

Poly(etherimide)/montmorillonite nanocomposites prepared by melt intercalation: morphology, solvent resistance properties and thermal properties

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Abstract

Polyimide-MMT (montmorillonite) nanocomposites has been prepared by melt blending an organo-modified MMT with a thermoplastic poly(etherimide) (PEI) in an internal mixer. The dispersion of the MMT layers within the PEI matrix was verified using X-ray diffraction and transmission electron microscopy, revealing an exfoliation morphology. Owing to the molecular dispersion of the MMT layers and the strong interaction between PEI and MMT, the nanocomposites exhibited a substantial increase at glass transition temperature and thermal decomposition temperature, and a dramatic decrease in solvent uptake compared to the virgin PEI. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Montmorillonite; Poly(etherimide); Nanocomposites

1. Introduction

Polymer melt intercalation is a promising approach to fabricate polymer-layered silicate (PLS) nanocomposites using conventional polymer processing techniques. The nanocomposites are formed by heating a mixture of polymer and layer silicate above the glass transition or melting temperature of the polymer. The ultrafine phase dimensions of the nanocomposites, typically ranging from 1 to 10 nm, leads to improved properties when compared to the virgin polymer or their macrocomposite counterparts. It has been reported that polymer-silicate nanocomposites exhibit increased modulus and strength [1,2], high heat distortion temperature [3], decreased thermal expansion coefficient [4,5], reduced gas permeability [6], increased solvent resistance [7], and enhanced ionic conductivity [8,9] compared to the pristine polymers. These performance improvements, though, depend greatly on the distribution, arrangement, and interfacial bonding between the silicate layers and the polymer.

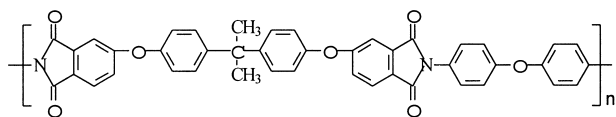
The structure of the PLS nanocomposites formed via polymer melt intercalation depends upon the thermodynamic interaction between the polymer and the silicate as

well as the transportation of polymer chains from the bulk melt into the silicate interlayers. Two typical nanocomposite structures can be identified by monitoring the position, shape, and intensity of the basal diffractions from the XRD pattern of the silicates. For the “intercalated” nanocomposites, extended polymer chains occupy the silicate interlayer space. The finite layer expansion results in the appearance of a new basal diffraction corresponding to the larger gallery height. For the “exfoliated” nanocomposites the silicate layers are delaminated and dispersed in a continuous polymer matrix. This results in the eventual disappearance of any X-ray diffraction peaks from the silicates [10,11].

Poly(etherimide) (PEI) resin is a type of amorphous thermoplastic material that has interesting physical and chemical properties, being an attractive candidate for many applications [12,13]. The ether units supply the chain flexibility and good melt flow characteristics to PEI. The aromatic imide units, meanwhile, provide thermal resistance and mechanical properties. Although PEI has good melt processability and solubility in some solvents, its relatively poor solvent resistance and thermal stability limited its application in the fields of aerospace and automotive. In this paper we studied the preparation of PEI-MMT nanocomposites by melt intercalation in an attempt to improve the solvent resistance and thermal property of the PEI. The pristine PEI was mixed with the organo-modified MMT in the HAAKE internal mixer, and the desirable intercalation

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Scheme 1.

capability of PEI and the strong shear field led to the exfoliated nanocomposites structure even at high MMT contents. Although many thermoplastic polymers have been used to prepare polymer-layered silicate nanocomposites using the melt intercalation approach [3,14,15], there are few reports on the PEI-layered silicate nanocomposites.

2. Experimental

2.1. Materials

Sodium montmorillonite (Na-MMT) was supplied by the Institute of Chemical Metallurgy, Chinese Academy of Sciences. The particle size is 40 μm . 1-Hexadecylamine ($\text{C}_{16}\text{H}_{33}\text{NH}_2$, lab reagent) is purchased from Merck. The thermoplastic PEI was provided by the Shanghai Research Institute of Synthetic Resin, whose chemical structure is shown in Scheme 1. Other analytical grade reagents, such as *N*-methyl-2-pyrrolidone (NMP), *N,N*-dimethylacetamide (DMA), *N,N*-dimethylsulfoxide (DMSO), ethanol and xylene, were purchased from Shanghai Reagent Company and used without further purification.

2.2. Preparation of organophilic-MMT

A dispersion of 30 g Na-MMT in 600 ml distilled water was added to a heated (80°C) solution of 17.23 g 1-hexadecylamine and 7.2 ml concentrated hydrochloric acid in 100 ml distilled water. The mixture was agitated vigorously for 2 h. Upon filtration, a white precipitate was obtained. It was then repeatedly washed with hot water and dried at 40°C in vacuum.

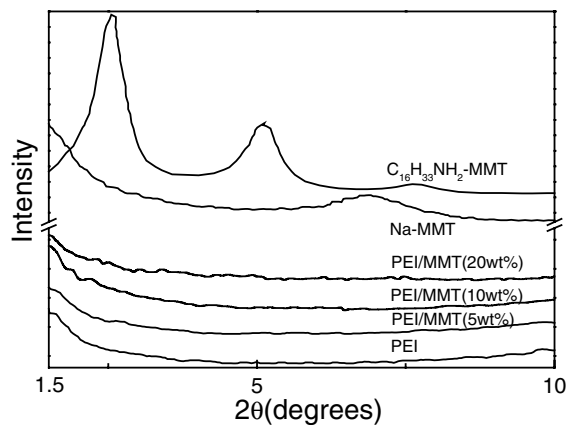


Fig. 1. XRD patterns of Na-MMT, $\text{C}_{16}\text{H}_{33}\text{NH}_2$ -MMT and PEI/MMT nanocomposites with various MMT contents.

2.3. Preparation of PEI/MMT nanocomposites

PEI and organo-MMT were dried at 120 and 40°C for 2 h, respectively, in vacuum before use. PEI and various amounts of organo-MMT were dry-mixed and melt-blended at 370°C for 30 min by using the internal mixer of a HAAKE Rheocord System.

2.4. Characterization

The wide angle X-ray diffraction (WAXD) patterns were recorded on a Rigaku Geiger Flex D/max-RB diffractometer using $\text{CuK}\alpha$ radiation (50 kV, 100 mA). The experiments were performed in a range of $2\theta = 1.5 - 40^\circ$ with a scan rate of $1^\circ/\text{min}$.

The epoxy block with the embedded powders of PEI/MMT nanocomposites was cut to form a triangular block face for microtoming. The ultrathin sections (100 nm or less) were microtomed from the epoxy block at room temperature using a LKB2088 ultramicrotome. The transmission electron microscopic (TEM) investigations were performed on a Philip CM120 TEM operating at an acceleration voltage of 80 kV.

The sorption experiments of the nanocomposites were carried out by the following procedure. The samples were dried in an oven at 105°C for 8 h, and then kept in the solvents at different temperatures for a given time, and blotted to remove the excess solvent. The amount of absorbed solvent was calculated from the increase in the weight of the samples.

The DSC analysis was conducted on a Perkin-Elmer Pyris I differential scanning calorimeter under the protection of N_2 . The heating rate was $20^\circ\text{C}/\text{min}$.

The thermal gravimetric analysis (TGA) was conducted on a Perkin-Elmer TGA 7 thermal analyzer under N_2 flow. The heating rate was $20^\circ\text{C}/\text{min}$.

3. Results and discussion

3.1. Organo-modification of MMT

MMT possesses the same structural characteristics as the well-known minerals, talc and mica, and hydrated inorganic cations in the galleries balance the layer charge, creating a hydrophilic interlayer environment [16]. Organo-modified MMT is produced by a cation-exchange reaction between the silicate and a surfactant molecule (1-hexadecylamine, quaternary ammonium salts, etc). The cationic head group of the surfactant molecule will preferentially reside at the layer surface and the aliphatic tail will radiate away from the surface [17]. The presence of these aliphatic chains in the galleries makes the originally hydrophilic silicate organophilic and increases the layer-to-layer spacing of MMT. The microchemical environment in the galleries is, therefore, appropriate to the intercalation of polymer molecules. The XRD patterns of Na-MMT and the organo-modified MMT

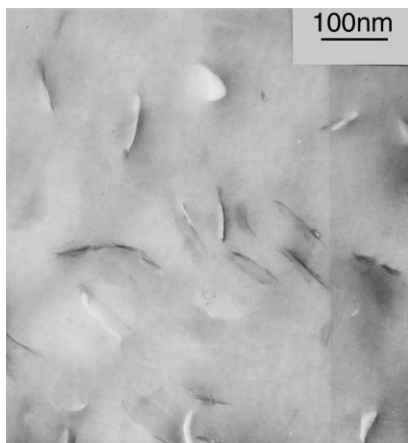


Fig. 2. TEM photograph of PEI/MMT (5 wt%) nanocomposite.

revealed the diffraction peaks at $2\theta = 6.78^\circ$, $2\theta = 2.62$, 5.16 and 7.64° , respectively. (Fig. 1) The basal spacing of MMT, which was calculated from the Bragg Equation, was obviously increased by the organo-modification. It was increased from 1.30 nm for an untreated MMT to 3.37 nm for MMT treated with 1-hexadecylamine ($C_{16}H_{33}NH_2$ -MMT).

3.2. Dispersibility of MMT layers in the nanocomposites

Direct evidence of the exfoliation of layered MMT is provided by the XRD patterns of the PEI/MMT nanocomposites (Fig. 1), in which the diffraction peaks of $C_{16}H_{33}NH_2$ -MMT disappeared completely. Most of the polyimide/MMT hybrid materials reported have been

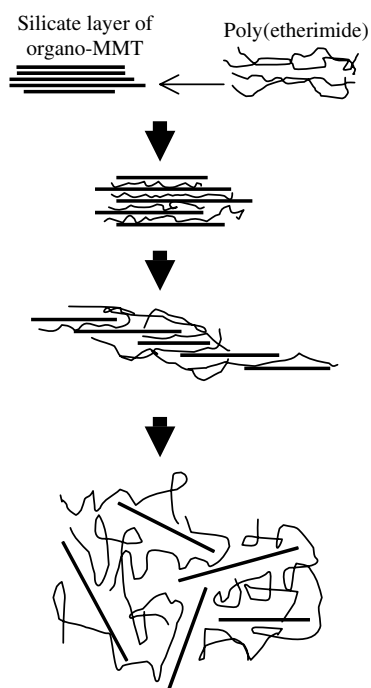


Fig. 3. Schematic representation of the intercalation process of PEI into the organo-MMT and the exfoliation of MMT.

using solution monomer or polymer intercalation approaches [5,18,19], in which only intercalation morphology could be achieved. In our study, no obvious aggregation of the MMT occurred in the PEI/MMT nanocomposites even with an MMT content as high as 20 wt%. The occurrence of this exfoliation morphology may be attributed to the strong shear field in the internal mixer, the high viscosity of molten PEI and the strong interactions between MMT and PEI.

The exfoliation morphology of the PEI/MMT composites was also supported by TEM (Fig. 2), in which the dark lines represented the intersections of MMT of about 1 nm thickness. It was observed that the MMT layers were dispersed homogeneously in PEI matrix.

3.3. Dispersion mechanism of the silicate layers

Fig. 3 presents a schematic representation of the mixing process of the thermoplastic PEI and organo-MMT. During melt blending, the PEI chains intercalate from the melt bulk into the silicate layer spaces. The driving force of the intercalation originates from the strong hydrogen bonding between the imide group in PEI and the polar surface of the MMT. The interlayer spacing of MMT increases, and the interaction among the layers is weakened. Meanwhile, the face-to-face associated silicate layers of the intercalated MMT stacking would orient and slip in a staircaselike fashion under strong shear field in the internal mixer (see Figs. 3 and 4). Finally, with the help of the shear field, the MMT layers were completely dissociated and homogeneously dispersed in the nanocomposites. The two factors, the intercalation capability of the polymer and the strong shear field, play important roles in the preparation of “exfoliated” polymer/MMT hybrids. The PP/MMT hybrids prepared by the melt intercalation method has an “intercalation” morphology because of the hydrophobic nature and the poor intercalation capability of PP [20]. This intercalation morphology was also obtained in the cool-pressed and annealed PEO/MMT hybrids because of the absence of the strong shear field [21]. However, the exfoliated nylon-6/MMT nanocomposites can be prepared by the melt intercalation approach [22]. Therefore, with the excellent intercalation capability and the strong shear field, the exfoliated structure of the PEI/MMT nanocomposites were successfully obtained.

3.4. Solvent resistance properties of PEI/MMT nanocomposites

The solvent uptake measurement was conducted by using two series of solvent. One series was conventional solvents, such as water, ethanol and xylene, while the other was non-protonic polar solvents, such as NMP, DMA and DMSO. The results of the measurement are listed in Table 1. The samples of known weight were treated by two different procedures. In one procedure the samples were immersed in solvents at 25°C for 24 h. It was observed that the solvent

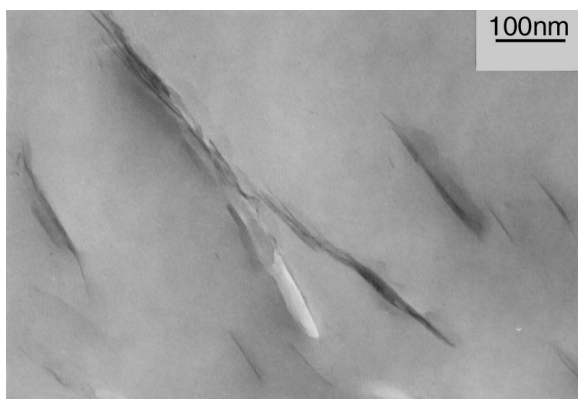


Fig. 4. TEM photograph of the MMT layer stacking with PEI molecule intercalated between the silicate layers. The spacing of the silicate layer increased to 6–7 nm and the face-to-face associated layers were oriented in the shear field and slipped in a staircaselike fashion. This PEI/MMT(5 wt%) nanocomposite sample was prepared by following route: PEI and MMT were dry-mixed and heated to 370°C. Then the melt mixture was blended for 1–2 min in the internal mixer.

uptake of the samples have not reached equilibrium. In another procedure the samples were immersed in solvents at 25°C for three days, and at 100°C for 1 h. Our intention is to investigate the solvent resistance properties at a relatively high temperature and the saturated solvent uptake of the PEI/MMT nanocomposites. In both cases, the introduction of MMT leads to an obvious decrease in the solvent uptake. For instance, as the MMT content was increased from 0 to 20 wt%, the ethanol uptake rate of the PEI/MMT nanocomposites decreased from 0.47%(25°C), 0.81%(100°C) to 0.35%(25°C), 0.39%(100°C), respectively. In addition, the virgin PEI could dissolve in non-protonic polar solvents, while the PEI/MMT nanocomposites could not be dissolved in these solvents at 25°C. The dramatic decrease in solvent uptake of the PEI/MMT nanocomposites compared to virgin PEI is due to the strong interactions between PEI and MMT, the excellent barrier properties of the large aspect ratio silicate layers and the exfoliated structure of MMT layers which maximizes the available surface area of the reinforcing phase. The interaction between PEI and MMT leads to

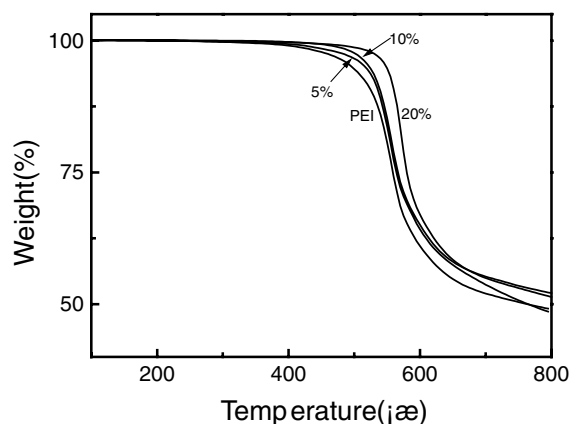


Fig. 5. TGA curves of the PEI/MMT nanocomposites with various MMT contents.

the formation of “bound polymer”, polymer in close proximity to the reinforcing filler (MMT) which is either physisorbed or chemisorbed and therefore restricts the solvent uptake [23]. Conventional non-reinforcing fillers prevent the formation of bound polymer, allowing large vesicles to form during solvent exposure, resulting in increased solvent uptake. Solvent uptake is inversely proportional to the filler reinforcing strength which strongly depends on filler surface area and agglomerate structure. Therefore, the exfoliated structure and the large surface of the layered silicate (750 m²/g) [24] are favorable to the solvent resistance properties of the PEI/MMT nanocomposites.

3.5. Thermal properties of the PEI/MMT nanocomposites

Fig. 5 shows the TGA analysis of PEI and the PEI/MMT nanocomposites with various MMT contents. The PEI/MMT nanocomposites showed delayed decomposition compared to PEI. The initial thermal decomposition temperature (on-set temperature) was increased from 514.2°C for the virgin PEI to 551.2°C for the nanocomposite containing 20 wt% MMT (cf. Table 2). MMT possesses high thermal stability and its layer structure exhibits great

Table 1
Solvent uptake rate of the PEI/MMT nanocomposites with various MMT contents

Solvent uptake rate (%)	PEI		5%		10%		20%	
	25°C ^a	100°C ^b	25°C	100°C	25°C	100°C	25°C	100°C
Water	0.68 ^c	1.02	0.58	0.72	0.49	0.61	0.37	0.65
Ethanol	0.47	0.81	0.36	0.72	0.37	0.55	0.35	0.39
Xylene	0.55	1.31	0.51	1.20	0.38	1.10	0.31	0.80
NMP	d		85		75		69	
DMSO	d		80		71		58	
DMA	d		78		65		61	

^a The sample was soaked in solvent at 25°C for 24 h.

^b The sample was soaked in solvent at 25°C for three days, 100°C for 1 h in a sealed vessel.

^c The calculation formula of the solvent uptake rate: $(W_{\text{wet}} - W_{\text{dry}})/W_{\text{dry}} \times 100\%$.

^d The sample was dissolved in this solvent.

Table 2
Thermal properties of the PEI/MMT nanocomposites with various MMT contents

MMT content (wt%)	0	5	10	20
T_d (°C) ^a	514.2	523.5	526.6	551.2
T_g (°C) ^b	174.0	200.1	209.5	210.4

^a Thermal decomposition temperature (on-set) from TGA measurement, scan rate: 20°C/min N₂ protection.

^b Obtained from DSC measurements, scan rate: 20°C/min N₂ protection.

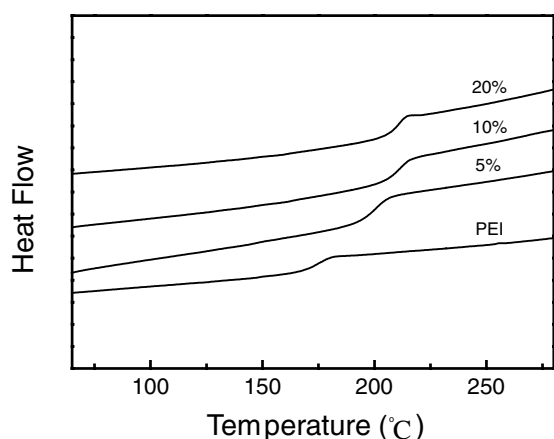


Fig. 6. DSC traces of the PEI/MMT nanocomposites with various MMT contents.

barrier effect to stop the evaporation of the small molecules generated in the thermal decomposition process and effectively limits the continuous decomposition of the PEI [7,19].

DSC analysis has been carried out to study the glass transition of the PEI/MMT nanocomposites (Fig. 6). The T_g of the nanocomposite was also increased remarkably as the MMT content was increased (cf. Table 2). This is clearly caused by the strong interaction between MMT and PEI, which limits the cooperative motions of the PEI main chain segments.

4. Conclusions

“Exfoliated” type PEI/MMT nanocomposites are

successfully prepared by melt intercalation in an internal mixer. Homogeneous dispersion of the MMT layers in PEI was verified by XRD and TEM analyses. Because of the good dispersion of the MMT layers and strong interaction between the PEI matrix and the MMT layers, the nanocomposites show higher T_g , better thermal stability and solvent resistance properties than the virgin PEI.

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