

Preparation and Properties of Hybrids of Organo-Soluble Polyimide and Montmorillonite with Various Chemical Surface Modification Methods

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INTRODUCTION

Intercalation composition is one of the most effective approach to prepare organic/inorganic hybrids, in which polymers are intercalated in between the sheets of inorganic materials such as mica and montmorillonite. Montmorillonite is composed of silicate sheets of 1nm thickness and with absorbed exchangeable sodium and potassium cations. The spacing between the two silicate sheets is 1-2 nm. The intercalation of polymers would increase the spacing of the silicate sheets and even lead to the complete dissociation of the sheets to form a polymer/montmorillonite composite with a nanometer scale¹. This type of organic/inorganic 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 pyromellitic anhydride type polyimide/clay hybrids which possess much lower thermal expansion coefficient (CTE) than the corresponding polyimide. They have also observed this decrease in CTE in other polymer hybrids⁴⁻⁷. Akalah et al.⁸ reported the preparation of PS/clay and rubber ATBN/clay hybrids. Giannelis et al.^{9,10} studied the polymer melt intercalation. Kato et al.¹¹ reported the study of PP oligomer/clay hybrids. Qi et al.¹²⁻¹⁵ also reported the successful preparation of nylon-6/clay, PET/clay and PBT/clay hybrids.

In this paper, we report the preparation, characterization and properties of organo-soluble polyimide/montmorillonite hybrids using a monomer intercalation polymerization method. Various intercalation agents were used to chemically "decorate" the surface of montmorillonite. The influence of the type of intercalation agents upon the effectiveness of chemical surface decoration and the properties of the hybrids were also studied.

EXPERIMENTAL

Materials

Sodium montmorillonite (Na-MMT) was supplied by the Institute of Chemical Metallurgy, Chinese Academy of Sciences. The particle size is 40 μ m. p-Aminobenzoic acid (ArNCO) (Analytical Reagent Grade) was purchased from Beijing Chemicals 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. Ethanolamine (HONH), 6-aminohexanoic acid (6NCO), 1-dodecylamine (12CNH), 1-hexadecylamine (16CNH), hexadecyltrimethylamine (HDTMA), and N,N-dimethylaminoethyl methacrylate (DMAEM) (all Chemical Reagent Grade) were purchased from Beijing Chemicals Company and used as received. N-methyl 2-pyrrolidone (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

(1). Montmorillonite organo-treated with amino acids

A mixture of 0.0673 mol of an amino acid (6-aminohexanoic acid or *p*-amino benzoic acid), 0.0584 mol 37% hydrochloric acid and 100ml distilled water was heated to 80 °C. To it, the heated (80 °C) dispersion of montmorillonite in water was added. The mixture was then 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 ammonium salt and dried.

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

A mixture of 0.0476 mol of a primary aliphatic amine (ethanolamine, 1-dodecylamine or 1-hexadecylamine), 0.056 mol 37% hydrochloric acid (phosphoric acid for ethanolamine) and 100ml distilled water was heated to 80 °C. To it, the heated (80 °C) dispersion of montmorillonite in water was added. The mixture was then 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 ammonium salt and dried.

(3). Montmorillonite organo-treated with HDTMA and DMAEM

1.8 mg phentiazine was dissolved in 0.1 mol DMAEM. To it, 20ml acetonitrile was added dropwisely with the agitation. The mixture was then heated to 50 °C. To it, 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 resultant white crystals was obtained by filtration followed by washing with acetonitrile. The aqueous solution of this white crystals (0.026 mol in 100 ml water) was then added with vigorous agitation to a warm (50 °C) dispersion of montmorillonite in water and the mixture was then stirred for 1 hour. The treated montmorillonite was collected by filtration followed by washing with distilled water until no I⁻ was detected by silver nitrate.

Preparation of polyimide/montmorillonite (PI/MMT) hybrids

Organophilic montmorillonite was added to DMAc and the mixture was heated to 90 °C and agitated for 3 hours. MMDA was dissolved in DMAc at room temperature

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conducted on a Perkin-Elmer TGA 7 Thermal Analyzer under the protection of N₂. 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

Thermal properties of PI/MMT hybrids

Table 1 lists the thermal decomposition temperatures of polyimide and MMT/polyimide. It is observed that the thermal stability of a MMT/polyimide hybrid is slightly higher than the corresponding polyimide. It is also observed that a hybrid seems to possess 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 as the dispersion of 16CNH-MMT in the hybrid is better than 12CNH-MMT. HDTMA-MMT/PI hybrid possesses a much lower thermal stability probably because of the poor dispersion of HDTMA-MMT.

Table 1 Thermal stability of PI/MMT hybrids using various intercalation agents (MMT content: 5wt%)

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

T_d: Decomposition temperature determined by TGA. a: 5% weight loss; b: 10% weight loss. N₂ protection; scan rate: 20 °C/min.

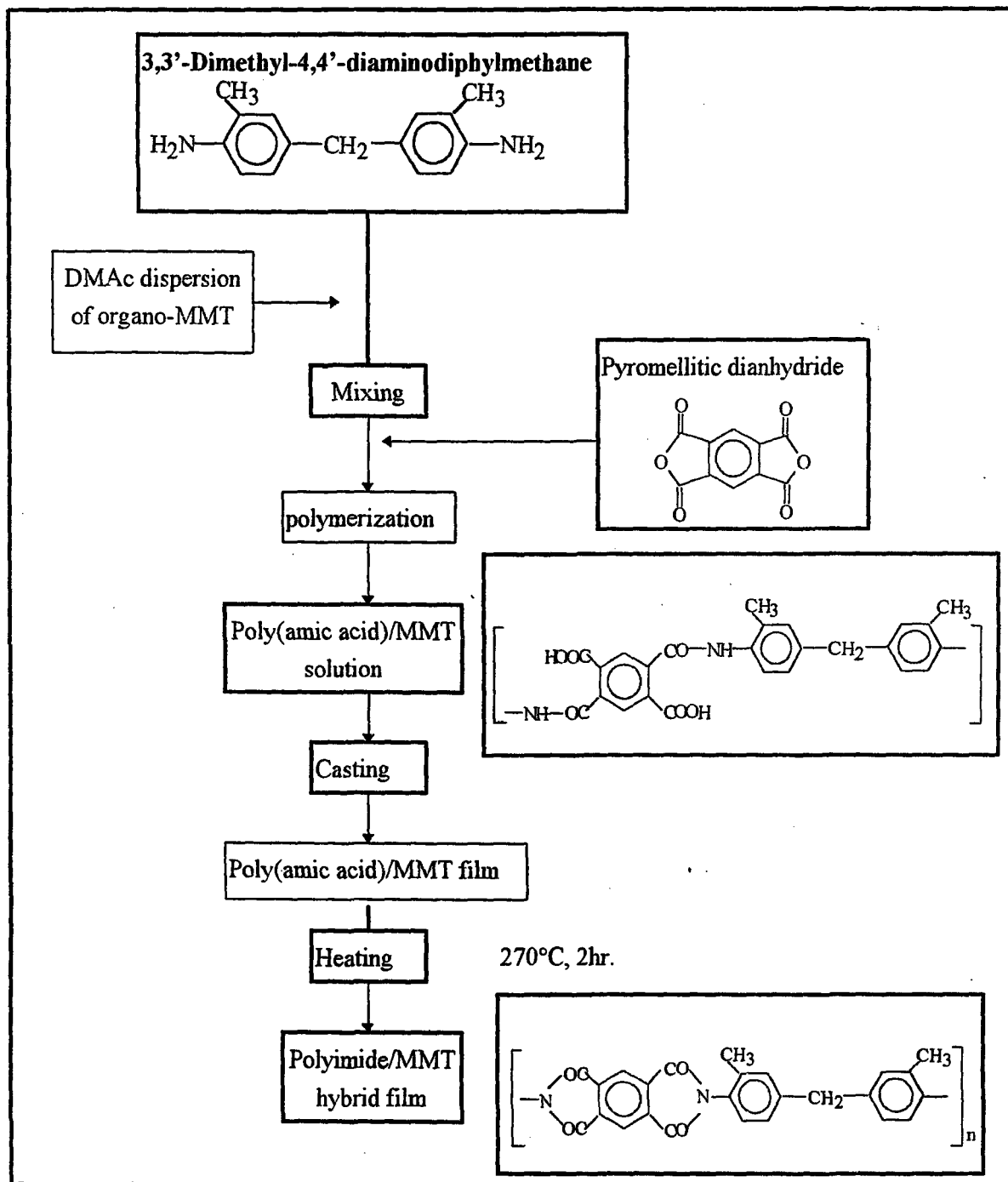
Table 2 is the thermal properties of 16CNH-MMT/PI hybrids with different MMT contents. It is observed that the introduction of a very small amount of 16CNH-MMT dramatically reduces the thermal expansion coefficient. The TEC of polyimide is decreased from $3.60 \times 10^{-5} \text{ K}^{-1}$ to $1.96 \times 10^{-5} \text{ K}^{-1}$ (a 45% decrease) when only 1 wt% of 16CNH-MMT is introduced. As the MMT content is increased, the TEC decreases continuously (cf. Fig.1). It is also found that the thermal stability of the hybrids increases with the increase of the MMT content. However, when the MMT content reaches 10%, the thermal stability decreases. This observation further support 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.

Mechanical and optical properties of PI/MMT hybrids

Table 3 is the mechanical properties of 16CNH-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 below 5 wt%, both tensile strength and the elongation at break are increased. The introduction of organo-treated MMT generates both the

and to it the organophilic montmorillonite/DMAc solution was added. The mixture was stirred for 30 minutes before equal molar of PMDA was added to it. This mixture was then stirred at room temperature for 6 hours.

The obtained polyamic acid/montmorillonite solution was cast in a glass substrate and then heated subsequently at 100 °C for 6 hours, 150 °C for 4 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.



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

property measurements of PI/MMT hybrids

The thermal gravimetric analysis (TGA) of PI and PI/MMT hybrids was