Synthesis and characterization of bismaleimide-polyetherimide-silica hybrid by sol-gel process

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A ternary hybrid of bismaleimide-polyetherimide-silica (BMI-PEI-SiO₂) was synthesized by sol-gel reaction and characterized by scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX), thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The results indicated that silica could be introduced into the blend of thermoplastic-thermosetting system by sol-gel reaction and dispersed uniformly as nanoparticles. The phase separation of BMI-PEI was not affected apparently by the presence of silica. The coupling agent 3-aminopropyl (triethoxy)silane was chosen to enhance the interaction between the polymer-matrix and silica. Thermal properties and mechanical properties of the hybrids both were improved with increasing silica content. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: nanoparticles; thermoplastics; thermosets; thermal properties; mechanical properties

INTRODUCTION

Organic-inorganic nanocomposites have become an effective source of advanced materials as they usually exhibit unique properties that traditional composites and conventional materials do not have. They combine the advantages of the inorganic materials (rigidity, high thermal stability) and the organic polymers (flexibility, dielectric, ductility, and processability). Moreover, they usually also contain special properties of nanoparticles that can be developed, leading to materials with improved properties for electrical, optical, structural, eletrooptical, non-linear-optical, or related applications. Sol-gel reaction is an effective method to prepare organic-inorganic hybrids. It has been extensively studied for over two decades. This technique has been attracting more and more interest because of its potential use in developing new ceramics or glasses. The major advantage of the technique resides in the fact that ceramics can be produced at relatively low temperature. The general method to prepare inorganic-organic hybrid is to carry out the sol-gel reaction in the presence of organic molecule, which are typically polymeric containing functional groups to improve their bonding to the ceramic-like phase. This is a very useful novel reinforcement technique that can generate reinforcing particles within a polymer matrix.

Bismaleimide (BMI) resins possess many desirable properties, including high tensile strength and modulus, excellent chemical and corrosion resistance, and hot/wet performance. It has attracted considerable attention as an important matrix resin for high-performance composites used in military aircraft and engines. However, due to the highly crosslinked structure, the cured BMI resins are extremely brittle. Researches usually focus on how to improve toughness without sacrificing other important properties such as high-temperature performance, and various attempts have been made.

Attribute to excellent properties, generally, aromatic polyimides have been considered as suitable polymer matrix materials for preparing advanced hybrid composites that have potential applications in the microelectronics and aircraft industries. The use of polyetherimide (PEI) to enhance the fracture toughness of the BMI resins has been studied in previous works and desirable results have been obtained. By the introduction of PEI, the impact and fracture toughness of BMI resin both can be greatly improved.

Although many papers on the synthesis of inorganic-organic hybrids have been published, most of them are concerned on the hybrid of SiO₂ with single component polymer. The synthesis of hybrid of SiO₂ with multi-component composite has seldom been reported.

In this present work, the synthesis and characterization of bismaleimide-polyetherimide-silica (BMI-PEI-SiO₂) hybrid...
by sol-gel process is reported and the relationship between the morphology and properties of the hybrids with the content of silica is discussed.

**EXPERIMENTAL**

**Materials**

The BMI resin was composed of two components. Component A is bis(4-maleimidodiphenyl)methane (BDM), supplied by Hubei Fengguang Chemical Factory. Component B is \(o,o'\)-diallyl bisphenol-A (DBA) supplied by Jiangyou Electric Engineering Material Factory. Bisphenol-A dianhydride (BISA-DA) and \(4,4'\-\{1,4\)-phenylenebis(1-methylethylidene)\}-bisaniline (BISP) provided by Shanghai Institute of Synthetic Resin (see Scheme 1). Tetraethoxysilane (TEOS, Beijing Chemicals Company) and 3-aminopropyl(triethoxy)silane (KH-550, Nanjing Shuguang Chemical Company) was used as received. N,N-Dimethylacetamide (DMAC, Shanghai Chemical Reagent Company) and N-methyl-2-pyrrolidone (NMP, Shanghai Reagent Chemical Company) were dried over molecular sieves (5 Å) and distilled before use.

**Synthesis of polyetherimide (PEI)**

PEI was synthesized by two steps from BISA-DA and BISP at a stoichiometric ratio in DMAc at room temperature for 6 hr to give a viscous poly(amid acid) solution, which was then converted to the required PEI by a chemical imidization reaction with excessive amounts of acetic anhydride and triethylamine (mole ratio \(=3:1\)) at room temperature for 16 hr. The PEI solution was then precipitated into methanol twice and dried at 70°C for 24 hr, the glass transition temperature (\(T_g\)) of the PEI is 210°C, the weight-average molecular weight (\(M_w\)) is 26,000. PEI of low molecular weight (\(M_w=5800\)) was synthesized from BISA-DA and BISP at a molar ratio of 1:0.96, \(T_g=205\)°C. The \(M_w\) values of PEI were determined in tetrahydrofuran (THF) at 25°C using gel permeation chromatography (GPC), the sample was run at 1 ml/min. The chemical structure of the PEI is shown in Scheme 2.

**Pre-polymerization of BMI resin**

DBA and BDM were mixed at the weight ratios of 43:57 and heated at 160°C for 30 min, then the pre-polymerized BMI resin was cooled to room temperature and crushed for preparing hybrids.

**Preparation of the BMI-PEI-SiO\(_2\) hybrid films**

To a 15% DMAC solution of BMI prepolymer and PEI (weight ratio of BMI/PEI = 100:30), KH-550 was added into the solution (with the weight ratio of PEI/KH-550 = 10:1), a certain amount of TEOS with distilled water (moles ratio of water/TEOS = 1:4) and hydrochloric (to keep the pH value at 4) were added. The mixture was then stirred at room temperature for 6 hr to give a transparent solution. The solution was cast in a glass substrate and dried under 70°C for 48 hr, then cured at 180°C for 2 hr, 200°C for 2 hr, 220°C for 2 hr. The films were removed from the glass substrate with the aid of deionized water and dried for 24 hr at 100°C in a vacuum oven. The procedure of the synthesis process is shown in Fig. 1.

**Analysis and characterization**

The thermal properties were characterized using a Perkin–Elmer Pyris1 thermogravimetric analyzer from room temperature to 800°C at a heating rate of 10°C/min in nitrogen and on a SETARAM DSC-141 differential scanning calorimeter from room temperature to 400°C at a heating rate of 10°C/min in nitrogen.
The morphology of the fracture surface of the hybrid was observed with a Philips XL 30 scanning electron microscope. All samples were gold coated (2–3 nm) and mounted on copper mounts.

Energy dispersive X-ray analysis (EDX) was performed on 1 µm thick samples with a LEICA Stereoscan 260 system. Before experiments, Co standard specimen was used to calibrate the machine.

The mechanical properties of the BMI-PEI and BMI-PEI-SiO\(_2\) hybrid films were recorded on an Instron-8500 universal tester according to China State Standard GB 1040-79. The films used were around 0.1 mm thick and had a rectangular shape (35 mm × 9 mm).

### RESULTS AND DISCUSSION

#### Hybrid preparation

Attribute to the insolubility of general polyimides in organic solvents, most of the polyimide-SiO\(_2\) hybrids reported are prepared from polyamic acid and then converted into polyimide by being heated up to 300°C.\(^1\) However, polyamic acid cannot be stored for a long time owing to its degradation, which certainly limits the use of polyamic acid for the preparation of hybrids. Thus in this work, the organosoluble PEI was used to prepare the hybrids without the polyamic acid route. Besides, the BMI resin was pre-polymerized to improve the solubility of the BMI resin in DMAC before preparing the hybrids, which could prevent BDM from precipitating during the removing of solvent.

There are many factors that affect the reaction of hydrolysis and condensation of TEOS in the sol-gel process, such as temperature, pH, nature of the solvent and the type of alkoxide precursors.\(^2\) Hydrolysis precedes the condensation reaction, but may not go to completion prior to the onset of condensation. The relative rates of the hydrolysis and condensation reactions determine the final structure of the hybrid material. The acid-catalyzed reaction provides relatively fast hydrolysis and slow condensation reaction, which results in slow network formation followed by a better environment for interpenetration of the phases. In this work, it was found that precipitation of silica will be found at the early stage of the sol-gel process in base media owing to the fast condensation of silicic acid, and so the sol-gel reaction was carried out in acidic media (pH 4) in the preparation of BMI-PEI-SiO\(_2\) hybrids.

The appearance of the hybrids with different contents of SiO\(_2\) and coupling agent KH-550 are listed in Table 1, the hybrids with KH-550 are transparent up to a TEOS content of 20 wt%, while the hybrids without KH-550 are opaque over 10 wt% of TEOS content. The function of coupling agent KH-550 can hydrolyze to form silanol groups that can polycondense with the hydrolysis product of TEOs, while the other end can react with the carbonyl groups in polyimide. Thus the interaction between the polymer-matrix and silica can be greatly improved by the introduction of KH-550.

#### Table 1. Effect of KH-550 on the appearance of the hybrids

<table>
<thead>
<tr>
<th>TEOS content (wt%)</th>
<th>0</th>
<th>5</th>
<th>10</th>
<th>15</th>
<th>20</th>
<th>25</th>
</tr>
</thead>
<tbody>
<tr>
<td>With KH-550</td>
<td>T</td>
<td>T</td>
<td>T</td>
<td>T</td>
<td>O</td>
<td>O</td>
</tr>
<tr>
<td>Without KH-550</td>
<td>T</td>
<td>T</td>
<td>O</td>
<td>O</td>
<td>O</td>
<td>O</td>
</tr>
</tbody>
</table>

Bismaleimide-polyetherimide-silica hybrid

Figure 2. The interaction of KH-550 with PEI segment.

### Morphology of the hybrids

As has been reported before, the BMI resin modified with PEI showed co-continues or phase-inversion structure with the BMI spherical particles dispersed in the PEI rich matrix when the content of PEI is over 15 phr (per hundred of BMI resin) (Fig. 3a).\(^3\),\(^4\)

From the scanning electron microscopy (SEM) image, it is shown (Fig. 3b) that when the silica is introduced into the blend of BMI-PEI with 15 phr PEI content, the hybrid maintains a phase inversion structure and the silica is dispersed uniformly with a mean diameter of 50 nm in both PEI rich phase and BMI rich phase (Fig. 3c and 3d), which suggests that the phase separation of BMI-PEI is not affected apparently by the introduction of silica. However, the size of the BMI particle in the hybrid with silica is about 3–5 µm in diameter, which is larger than that of BMI (1–2 µm) in the blend of PEI-BMI without silica owing to the presence of silica.

Furthermore, according to previous studies, the molecular weight of PEI has a great effect on the morphology of the blends of PEI-BMI,\(^5\),\(^6\) and the same phenomena is also observed in the hybrids of BMI-PEI-SiO\(_2\). As far as the hybrid with 30 phr PEI content is concerned, the phase-inversion structure is observed in the sample with high molecular weight (\(M_w=26,000\), shown in Fig. 3b), while the spherical structure is obtained in the sample with low molecular weight (\(M_w=5800\), shown in Fig. 3e).

#### The distribution of silica in the hybrids

To study the distribution of silica in both phases of PEI and BMI, EDX analysis was used to measure the content of silicon element in the hybrids (Fig. 4). Major elements in the hybrids, such as oxygen, nitrogen, silicon and carbon, are tracked by EDX. As far as the hybrid with 5 wt% TEOs is concerned, the mean content of silica is about 2.2% in the BMI rich phase and about 8.6% in the PEI rich phase respectively, which indicates that silica tends to be dispersed in PEI phase due to the improved interaction introduced by KH-550 as mentioned earlier (Fig. 3).

#### Thermal properties

Thermogravimetric analysis (TGA) was used to measure the thermal decomposition temperature (\(T_d\)) of the hybrid films (Table 2). There is no weight loss shown in TGA curves below 100°C, indicating no water or ethanol remained in the films and the TEOs has been completely hydrolyzed. In this work,
The $T_{d}$ of the hybrids increased with the content of silica from 382°C (0% TEOS) to 418°C (20 wt% TEOS) (Table 2), which suggests that the introduction of inorganic components into organic materials can improve their thermal stability.

Because of the high crosslink of BMI, differential scanning calorimetry (DSC) could not observe the $T_g$ of BMI, however, the $T_g$ of PEI in the hybrids was found in DSC. Table 2 shows that the $T_g$ of PEI increased with increasing content of silica, which strongly supports the aforementioned discussion that the interaction between the polymer-matrix and silica can be greatly improved by the introduction of KH-550 as shown in Fig. 2.

The onset temperature of curing reaction ($T_c$) of the hybrids with different content of SiO$_2$ was measured by DSC, the results suggested that the introduction of the SiO$_2$ did not affect initiation of the curing reaction (Table 2).

**Mechanical properties**

An Instron 8500 universal tester was used to study tensile properties of the hybrid films. The influence of the silica...
content on the mechanical properties of the hybrids is shown in Table 3 and Fig. 5.

It is found that the Young’s moduli and tensile strength both increase greatly with the silica content. The phenomenon could also be attributed to the improved interaction between the polymer matrix and the silica, which resulted from the high surface-mass ratio of SiO₂ nanoparticles and the chemical bonds induced by the coupling agent. In contrast, the elongations at break of the hybrids decreased with the content of silica due to the formation of the physical crosslinking between SiO₂ and polymer matrix.

Table 2. Thermal properties of hybrids

<table>
<thead>
<tr>
<th>TEOS content (wt%)</th>
<th>T_d (°C)</th>
<th>T_g-PEI (°C)</th>
<th>T_c (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>382</td>
<td>210</td>
<td>135</td>
</tr>
<tr>
<td>5</td>
<td>390</td>
<td>215</td>
<td>134</td>
</tr>
<tr>
<td>10</td>
<td>394</td>
<td>219</td>
<td>136</td>
</tr>
<tr>
<td>15</td>
<td>403</td>
<td>228</td>
<td>133</td>
</tr>
<tr>
<td>20</td>
<td>418</td>
<td>239</td>
<td>135</td>
</tr>
</tbody>
</table>

T_d determined by TGA in N₂; T_g, determined by DSC; T_c, determined by DSC.

Table 3. Mechanical properties of BMI-PEI-SiO₂ hybrid films

<table>
<thead>
<tr>
<th>TEOS content (wt%)</th>
<th>Modulus (GPa)</th>
<th>Tensile strength at break (MPa)</th>
<th>Ultimate elongation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.09</td>
<td>25.1</td>
<td>2.54</td>
</tr>
<tr>
<td>5</td>
<td>1.22</td>
<td>28.4</td>
<td>2.35</td>
</tr>
<tr>
<td>10</td>
<td>1.36</td>
<td>30.1</td>
<td>2.03</td>
</tr>
<tr>
<td>15</td>
<td>1.49</td>
<td>34.0</td>
<td>1.76</td>
</tr>
<tr>
<td>20</td>
<td>1.65</td>
<td>35.2</td>
<td>1.58</td>
</tr>
</tbody>
</table>

Figure 4. EDX results of BMI-PEI-SiO₂ hybrid with 5 wt% TEOS: (a) PEI rich phase, (b) BMI rich phase.

CONCLUSIONS

In this study, the ternary hybrid of BMI-PEI-SiO₂ was synthesized by sol-gel reaction. The phase separation of BMI-PEI was not affected by the presence of silica. The coupling agent KH-550 was chosen to enhance the interaction between polymer matrix and silica. The silica particle, with a diameter about 50 nm, dispersed in the hybrid uniformly and the silica...
content in the PEI rich phase was higher than that in the BMI rich phase. The thermal properties and mechanical properties of the hybrid were improved by the introduction of silica into the hybrids.

REFERENCES