Research Article

Yiming Sun, Jie Mei, Huan Hu, Jiru Ying, Weiye Zhou, Xipo Zhao*, and Shaoxian Peng

In-situ Polymerization of exfoliated structure PA6/organo-clay nanocomposites

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Abstract: Montmorillonite (MMT) was modified with cetyl trimethyl ammonium bromide (CTAB) to obtain organo-montmorillonite (OMMT) by stirring and pulsed ultrasonic mixing. Polyamide 6 (PA6)/OMMT nanocomposites were then prepared via in-situ polymerization. The resulting OMMT and PA6/OMMT nanocomposites were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM) and scanning electron microscopy (SEM). The results suggested that the OMMT interlayer distance was greatly increased to 3.13 nm due to CTAB being intercalated into the MMT galleries. The OMMT interlayer distance was further enlarged to 10–20 nm during the polymerization process. The OMMT layers were exfoliated into nanoscale layers and uniformly dispersed in the molten ϵ -caprolactam and PA6 matrix, and exfoliated structure nanocomposites were formed.

Keywords: Polyamide 6 (PA6); Organo-montmorillonite (OMMT); In-situ; Nanocomposites

1 Introduction

Since the development of PA6/clay nanocomposites by Toyota researchers [1–5], polymer layered silicate nanocomposites have attracted considerable interest from a wide range of scientific and practical viewpoints due to their unexpected hybrid properties synergistically resulting from their parent components. Polymer layered silicate nanocomposites synthesized by adding just a small frac-

tion of clay to a polymer matrix exhibit dramatic increase in mechanical properties as well as gas barrier properties, the reason being generally attributed to the uniform dispersion of the 1-nm thick clay silicate layers in the polymer matrix [6]. Polymer/clay nanocomposites have been produced via either in-situ polymerization or melt intercalation [7–9]. The in-situ polymerization of monomer in the clay galleries, so called intercalation polymerization, is one of the very useful methods to synthesize polymer/clay nanocomposites.

PA6 is a type of aliphatic polyamide with good performance. The main applications of PA6 are for fiber, film and a range of injection molded products. PA6 crystallizes very rapidly, usually with a crystallinity of more than 30–40%. Therefore, PA6 still has a high modulus above the glass transition temperature (T_g), at the same time with high hardness (for thermoplastic materials) and low production cost [10].

The type of PA6/clay nanocomposite based on montmorillonite (MMT) is one of the most promising layered silicate based polymer nanocomposites [11–15]. PA6/MMT nanocomposites have superior performance of physical and mechanical properties. They have been extensively used in areas of electronics, transportation, packaging, etc.

The layered structure of MMT is constructed of two silica tetrahedral sheets to an edge-shared octahedral sheet of either aluminum or magnesium hydroxide [3]. On account of the hydrophilic nature of MMT, its organo-modification is an important step in the preparation of polymer/MMT composites to generate a micro-chemical environment for the intercalation of polymer or monomer. The intercalation of organic materials increases the spacing distance between the silicate sheets. The organic montmorillonite (OMMT) can be broken down into its nanoscale building blocks and uniformly dispersed in the polymer matrix to form exfoliated nanocomposites during the polymerization process.

Many works [16–18] have proved that complete exfoliation of silicate layers is the key to achieving polymer/clay nanocomposites with high performance. Therefore, the intercalation and exfoliation behavior of organo-

***Corresponding Author: Xipo Zhao:** Hubei Provincial Key Laboratory of Green Materials for Light Industry, Collaborative Innovation Center of Green Light-weight Materials and Processing, Hubei University of Technology, Wuhan 430068, China; Email: xpzhaol23@163.com

Yiming Sun, Jie Mei, Huan Hu, Jiru Ying, Weiye Zhou, Shaoxian Peng: Hubei Provincial Key Laboratory of Green Materials for Light Industry, Collaborative Innovation Center of Green Light-weight Materials and Processing, Hubei University of Technology, Wuhan 430068, China

montmorillonite in ϵ -caprolactam and PA6 matrix was studied. In this paper, sodium montmorillonite (Na-MMT) was modified with cetyl trimethyl ammonium bromide (CTAB) as intercalation reagent to obtain organic-montmorillonite (OMMT) by ion exchange reaction with stirring and pulsed ultrasonic mixing. The exfoliated PA6/OMMT nanocomposites were prepared via in-situ intercalative polymerization. In the present research, a super-dispersed phenomenon in the ϵ -caprolactam and PA6/MMT nanocomposite samples is shown. The phenomenon was characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM) and scanning electron microscopy (SEM).

2 Experimental

2.1 Materials

Sodium montmorillonite (Na-MMT) with a cation-exchange capacity of 110 mequiv / 100 g and interlayer distance of 1.27 nm was purchased from Zhejiang Fenghong New Material Co., Ltd. Cetyl trimethyl ammonium bromide (CTAB), isopropanol and HCl (analytical reagent grade) were purchased from Sinopharm Group Chemical reagent Co., Ltd. ϵ -caprolactam (industrial reagent grade) was purchased from the Baling company division of China Petroleum and Chemical Co., Ltd.

2.2 Preparation of OMMT

1.44 g of CTAB and 0.5 g of isopropanol were dissolved in 60 g deionized water. 3.6 g Na-MMT was dispersed in 120 ml deionized water under vigorous stirring to form a uniformly dispersed mixture, then the pH value was regulated to 6 with HCl, and the CTAB and isopropanol solution was added. The mixture was then stirred for 1 h at 70°C and subjected to pulsed ultrasonic mixing for 15 minutes. The mixture was filtered and repeatedly washed with deionized water to remove excess intercalative reagent until there was no precipitation observed in the wash water tested with 0.1 mol/L AgNO₃ solution. The product was then vacuum-dried to constant weight at ambient temperature and ground into power (diameter about 75 μ m) to obtain the organic-montmorillonite (OMMT).

2.3 Synthesis of PA6/MMT nanocomposites

OMMT (3.5wt%) and deionized water (5wt%) was added to the ϵ -caprolactam/catalyst system, the mixture was stirred at 100°C for 30 minutes until the catalyst and montmorillonite were dispersed in the caprolactam melt. Then the mixture was reacted under 240°C for 5 hours in the sealed reactor. Subsequently, the system was vented and then vacuumed, and heated to 250°C for 2 hours under vacuum conditions to obtain PA6/OMMT nanocomposites. The PA6/Na-MMT composites were prepared using the same procedure.

3 Characterizations

The interlayer distances of the Na-MMT, OMMT and PA6/MMT nanocomposites were obtained by X-ray diffraction (XRD) using a Rigaku D/Max 2500 X-ray diffractometer with CuK α radiation ($\lambda = 0.154$ nm) and diffraction angle from 1-10°, operated at 30 kV and 40 mA.

The interlayer spacing and dispersibility of the OMMT and PA6/OMMT nanocomposites were studied by means of transmission electron microscopy (TEM) using a Hitachi H-800, operated at an acceleration voltage of 100 kV.

Scanning electronic microscope (SEM) photographs of the MMT powder were taken on a Hitachi S-570. Raw material surfaces were sputter coated with gold before measurements. The acceleration voltage was 20 kV.

The tensile properties of PA6 and PA6/OMMT nanocomposites were tested in accordance with ISO 527-2 on a universal tensile machine (CMT 4000, Metis Industrial Systems (China) Co., Ltd) at a rate of 20 mm/min.

The PA6 and PA6/OMMT nanocomposites were tested for flexural performance in accordance with ISO 178 using the CMT 4000 machine.

The notched impact strength of PA6 and PA6/OMMT nanocomposites was carried out in accordance with ISO 180 using a simple beam impact tester (XJJD-5, Chengde Jinjian Testing Instrument (China) Co., Ltd).

The temperature of deflection under load (HDT) of PA6 and PA6/OMMT nanocomposites was tested based on ISO 75-2 at a bending stress of 0.45 MPa and heating rate of 2°C/min (RV-300B, Jiangcheng Tianyuan Machinery (China) Co., Ltd).

4 Results and Discussion

4.1 The interlayer distance of MMT and PA6/MMT nanocomposites

The change of the interlayer distance of MMT and PA6/MMT composites can be detected by XRD, as are shown in Figure 1. It reveals that the diffraction peaks of OMMT and PA6/MMT composites shift in the low angle direction after the ion exchange reaction. The characteristic diffraction peaks of Na-MMT and OMMT are clearly observed at 2θ of 6.95° and 2.82° , respectively, corresponding to the (d001 value) diffraction of the layer structure of the Na-MMT and OMMT, respectively. The interlayer distance can be calculated according to the Bragg equation to be 1.27 nm for Na-MMT and 3.13 nm for OMMT. This did not destroy the layer structure of the MMT, indicating that the basal spacing had been expanded due to CTAB molecules intercalating into the silicate layers of Na-MMT, which facilitated intercalation of ϵ -caprolactam into the galleries.

Figure 1: XRD spectra of MMTs and PA6/MMT nanocomposites

Figure 1 shows the XRD patterns of PA6/Na-MMT and PA6/OMMT nanocomposites. The characteristic diffraction peaks of PA6/Na-MMT are indicated at 2θ of 4.09° and 5.9° . Based on the Bragg equation, the interlayer distances of the Na-MMT are 2.16 nm and 1.5 nm, indicating that the order structure of Na-MMT still remained in the composites, the interlayer distance of Na-MMT was evidently not changed, and the layers were not exfoliated during the in-situ polymerization process. However, the

characteristic peak disappears entirely in the range of 1° – 10° in the XRD pattern of the PA6 OMMT nanocomposites, suggesting that ϵ -caprolactam intercalated into OMMT galleries. The ϵ -caprolactam molecules formed PA6 macromolecules during the polymerization process and then the layered structure of the MMT was destroyed. The results also indicated that the organo-modification of Na-MMT allows ϵ -caprolactam to be intercalated into the galleries and enlarge the gallery distance. The clay nanocomposites are commonly considered as exfoliated nanocomposites as the OMMT gallery distance in the nanocomposites is not less than 8.8 nm (corresponding to $2\theta=1.5^\circ$) [12]. These results illustrate that the layer structure of the OMMT was destroyed and the layers were completely exfoliated and uniformly dispersed at the nanoscale in the PA6 matrix.

4.2 The morphology of Na-MMT and OMMT

SEM micrographs (Figure 2, 3) showed the morphologies of Na-MMT and OMMT. The agglomerated particles of Na-MMT and OMMT were detected in the images. The morphology of Na-MMT is similar to that of OMMT, indicating that organo-modification by CTAB just enlarged the interlayer distance and did not change the Na-MMT structure. This is consistent with previous studies of XRD of MMT.

More details of the morphology of Na-MMT and OMMT were observed. The surface of OMMT is much more even and smooth, the dispersion of particles is more uniform, and the OMMT interlayer is unfolded like a petal, looser and softer than that of Na-MMT. These results indicate that the structure of interlayers was exfoliated due to intercalation of CTAB into the galleries during stirring and ultrasonic treatment in the organo-modification process.

4.3 TEM for the morphology of OMMT in ϵ -caprolactam

Figure 4 shows TEM image of OMMT in molten ϵ -caprolactam. The dark region and the bright field represent MMT particles and ϵ -caprolactam, respectively. It is clearly seen that the silicate layers were exfoliated on a nanometer scale, and also that the layers were greatly unfolded. In addition, the silicate layers displayed substantial flexibility, more like stacks of petals with some overlapping. These results indicate that the layers of MMT are unfolded and completely exfoliated into nanoscale layers. The OMMT exhibits good dispersion in the ϵ -caprolactam and the dispersion behavior is improved as the interlayer distance is increased.

Figure 2: SEM micrographs of Na-MMT

Figure 3: SEM micrographs of OMMT

Figure 4: TEM images of OMMT in molten ε-caprolactam

Figure 5: TEM image of PA6/OMMT nanocomposite (3.5 wt.% MMT)

4.4 TEM for PA6/OMMT nanocomposites

TEM could provide information in real space on the spatial distribution of the silicate layers in a local area in the composite. Figure 5 shows TEM image of the PA6/OMMT nanocomposite with 3.5wt% OMMT. The narrow dark lines represent individual silicate layers, the light regions represent the PA6 [3, 4]. It can be seen that the layers of OMMT were exfoliated into nanoscale layers and dispersed uniformly in the PA6 matrix. The exfoliated layers display some degree of flexibility. The thickness of individual dark lines is about 1.0 nm, and is in agreement with the known crystal thickness of a single silicate layer, 0.96 nm. The PA6/OMMT composites obtained are nanocomposites according to the definition of Vaia *et al.* [19]. Furthermore, the interlayer distance was greatly increased during in-situ polymerization due to PA6 chain intercalation, and is in the range of 10–20 nm, which is consistent with the results determined by XRD of PA6/OMMT composites. Generally speaking, the large interlayer distance would be an advantage of the intercalation of a monomer or polymer. This can lead to easy dissociation of MMT which would result in hybrids with better MMT dispersion. The interlayer distance was greatly enlarged due to the monomer and PA6 chains intercalating into the OMMT interlayer during the polymerization process. The stacked clay layers of OMMT were exfoliated into nanoscale layers and uniformly dispersed in the PA6 matrix. From these results, it was concluded that the MMT layers are randomly dispersed on a nanoscale in the PA6 matrix.

4.5 Mechanical properties of PA6/OMMT nanocomposites

The mechanical properties of PA6/MMT (3.5wt%) nanocomposites and PA6 were showed in Table 1. The results show that the PA6/MMT nanocomposite produced by one-step in-situ interpolation polymerization has better mechanical properties than PA6. The tensile strength was increased from 75 MPa to 100 MPa, an increase of 33.3%. The notched impact strength was increased from 4.2 KJ/m² to 9.2 KJ/m², an increase of 120%. Flexural strength increased from 125 MPa to 138 MPa, an increase of 10%, and flexural modulus increased from 2.8 GPa to 4.5 GPa, an increase of 60.7%. Using the one-step in situ interpolation polymerization process, MMTs were evenly dispersed in the PA6 substrate and had good compatibility with the PA6 substrate, thus realizing dispersion at the nanoscale. Because of the small size effect of nanocomposites and better interface performance, the material's comprehensive performance was greatly improved.

Table 1: Mechanical properties of PA6/MMT (3.5wt%) nanocomposites by one-step in-situ intercalation polymerization

	Standard	PA6	PA6/OMMT
Tensile strength (MPa)	ISO 527-2	75	100
Flexural strength (MPa)	ISO 178	125	138
Flexural modulus (GPa)	ISO 178	2.8	4.5
Charpy impact strength (KJ/m ²)	ISO 180	4.2	9.2

4.6 Heat deflection temperature (HDT) of PA6/OMMT nanocomposites

The static load was 0.45 MPa

The HDT is the temperature at which a polymer sample deforms under a specific load. This property is relevant to many engineering products. In general, adding clay to a polymer increases the stiffness of the material, which in turn affects its HDT. As shown in Table 2, the heat deformation temperature increased from 65°C to 142°C, an increase of 118%. From an engineering point of view, the application field of materials (automotive, aerospace, etc.) will be greatly expanded as the thermal deformation temperature of the material increases. Paz *et al.* [20] studied composite materials prepared with different grades of PA 6 and MMT, indicating an upward trend in HDT as the MMT content increased.

Table 2: HDT of PA6/OMMT nanocomposites

	Standard	PA6	PA6/OMMT
Heat deflection temperature (°C)	ISO 75-2	65	142

5 Conclusions

OMMT was prepared by stirring and pulsed ultrasonic mixing, and PA6/OMMT nanocomposites were successfully synthesized via in-situ polymerization. The OMMT interlayer distance was greatly enlarged from 1.27 nm to 3.13 nm and the layers were exfoliated. The layers of OMMT were unfolded in molten ϵ -caprolactam and uniformly dispersed in exfoliated PA6/OMMT nanocomposites. A super-dispersion phenomenon in the CTAB in molten ϵ -caprolactam system and exfoliated PA6/CTAB-OMMT nanocomposites was detected. The PA6/OMMT nanocomposites has excellent mechanical and thermal properties

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