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Disordering of Clay Layers in the Nylon 6 / Clay Nanocomposites Prepared by Anionic Polymerization

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Abstract: As a preliminary work for the preparation of nylon 6/clay nanocomposites by reactive extrusion, nylon 6/clay nanocomposites were prepared by anionic polymerization in a flask. In order to investigate the effect of the intercalation of clay layers, the clay feeding times, such as in pre-mixing where the clay was fed before initiation of polymerization and in after-mixing method where the clay was fed after initiation of polymerization, were changed. The appearance of the WAXD peak of nanocomposites prepared by the pre-mixing method was obvious and the tensile strength was decreased compared with that of pure nylon 6, which indicates that the clay layers were not dispersed and distributed. During the preparation of the nanocomposites by the after-mixing method, disordering of the clay layers was observed with increasing clay addition time and was suspected to result from the rapid polymerization of nylon 6 within the clay layers.

Keywords: anionic polymerization, nanocomposite, intercalation, disordering, nylon.

Introduction

In the last decade of the 20th century, polymer / clay nanocomposites emerged as a new class of materials. These nanocomposites have attracted much attention as they frequently show unexpected synergistic properties. An additional advantage of nanocomposites is that relatively small amounts of clay, typically 3~5 wt%, are required to improve the properties through nano scale dispersion. This advantage is believed to stem from the high aspect ratio and surface area of the exfoliated clay layers.^{1,2}

Polymer/clay nanocomposites have their origin in the pioneering research conducted at Toyota central research center where these organic and mineral materials have been successfully integrated. Their first practical application of a nylon 6/clay nanocomposite for use was a timing belt cover on automobiles, and the mechanical properties of nylon 6/clay nanocomposites were demonstrated.³⁻⁵ Yang *et al.* reported the mechanical properties of nylon 6/clay nanocomposites prepared by in situ polymerization. In this article, the mechanical properties of nanocomposites showed maximum values with a 5 wt% clay content.⁶ Kojima *et al.* suggested that during the preparation of nylon 6/clay nanocomposites by *in-situ* polymerization, the polymer matrix of

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the nanocomposite was not only a nylon 6 homopolymer, but also a copolymer of nylon 6 and nylon 12. They revealed that the nylon 6/clay nanocomposite, composed of a nylon 6 homopolymer, exhibited good mechanical properties as successive polymerization could be performed.⁷ Fornes *et al.* reported the effect of matrix molecular weight on the intercalation of the clay layers in nylon 6/clay nanocomposites prepared by melt processing. They suggested that the nanocomposite with a high matrix molecular weight showed an intercalated structure of the clay layers due to the high viscosity.⁸ Cho *et al.* reported the mechanical properties and morphology of nylon 6/clay nanocomposites prepared by melt processing. In this work, the nanocomposites prepared by melt processing showed an improved property compared with those prepared by *in-situ* polymerization.⁹

Until now, as mentioned above, nylon 6/clay nanocomposites have been prepared by various processing technique, such as *in-situ* polymerization and melt processing. *In-situ* polymerization is regarded as a very effective method, and the melt processing is usually carried out using existing processing equipment.¹⁰ However, these two techniques also have weaknesses with regard to the productivity of nanocomposite and the effectiveness in forming intercalated clay layers, respectively.

In order to compensate for these weak points, new methods, such as reactive extrusion (REX), may be useful. In this work, as preliminary works in nylon 6/clay nanocomposites preparation, the nylon 6/clay nanocomposites were prepared by anionic polymerization, and the disordering phenomena of clay layers was observed during the polymerization.

Experimental

Materials. The monomer used in this study was an industrial grade ϵ -caprolactam supplied by Capro Ltd. The ϵ -caprolactam is a very hygroscopic material, so it should be dried in a convection oven at 60°C for 7 days, in order to remove the absorbed moisture thoroughly before use.

The sodium-caprolactam used as a catalyst was prepared by adding sodium hydride (supplied by Aldrich) into molten caprolactam at 100°C. They were agitated until completely dissolved. Since the anionic polymerization of caprolactam is very sensitive to moisture, the preparation of sodium caprolactam should be carried out without contact of moisture, and the prepared sodium caprolactam should be kept inside the dry box. The *N*-acetylcaprolactam, used as a monofunctional chain initiator, was supplied by Sigma-Aldrich. Because this initiator exists in a liquid state at room temperature, it was added after the caprolactam and catalyst had fully melted.

The clay (sodium montmorillonite : Na⁺-MMT) was supplied by Southern Clay Products. The clay was a fine powder with a cation exchange capacity (CEC) of 92 mequiv./100 g, and was so hygroscopic that it was dried in a vacuum oven

at 90°C for 1 day before use.

Preparation. In this study, the anionic polymerization of nylon 6/clay nanocomposites was carried out in a three-neck flask, with nitrogen gas purging, to protect from contact with moisture. The reaction mechanism of nylon 6 was described in Figure 1.

During the polymerization, mechanical agitation was used to mix the monomer, catalyst, initiator and clay. As shown in Figure 2, the initiator was added to the molten mixture after the monomer and catalyst had fully melted at 100°C, and then the polymerization proceeded at 240°C. The clay was added to the flask after the polymerization had started at 240°C. In order to investigate the effect of the intercalation of the clay layers, the clay feeding time was changed as the following two methods.

(1) Pre-mixing method: The monomer and catalyst were

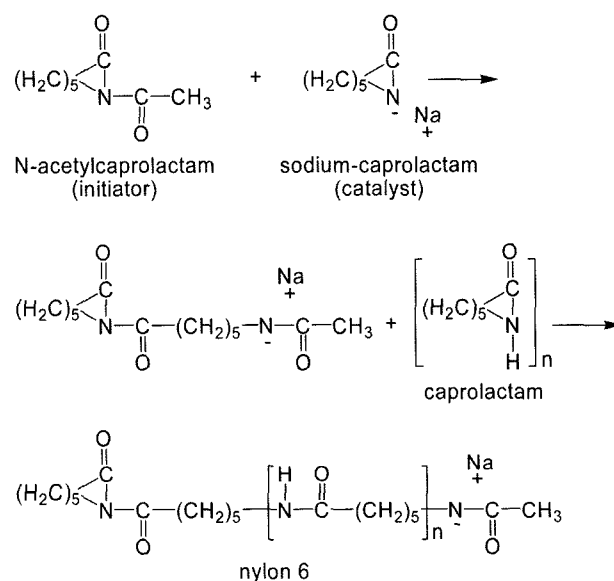


Figure 1. Reaction mechanism for the anionic polymerization of nylon 6.

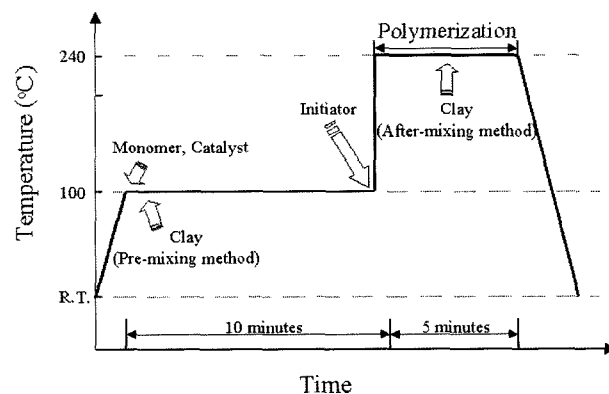


Figure 2. A schematic diagram for the preparation of nanocomposites by the pre-mixing and after-mixing methods.

melted in a flask at 100 °C, and then the initiator and clay were added to the molten mixture. When the temperature was increased to 240 °C, the polymerization was started in a flask.

(2) After-mixing method: After the monomer and catalyst were melted in a flask at 100 °C, the initiator only added to the molten mixture. The clay was added to the flask after the polymerization in the flask had started at 240 °C. In this study, the nanocomposites were prepared by varying the clay addition time every 20 sec.

Characterization. The dispersion of the clay layers in the nanocomposites was investigated using a wide angle X-ray diffractometer (WAXD: Model MXP-18, Mac Science). Measurements were performed using $\text{CuK}\alpha$ as an X-ray source, with the generator operated at 40 kV and 100 mA. WAXD scans were obtained in the reflection mode, using an incident X-ray wavelength of 1.54 Å, at a scan rate of 1.0 deg/min. The d -spacing was calculated by Bragg's law, $d = n\lambda/2\sin\theta$, from the position of the (001) plane peak in the WAXD pattern.

The molecular weight of nylon 6 was obtained from the intrinsic viscosity measurement at 25 °C by using formic acid. During the polymerization, the samples were collected from the flask every 20 sec and quenched in liquid nitrogen to prevent the further polymerization. The residual caprolactam in the sample was removed by washing the sample with the deionized water. The samples were dissolved in formic acid, and the clay was separated by using rotary centrifuge. The clay removed from the sample, and the pure nylon 6 was obtained by evaporating the formic acid.

The tensile strength was measured by using an Instron 4467 universal test machine at room temperature. The cross-head speed was 5 mm/min according to the ASTM D638.

Results and Discussion

Preparation of Nylon 6/Clay Nanocomposites by Pre-mixing Method. The anionic polymerization of the caprolactam was completed within a few minutes, so it was possible to prepare the nylon 6 by a continuous process, such as reactive extrusion (REX).¹¹⁻¹³ In the anionic polymerization of caprolactam, the nylon 6 was polymerized by a ring-opening mechanism of the caprolactam.^{14,15} In the pre-mixing method, the clay was mixed with a catalyst before the initiation of the polymerization. The preparation of nylon 6/clay nanocomposites using the pre-mixing method was carried out with a clay content of up to 5 wt%. The polymerization was not possible above 5 wt% of clay. Since it was very difficult to dry the clay completely even though the clay was dried in a vacuum oven at 90 °C for 1 day, the remaining moisture may attack the reaction site and the polymerization was not proceeding. Generally most of all nanocomposites contain some wt% of water in clay layers.¹⁶

The WAXD patterns for the nylon 6/clay nanocomposites

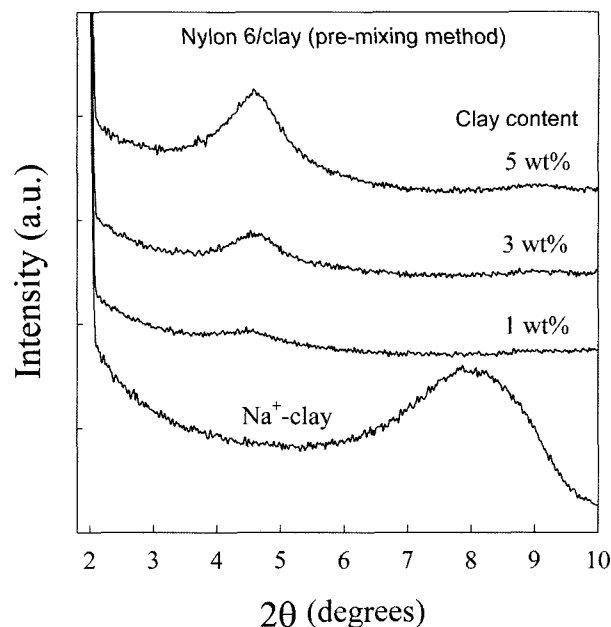


Figure 3. WAXD patterns of the Na^+ -clay and nylon 6/clay nanocomposites prepared by the pre-mixing method by varying the clay content.

prepared by pre-mixing method are shown in Figure 3. From Figure 3, the nanocomposites for all of the clay contents (1, 3, and 5 wt%) show a characteristic basal reflection, corresponding to the intercalation of the clay layers.

When the clay was added to the melted monomer, the clay layers were intercalated by the melted caprolactam monomer. In order to investigate the intercalation phenomena of clay by the melted caprolactam, the samples were collected every 20 sec from the flask. The WAXD patterns of caprolactam/clay mixtures were obtained and shown in Figure 4. The peak position and height was unchanged regardless of the mixing time. This means that the clay layers were quickly intercalated by the melted caprolactam, so it is considered that the caprolactam molecules are easily diffused in and out the gallery of the clay layers. The d -spacing of clay layers in caprolactam/clay mixtures was 18.4 Å, and the d -spacing of the nylon 6/clay nanocomposites prepared by the pre-mixing method was 19.6 Å as shown in Figure 3. We could see that the d -spacing was slightly increased after polymerization.

Figure 5 shows the tensile strength of nylon 6/clay nanocomposites prepared by pre-mixing method. The tensile strength of the nanocomposites showed lower values than that of pure nylon 6. This means that the pre-mixing method did not affect the dispersion of clay and also showed the poor distribution of clay.

Preparation of Nylon 6/Clay Nanocomposites by after-Mixing Method. It has been reported that moisture prohibits the anionic polymerization of caprolactam by eliminating the active primary amine.^{14,17} And, the catalyst also reacts to

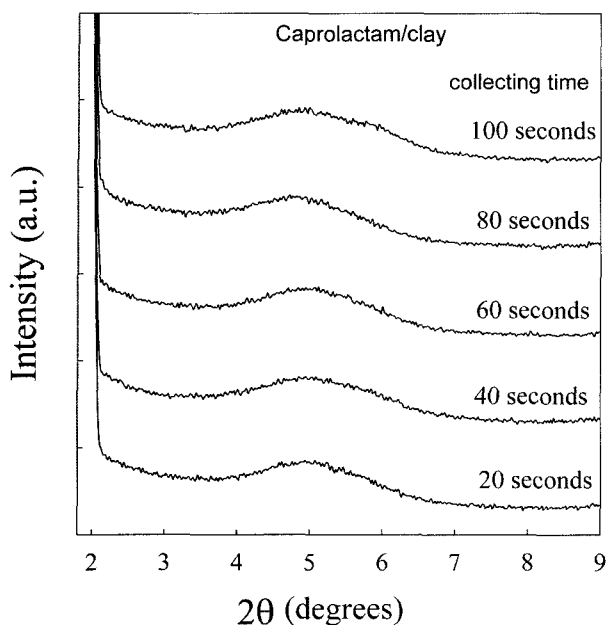


Figure 4. WAXD patterns of 3 wt% clay in caprolactam nanocomposites with different collecting times.

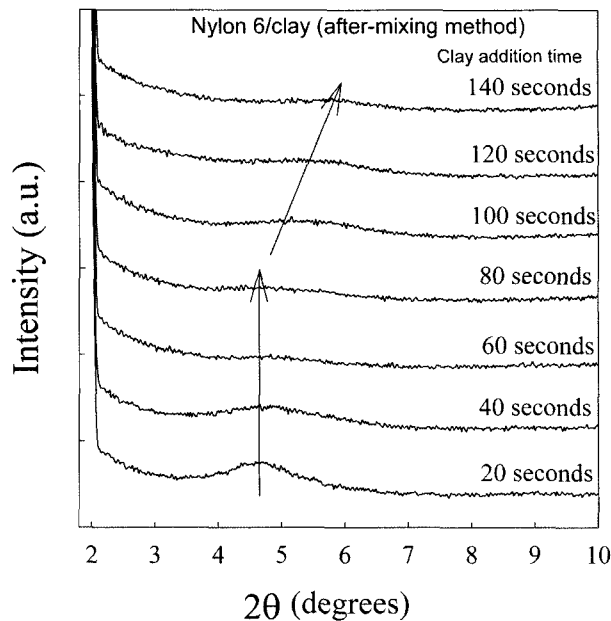


Figure 6. WAXD patterns of the nylon 6/clay nanocomposites prepared by the after-mixing method for the different clay addition time.

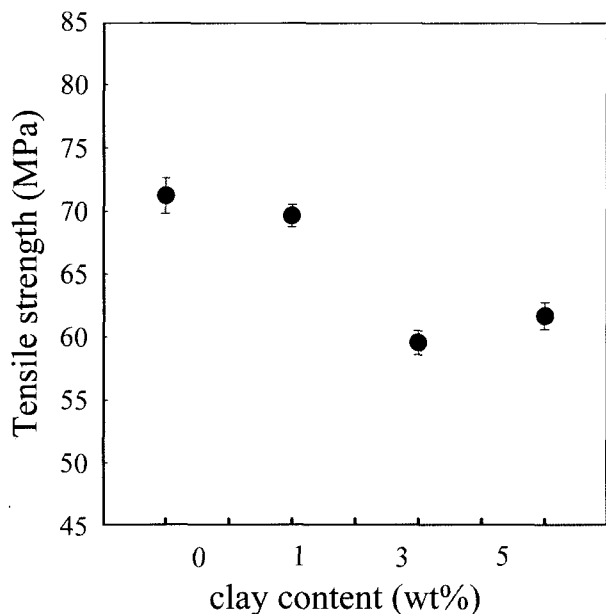


Figure 5. Tensile strength of nylon 6/clay nanocomposites prepared by the pre-mixing method.

moisture prior to the initiator. Therefore, the anionic polymerization of caprolactam should be carried out after drying of the raw materials, such as the caprolactam, catalyst and clay.¹¹ The clay is a very hygroscopic material, so it is very difficult to dry completely. The nylon 6/clay nanocomposites prepared by after-mixing method were successfully polymerized with clay content up to 5 wt%. The nylon 6/

clay nanocomposites were investigated for various clay adding time and clay content.

The WAXD patterns for the nylon 6/clay nanocomposites prepared by the after-mixing method were investigated and shown in Figure 6 for the different clay addition time. In this experiment, the clay was added at different time. The clay addition time means elapsed time from the initiation of polymerization. Because the polymerization was initiated on addition of the initiator, the clay addition time was counted from the addition of the initiator to the flask.

From Figure 6, the 2θ values of WAXD peaks were similar to the caprolactam/clay mixture for clay addition time up to 80 sec. That means the d -spacing of the clay layers in the nanocomposites were not increased. But, the intensity of the WAXD peaks gradually decreased with increase of the clay addition time, until 80 sec. This suggested that the *in-situ* polymerization could not increase the d -spacing of clay layers but break the layered structure of clay layers into a disordered structure.

When the clay addition time was about 80 sec, the intensity of the WAXD pattern became very low, but the 2θ value of WAXD peak did not changed. Its intensity was too low so it could be regarded as a disordered structure for the clay layers. In the WAXD measurement of the clay nanocomposites, it has been reported that the peak intensity represents the degree of disordering of the clay layers.^{2,18,19} Therefore, in the preparation of the nanocomposites by anionic polymerization, the after-mixing method was more effective than the pre-mixing method.

As the clay addition time was increased above 80 sec the

WAXD peaks of the nanocomposites shifted to higher 2θ values, corresponding to the decrease of a d -spacing. As the clay addition time was increased in this experiment, the size of the nylon 6 molecules increased, so it became very difficult for the large molecules to enter the gallery of the clay. Therefore, the d -spacing of the clay layers decreased with increase of clay addition time.

When the clay was added into the flask, some of nylon 6 oligomers were deactivated by the remaining water inside the clay. So the chain lengths of deactivated nylon 6 oligomers were increased with the clay addition time, and these deactivated oligomers would strongly affect the molecular weight of the nanocomposites. Table I shows the molecular weight of the nanocomposites prepared with the clay addition time. From the Table I, the molecular weight of the nanocomposites was decreased as the clay addition time was increased to 80 sec. It suggested that the decrease of molecular weight of nanocomposite was induced from the increase of molecular chain length of deactivated nylon 6 oligomers.

Figure 7 shows the WAXD patterns of the nylon 6/clay nanocomposites prepared by after-mixing method, by varying the clay content (1, 3, and 5 wt%). In the preparation of these nanocomposites, the clay was added to the flask after 80 sec were passed from initiation of polymerization. From Figure 7, no characteristic basal reflection was shown in the nanocomposite with clay content of 1 wt%, but as the clay content was increased from 3 to 5 wt%, the characteristic basal reflection appeared. The 2θ value of clay layers in these nanocomposites was similar to that of the nanocomposites prepared by the pre-mixing method, but the intensity of WAXD peak was much smaller.

Figure 8 shows the tensile strength of nylon 6/clay nanocomposites prepared by after-mixing method. The tensile strength of the nanocomposites showed higher values than that of pure nylon 6. The tensile strength of nanocomposites largely increased up to the clay content of 3 wt%. Therefore we can consider that the layered structure of clay layers was partially disordered and uniformly distributed during poly-

Table I. Molecular Weight of the Nanocomposites Prepared with Varying the Clay Addition Time

Clay Addition Time (sec)	"Molecular Weight (M_n)
20	3.05×10^4
40	2.88×10^4
60	2.82×10^4
80	2.74×10^4
100	2.99×10^4
120	3.09×10^4
140	3.20×10^4

^aFrom intrinsic viscosity measurement using $[\eta] = 0.023 \times [M_n]^{0.82}$

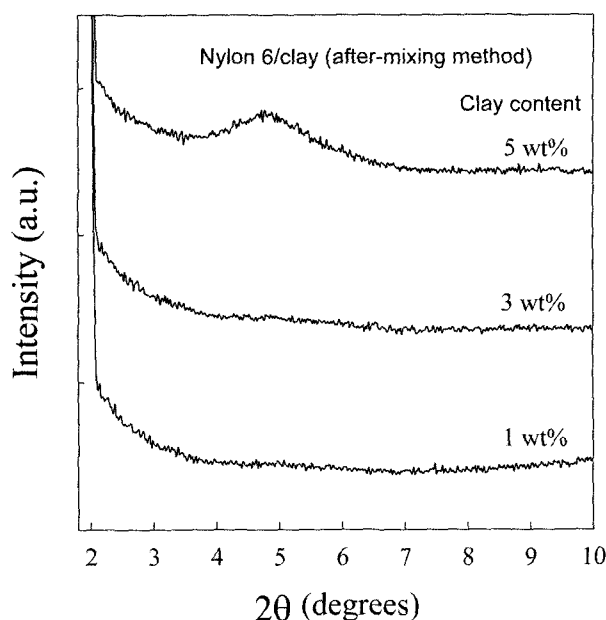


Figure 7. WAXD patterns of the nylon 6/clay nanocomposites prepared by the after-mixing method for the different clay content.

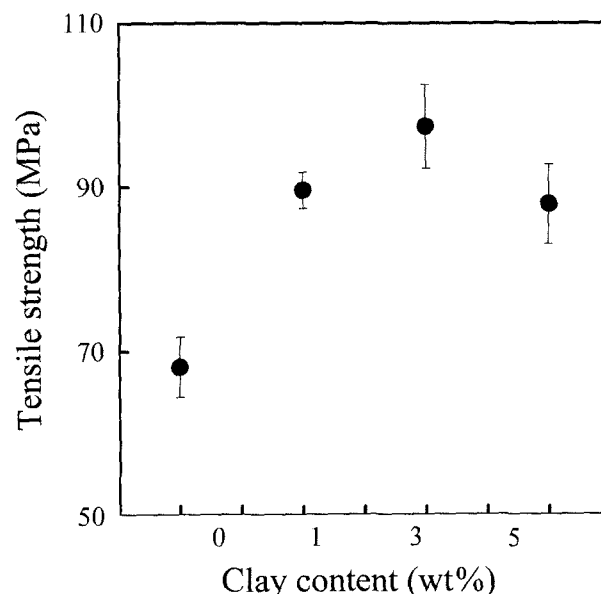


Figure 8. Tensile strength of nylon 6/clay nanocomposites prepared by the after-mixing method.

merization of the nylon 6/clay nanocomposites by using the after-mixing method. This phenomenon was also investigated from the TEM experiments. Figure 9 shows the TEM photos for the nylon 6/clay nanocomposites manufactured by using the pre-mixing method and the after-mixing method. Comparing with Figures 3 and 7, the peak height becomes slightly lower and the peak width becomes more broaden in

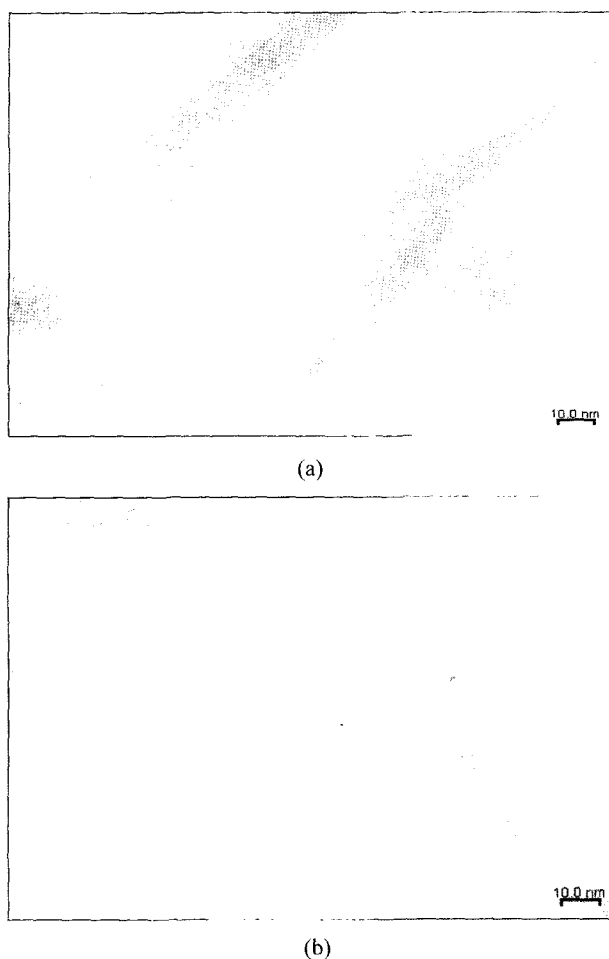


Figure 9. TEM photos for nylon 6/clay nanocomposites. (a) pre-mixing method and (b) after-mixing method (clay content; 5 wt%).

nanocomposite prepared by after-mixing method. So ordering structure of clay seems to be partly broken during polymerization of nylon 6.

Conclusions

The new and significant result of this paper is that tensile strength of clay/nylon nanocomposites showed the very reverse results depending on the processing conditions as you can see in Figures 5 and 8. The tensile strength of nylon 6/clay nanocomposites was increased when the clay was fed by using the after-mixing method. So we performed an experiment by changing the feeding time of clay during polymerization of nylon 6. And we obtained the very interesting X-ray result (Figure 6) which showed that the *d*-spacing and peak height have changed according to the feeding time of clay.

But the x-ray result of nanocomposites made by pre-mixing condition and after-mixing condition showed small change in peak height and width. Also the TEM photos showed small difference, where the nanocomposite made by pre-mixing method showed a little more agglomeration of clays comparing to that made by after-mixing method.

During the preparation of the nanocomposites by the after-mixing method, the disordering behavior of clay layers was affected by the clay feeding time. The after-mixing method showed better dispersion of the clay layers than pre-mixing method. The tensile strength was increased when the after-mixing method was used. Therefore it was concluded that the feeding time of clay became very important in the fast reaction of the nylon 6/clay nanocomposite by anionic polymerization.

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