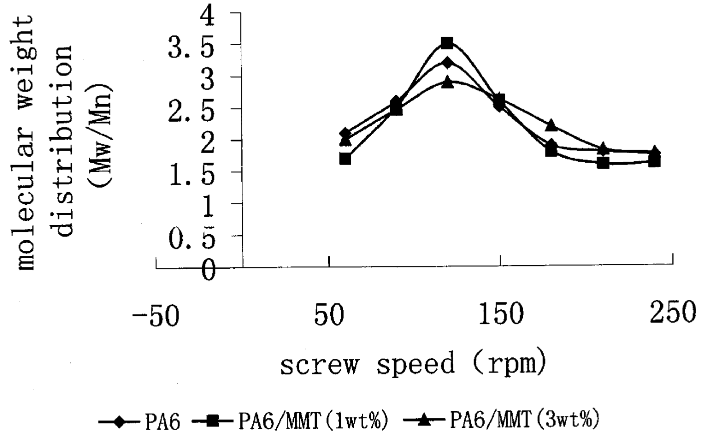

FIGURE 3 Effect of screw speed on molecular weight distribution.

were cut short due to the high shear force and as a result molecular weight distribution became narrower at the screw speed reached a high speed (150 rpm). The molecular weight was simultaneously decreased owing to thermal degradation caused by too high shear rate. Conversely, thermal degradation would also happen when the screw speed decreased to a too low level (60 rpm) because the increase of residence time would also cause molecular weight decreases. Lower shear rate would reduce the blending efficiency and consequently the molecular weight distributions became broader.

X-ray Diffraction

It is well known that PA6 is polymorphic and has several crystal forms [4]. The main one is α-form and the other is γ-form. Usually α form is more stable than its γ-form. To further investigate the structure of the PA6/MMT, X-ray diffraction measurements were made.

Figure 4 shows WAXD patterns of pure PA6 and the PA6/MMT fiber-grade chips with 1 wt% and 3 wt% MMT, respectively. Two main diffraction peaks can be observed for pure PA6 chip at $2\theta = 20.75^\circ$ and 24.7°, which are attributed to (100) and (002/202) diffractions [10–12]. It is clear that the α-form is the dominant crystalline phase for the extruded pure PA6 polymer. However, for nylon6/MMT fiber-grade chips with 1 wt% and 3 wt% MMT, two more diffraction peaks at $2\theta = 21.8^\circ$ and 21.85° were observed, as shown in curves b and c. These two peaks were attributed to γ (011) and γ (200) diffractions [13–14].

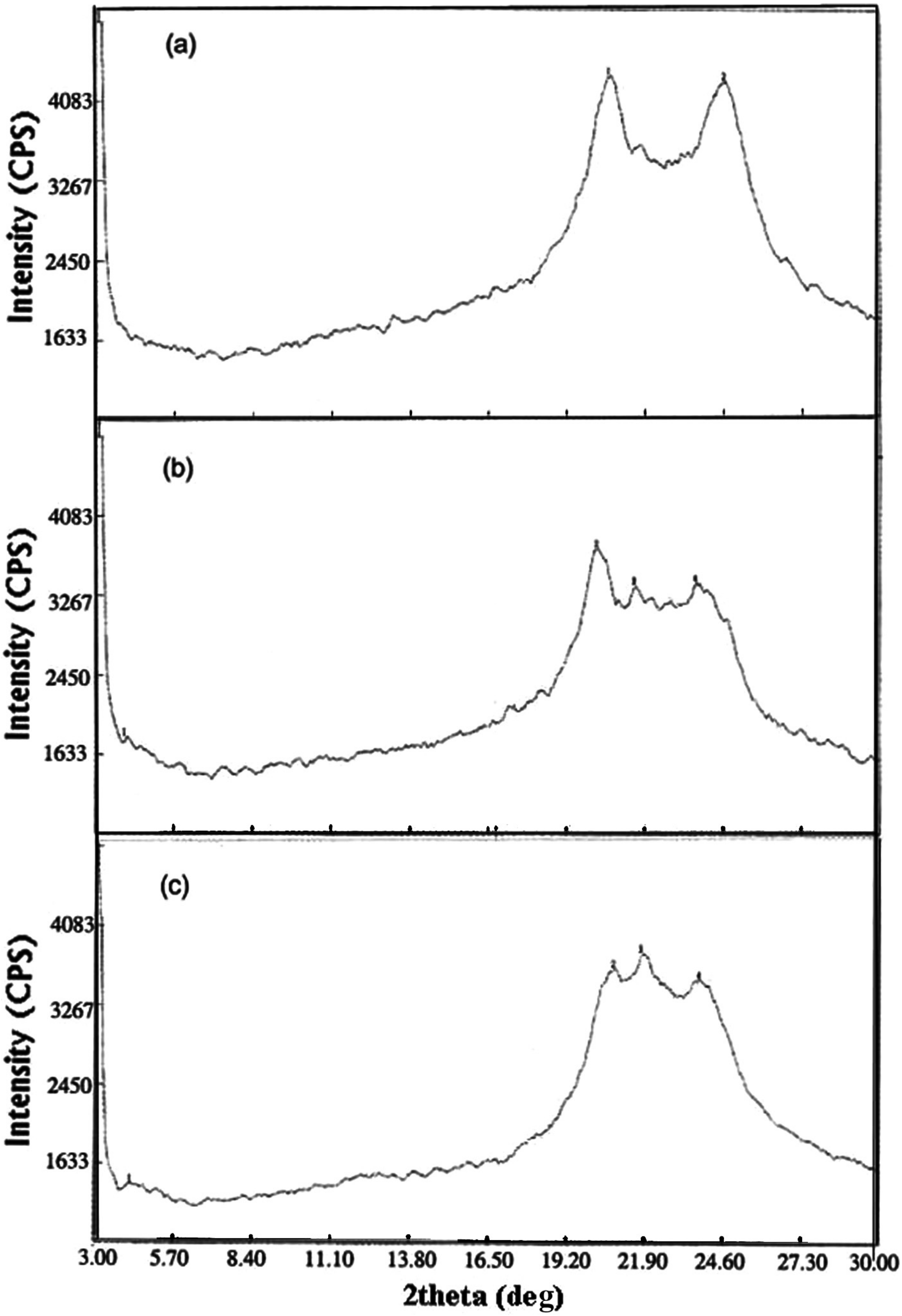

FIGURE 4 WAXD patterns of PA6 (a) and PA6/MMT, (b) 1 wt%, (c) 3 wt%.

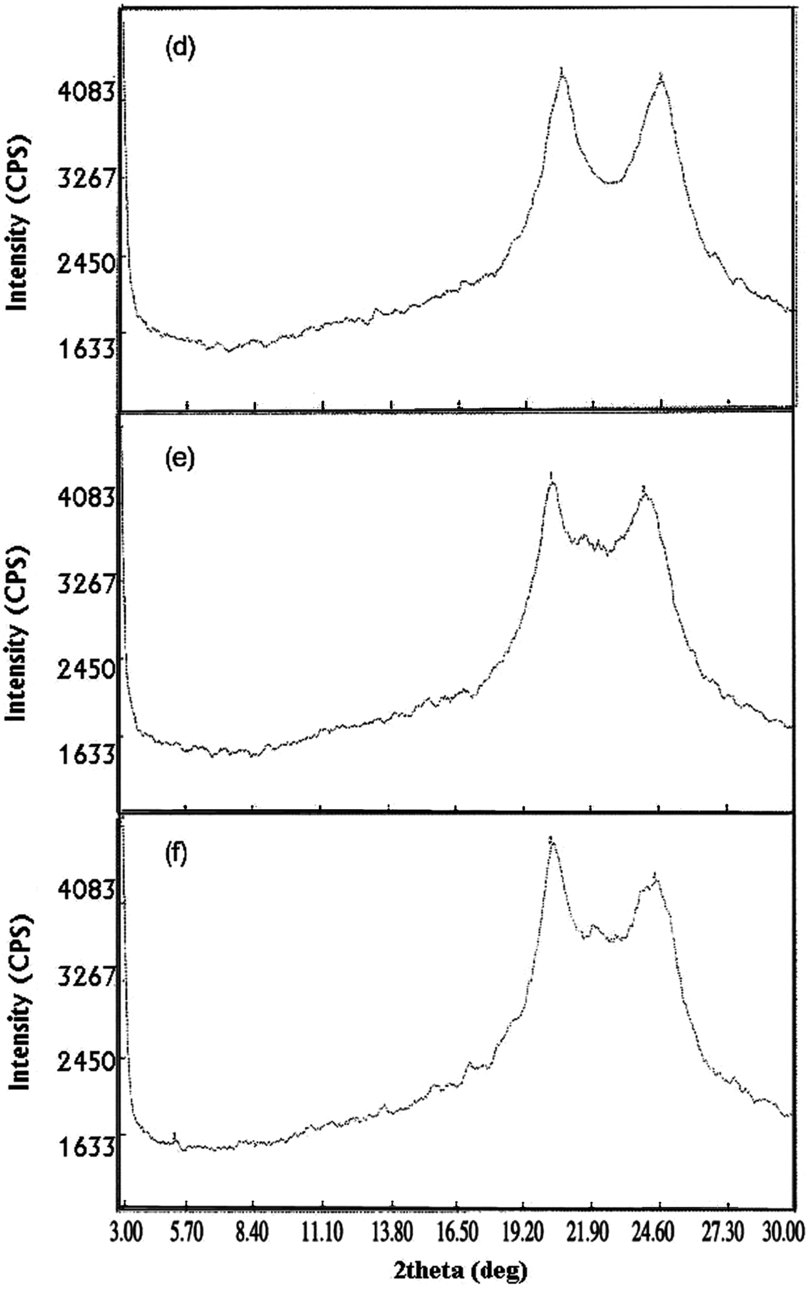

FIGURE 5 (d) PA6 drawn fiber; (e) PA6/MMT (1 wt%) drawn fiber; (f) PA6/MMT (3 wt%) drawn fiber.

It was therefore proposed that the addition of MMT silicates induces the formation of γ-form crystals according to a heterogeneous nucleation mechanism.

Figure 5 shows that WAXD patterns of pure PA6 drawn fiber, PA6/MMT (1 wt%) drawn fiber and PA6/MMT (3 wt%) drawn fiber. It can be seen that the neat PA6 drawn fiber shows two main diffraction peaks (α-form) at $2\ \theta = 20.8^\circ$ and 24.2°. Whereas the PA6/MMT (1 wt%) drawn fiber shows two main peaks (α-form) at $2\theta = 20.4^\circ$ and 24.1° and relatively weak γ-form peak at $2\theta = 21.85^\circ$ and PA6/MMT (3 wt%) drawn fiber has the same peaks at 20.3° and 24.45° and a trace of γ-form peak at 21.8°. The XRD results indicate that certain amount of polymorphic crystalline forms exists in PA6/MMT depending on thermal history and processing condition. Moreover, the crystal structure could be transformed from unstable γ-form to the more stable α-form.

DSC

Differential scanning calorimetry (DSC) measurement for PA6, PA6/MMT (1 wt%), and PA6/MMT (3 wt%) are shown in Figure 6. The DSC scan of PA6 exhibited a sharp melting endotherm at 220°C and also a weak shoulder at 210°C. The sample of PA6/MMT (1 wt%) had two melting endotherms at the same temperatures. However, the PA6/MMT (3 wt%) sample displayed four endotherms. When compared with PA6 and PA6/MMT (1 wt%), the most noticeable difference for PA6/MMT (3 wt%) is a higher endotherm peak around 230°C. It is obvious that the abnormal endotherm peak is attributed to the presence of montorillionite in the PA6 matrix. The silicates induced γ-form crystals by heterogeneous nucleation mechanism, which may result in a more stable morphology through the interreaction between clay and polymer crystal surface.

Mechanical Property Characterization

The mechanical properties of the fibers are given in Table 3.

Pure PA6 and PA6/MMT composite chips with different MMT contents were spun and drawn into fibers. Fiber mechanical properties were tested and the results are shown in Table 3. It shows that the addition of nano-MMT could improve fiber mechanical properties. Compared with pure PA6 fiber, the tensile strengths of fibers with 1 and 3 wt% MMT have increased by 8% and 7% whereas fiber Young's modulus was increased by 18.4% and 29.3%, respectively. However, too much MMT would destroy fiber properties. The enhancing effect

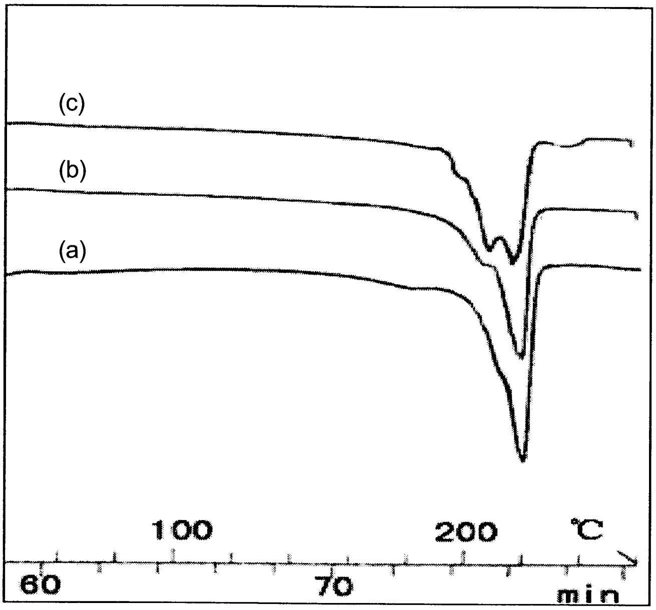

FIGURE 6 DSC scans of PA6 samples: (a) PA6, (b) PA6/MMT (1 wt%), (c) PA6/MMT (3 wt%).

of montorillionite on mechanical properties is probably due to the incorporation of clay with PA6 polymer chains. However, elongation at break decreased continuously with the increase of montorillionite content. Decreased elongation at break will be discussed in a separate article.

TABLE 3 Mechanical Properties of Different PA6 Fibers

MMT content (%)	Tensile strength (CN/dtex)	Elongation at break (%)	Modulus (CN/dtex)
1#*	5.24	22.2	39.57
0 wt%	5.52	23.7	42.32
1 wt%	5.66	26.9	46.84
2 wt%	5.72	24.5	49.42
3 wt%	5.61	22.1	51.16

*1# is the hydrolytic polymerized PA6 chips provided by Yuyang Petrochemical Complex.

CONCLUSIONS

By controlling polymerization parameters such as temperature and screw profile, fiber grade PA6/MMT nanocomposites could be continually prepared by twin-screw reactive extrusion in a quite short time, compared with that by classical hydrolytic ring polymerization method.

Relation between screw speed and molecular weight (Mn) and molecular weight distribution were discussed. The results show that molecular weight (Mn) and molecular weight distribution increased up to a screw speed of 150 (r/m) and 125 (r/m), respectively, and decreased beyond that.

The XRD results indicate that there were some polymorphic crystalline forms in PA6/MMT depending on thermal history and processing conditions. Moreover, the crystal structure can be changed from unstable γ-form to the more stable α-form.

Compared with PA6 and PA6/MMT (1 wt%) the most noticeable difference for PA6/MMT (3 wt%) was the higher endotherm peak around 230°C. It is therefore deduced that the silicates induced γ-form crystals by heterogeneous nucleation mechanism may result in a more stable morphology through the inter-reaction between clay and polymer crystal surface.

Fiber mechanical properties studies showed that addition of nano-MMT somewhat improves fiber mechanical properties. Compared with pure PA6 fiber, fiber Young's modulus with 1 and 3 (wt%) have increased by 18.4% and 29.3%, respectively.

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