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# Study on PI/$SiO_2$ Hybrid Materials Prepared from Basic Catalyzed TEOS *

Jiaqiang Qin, Jian Ding, Rongqi Zhu, Yi Gu**
State key laboratory of Polymer Materials Engineering
College of Polymer Science and Engineering, Sichuan University, Chengdu, 610065, P. R. China

## Abstract

Copolyimides containing phenolic hydroxyl groups were used to prepare the polyimide/$SiO_2$ hybrid films by sol-gel method under the basic catalyst system. Morphology and microstructure of the hybrid films were studied carefully adopting Optical Microscope and SEM. Results from these tests revealed that the interaction between polyimide and silica components create physical and chemical bonding between PI and silica. With the catalyst of TEA, the morphology of silica is the continuous-global particle, which evaluation process is from disperse structure to the continuous structure.

**Key word**: Polyimide/Silica Basic Catalyst, Sol-Gel, Morphology,

## 1. Introduction

In recent years, the organic/inorganic hybrid materials have been recognized as a new class of advanced materials because of the versatile approaches on synthesis, processing and tunable properties. The structure of organic component and the morphology of inorganic particle in the hybrid materials could be controlled by the synthetic process. The interaction between organic and inorganic component was strengthened by addition of coupling agents, such as γ -glycidyloxypropyltrimethoxysilane(GOTMS)[1], (aminophenyl)trimethoxy- silane (APTMOS)[2].

PI is a type of high–performance polymer used in microelectronic industries because of their outstanding characteristics, such as their excellent mechanical properties, lower thermal expansivity, dielectric constant and good resistance to organic solvents [3]. The alkoxide hydrolysis with acid catalyst is taken place usually [1-4], and few references to report that alkoxide hydrolyzed with base catalyst in process of preparing PI/$SiO_2$ hybrid with sol-gel reaction,

In this paper, a new kind of copolyimide/silica hybrid materials was prepared by diamine containing phenolic hydroxyl groups, BTDA, ODA, TEOS and GOTMS, with based catalyst system through sol-gel process. Morphology and evaluation process of the hybrid would be researched.

## 2.Experimental

### Materials

4,4'-diamino-4''-hydroxyltriiphenylmethane(DHTM) was synthesized by the method described in literature[5]. 3,4,3',4'-benzophenone dianhydride(BTDA), from ACROSOGANICS, was used after drying at 180°C under vacuum for 5h. ODA (from the Shanghai research Institute of Synthetic Resins) was used as received. Tetraethoxysilane(TEOS) was purchased from Shanghai Chemical Reagent Co. γ -glycidyloxypropyltrimethoxysilane (GOTMS) was obtained

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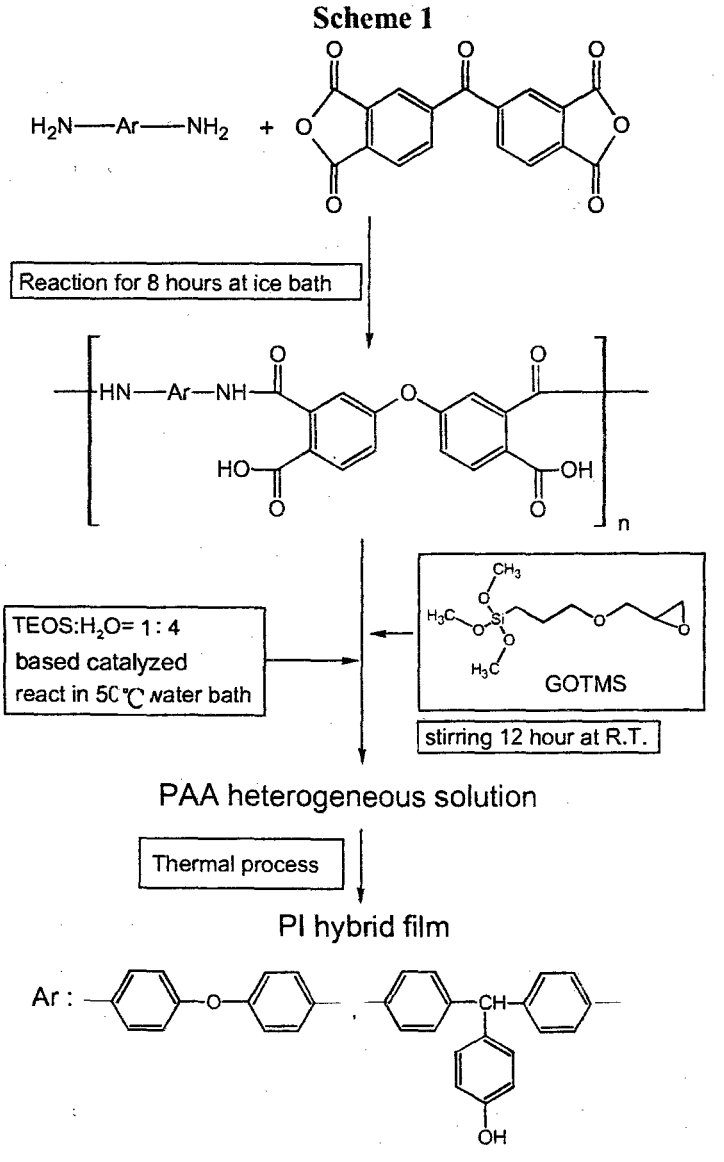
** To whom the correspondence should be addressed.

from Guangdong Daoning Chemical Co. Guangdong, China.. TEA was purchased from Chengdu Kelong Chemical Reagent Co. (Chengdu, China), N-methyl-2-pyrrolidinone (NMP, Qunli Chemical Reagents Corp., Shanghai, China) was purified by vacuum-distillation over phos-phorus pentoxide and stored over 4-Å molecular sieves.

## Preparation of PI/$SiO_2$ hybrid films

An equimolar amount of BTDA was added to the NMP solution of ODA (or ODA and DHTM) which was cooled with an ice-water base. The solid content of the solution was 15 wt%. The mixture was stirred at 0℃ for 12 h to get a viscous polyamic acid solution. TEOS, water and GOTMS, which is added by calculated contents in proportion as the diamine with basic condition, were added and further stirring for 6 h was needed to recover a homogeneous solution. The amount of TEOS is decided by the $SiO_2$ content desired in the hybrid. The mole ratio of water to TEOS was 4. The transparent solution was spun onto a glass plate and subsequently dried at 80℃ for 3 h in atmosphere. Then the film was dryed and imidized in a nitrogen atmosphere for 2 h at 130℃, 2 h at 220℃ and 1 h at 350℃. The reaction route is shown in Scheme 1.

**Scheme 1**



## 2.3 Measurements

Fourier transform infrared spectra (FTIR) of PI and hybrid films were recorded on a Nicolet 560 FTIR spectra photometer.The evaluatin process was researched by Optical Microscope(OM). The morphology of the cross section was investigated by scanning electron microscopy (SEM) using a Hitachi X-650 operating at 20 KV.

## 3 Results and discussion

### 3.1 TEOS pre-hydrolysis with basic catalyst

Because polyimide and polyimide/$SiO_2$ hybrid are insoluble in organic solvents, the sol-gel reaction is carried out in the NMP solution of polyamic acid (PAA). Choosing catalyst is very important to catalyze the hydrolysis and condensation of alkoxide in sol- gel process. The properties of PI/$SiO_2$ are decreased obviously because decomposition reaction of PAA will take place with acid catalyst。

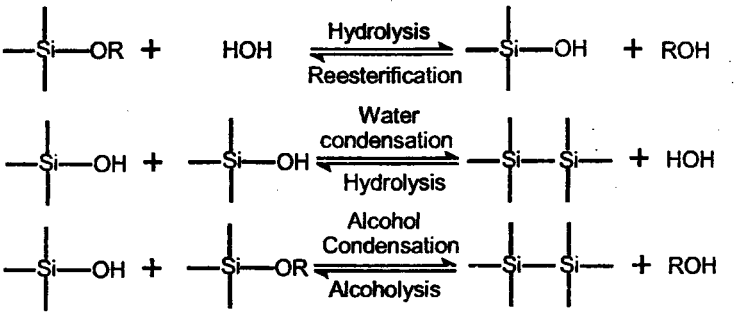



**fig.1 Hydrolysis and condensation process of TEOS**

A three-dimensional network is formed by the hydrolysis of tetraethoxysilane (TEOS), which is the most common ceramic precusor, and susequent polycondensation (fig.1). These reactions are concurrent and their relative rates are governed, for example, the mole ratio of water to alkoxide, type of catalyst and PH. Obvious differences in structures can be found depending on whether the processing is carried out under acidic or basic ccditions [6]. Based catalyst system tends to form high branched non-interpenetrating clusters. This structure of silica results that because under basic conditions, the hydrolysis is slower than either of the two condensation reactions[7]. The continuous-global structure is formed promptly with the hydrolysis of TEOS and the morphology agrees with the result of SEM.

### 3.2 FT-IR analysis

FTIR spectroscopy is used to study the chemical structure of the matrix polymer. Figure 2 shows the FTIR spectra of the polyimide, and polyimide/$SiO_2$ (with $SiO_2$ 7 wt % and 16 wt %). The characteristic absorption bands of the imide group near 1775,1772,1378,1119,and 721 $cm^{-1}$ and silica characteristic absorption bands near 830 and 450 $cm^{-1}$ were observed in the FTIR spectra of the cured samples. The characteristic absorption of the amide carbonyl at 1650 $cm^{-1}$ don't appear in the spectra, meaning that the imidization reaction was complete. The characteristic absorption bands of the hydrolysis product of TEOS were observed too. The spectrum showed absorption bands due to O-H bond stretching at 3485 $cm^{-1}$, Si-O bond warping at 450 $cm^{-1}$, and typical absorption bands for Si-O-Si network vibrations at 1100 and 830 $cm^{-1}$. The chemical structure of the matrix polymer was confirmed by FTIR spectroscopy.

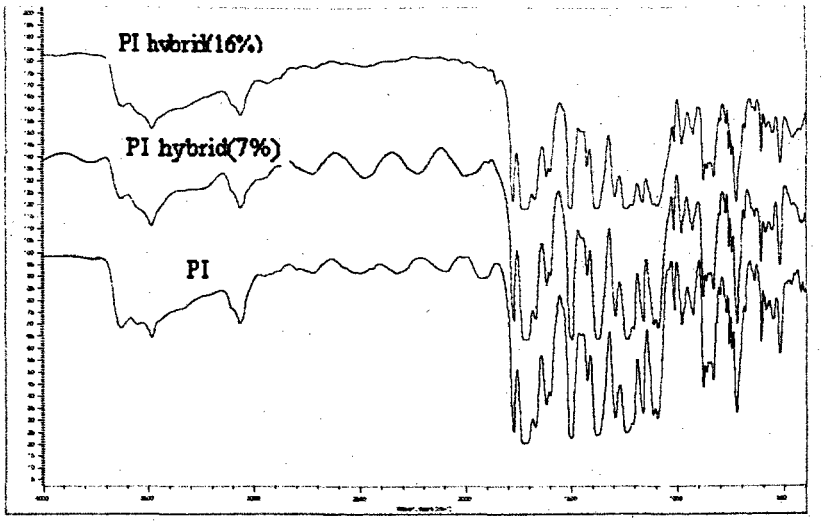



Fig2. FTIR spectra of PI, and PI/Silica hybrid films

### 3.3 Appearance of hybrid films

Two series of polyimide-silica hybrid films were prepared from DHTM-ODA-BTDA and ODA-BTDA with the same experimental conditions. The transparency of the films was compared (Table 1). Hybrid film 2 containing 11wt % silica becomes almost transparent, and the film containing 30 wt % silica is almost transparent when DHTM is used to replace 30 mol % ODA. This indicates that PI/$SiO_2$ hybrids with higher silica contents showing no obvious phase separation can be obtained due to the presence of phenolic hydroxyl groups.

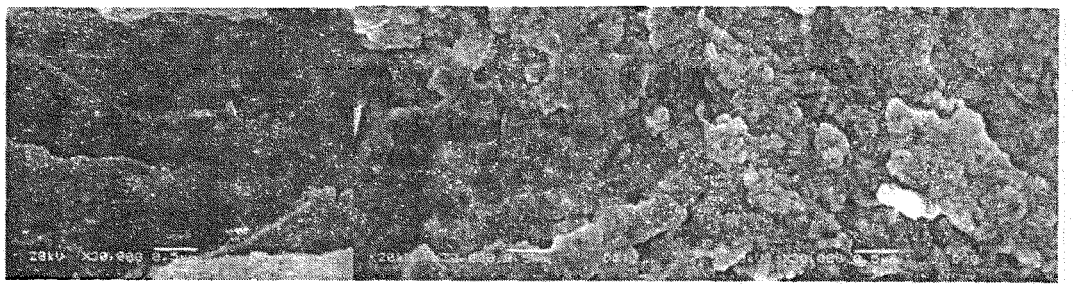
**Table 1 The Transparency of Hybrid Films ***

| | PI composition | Silica Content (wt %) | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | 0 | 3 | 7 | 11 | 16 | 22 | 30 |
| 1 | DHTM-ODA-BTDA | T | T | T | T | T | T | Ta |
| 2 | ODA-BTDA | T | T | T | Ta | Ta | Ta | O |

* T - transparent; Ta - almost transparent; O - opaque

### 3.4 SEM analysis

Scanning electron microscopy (SEM) is used to analyze the morphology of the hybrids. Figure 3 shows the SEM photographs of the fracture surface of the hybrid films containing 7-30 wt % silica. When the content of silica component is 7wt %, the diameter of silica is below 100nm(Figure 4a), which forms the nano-scale PI composite. The silica particles in the hybrid containing 11wt% silica have a size distribution ranging from 100-200nm (Figure 4b), which is linked obviously by PI. When the silica content reachs 30 wt % (Figure 4c), the diameter of silica is about 200 nm, which forms the continuous two phases structure with PI. This hybrid material with the connected globule structure is almost transparent because the silica particle aligned tightly.



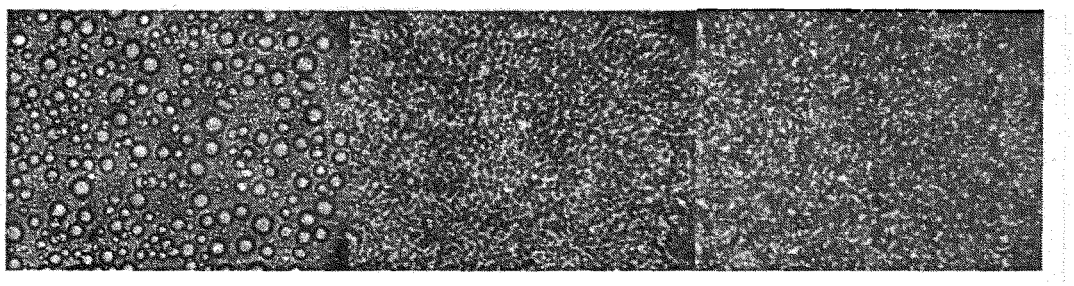
(a) (b) (c)

**Fig.3 SEM Photograph of PI/$SiO_2$ hybrid films**

DHTM:ODA: BTDA=0.3:0.7:1; silica: a - 7%, b - 11%, c - 30%

### 3.4 Phase separation process of hybrid

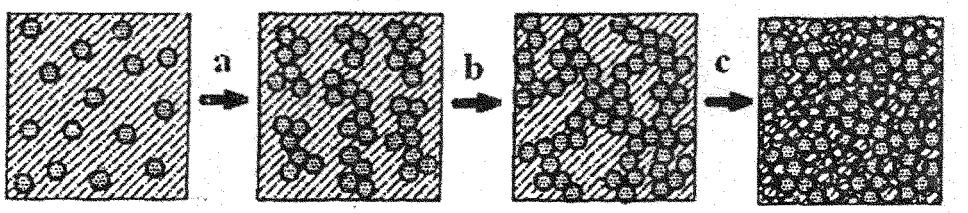
The evaluation process of phase separation is investigated by Optical Microscope (OM), which detects gel process of silica. In fig.4(a). it can be found that there have spherical or disk shaped particles, which is composed by residual solvent and silica/ cr silanol, when the hybrid film was heated in air atmosphere for 2h at 80℃. The continued structure was detected after dealing with 130℃ for 2h, which is the result of gel degree increased. The silica particles become continuous dispersion with increasing temperature, as shown fig.4(b). The silica particles in fig.4(c) connect more tightness each other than fig.4(b), and according with the result of SEM, when drying temperature of hybrid reaches 230℃.



a b c

Fig. 4 Photomicrographs of PI(DHTM/ODA/BTDA)/$SiO_2$ (50wt%) films (400×)

a: 80℃ b: 130℃ c: 230℃




a.Aggregation b.gelation c.aging (solvent removed)

**Fig. 5. Structural transformations in the sol-gel procedure to obtain homogeneous PI/silica hybrid**

In the procedure of preparing monolithic homogeneous and porous glasses with sol-gel process, it involves several stages, that is monomer aggregation, gelation, aging, drying, and sintering. [8] It is different to prepare PI/$SiO_2$ hybrids that the imidisation reaction occurs simultaneously, when the sol-gel reaction is taken place. In the sol-gel reaction, PI precursors with phenolic hydroxyl group plays an important role. It can induce phase separation and affect the phase separation

kinetics. It forms strong hydrogen bonds and chemical bonds with silanol. In the basic condition, the sol-gel process starts from liquid solution of alkoxide, water and NMP. A schematic picture of the method is given in fig.5. Aggregation, or clustering, and gelation, process by the hydrolysis of the alkoxide monomers and further polycondensation in liquid phase. The gelation is aging after residual solvent removed, and continuous-global structure was formed.

## Conclusions

A new series of copolyimide/silica hybrid materials was prepared. The interaction between polyimide and silica component create physical and chemical bonding between PI backbone and silica. With the catalyst of TEA, the morphology of silica is the continuous-global particle, which evaluation process is from disperse structure to the continuous structure.

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# 碱催化 TEOS 制备 PI/$SiO_2$ 杂化材料的研究*

秦家强，丁键，朱蓉琪，顾宜**
(高分子材料科学与工程国家重点实验室，高分子科学与工程学院,四川大学 610065
中国 成都)

本文在碱催化条件下采用溶胶-凝胶法制备了一系列的含有酚羟基的共聚型聚酰亚胺/二氧化硅杂化材料。采用 FTIR 表征了杂化材料的结构，用光学显微镜和扫描电镜观察了杂化材料的形貌及其变化过程。研究结果表明：聚酰亚胺和二氧化硅在偶联剂和酚羟基存在下产生了物理和化学交联。在三乙胺催化 TEOS 条件下，二氧化硅形成了颗粒大小基本一致的连续球分布的微观结构，其变化过程是先形成分散相结构再逐步转化为连续相结构。