

## **A new process for the preparation of polyimide/silica hybrid films**

Li Y., Fu S. Y. \*, Pan Q. Y., Zhang Y. H., and Lin D. J.

Cryogenic Materials Division, Technical Institute of Physics and Chemistry,  
Chinese Academy of Science, Beijing 100080, China

In this article a new process was introduced to prepare a series of transparent PI/silica hybrid films. The mechanical properties at 77 K were studied and compared with the films prepared by the traditional process. It was shown that the tensile strength of the films prepared by the new process were superior to the films prepared by the traditional process. The morphology of the films was characterized by scanning electron microscopy (SEM) observation.

### **INTRODUCTION**

In recent years, the cryogenic properties of polymers and polymer composites have drawn much attention with rapid developments in space, superconducting magnet and electronic technologies<sup>[1-3]</sup>. Polyimide (PI) films are used as insulating materials in superconducting magnet systems because of their high mechanical properties and excellent electrical properties etc. Electrical insulation in superconducting magnet systems is subjected to uncommon synergetic conditions: high electrical stress, high magnetic stress, high mechanical stress by electromagnetic force, thermo-mechanical stress caused by the cryogenic environment, phase transition of coolant and high energy radiation etc. So study on the mechanical properties of the insulating materials at cryogenic temperature is of great importance. Recently, the properties of PI/SiO<sub>2</sub> hybrid films prepared by sol-gel process has been studied extensively<sup>[4-10]</sup>. The PI/silica hybrid films possess lower coefficient of thermal expansion, higher thermal stability and better mechanical properties at room temperature compared with neat PI films. However, the mechanical properties of PI/SiO<sub>2</sub> hybrid films by the traditional process decreased fast by the addition of SiO<sub>2</sub> particles at higher silica content because of the fast increase of particle size; moreover, few studies have been carried out on cryogenic properties of the PI/ SiO<sub>2</sub> hybrid films.

In this article, a new process, which would lead to a smaller particle size than the traditional process, was developed for the preparation of PI/SiO<sub>2</sub> hybrid films. The mechanical properties at 77 K of the films prepared by the new process were studied. The morphology of the films was characterized by scanning electron microscopy (SEM) observation.

### **EXPERIMENTAL**

#### **Materials**

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) were provided by Tecnid Enterprise co. Ltd. N,N-dimethylacetamide (DMAc, [(CH<sub>3</sub>)<sub>2</sub>NCOCH<sub>3</sub>]) was desiccated by molecular sieve before use. Tetraethoxysilane (TEOS), ethanol (EtOH) and catalyst were purchased from Beijing Chemical Co. LTD., and used without further purification.

## Preparation of PI/SiO<sub>2</sub> hybrids

### A: Traditional process

ODA was first dissolved in DMAc. PMDA was then added to the reaction mixture under a nitrogen atmosphere and stirred at room temperature for 6 h. Then, the TEOS, water and catalyst were added to the solution. After the addition of TEOS, water and catalyst, further stirring was needed to recover a homogeneous solution. The transparent solution was spun onto a glass plate and subsequently dried respectively at 80, 100, 120, 150, 180, 240 and 270 °C for 1 h. The formulations for the PS1 hybrid films prepared using the traditional process are shown in Table 1.

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
PS2-3	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

a: 15wt% DMAc solution.

b: Weight percentage of hydrochloric acid based on the amount of water added.

c: The appearance of hybrid films, T: transparent, S: translucent, O: Opaque.

### B: New process

ODA was first dissolved in DMAc under a nitrogen atmosphere. TEOS, ethanol (EtOH) and catalyst were then added. PMDA were added after stirring for about 30 min. Subsequently stirring of about 6h was needed in order to gain a homogeneous solution. The hybrid films can be obtained through the same thermal treatment as above. The formulations for the PS2 hybrid films prepared using the new process are also given in Table 1.

## Measurement and characterization

Mechanical properties were measured with a RGT-20A testing machine at a rate of 2 mm/min. The morphology of the fracture surfaces of samples was investigated by scanning electron microscopy (SEM) with a Hatachi S-4300 microscope (Japan), operating at 10.0 kV.

## RESULTS AND DISCUSSION

### Mechanical properties

The influence of the silica content on the tensile strength at 77 K is shown in Figure 3 (a). The tensile strength at 77 K increased initially with the increase of silica content for both systems. The tensile strength at 77 K of the PS1 films was increased by about 8% when the 3 wt% silica content was added. A further increase was observed for the PS2 system. When 5 wt% silica was added, the tensile strength of

the hybrid films reached 184 MPa (an increase of about 34%). This effect might result from the stronger physical interaction between organic and inorganic phase in the PS2 system.

The influence of the silica content on the elongation at break at 77K is shown in Figure 3 (b). The elongation at break at 77 K of the PS1 system decreased with the increase of the silica content. While the elongation at break of the PS2 system increased initially and decreased with the increase of SiO<sub>2</sub> content. The elongation at break was increased by about 21% when 3 wt % silica was introduced.

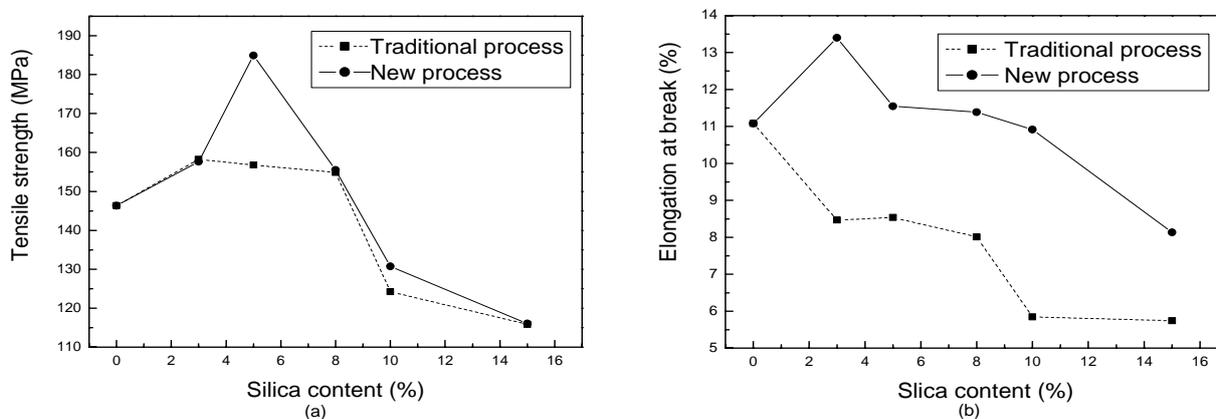
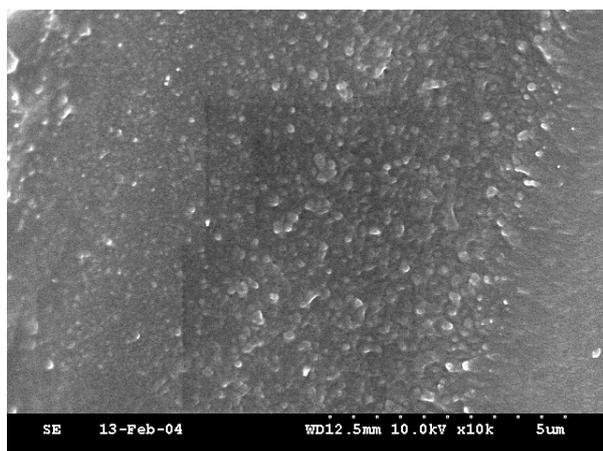


Figure 1. The mechanical properties at 77K of hybrid films for two systems.  
(a) Tensile strength, (b) elongation at break.

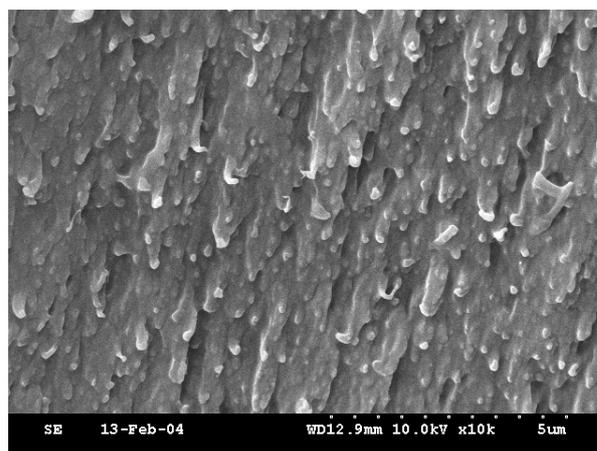
### SEM analysis

Figure 2 shows the SEM photographs of the tensile fracture surfaces of PI/SiO<sub>2</sub> hybrid films. The dispersed silica particles could be seen as white beads with an average diameter of about 40 nm, 1  $\mu$  m, 30 nm and 600 nm respectively for PS1-3, PS1-15, PS2-3 and PS2-15 films. The increase in silica particle size clearly resulted from the increase in the aggregation tendency as the increase of silica content. A fine interconnected phase morphology of PS1-3 and PS2-3 could be seen in Figure 2 (a) and (b), The morphology of PS1-15 and PS2-15 reveals that the silica particles are very smooth and completely debonded from the surrounding polyimide matrix, indicating a very poor interfacial adhesion between particles and matrix.

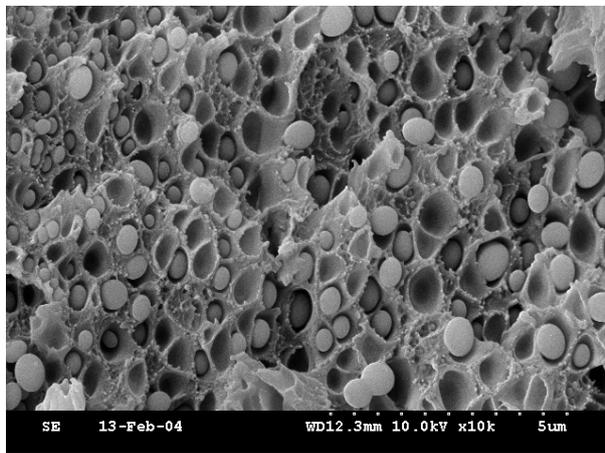
On the basis of the morphological observations, it is evident that the reduction in ultimate properties observed for the films with high SiO<sub>2</sub> contents can be attributed to weak interfacial adhesion between particles and matrix, which allows the silica particles to act as stress-concentration defects, rather than as effective reinforcing filler. On the contrary, for the films with low silica contents, the increased tensile



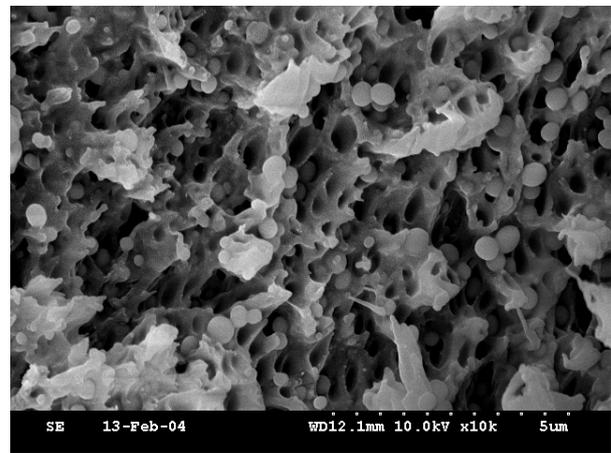
(a)



(b)



(c)



(d)

Figure 2. The morphology of the tensile section of the films by SEM.

(a) PS1-3, (b) PS2-3, (c) PS1-15 and (d) PS2-15 films

strength is the result of both a better interfacial adhesion and the formation of co-continuous morphologies, which improve the efficiency of stress transfer mechanisms between the two components. At a given silica content, the size of the SiO<sub>2</sub> particles is smaller and then the interfacial area is larger in the PS2 films than in the PS1 films, so the silica particles would have better reinforcing and toughening effects for the PS2 films than for the PS1 films.

## CONCLUSIONS

PI/silica hybrid films have been prepared with the traditional and newly developed sol-gel process. It was shown that the newly developed sol-gel process led to smaller silica particle sizes than the traditional sol-gel process did. The PI/SiO<sub>2</sub> hybrid films prepared by the new process showed better cryogenic mechanical properties than the hybrid films prepared by the traditional sol-gel process.

## REFERENCES

1. H. Yamaoka, K. Miyata and O.Yano, Cryogenic properties of engineering plastic films, *Cryogenics* (1995) **35** 787-789.
2. Takefumi Horiuchi and Tsutomu Ooi, Cryogenic properties of composite materials, *Cryogenics* (1995) **35** 677-679.
3. Okimichi Yano and Hitoshi Yamaoka, Cryogenic properties of polymers, *Prog.Polym.Sci.*(1995)**20** 585-613.
4. Yi Huang, Yi Gu, New Polyimide-silica Organic-Inorganic Hybrids, *J.Polym. Sci.*( 2003) **88** 2210-2214.
5. Ging-Ho Hsiue, Jem- Kun Chen, Ying-Ling Liu, Synthesis and Characterization of Nanocomposite of Polyimide-Silica Hybrid from Nonaqueous Sol-Gel Process, *J.Appl.Polym.Sci.*(2000) **76** 1609-1618.
6. Jing Liu, Yan Gao, FuDong Wang, Ming Wu, Preparation and Characteristics of Nonflammable Polyimide Materials *J.Appl.Polym.Sci.*(2000) **75** 384-389.
7. Zi-Kang Zhu, Yong Yang, Jie Yin, Zong-Neng Qi, Preparation and Properties of Organosoluble Polyimide/Silica Hybrid Materials by Sol-Gel Process, *J. Appl. Polym. Sci.*(1999) **73** 2977-2984.
8. Atsushi Morikawa, Yoshitake Iyoku, and Masa-aki Kakimoto etc.Preparation of a new Class of Polyimide-silica Hybrid Films by sol-Gel process *Polym. Jour.* (1992)**24** 107-113.
9. L.Mascia and A.Kioul, Influence of siloxane composition and morphology on properties of polyimide-silica hybrids, *Polymer* (1995) **36** 3649-3659.
10. T.A.Shantalii, I.L.Karpova, K.S.Dragan,etc,Synthesis and thermomechanical characterization of polyimides reinforced with the sol-gel derived nanoparticles, *Sci. and Tech. of Adv. Mater.* (2003) **4** 115-119.