

Interaction of Nylon 6-Clay Surface and Mechanical Properties of Nylon 6-Clay Hybrid

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SYNOPSIS

We synthesized nylon 6-clay hybrid materials using four types of clay minerals, montmorillonite, saponite, hectrite, and synthetic mica. The mechanical properties of their injection molded specimens were measured according to ASTM. Nylon 6-clay hybrid using montmorillonite was superior to the other hybrids in mechanical properties. This might result from the difference in the interaction between nylon molecules and silicates in the hybrids. To clarify this hypothesis, we synthesized intercalated compounds of the clay minerals with glycine as the model of the hybrids, and analyzed the interaction using ^{15}N cross polarization magic angle spinning (CP/MAS) NMR spectroscopy. The ^{15}N -NMR result reveals that the positive charge density on the nitrogen of the intercalated compound based on montmorillonite was largest in all the intercalated compounds. It was suggested that montmorillonite interacted strongly with nylon 6 by ionic interaction. This ionic interaction was one of the reasons why these hybrid materials had superior mechanical properties. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Nylon 6-clay hybrid is a new type of engineering polymer in which layered clay minerals are uniformly dispersed in nylon 6 matrix.^{1,2} The features of this polymer are high strength, high modulus, high distortion temperature,³ and low gas permeability.⁴ The silicate layers hinder the permeation of gases for low gas permeability. However, on what these superior mechanical properties were based was not understood. In this study, we synthesized nylon 6-clay hybrid materials based on four types of clay minerals, montmorillonite, saponite, hectrite, and mica. These four nylon hybrids were characterized by measuring standard mechanical properties. The strength of interaction between nylon 6 and clay minerals were estimated using ^{15}N cross polarization magic angle spinning (CP/MAS) NMR of model intercalated compounds. Glycine is the most elementary amino acid and can be considered as the simplest chemical structure of polyamide. We used glycine as the model compound of the hybrid. Gly-

cine was intercalated into four types of clay minerals, and ^{15}N -NMR of these intercalated compounds were measured. The aim of this study was to clarify the origin of the difference in the mechanical properties among four nylon hybrid materials.

EXPERIMENTAL

Materials

Caprolactam was purchased from Wako Co. Montmorillonite "Kunipia F" and saponite "Sumecton SA" were supplied by Kunimine Ind. Co. Hectrite "Laponite RD" and synthetic mica were supplied by Kakuhachi Co. and Topy Ind. Co., respectively. Exchangeable sodium ions exist in these clays. Their cation exchange capacities are about 120, 100, 50, and 100 meq/100 g, respectively. Isotopic ^{15}N enriched glycine was purchased from Aldrich Co. and used for synthesis of model intercalated compounds.

Nylon 6-Clay Hybrid

The sodium ions of montmorillonite, saponite, hectrite, and synthetic mica clays were exchanged for

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ammonium ions of 12-aminolauric acid by following the reported method.¹ Then we polymerized ϵ -caprolactam using four types of the organophilic clays by following the reported method.² The contents of organophilic clay were about 5 wt %. To expedite ring-opening polymerization of ϵ -caprolactam, 10% of 6-aminocaproic acid was added. The polymerizations were carried out at 250°C for 6 h. The resulting products were mechanically crushed and washed with hot water. After being dried *in vacuo*, the products were molded on test pieces. Nylon 6 "1013B" was supplied by UBE Ind. Co.

Tensile strength and other mechanical properties of the injection molded samples were measured according to ASTM. End group analysis of nylon 6 was performed using a titration method. The car-

boxyl ends were titrated with N/20 sodium hydroxide solution in a benzyl alcohol solution of nylon. The amino ends were titrated with N/20 hydrochloride solution in a phenol and methanol mixed solution of nylon. To confirm the dispersion of clays in nylon 6 matrix, we observed transmission electron micrographs (TEMs) of intersections of the injection molded samples. TEMs were obtained with a Jeol-200CX TEM using an acceleration voltage of 200 kV. A differential scanning calorimeter (DSC) was used to measure the crystallinity of nylon 6. A Perkin-Elmer DSC-7 was used for all DSC measurements and was calibrated with indium. Heat of fusion of nylon 6 was calculated by using a TAS 7 data station Model PE 7000. Heating rate was 10°C/min.

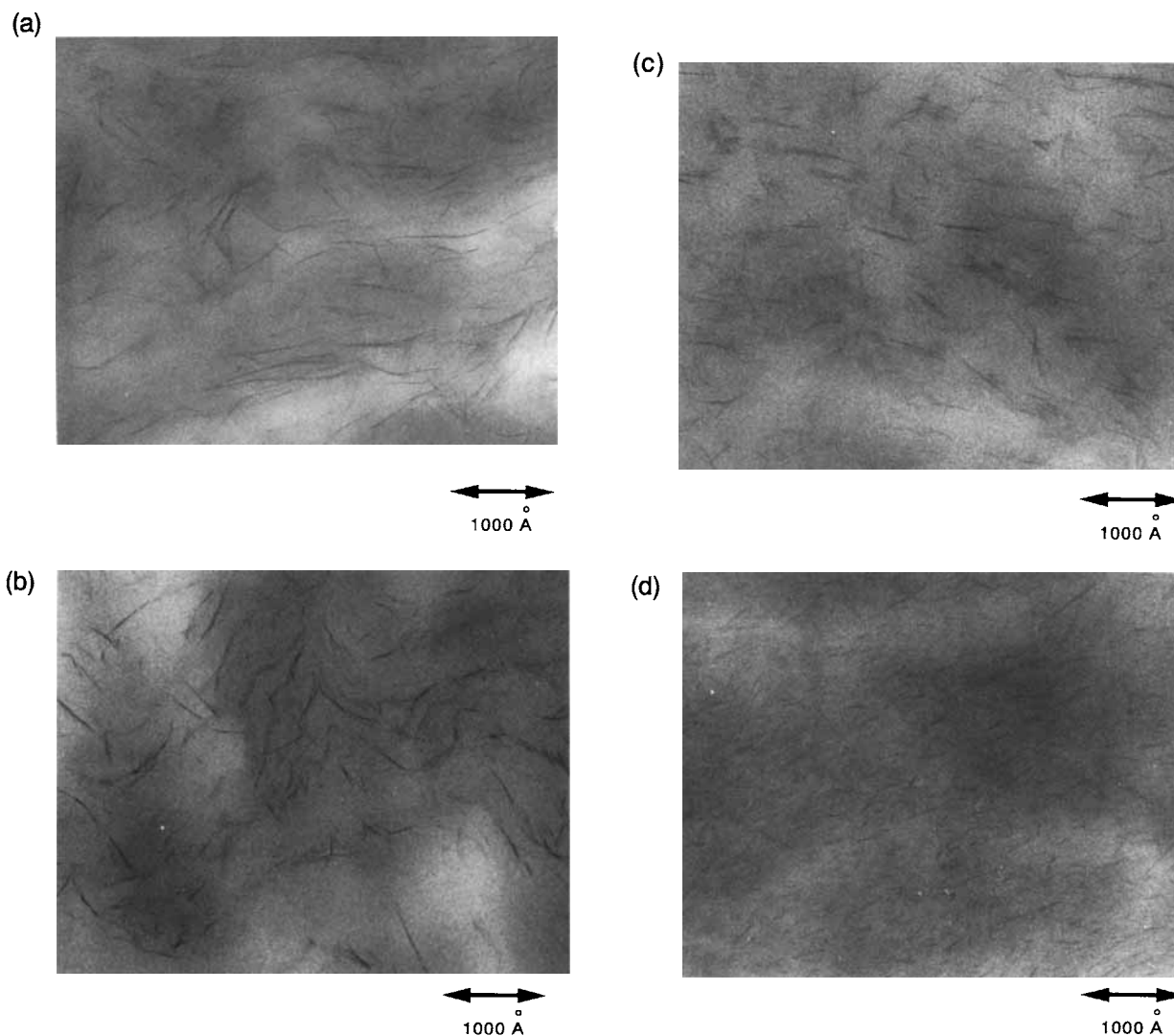


Figure 1 Photograph of transmission electron micrographs of molded nylon 6-clay hybrids, used clay minerals: (a) montmorillonite, (b) mica, (c) saponite, (d) hectrite.

Table I Mechanical and Thermal Properties of Nylon 6-Clay Hybrids and Nylon 6

Properties	Clays				
	NCH Montmorillonite	NCHM Mica	NCHP Saponite	NCHH Hectrite	Nylon 6 No
Tensile strength (MPa)					
23°C	97.2	93.1	84.7	89.5	68.6
120°C	32.3	30.2	29.0	26.4	26.6
Elongation (%)					
23°C	7.3	7.2	>100	>100	>100
Tensile modulus (GPa)					
23°C	1.87	2.02	1.59	1.65	1.11
120°C	0.61	0.52	0.29	0.29	0.19
Heat distortion temperature (°C)	152	145	107	93	65
Heat of fusion (J/g)	61.1	57.2	51.5	48.4	70.9
Heat of fusion (J/nylon 6 1 g)	63.6	59.6	53.4	50.4	70.9

Interlayer Compounds Intercalated with Glycine

The interlayer compounds intercalated with glycine were synthesized to measure the ion-bonding strength between clay and ammonium cations of glycine by using ^{15}N -NMR. In a 100 mL beaker were placed 1.0 g of clay, 1.3 mL of 1 NHCl, 50 g of water, and 0.1 g of ^{15}N labeled glycine. This mixture was stirred vigorously for 10 min, and it became a milky turbid suspension. The suspension was filtered and the residue was freeze-dried.

^{15}N NMR Measurement

^{15}N CP/MAS NMR measurements were performed on a Bruker MSL-300 NMR spectrometer equipped with a Bruker MAS probe operating at a field strength of 7.0 T. The ^{15}N resonance frequency was 30.41 MHz. Crystalline ammonium nitrate was used as an external chemical shift reference (at 0 ppm; $^{15}\text{NH}_4$).

RESULTS AND DISCUSSION

We prepared the nylon 6-clay hybrids in which layered clay minerals were dispersed in nylon 6 matrix. The content of the organophilic clay ion exchanged with 12-aminolauric acid was 5 wt % at the preparation of the hybrids. The actual amounts of the clays in the hybrids were measured by weighing the residue after burning them. They were about 4 wt %. These nylon 6-clay hybrids based on montmorillonite, saponite, hectrite, and synthetic mica were termed NCH, NCHP, NCHH, and NCHM, respec-

tively. These polymers were molded at 250°C to prepare the test pieces.

The TEMs of the injection molded samples are shown in Figure 1. The dark lines in the figure correspond to the intersections of sheet layers of 1 nm thickness. All clay minerals were dispersed in nylon 6 matrix at a microscopic level similarly to montmorillonite.² The size of the clay layers that could be observed in the TEM photographs were slightly different. It was noted that the montmorillonite layer was nearly equal to the mica layer and saponite layer, and the size of layer was about 1000 Å. The hectrite layer was the smallest in the clays, about 500 Å.

The tensile test of nylon 6-clay hybrids (NCH, NCHP, NCHH, and NCHM) and nylon 6 were performed at 23 and 120°C, and their heat distortion temperatures were measured. These results are shown in Table I. NCH was superior to the other hybrids in mechanical properties.

The results of the end group analysis are shown in Table II in the case of NCH, NCHP, and nylon 6. The concentration of carboxyl ends is equal to that of amino ends in nylon 6. However, the con-

Table II End Group Analysis of Nylon 6-Clay Hybrids and Nylon 6

	NCH	NCHP	Nylon 6
COOH	9.46	8.37	5.14
NH ₂	4.86	3.17	5.09
NH ₃ ⁺	4.6	5.2	—

Values are $\times 10^{-5}$ mol/g.

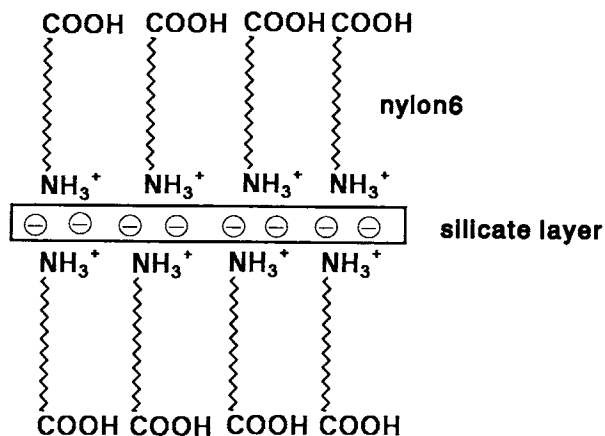


Figure 2 Conceptual figure of nylon 6-clay surface.

centration of carboxyl ends was larger than that of the amino ends in NCH and NCHP. The carbon ends of nylon 6 propagated from 12-aminolauric acid were only carboxyl ends, COOH in the hybrids. However, the nitrogen ends could exist as neutral amino ends (NH_2) or cationic ammonium ends (NH_3^+). Neutral amino ends developed from the amino groups of 6-aminocaproic acid through polymerization. The difference between the concentration of the carboxyl COOH and amino NH_2 ends was equal to the concentration of the ammonium NH_3^+ end.⁵ This ammonium end group in nylon 6 should interact with the negative charge of the sil-

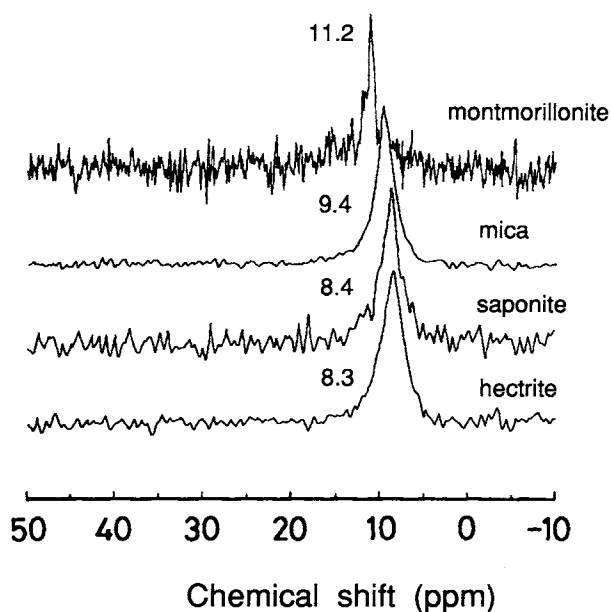


Figure 3 ^{15}N NMR spectra of intercalated compounds.

icate layer. The conceptual figure is shown in Figure 2. The superior mechanical properties of the hybrids might result from the strong interaction between nylon molecules and clay layers.

In order to clarify this hypothesis, it was desirable to measure ^{15}N -NMR to evaluate the ion bonding strength between the clay layer and nylon 6. However, the amount of the ammonium ends bonded to the silicate layer was too small to be detected by ^{15}N NMR in the nylon 6-clay hybrid. In this study, we selected glycine as a hybrid model and diamine as a nylon 6 molecule model. Hexamethylenediamine (HMDA) was used for the model compound of ordinary nylon 6 because HMDA has neutral amine ends and is solid at room temperature. Thus, we synthesized intercalated compounds of four clay minerals with glycine.

Figure 3 shows ^{15}N -NMR spectra of clays intercalated with glycine. Table III summarizes ^{15}N -NMR chemical shifts of these compounds. The neutral amine, HMDA, showed a resonance at 7.0 ppm, and the ammonium ion, glycine hydrochloride, had a peak at 15.6 ppm. The peaks of the glycine intercalated in the clays appeared around the region between HMDA and glycine hydrochloride. In montmorillonite, the shoulder on the low field side of the main peak at 11.2 ppm was an unresolved signal. Among the main four peaks, the glycine intercalated in montmorillonite had the most downfield resonance. The large down field resonance means that there is less shielding by the electrons at the nucleus. The chemical shift becomes larger as the electron charge density of the nitrogen atom becomes smaller.⁶ The ^{15}N -NMR result reveals that the electron charge density on the nitrogen of glycine in montmorillonite was the smallest in all the intercalated compounds. In other words, the nitrogen atoms in montmorillonite have much positive polarization and largely interact to silicate layer.

Table III ^{15}N -NMR Chemical Shift of Model Compounds

Compounds	Chemical Shift (ppm)
$\text{Cl}-\text{NH}_3^+\text{CH}_2\text{COOH}$	15.6
Montmorillonite- $\text{NH}_3^+\text{CH}_2\text{COOH}$	11.2
Mica- $\text{NH}_3^+\text{CH}_2\text{COOH}$	9.4
Saponite- $\text{NH}_3^+\text{CH}_2\text{COOH}$	8.4
Hectrite- $\text{NH}_3^+\text{CH}_2\text{COOH}$	8.3
HMDA	7.0

ppm relative to $^{15}\text{NH}_4\text{NO}_3$.

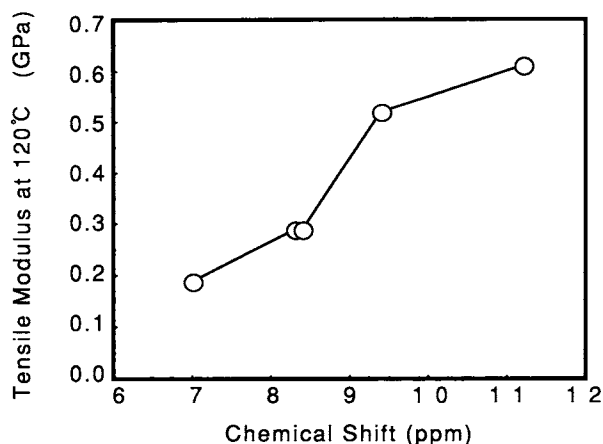


Figure 4 Relation between ^{15}N -NMR chemical shift of intercalated compounds and tensile modulus at 120°C of nylon hybrids.

It is thought that these ionic interactions influence the mechanical properties at high temperature and crystallization. Figure 4 shows the correlation of the ^{15}N -NMR chemical shift with the tensile modulus at 120°C of the four nylon hybrids. The ^{15}N -NMR chemical shifts of the four intercalated compounds correlate with the mechanical properties of the corresponding nylon hybrids. On the other hand, the silicate layers could act as nucleating agents during crystallization, thus affecting crystallinity. The heat of fusion of the hybrids and nylon 6 are shown in Table II. The heat of fusion of 1 g nylon 6 in the hybrids (J/1 g nylon 6) was calculated from clay contents and the heat of fusion of the hybrids (J/g). The heat of fusion of nylon 6 in all the hybrids decreased compared to that of nylon 6.

From this result, the crystallinity of all the nylon 6 hybrids is lower than that of nylon 6. The mechanical properties of the hybrids were excellent notwithstanding the decrease in crystallinity. The main factor that determines the mechanical properties of the hybrids is considered to be the reinforcement due to the dispersion of silicate nano layers. However, the hybrid based on montmorillonite (NCH) possesses the highest crystallinity among the hybrids. Montmorillonite interacted most strongly with nylon 6 through ionic interaction. We suppose that the crystallinity was affected by ionic interaction between nylon 6 and silicate layers. It is considered that the superior mechanical properties of these hybrid materials can be attributed to the strong ionic interaction.

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