Research Article

Preparation of Nanocomposite Based on Exfoliation of Montmorillonite in Acrylamide Thermosensitive Polymer

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Poly(*N*-isopropylacrylamide) (PNIPAM) was synthesized in the presence of AIBN as radical initiator. The structure of polymer was elucidated using IR, ¹H NMR, and ¹³C NMR spectroscopies and TGA thermogram. Exfoliated nanocomposite based on thermosensitive polymer (PNIPAM) was prepared utilizing montmorillonite (MMT) by solution blending. Its dispersion characteristics were investigated using SEM, X-ray diffraction, and particle size analysis. XRD showed exfoliation of MMT in polymer matrix above lower critical solution temperature (LCST). SEM indicated that polymer chains were dispersed among the layers of MMT. Particle size analysis showed two distinctive regions at 311 (31/5%) and 1160 (68/5%) nm.

1. Introduction

The production of clay-polymer nanocomposites is an active area of research which benefits from the high surface area ratio of nanoclay particles to greatly improve the thermo-mechanical properties of the polymer matrix, even with low filler contents [1]. The success in the development of clay-polymer nanocomposites requires two key conditions: first, achieving a correct dispersion of nanoparticles in the matrix in order to obtain a high fraction of interfacial clay-polymer region within the material, and second, controlling the interfacial interactions between silicate particles and the polymer matrix, so that highly interacting polymer chains can either intercalate between the silicate layers or even break the stacking of the basal planes to induce exfoliation [2–4].

The ultimate goal for the preparation of nanocomposites is to achieve a very high degree of dispersion (exfoliation) of the aggregates of layered silicates. However, perfect exfoliation of the aggregates of layered silicates is very difficult to

be achieved, if not impossible [5]. There are three ways of preparing nanocomposites, namely, (1) in situ polymerization of a monomer using an initiator tethered to the silicate surface or copolymerization of monomers by a silicate-anchored bifunctional initiator, (2) solution blending, and (3) melt blending [2].

It is well established that layered silicates (e.g., montmorillonite (MMT)) are hydrophilic [6, 7]. Therefore, they do not have chemical affinity with hydrophobic organic polymers and thus the two are incompatible.

Thermosensitive polymers [8], such as poly(*N*-isopropyl acrylamide) (PNIPAM) [9–11], exhibit a volume phase transition at a critical temperature, which causes a sudden change in the solvation state. Such polymers, which become insoluble and hydrophobic upon heating, have a lower critical solution temperature (LCST) [11].

PNIPAM is hydrophilic below the LCST (about 32°C) and there is no considerable interaction between polymer

SCHEME 1

and the suspended particles, but above LCST hydrophobic-hydrophobic interactions occur between polymer and particles, which lead to shrinkage of the polymer and sorption of suspended particles [12].

To our knowledge, some studies have been reported on the preparation of exfoliated MMT nanocomposites based on thermosensitive polymers [13, 14]. This paper aims to summarize the highlights of our findings from the investigation on exfoliation ability of PNIPAM as thermosensitive polymer using XRD and SEM techniques and particle size analysis.

2. Materials and Methods

Montmorillonite (MMT) nanoclay powder with cation exchange capacity of 92 meq/100 g of clay was provided by Southern Clay Products (under the trade name of Na-Cloisite, USA). The average dry particle size is $8\mu\text{m}$, composed of millions of individual platelets that only appear separately after a good dispersion in a polymer or a liquid dispersant. IR spectra were measured by a Shimadzu IR 460 spectrometer. ^1H and ^{13}C NMR spectra were measured with BRUKER DRX-500 AVANCE spectrometer at 500 and 125.8 MHz, respectively. XRD patterns were obtained at ambient temperature using a XRD 6000 Shimadzu diffractometer, at $1^\circ/\text{min}$ in a 2θ range between 2 and 24° using Ni-filtered Cu KR radiation. SEM images were obtained with VEGA//TESCAN—LMU, using an accelerating voltage of 25 kV. Mettler Toledo TGA/DSC 1 Star System was used for TGA analysis. Master sizer (Zen 3600 Malvern) was employed for particle size analysis.

2.1. The Procedure for the Synthesis of NIPAAm (1) [15]. Acryloyl chloride (0.4 mol) and isopropylamine (0.8 mol) were added to 15 mL ethyl acetate in a 100 mL reactor equipped with a magnetic stirrer. The reactor was placed in an iced water bath to control the reaction temperature at 0°C for 4 h. The mixture was filtered and the obtained filtrate solution remained 24 h in a refrigerator; after vacuum distillation at 80°C , the collected precipitate was filtered and dried at room temperature (r.t.).

2.2. The Procedure for the Synthesis of PNIPAM (3). A solution of NIPAAm (4 gr in 16 mL THF) and AIBN (0.5 gr) was magnetically stirred and refluxed at 70°C for 12 hrs under N_2 effluent. Precipitated solid was filtered and washed by 2×10 mL diethyl ether and dried at r.t. (3.76 g, 94%). IR (ν_{max} , cm^{-1}) (3) (KBr): 3277 (NH), 1680 (C=O). ^1H NMR (500 MHz, CDCl_3) δ : 1.12 and 1.13 (6H, 2d, $^3J_{\text{HH}} = 7.1$ Hz, 2 CH_3), 1.71 (1H, dd, $^2J_{\text{HH}} = 3.0$ Hz, $^3J_{\text{HH}} = 7.1$ Hz, CH_2), 1.84 (1H, dd, $^2J_{\text{HH}} = 5.2$ Hz, $^3J_{\text{HH}} = 7.1$ Hz, CH_2), 2.11 (1H, dd, $^3J_{\text{HH}} = 5.2$ Hz, $^3J_{\text{HH}}$

TABLE 1: Distinctive peaks of the stretching vibrations (cm^{-1}).

	O-H	C=O	Si-O-Si
MMT	3626	—	1100
PNIPAM	—	1680	—
PNIPAM/MMT	3630	1680	1080

= 7.1 Hz, CHCO), 3.73 (1H, m, CHN), 8.48 (NH). ^{13}C NMR (125.8 MHz, CDCl_3) δ : 19.1 and 19.3 (2 CH_3), 25.1 (CH_2), 29.6 (CH), 44.2 (CH-N), 174.6 (C=O).

2.3. MMT Exfoliation in Polymer (3) Matrix. A solution of 2 g PNIPAM (3) in water (1% w/v) was prepared at room temperature. Nanoclay mixture of MMT in water (0.1 g in 5 mL water) was added to the solution (60 ml) and mixed seriously. After 3 hours temperature was raised slowly to 70°C . At 32°C , turbidity of the mixture increased; however, no precipitate or flocculation was observed up to 70°C after 8 hours. A layer (200 microns) of suspended mixture was applied on a glass plate, water was evaporated at 20°C , and subsequently the residue (composition of 15% W/W of MMT/PNIPAM, theoretically) remained as a transparent film. In this paper, exfoliation ability of the thermosensitive polymer (3) was intended to evaluate in MMT-water suspension mixture at below and above LCST.

3. Results and Discussion

Polymerization of NIPAAm (1) in the presence of AIBN (2) as radical initiator led to formation of PNIPAM (3) in good yield (94%) (Scheme 1) [16, 17].

The structure of polymer (3) was elucidated by IR, ^1H NMR, and ^{13}C NMR spectroscopies. In IR spectrum, stretching vibration of NH and C=O groups appeared at 3277 and 1680 cm^{-1} , respectively. In ^1H NMR resonance of CHCO and CHN, polymer backbone was at 2.11 and 3.73 ppm, and resonance of NH moiety appeared at 8.48 ppm. ^{13}C NMR spectrum of product was in good agreement with corresponding polymer structure (3) (experimental).

An important key to obtain a polymer-clay nanocomposite is to achieve a satisfactory dispersion of the nanoclay in the polymer matrix. This requires an efficient interaction between nanoclay and matrix allowing the polymer chains to be inserted within the interlayer of the MMT structure leading to intercalated or exfoliated structures.

Polymer (3) was employed to prepare nanocomposite using MMT (experimental). Some investigations were carried out to investigate the existence, intercalation and/or

FIGURE 1: (a) TGA thermograph of (3), and (b) MMT/PNIPAM nanocomposite.

TABLE 2: TGA results of PNIPAM-copolymer and the organoclay/PNIPAM nanocomposite.

	PNIPAM	MMT/PNIPAM
Initial weight loss (°C)	95–106	97–106
%W/W loss (weight loss)	9.09	9.86
The first degradation °C	225–415	320–415
%W/W loss (final degradation)	86.11	75.00

exfoliation of organoclay layer in PNIPAM matrix. Considering IR spectra, distinctive peaks of organoclay, PNIPAM, and MMT/PNIPAM nanocomposite showed the presence of organoclay in PNIPAM-matrix (Table 1).

The results of TGA thermograms of PNIPAM (Figure 1(a)) and MMT/PNIPAM (Figure 1(b)) have been summarized in Table 2. Initial weight loss of (3) and nanocomposite occurred at about 100°C, which was due to departure of H₂O imbedded in the polymer. In the second phase, degradation of (3) and nanocomposite commenced at 225 and 320°C for, respectively, and finalized at 415°C for both of them. Approximately the whole (3) degraded at less than 430°C. However, 15.14% of the composite remained unchanged up to 600°C which was due to MMT. This result was in good agreement with theoretical value (experimental). On the other hand, dispersion of MMT in PNIPAM improved the heat stability of polymer 95°C (225 to 320°C) (Table 2).

Particle size analysis showed two distinct regions at 311 and 1160 nm with 31/5% and 68/5% intensities which were due to MMT and PNIPAM particles, respectively (Figure 2). Although particle size distribution was not completely in nanotechnology scale (less than 100 nm), it is roughly acceptable to be considered as nano dispersion.

The surface morphology and external structure of PNIPAM/MMT were investigated by scanning electron micrographs which are given in Figure 3. The surface of PNIPAM/MMT had a smooth and relatively homogeneous appearance. As clearly seen here, the surface of the exfoliated MMT had a layer shape. The size of the pores between the clusters as shown in Figure 3 was variable (e.g., 422, 960, and 2134 nm). It is evident that layers of MMT had been exfoliated in PNIPAM matrix.

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FIGURE 2: Particle size analysis of PNIPAM/MMT suspension.

Dispersion characteristics of solution-blended nanocomposite were studied based on XRD patterns. It can be seen in Figure 4 that the XRD patterns of the nanocomposite showed reflection peaks at 20.1 suggesting that this composite had no dispersion of MMT aggregates below LCST. In spite, above LCST for MMT-hybrid material, MMT characteristic peaks decreased in intensity or even disappeared, meaning a high degree of intercalation and/or exfoliation of the silicate layers in PNIPAM matrix [18]. An explanation for the observed exfoliation is that above LCST intercalated PNIPAM chains had to change their conformation and this provided sufficient energy to exfoliate MMT layers.

4. Conclusions

PNIPAM was synthesized via free radical polymerization and its exfoliation ability has been evaluated in MMT-water suspension. Surprisingly in spite of the common coagulation character of thermosensitive polymers, homogeneous suspension of polymer and MMT was formed and was stable within a week. An explanation may be that tendency of thermosensitive polymers to change their conformation above LCST after intercalation to layers of MMT forced the clay to be exfoliated in PNIPAM matrix. Scanning electron microscopy (SEM) images, X-ray diffraction (XRD), and size distribution spectra were carried out and showed that MMT had been exfoliated in polymer matrix. It is suggested to

FIGURE 3: SEM image of (a) PNIPAM and (b) exfoliated MMT dried film.

FIGURE 4: XRD patterns of PNIPAM/MMT hybrid (a) below LCST and (b) above LCST.

use modified clay, named organoclays, to achieve perfect exfoliated nanocomposite.

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