

# Preparation of Nylon 6 / Clay Nanocomposites by Reactive Extrusion

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## Abstract

As the preliminary works for the preparation of exfoliated nanocomposites by reactive extrusion (REX), the modified anionic polymerization proceeded in a flask using an  $\epsilon$ -caprolactam, catalyst, initiator, and clay. Polymerization methods were classified with a variation of the clay adding time. Intercalation mechanism of clay layers was investigated by measuring the WAXD peaks of clay with polymerization. In the preparation of nanocomposites, the molecular weight of nylon 6 was affected by the clay content. From the mechanical property measurement, improved properties were obtained in comparison to the neat nylon 6, and these properties were also affected by the molecular weight.

## 1. Introduction

Nanocomposites have recently emerged as a very efficient strategy to upgrade properties of common polymer to the point where the properties exceed the ones of conventional composites. The advantage of nanocomposite

is that relatively small amount (1 ~ 5 wt%) of filler is required to reach the properties which is comparable to the conventional composite. The improved properties of nanocomposite depend on many factors including aspect ratio of the filler, its orientation and dispersion in polymer matrix, and adhesion at the interface between polymer and inorganic filler.

The polymerization methods of nylon6 are generally divided into two methods hydrolytic polymerization and anionic polymerization. In a hydrolytic polymerization, a mixture of caprolactam,

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water, and initiator is fed into a reactor. The mixture is maintained at about 250 °C for 12 hours and a pressure of 15 atmospheres is applied to the reactor. This method has been used as a conventional process to produce a commercial nylon6. In an anionic polymerization, a mixture of caprolactam, catalyst, and initiator is fed into a reactor. The polymerization is rapidly executed by the use of anionic initiator. The reaction temperature is initially about 150 °C, but during polymerization it rises to above 220 °C. The anionic polymerization is so fast (below 10 min) that it can be applied to a continuous process such as reactive extrusion (REX) and reaction injection molding (RIM).

Until now, any research team has not made an attempted to produce the nylon 6 / clay nanocomposites by the method of anionic polymerization. In this study, nylon 6 / clay nanocomposites, prepared by anionic polymerization, have been investigated. We focus on the mechanism of clay intercalation during anionic polymerization by measuring the d-spacing of clay layers and the rheological property. And, according to the mechanical test, the reinforcing effect of clay on nanocomposites will be investigated.

## 2. Experiment

The anionic polymerization of caprolactam is very sensitive to moisture, since the moisture prohibits anionic polymerization by eliminating the active primary amine anion which is induced from the catalyst. In this study, all materials, including monomer, catalyst, and clay were dried to remove the moisture before use. Monomer used in this study is an industrial grade  $\epsilon$ -caprolactam

supplied by Capro Ltd. Sodium-caprolactam used as a catalyst was prepared by adding sodium hydride, supplied by Aldrich, into the molten caprolactam at 100 °C, and agitated until it was completely dissolved. The mixture was poured into a stainless tray, and cooled down to obtain solid state of sodium. N-acetylcaprolactam used as a mono-functional chain initiator was supplied by Sigma-Aldrich company. The sodium montmorillonite (Na<sup>+</sup>-MMT), used in this study was supplied by Southern Clay Products company.

During polymerization, mechanical agitating stirrer was used to mix the monomer, catalyst, initiator, and clay. Monomer and catalyst were melted in a flask at 100 °C and then initiator was added into the molten mixture. The clay was added into a polymerization after the polymerization had been started in a flask at 240 °C.

## 3. Results and Discussions

Clay addition time was subdivided from the initiation to the termination of polymerization at the intervals of 20 sec. Because polymerization was initiated when the initiator was added, the clay addition time was counted from the addition of the initiator. WAXD peak of the nanocomposites exhibited almost same  $2q$  quantities while the clay addition time was increased until 80 seconds, but these peak intensities were decreased as the clay addition time was increased. It might be considered that the molecular chains of nylon 6 diffused into the clay layers, and then the chain entanglement proceeded with a further polymerization. Since, the chain entanglement proceeded

between clay layers, the layered structure of clay layers might be broken into the disordered structure. As the clay addition time was increased above 100 seconds, the WAXD patterns of nanocomposite showed a reflection peak shifted to the higher  $2\theta$  quantities, which is corresponding to the decrease of a d-spacing. Since the clay was added when the molecular weight and the viscosity of nylon6 were fully increased, the molecular chains of nylon 6 could not diffuse into the clay layers. So they could not break the ordered structure of clay layers with further polymerization.

To investigate the effect of clay content on the intercalation of clay, the preparation of nylon 6 / clay nanocomposites which clay addition time was 80 seconds was executed with varying the clay contents. From the WAXD patterns, a characteristic basal reflection was not shown in the nanocomposite which clay content was 1 wt%, but as the clay content was increased from 3 wt% to 5 wt%, a characteristic basal reflection was appeared and its peak intensity was also increased. Since the polymerization was already initiated before addition of the clay, the catalyst was reacted with the initiator prior to the diffusion into the clay layers. During the polymerization, it could be considered that the inserted oligomers, were not deactivated, played an important role in changing layered structure of clay layers into disordered structure with inducing the chain entanglement by increasing the molecular weight. But, as the clay content was increased above 3wt%, the disordered clay structure in nanocomposite might be decreased because of the restriction of chain growth by the moisture and steric

hindrance of clay layers.

When the clay was added into the polymerization, since the polymerization was initiated before the addition of clay into polymerization, the nylon 6 oligomers were diffused into the clay layers. And then the diffused oligomers might be deactivated with the contact of moisture in clay layers or further polymerized between the clay layers. The molecular chain growth between the clay layers might be restricted by insufficient supply of the caprolactam into the clay layers, because of the steric hindrance of clay layers and the presence of deactivated oligomer between the clay layers. As a consequence, it could be considered that the molecular weight of nanocomposites exhibited lower quantity than that of neat nylon 6, and it was decreased as the clay content was increased.

The mechanical properties of the nylon 6 / clay nanocomposites were increased when the clay content was less than 3 wt%, and then decreased when the clay content was 5 wt%. In spite of the increase of clay content in nanocomposites, the mechanical properties were decreased because of the decrease of molecular weight.

#### 4. Conclusions

In preparation of nylon 6 / clay nanocomposites by anionic polymerization, the moisture content in clay layers strongly affected the anionic polymerization of nylon 6.

The intercalation behavior of clay layers was strongly affected by the clay addition time. Since the molecular chain length of

nylon 6 was closely related to the clay addition time, the optimum clay addition time which induced the well intercalated nylon 6 / clay nanocomposites was existed.

The layered structure of clay layers in nanocomposites was disordered with the entanglement of nylon 6 occurred between clay layers. The more clay content was added, the more disordered clay structure was investigated.

Owing to the decrease of molecular weight in nanocomposite which the clay content was 5 wt%, the mechanical properties exhibited lower quantities than those of neat nylon 6.

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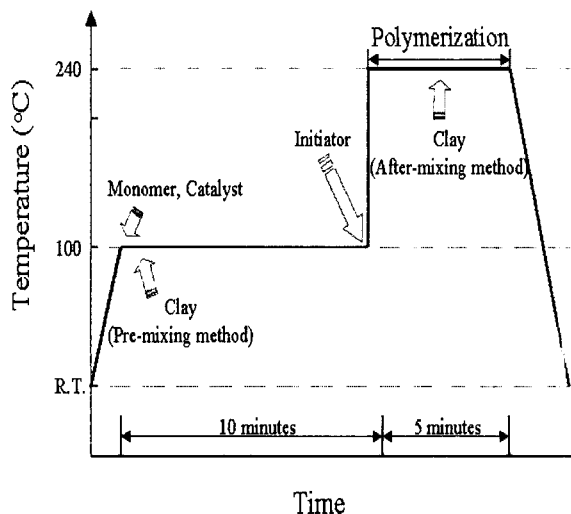


Figure A schematic diagram for the nano- composites preparation by the pre-mixing and after-mixing methods.

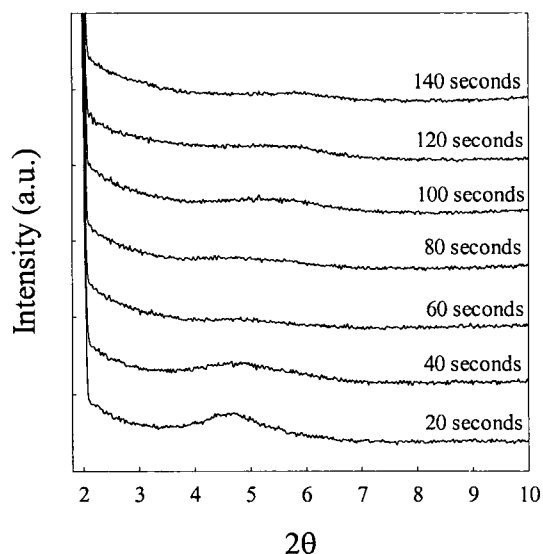


Figure WAXD patterns of the nylon 6 / clay nanocomposites prepared by the after-mixing method by varying the clay addition time.

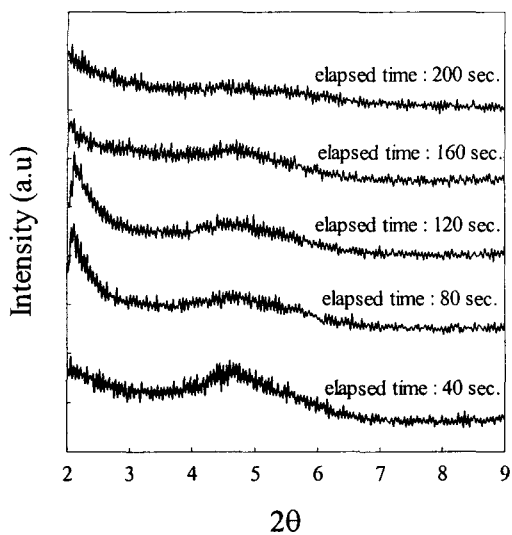


Figure WAXD patterns of the nylon 6 / clay nanocomposites prepared by the after-mixing method during anionic polymerization.