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ORIGINAL PAPER

Synthesis and characterization of polyvinyl acetate/montmorillonite nanocomposite by in situ emulsion polymerization technique

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Abstract Exfoliated polyvinyl acetate/montmorillonite nanocomposite (PVAc/MMT) was prepared via in situ emulsion polymerization. The resulting PVAc with various organophilic MMT contents was investigated. In the nanocomposite latex preparation, sodium lauryl sulfate (SLS), ammonium persulfate (APS), and poly (vinyl alcohol) (PVA) are used as anionic emulsifier, conventional anionic initiator, and stabilizer, respectively. The samples were characterized using elemental analysis, X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM). The XRD and AFM results demonstrate that the MMT well dispersed at molecular level in the PVAc matrix. Thermal properties of the nanocomposite were studied by using differential scanning calorimetric analysis (DSC). The exfoliated PVAc/MMT nanocomposite showed a higher glass transition temperature and a better thermal stability compared to the pure PVAc.

Keywords Nanocomposite · Emulsion polymerization · Polyvinyl acetate · Montmorillonite · Exfoliation · Thermal properties

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Introduction

Polymer–inorganic nanocomposites are an attractive set of organic–inorganic materials which have emerged as a new class of advanced materials containing a low inorganic filler concentration. The most important advantage of synthesis polymer–inorganic nanocomposites is related to combination of the properties of inorganic material (e.g., rigidity and thermal stability) with the organic polymer (e.g., flexibility, ductility, and processability) [1–4].

The traditional polymer–inorganic microcomposites containing micron size inorganic fillers often show improved modulus and yield strength, and a corresponding increase in heat distortion temperature. However, enhancement in the desired materials properties is often accompanied by losses in other properties such as ductility and toughness [5]. The basic feature of polymer nanocomposites is that the nano-size fillers lead to increase in interfacial area as compared with traditional composites [6]. Actually, nano-sized fillers have high potential for use in polymer–inorganic nanocomposites in which enhanced thermal and mechanical properties are required. A significant amount of work has been focused on the synthesis and characterization of these nanocomposites for better understanding of the mechanism of intercalating polymers in layered inorganic hosts to fabricate modified polymer–inorganic nanocomposites. In the polymer–inorganic nanocomposites, strong molecular interactions such as chemical bonds, hydrogen bonding, and electrostatic forces cause to fabricate some novel nanocomposites with improved optical and electrical properties [7–9]. The properties of the synthesized polymer–inorganic nanocomposites are affected by the type, molecular structure, and size of inorganic fillers as well as the synthesis conditions. Therefore, nanostructured polymer–inorganic composites may be much different from the conventional composites with incorporation of a variety of additives in the polymer matrices [10, 11].

Nanoclays have been widely used as an inorganic reinforcement for polymer matrices with nanoscale dispersion of the inorganic phase within the polymer matrix [2–4]. Three approaches have been employed to fabricate polymer–clay nanocomposites, such as in situ polymerization [12], melt compounding [13], and solution blending [14]. In general, in situ polymerization and melt compounding have been proved to be conventional and efficient methods for preparing polymer matrix nanocomposites. The exfoliated structure of layered silicates in nanocomposites was studied to get the high performance polymer matrix nanocomposites [15].

The desired properties of polymer–clay nanocomposites can be enhanced by complete exfoliation nanoscale dispersion of clay in the polymer matrix. However, it is found that this is not always reproducibly achieved using existing methods for synthesis of nanocomposites [16]. Generally, the polymer–clay nanocomposite preparations are limited to hydrophilic polymers which are sufficiently polar to be intercalated between the aluminosilicate layers of the clay [17].

In this study, we prepared the exfoliated PVAc/MMT nanocomposite latexes by the emulsion polymerization. The morphology of the prepared PVAc/MMT nanocomposite latex was investigated by atomic force microscopy (AFM), X-ray diffraction (XRD), transmission electron microscopy (TEM), and scanning electron microscopy (SEM). TEM was used to see the distribution of the clay in the polymer matrix. The obtained results indicate that the polymerizing chains were aggregated into the clay interlayer regions and consequently the exfoliation of MMT was almost completed.

Experimental

Materials

Commercial grade of VAc and PVA (degree of hydrolysis 88%, degree of polymerization 580) were supplied from Iranian petrochemical Co. and Kuraray Chemical Co., Japan, respectively.

The nano-MMT, cloisite 30B (C30B) was obtained from Southern Clay Products, USA. The closite 30B is modified with methyl tallow bis-2-hydoxyethyl quaternary ammonium chloride, and it is a layered silicate with silicate layers of 1.7 nm in thickness and 300–350 nm in lateral and the cation exchange capacity of cloisite 30B is 90.0 mequiv/100 g. Sodium lauryl sulfate (SLS 99%) was supplied by Fluka. APS and sodium bicarbonate ($NaHCO_3$) were supplied by Merck Co. Inc., Germany. All chemicals were used without further purification. Water was distilled after being ion-exchanged.

Preparation of PVAc/MMT nanocomposites

We have prepared PVAc/MMT nanocomposite via in situ emulsion polymerization, nanoclay was dispersed in 50 mL deionized water, and the dispersion was stirred vigorously overnight and then was dispersed by ultrasonication to prevent aggregation of nanoparticles. Then, this solution was added to a three-necked flask with a water jacket to maintain a constant temperature (±0.1 °C). MMT for preparation of PVAc/MMT nanocomposite lattices containing 0, 0.5, 1, and 2 wt% MMT, respectively.

The glass reactor was fitted with a reflex condenser, funnel, and mechanical stirrer. The speed of agitation with stirring was stable at 200–300 rpm. 47 g Monomer poured into the dropping funnel, a quantity of distilled water was poured into the glass reactors and 0.1 g initiator (APS) and 0.1 g buffer solution of $NaHCO_3$ were added and maintained under constant agitation (200–300 rpm). The aqueous emulsified solution containing 2 g PVA and 0.2 g SLS were added to the reaction system. The mixture was stirred at 300 rpm and heated up to75 °C. Afterwards, the monomer was fed into the reactor in a separate stream with constant flow rates to maintain the reaction system at 75 °C. The time of feeding was almost 70 min and after addition of the monomers, the polymerization was carried out under an inert nitrogen atmosphere for 4 h. Then, the system was cooled to room temperature and the final latex was obtained without any post preparative treatments. The calculated monomer conversion were 70.9, 72.4, 73.7, and 76.1% for PVAc/MMT nanocomposite lattices containing 0, 0.5, 1, and 2 wt% MMT, respectively [18].

Figure 1 shows the conceptual approach to the monomer intercalation. According to this figure, the intercalated structure in which the extended polymer chain is intercalated between the MMT layers results in a well-ordered multilayer morphology built up with alternating polymeric and inorganic layers. The exfoliated structure refers to the complete dispersion of the MMT layers in a continuous polymer matrix [1].

Characterization

X-ray diffraction (XRD) measurements

The diffraction behavior of the synthesized PVAc/MMT nanocomposites was studied by A Philips X'Pert MPD X-ray Diffractometer with Cu-Kα radiation ($\lambda = 1.54$ Å) at a generator voltage of 40 kV and a generator current of 40 mA was used to study the diffraction behavior of MMT and PVAc/MMT nanocomposites. All experiments were carried out in the reflection mode at ambient temperature with 2θ varying between 1 and 10°. The scanning speed was 1° min^{-1} and the step size was 0.01°.

Morphology observations

The surface morphology and particle diameters of the synthesized PVAc/MMT nanocomposite specimens was investigated using a scanning electron microscope (SEM, JSM 5800-LV, JEOL, Japan). Prior to SEM examination; the samples were dried at room temperature and coated with a thin layer of gold, using a JEOL ion-sputter JFC-1100 coating machine.

Considering the importance of the uniform dispersion of MMT into the PVAc matrix, the synthesized PVAc/MMT nanocomposite analyzed using transmission electron microscope (TEM) operating at an accelerating voltage of 120 kV. The

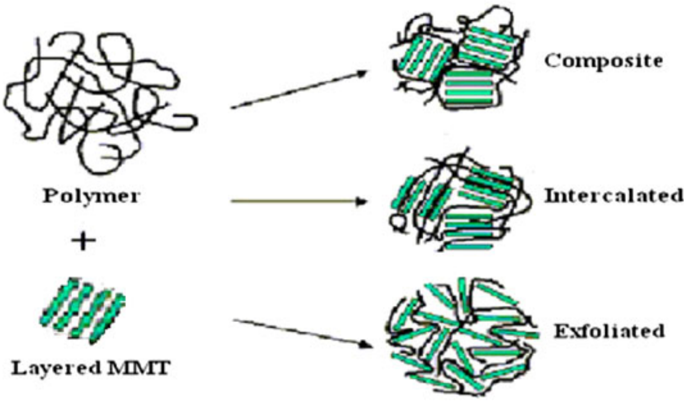

Fig. 1 The conceptual approach to the formation of intercalated and exfoliated nanocomposites

samples were prepared as follows: fine power of the nanocomposite was dispersed in ethanol under ultrasonication at 25°C for 10 min, and then one drop of the dilute suspension of colloid was suspended and evaporated on a carbon-coated copper grid and placing in the Phillips CM-120 TEM.

AFM is an effective tool to characterize nanocomposites by providing the morphological information. To characterize the shape of the nanocomposite and the morphological feature, AFM (TS-150, Russia) is used. The AFM consists of a sharp tip (10–20 nm diameter) attached to a stiff cantilever. The tip is brought close to the surface, and the sample is scanned beneath the tip. The tip moves in response to tip–surface interactions, and this movement is measured by focusing a laser beam onto the back of the cantilever and detecting the position of the reflected beam with a photodiode. Different modes of operation can be used [15]. In the AFM analysis, sample preparation is quite simple and does not require a conductive coating as for SEM [16].

Differential scanning calorimetry

Differential scanning calorimetry provides the quantitative and qualitative information about chemical and physical changes that involve endothermic and exothermic transitions.

The thermal properties of the synthesized PVAc/MMT nanocomposites were investigated by DSC (NETZSCH, Germany-200F 3 Maia). The samples for DSC

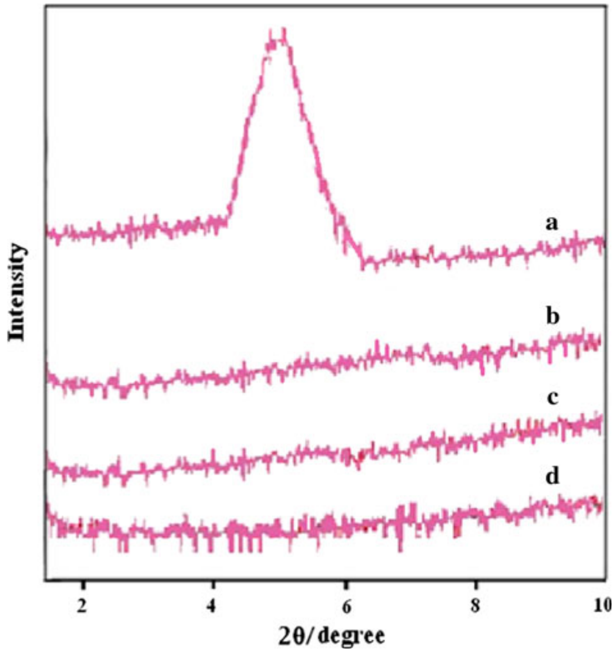

Fig. 2 XRD patterns of PVAc/MMT nanocomposite: *a* 1% MMT(non-exfoliated), *b* 0.5% MMT (exfoliated), *c* 1% MMT (exfoliated), *d* 2% MMT (exfoliated)

analysis were initially scanned from −50 to 350 °C under nitrogen atmosphere at a heating rate of 10 °C/min. The glass transition (T_g) was determined at the deflection point in the transition region.

Results and discussion

Morphology

X-ray diffraction (XRD) method was used to characterize the formation and structure of the synthesized PVAc/MMT nanocomposites. Figure 2 compares the XRD patterns of the exfoliated and non-exfoliated PVAc/MMT nanocomposite samples, in this figure the non-exfoliated sample exhibits a single peak at an angle 2θ of 4.92°.

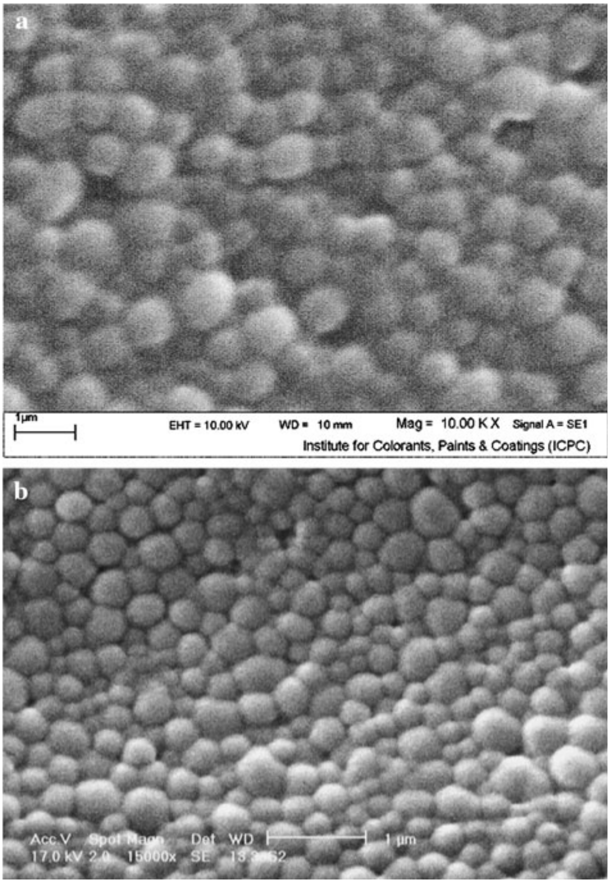

Fig. 3 Scanning electron microscopic (SEM) images of the **a** pure PVAc and **b** PVAc/MMT nanocomposite

According to Fig. 2, for the exfoliated synthesized PVAc/MMT nanocomposites, the characteristic diffraction peak disappeared indicating that the MMT has been exfoliated in the PVAc matrix. It is found that in all systems, the interlayer spacing increases due to the intercalation of polymer into the layers of MMT. Enhanced interlayer distance indicates that the layered structure is retained.

Morphological properties

The morphology of the surfaces was observed by SEM, Fig. 3a and b shows the representative scanning electron micrographs of PVAc and PVAc/MMT nanocomposite from the dispersion polymerization, respectively.

The PVAc obtained from the polymerization was in the form of spherical particles with an average particle size of 600 nm and showed relatively broad particle size distribution. SEM image of PVAc/MMT (Fig. 3b) nanocomposite showed that when the MMT was incorporated in the PVAc matrix, the average particles size of the spherical nano-size composite was reduced to 250 nm.

Figure 4 shows a TEM micrograph of PVAc/MMT nanocomposite having 2.0% wt of MMT, where the dark lines in the picture correspond to the MMT layers. It is clear that the MMT layers were exfoliated and dispersed in the PVAc matrix.

The homogeneity of the dispersion of MMT in the PVAc/MMT nanocomposites was determined by AFM measurements of spin-coated thin films. AFM images were analyzed using the plug-in functions of the Adobe Photoshop image processing program that calculates the specific surface area and edge-to-edge nearest neighbor length correlation distance through the size, shape, position of each feature in the images. We emphasize at this moment that the AFM images do not display the entire surface area for all the platelets as portions of these surfaces may be buried in

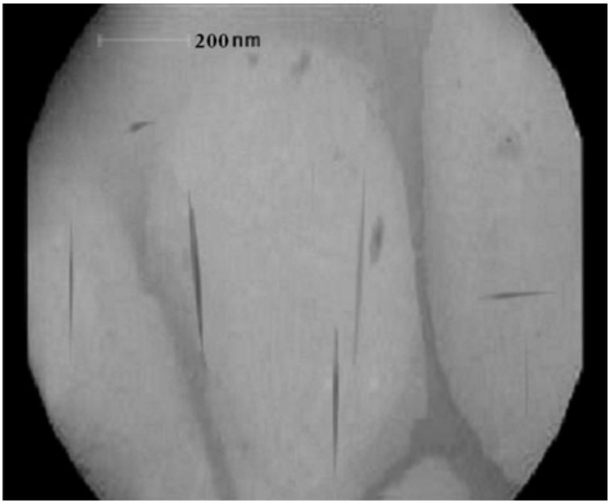

Fig. 4 Transition electron microscopic (TEM) images

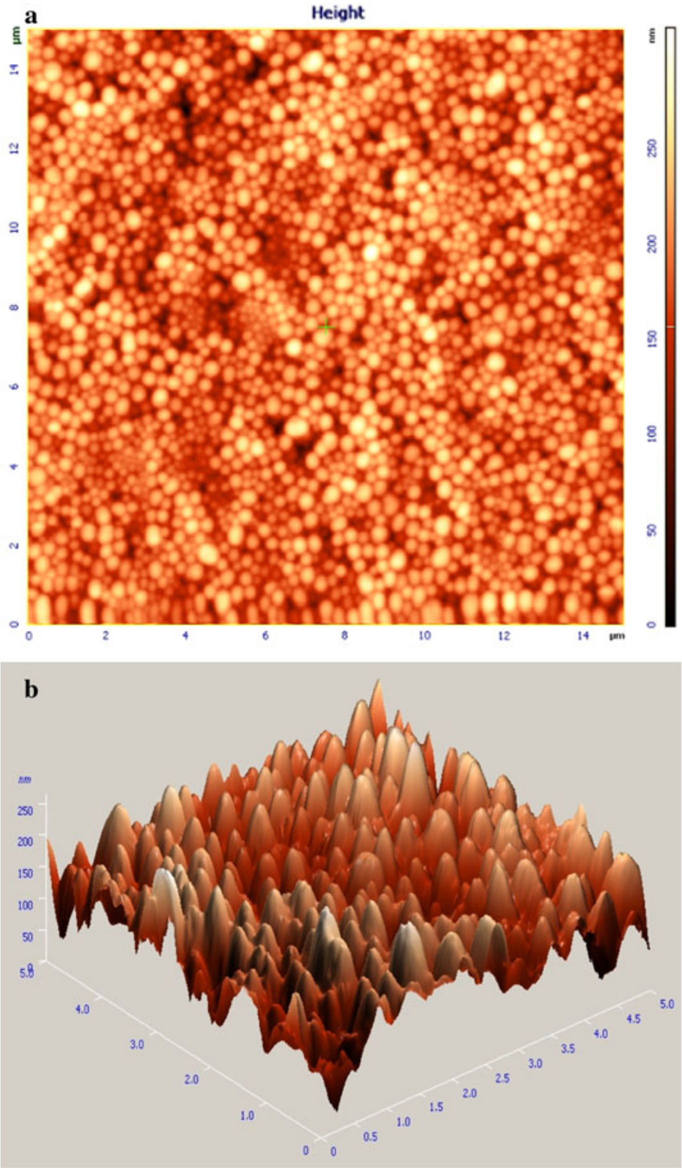

Fig. 5 AFM topographic images for the nanocomposite with a MMT concentration of 1%: **a** flat image 15 µm × 15 µm, **b** spatial image, 5 µm × 5 µm × (0–300) nm

the PVAc. Therefore, these images represent apparent surface areas of the MMT particles.

Figure 5a and b show the AFM height images of the samples. The AFM height images (topographic nature) cannot offer information about the presence of MMT and exfoliated layers. Thus, the AFM phase image that should differentiate MMT

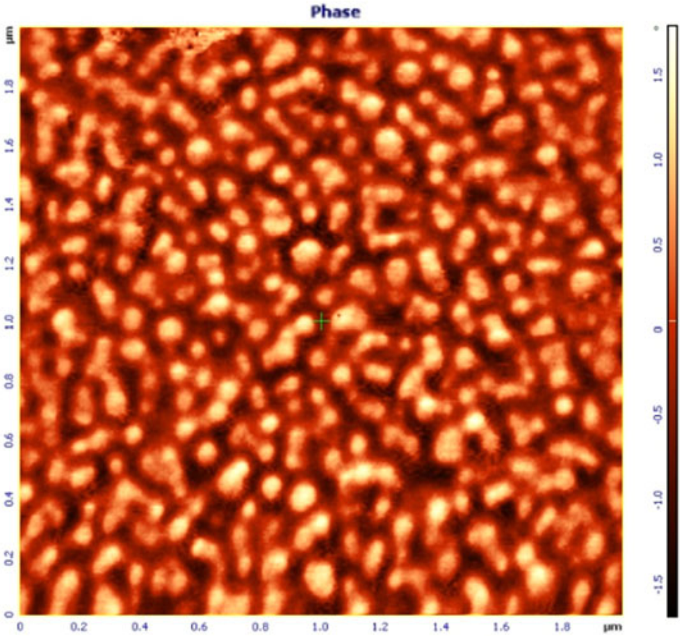

Fig. 6 AFM phase image for the nanocomposite with a MMT concentration of 1%

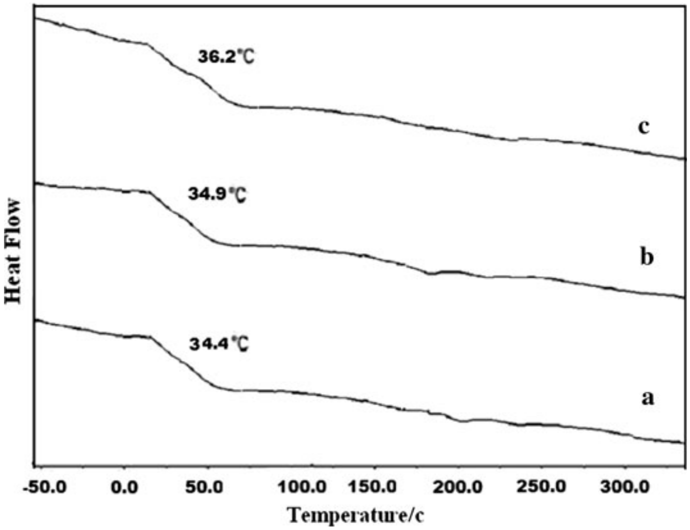

Fig. 7 DSC thermogram of PVAc/MMT samples with different clay contents: **a** 0.5% MMT, **b** 1%MMT, **c** 2% MMT

from PVAc due to their materials contrast is presented Fig. 6. The phase contrast is likely caused by repulsive tip–MMT interactions, resulting in a brighter areas or features, and an attractive tip–PVAc interaction, resulting in the darker areas. The phase image indicates that relatively good dispersion was achieved and this finding has a good consistency with the TEM and XRD results.

Thermal analysis

The thermal properties of the nanocomposite materials have been evaluated by DSC as shown in Fig. 7. The measurements were made with 3–4 mg sample on a DSC plate, DSC analysis does not reveal melting phenomena, thus suggesting that all the materials are in amorphous structure. All the investigated materials show that glass transition temperatures (T_g) were determined at the midpoint of the transition point. The obtained T_g values of the synthesized PVAc/MMT nanocomposites were compared with that for the pure PVAc synthesized by the same processing route. The T_g value of pure PVAc was 32.2°C. Therefore, with increasing of the content of MMT in the synthesized PVAc/MMT, the T_g values were increased. Increase of T_g values with the MMT content for the synthesized nanocomposites can be explained by an increase of the network rigidity which can be referred as a thermal stability criterion.

Conclusions

The exfoliated PVAc/MMT nanocomposites were synthesized by in situ emulsion polymerization of vinyl acetate (VAc) in the presence of modified MMT. The VAc monomer conversion increases with an increase in the content of MMT in the synthesized PVAc/MMT. The synthesized PVAc/MMT nanocomposites were characterized by XRD, SEM, TEM, and AFM. XRD results showed a disorder layer structure due to intercalation of polymer into the layered silicate. TEM images showed good dispersion of MMT in PVAc matrix, resulting in an exfoliated structure. Thermal properties of the nanocomposite were studied by using DSC. According to the obtained results, the glass transition temperature, T_g, for the synthesized PVAc/MMT nanocomposites increased with the content of MMT.

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