

# Studies on the Compatibilization of the Soluble PI/SiO<sub>2</sub> Nanocomposite

Xiu-yong SHANG<sup>1\*</sup> Zi-kang ZHU<sup>2</sup> Jie YIN<sup>2</sup> Xiao-dong MA<sup>2</sup>

<sup>1</sup> Engineering Research Center in Organic Synthesis, Chinese Academy of Sciences, 476 Zhenbei Road, Shanghai 200062, P. R. China.

<sup>2</sup> College of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, P. R. China

## 1. INTRODUCTION

It is known that the properties of composites depend not only on their components but also on their morphology and the interaction at the interface. For organic/inorganic nanocomposites, they usually exhibit new and different properties which the traditional macroscale composites and conventional materials do not have. They can combine the advantages of inorganic material and organic polymers. For examples, they combine the rigidity, high thermal stability of inorganic material and the flexibility, dielectric, ductility, and processability of polymers. In addition, the nanocomposite usually contain special properties of nanoparticles which can be developed leading to materials with properties for electrical, optical, structural, electro-optical, non-linear optical, or related applications. Fortunately, the nanometer size of the components or phases will greatly increase the interface area and greatly strengthen the adhesion strength at the interface because of their tiny scales, which can lead them toughening coupled with strengthening effect.

A facile procedure to obtain organic-inorganic hybrids is mixing an organic polymer with a silicon alkoxide such as tetraethoxysilane (TEOS) followed by sol-gel reaction involving hydrolysis and polycondensation of TEOS. However, it is worthy to note that the thermodynamic incompatibility for the two components of polyimide/silica (PI/SiO<sub>2</sub>) hybrids is disadvantageous for the inorganic SiO<sub>2</sub> particles dispersing in the polyimide base. This is obviously not a favorable factor in the preparation of transparent free standing PI/ SiO<sub>2</sub> hybrid films without phase separation. Additionally, the morphology and interface property of the separated two phases will not lead to a composite with excellent properties<sup>[1-4]</sup>. So it is important to improve the compatibility between the two phases for the preparation of organic-inorganic hybrid with good properties. There are several ways to improve the compatibility between the two phases. Firstly, introducing siloxane or epoxy group to the polymer chain by molecular designing which can take part in chemical reactions in the sol-gel process and form chemical bond with SiO<sub>2</sub> phase<sup>[5-7]</sup>. Secondly, introducing functional group to the polymer chain<sup>[8-11]</sup> which can form hydrogen bond with the hydrolysis product of siloxane. Additionally, coupling agent can also improve the compatibility between the two phases. Mascia and Kioul have found that coupling agent can greatly reduce the size of the disperse phase in their studies<sup>[12-14]</sup>.

In this paper, a kind of organo-soluble polyimide was chosen as polymer matrix and a new serial of soluble polyimide/silica nanocomposites were prepared by sol-gel process with coupling agent. Furthermore, the effects of coupling agent on the size of SiO<sub>2</sub> particle, the distribution of particle size and the properties of PI/ SiO<sub>2</sub> nanocomposites were also studied.

## 2. EXPERIMENTAL

### 2.1. Materials

Benzophenone-3,3',4,4'-tetracarboxylic dianhydride (BTDA) was prepared from benzophenone-3,3',4,4'-tetracarboxylic acid (Industrial product, purchased from Beijing Tar Chemicals Company, Beijing, China) by refluxing with an excessive amount of acetic anhydride. 4,4'-Diamino-3,3'-dimethyldiphenyl methane (MMDA) was prepared from o-methyl aniline and formalin<sup>[15]</sup>. Tetraethoxysilane (TEOS, chemical reagent grade, purchased from Beijing Chemicals Company,

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To whom all correspondences should be addressed

Tel.: 021-52810088-2013

E-mail: :xy-shang@online.sh.cn

Beijing, China) was used as received. N-Methyl-2-pyrrolidone (NMP, analytical reagent grade, purchased from Shanghai Reagent Company, Shanghai, China) was dried over molecular sieves before use.  $\gamma$ -glycidyloxypropyltrimethoxysilane (GOTMS, analytical reagent grade, purchased from Nanjing Shuguang Chemicals Company, Nanjing, China) was used directly without purification. Common reagents such as acetic acid and acetic anhydride were used without purification.

## 2.2. Preparation of PI/silica hybrids

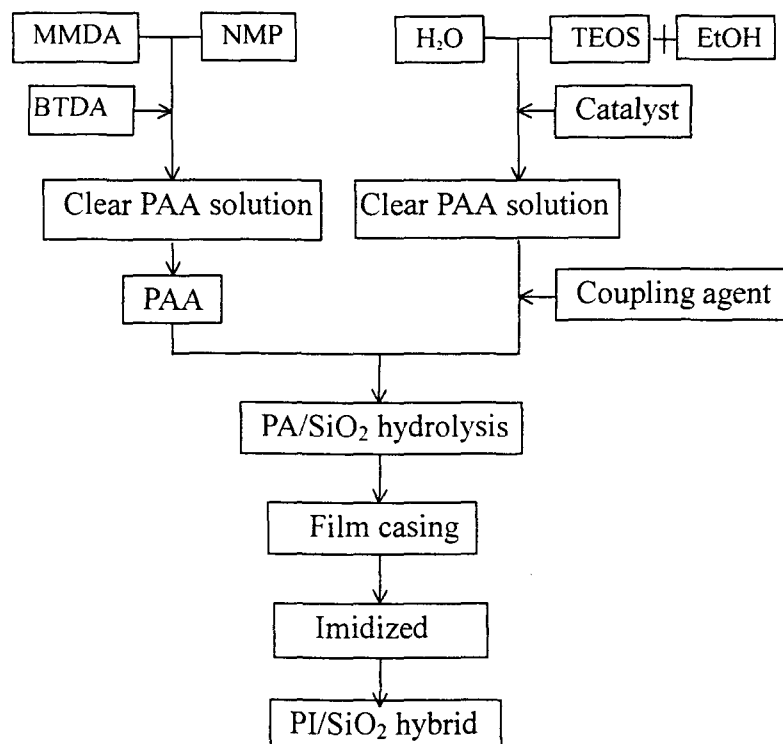


Fig. 1 Sol-gel process for the preparation of PI/SiO<sub>2</sub> hybrids

Table 1 The recipe of preparation of PI/SiO<sub>2</sub> hybrids

	Silica <sup>a</sup> (wt%)	GOTMS/TEOS (mol ratio)	Remarks <sup>b</sup>
Soa2	5	0	T
Soa3	10	0	T
Soa4	20	0	O
Soa5	30	0	O
Soa6	40	0	O
Sob1	10	1/10	T
Sob2	20	1/10	T
Sob3	30	1/10	O
Sod1	20	1/4	T
Sod2	20	1/7	T
Sod3	20	1/15	O

Notes: a. The contents of Silica were calculated theoretically; b. T: transparent O: opaque.

In this paper, PI/SiO<sub>2</sub> hybrids were prepared by sol-gel process described in figure 1. An equal mole of BTDA was added to the MMDA/NMP solution (solid content: 10wt%). The mixture was kept at room temperature for 16 hours and a viscous polyamic acid (PAA) solution was obtained. To this PAA solution, the mixture of TEOS with distilled water (4/1 based on TEOS mole) and acetic acid (to keep the pH value at 4) was added. The mixture was then stirred at room temperature for 6 hours to give a transparent solution. The solution was cast on a glass substrate and thermally treated stage by stage to form the

PI/silica hybrid films with 20wt% SiO<sub>2</sub> (if it is assumed that TEOS was fully hydrolyzed and condensed). The recipe of PI/SiO<sub>2</sub> hybrid samples was listed in table 1.

### 2.3. Instrumentation and Characterization

The chemical structures of the hybrids were identified by FT-IR spectra, which were recorded on a Perkin Elmer Paragon 1000 FT-IR Spectrophotometer using KBr pellets. UV-Vis spectra of the PI/silica hybrid films were recorded on a Perkin Elmer Lambda 20 UV-Vis Spectrophotometer.

The morphology of the fractured surfaces of the hybrid materials were observed by a JSM-6300 Scanning Electronic Microscope (SEM).

The thermal properties of the hybrid samples were characterized by DSC and TGA, which were performed on PERKIN-ELMER Pyris 1 DSC and PERKIN-ELMER TGA 7 respectively. The DSC and TGA measurements were performed at a heating rate of 20°C/min in nitrogen. The temperature range for TGA measurements is from 50 to 900°C.

The solubility of PI and PI/SiO<sub>2</sub> hybrids in various organic solvents at room temperature were also measured.

The linear thermal expansion coefficient (TEC) of PI and the PI/SiO<sub>2</sub> hybrids was measured on a Perkin-Elmer TMS-2 Thermal Mechanical Analyzer at a heating rate 10°C/min.

The stress-strain curves of PI and PI/SiO<sub>2</sub> hybrids were recorded on an Instron-8500 Universal Tester at room temperature at a drawing rate of 5mm/min.

## 3. Result and discussion

### 3.1. Optical behavior of PI/ SiO<sub>2</sub> hybrids

The appearances of PI/ SiO<sub>2</sub> hybrid films with different PI/SiO<sub>2</sub> content and different amount of coupling agent (GOTMS) are listed in table 1. It is observed that the transparency of the PI/ SiO<sub>2</sub> hybrid films is improved by coupling agent. A hybrid film will become translucent when the silica content is more than 10wt% without GOTMS. However, this critical point is moved higher to 20wt% by the adding of GOTMS. Figure 2 shows the effect of GOTMS on the UV-Vis spectra of the PI/SiO<sub>2</sub> hybrid film. The transparency of the PI/ SiO<sub>2</sub> hybrid film is greatly improved by GOTMS. This reveals that the transparency of PI/SiO<sub>2</sub> hybrid films can be increased by the addition of coupling agent. It is because that GOTMS will hydrolyze to form silanol group which can polycondense with the hydrolysis product of TEOS. Moreover, the other end of GOTMS will hydrolyze to form hydroxyl group which is compatible with polyimide. All these two will lead to the reduction of the particle size and high dispersion of SiO<sub>2</sub> particle in the polyimide base.

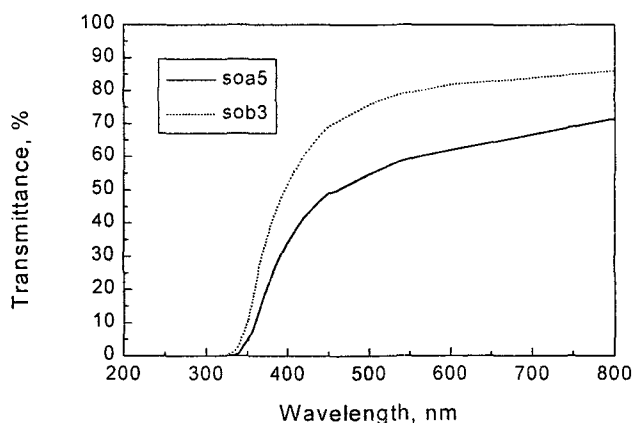


Fig. 2 The effect of coupling agent on the UV-vis spectra of PI/SiO<sub>2</sub> hybrid films (SiO<sub>2</sub>=30wt%)

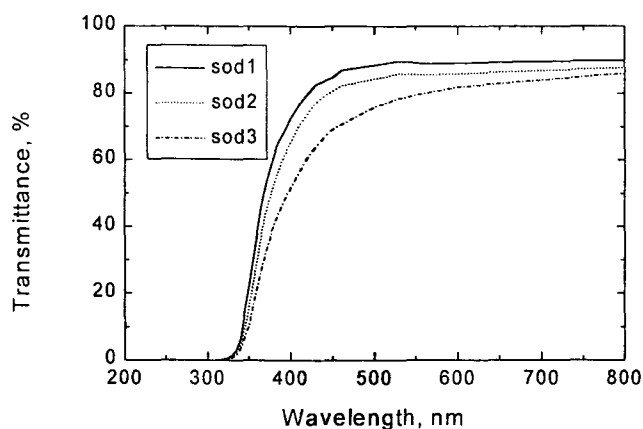


Fig. 3 The effect of coupling agent content on the Uv-vis spectra of PI/SiO<sub>2</sub> hybrid films

As shown in figure 3, the transparency of the PI/SiO<sub>2</sub> hybrid film increases with the amount of coupling agent. This may results from the improved compatibilization between the two components of PI and SiO<sub>2</sub> with the increasing amount of coupling agent, which leads to the smaller size of SiO<sub>2</sub> particles and better dispersion in PI. From figure 3, it is also observed that the effect of coupling agent reaches a constant level when the amount is large enough.

### 3.2. Influence of GOTMS on the structure of PI/SiO<sub>2</sub> hybrids

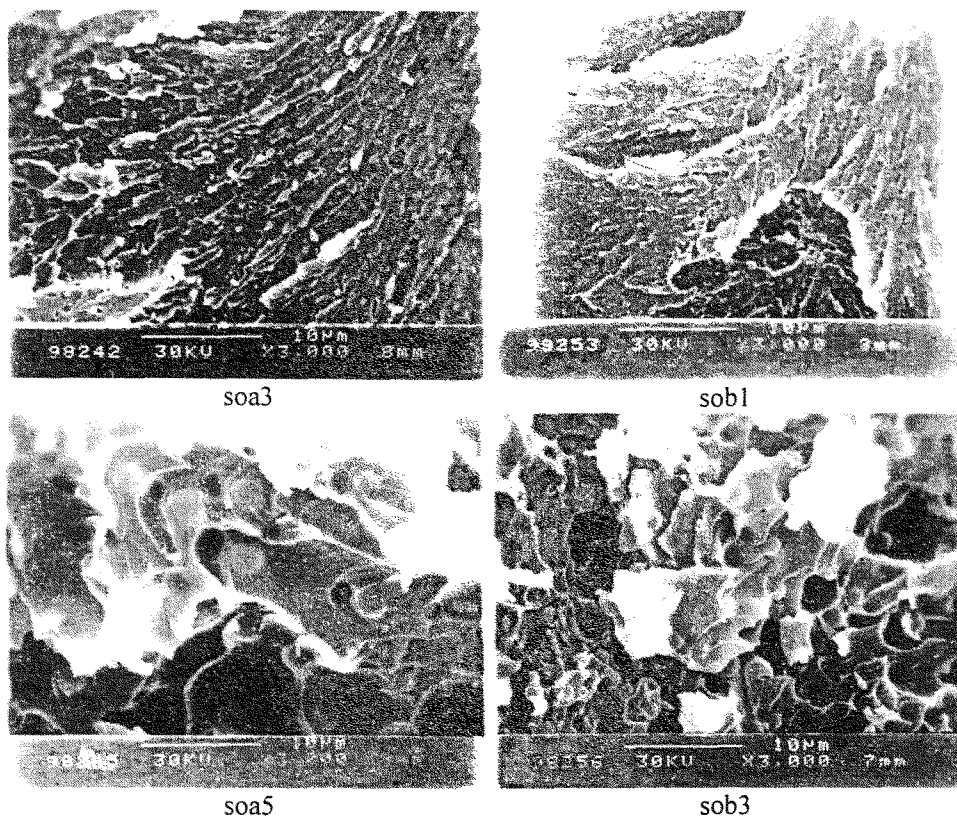


Fig. 4 SEM photographs of PI/ SiO<sub>2</sub> hybrids

Fig. 4 shows the SEM photographs of PI/SiO<sub>2</sub> hybrid samples of different silica content without and with GOTMS. Comparing the samples with their counterparts (soa3 with sob1, soa5 with sob3), it is observed that the particle size of SiO<sub>2</sub> particles in the hybrids decreases remarkably with the addition of

GOTMS. It is also observed that the dispersion of  $\text{SiO}_2$  particles in the hybrids becomes more even, narrower size distributed and less aggregated with the addition of GOTMS. Fig. 5 shows the photographs of PI/ $\text{SiO}_2$  hybrid samples with different amount of GOTMS. It is observed that the compatibility between the two phases of PI and  $\text{SiO}_2$  is greatly improved with the amount of GOTMS. Accordingly, this results in the reduced particle size and well dispersion behavior of  $\text{SiO}_2$  in the hybrid.

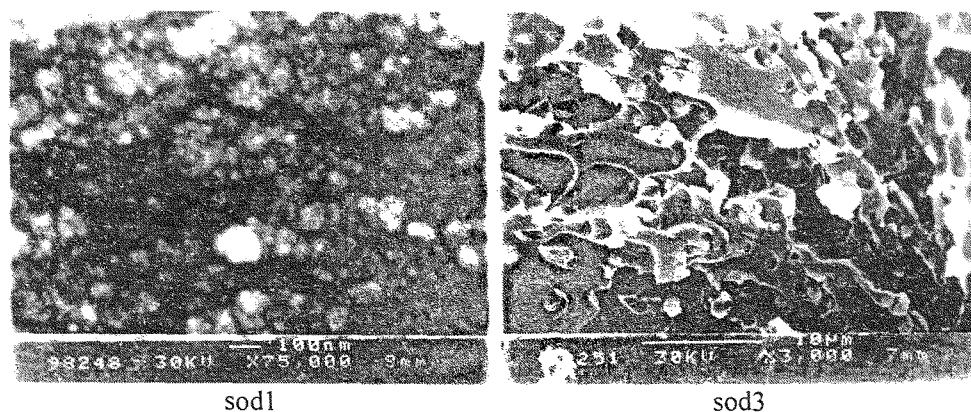


Fig. 5 SEM photographs of PI/ $\text{SiO}_2$  hybrids with different content of GOTMS ( $\text{SiO}_2$  20wt%)

### 3.3. IR characterization of PI/ $\text{SiO}_2$ hybrids

Fig. 6 shows the IR spectra for PI/ $\text{SiO}_2$  hybrids. It is observed that there is no noticeable effect of GOTMS on the thermal imidization process of polyamic acid. The characteristic absorption band of Si-O-Si asymmetric stretching ( $1130\text{cm}^{-1}$ ) becomes stronger and moves to higher wavenumber with the addition of coupling agent. This indicates that more Si-O-Si bonds are formed which results in a more compact silica network in the hybrid.

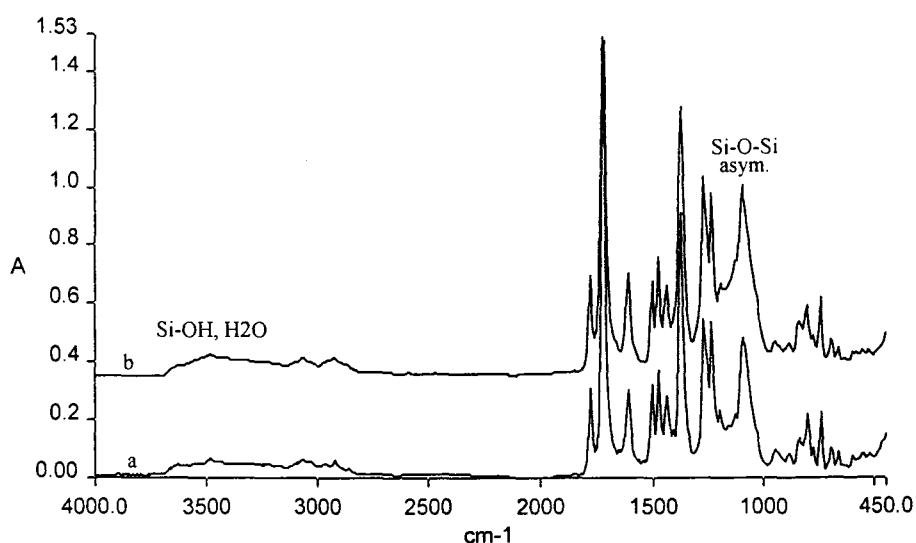


Fig. 6 FTIR spectra of PI/ $\text{SiO}_2$  hybrids  
(a: without coupling agent, b: with coupling agent)

### 3.4. Solubility of PI/ $\text{SiO}_2$ hybrids

Because of the high aromaticity of the BTDA moiety, the conventional polyimides based on BTDA 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 BTDA. 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 BTDA and MMDA is organo-soluble<sup>[15]</sup>.

It is known that the solubility of a hybrid is mainly decided by the dispersion behavior of inorganic particles. Fortunately, all the above results show that the addition of coupling agent has greatly improved the dispersion behavior of silica in the polyimide base. So the effect of coupling agent on the solubility of PI/SiO<sub>2</sub> hybrids were also investigated. The solubility data of PI/SiO<sub>2</sub> hybrids are presented in table 2. It is observed that only when the silica content is less than 5wt% a hybrid without coupling agent can be soluble in aprotic polar solvents. This must be attributed to that when the silica content is low the size of SiO<sub>2</sub> particle is small enough and will not affect the solubility of the PI/SiO<sub>2</sub> hybrid. However, the high content of silica will form large size of SiO<sub>2</sub> particles which will restrict polyimide molecules and resulting in bad solubility of PI/SiO<sub>2</sub> hybrids. The solubility is increased by the decreased size and less aggregation of SiO<sub>2</sub> particles resulting from the addition of coupling agent.

Table 2 Solubility of PI/SiO<sub>2</sub> hybrids (at 25°C)

	Soa2	Soa3	Soa4	Sod1	Sod2	Sod3
SiO <sub>2</sub> , wt%	5	10	20	20	20	20
GOTMS/TEOS	0	0	0	1/4	1/7	1/15
NMP	+	+ -	-	+	+ -	+ -
DMAc	+	+ -	-	+	+ -	+ -
DMF	+	+ -	-	+	+ -	+ -
DMSO	+	+ -	-	+	+ -	+ -

notes: +: soluble, + -: partly soluble. -: insoluble

### 3.5. Thermal properties of PI/SiO<sub>2</sub> hybrids

Table 3 The effects of coupling agent on the thermal properties of PI/SiO<sub>2</sub> hybrids

Run	SiO <sub>2</sub> <sup>a</sup> , wt%	GOTMS/TEOS	T <sub>d</sub> <sup>b</sup> , °C	CTE, 10 <sup>-5</sup> K <sup>-1</sup>	Tg <sup>c</sup> , °C
b0	0	0	561	5.41	289
b2	10	0	581	4.86	294
b3	20	0	588	3.45	301
b4	30	0	600	—	310
b6	10	1/10	572	2.53	298
b7	20	1/10	576	—	309
b8	30	1/10	592	—	316

a. Calculated silica contents in hybrid films; b. T<sub>d</sub> determined by TGA in N<sub>2</sub>, on-set;  
c. Tg, determined by DSC.

The glass transition temperatures (Tg) of PI/SiO<sub>2</sub> hybrids obtained by DSC are listed in Table 3. The thermal decomposition temperatures (Td) determined by TGA and the coefficient of thermal expansion (CTE) of the hybrid samples are also listed in Table 3. It is observed that the Tg of a hybrid increases with the content of silica. The hybrid films with coupling agent exhibit higher Tg and much lower CTE than their counterpart. These phenomena may be explained as follows: Firstly, the coupling agent strengthens the interaction between the organic polymer matrix and the inorganic mineral which means the increasing restricting strength of SiO<sub>2</sub> to PI molecules. Secondly, the coupling agent reduces the size of SiO<sub>2</sub> particles and greatly increases the interface area with the same silica content. Furthermore, the reduced size of SiO<sub>2</sub> particle, to some extent, means the increasing of the crosslinking density. All these effects lead to the higher Tg and lower CTE values of the PI/SiO<sub>2</sub> hybrids with coupling agent than their counterparts. From table 3, it can also be found that the hybrids possess higher thermal stability than the corresponding PI. It is also observed that the thermal decomposition temperature (T<sub>d</sub>) of a hybrid increases with its silica content. The thermal stability of the hybrids with coupling agent are slightly lower than their counterparts without coupling agent owing to the alkyl chain of GOTMS, but still higher than the corresponding PI.

### 3.6 Mechanical properties of PI/SiO<sub>2</sub> hybrids

The influence of the silica content on the mechanical properties of the hybrids is shown in Table 4, Fig. 7 and Fig. 8. As shown in table 4, it can be observed that the modulus of the hybrid films increase linearly with the silica content. It can be found in Fig. 7 and Fig. 8 that when the silica content is less than 20wt%, both tensile strength and the elongation at break increase with the silica content. However, both of them begin to decline when the silica content exceeds 20wt%. These phenomena may be the distinct features of a nanometer composite. However, this critical point is only 10wt% for PI/SiO<sub>2</sub>

Table 4 The effects of coupling agent on the mechanical properties of PI/SiO<sub>2</sub>

SiO <sub>2</sub> , wt%	Without coupling agent			With coupling agent		
	M, GPa	T <sub>b</sub> , MPa	E <sub>b</sub> , %	M, GPa	T <sub>b</sub> , MPa	E <sub>b</sub> , %
0	2.09	59.4	6.1	—	—	—
5	2.18	116.4	7.9	2.74	105.1	3.6
10	2.46	122	12.3	2.85	135.6	6.5
20	2.78	105.3	9.7	3.08	143.4	7.9
30	3.54	45.5	3.5	3.38	74.7	2.9
40	—	—	—	3.49	51.9	1.8

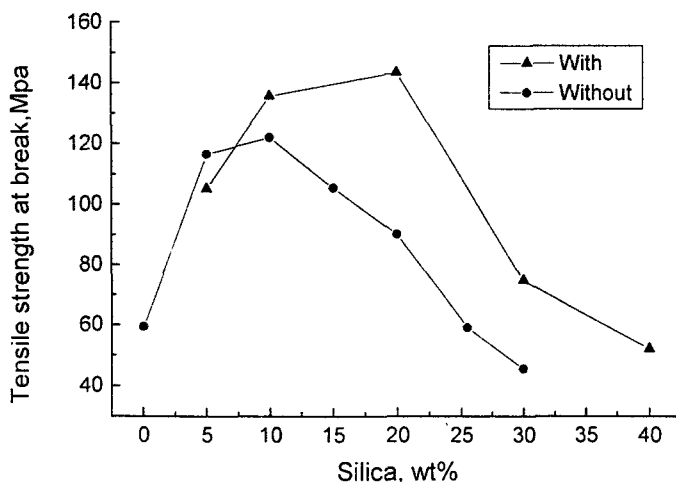


Fig. 7 The effect of coupling agent on the tensile strength at break of PI/SiO<sub>2</sub> films

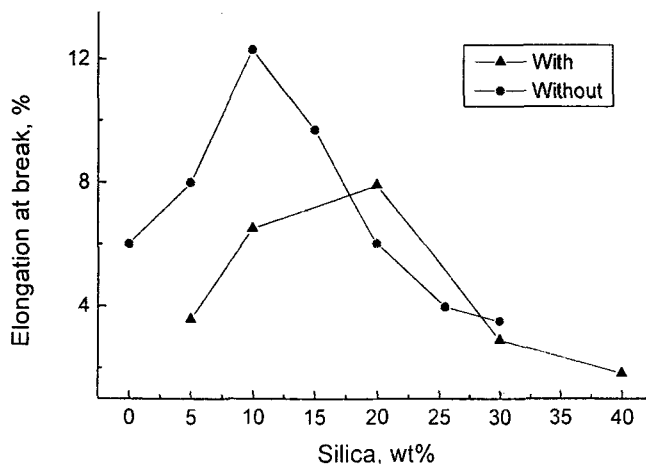


Fig.8 The effect of coupling agent on the elongation at break of PI/SiO<sub>2</sub> films

hybrids without coupling agent. Most of the modulus and tensile strength are higher than their counterparts without coupling agent. This may be attributed to the improved interaction between the PI matrix and the silica resulting from the reduced size of SiO<sub>2</sub> particles and the chemical bonds introduced by the coupling agent. On the contrary, the elongation at break (E<sub>b</sub>) of the hybrids decrease dramatically with the addition of coupling agent. This can be explained by the increased “crosslinking density” resulting from the reduced particle size.

#### 4. Conclusions

The properties of PI/SiO<sub>2</sub> hybrids are greatly improved by the addition of coupling agent GOTMS. GOTMS has greatly compatibilized the two phases of the hybrid and results in remarkable reduced size of SiO<sub>2</sub> particles. The addition of GOTMS can provide a PI/SiO<sub>2</sub> hybrid good properties such as simultaneous strengthening and toughening with high silica content (20wt%), decreased thermal expansion coefficient, retention of the solubility of polyimide matrix and high optical transparency.

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