The Preparation and Properties of Organo-Soluble Polyimide/Clay Hybrid Materials

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INTRODUCTION

Montmorillonite (MMT) is a type of clay made of silicate sheets with a thickness of about 1 nm. It has been reported that some organic compounds such as styrene, acrylic acid and acrylnitrile may enter in between the silicate sheets and undergo polymerization¹⁻⁴. According to this feature, it is possible to disassociate montmorillonite to particles with nanometer size. This may provide a novel route (intercalation method) to prepare polymer/clay nanometer composites.

In comparison with conventional polymer-matrix composites, polymer layered silicate (PLS) nanocomposites prepared by the intercalation method possess following features: Very small fraction of silicate filler would give obvious improvements in the strength and toughness to the materials⁵⁻⁹; The composites possess excellent thermal stability and size stability⁵⁻⁹; The composite films possess excellent barrier property because of the planer orientation of the silicate sheets¹⁰⁻¹².

Aromatic polyimides exhibit outstanding dielectric and mechanical properties at elevated temperature^{13,14}. The study on polyimide/ montmorillonite hybrids has been reported by Yano et al.^{5,15}. In their studies, a conventional aromatic polyimide based on pyromellitic dianhydride (PMDA) and 4,4-diaminodiphenylether (ODA) was used as the polymer matrix. This polyimide and the corresponding hybrids would be neither soluble nor fusible after the imidization process. This causes difficulties in fabrication and may limit their applications. In this study, an organo-soluble polyimide is used as the matrix to prepare novel organo-soluble polyimide/montmorillonite hybrids through a monomer solution intercalation polymerization method in an attempt to obtain materials with improved thermal stability, mechanical properties and lower thermal expansion coefficient than conventional polyimides. The materials may find good applications in microelectronic industry.

EXPERIMENTAL

Materials

Sodium montmorillonite (Na-MMT) was supplied by the Institute of Chemical Metallurgy, Chinese Academy of Sciences. The particle size is $40 \ \mu$ m. p-Aminobenzoic acid (Analytical Reagent Grade) was purchased from Beijing Chemical Company and used as received. Pyromellitic dianhydride (PMDA) (Chemical Reagent Grade) was purchased from Beijing Chemicals Company and recrystallized from acetic anhydride before use. 3,3'-Dimethyl-4,4'-diamino diphenylmethane (MMDA) was

synthesized by the reaction between o-methyl aniline and formaldehyde. N-methyl-2pyrrolidone (NMP) (Analytical Reagent Grade), N,N-dimethyl acetamide (DMA) (Analytical Reagent Grade), N,N-dimethyl formamide (DMF) (Analytical Reagent Grade) and dimethyl sulfone (DMSO) (Analytical Reagent Grade) were purchased from Shanghai Reagent Company and dried over molecular sieves before use. Common reagents, such as acetic anhydride were used without further purification.

Preparation of organophilic-montmorillonite

A mixture of 8.82 g (0.0584 mol) p-aminobenzoic acid, 4.8ml 37% (0.0584 mol) hydrochloric acid and 100 ml distilled water was heated to 80 °C. To it, a dispersion of montmorillonite in distilled water (heated to 80 °C) was added. The mixture was agitated vigorously for 1 hour. The organophilic MMT was then collected by filtration and washed with 400ml hot water for three times to remove the residual p-aminobenzoic acid and dried.

Preparation of polyimide/montmorillonite (PI/MMT) hybrids

3.14g organophilic montmorillonite was added to 90.0g DMAc and the mixture was heated to 90 °C and agitated for 3 hours. 1.045g (0.00462 mol) MMDA was dissolved in 18.6g DMAc at room temperature and to it organophilic montmorillonite/DMAc solution was added. The mixture was stirred for 30 minutes before 0.982g (0.00450 mol) PMDA was added to it. This mixture was then stirred at room temperature for 5 hours.

The obtained polyamic acid/montmorillonite solution was cast in glass and then heated subsequently at 100 °C for 6 hours, 150 °C for 2 hours and 270 °C for 2 hours under the protection of N₂ to obtain polyimide/montmorillonite hybrids. The preparation of the hybrids was described in Scheme 1.

Structure characterization and property measurements of PI/MMT hybrids

The FT-IR spectra of PI/MMT hybrid film samples were recorded on a Perkin Elmer 180 Infrared Spectrophotometer.

The thermal gravimetric analysis (TGA) of PI and PI/MMT hybrids was conducted on a Perkin-Elmer TGA 7 Thermal Analyzer under the protection of N_2 . The scan rate was 20 °C/min.

The linear thermal expansion coefficients (TECs) of PI and PI/MMT hybrids were measured on a Perkin-Elmer TMS-2 Thermal Mechanical Analyzer. The scan rate is 10 °C/min.

The stress-strain curves of PI and PI/MMT 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 PI/MMT hybrids were decided by the observation of the solubility of samples in various organic solvents at the room temperature.

RESULTS AND DISCUSSION

FT-IR Spectra

Fig. 1 is the FT-IR spectrum of a PI/MMT hybrid (MMT content: 5wt%). The

increased with the increase of the MMT content in the range studied. The temperature at 5 wt% loss of a PI/MMT is increased by 20 °C and 36 °C on the basis of PI for a MMT content of 1wt% and 5 wt%, respectively. This increase in the thermal stability by the introduction of MMT may firstly caused by the "barrier" effect⁴ of the montmorillonite layer structure which prevents the mobility of the small molecules produced during the thermal decomposition of polyimide molecules. The increase in the thermal stability of the hybrids may also result from the strong interaction between the organophilic montmorillonite and polyimide molecules. This strong interaction may make montmorillonite particles act as the crosslink points, which leads to the increase of the thermal stability of the hybrids with the increase of the MMT content. This explanation could be further supported by the observation that the thermal stability of a PI/Na-MMT hybrid is not increased compared to the corresponding PI.

It was also observed from Table 1 that the thermal expansion coefficients (TECs) of PI/MMT hybrids are effectively decreased compared to corresponding PI. The TEC of a hybrid is decreased with the increase of the MMT content. The TEC of the hybrid is decreased by about 40% and above 50% when only 1wt% and 5wt% of MMT, respectively, is introduced.

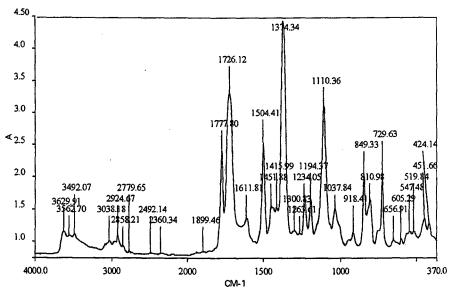


Fig. 1 IR Spectrum of PI/MMT Hybrids

MMT content (wt %)	0	1	5	5°
$T_d^{a}(^{\circ}C)$	510	530	546	501
T _d ^b (℃)	573	577	581	566
TEC (\times 10 ⁻⁵ K ⁻¹)	3.60	2.20	1.76	2.40

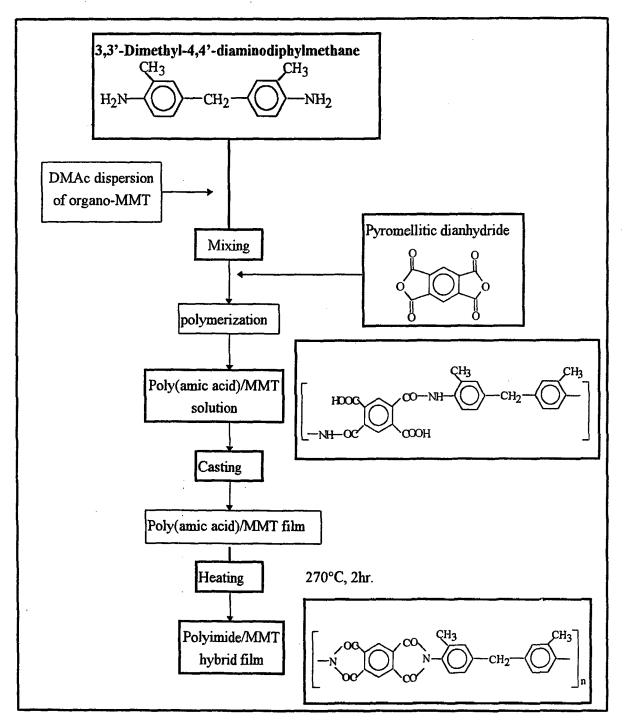
Table 1 Thermal properties of PI/MMT hybrids

 T_d : Decomposition temperature determined by TGA: a. 5% weight; b. 10% weight loss, scan rate: 20 °C/min., N₂ protection. c: PI/Na-MMT hybrid.

Mechanical properties of PI/MMT hybrids

The tensile strength and the elongation at break of PI and PI/MMT hybrids are listed in Table 2. It was observed that the tensile strength of the polyimide is clearly

clear appearance of the bands at 1778 cm⁻¹ and 1726 cm⁻¹, which are characteristic of C=O stretch in imide groups, and the disappearance of the 1660 cm⁻¹ and 1605 cm⁻¹ bands clearly indicate that the polyamic acid has been converted to polyimide after the thermal treatment.



Scheme 1 Preparation of MMT/PI hybrids using monomer intercalation polymerization method

Thermal properties of PI/MMT hybrids.

The thermal properties of PI/MMT hybrids were listed in Table 1. It was observed that the thermal resistance of PI/MMT hybrids is obviously increased compared to the corresponding PI. The thermal decomposition temperature of a PI/MMT hybrid is

increased with the introduction of MMT and also with the increase of the MMT content (in the range studied). However, the more interesting result comes from the observation that the introduction of 1wt% of MMT leads to a 60% increase in the elongation at break as well as a 13% increase in the tensile strength. The further increase in the MMT content would lead to the decrease in the elongation at break. Even though, the elongation at break of the hybrid containing 5wt% of MMT is still much higher than the polyimide. It can be concluded from above observation that in a certain MMT content range, the introduction of MMT would lead to both strengthening and toughening to the polyimide matrix. This may be regarded as the feature of a nanometer-composite. In this study, the decrease in the elongation at break of the hybrid as the MMT content is increased from 1wt% to 5wt% may be caused by the aggregation of the MMT particles. The aggregation leads to the increase in the particle size and as a result, the disappearance of the "nanometer effect". It could be expected, therefore, that the observation of both the strengthening and the toughening effects may extend to a wider MMT content range if the aggregation of MMT can be controlled and the MMT particle size can be restricted to the nanometer range as the content is increased. The improvements in the mechanical properties may result from the strong interfacial interaction between polyimide and MMT. This explanation may be supported by the fact that no obvious improvement in the mechanical properties on the したみいわしたりわ KATE TO basis of the polyimide was observed for PI/Na-MMT.

Table 2 Mechanical properties of PI/MMT hybrids (25 °C)

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MMT content (wt %)	0	1	5	(5)	(达)
tensile strength (MPa)	78	88	95	75	d-street
elongation at break (%)	15	24	20	17	いまれた
remarks	Т	T	<u> </u>	Т	1.

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a: PI/Na-MMT hybrid film; T: transparent.

Solubility of PI/MMT 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, a 3,3'-dimethyl substituted 4,4'-diamino / (f,f), f,fdiphenylmethane (MMDA) was used to prepare polyimide with PMDA. The for 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 molecules. Because of the above reason, polyimide based on PMDA and MMDA is organo-soluble¹⁶.

The solubility of PI/MMT hybrids before and after the imidization process was listed in Table 3. It was observed that solubility of PA/MMT hybrids is basically unaffected by the introduction and the content of MMT. PI/MMT hybrids also exhibit good solubility in strong aprotonic polar solvents such as NMP, DMAc, DMF and DMSO when the MMA content is below 5wt%. It was also observed that the solubility of a PI/MMT hybrid is even better than the polyimide when the MMT content is 1wt%.

17 Proceedings of the 2nd China-Japan Seminar on Advanced Aromatic Polymers This improvement in the solubility may be caused by the existence of small amounts of nanometer size MMT particles, which reduces the strong intermolecular interactions of polyimide and, as a result, increases the solubility.

MMT content (wt %)	PA/I	PA/MMT		PI/MMT			
	0	5	0	1	5	5ª	
NMP	+	+	+	+	+-	_	
DMAc	+	+	+	+	+-	—	
DMF	+	+	+	+	+		
DMSO	+	+-	+	+	+-	_	

Table 3 Solubility of PI/MMT hybrids (25 $^{\circ}$ C)

+: soluble; +-: partially soluble; -: insoluble; a: PI/Na-MMT.

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