

PREPARATION AND CHARACTERIZATION OF POLYAMIDE 11/CLAY NANOCOMPOSITES*

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Abstract Polyamide 11 (PA 11) is a widely used polyamide resin, but its application is limited since the impact properties, tensile strength, and thermal properties are not very satisfactory for industrial application. In order to improve the mechanical properties of PA 11, in this paper, the preparation of polyamide 11/clay nanocomposites (PACN) via *in-situ* intercalated polymerization was reported. SEM, TEM and XRD were employed to investigate the dispersion of clay sheet in the matrix. The results indicate that clay layers were homogeneously dispersed in PA11 matrix on a nano-scale, and an exfoliated and intercalated structure co-existed in the composites. The mechanical and thermal properties of the obtained nanocomposites were improved to certain extent by the addition of clay.

Keywords Polyamide 11, Nanocomposites, *In-situ* intercalated polymerization, Dispersion

INTRODUCTION

In recent years, polymer/clay nanocomposites have attracted great interest from researchers since they frequently exhibit unexpected hybrid properties synergistically derived from the two components. Compared to their micro counterparts and the pristine polymer matrix, polymer/clay nanocomposites exhibit improved tensile strength and modulus, decreased thermal expansion coefficient, decreased gas permeability, increased swelling resistance, enhanced ion conductivity, and reduced flammability.

Many approaches have been employed to prepare polymer/clay nanocomposites. As is well known, polymer chains can be intercalated into the layered silicates of clay either by the insertion of an appropriate monomer and subsequent polymerization or by the direct insertion of polymer chains from the solution or melt. *In-situ* intercalation polymerization was first successfully used in manufacturing nylon 6/montmorillonite nanocomposites, which show greatly improved thermal, mechanical, barrier, and even flame-retardant properties compared with their conventional inorganic particle-filled counterparts^[1–3]. This approach has since been extended to other thermoplastics such as polyimide^[4–6], PMMA^[7], PCL^[8], PS^[9–11], and polysiloxane^[12], etc.

When the silicate layers are dispersed in the polymer matrix, two types of nanocomposite structures can be obtained. Intercalated nanocomposites are formed when there is limited inclusion of polymer chain between the clay layers with a corresponding small increase in the interlayer spacing of a few nanometers. On the other hand, exfoliated structures are formed when the clay layers are well separated from one another and individually dispersed in the continuous polymer matrix. Because exfoliated nanocomposites have higher phase homogeneity than the intercalated counterpart, the exfoliated structure is more desirable in enhancing the properties of the nanocomposites. However, it is not easy to achieve complete exfoliation of clays and, indeed with few

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exceptions, the majority of the polymer nanocomposites reported in the literature were found to have partly intercalated and partly exfoliated nanocomposites.

Polyamide 11 (PA 11) is a kind of polyamide, which is widely used for industrial applications. Polyamide 11 possesses excellent piezoelectricity, good cryogenic properties, oil resistance and water resistance, but impact properties, tensile strength, and thermal properties are not satisfactory for engineering plastics. Some modifications have been done to improve these inferior properties. In recent years, a new method of introducing clay as filler has attracted much attention. As a typical example, PA 6/clay nanocomposite is perhaps the most successful system demonstrating dramatic improvement in properties. Other polyamides, such as PA 66 and PA12 have also been used to introduce clay and to make nanocomposites which show excellent properties, also on an industrial scale. The preparation of PA 11/clay nanocomposites would be of great benefit, just as in the case of other polyamides.

The objective of this study is to investigate the possibility of synthesizing materials with nanocomposite structure based on PA 11 and clay. In this paper, PA 11/clay nanocomposites (PACN) were prepared via *in-situ* intercalated polymerization. X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM) and the Molau test were introduced to characterize the clay layer dispersion. The effect of clay content on mechanical and thermal properties will then be investigated.

EXPERIMENTAL

Materials

Sodium montmorillonite (MMT) having a cation-exchange capacity of 64.5 meq/100 g, and 11-aminoundecanoic acid were commercially available.

Preparation of Cation-Exchanged Montmorillonite

50 g MMT was dispersed into 1000 mL hot water using a stirrer. 7.0 g 11-aminolauric acid and 3.5 mL concentrated hydrochloric acid were dissolved in hot water (200 mL) and then poured into the montmorillonite-water suspension under vigorous stirring for 2 h. The product was filtered off and washed three times. The obtained MMT is termed 11-MMT. Pure and treated MMT were dried for X-ray diffraction measurement.

Synthesis of PA11/MMT Nanocomposites

11-Aminoundecanoic acid (monomer), other ingredients and different amounts of 11-MMT were mixed in a vessel. These mixtures were heated at 100–180°C to drive off water. Then catalyst and other ingredients were added. The mixture was again heated at 180–280°C for 6 h to achieve polymerization. The amounts of 11-MMT were chosen as 1 wt%, 3 wt%, 5 wt% and 10 wt%. The products with different MMT contents are termed PACN1, PACN3, PACN5, PACN10, respectively. For comparison, pure PA 11 was also prepared under the same conditions.

Characterization of Dispersed MMT in PA11/MMT Nanocomposites

The dispersion of 11-MMT sheets in the matrix was evaluated by SEM, XRD, TEM, and the Molau test.

The injection-molded PACN3 sample for SEM experiments was fractured in liquid nitrogen. The fractured surfaces were then gold coated to prevent charging of the samples, and investigated in an SEM (JEOL JSM-5900LV SEM) using an acceleration voltage of 20 kV.

The XRD analysis was performed by using a Rigaku Denki RAD-B instrument with Cu-K α ($\lambda = 0.154$ nm) radiation at room temperature. The basal spacing of the montmorillonite was estimated from the (001) peak in the XRD pattern. PACN with different 11-MMT contents, pure MMT and cation-exchanged MMT were scanned at room temperature. The scanning rate was 2.5 °/min and the scanning range was 1–10°.

TEM observations of the hybrids were performed for the injection-molded samples with a 500 nm thickness by a JEM-100SX TEM instrument using an acceleration voltage of 70 kV.

In the Molau test, the samples with different 11-MMT contents were separately added to the methyl hydroxybenzene solvent. Then the samples were examined after being completely dissolved.

Measurements of Properties

The standard specimens of PA11 and PACN3 were prepared by injection molding in a PS40E5ASE injection-molding machine. The temperatures of the machine were maintained at 190, 220 and 215°C from hopper to die. The mold was kept at room temperature. Prior to testing, all specimens were dried in a vacuum oven at 90°C for 10 h.

The tensile strength and tensile modulus of the specimens were measured using an AG-10TA tensile tester with a speed of 50 mm/min and 5 mm/min, respectively, according to GB/T 1040-92 standard. The Izod impact test of notched specimens was carried out on a VJ-40 impact tester, according to GB/T 1834-1996 standard. The flexural strength and flexural modulus were measured using an AG-10TA flexural testing machine with a speed of 2 mm/min according to GB 9341-88 standard. The tests were performed at room temperature. A RW-3 heat distortion testing machine was used to measure the heat distortion temperature of PA11 and PACN3 according to GB 1634-79 standard.

RESULTS AND DISCUSSION

The Dispersion of MMT in Composites

The key question regarding the structure of PA11/clay is whether a true nanocomposite is formed or not. If not, the material is comparable to a conventional, filled polymer microcomposite. In order to obtain the overall macroscopic view of dispersion of the 11-MMT layers in the PA11 matrix, SEM observation was performed. Figure 1 shows the fractured specimens of PACN3. Some primary MMT particles having a size of 50–200 nm are quite homogeneously dispersed in PA 11 matrix. But 11-MMT sheets are not clearly seen as a result of the strong interaction between 11-MMT sheets and the matrix.

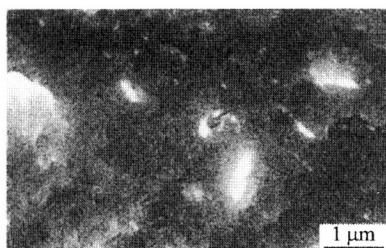


Fig. 1 SEM photo of fractured surface of PA11/clay nanocomposites (clay content: 3 wt%)

Due to the low resolution of SEM, one doesn't know whether the observed particles have an intercalated-structure, or an exfoliated structure exists in the remaining area. So other experiments are needed. XRD and TEM are two predominant methods to characterize the dispersion of 11-MMT in nanocomposites.

An important method of characterization is X-ray diffraction. It is advisable to observe the MMT layer spacing changes before and after cation exchange processes. Figure 2 presents the X-ray diffraction patterns for pure MMT and 11-MMT. The peaks correspond to the (001) reflections of the clay (the interlayer gallery height). The basal spacing of the cation-exchanged MMT increases from 1.47 nm for the pure MMT, to 1.75 nm for the 11-MMT. This indicates that 11-aminolauric acids enter into the interlayer spacing and increase the *d*-spacing.

Figure 3 shows the XRD profiles of PA 11/clay composites with different content of 11-MMT. PACN samples with different content of 11-MMT show the (001) reflections of 11-MMT. With the increasing 11-MMT content, the peak of 11-MMT further expands from 1.75 nm to 1.84 nm (PACN5) and 2.05 nm (PACN10), suggesting that the intercalation of PA11 into the gallery indeed takes place. There exists a clear regular layered structure, demonstrated by the presence of the d_{001} and higher-order diffraction peaks. But in PACN1 and PACN3, the peak of MMT is not obvious. The reason may be that MMT content is so low that reflections can not be detected by XRD or that the exfoliation of MMT sheets has taken place.

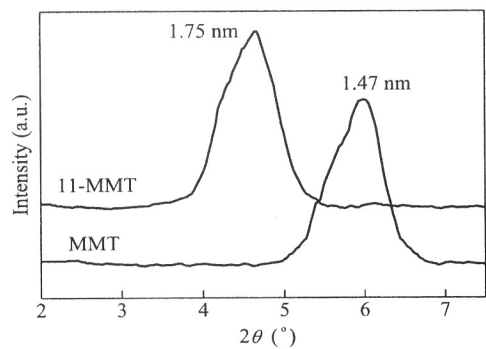


Fig. 2 The XRD profiles of MMT and 11-MMT

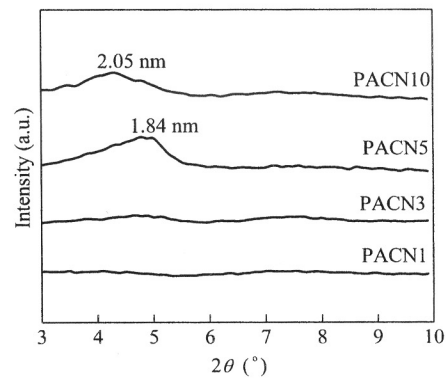


Fig. 3 The XRD profiles of PACN with different clay contents

More direct evidence for the formation of a true nanocomposite is provided by TEM of an ultramicrotomed section. TEM photographs of injection-molded sample with 3 wt% 11-MMT content are shown in Fig. 4, where the dark lines are the interfaces of the MMT sheets. MMT layers are dispersed homogeneously in the PA11 matrix. One finds some MMT sheets with 10–50 nm thickness, but in some areas, the intercalated layers with sizes of 50–200 nm are also observed, which indicates the existence of a partly exfoliated and partly intercalated structure in the nanocomposties.

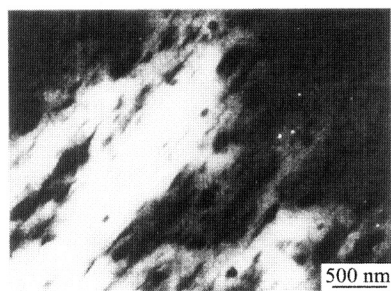


Fig. 4 TEM micrograph of PACN3

Molau Test

In order to study the interaction between MMT and matrix, the Molau test was performed. Table 2 lists the dissolution phenomena of PA11 and PACN with various MMT contents in the solvent. The solutions of PACN1 and PACN3 are stable. One can not find any sediment and delaminating, which indicate that the interaction between the MMT sheets and PA11 is strong at lower MMT content. But we can find some MMT precipitated in the PACN5 and PACN10 solutions. It indicated that some aggregated MMT layers exist at higher MMT content of PACN, which lead to poor interaction between MMT layers and matrix.

Table 2. Molau test results	
Solution	Phenomena
PA11	Dissolve, stable
PACN1	Dissolve, stable
PACN3	Dissolve, stable
PACN5	Precipitate
PACN10	Precipitate

Combining with the results of SEM, XRD, TEM, and the Molau test, we can conclude that the PA 11/clay nanocomposites were successfully produced. Intercalated and exfoliated MMT layers coexist in PACNs. With

the increasing MMT contents, more intercalated layers exist, which lead to bad dispersion and poor interaction between MMT and PA 11.

Mechanical and Thermal Properties

Table 1 summarizes the mechanical and thermal properties of PA11 and PACN3. Compared with PA11, PACN3 shows an increase of 26% in impact strength and a slight increase in tensile strength and tensile modulus, but the elongation at break is decreased. Flexural strength is improved with 22.2% increasing. And the flexural modulus is also increased. The results can be attributed to the uniform dispersion of MMT sheets and the strong interaction between MMT and matrix, which reinforces the mechanical properties of PA11.

Table 1. Mechanical and thermal properties of PA11 and PACN3

Samples	PA11	PACN3
Izod impact strength (kJ/m ²)	11.5	14.5
Tensile strength (MPa)	44.2	46.1
Tensile modulus (GPa)	0.91	1.1
Elongation at break (%)	104.7	78.0
Flexural strength (MPa)	30.6	37.4
Flexural modulus (GPa)	0.96	1.23
Heat deformation temperature (°C)	51	58

Since PA6/clay nanocomposites show greater improvement in heat distortion temperature (HDT), we also examined the HDT of PA11/clay nanocomposites. As shown in Table 1, the HDT of PACN3 is only 7°C higher than that of PA11. Compared with Nylon6/clay hybrid^[2], of which the HDT increased from 65°C to 152°C, the thermal property of PA11 nanocomposites is slightly improved. The reason for this slight improvement on HDT of PA11 nanocomposites has not been clearly understood but PA6 nanocomposites show much greater improvement. More work is needed to find out the reason.

CONCLUSIONS

Polyamide 11/MMT nanocomposites can be successfully achieved via *in-situ* intercalated polymerization. MMT layers are homogeneously dispersed in the PA11 matrix on the nano-scale, and an exfoliated and intercalated structure co-exists (also called incomplete exfoliation) in the composites. The mechanical and thermal properties of PACN have been improved, due to the strong interaction between MMT and PA11 matrix, but the improvement is not satisfactory compared with PA-6 nanocomposites.

REFERENCES

1 Okada, A., Kawasumi, M., Kurauchi, T. and Kamigaiti, O., Polym. Prepr., 1987, 28: 447
2 Usuki, A. and Kawasumi, M., J. Mater. Res., 1993, 8: 1179
3 Usuki, A., Kojoma, Y. and Kawasumi, M., J. Polym. Sci., Part A, Polym. Chem., 1993, 31: 1755
4 Yano, K., Usuki, A. and Okada, A., J. Polym. Sci., Part A, Polym. Chem., 1997, 35: 2289
5 Yang, Y., Zhu, Z.K., Yin, J., Wang, X.Y. and Qi, Z.N., Polymer, 1999, 40: 4407
6 Liu, J., Gao, Y., Wang, F.D. and Wu, M., J. Appl. Polym. Sci., 2000, 75: 384
7 Lee, D.C. and Jang, L.W., J. Appl. Polym. Sci., 1996, 61: 1117
8 Messersmith, P.B. and Giannelis, E.P., Chem. Mater., 1993, 5: 1064
9 Akelah, A. and Moet, A., J. Mater. Sci., 1996, 31: 3589
10 Porter, T.L., Hagerman, M.E., Reynolds, B.P., Eastman, M.P. and Parnell, R.A., J. Polym. Sci., Part B: Polym. Phys., 1998, 36: 637
11 Vaia, R.A. and Ginnelis, E.P., Macromolecules, 1997, 30: 8000
12 Burnside, S.D. and Giannelis, E.P., J. Polym. Sci., Part B: Polym. Phys., 2000, 38: 1595