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Nylon 6/Na–montmorillonite nanocomposites prepared by compounding Nylon 6 with Na–montmorillonite slurry

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Abstract

We report a novel compounding process using Na–montmorillonite water slurry for preparing novel nylon 6/Na–montmorillonite nanocomposites. In this compounding process, the Na–montmorillonite slurry was blended with melting nylon 6 using an extruder, followed by removing the water. The Na–montmorillonite silicate layers were found to be exfoliated and dispersed homogeneously at nanometer level in the nanocomposites with an electron transmission microscope. The exfoliated Na–montmorillonite silicate layers were fixed in the nylon 6 matrix almost as they were in water. The nylon 6/Na–montmorillonite nanocomposites, loaded with only 1.6 wt% clay silicate layers, exhibited high strength, high modulus, high heat distortion temperature and low gas permeability compared to neat nylon 6. The properties of the nylon 6/Na–montmorillonite nanocomposites were nearly equal to those of conventional nylon 6/clay nanocomposites prepared by dry-compounding nylon 6 and organophilic clay ion-exchanged with alkylammonium ions.

Keywords: Clay; Nanocomposite; Nylon

1. Introduction

In recent years, organic–inorganic nanometer-composites have attracted great interest to researchers since they frequently exhibit unexpected hybrid properties synergistically derived from the two components [1–4]. One of the most promising composite systems would be polymer–clay nanocomposites based on organic polymers and inorganic clay minerals consisting of silicate layers [4–21]. In our previous work, we synthesized a nylon/clay nanocomposites (nylon/clay hybrids, abbreviated to NCH) wherein 1 nm thick silicate layers of the clay minerals exfoliated and homogenously dispersed at nanometer level [5,6]. The NCH exhibited various superior properties such as high strength, high modulus, high heat resistance and low gas permeability compared to nylon 6 resin [6]. Since then, other polymer–clay nanocomposites such as polyimide [7], epoxy resin [8], polystyrene [9], polycaprolactone [10], acrylic polymer [11], polyurethane [12], poly(ethylene terephathalate) [13], polypropylene [14], were reported. Various kinds of methods such as polymerization methods, compounding methods, and solution methods were also reported for preparation of these polymer–clay nanocomposites.

The NCHs have been prepared by several methods. A polymerization method was first reported, wherein caprolactam was polymerized in the presence of organophilic montmorillonite ion-exchanged with ammonium ions of ω-aminoacid [5]. Recently, compounding processes have attracted a great deal of attention industrially, wherein organophilic clay ion-exchanged by organoammonuim ions were melt compounded with nylons [15]. In these compounding processes, the organophilic clay was necessarily used to yield the exfoliated-type NCHs, because the silicate layers without organo-modification do not exfoliate during compounding.

It is worth developing a general compounding process using the natural clay minerals without organo-modification to reduce the cost on producing polymer/clay nanocomposites industrially. Recently, compounding processes using the clay minerals were reported, wherein the clay minerals and polymers were compounded with compatibilizers such as alkyl ammonium salt [16], maleic anhydride [17].

It is well known that the clay minerals, such as Na–montmorillonite, Na–fluoromica, exfoliate in water to form

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clay slurry (clay dispersion). Some polymer/clay nanocomposites prepared using the clay slurry were reported; however the applies were limited to hydrophilic polymers, such as poly(vinyl alcohol) [18], poly(ethylene oxide) [19], and to emulsion polymerizations. Emulsion polymerizations were carried out in the clay slurry for poly(methyl methacrylate) [20] and polystyrene [21]; however, exfoliated-type nanocomposites were not obtained. In this study, we report a novel compounding process using the Na–montmorillonite slurry and demonstrate preparing a NCH based on nylon 6 and Na–montmorillonite, wherein the Na–montmorillonite silicate layers exfoliate and homogeneously disperse at nanometer level. The most merit of this compounding process is that the NCH consisted of nylon 6 and Na–montmorillonite is prepared without any surfactants of the clay minerals and additives.

2. Experiment

2.1. Materials

The materials used for preparation of the samples were purified Na–montmorillonaite (Kunipia-F) from Kunimine Industries. Co. and nylon 6 (1015B) from Ube Industries. Co.

2.2. Clay slurry

The clay slurry was prepared by dispersing Na–montmorillonite powder (40 g) into water (1960 ml) by using a homogenizer for 10 min. The inorganic content in the slurry was 2 wt%.

2.3. Preparation of NCH using clay slurry

The co-rotating twin-screw extruder TEX30 α-45.5BW from Japan Steal Works LTD was used to prepare composites. Its screw length was 1365 mm and its L/D was 45.5. Fig. 1 shows schematic figure depicting a compounding process for preparing the NCH using the clay slurry. Nylon 6 was put into the extruder at 2 kg/h and melted in the melting zone. The clay slurry was pumped into the cylinder of the extruder at 2 kg/h and compounded with the melting nylon 6 in the compounding zone at 240–250 °C. The screw rotation speed was 200 rpm. The residence time in the cylinder was approximately 10 min. Sealing zone was set by using a sealing ring to prevent water back flow for the hopper. The water of the slurry was removed from the vent by vacuum to obtain the NCH consisted of nylon 6 and Na–montmorillonite. The obtained strands were pelletized and dried under vacuum at 80 °C. This NCH prepared using clay slurry is abbreviated to Nylon/Clay Hybrid-Clay Slurry (NCH-CS). The inorganic clay content in the NCH-CS was 1.6 wt% obtained by measuring the weights before and after burning its organic part. For the sake of comparison, a composite dry-compounded nylon 6 with the Na–montmorillonite powder and a conventional nanocomposite dry-compounded nylon 6 with organophilic montmorillonite powder intercalated with stearylammonium ions were prepared. These samples are abbreviated to Nylon/Clay Composite (NCC) and Nylon/Clay Hybrid-Organophilic Clay (NCH-OC), respectively. The inorganic clay contents in the NCC and the NCH-OC were 2.0 and 1.8 wt% obtained by measuring the weights before and after burning their organic parts, respectively.

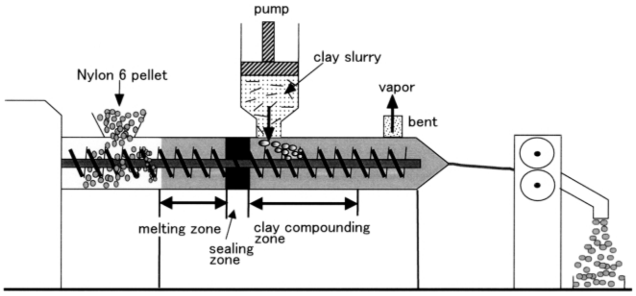

Fig. 1. Schematic figure depicting the compounding process for preparing the NCH-CS using the clay slurry.

2.4. Evaluation of dispersibility of clay

The dispersibility of the silicate layers of Na–montmorillonite in the samples was evaluated by X-ray diffraction (XRD) measurements, optical microscopy and transmission electron microscopy (TEM) observation. The XRD measurements were performed for films of the samples by using a Rigaku RAD-B diffractometer with Cu Kα radiation generated at 30 kV and 30 mA. The films were prepared by compression molding at 240 °C. Their thicknesses were 0.4–0.6 mm. The TEM observation was performed for the ultra thin sections of the films by a Jeol-200EX using an acceleration voltage of 200 kV.

2.5. Measurement of properties

The properties of the samples were measured according to the standard methods shown in Table 1. Tensile, flexile and Izod impact tests were carried out at 23 °C. Gas permeability measurements were performed for the films with 40 μm thickness using oxygen at 23 °C.

3. Results and discussion

3.1. Dispersibility of Na–montmorillonite

Fig. 2 shows the optical microscopy photographs of the NCC and the NCH-CS. The observation under cross-Nicol was performed for the melting samples at 240–250 °C. In the NCC, aggregated clay particles were found

Table 1
Tablel Properties of the NCHs and nylon 6

	Unit	Measurement method	Sample		
			Nylon 6	NCH	
				Organophlic clay	Clay slurry
Inorganic content	wt%	–	0	1.8	1.6
Relative viscosity	–	JIS K-6810	2.83	–	2.79
Tensile strength	MPa	ASTM D-638	68	82	82
Tensile modulus	GPa	ASTM D-638	1.08	1.41	1.38
Tensile elongation	%	ASTM D-638	>200	>200	>200
Flexural strength MPa	MPa	ASTM D-790	110	132	123
Flexural modulus	GPa	ASTM D-790	2.85	3.58	3.26
Izod impact strength	kg cm/cm	ASTM D-256	50	42	44
Heat distortion temperature	°C	ASTM D-648	75	135	102
O_2 permeability	ml/m^{2}D	ASTM D-3985	48	31	33

at the micrometer level. On the other hand, aggregates of the clay were not observed in the NCH-CS. Fig. 3 shows the TEM images of the NCH-CS in which the dark lines are the cross-sections of the Na–montmorillonite silicate layers with about 1 nm thickness. In the NCH-CS, the Na–montmorillonite silicate layers exfoliated and homogeneously dispersed at the nanometer level. Some silicate layers dispersed at a few layers gathering and some silicate layers dispersed at monolayer. Fig. 4 shows X-ray diffraction patterns of the Na–montmorillonite powder, the NCC and the NCH-CS. The NCC exhibited an apparent peak at $2\theta = 7.1°$ corresponded to 001 diffraction peak of the layered structures of Na–montmorillonite. The interlayer spacing of Na–montmorillonite in the NCC was 1.25 nm and the spacing was the same as the Na–montmorillonite powder. It indicates that nylon 6 polymer chains did not intercalate into the galleries of the Na–montmorillonite silicate layers during dry-compounding. On the other hand, there was no peak in the XRD pattern of the NCH-CS. It indicates that the silicate layers of Na–montmorillonite in the NCH-CS were not stacked regularly, though there were a few silicate layers gathering as shown in the TEM image. An exfoliated-type NCH is successfully prepared by compounding nylon 6 with the Na–montmolironite water slurry.

Fig. 5 shows schematic figures depicting dispersion of the Na–montmorillonite silicate layers of the clay slurry into nylon 6 during compounding by an extruder. We guess that the exfoliated Na–montmorillonite silicate layers disperse into nylon 6 as following. The clay slurry is first pumped into the melting nylon 6 under vigorous shear (Fig. 5a). The clay slurry would get into finer drops during blending and, at the same time, the water of the slurry drops would begin to evaporate on contact with melting nylon 6 (Fig. 5b and c). The evaporated water was removed quickly by vacuum from the bent. During the evaporation of water, some silicate layers are fixed into melting nylon 6 and disperse at monolayer, and some silicate layers gather and disperse at a few layers gathering (Fig. 5d). It is thought that,

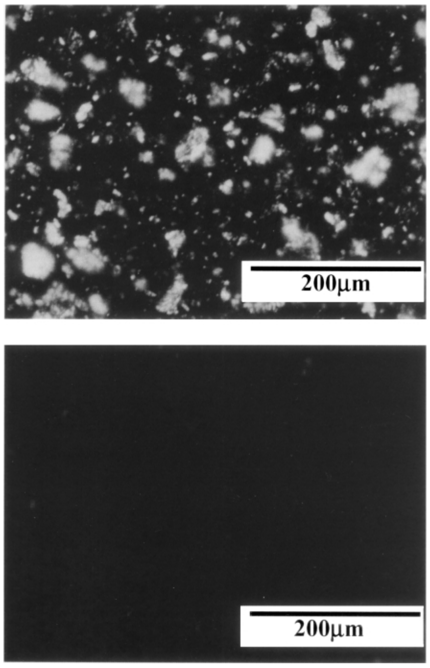

Fig. 2. Optical microscopy photographs (a) the NCC, (b) the NCH-CS.

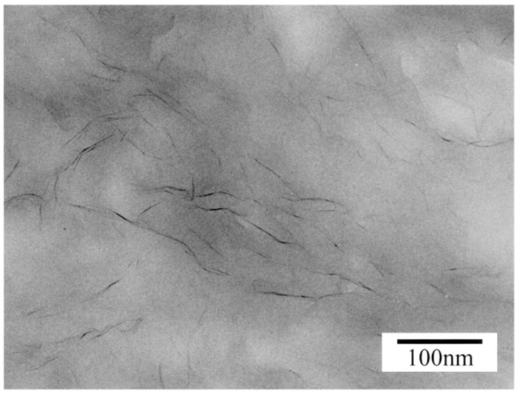

Fig. 3. TEM image of the NCH-CS.

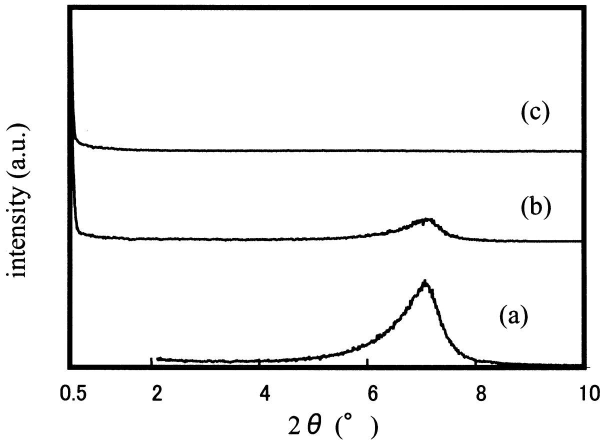

Fig. 4. X-ray diffraction patterns (a) the Na–montmorillonite powder, (b) the NCC, (c) the NCH-CS.

by blending with nylon 6 vigorously and removing the water quickly, the exfoliated Na–montmorillonite silicate layers are fixed into the nylon 6 matrix almost as they were in water. The key point of silicate layer dispersion in this compounding process is quite different from that of the conventional compounding processes using the organophlic clay. In the conventional processes, the key point is that polymer chains intercalate into the galleries of stacked layered silicates and the silicate layers exfoliate into the polymer matrix. On the other hand, in this process, the key point is that the exfoliated silicate layers in water are fixed into the polymer matrix without aggregation of the silicate layers.

As for thermal stability of the NCH-CS, the dispersed Na–montmorillonite silicate layers did not aggregate after injection and compression molding. It indicates that the exfoliated Na–montmorillonite silicate layers existed stably in melting nylon 6, even though the silicate layers were not organo-modified.

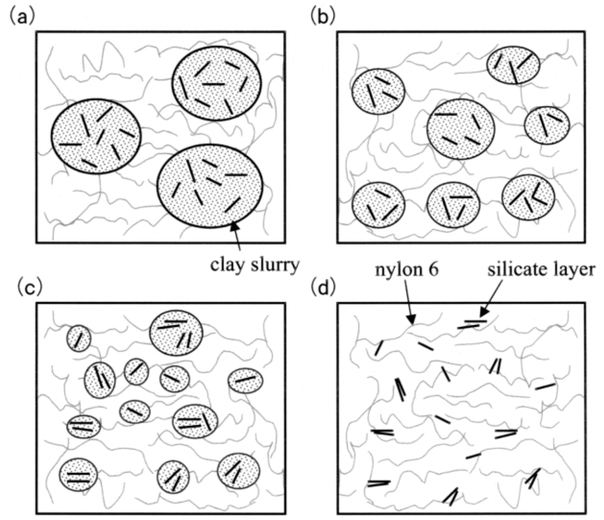

Fig. 5. Schematic figures depicting dispersion of the Na–montmorillonite silicate layers of the slurry into nylon 6 during compounding.

3.2. Study of properties

The properties of the samples are summarized at Table 1. Relative viscosity of the NCH-CS was almost equal to that of neat nylon 6, thus hydrolysis of nylon 6 did not nearly occur in the compounding process using the clay slurry. It is thought that hydrolysis of nylon 6 was prevented by removing the water quickly under vacuum from the vent.

Tensile and flexural moduli of the NCH-CS were 28 and 14% higher than those of neat nylon 6, respectively. Tensile and flexural strength of the NCH-CS were also 28 and 12% higher than those of neat nylon6, respectively. The strength and modulus of the NCH-CS were superior to those of neat nylon 6. The NCH-CS, loaded with only 1.6 wt% clay, was much improved in strength and modulus as well as the conventional NCH-OC. Meanwhile, Izod impact strength of the NCH-CS was 12% lower compared to neat nylon 6 as well as the NCH-OC. Heat distortion temperature (HDT) of the NCH-CS was 102 °C. The HDT was much higher than that of neat nylon 6, but it was lower than that of the NCH-OC. Gas permeability of the NCH-CS was 31% lower than that of neat nylon 6. Gas barrier effect caused by the dispersed silicate layers in the NCH-CS was almost equal compared to that of NCH-OC.

4. Summary

We reported a novel compounding process using the Na–montmorillonite water slurry for preparing the NCH consisted of nylon 6 and Na–montmorillonite. The Na–montmorillonite silicate layers exfoliated and dispersed homogeneously at nanometer level in the NCH-CS. With only 1.6 wt% clay silicate layers loading, its strength, modulus, and heat distortion temperature were much higher than those of neat nylon 6, though its impact strength was lower. The properties of the NCH-CS were nearly equal to those of the conventional NCH-OC except for heat distortion temperature. We are in progress to apply this novel compounding process using the clay slurry to other polymer resins for preparing various kinds of polymer/clay nanocomposites.

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