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A new approach to polymer/montmorillonite nanocomposites

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Abstract

A novel method for preparation of exfoliated/intercalated nanocomposites is reported based on two steps, i.e. preparation of treated-montmorillonite (MMT) solution and solution blending with polymers. After in situ polymerization of dimethyldichlorosilane between layers and separation of most polydimethylsiloxane (PDMS), the treated-MMT solution shows good storage stability. Although elemental analyzer shows no residue PDMS, NMR proves residue PDMS still exists in the solution. The residue PDMS is believed to graft onto the MMT layer surface via condensation of hydroxyl groups of PDMS and those that existed on MMT surface. Lower relaxation time of end-capped CH_3 of alkyl ammonium grafted onto layer surface via ion exchanging in the solution shows that the layer spacing was increased significantly or even exfoliated. When the solution was blended with some polar polymers, exfoliated nanocomposites were found. When it was blended with some nonpolar polymers, however, intercalated nanocomposites were obtained. The reason was explained in the light of compatibility between polymer matrix and MMT as well as alkyl ammonium and PDMS grafted on the layer surface. For intercalated nanocomposites, different layer spacing corresponds to different chain flexibility and the presence of multi-peaks is caused by the processing of these blends.

Keywords: Montmorillonite; Exfoliation; Nanocomposite

1. Introduction

Nanocomposites are a relatively new class of materials with ultrafine phase dimensions, typically of the order of a few nanometers [1–4]. Depending on the organization of the silicate layers in a polymer matrix, two types of morphology can be achieved in nanocomposites: intercalated or exfoliated. Generally, there are four strategies used to prepare polymer/montmorillonite (MMT), i.e. exfoliation–adsorption, in situ intercalative polymerization, melt intercalation and template synthesis [5]. Exfoliation–adsorption has been widely used with water-soluble monomer, prepolymer and polymer to produce intercalated nanocomposites [6–8]. These molecules can be intercalated in the untreated MMT and then converted into the desired polymer. In the second method, the layered silicate is swollen within the liquid monomer (or a monomer solution) so that polymer formation can occur in between the intercalated sheets. This method is suitable for some polymers, such as nylon [9,10], polycaprolactone [11–13] and epoxy [14–21]. Melt intercalation is to enable the layered silicate mixed with the polymer matrix in the molten state. This solvent-free method requires the polymer to be compatible with the layer surfaces. The last technique is in situ hydrothermal crystallization of the clay layers (hectorite) in an aqueous polymer gel medium where the polymer often acts as a template for layer formations [22].

Exfoliated nanocomposites attain a particular degree of stiffness, strength, and barrier properties with far less clay content than in conventionally filled polymers [23]. Researchers at the Toyota Research Center first demonstrated that exfoliated MMT/nylon nanocomposites exhibit substantial improvements in strength and modulus [9,10]. However, it is difficult to achieve complete exfoliation of MMT in a continuous polymer matrix, because of the strong electrostatic attraction between the silicate layers and the inter-gallery cations. The general way to prepare an exfoliated nanocomposite is to use an appropriate in situ polymerization method. It does mean that for every type of polymer, one has to find the right layered clay, organic

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modifier and solvent. In this paper, a new approach to prepare polymer/MMT nanocomposites was proposed, which included preparation of a treated-MMT solution and blend processing of nanocomposites. The MMT solution is prepared via in situ polymerization of dimethyldichlorosilane inside the galleries of layered silicate hosts and thereafter most of polydimethylsiloxane (PDMS) was separated from the solution. Then the solution was blended with several polymers, which produced exfoliated or intercalated polymer/MMT nanocomposites depending on the compatibility between polymer and PDMS grafted on MMT surfaces. The technique permits various polymer/MMT nanocomposites to be prepared while using the same procedure. The toxic solvent and macromolecules washed away in the process could be recycled.

2. Experimental work

2.1. Materials

Dimethyldichlorosilane (monomer) was ordered from Tongji University and used as received. Na^+-montmorillonite (MMT) from Qinghe Chemical Factory of Zhangjiakou in Hebei Province was modified by hexadecyltrimethylammonium bromide according to ref [24]. The modified MMT is denoted as org-MMT. Polymers, such as polydimethylsiloxane (PDMS), polyvinylchloride (PVC), styrene–butadiene rubber (SBR), polystyrene (PS), ethylene–propylene diene monomer rubber (EPDM), and polycarbonate (PC), are all commercial products.

2.2. Preparation of treated-MMT solution

2.2.1

5 g of org-MMT was immersed in 50 g of chloroform for 10 h and then 25 g of monomer was added to the solution followed by sonication using an ultrasonic generator for about 1 hr. 10 ml of H_2O, 30 ml of CH_3OH and 30 ml of $CHCl_3$ were mixed in a three-neck reactor. The above sonicated solution was then dropped into this reactor at a speed of 1 drop/s at 0 °C while under vigorous stirring.

2.2.2

After stirring, the resultant solution was washed several times with de-ionised water until no chloride ion was detected by one drop of 0.1N $AgNO_3$ solution. After washing, a desired amount of solution was used for characterization.

2.2.3

The solution was mixed with 200 ml of tetrahydrofuran (THF), which is a good solvent for PDMS but poor solvent for org-MMT, by stirring for 5 min. Then the mixture was loaded into PP tubes and centrifuged at 3000 rpm for 5 min.

2.2.4

The opaque whitish layer accumulated at the bottom of the tubes was dissolved in 500 ml of $CHCl_3$ by stirring for 10 min. The resultant solution is called the treated-MMT solution.

2.3. Preparation of polymer/MMT nanocomposites

A given amount of the treated-MMT solution was placed in a three-neck reactor. Polymer, such as PDMS, PVC, SBR, PS and EPDM, was added to the solution and kept at 50 °C under stirring for 1 h. Then polymer/MMT was precipitated by a large amount of methanol. Since PC was poorly dissolved in chloroform, toluene and higher blending temperature were employed to prepare PC/MMT nanocomposites.

2.4. Characterization of the treated-MMT solution and polymer/MMT nanocomposites

100 ml of the treated-MMT solution was vacuum-dried to a constant weight at 50 °C and then the residue was weighed carefully. The yield was about 70%.

Derived from section 2.2.2, some amount of the solution was vacuum-dried to a constant weight at 50 °C. As a reference, some amount of the treated-MMT solution was also dried via the same method. Elemental analysis of the above two samples and org-MMT was performed by using an elemental analyzer (EA). Carbon and hydrogen were determined by combustion in oxygen using an induction furnace technique and gel chromatography.

The treated-MMT solution for NMR measurements was prepared in the specific NMR tube with deuterium chloroform as solvent. The measurements were carried out with a Bruker DMX-300 NMR spectrometer at room temperature. The resonance frequency for ^1H was 300.13 MHz.

X-ray measurement (XRD) was conducted with Cu Kα radiation, operated at 40 kV and 12 kW. Polymer/MMT samples for X-ray diffraction measurement were processed as pellets with a smooth surface and dimensions of $1 \times 1 \times 0.1\ cm^3$.

Transmission electron microscopy (TEM) experiments were performed using a H-800 transmission electron microscope, in order to acquire direct visualization of the particular layer characteristics of the nanocomposites. Ultrathin sections of bulk samples were produced at −100 °C using a Leica Ultracut UCT with EMFCS cryo-attachment. The sections were floated off the diamond knife and transferred to the grids.

Thermogravimetric analysis (TGA) was conducted in flowing nitrogen ($30\ cm^3\ min^{-1}$) at a heating rate of $10\ °C\ min^{-1}$ using a Perkin–Elmer TGA 7.

3. Results and discussion

3.1. Analysis of treated-MMT solution

EA was performed to detect if there was any residual

PDMS in the treated-MMT solution arising from in situ polymerization. Table 1 presents the EA data derived from org-MMT, solutions from section 2.2.2 and from the treated-MMT solution, respectively. After in situ polymerization and washing, the percentage of carbon element increased only to 32.3% in comparison with 19.7% in org-MMT. It indicates that much of PDMS was washed away and there were still some PDMS existing at the end of section 2.2.2. The value of 19.6% derived from the treated-MMT solution was very similar to that derived from org-MMT. It shows that there were few or even no PDMS in the treated-MMT solution. However, NMR shows that residue PDMS still exists in this solution as NMR has much higher resolution than EA.

Solution taken from section 2.2.2 (denoted as solution A) has excellent storage stability, because no precipitation was observed even after one year of storage. For the treated-MMT solution (denoted as solution B), the storage stability was good since precipitation was observed only after six months of storage. As a reference, 0.7 g of org-MMT was dissolved in 100 ml of chloroform (denoted as solution C) followed by 30 min of sonication. After 3 h of storage, however, obvious precipitation was observed in solution C. The discrepancy between these storage stabilities may rise from different MMT layer structures in solutions. Through in situ polymerization of monomer, the strong electrostatic attraction between the silicate layers and the inter-gallery cations was destroyed and interlayer spacing was increased significantly or the layers were exfoliated. Some PDMS chains were grafted onto MMT surface because hydroxyl groups on MMT surface [4] could react with hydroxyl groups of PDMS via condensation. The amount of grafted PDMS might be small, which cannot be detected by EA, but its existence between layers is very important to the storage stability. In solution A, a large quantity of PDMS existed between layers as shown in Table 1, which could effectively prevent layered MMT from re-aggregating. In solution B, although most of PDMS was removed during extraction and centrifugation, PDMS grafted onto MMT surface could somewhat prevent layered MMT from re-aggregating. In solution C, however, no in situ polymerization proceeds and layered structure still exists because of the strong electrostatic attraction between the silicate layers and the inter-gallery cations and therefore layer silicate MMT is easy to aggregate and to precipitate.

Layered MMT offers a unique avenue for studying the properties of small molecules or macromolecules in a confined environment. Zax reported that slow relaxing moieties are concentrated in denser regions in the immediate vicinity of the confining surfaces [25]. Understanding the changes in the dynamics due to this extreme confinement (layer spacing $\ll$ layer radius) would provide complementary information to the nature of those solutions in this study. The local chain dynamics was probed using ^{1}H NMR. T_1 relaxation time of end-capped CH_3 of alkyl ammonium grafted via ion exchange on the surface of MMT might most represent local dynamics of chains in different spaces. T_1 relaxation times are 1.001 and 3.058 s, respectively, for solution B and solution C. In solution C, the higher T_1 relaxation time indicates that the spatial motion of the chain is confined due to the layered structure, which still exists after 30 min of sonication because of the strong electrostatic attraction between the silicate layers and the inter-gallery cations. Topologically, the surfaces of the silicate layers will restrict the motions of the chains of the opposing silicate layers. After in situ polymerization of the monomer, however, layer spacing was increased significantly or even the layered structure became exfoliated. Although most of PDMS was removed from the exfoliated solution via centrifugation mentioned in Section 2.2.3, which might induce layer re-aggregating according to present clay theory [26], PDMS grafted onto MMT surface via hydroxyl group condensation prevented layered MMT from re-aggregating. The change of structure corresponds to the significant decrease of the time from 3.058 s in solution C to 1.001 s in solution B. The enhanced local chain dynamics of the chain reflects the absence of chain motion confinement as associated with the importance of PDMS grafted on layered MMT surface via condensation of hydroxyl groups.

3.2. Polymer/MMT nanocomposites via solution blending

To confirm the fine construction of the treated-MMT solution and extend its application, several nanocomposites, such as possibly exfoliated nanocomposites, including PDMS/MMT, PVC/MMT and SBR/MMT, and intercalated nanocomposites, including EPDM/MMT, PS/MMT and PC/MMT, were made via solution blending.

An important measure of the degree of silicate dispersion and exfoliation is usually obtained by XRD measurements. Generally intense reflections in the range $2\theta = 3-9°$ indicate an ordered intercalated system with alternating polymer/silicate layers. In exfoliated hybrids, on the other hand, where single silicate layers (1 nm thick) are homogeneously dispersed in the polymer matrix, XRD patterns

Table 1
Elemental analysis of MMT derived from different preparation steps

Samples	Carbon element (%)	Hydrogen element (%)	Nitrogen element (%)
org-MMT	19.7	3.7	1.0
MMT from section 2.2.2	32.3	4.0	0.7
MMT from the treated-MMT solution	19.6	3.7	1.0

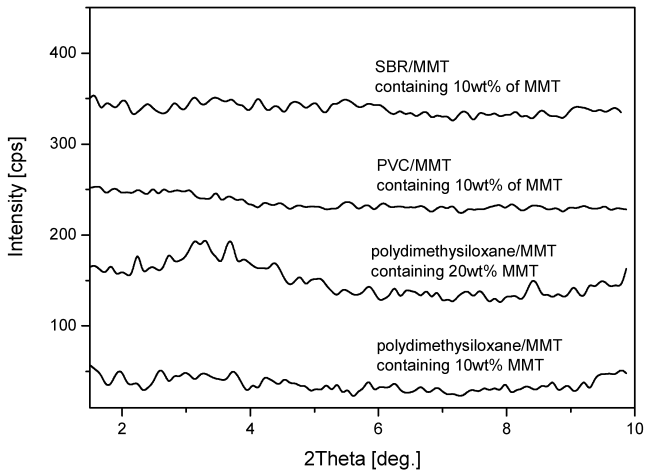

Fig. 1. XRD patterns of PDMS/MMT, PVC/MMT and SBR/MMT nanocomposites.

with no distinct features in the low 2θ range are anticipated due to the loss of structural registry. Shown in Fig. 1 are a series of XRD patterns of treated-MMT nanocomposites containing various polymer matrix. The featureless patterns of nanocomposites suggest that exfoliated hybrids might be present as opposed to the diffraction peak at 2 nm for org-MMT in Fig. 2, indicating the possibility of having exfoliated silicate layers of MMT dispersed in the polymer matrix.

In contrast to the global averaging of XRD, conventional TEM can directly provide information in real space, in a localized area, on morphology and defect structures. Fig. 3 shows TEM images of SBR/MMT nanocomposite prepared as above. Since the silicate layers are composed of heavier elements (Al, Si, O) than the interlayer and surrounding matrix (C, H, N), they appear darker in bright field images [27]. The low magnification view in Fig. 3(a) reveals that the MMT is uniformly dispersed in the matrix. Fig. 3(b) shows a higher magnification picture which reveals that MMT is well exfoliated in the matrix and the individual layers are aligned along the flow axis during cross-linking of SBR, which corresponds to XRD pattern analysis. The dark lines in Fig. 3(a) are the cross-sections of single or possibly multiple silicate platelets. The platelets are flexible and, thus, show some curvature. The average thickness of the MMT platelets appears to be approximately 3 nm while the average length is about 120 nm. The thickness deduced from these photomicrographs is somewhat higher than that of a single MMT layer, which should be about 1 nm. This phenomenon was mentioned by Paul [28] and possible unconfirmed reasons were given below. One possibility is that the platelets appearing in the image to be larger than they actually are due to inaccurate focusing in the TEM. Another is that the MMT platelets are not fully exfoliated. The last is that the microtoming direction is not perfectly perpendicular to the surface of the platelets and therefore the image is of such a tilted platelet that appears to be thicker than it actually is. In this study, however, TEM was calibrated before characterization. If MMT in these composites is not exfoliated, an obvious peak should be observed in Fig. 1 corresponding to 3 nm of MMT platelets. Therefore, the third possibility could be the reason for the discrepancy found in TEM observation. Based on analysis of XRD and TEM, the structure of exfoliated SBR/MMT nanocomposite was confirmed. It might prove that the layered structure in the treated-MMT solution is exfoliated. Since SBR is one of main components of tire materials and exfoliated MMT plays an important role in reducing the gas permeability of polymer [29–32], the exfoliated SBR/MMT nanocomposite prepared in this study might find possible application in the tire industry.

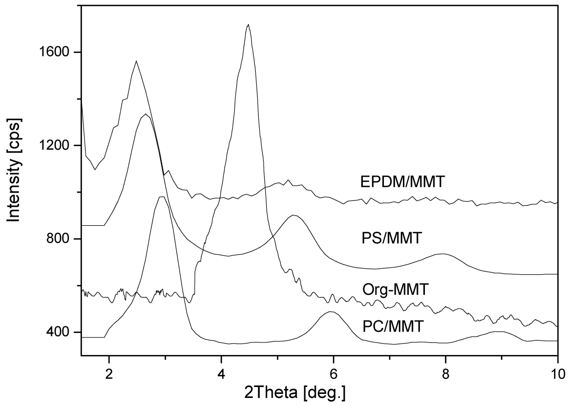

Fig. 2. XRD patterns of org-MMT and PC/MMT, PS/MMT and EPDM/MMT nanocomposites containing 10 wt% of MMT.

The superior mechanical properties of siloxanes at elevated temperatures usually justify their increased cost over conventional elastomers. Therefore, thermal stability especially at elevated temperatures is an important characteristics in these composites. Burnside and Giannelis show an increase and broadening of the glass-transition temperature for exfoliated PDMS/MMT nanocomposite in comparison with pristine PDMS [33,34]. Table 2 shows the TGA analysis for both pristine SBS and PDMS and their nanocomposites containing 10 wt% MMT. An increase in decomposition temperature of 68.2 °C was observed for PDMS/MMT nanocomposite while SBR/MMT nanocomposite showed only 13.0 °C of decomposition temperature increase with the same amount of MMT. The nanocomposites show delayed decomposition temperature compared to the pristine polymers, which should be attributed to hindered diffusion of the volatile decomposition products.

XRD of intercalate polymer/MMT are shown in Fig. 2 and the detailed data are provided in Table 3. It should be noted that, although exfoliated SBR/MMT, PDMS/MMT and PVC/MMT were obtained as discussed above, intercalate nanocomposites were still processed while using almost the same method. The difference between them should be found in the compatibility. Both PDMS grafted on MMT surface via hydroxyl group condensation and silicate layers composed of silicone, oxygen and carbon are polar. Therefore, both have good compatibility with polar chains

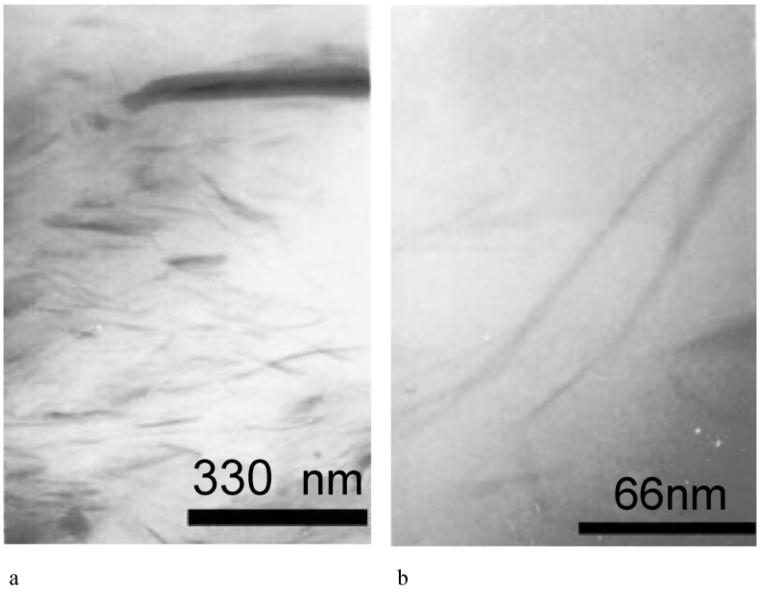

Fig. 3. TEM images of styrene–butadiene rubber/MMT nanocomposite.

of SBR, PDMS and PVC. The good compatibility promoted blending of polymer and silicate nanolayer and so exfoliated nanocomposites were present. PC, PS and EPDM are nonpolar polymers, which are not compatible with MMT and grafted molecules. The poor compatibility impedes blending of polymer and nanolayer and results in intercalate nanocomposites.

As shown in Fig. 2 and Table 3, layer spacing of intercalate nanocomposites decreased in the order: EPDM/MMT > PS/MMT > PC/MMT, which should be explained according to macromolecular flexibility. EPDM is an excellent elastomer that has a high molecular weight and flexible chain, which makes EPDM molecules easy to move into the layer spacing of silicates during solution blending. PS chain is not flexible because of the large volume of styrene and so it is not easy to intercalate into MMT layers. PC chain is so rigid that it is the most difficult to intercalate.

For PC/MMT and PS/MMT nanocomposites, multi-peaks are shown in Fig. 2 and the reason could be found in the processing of these nanocomposites. When nanocomposites were precipitated from solution by large amount of methanol, the polymer either stayed in the silicate layer space or moved out of the space. It is well known that layer spacing of MMT could be increased from 1 to 2 nm or so

Table 2
Thermal decomposition temperatures of pristine polymers and their nanocomposites containing 10 wt% of MMT

Polymer type	Decomposition temperature of pristine polymer	Decomposition temperature of nanocomposite	Increase of decomposition temperature after adding MMT
SBR	428.7	441.7	13.0
PDMS	395.4	463.6	68.2

Table 3
XRD data of PC/MMT, PS/MMT and EPDM/MMT nanocomposites as well as Org-MMT (standard deviation 0.002°)

Peak		2θ (degree)	Layer spacing (nm)	Relative intensity
Peak of org-MMT		4.48	1.97	1
Peaks of PC/MMT	Peak 1	2.96	2.98	0.72
	Peak 2	5.90	1.50	0.20
	Peak 3	8.80	1.00	0.08
Peaks of PS/MMT	Peak 1	2.64	3.34	0.67
	Peak 2	5.24	1.69	0.26
	Peak 3	7.64	1.16	0.07
Peak of EPDM/MMT		2.48	3.56	–

while treated with ammonium surfactants. In this study, the increase of MMT layer spacing could be due to the existence of organic ammonium molecules and PDMS grafted onto MMT surface. When the polymer moves out of the space, some grafted molecule might also be taken out of the space because of the movement. Therefore, the layer spacing of some part of org-MMT might be decreased after polymerization. Similar situation was also encountered by some researchers when preparing polymer/MMT nanocomposites [26,29].

4. Conclusion

The method involving in situ polymerization of dimethyldichlorosilane and blending the treated-MMT solution with several polymers yields storage-stable treated-MMT solution and exfoliated/intercalated nanocomposites. The in situ polymerization destroys the strong electrostatic attraction between the silicate layers and the inter-gallery cations. PDMS grafted onto MMT layer surface via condensation of hydroxyl groups of PDMS and those hydroxyl groups existed on MMT layer surface prevents nanolayers of MMT re-aggregating, which could be proved by comparison of storage stability and relaxation time. When the treated-MMT solution was blended with other polymers, exfoliated or intercalated nanocomposites were obtained according to the discrepancy of compatibility between polymer and MMT as well as alkyl ammonium and PDMS grafted on the layer surface.

Acknowledgements

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