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Preparation and properties of hybrids of organo-soluble polyimide and montmorillonite with various chemical surface modification methods

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Abstract

Montmorillonite (MMT)/Organo-soluble polyimide (PI) hybrids were prepared using a monomer solution intercalation polymerization method. The organo-soluble polyimide was based on pyromellitic dianhydride and 4,4′-diamino-3,3′-dimethyldiphenylmethane. The MMT was organo-modified with three types of intercalation agents: amino acids, primary aliphatic amines and quaternary ammonium salt. The dispersion behavior of MMT in organic solvents and polyimide depends on the type of the functional group and the bulky group of the intercalation agent. The MMT modified with 1-hexadecylamine is observed to possess the best dispersion behavior. The properties of a MMT/PI hybrid are also greatly dependent upon the dispersion behavior of MMT particles. When the MMT is well dispersed, a MMT/PI hybrid would possess desired properties such as strengthening and toughening at the same time, improved thermal stability, decreased thermal expansion coefficient, retaining of the solubility of the polyimide matrix and high optical transparency. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Montmorillonite; Polyimide; Hybrid

1. 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 (MMT). MMT is composed of silicate sheets of 1 nm 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 MMT/organic composite with a nanometer scale [1]. This type of inorganic/organic hybrids possesses following features: the introduction of very small fraction of inorganic material would lead to dramatic property improvement [2]; the hybrids possess excellent ‘‘barrier’’ property because of the two dimensional sheet structure of the inorganic materials introduced [1]. This type of composites have been topics of intense study in the past few years [2]. Yano et al. [3] prepared clay/polyimide hybrids which possess much lower thermal expansion coefficient (TEC) than the corresponding polyimide. They have also observed this decrease in CTE in other polymer hybrids [4–7]. Akelah et al. [8] reported the preparation of clay/PS and clay/rubber ATBN hybrids. Giannelis et al. [9,10] studied the polymer melt intercalation. Kato et al. [11] reported the study of clay/PP oligomer hybrids. Qi and co-workers [12–15] also reported the successful preparation of clay/nylon-6, clay/PET and clay/PBT hybrids.

On account of hydrophilic nature of MMT, its organo-modification is an important step in the preparation of MMT/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 [16,17]. Yano et al. used a conventional PI based on pyromellitic dianhydride (PMDA) and 4,4-diaminodiphenylether (ODA) in MMT/polymer hybrids [3]. This polyimide and the corresponding hybrids are neither soluble nor fusible because of 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 MMT/organo-soluble polyimide hybrids using a monomer solution intercalation polymerization

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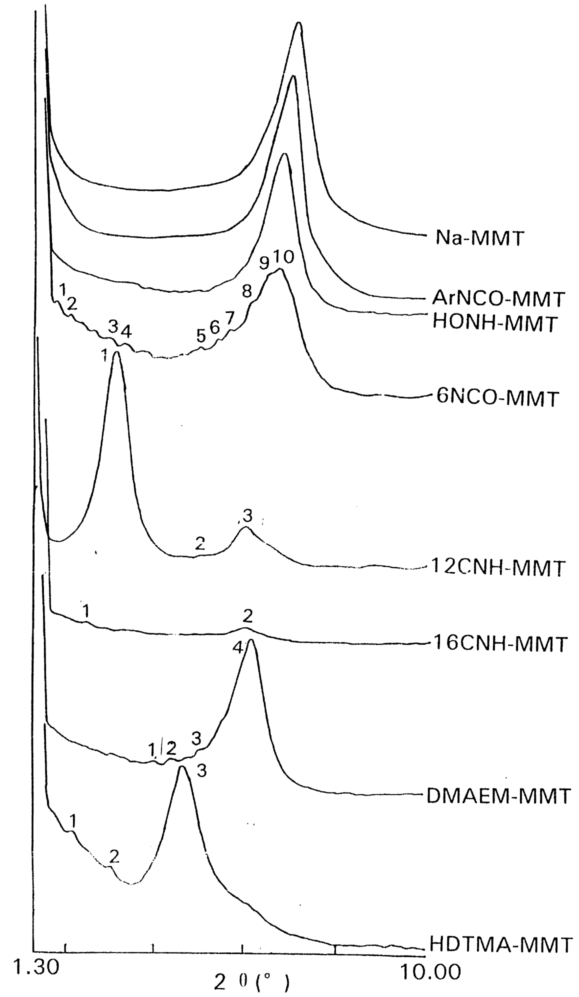
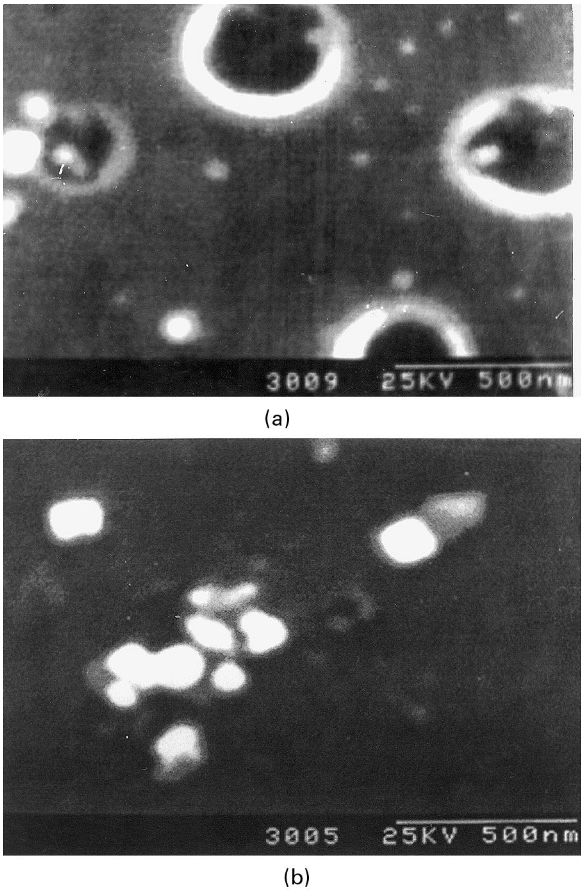


Fig. 1. WAXD patterns of MMT modified with various intercalation agents.



(a)

(b)

Fig. 2. TEM photographs of MMT/PI hybrids. A: ArNCO/PI hybrid (1 wt% MMT). B: 16CNH-MMT/PI hybrid (1 wt% MMT).

method. Various intercalation agents were used to chemically ‘‘modify’’ the surface of the MMT. An influence of the intercalation agents upon the effectiveness of chemical surface modification, the structure and the properties of the hybrids were studied.

2. Experimental

2.1. Materials

A sodium montmorillonite (Na-MMT) was supplied by the Institute of Chemical Metallurgy, Chinese Academy of Sciences. The particle size is 40 μm. Pyromellitic dianhydride (PMDA) (Chemical Reagent Grade) from Beijing Chemicals Company was recrystallized from acetic anhydride before use. 4,4′-Diamino-3,3′-dimethyldiphenylmethane (MMDA) was synthesized by a reaction of *o*-methyl aniline with formaldehyde [18]. *p*-Aminobenzoic acid (ArNCO) (Analytical Reagent Grade) from Beijing Chemicals Company was used without any purification. Ethanolamine (HONH), 6-aminohexanoic acid (6NCO), -dodecylamine (12CNH), 1-hexadecylamine (16CNH), hexadecyltrimethylamine (HDTMA), and N,N-dimethylaminoethyl methacrylate (DMAEM) (all Chemical Reagent Grade) from Beijing Chemicals Company were used as received. N-methyl-2-pyrrolidone (NMP), N,N-dimethyl acetamide (DMA), N,N-dimethyl formamide (DMF) and dimethyl sulfone (DMSO) (all Analytical Reagent Grade) from Shanghai Reagent Company were dried over molecular sieves before use.

2.2. Preparation of organophilic-montmorillonite

2.2.1. 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 (0.0584 mol HCl) and 100 ml distilled water was heated to 80°C followed by a vigorous agitation with aqueous dispersion of Na-MMT for 1 h. The organophilic MMT was then collected by filtration and washed with 400 ml hot water three times to remove the residual ammonium salt and dried.

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

Entry	2θ (°)	*d*-value (nm)
Na-MMT	7.01	1.26
ArNCO-MMT	6.94	1.27
HONH-MMT	6.86	1.29
6NCO-MMT	1.78	4.96
	2.08	4.24
	2.90	3.04
	3.26	2.71
	4.96	1.78
	5.32	1.66
	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
16CNH-MMT	2.38	3.70
	5.90	1.50
MIX-MMT	5.70	1.55
DMAEM-MMT	4.08	2.16
	4.46	1.98
	5.06	1.75
	6.22	1.42
HDTMA-MMT	2.18	4.05
	3.04	2.90
	4.68	1.89

Table 2
Dispersion behavior of organo-MMT in DMA and polyimide. ○: dispersible; △: partially dispersible; ×: not dispersible

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

2.2.2. 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 100 ml distilled water was used. Further process was the same as that described in the former section.

2.2.3. Montmorillonite organo-modified with quaternary ammonium salts

Phenthiazine (1.8 mg) was dissolved in 0.1 mol DMAEM. 20 ml acetonitrile was added dropwise with simultaneous agitation. The mixture was then heated to 50°C The solution of 21.9 g (0.154 mol) methyliodide in 20 ml acetonitrile was slowly added over a period of 3 h. The mixture was then stirred for a further 30 min before being cooled to room temperature. A 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 h. The modified MMT was collected by filtration followed by washing with distilled water until no I^- was detected by silver nitrate.

2.3. Preparation of montmorillonite/polyimide (MMT/PI) hybrids

The organophilic MMTs were added to DMA and the mixtures were heated to 90°C and agitated for 3 h. MMDA was dissolved in DMA at room temperature and the organophilic MMT/DMA solution was added. The mixture was stirred for 30 min followed by addition of PMDA. This mixture was then stirred at room temperature for 6 h.

The obtained montmorillonite/polyamic acid (MMT/PA) mixture was cast on a glass substrate and subsequently heated at 100°C for 6 h, 150°C for 4 h and 270°C for 2 h under N_2 to obtain MMT/PI hybrids.

2.4. 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 CuKα radiation

Table 3
Thermal stability of MMT/PI hybrids using various intercalation agents. (MMT content: 5 wt%; N_2 protection; scan rate: 20°C/min)

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.

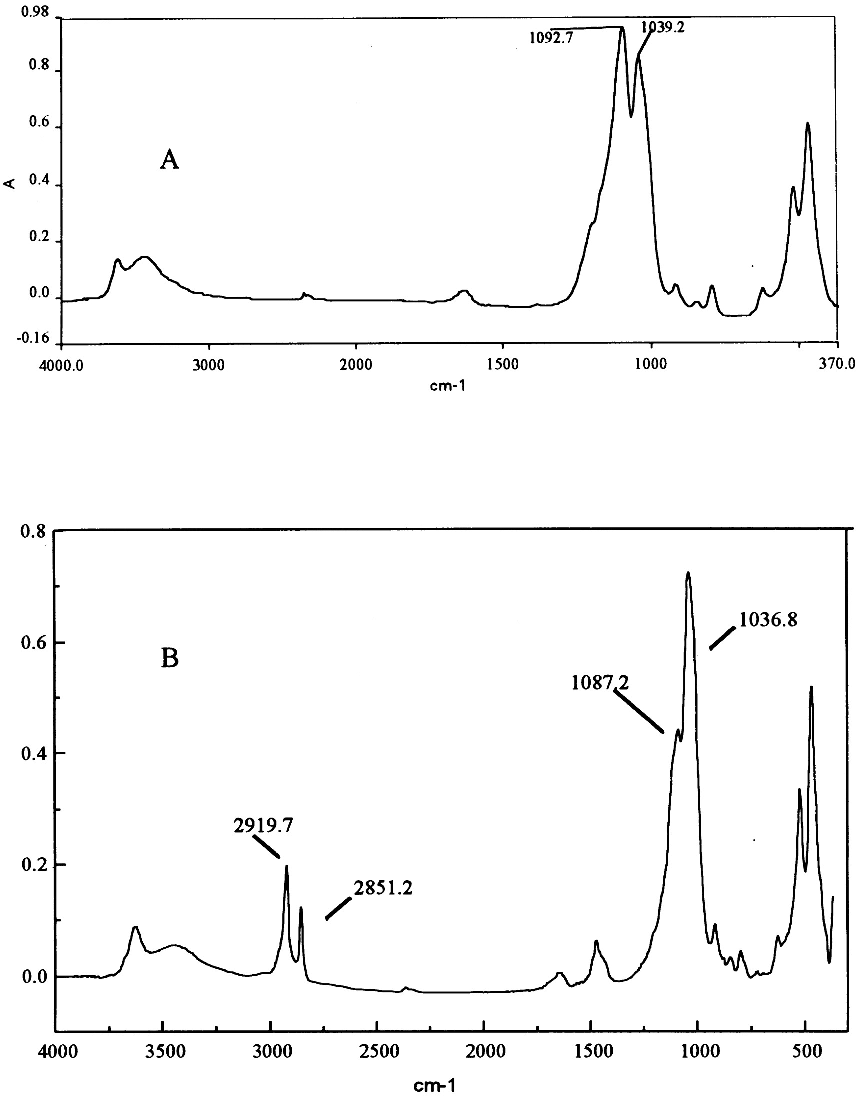


Fig. 3. IR spectra of Na-MMT (A), 16CNH-MMT (B), 16CNH-MMT/PA (C) and 16CNH-MMT/PI (D).

(50 kV, 100 mA). The experiments were performed in a 2θ range of 1–40° with a scan rate of 2°/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 N_2.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 was 10°C / min.

The stress–strain curves of PI and MMT/PI hybrids were recorded on an Instron-8500 Universal Tester at room temperature at a drawing rate of 5 mm/min.

The solubility of PI and MMT/PI hybrids in various organic solvents at room temperature were also measured.

3. Results and discussion

3.1. Influence of intercalation agent on the structure of MMT

Fig. 1 shows the WAXD patterns of MMT samples without the organo-modification and modified with various intercalation agents. Table 1 lists the basal spacings. 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

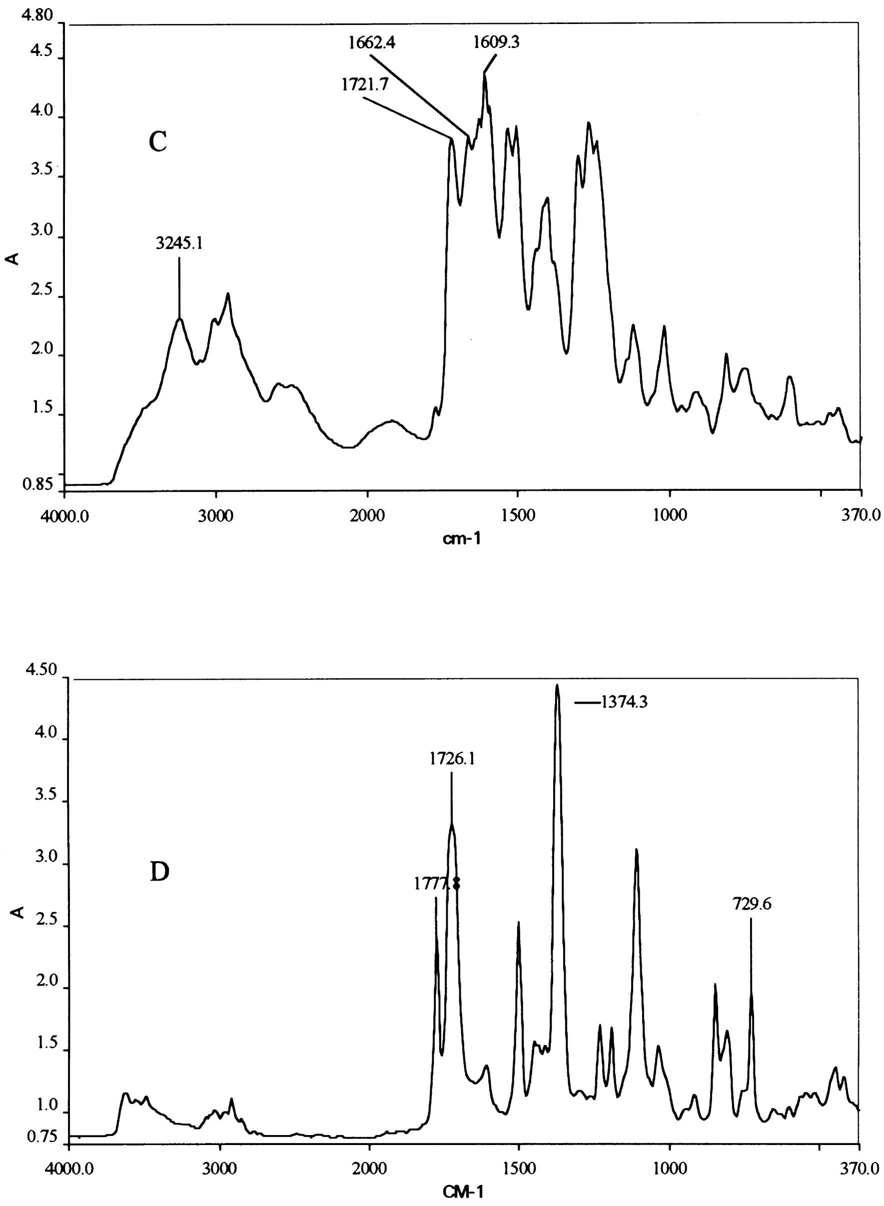


Fig. 3. Continued.

length of the alkyl group in an intercalation agent. For amino acids, the basal spacing increases from 1.27 nm for a MMT modified with ArNCO (ArNCO-MMT) to 1.33–4.96 nm for a MMT modified with 6NCO (6NCO-MMT). For the primary aliphatic amine series, the spacing is increased from 1.47–2.87 nm for a 12CNH-MMT to 1.50–3.70 nm 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 was also observed in the quaternary ammonium salt series: the

Table 6
Solubility of MMT/PI hybrids (at 25°C) + : soluble; ± : partially soluble; − : insoluble

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

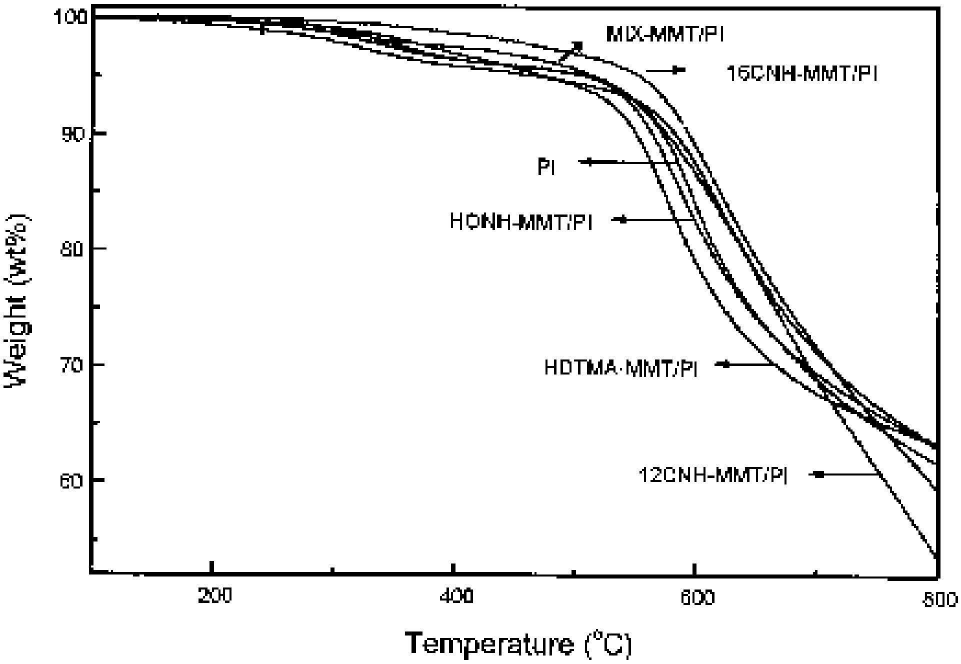


Fig. 4. TGA curves of MMT/PI hybrids with various surface modification methods. MMT content: 5 wt%; N_2 protection; scan rate: 20°C/min.

MMTs modified with DMAEM have spacings of 1.42–2.16 nm while those modified with HDTMA have spacings of 1.89–4.05 nm.

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. Fig. 2 shows the TEM photograph of MMT/PI hybrids. It is observed that the particle size of MMT in 16CNH-MMT/PI hybrid is about 150 nm while that in ArNCO-MMT/PI is about 400 nm. 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

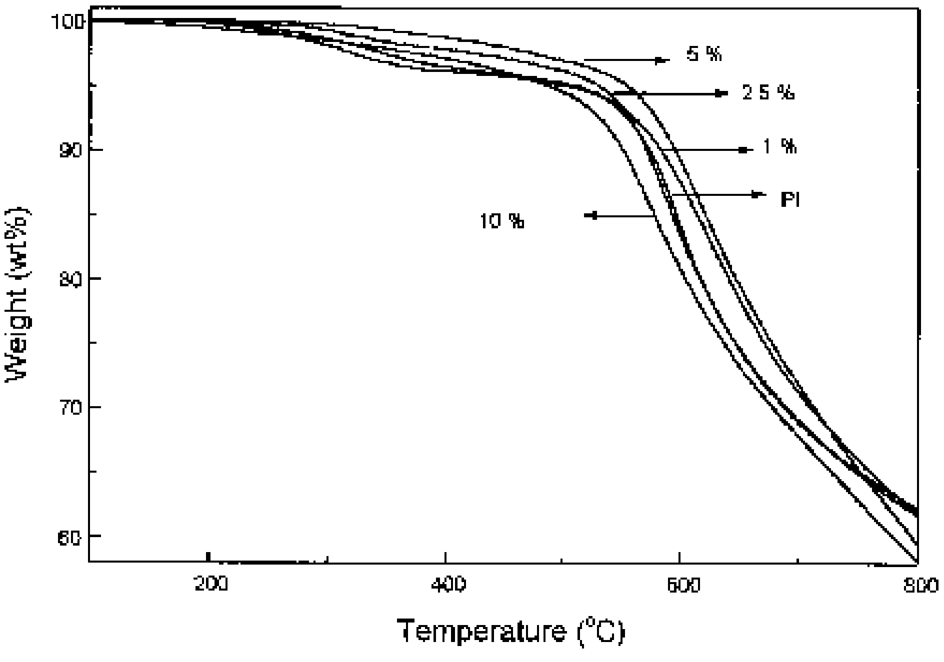


Fig. 5. TGA curves of 16CNH-MMT/PI hybrids with various MMT contents. N_2 protection; scan rate: 20°C/min.

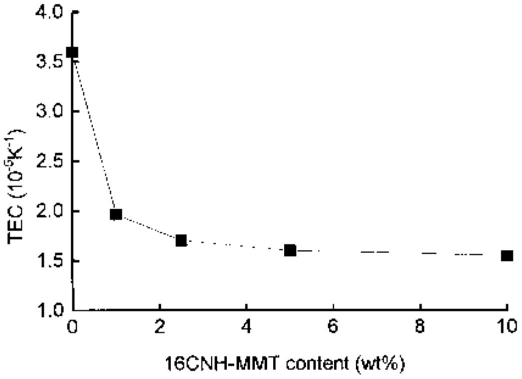


Fig. 6. Relationship between 16CNH-MMT content and thermal expansion coefficient of the 16CNH-MMT/PI hybrids.

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.

3.2. IR characterization of MMT/PI hybrids

Fig. 3 shows the IR spectra for Na-MMT, 16CNH-MMT, 16CNH-MMT/PA hybrid and 16CNH-MMT/PI hybrid. Bands at 1092 cm^{-1} and 1039 cm^{-1} are the characteristic absorption bands of Na-MMT (Fig. 3A). After the treatment with 16CNH, the sample exhibits characteristic bands of C–H stretching at 2920 cm^{-1} and 2851 cm^{-1} (Fig. 3B). In the IR spectrum for 16CNH-MMT/PA hybrid, the characteristic bands of amide groups at 1721, 1662 and 1609 cm^{-1} are observed. In the thermal imidization process, polyamic acid is converted to polyimide upon a ring closure reaction. This is confirmed by the observation of the characteristic absorption bands of C=O stretching in imide groups (1778 and 1726 cm^{-1}) and C–N stretching in imide groups (1374 cm^{-1}).

Table 4
Thermal properties of 16CNH-MMT/PI hybrids with various MMT contents. (N_2 protection; scan rate: 20°C/min)

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 (× 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.

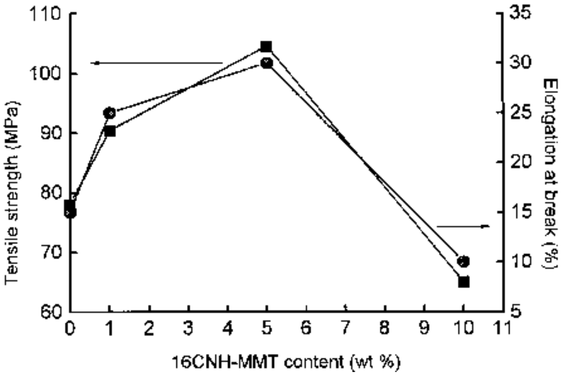


Fig. 7. Relationship between 16CNH-MMT content and the mechanical properties of 16CNH-MMT/PI hybrids.

3.3. Thermal properties of MMT/PI hybrids

Fig. 4 shows the TGA curves of MMT/PI hybrids with identical MMT content (5 wt%) but various organo-modification methods. The thermal decomposition temperatures obtained 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, owing to the better dispersion of 16CNH-MMT in the hybrid than 12CNH-MMT (cf. Table 2). HDTMA-MMT/PI hybrid possesses a much lower thermal stability probably because of the poor dispersion of HDTMA-MMT (cf. Table 2).

Fig. 5 shows the TGA curves of 16CNH-MMT/PI hybrid with various MMT contents and the thermal decomposition temperatures 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 affects the thermal stability of the hybrid. As the MMT content increases, the aggregation tendency of MMT increases.

Fig. 6 is the relationship between the MMT content and the TEC of 16CNH-MMT/PI hybrids. It is observed that the introduction of only a small amount of 16CNH-MMT dramatically reduces the TEC. The TEC of PI is decreased from 3.60 × 10^{-5} K^{-1} to 1.96 × 10^{-5} K^{-1} (a 45% decrease) when only 1 wt% of 16CNH-MMT is introduced.

Table 5
Mechanical and optical properties of 16CNH-MMT/PI hybrids with various MMT contents (at 25°C); T: transparent; Tr: translucent

16CNH-MMT content (wt%)	0	1	5	10
Tensile strength (MPa)	78.0	90.4	104.5	65.0
Elongation at break (%)	15	25	30	10
Remarks	T	T	T	Tr

As the MMT content is increased, the TEC decreases continuously.

3.4. Mechanical and optical properties of MMT/PI hybrids

The influence of the MMT content on the mechanical properties of the hybrids is shown in Table 5 and Fig. 7. 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.

As shown in Table 5, the hybrid films with low MMT content are transparent. The high transparency of the hybrid comes from the nanometer scale dispersion of the MMT particles. A high MMT content leads to aggregation of MMT particles, which reduces the transparency of a visible light.

3.5. 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 an increase in the free volume and resultant 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. On account of these reasons, polyimide based on PMDA and MMDA is organo-soluble [18].

The solubility data of MMT/PI hybrids are presented in Table 6. 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 is reduced by the aggregation of MMT particles resulting from either increased MMT content or inappropriate selection of the intercalation agent.

4. Conclusions

The properties of MMT/PI hybrids are greatly dependent on the dispersion behavior of MMT particles. Only when the MMT is well dispersed, that an MMT/PI hybrid can possess good properties such as simultaneous strengthening and toughening, improved thermal stability, decreased thermal expansion coefficient, retention of the solubility of the polyimide matrix and high optical transparency. The chemical structure of an intercalation agent imposes great influence on the dispersion of MMT. 1-Hexadecylamine is the best selection for MMT/PI hybrid system studied.

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