

# Study on Morphology Control and How to Affect Mechanical Properties of Polyimide/Silica Hybrid Films

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**ABSTRACT:** A series of polyimide (PI)/silica hybrid films were prepared by sol-gel method, using hydrolyzed tetraethoxysilane and poly amic acid-imides (PAA-Is), which were different imidization degree controlled by chemical imidization method. The imidization degree was characterized by Fourier transform infrared spectra and their corresponding morphology was characterized by scanning electron microscopy. The results show that there are two kinds of silica particles and their formative morphology obeys the double phase separation mechanism. According to the increase of PAA-I imidization degree, amount of nano silica particles decreased and the diameter

of macro silica particles increased in the hybrid films. Tensile testing, dynamic mechanical analysis, and thermal mechanical analysis results show that, according to the amount of nano silica particles increasing, the hybrids have the higher the mechanical properties, glass transition temperature ( $T_g$ ), and thermal expansion coefficient. Through controlling PI/silica hybrid films microstructure, its mechanical properties can be controlled. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 2772–2777, 2010

**Key words:** polyimide/silica hybrid; morphology; mechanical properties; nano effect

## INTRODUCTION

Polyimide (PI) is a novel material owning excellent mechanical properties and thermal resistance in modern industry, broadly applied in aerospace, and electronic industry.<sup>1–3</sup> PI/inorganic hybrid materials combine advantages of PI and inorganic component and show more excellent properties, which attracts much attention on lots of researchers.<sup>4–6</sup>

In previous studies, PI/silica hybrid materials were prepared by the sol-gel route and characterized in terms of their curing behaviour, morphology, and mechanical properties. It was established that the morphology of the PI/silica hybrid can be controlled by introducing silicic structure onto main and side chain of PI molecule,<sup>7–9</sup> adding coupling agents (such as GOTMS),<sup>10,11</sup> and using PI with the hydroxyl and carboxyl groups.<sup>12–14</sup> Above researches were concentrated on improving the interfacial interaction between organic and inorganic components to make silica inorganic particles disperse in PI matrix. Furthermore, researchers also attend to control the morphology and gain higher properties of PI/silica hybrid. Such results were reported that with the

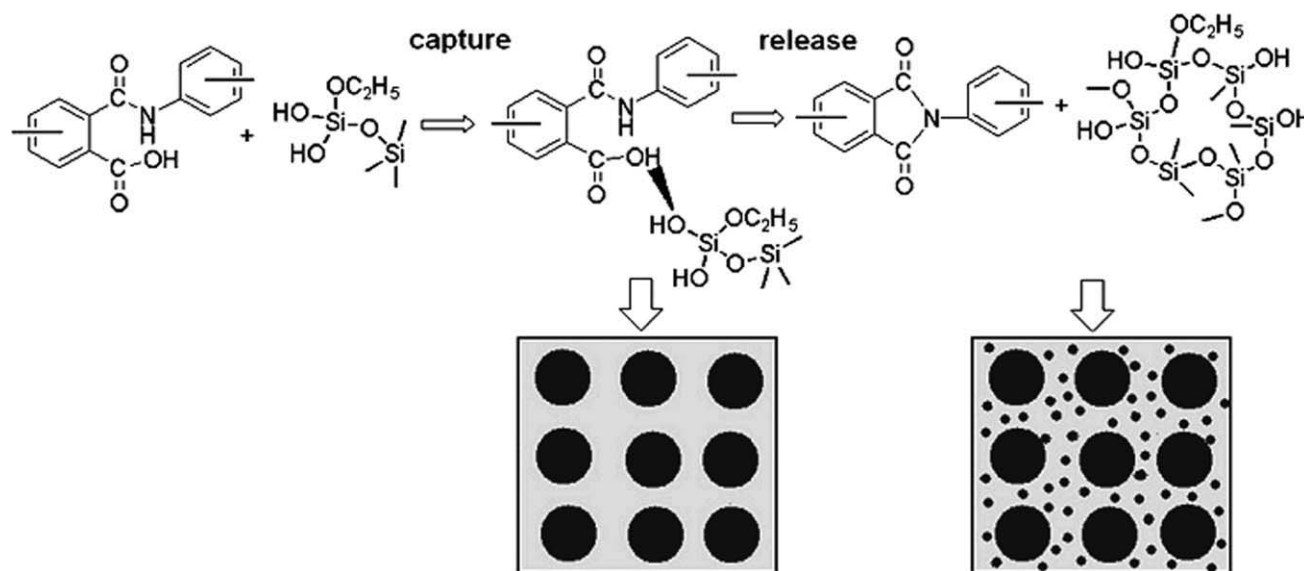
silica content increasing, the tensile mechanical properties of hybrids increased and when silica content exceed certain point, the properties would obviously decrease.<sup>13,15–20</sup> That explanation of maximal mechanical property was presumed by the nano effect of nano silica particles, such as the nano scale effect, the nano surface effect, the macroscopic quantum tunnel effect. But it was not supported by experimental results.

In our previous research,<sup>21</sup> we found that double phase separation phenomenon exists when fabricating PI/SiO<sub>2</sub> hybrid materials via polyamic acid (PAA) and hydrolyzed TEOS and proved that it results from two different stages. The mechanism is shown by Figure 1. This phenomenon has repeated in lots of systems, such as BTDA/ODA, BTDA/ODA/DHTM, ODPA/ODA, ODPA/ODA/DABBE, PMDA/ODA.

The purpose of this study is, with the same silica content in PI/silica hybrid film, to design and control the different morphology by double phase separation mechanism and further study the relationship of nano silica particle and the mechanical properties. Herein, we need to fabricate nano silica particles and make the scale of silica particles change, and track the corresponding mechanical properties. In double phase separation mechanism, the carboxyl groups in PAA by hydroxyl bond “capture” the hydrolyzed TEOS and finally “release” this part of inorganic component and form nano scale silica particle. The carboxyl group acts as very special and key role in double phase separation phenomenon. Its contents of PAA intermediate

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**Figure 1** Schematic representation of double phase separation of PI/SiO<sub>2</sub> hybrid.<sup>21</sup>

decide the amount of nano silica particles. We utilize this mechanism, through controlling the content of carboxyl group in PAA, to control the content of nano silica particle. Furthermore, we also hope this study result find a direct experimental proof to make clear the relationship of the mechanical property and the nano silica particles.

## EXPERIMENTAL

### Materials

4,4'-Oxydiphthalic anhydride (ODPA, ACROSOGANICS) was used after drying at 180°C under vacuum for 5 h. 4,4'-Oxydianiline (ODA, Shanghai Research Institute of Synthetic Resins) and tetraethoxysilane (TEOS, Shanghai Chemical Reagent Co.) were used as received. *N*-Methyl-2-pyrrolidinone (NMP, Qunli Chemical Reagents Corp., Shanghai, China) was purified by vacuum-distillation over phosphorus pentoxide and stored over 4-Å molecular sieves.

### Preparation of PI/SiO<sub>2</sub> hybrid films

Dianhydride (ODPA) was added to the NMP solution containing an equimolar amount of diamines (ODA) (solid content 15 wt %). The mixture stirred at room temperature for 12 h, and a viscous PAA solution was obtained. Series of PAA-Is with different imidization degree were prepared by controlling the amount of the dehydration agent which is a blend of acetic anhydride and pyridine. Theoretically, the imidization degree is controlled by changing the mole amount of acetic anhydride (0, 20, 40, 60, 80, and 100 mol %). When the mole ratio of added acetic anhydride to carboxyl group is 1.00, the theoret-

cal imidization degree is 100%. The hydrolyzed TEOS solutions were added into the PA-I solutions, respectively. The series solutions were coated on the glass substrates and subsequently dried at 80°C for 3 h, 140°C for 2 h, 220°C for 2 h, and 300°C for 1 h under vacuum and then got the hybrid films with silica content of 8 wt %. The PI/SiO<sub>2</sub> hybrid films synthesis process is shown in Scheme 1.

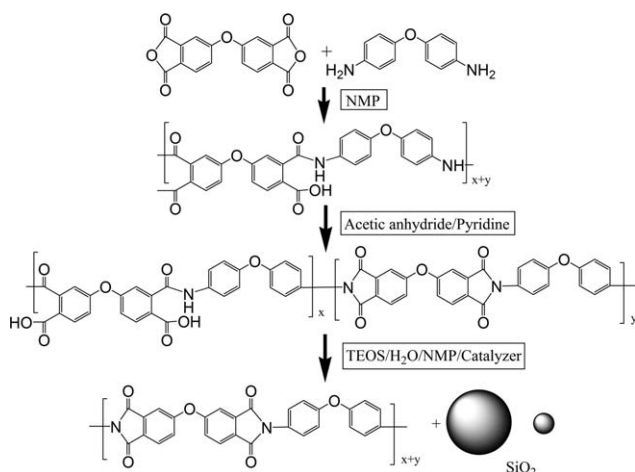
### Measurements

Fourier transform infrared spectra (FTIR) of hybrid films were recorded on a Nicolet 560 FTIR spectrophotometer. The morphology was investigated by scanning electron microscopy (SEM) using a LSM-5900LV (Japan) operating at 20 kV. The tensile strain-stress test of PI/SiO<sub>2</sub> hybrid films was determined on a XLL-50 tester at room temperature. The load cell used was 5 kg and the drawing rate was 5 mm/min. Measurements were performed with film specimens (1 cm wide, 7 cm long, and 25–40 μm thick). The gauge length was 3 cm. The dynamic mechanical analysis (DMA) and thermal mechanical analysis (TMA) were obtained with a TA Instruments DMA 983. A sample 10 mm long and 4 mm wide was used. The DMA experiment was performed at a heating rate of 5 K/min from 150°C to the maximal temperature of 350°C using a frequency of 10 Hz. The TMA experiment was carried out at a heating rate of 10 K/min from 50 to 300°C using a static force of 0.8 N.

## RESULTS AND DISCUSSION

### Factual imidization degree of the PA-Is

Series of part imidized PAAs (PA-Is, ODPA/ODA) were characterized by FTIR. To measure the factual



**Scheme 1** Synthesis process of PI/SiO<sub>2</sub> hybrid films.

imidization degrees of PA-Is, technique of Ref. 15 was introduced. The results (Fig. 2) substantiated that the factual imidization degrees of the PA-Is are 0%, 27.7%, 45.5%, 55.4%, 72.67% and 100%, respectively. The results show that the actual imidization degree consistent with the expected results.

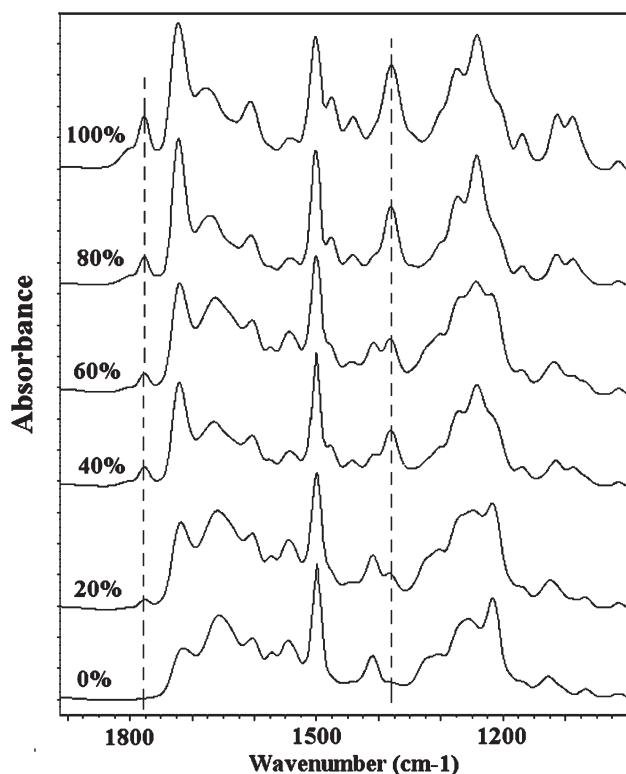
### Morphology of PI/SiO<sub>2</sub> hybrid films

With the imidization degree increasing of PI, the transparency of PI/SiO<sub>2</sub> hybrid films decreased. It can be proved by the SEM photographs (Fig. 3). There are two populations of SiO<sub>2</sub> particles in the hybrid films when PAA was used in hybrid solution [Fig. 3(a)]. Decreasing carboxyl group content, morphology of hybrid films changes: the size of bigger SiO<sub>2</sub> particles increases from 300 nm [Fig. 3(a)] to 1 μm [Fig. 3(d)]; however, the amount of SiO<sub>2</sub> nanoparticles in the hybrids decreases and almost disappears when the imidization degree reaches 55.4%. This result confirms that the silica particles size can be controlled by the double phase separation mechanism. The silica particle size with higher imidization degree PA-I is bigger than that of low imidization degree PA-I. The relationship of PI/SiO<sub>2</sub> hybrid film's morphology and imidization degree is shown in Scheme 2.

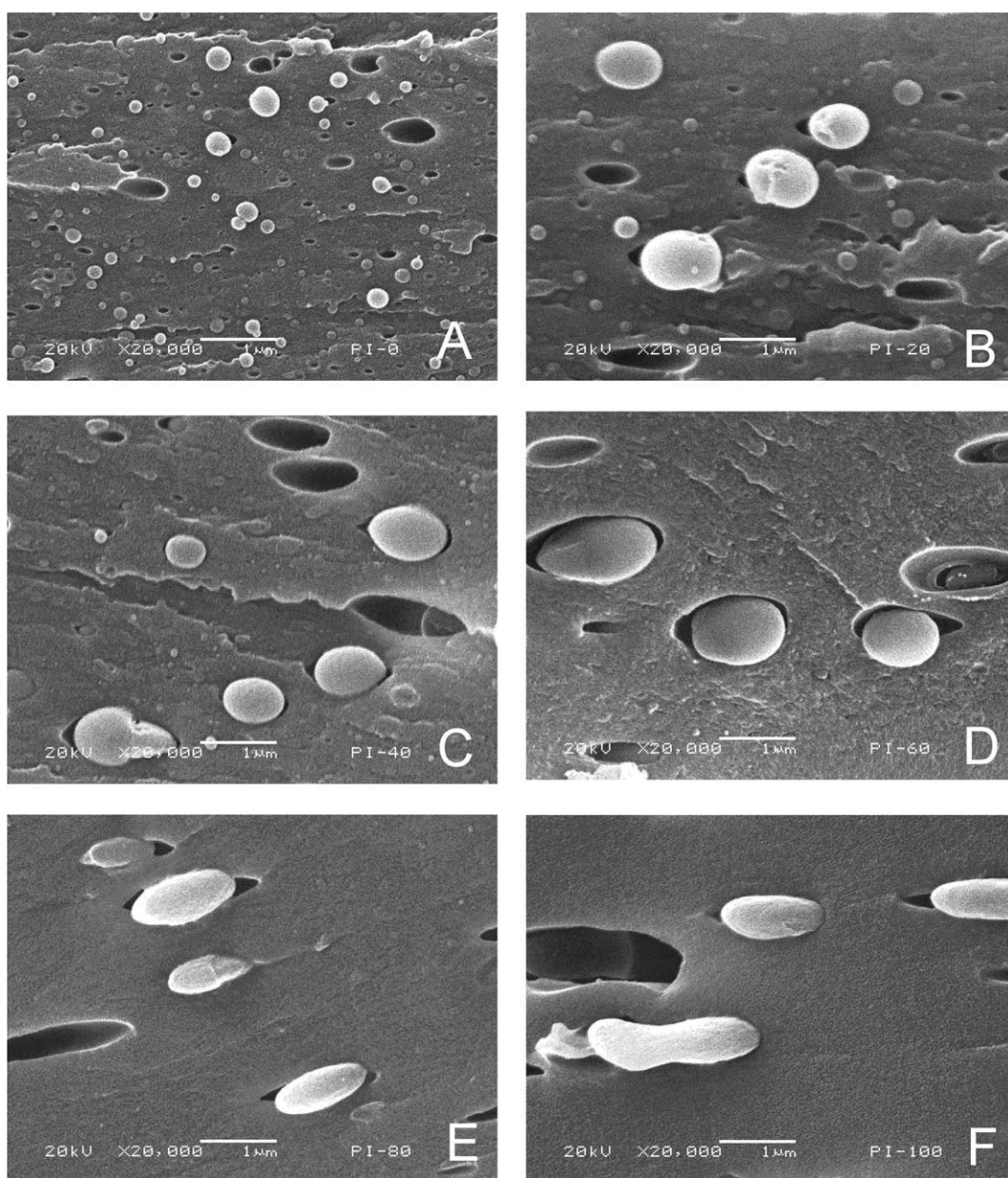
### Mechanical properties of PI/SiO<sub>2</sub> hybrid films

Figure 4 shows the test results of mechanical properties of above PI hybrid films. It indicates that with increase of imidization degree, tensile strength decreases, elongation at break increases. The corresponding PI films prepared by different imidization degree PA-I were tested by strain–stress test. The result shows in Table I. Comparison of the results, it shows that tensile strength and Young's modulus of hybrid system are both higher than that of pure PI,

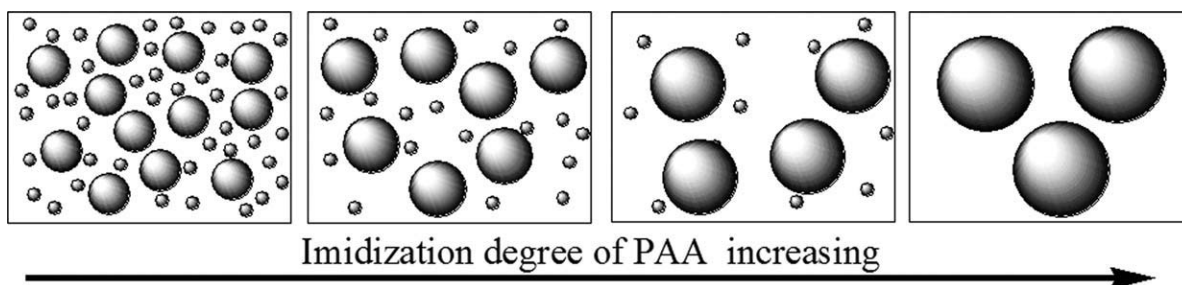
yet with the increase of imidization degree of PI, this discrepancy becomes smaller; correspondingly, its elongation at break is higher than that of pure PI and then lower than that of pure PI. Compositions of all hybrid samples are the same, so the influence of PI matrix can be excluded. It shows that the morphology of silica particles influence the mechanical properties of hybrid materials. Microscopic morphology in Figure 3 shows that with the increase of imidization degree of PI, the number of smaller silica particles decreases, and the size of larger silica particles increases. Two kinds of silica particles form with different mechanism: larger particles derive from volatilization of solvent, and smaller ones derive from phase separation induced by imidization reaction. The formation of larger silica particles is results from phase separation when the system changes from solution to solid state, which is a process in micron order; the formation of smaller ones is due to the chemical structure change of polymer and inorganic component at solid state. *In situ* produced silica particles release from polymer molecule. These two different size silica particles contribute to the different effect on mechanical properties. The nano scale silica particle act in PI/silica hybrid as physical crosslinking points to restrict PI molecule's mobility. So, it is a positive effect on the tensile strength and Young's modulus and a negative factor for the elongation at break.



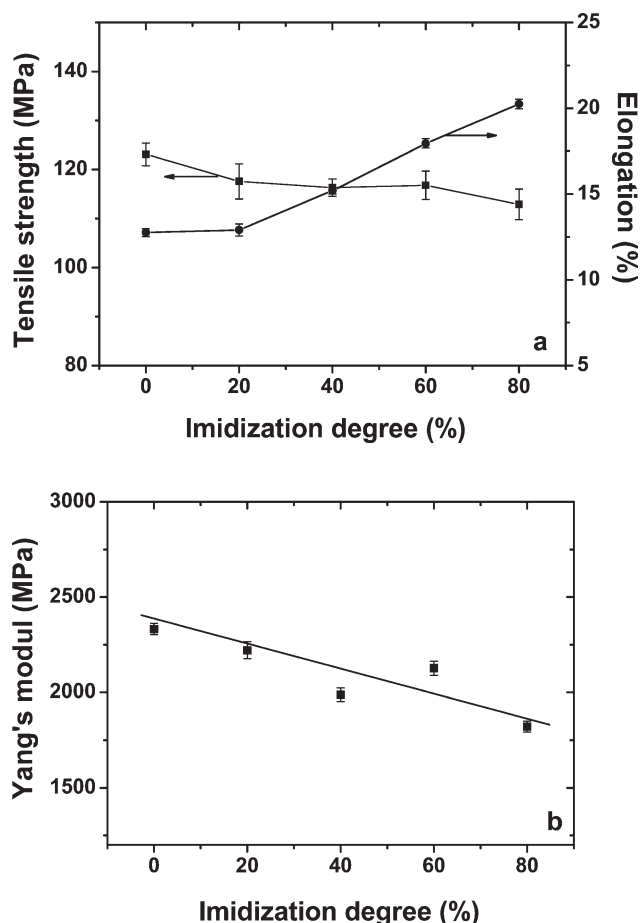
**Figure 2** FTIR spectra of PA-Is cured at 60°C for 6 h.



**Figure 3** SEM photograph of the PI/SiO<sub>2</sub> hybrid from different imidization degree cured at 300°C. (a) PAA; (b) PA-I with 20% imidization degree; (c) PA-I with 40% imidization degree; (d) PA-I with 60% imidization degree; (e) PA-I with 80% imidization degree; and (f) PI.



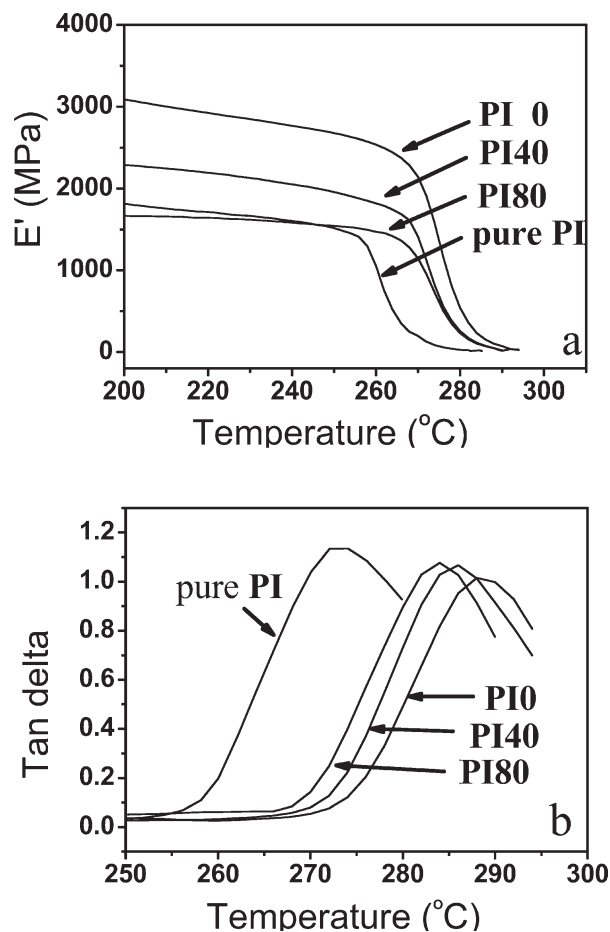
**Scheme 2** Relationship of PI/SiO<sub>2</sub> hybrid film's morphology and imidization degree of PAA.



**Figure 4** Tensile test results of PI/SiO<sub>2</sub> hybrids with different imidization degree of PI. (a) Tensile strength and elongation at break; (b) Young's modulus.

#### DMA analysis of PI/SiO<sub>2</sub> hybrid films

DMA test can further make clear the morphology effect on the mechanical property. Dynamic mechanical test results are shown in Figure 5. The result shows that the modulus of hybrid films decrease with the increasing of imidization degree. According to FTIR and SEM result, the imidization degree increasing, the amount of the nano scale silica particle decrease, while the micron scale silica particle size gradually increased, the modulus of the hybrid is more and more close to that of pure PI. This result indicates that nano silica particles act as efficient physical crosslinking points to restrict the mobility of PI molecule. It is agreed with the stress-strain test results. Furthermore, the peak intensity and move-



**Figure 5** DMA results of PI/SiO<sub>2</sub> hybrid with different imidization degree of PAA. (a) E'; (b) tan  $\delta$ .

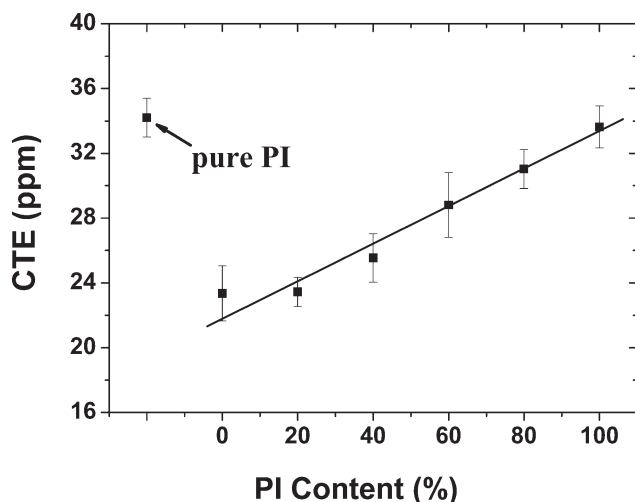
ment of tan  $\delta$  ( $T_g$ ) changes also can prove it. The effect of nano silica and micro silica on the PI molecular movement ability is different. Nano silica can be more effective restrictions on PI molecular motion. As the imidization degree of PA-I increase gradually, the number of nano silica reduces and micro silica particle size increase. Therefore, the hybrid films of the peak intensity increased with the imidization degree of PA-I gradually increased and the peak moves from the higher temperature to the lower temperature.

#### Thermal expansion coefficient of PI/SiO<sub>2</sub> hybrid films

In the same composition of PI/silica hybrid film, TMA experiment can directly test the molecule

**TABLE I**  
Tensile Test Results of Pure PI and PI/SiO<sub>2</sub> Hybrid films

Degree of Imidization (%)	Tensile strength (MPa)		Moduli (MPa)		Elongation at break (%)	
	Pure PI	PI hybrid	Pure PI	PI hybrid	Pure PI	PI hybrid
0	110.6	123.1	1829	2333	12.75	14.25
40	115	116.3	1777	1988	19.76	16.2
80	111.9	112.9	1811	1881	23.94	20.25



**Figure 6** TMA results of PI/SiO<sub>2</sub> hybrid from different imidization degree of PAA.

mobility of PI. TMA test results are shown in Figure 6. It shows that, with the increase of imidization degree, thermal expansion coefficient increases markedly. The reason is that the amount of nano silica particles decreases with the increasing of imidization degree and the size of micron silica particle (shown in Fig. 3). This results evidently shows that more nanoparticles could restrict polymer molecule' mobility more effectively, which is consistent with DMA results.

### CONCLUSIONS

In summary, we have successfully controlled the morphology of PI/silica hybrid film and get nano and micron scale silica particles simultaneously with double phase separation mechanism. These two kinds of silica particles with different size contribute to the different effect on mechanical properties. This work finds a direct experimental proof to prove the maximal mechanical property caused by the nano silica particles, which shows the nano effect in hybrid. Furthermore, previous researchs are focus

on designing PI with novel structure to improve the interface between silica and PI, which may weaken the intrinsic properties of PI. Our research finds a novel way to control the morphology of PI/silica hybrid and further control their properties. This research result may offer a new idea to prepare other high performance PI hybrid materials by sol-gel method.

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