

Preparation and Properties of Organo-Soluble Polyimide and Montmorillonite Hybrids

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INTRODUCTION

An intercalation is one of the most effective approach to prepare inorganic/organic hybrids, in which organic materials are intercalated between sheets of inorganic materials such as mica and montmorillonite. Montmorillonite is composed of silicate sheets of 1nm thickness with adsorbed exchangeable cations. The spacing between the two silicate sheets is 1-2 nm. The intercalation with organic materials increases the spacing between the silicate sheets and even lead to the complete dissociation of the sheets to form a montmorillonite/organic composite with a nanometer scale¹. This type of inorganic/organic hybrids possess following features: The introduction of very small fraction of inorganic material would lead to dramatic property improvement²; The hybrids possess excellent "barrier" property because of the two dimensional sheet structure of the inorganic materials introduced¹. This type of composites are of intense study in the past few years². Yano et al³. prepared clay/polyimide hybrids which possess much lower thermal expansion coefficient (CTE) than the corresponding polyimide. Because of a hydrophilic nature of montmorillonite, the organo-modification of montmorillonite is an important step in the preparation of montmorillonite/polymer hybrids to generate a micro chemical environment for the intercalation of a polymer or a monomer.

Aromatic polyimides (PI) exhibit outstanding dielectric and mechanical properties at elevated temperature^{4,5}. Yano et al. used a conventional aromatic polyimide based on pyromellitic dianhydride (PMDA) and 4,4-diaminodiphenylether (ODA) in montmorillonite/polymer hybrids³. This polyimide and the corresponding hybrids would be neither soluble nor fusible due to the high rigidity and conjugation of the polyimide backbone. This causes difficulties in fabrication and may limit their applications.

In this paper, we report the preparation, characterization and properties of montmorillonite/organo-soluble polyimide hybrids using a monomer solution intercalation polymerization method.

EXPERIMENTAL

Preparation of organophilic-montmorillonite

(1). Montmorillonite organo-modified with amino acids

A mixture of 0.0673 mol of an amino acid (6-aminohexanoic acid or *p*-aminobenzoic acid), 5.05 ml of 37 wt% hydrochloric acid aqueous solution (0.0584 mol HCl) and 100ml distilled water was heated to 80°C followed by an agitation vigorously with aqueous dispersion of Na-MMT for 1 hour. The organophilic MMT was then collected by filtration and washed with 400ml hot water for three times to remove the residual ammonium salt and dried.

(2). Montmorillonite organo-modified with primary aliphatic amines

A mixture of 0.0476 mol of a primary aliphatic amine (ethanolamine, 1-dodecylamine or 1-hexadecylamine), 4.85 ml 37 wt% hydrochloric acid aqueous solution (0.056 mol HCl) (phosphoric acid for ethanolamine) and 100ml distilled water was used. The further process was the same with the former section.

(3). Montmorillonite organo-modified with quaternary ammonium salts

1.8 mg phenthiazine was dissolved in 0.1 mol DMAEM. 20ml acetonitrile was added dropwisely with the agitation. The mixture was then heated to 50°C. The solution of 21.9g (0.154 mol) methyl iodide in 20 ml acetonitrile was slowly added in a period of 3 hours. The mixture was then stirred for another 30 minutes

before cooled to room temperature. The white crystal was obtained by filtration followed by washing with acetonitrile. The aqueous solution of this white crystal (0.026 mol in 100 ml water) was agitated with a warm (50°C) aqueous dispersion of Na-MMT for 1 hour. The modified montmorillonite was collected by filtration followed by washing with distilled water until no I⁻ was detected by silver nitrate.

Preparation of montmorillonite/polyimide (MMT/PI) hybrids

The organophilic montmorillonites were added to DMA and the mixtures were heated to 90°C and agitated for 3 hours. MMDA was dissolved in DMA at room temperature and the organophilic montmorillonite/DMA solution was added. The mixture was stirred for 30 minutes and PMDA was added. This mixture was then stirred at room temperature for 6 hours.

The obtained montmorillonite/polyamic acid (MMT/PA) mixture was cast on a glass substrate and subsequently heated at 100°C for 6 hours, 150°C for 4 hours and 270°C for 2 hours under N₂ to obtain MMT/PI hybrids.

Characterization and property measurements of MMT/PI hybrids

The wide angle X-ray diffraction (WAXD) patterns of MMT/PI hybrid films were recorded on a Rigaku Geiger Flex D/max-RB diffractometer using Cu K α radiation (50kV, 100mA). The experiments were performed in a range of $2\theta = 1-40^\circ$ with a scan rate of $2^\circ/\text{min}$. The FT-IR spectra of MMT/PI hybrid film samples were recorded on a Perkin Elmer 180 Infrared Spectrophotometer. Transmission electron microscope (TEM) photographs of ultrathin sectioned MMT/PI hybrid samples were taken on a Hitachi-800 Transmission Electron Microscope. The thermal gravimetric analysis (TGA) of PI and MMT/PI hybrids were conducted on a Perkin-Elmer TGA 7 Thermal Analyzer under N₂ flow. The heating rate was 20°C/min. The linear thermal expansion coefficient (TEC) of PI and MMT/PI hybrids was measured on a Perkin-Elmer TMS-2 Thermal Mechanical Analyzer. The heating rate is 10°C/min. The stress-strain curves of PI and MMT/PI hybrids were recorded on an Instron-8500 Universal Tester at the room temperature at a drawing rate of 5mm/min. The solubility of PI and MMT/PI hybrids in various organic solvents at the room temperature were also measured.

RESULTS AND DISCUSSION

Influence of intercalation agent on the structure of MMT

Table 1 lists the basal spacings of MMT samples without the organo-modification and modified with various intercalation agents obtained from WAXD patterns. The basal spacing of the MMT is increased by the organo-modification. For a certain type of intercalation agent, the basal spacing of an organo-modified MMT is increased with the length of the alkyl group in an intercalation agent. For amino acids, the basal spacing increases from 1.27nm for a MMT modified with ArNCO (ArNCO-MMT) to 1.33-4.96nm for a MMT modified with 6NCO (6NCO-MMT). For the primary aliphatic amine series, the spacing is increased from 1.47-2.87nm for a 12CNH-MMT to 1.50-3.70nm for a 16CNH-MMT. (MIX-MMT is a MMT modified with a mixture of primary aliphatic amine with carbon numbers from 12 to 24). This trend is also observed in the quaternary ammonium salt series: the montmorillonites modified with DMAEM have spacings of 1.42-2.16nm while those modified with HDTMA have spacings of 1.89-4.05nm.

Generally speaking, the greater spacing would be an advantage of the intercalation of a monomer or polymer. It would also lead to easy disassociation of MMT, which would result in hybrids with better dispersion of MMT. From TEM photographs, it is observed that the particle size of MMT in 16CNH-MMT/PI hybrid is about 150nm while that in ArNCO-MMT/PI is about 400nm. It is also observed that the dispersion of MMT in a hybrid depends on functional groups of the intercalation agents. Table 2 lists the dispersion behavior of MMT modified with various intercalation agents. It is observed that MMTs modified with amino acids and primary aliphatic amines exhibit good dispersion behavior in the hybrids and the dispersion behavior is improved as the spacing of MMT is increased. When the amino hydrogen atoms of the intercalation agent are substituted, the modification of MMT with such an intercalation agent would lead to large spacings. However, the dispersion behavior of the modified MMT in a hybrid is not satisfactory. This "bad" dispersion behavior may be attributed to the difference in the structure between an intercalation agent and the diamine monomer, which reduces the affinity of the modified MMT with polyimide monomers.

Table 1 d-Value of MMT modified with various intercalation agents

Entry	2 θ (°)	d-value (nm)	Entry	2 θ (°)	d-value (nm)
Na-MMT	7.01	1.26	16CNH-MMT	2.38	3.70
				5.90	1.50
ArNCO-MMT	6.94	1.27	MIX-MMT	5.70	1.55
HONH-MMT	6.86	1.29	DMAEM-MMT	4.08	2.16
6NCO-MMT	1.78	4.96		4.46	1.98
	2.08	4.24		5.06	1.75
	2.90	3.04		6.22	1.42
	3.26	2.71	HDTMA-MMT	2.18	4.05
	4.96	1.78		3.04	2.90
	5.32	1.66		4.68	1.89
	5.58	1.58			
	6.06	1.46			
	6.48	1.36			
	6.60	1.33			
12CNH-MMT	3.08	2.87			
	5.02	1.76			
	6.00	1.47			

Table 2 Dispersion behavior of organo-MMT in DMA and polyimide

sample	dispersability in DMA	dispersability in polyimide
HONH-MMT	○	○
ArNCO-MMT	○	○
6NCO-MMT	○	○
12CNH-MMT	△	△
16CNH-MMT	○	○
MIX-MMT	○	○
DMAEM-MMT	×	×
HDTMA-MMT	×	×

○: dispersible; △: partially dispersible; ×: not dispersible.

Thermal properties of MMT/PI hybrids

The thermal decomposition temperatures of MMT/PI hybrids obtained from their TGA curves are listed in Table 3. It is observed that most of the hybrids possess slightly higher thermal stability than the corresponding PI. It is also observed that the hybrid possesses higher thermal stability when MMT is well dispersed. The thermal stability of 16CNH-MMT/PI hybrid is higher than that of 12CNH-MMT/PI hybrid, due to the better dispersion of 16CNH-MMT in the hybrid than 12CNH-MMT. HDTMA-MMT/PI hybrid possesses a much lower thermal stability probably because of the poor dispersion of HDTMA-MMT.

The thermal decomposition temperatures of 16CNH-MMT/PI hybrid with various MMT contents are listed in Table 4. It is found that the thermal stability of a hybrid increases with the increase of the MMT content when the MMT content is less than 10%. This observation again supports the claim that the dispersion behavior would affect the thermal stability of the hybrid. As the MMT content increases, the aggregation tendency of MMT increases.

Fig. 1 is the relationship between the MMT content and the thermal expansion coefficient (TEC) of 16CNH-MMT/PI hybrids. It is observed that the introduction of an only small amount of 16CNH-MMT dramatically reduces the thermal expansion coefficient. The TEC of PI is decreased from $3.60 \times 10^{-5} \text{ K}^{-1}$ to $1.96 \times 10^{-5} \text{ K}^{-1}$ (a 45% decrease) when only 1 wt% of 16CNH-MMT is introduced. As the MMT content is increased, the TEC decreases continuously.

Table 3 Thermal stability of MMT/PI hybrids using various intercalation agents (MMT content: 5wt%)

Intercalation agent	HONH	ArNCO	HDTMA	12CNH	16CNH	MIX	PI
T_d^a (°C)	510	546	474	516	554	518	510
T_d^b (°C)	564	581	551	577	595	584	573

a: Temperature at 5% weight loss determined by TGA;

b: Temperature at 10% weight loss determined by TGA;

N_2 protection; scan rate: 20°C/min.

Table 4 Thermal properties of 16CNH-MMT/PI hybrids with various MMT contents

MMT content (wt%)	0	1	2.5	5	10
T_d^a (°C)	510	501	530	554	486
T_d^b (°C)	573	582	570	595	550
TEC ($\times 10^{-5} K^{-1}$)	3.60	1.96	1.70	1.60	1.55

a: Temperature at 5% weight loss determined by TGA;

b: Temperature at 10% weight loss determined by TGA;

N_2 protection; scan rate: 20°C/min.

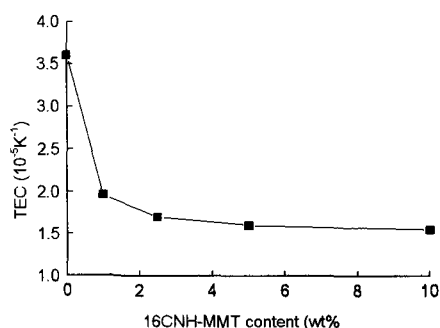


Fig. 1 Coefficient of thermal expansion of 16CNH-MMT/PI hybrids

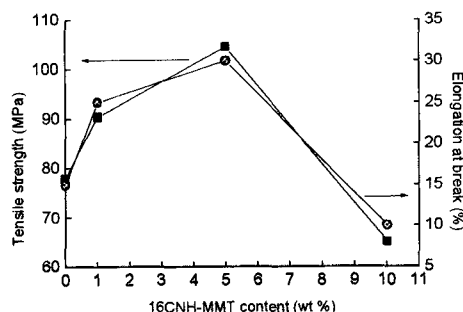


Fig. 2 Mechanical properties of 16CNH-MMT/PI hybrids

Mechanical and optical properties of MMT/PI hybrids

The influence of the MMT content upon the mechanical properties of the hybrids is shown in Fig. 2. When the MMT content is less than 5 wt%, both tensile strength and the elongation at break are increased with MMT content. When the MMT content exceeds 5 wt%, both the tensile strength and the elongation at break are decreased. These decreases may be caused by the aggregation of MMT, which leads to the loss of the features of a nanometer composite.

Solubility of MMT/PI hybrids

Because of the high aromaticity and rigidity of the pyromellitic dianhydride moiety, the conventional polyimides based on PMDA are neither soluble nor fusible and are difficult to process. In this study, 4,4'-diamino-3,3'-dimethyldiphenylmethane (MMDA) was used to prepare polyimide with PMDA. The incorporation of the two substitute methyl groups leads to the increase in the free volume and the decrease of the molecular packing. The steric hindrance from the methyl groups may also lead to the distortion of the conjugation of the polyimide backbones. Because of above reasons, polyimide based on PMDA and MMDA is organo-soluble⁶.

Table 5 is the solubility of MMT/PI hybrids. The solubility of a hybrid is mainly decided by the dispersion behavior of MMT particles. When the MMT content is low and an appropriate intercalation agent is used, the hybrid is observed to be soluble in aprotic polar solvents. The solubility would be reduced by the aggregation of MMT particles resulting from either increased MMT content or inappropriate selection of the intercalation agent.

Table 5 Solubility of MMT/PI hybrids (25°C)

MMT content (wt%)	ArNCO-MMT/PI		16CNH-MMT/PI				MIX-MMT/PI	12CNH-MMT/PI	HDTMA-MMT/PI
	0	5	0	1	5	10	5	5	5
NMP	+	+	+	+	+	+-	+	+-	-
DMA	+	+	+	+	+	+-	+	+-	-
DMF	+	+	+	+	+	+-	+	+-	-
DMSO	+	+	+	+	+	+-	+	+-	-

+: soluble; +-: partially soluble; -: insoluble.

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