

# Low temperature properties of PI/SiO<sub>2</sub> nanocomposite films

Z.D. Wang<sup>a,c,\*</sup>, J.J. Lu<sup>a</sup>, Y. Li<sup>b</sup>, S.Y. Fu<sup>b</sup>, S.Q. Jiang<sup>a</sup>, X.X. Zhao<sup>a</sup>

<sup>a</sup> Institute of Engineering Mechanics, Beijing JiaoTong University, Chinese Academy of Sciences, Beijing 100044, China

<sup>b</sup> Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100080, China

<sup>c</sup> Institute of Mechanics, Chinese Academy of Sciences, Beijing 100080, China

Received 9 December 2004; received in revised form 7 July 2005; accepted 7 August 2005

## Abstract

In this paper, the mechanical properties of PI/SiO<sub>2</sub> nanocomposite hybrid films with different silica doping levels are experimentally studied at low temperature. Experimental results show that the coefficient of thermal expansion (CTE) of the PI/SiO<sub>2</sub> nanocomposite hybrid films gradually reduces when the ambient temperature is decreased. At the liquid nitrogen temperature (77 K), the CTE value is about five times less than that at room temperature (287 K). The measured CTEs of hybrid films greatly decrease when doped with inorganic silica, especially when the silica doping level is more than 1 wt.%. However, too high silica contents (more than 10 wt.%) can cause problem to disperse effectively and the specimens become quite opaque. Experimental results also show that the effects of the pre-applied stress levels can be neglected on the CTE testing. When the ambient temperature changes from 287 to 77 K, the measured average values of the films' ultimate tensile strength (UTS) and Young's modulus increase about 60 and 90%, respectively, while the breaking elongation decreases about 42%.  
© 2005 Elsevier B.V. All rights reserved.

**Keywords:** Coefficient of thermal expansion (CTE); Low temperature; Mechanical properties; Film

## 1. Introduction

Polyimide (PI) films have attracted great research interests because of their special properties, such as low dielectric constant, excellent electrical and mechanical properties, which have broad applications in microelectronics industry as buffer coatings, passive layers, interlayer dielectrics and wafer scale packages [1,2]. In order to further improve the related mechanical properties, such as decreasing coefficient of thermal expansion (CTE) and improving fracture property, recent works have been focused on how to produce nano-structure PI hybrid organic–inorganic films which can combine desirable organic and inorganic characteristics together by using different fabrication techniques [3–8].

Besides their applications at room and high temperatures [9–17], PI films are also regarded as important thermal and electrical insulating materials in cryogenic engineering, such as spacecraft, superconducting magnet devices and some related electrical components. The requirements for PI films in these unique applications are extremely severe and complicated, and

their related mechanical properties at low temperature are very critical. There are some research reports involved in the cryogenic properties of PI films [18–20], but not much about PI/SiO<sub>2</sub> nanocomposite films.

In this paper, we report research results of cryogenic mechanical properties of PI/SiO<sub>2</sub> nanocomposite films doped with different silica contents and provide some necessary information for their applications in cryogenic engineering. Considering the liquid nitrogen is commonly used as the medium in cryogenic engineering, CTEs are measured from room temperature to liquid nitrogen temperature (77 K). The Young's modulus, elongation and ultimate tensile strength (UTS) are only tested at 77 K. However, related room temperature data are also introduced for comparison.

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

Like most of organic polymers, the much higher CTE of PI films compared with that of metallic substrates is one of the major disadvantages for their application in cryogenic engineering. The higher CTE can cause high interfacial stresses during thermal cycling and sometimes even lead to mechanical failures, such as film degradation or crack and affects the reliability of the whole structure. Doping with inorganic material is a promis-

\* Corresponding author. Tel.: +86 1051687257; fax: +86 1051682094.  
E-mail address: zhdwang@center.njtu.edu.cn (Z.D. Wang).

ing solution to reduce PI film's CTE and improve the fracture toughness and other properties.

The traditional PI/SiO<sub>2</sub> hybrid films fabricated by sol-gel technique possess lower CTE, higher thermal stability and better mechanical properties at room temperature compared with pure PI films. However, the PI/SiO<sub>2</sub> hybrid film's mechanical properties will decrease quickly at higher silica doping level because of the increased particle size. In order to improve the properties of PI/SiO<sub>2</sub> hybrid films, a new process which would lead to a smaller particle size was developed for the preparation of PI/SiO<sub>2</sub> hybrid films in this study.

### 2.1. Materials

In our experiments, some commercial available materials are used, namely, pyromellitic dianhydride (PMDA, C<sub>10</sub>H<sub>2</sub>O<sub>6</sub>) and diphenylene diamine (ODA, C<sub>12</sub>H<sub>12</sub>N<sub>2</sub>O) from Technid Enterprise Co. Ltd., tetraethoxysilane (TEOS), ethanol (EtOH) and catalyst from Beijing Chemical Co. Ltd. *N,N*-Dimethylacetamide (DMAc, [(CH<sub>3</sub>)<sub>2</sub>NCOCH<sub>3</sub>]) was desiccated by molecular sieve before use.

### 2.2. Traditional processing technique

After dissolving ODA in DMAc, PMDA is added into the reaction mixture under a nitrogen atmosphere and stirred for 6 h at room temperature. Then, TEOS, water and catalyst are added to the solution, and further stirring is conducted to produce a homogeneous solution. Spinning the transparent solution onto a glass plate and subsequently dried for 1 h at 80, 100, 120, 150, 180, 240 and 270 °C. Table 1 gives the formulations for the PS1 hybrid films prepared using the traditional processing technique.

### 2.3. New processing technique

ODA is first dissolved in DMAc under a nitrogen atmosphere. TEOS, ethanol and catalyst are then added to form the solution. After stirring for about 30 min, PMDA are added and subse-

quently stirred for about 6 h to produce a homogeneous solution. Hybrid films are obtained through the same thermal treatment as above. The formulations for the PS2 hybrid films prepared using the new processing technique are also given in Table 1.

## 3. Coefficient of thermal stress

The mechanical properties of polymer films, such as the CTE, the residual stresses and the elastic constants, are generally not the same as those of the bulk materials [21,22]. Therefore, it is preferable to characterize the CTE of the films at low temperature directly. In this study, a new device was designed to test the CTE values of PI/SiO<sub>2</sub> nanocomposite hybrid films.

### 3.1. Testing device

Fig. 1 shows the schematic of the CTE testing device. The specimen (11) is fixed by four magnets and magnet-sheaths (the magnet and magnet-sheath are wholly shown as part 7 in

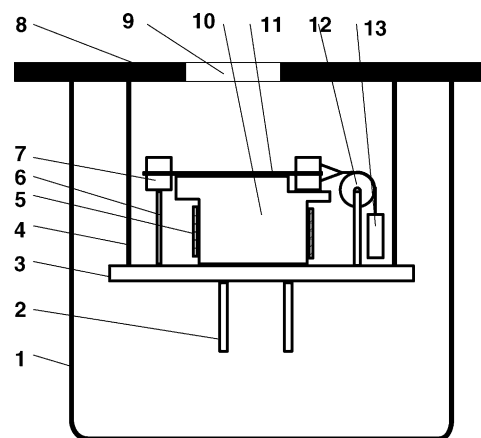


Fig. 1. Schematic depiction of the device for measuring CTE of thin films at low temperature: (1) Dewar; (2) fixed rod; (3) foundation; (4) connecting rod; (5) heater; (6) supporting rod; (7) magnet and its sheath; (8) flange; (9) glass window; (10) temperature-controlled block; (11) specimen; (12) pulley system; (13) weight.

Table 1  
Preparation of PI/SiO<sub>2</sub> hybrid films

Sample name	PAA <sup>a</sup> (g)	TEOS (g)	H <sub>2</sub> O (ml)	Catalyst <sup>b</sup>	EtOH (ml)	Silica content (wt.%)	Remarks <sup>c</sup>
PI	15	0	–	–	–	0	T
PS1-1	15	0.035	0.012	5.0	–	1	T
PS1-3	15	0.106	0.037	5.0	–	3	T
PS1-5	15	0.182	0.063	5.0	–	5	T
PS1-8	15	0.301	0.103	5.0	–	8	S
PS1-10	15	0.385	0.132	5.0	–	10	O
PS1-15	15	0.612	0.210	5.0	–	15	O
PS2-1	15	0.035	–	37	0.100	1	T
PS2-3	15	0.106	–	37	0.301	3	T
PS2-5	15	0.182	–	37	0.494	5	T
PS2-8	15	0.301	–	37	0.791	8	T
PS2-10	15	0.385	–	37	0.987	10	T
PS2-15	15	0.612	–	37	1.571	15	O

<sup>a</sup> 15 wt.% DMAc solution.

<sup>b</sup> Weight percentage of hydrochloric acid based on the amount of water added.

<sup>c</sup> The appearance of hybrid films: T, transparent; S, translucent; O, opaque.

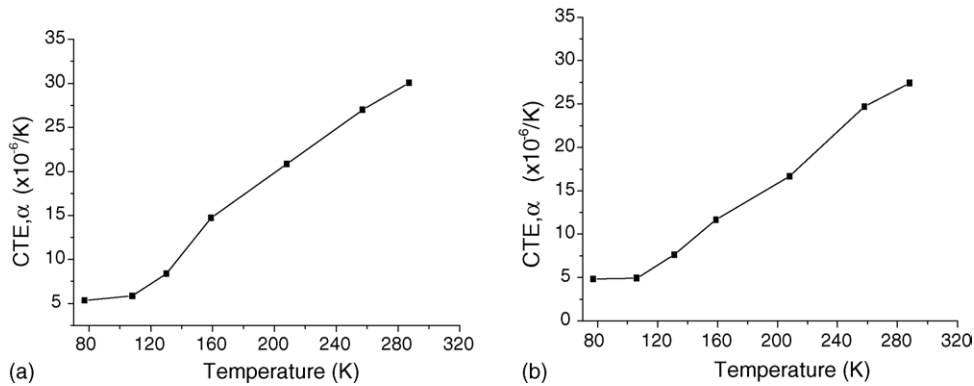


Fig. 2. Measured CTEs of pure PI film and PI/SiO<sub>2</sub> nanocomposite film with different testing temperatures: (a) 0 wt.% and (b) 8 wt.%.

Fig. 1). The left-side magnet and magnet-sheath are installed on the foundation (3) by the supporting rod (6) and cannot move during the experiment. The right-side magnet is connected with the weights (13) by a wire and can move smoothly along the surface of the temperature-controlled block (10) by a pulley system (12). The pulley system is specially designed for the application at low temperature with all parts made of same material (stainless steel) to avoid the influence caused by different CTEs. The force level applied on the specimen can be adjusted by selecting different weights (13) (according to our test, the resistance caused by the pulley system can be neglected). The fixed rod (2) and the foundation (3) are made of stainless steel and have a lower thermal conductivity than that of copper. There are two functions for the fixed rod (2). Its upper part is a screw-thread structure, which can ensure that the temperature-controlled block (10) and the foundation (3) contact each other firmly. Another function is to prevent the testing temperature from increasing too quickly while the altitude of liquid nitrogen is lower than that of the lower surface of the foundation (3). In this experiment, liquid nitrogen was used as cooling medium to decrease the testing temperature. However, some other cooling medium, such as liquid helium, may also be used instead of liquid nitrogen for temperature control.

The specimen (11) keeps contacting with the temperature-controlled block (10) tightly through a notch in the middle of the temperature-controlled block (10) so that the temperature of the specimen is more homogeneous. The temperature-controlled block (10) is made of copper which has a very high thermal conductivity. In the experiment, every temperature point was kept for 5 min for achieving good temperature stability. Considering the direct contact between the temperature-controlled block (10) and the specimen (11) and the micrometer thickness of the specimen, it is reasonable to believe that there was no temperature difference between (10) and (11). The testing temperature can be controlled by a heater (5) and recorded by a thermometer, which is installed in the temperature-controlled block (10) and not shown in Fig. 1. The power of the heater (5) is controlled by a standard temperature-controller installed in the outside of the liquid nitrogen Dewar (1).

Two parallel lines are made on the specimen before the experiment as reference. During the testing process, the distance of the two reference parallel lines decreases or increases due to the thermal deformation of the film specimen when the temperature drops or rises, which is recorded by a microscope through the glass window (9). The microscope is installed in the outside of the liquid nitrogen Dewar (1) and not shown in Fig. 1.

### 3.2. Experimental result and discussion

Fig. 2(a and b) shows measured CTEs of pure PI film and PI/SiO<sub>2</sub> nanocomposite film (8 wt.% silica content) versus different testing temperatures. The CTEs for both types of specimens decrease when the temperature drops, and which shows very good linear relationship from room temperature to 100 K. Further decreasing the testing temperature, the change of CTEs becomes slowly. The CTE value at liquid nitrogen temperature (77 K) is less than one-fifth of that at room temperature (287 K).

The average CTEs of different silica-content nanocomposite films from 287 to 77 K are shown in Fig. 3. For the PI/SiO<sub>2</sub> film with 1 wt.% silica content, the CTE is higher than that of pure PI film. The CTE of the composite films shows significant reduce when the silica content changed from 3 to 15 wt.%. However, the variation of the measured CTE values becomes very small

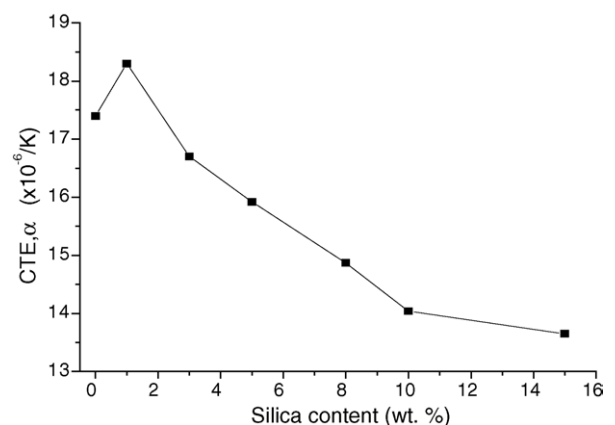


Fig. 3. Average CTE of the PI/SiO<sub>2</sub> nanocomposite films with different silica contents from 287 to 77 K.

when the silica contents increase from 10 to 15 wt.%, because it is difficult to effectively disperse silica into PI matrix when the silica content is too higher. From below Eq. (1), we can theoretically explain the relationship between the CTE and doping level [23–25]. For traditional macroscopically isotropic composites, the effective CTE value can be derived from:

$$\alpha = \alpha_2 + (\alpha_1 - \alpha_2) \frac{(1/K) - (1/K_2)}{(1/K_1) - (1/K_2)} \quad (1)$$

where  $\alpha$  and  $K$  represent material's effective CTE and bulk modulus, respectively. The subscripts 1 and 2 refer to the two phases of the composite. The lower and upper bounds can be derived on the basis of Hashin–Shtrikman theory. According to Eq. (1), the CTE of the composite is not only decided by the CTEs of the components, but also affected by the bulk moduli of the components. For organic–inorganic hybrid composites, the bulk modulus of the inorganic reinforced component is often much higher than that of inorganic matrix, which leads to a higher composite CTE at a lower inorganic content. With increasing of volume fractions of the reinforced component, the CTE of the reinforced component plays a more important role than its bulk modulus. Generally, the effective CTE decreases with increasing of volume fractions of inorganic reinforcement. Although we cannot use Eq. (1) to accurately calculate the composite CTEs in our experiments due to the nano-size of the reinforcement, the basic changing tendency is coincident with the theoretical result.

Fig. 4 shows photos of the PI/SiO<sub>2</sub> films fabricated using the new processing technique. Most of the films have light colors which imply good transparency except that of the film with 15 wt.% silica content which is quite opaque. The tensile fracture surfaces of the PI/SiO<sub>2</sub> hybrid films are examined by SEM and the photographs are shown in Figs. 5 and 6. There are notice-

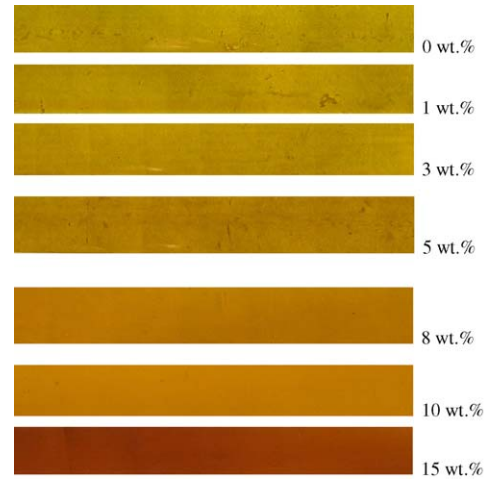


Fig. 4. Photos of PI/SiO<sub>2</sub> nanocomposite films.

able white beads in the photographs of 15 wt.% silica-content films, which means that the average diameter of the dispersed silica particles is no longer in the nano-size level. This also demonstrates that too higher silica content can cause difficulty to disperse silica into the PI matrix effectively.

The above results were obtained under fixed pre-apply stress of 3–4.5% material's UTS (the percentage variation is due to the material's UTS changing at different temperatures). The available testing techniques on CTEs are taken on a constant-stressed-body or a free-body. The question asked here is that whether the CTEs may be affected by the pre-stress level. For bulk materials, the working stresses are normally much lower than the failure strength of materials and the stress effect can be neglected. However, for thin film materials, it is preferred to investigate the CTE at different stress levels. To answer this

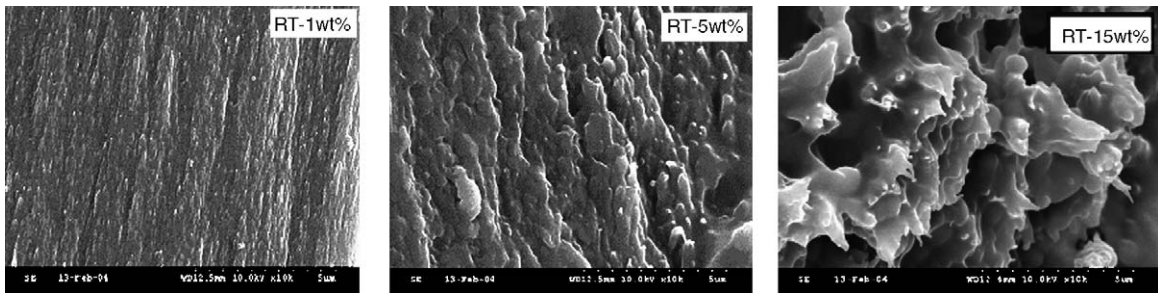


Fig. 5. Fractured surface morphology of composite films with different silica contents at 287 K.



Fig. 6. Fractured surface morphology of composite films with different silica contents at 77 K.



Table 2  
CTEs of pure PI film at different applied stress levels

$T$ (K)	$\alpha \times 10^{-6}$ (K)		
	3.0–4.5% UTS	9.0–13.5% UTS	15.0–22.5% UTS
287	30.05	30.02	29.86
257	26.99	26.55	26.33
208	20.85	20.63	20.38
159	14.72	14.70	14.49
131	8.4	8.13	7.22
107	5.86	5.80	5.25
77	5.34	5.23	4.81

Table 3  
CTEs of film with 8 wt.% SiO<sub>2</sub> at different applied stress levels

$T$ (K)	$\alpha \times 10^{-6}$ (K)		
	3.0–4.5% UTS	9.0–13.5% UTS	15.0–22.5% UTS
287	27.40	27.20	27.01
257	24.71	24.05	23.79
208	16.67	16.09	15.85
159	11.65	10.96	10.55
131	7.61	6.80	6.55
107	4.85	4.68	4.20
77	4.82	4.41	4.02

question, we applied different stress levels to the pure PI film and the hybrid film (8 wt.% silica content), measured CTE values are listed in Tables 2 and 3, respectively. The testing results demonstrate that the film's CTE value reduces slightly when the pre-applied stress is increased, but the difference is very small and can be neglected. In the testing, no further higher stress was applied, because stress loadings of PI films are usually lower than 10% of material's UTS under normal working condition.

#### 4. Tensile properties

Tensile experiments were carried out with a Sans universal testing machine at a rate of 2 mm/min. The measured UTS values of the PI/SiO<sub>2</sub> hybrid films with different silica doping levels at 287 and 77 K are shown in Fig. 7. It is noticeable that the UTS values increase in a range of appropriate silica doping level (0–8 wt.%), then it drops significantly when the doping level is too high (more than 10 wt.%). The maximum UTS values are obtained from the films with 3 wt.% silica content at both temperatures of 77 and 287 K. Fig. 7 also shows that the UTS values of PI/SiO<sub>2</sub> hybrid films with 3 wt.% silica content have more than 70% increase when temperature changes from 287 to 77 K.

The measured Young's moduli increase with increasing of silica content at temperature 287 and 77 K, as shown in Fig. 8. At 77 K, the Young's modulus increases dramatically when the silica content changes from 0 to 5 wt.%, then the value is kept almost constant with further increase of silica content. However, the Young's moduli of the hybrid films with different silica contents generally changes much smaller at 287 K compared to at 77 K, especially in the lower silica doping level.

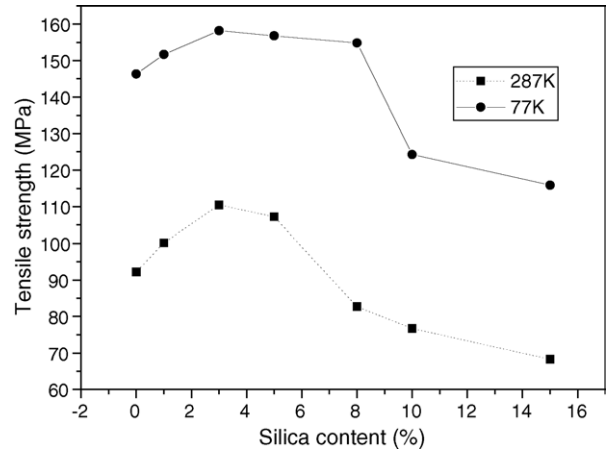


Fig. 7. Ultimate tensile strength of PI/SiO<sub>2</sub> nanocomposite films with different silica contents.

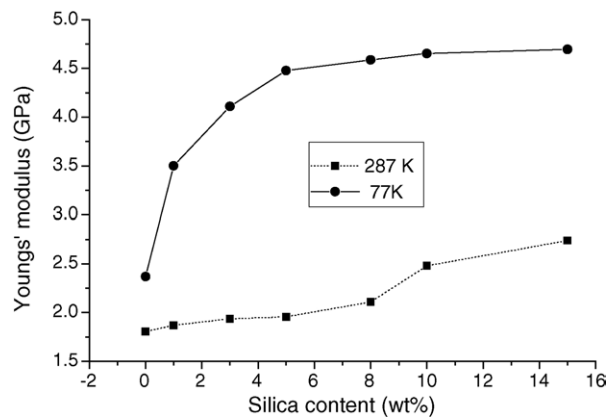


Fig. 8. Young's moduli of PI/SiO<sub>2</sub> nanocomposite films with different silica contents.

The breaking elongations of the hybrid films at 287 and 77 K are shown in Fig. 9. The maximum values are also obtained from the films with 3 wt.% silica content, similar as the UTS result. But the changing tendency of the breaking elongation is much more slowly with different silica contents at 77 K. It is not clear why the measured breaking elongation for the film with 3 wt.% silica content is much higher than the other values at 287 K.

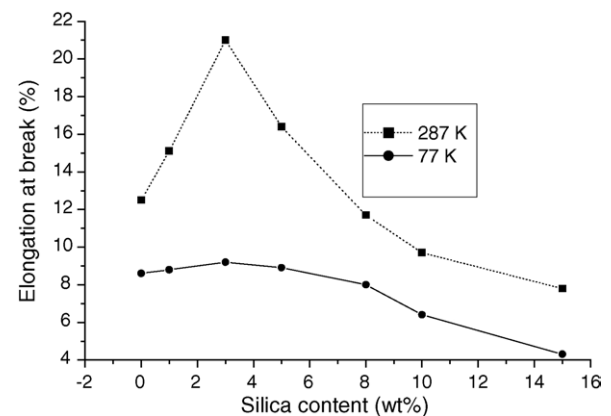


Fig. 9. Elongations at break of PI/SiO<sub>2</sub> nanocomposite films with different silica contents.

## 5. Conclusions

In this paper, the mechanical properties of PI/SiO<sub>2</sub> nanocomposite thin films at low temperature are presented. PI/SiO<sub>2</sub> nanocomposite films with different silica contents are synthesized by a new sol–gel processing technique. A new testing device is designed to characterize the CTEs of the thin PI/SiO<sub>2</sub> nanocomposite films applied with different stress levels at temperature range from 287 to 77 K. Testing results show that appropriate silica doping levels should be selected to decrease the CTE of composite films. On one hand, too low silica content can lead to a high composite CTE value, because the modulus influence of the reinforcement is much higher than that of PI matrix. On the other hand, too high silica content can also cause problem for the doping silica to be effectively dispersed into PI matrix, and decrease other properties of the hybrid films, such as the UTS and the Young's modulus. The measured CTEs show slight decrease with increasing of the applied stress level, but the change is very small and can be neglected.

The tensile testing results show that the average UTS and the Young's modulus increase about 70 and 90% from room temperature (287 K) to low temperature (77 K), respectively. However, the changing tendency is not linear. At 77 K, the Young's modulus of the films have a significant improvement with silica content changing from 0 to 5 wt.%, then the value changes very small with further increasing the silica content. At 287 K, the Young's modulus of the films generally changes much slowly. The measured breaking elongation curves of the films are quite different at 287 and 77 K; both curves have the maximum values at 3 wt.% silica content, but the former curve has a much higher maximum value, and the later curve changes very slowly in all range.

Commonly speaking, the mechanical properties of PI/SiO<sub>2</sub> nanocomposite thin films at low temperature are much different from that at room temperature and the changing tendency is also much different. In order to promote their application in

cryogenic engineering, some necessary researches about their cryogenic properties must be carried out.

## Acknowledgement

This work was funded by NJTU Paper Foundation, Beijing Jiaotong University (No. TJJ05005).

## References

- [1] D. Wilson, H.D. Stenzenberger, P.M. Hergenrother (Eds.), *Polyimides*, Blackie, Glasgow, 1990.
- [2] W. Volksen, P.M. Hergenrother (Eds.), *High Performance Polymers*, Springer, Berlin, 1994.
- [3] J.E. Mark, *Polym. Eng. Sci.* 36 (1996) 2905.
- [4] Y. Imai, *J. Macromol. Sci. Chem.* A280 (1991) 1115.
- [5] V.A. Bershtein, et al., *Macromol. Symp.* 146 (1999) 9.
- [6] Z.K. Zhu, et al., *Adv. Mater.* 12 (14) (2000) 1055.
- [7] C.S. Ha, W.K. Cho, *Polym. Adv. Technol.* 11 (3) (2000) 145.
- [8] T.C. Huang, et al., *Polymer* 42 (3) (2001) 873.
- [9] F. Wang, J.A. Wickert, *J. Micromech. Microeng.* 6 (1996) 301.
- [10] J.J. Vlassak, M.D. Drory, W.D. Nix, *J. Mater. Res.* 12 (1997) 1900.
- [11] T.Y. Zhang, L.Q. Chen, R. Fu, *Acta Mater.* 47 (1999) 3869.
- [12] F. Wang, H.C. Tsai, C.Y. Lo, *Sens. Actuators A77* (1999) 21.
- [13] T. Agag, T. Koga, T. Takeichi, *Polymer* 42 (2001) 3399.
- [14] K.L. Mittal (Ed.), *Polyimide: Synthesis, Characterization, and Applications*, Plenum Press, New York, 1993.
- [15] C. Feger, M.M. Khojasteh, J.E. McGrawth, Elsevier, Amsterdam, 1989.
- [16] M.K. Gosh, K.L. Mittal, *Polyimides: Fundamentals and Applications*, Marcel Dekker, New York, 1996.
- [17] D. Wilson, H.D. Stenzenberger, P.M. Hergenrother (Eds.), *Polyimide*, Blackie, Glasgow, 1999.
- [18] H. Yamaoka, K. Miyata, O. Yano, *Cryogenics* 35 (1995) 787.
- [19] K. Ahlborn, *Cryogenics* 28 (1988) 234.
- [20] E. Tschegg, K. Humer, H.W. Weber, *Cryogenics* 31 (1991) 878.
- [21] W. Fang, J.A. Wickert, *J. Micromech. Microeng.* 6 (1996) 301.
- [22] O. Tabata, et al., *Sens. Actuators A* 20 (1989) 135–141.
- [23] V.M. Levin, *Mech. Solids* 2 (1967) 58.
- [24] R.A. Schapery, *J. Compos. Mater.* 2 (1968) 380.
- [25] B.W. Rosen, Z. Hashin, *Int. J. Eng. Sci.* 8 (1970) 157.