

SYNTHESIS AND CHARACTERIZATION OF ORGANOMONTMORILLONITE AND POLYAMIDE 66/MONTMORILLONITE NANOCOMPOSITES*

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Abstract The montmorillonites (MMTs), layered, smectite-type silicates, were premodified by two different methods prior to the polymer melt intercalation. In one case MMTs were modified with cetyltrimethylammonium bromide (CTAB), and termed as organomontmorillonites (OMMTs); in the other case MMTs were modified by nylon, and the products were called modified montmorillonites (MMMTs). The effects of CTAB and nylon on the MMTs were investigated by using TG and WAXD. The results show that interlayer spacings of CTAB and nylon modified MMTs are larger than that of sodium MMTs. Then, polyamide 66 (PA 66)/MMT nanocomposites were obtained through the method of melt intercalation of polymers. The nanocomposites were characterized by WAXD, TEM and Molau experiments. The results indicate that the MMTs disperse homogeneously in the PA 66 matrix. The mechanical properties of nanocomposites, such as tensile properties and flexural properties, were also measured and show a tendency to increase with increase of MMT content and reach the maximum values at 5phr MMT content. The heat distortion temperature (HDT) of the nanocomposites (7 phr) is about 32 K higher than that of pure PA 66.

Keywords Montmorillonite, Polyamide 66, Nanocomposites. Melt intercalation

INTRODUCTION

In recent years, organic-inorganic nanometer composites have attracted great interest of many researchers since they frequently exhibit unexpected hybrid properties synergistically derived from the two components^[1–8]. One of the most promising composite systems would be hybrids based on organic polymers and inorganic clay minerals consisting of silicate layers^[3–8]. Polymer/layered-silicate hybrids — nanocomposites — become possible which achieve impressive enhancements of material properties compared to those of the pure polymers, especially when these properties depend on the surface area of the filler particles. Small amounts (typically, less than 5%) of nanometer-thin layered inorganic fillers give rise to the same level of mechanical and thermal improvements as are typically achieved with loadings of 30%–50% of micron-sized fillers. Examples of such material enhancements are increased thermal stability, improved mechanical properties, decreased permeability to gases and liquids, and better resistance to solvents.

Sodium montmorillonite (Na-MMT) is a smectite-type silicate mineral composed of extremely small crystalline particles. It belongs to the smectite family. Its structure consists of two fused silica tetrahedral sheets sandwiching an edge-shared octahedral sheet of aluminum hydroxide (Fig. 1 and Fig. 2). Stacking of the layers by weak dipolar or Van der Waals forces leads to interlayers or galleries between the layers^[9]. The galleries are normally occupied by inorganic cations (Na^+ , Ca^{2+}), balancing the charge of the oxide layers. These cations are readily ion exchanged with a wide variety of positively charged species.

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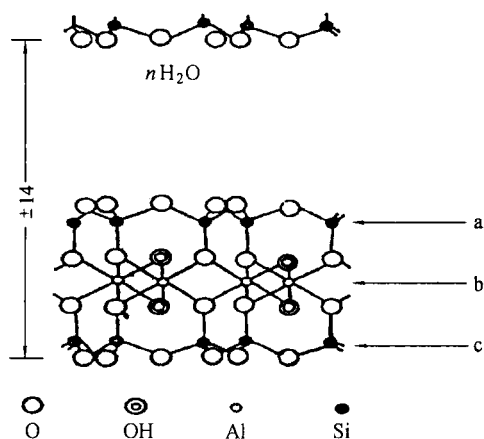


Fig. 1 Structure of montmorillonite crystal

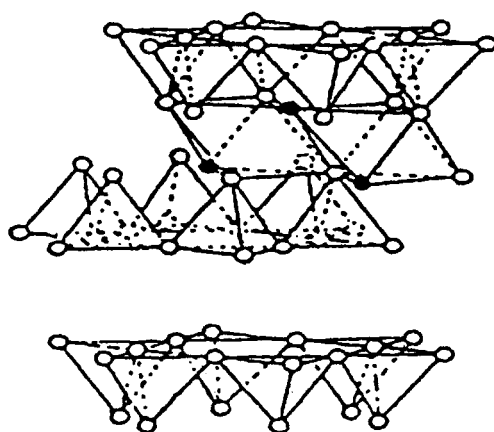


Fig. 2 Ideal crystal structure of montmorillonite

MMT has a high swelling capacity, which is essential for an efficient intercalation of the polymer. Because of its hydrophilic behavior, MMT often must be chemically treated in order to make it organophilic and compatible with the polymer matrix. The modification of the interlayers' surfaces is realized by replacing the hydrophilic Na^+ and Ca^{2+} exchangeable cations of the native clay with more hydrophobic anions. The modified clay is called the organomontmorillonite (OMMT).

At present, organic/inorganic nanocomposites are prepared mainly via two methods: (I) *In situ* intercalation polymerization^[10–13], which is a method whereby nanometer scale inorganic filler or reinforcements are dispersed in the monomer first; then, this mixture is polymerized using a technique similar to bulk polymerization. It is obvious that the most important factors that affect the properties of composites are the dispersion and the adhesion at the polymer and filler interfaces^[10, 14, 15]. Inorganic particles may disperse homogeneously in the polymer matrices when they are premodified by a coupling agent. (II) Polymer intercalation, which can be divided into solution intercalation and melt intercalation. Solution intercalation utilizes the method of growing hybrid crystallites of polymers and inorganic components from a common solution or dispersion^[16]. However, both *in situ* polymerization and solution intercalation of polymers have associated drawbacks. *In situ* polymerization works for very specific systems and conditions, and solution methods often result in the intercalation of small molecules (such as organic solvents or water) rather than the desired macromolecule into

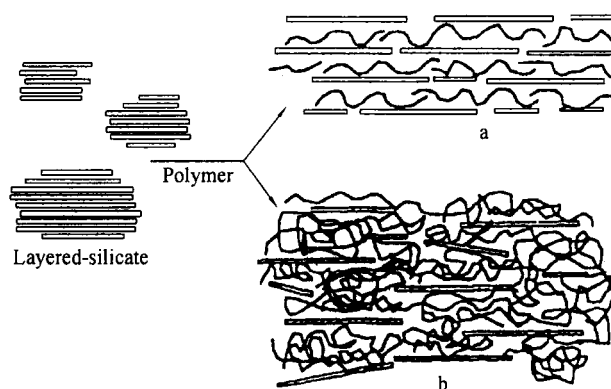


Fig. 3 A conceptual picture of melt intercalation

a) Single polymer layer intercalates in the silicate galleries

b) Composites obtained by exfoliating of the silicate particles and dispersion in a continuous polymer matrix

the inorganic. Giannelis advanced a new and promising technique of direct melt intercalation of polymers in layered silicates^[17]. With this methodology, a mixture of silicate powder and polymer is heated above the glass transition temperature of the polymer, and intercalation of the polymer chains into the galleries between the silicate layers takes place. The galleries are expanded to accommodate the polymer layers, giving rise to a new characteristic dimension of the hybrid material that remains constant over time (Fig. 3).

In general, two idealized polymer/layered-silicate structures are possible: *intercalated* and *exfoliated*. The greatest enhancement of properties was observed for exfoliated nanocomposites. This structure consists of individual nanometer-thick silicate layers suspended in a polymer matrix resulting from extensive polymer penetration and delamination of the silicate crystallites. In contrast, polymer penetration resulting in finite expansion of the silicate crystallites produces intercalated hybrids consisting of well-ordered multilayers with alternating polymer/silicate layers and a repeat distance of a few nanometers. In practice, many systems fall short of the idealized exfoliated morphology. More commonly, *partially exfoliated* nanocomposites, containing small stacks of 2–4 layers uniformly dispersed in the polymer medium, are obtained. These *partially exfoliated* structures can be associated with inhomogeneities (size and composition) existing in the natural smectites or arise from processing factors. Nevertheless, these systems may still exhibit substantial physical property enhancements^[18].

Polyamide resins have been widely used as injection and extruding molding materials — particularly for parts of automobiles and electrical goods — because the molded materials have excellent mechanical properties^[19]. Polyamide has been successfully reinforced by using glass fiber and other inorganic additives^[19]. In these composites, the polymer and additives are not homogeneously dispersed on the microscopic level. In 1987, the unparalleled ability of smectite clays to boost the mechanical properties of polyamide 6 (PA6) was first demonstrated in a stunning example by Toyota researchers^[4, 5, 20]. However, another kind of polyamide, polyamide 66 (PA 66) has not been reported to be reinforced by layered-silicates. In this article, we employed melt intercalation to prepare PA 66/montmorillonite nanocomposites. The effects of the CTAB and nylon on the MMTs and the properties of nanocomposites such as their mechanical properties were characterized to show the efficiency of this method.

EXPERIMENTAL

Materials

The montmorillonite (MMT) used in this experiment was supplied by the Institute of Chemical Metallurgy, Chinese Academy of Sciences. MMT is a natural clay mineral with a cation exchange capacity of 100 meq/100 g. In 1 L of water, MMT (35.0 g) was dispersed at room temperature (3.38% dispersion in water). PA 66 with a relative viscosity of 3.22 was purchased from China Shenma Group Nylon 66 Salt Co. Ltd. Cetyltrimethylammonium bromide was purchased from Tianning Chemical Reagent Co. Ltd. of Jining City Qinghai Province in China.

Preparation of Composites

The surfaces of the MMTs were premodified by two different methods prior to the polymer melting intercalation. In one of them MMTs were first modified with CTAB, then, the modified MMTs were washed and filtered under vacuum and we termed them as organomontmorillonites (OMMTs); in the other MMTs were modified with nylon, and the products were called modified montmorillonites (MMMTs). MMMTs were washed with water at 80°C to remove the remaining nylon and dried under vacuum at 100°C for 12 h.

The pellets of PA 66 and MMMT were melt-blended at 260–280°C using TE-34 twin-screw extruder to yield the composites. The TE-34 twin-screw extruder was purchased from the Institute of Extrusion Machines, Institute of Chemical Machines, Department of Chemical Industry of China. The obtained strands were pelletized and dried under vacuum at 90°C. The dried pellets of the composites were injection-molded into test pieces for mechanical tests using an HTF-80-Wz injection molder (Haitian Co. Ltd. of Ningbo City). The temperatures of the cylinders were 260–280°C and that of the mold was 30°C. The PA 66/unmodified-MMT composites can also

be prepared by this method.

Characterization

Thermogravimetric analysis (TGA) was performed using a Netzsch TG209 instrument with a heating rate of 10 K/min and a heating range from 30°C to 600°C under N₂ atmosphere. X-ray diffraction (WAXD) patterns were recorded by monitoring the diffraction angle 2θ from 1.4 to 20 degree on a Rigaku D/MAX-IIIB X-ray diffractometer using CuK α radiation ($\lambda = 0.154$ nm) operated at 35 kV and 30 mA. The scanning rate is 4°/min. The Molau experiments were performed by dissolving 0.5 g composites in 5 mL formic acid. Their emulsification phenomenon was observed under microscope after standing for a week. Transmission electron micrographs were obtained with a JEM-100SX using an acceleration voltage of 80 kV.

Mechanical Tests

The tensile and flexural tests were carried out on a CMT5104 universal testing machine (Shenzhen Sans Testing Machine Co. LTD.) according to ASTM D638-97 and ISO178: 1993(E), respectively. The tensile testing was performed at a speed of 5 mm/min and the flexural testing at a speed of 2 mm/min. Notched impact tests were carried out on a XJU-22 impact machine according to ISO180: 1993. Heat distortion tests were carried out on a XWB-300G heat distortion machine (Chengde Testing Factory Hebei) according to ISO75-2: 1993(E).

RESULTS AND DISCUSSION

The Heat Resistance and the Gallery Height of OMMT and MMMT

Figure 4 shows the results of TG and DTG of the native MMT, OMMT and MMMT. As shown in Fig. 4(A), the pristine Na-MMT has a loss of 3.2% in weight within the temperature range of 20–600°C, while OMMT and MMMT lose 33.43% and 49.12%, respectively. These considerable weight losses of OMMT and MMMT are regarded as the loss or decomposition of CTAB and nylon intercalated between the interlayers of clay or adsorbed by the surface of clay. Fig. 4(B) shows the decomposition temperatures of OMMT are 254.4°C and 268°C, while that of MMMT is 337.7°C.

Since the decomposition temperature of MMMT is higher than the processing temperature, MMMT can be used as the reinforcer for PA 66. Because of the decomposition of CTAB, there are plenty of detrimental decomposition products in the matrix, which will impair the mechanical properties of composites if we select OMMT as the reinforcer. Therefore, we should choose MMMT to reinforce PA 66. Besides, nylon is more compatible with the matrix than CTAB, so nylon will perform a role of interfacial agent. That is, the molecule of nylon can reduce the polarity of layers of MMT through reactions between the functional groups of those two kinds of material. The outstanding compatibility of nylon and PA 66 can improve the interfacial structure of the composites. Thus, MMMT can improve the properties of PA 66/MMMT nanocomposites.

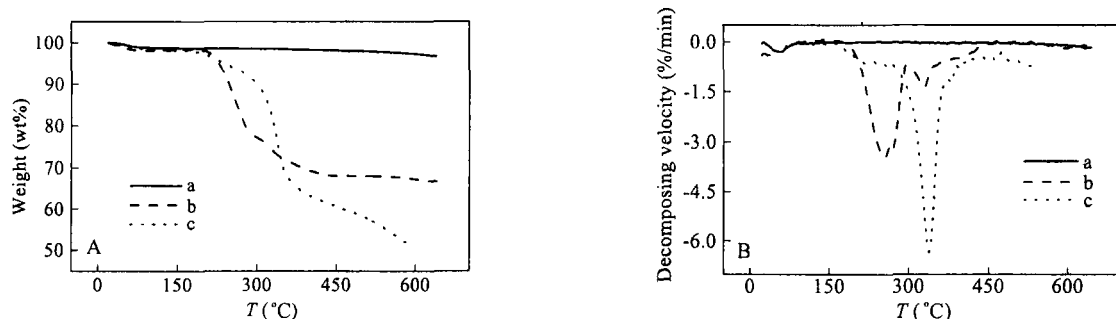


Fig. 4 The thermogravimetric curves and the derivative thermogravimetric curves of (a) Na-MMT; (b) OMMT; (c) MMMT

The periodic intercalated structure can be quantified through powder WAXD. Figure 5 shows the X-ray diffraction intensity curves of MMT, OMMT, MMMT and a kind of nanocomposite. The gallery height was

obtained from the peak position of the curve according to the Bragg equation:

$$2d/\sin\theta = \lambda \tag{1}$$

where, d , the average interlayer spacing of the silicate; 2θ , the diffraction angle; λ , the wavelength of the incident X-ray ($\lambda = 0.154 \text{ nm}$).

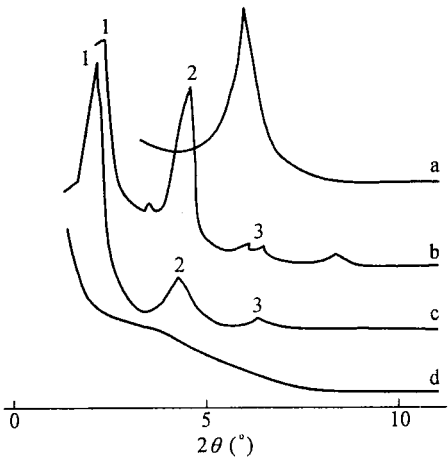


Fig. 5 WAXD patterns of (a) Na-MMT;(b) OMMT; (c) MMT and (d) nanocomposite (MMT content: 9.0 phr)

Na-MMT exhibits a single peak at about 5.46° , while the samples of OMMT, MMT show three characteristic peaks at 2θ values of 2.1° , 2.28° , 4.62° and 2.26° , 4.58° , 6.76° , which, in turn, correspond to three diffraction peaks of crystal structures of MMT layers. Thus, MMT, OMMT and MMT have interlayer spacings of 1.62 nm, 4.20 nm and 3.91 nm, respectively. The gallery heights of OMMT and MMT expand for the reason that some bulky organic ions replace the Na^+ and Ca^{2+} exchange cations of the native clay.

Dispersibility of the Clay in PA 66

To study the intercalation between the montmorillonite layers and the matrix, we performed the Molau experiments. Figure 6 shows one of the results of the experiments. The MMTs of the nanocomposites disperse in formic acid to form a well-distributed and stable colloid. This indicates that there exists a strong intercalation between the MMTs and the PA 66 matrix.

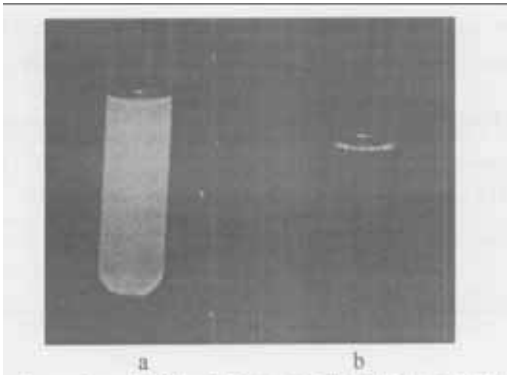


Fig. 6 The dispersive stability of formic acid solutions containing (a) PA 66/MMMT nanocomposite(MMT content:5.0 phr) and (b) PA 66

The WAXD results of the nanocomposite are also shown in Fig. 5 curve (d). However, in the range of $2\theta = 1.4^\circ\text{--}10^\circ$, no peak was observed on curve (d). That phenomenon can be attributed to two different kinds of

situations. One of them is that the MMT content of that sample is so low that the diffracted intensity is too weak to show a diffraction peak. The other is that layers of MMT have been exfoliated into the matrix, so the 2θ value of the diffraction peak is smaller than 1.4° or does not show a diffraction peak on the curve. According to the TEM photograph, which will be discussed in the next paragraph, the nanocomposite is partially exfoliated, so we can conclude that the low content of MMT is responsible for such a phenomenon.

More direct evidence for the formation of a true nanocomposition is provided by transmission electron microscopy of an ultramicrotomed section. Figure 7 shows a TEM photograph of the PA 66/MMMT nanocomposites, where the dark lines are the cross sections of silicate layers of 10–50 nm thickness. Some of the particles of montmorillonite layers were dispersed at the nanometer level — 7–15 nm. As is evident from this picture, the polymer chains of PA 66 can not only intercalate into the montmorillonite layers to make them expand but also make them exfoliate into nanoscale dispersion in the matrix. However, there are still signs of the original ordering of the silicate layers. For this reason, we interpret the micrograph as a section of a partially exfoliated nanocomposite.

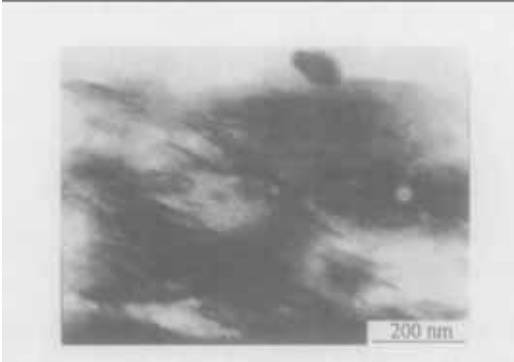


Fig. 7 The transmission electron micrograph of the PA 66/MMMT nanocomposites (MMT content:5.0 phr)

Mechanical Properties of PA 66/MMMT Nanocomposites

Table 1 summarizes the mechanical properties of PA 66/MMMT nanocomposites. The tensile modulus of PA 66/MMMT nanocomposites at 23°C is 58% higher than PA 66 and the strength substantially increases. This is because the nanocomposites have good dispersion and interfacial adhesion, so when they are subjected to tensile stress, the force is transferred to silica particles through the interphase and the silica particles become the receptor of the tensile force. When the tensile stress applied on the composites is beyond a critical value, damage occurs in the composite resulting from the destruction of the interphase between PA 66 and the silicas. The heat distortion temperature (HDT) — an index of heat resistance — of PA 66/MMMT nanocomposites increases by 23.2 K (mont- morillonite content: 5.0 phr) and almost 32 K (montmorillonite content: 7.0 phr).

Table 1. Properties of PA 66/MMMT nanocomposites

Properties	Tensile strength (MPa)	Tensile modulus (GPa)	Flexural modulus (GPa)	Impact strength* (kJ/m ²)	Heat distortion temperature (°C)
PA 66	74.61	2.76	2.53	3.63	57.2
PA 66/MMT (6 phr)	—	—	—	3.00	63.0
PA 66/MMMT (5 phr)	84.21	3.80	3.08	3.23	80.4

* Notched Izod impact strength

CONCLUSION

Melt intercalation of polymers is a good method for the preparation of inorganic/organic nanocomposites which is simple and environmentally friendly. We prepared PA 66/MMMT nanocomposites by this method. The montmorillonite layers of PA 66/MMMT nanocomposites dispersed homogeneously in the PA 66 matrix. And PA 66/MMMT nanocomposite has improved mechanical properties.

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