Effect of Chemical Interaction on Morphology and Mechanical Properties of CPI-OH/SiO$_2$ Hybrid Films with Coupling Agent

Jiaqiang Qin,[1] Hui Zhao,[1] Rongqi Zhu,[1] Xinyuan Zhang,[2] Yi Gu[1]

[1]State key laboratory of Polymeric Materials Engineering, College of Polymer Science and Engineering, Sichuan University, Chengdu 610065, People's Republic of China
[2]Sichuan University Analytical Testing Center, Chengdu 610065, People's Republic of China

ABSTRACT: A novel hybrid film composed of copolyimide with hydroxyl group, silica and γ-glycidyloxypropyltrimethoxysilane (CPI-OH/SiO$_2$/GOTMS) was prepared by the sol–gel process based on hydrolyzed tetraethoxysilane (TEOS) under acidic condition. GOTMS, as the coupling agent, and hydroxyl group in PI chain were used to improve the compatibility between the PI and SiO$_2$. The components, morphologies, and mechanical properties of the hybrids were investigated by FTIR, UV–vis, SEM, stress–strain tests, and DMA. The results showed that SiO$_2$ particle size significantly decreased, fractured cross sections of hybrid were rougher, and the surfaces of spherical SiO$_2$ particles were more widely covered by PI component. The tensile mechanical properties of hybrids increased when adding GOTMS. The critical points of maximum tensile strength and elongation at break move from 11 to 16 wt % SiO$_2$ content. DMA results showed that the storage moduli of hybrids with GOTMS, when above 260°C, were obviously higher than those without GOTMS; the tan δ transition temperature of hybrid films went up from 317 to 337°C. It suggests that chemical interaction between CPI-OH and SiO$_2$ is formed and the PI molecular mobility is restricted by the chemical interaction. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 3530–3538, 2007

Key words: organic/inorganic hybrids; sol–gel process; coupling agent; morphology and properties

INTRODUCTION

Organic/inorganic hybrid materials have been widely studied recently because such novel materials can be fabricated through systematic design of the organic and inorganic structures.[1] Moreover, the hybrid materials combine the advantages and overcome the disadvantages of the two different materials. Sol–gel method is widely used to prepare the organic/inorganic hybrid materials.[2–8] This complex process consists of hydrolysis and condensation reactions of metal alkoxide. The final morphologies and properties of the inorganic gel and subsequent glass depend on many interdependent variables,[9–14] which include the type of alkoxide precursors,[4,10] the pH of the reaction medium,[11] nature of the solvent,[12] the ratio of water and catalyst to the alkoxide,[13] the reaction temperature and pressure, and the overall concentration of reactants.

The morphologies and physical properties of organic/inorganic hybrid materials have been studied in a number of polymeric systems,[2,14–16] such as

polyimide (PI),[2] poly(vinyl alcohol) (PVA),[14] poly(methyl methacrylate) (PMMA),[15] and epoxy.[16] Because of their excellent properties, aromatic PIs have been considered as suitable polymer matrix materials for advanced hybrid materials that have potential applications in the microelectronics and aircraft industries since the first report by Nandi et al.[2] Controlling the physical properties of the hybrid materials highly depends on the improvement of compatibility between the organic and the inorganic phases. One of the primary challenges for preparing the hybrid materials is the phase separation between organic and inorganic components.[5–7,17–23]

The previous attempts by Morikawa et al.[17] to prepare PI/SiO$_2$ hybrid materials via sol–gel reactions using TEOS and a polyamic acid resulted in a hybrid material with considerably decreased tensile strength and elongation at break. The results are attributed to poor interfacial bonding between the SiO$_2$ particles and the PI matrix, and inorganic phase separation characterized by particles at 3–7 μm diameter. Ahmad and Park[6,18] produced homogenous PI/SiO$_2$ hybrid materials by employing functionalized PIs with low molecular weight. However, the PI oligomer is a low molecular compound, which influenced the intrinsic properties of PI. Morikawa and

Correspondence to: Y. Gu (guyi@scu.edu.cn).

Beecroft[7,19] greatly improved the properties of the PI hybrids by introducing different types and concentrations of pendant alkoxysilanes along the PI backbone. These pendant groups react with silane alkoxide and form crosslinking points between PI matrix and silica particles, which increased the homogeneity of the PI/SiO₂ hybrid and produced a much finer dispersion of SiO₂ particles. Some studies demonstrated that silane coupling agents could be used to improve the compatibility of PI/SiO₂ hybrid materials.[20–22] Silane coupling agents could interact with PI and silica simultaneously, and minimized the phase separation of hybrid. However, in terms of controlling the morphology of hybrids and in a higher degree to keep the mechanical properties, as well as the relationship between morphology and mechanical properties of PI and SiO₂, it is not clear and open to further study.

In our previous work,[5,23] we found that the introduction of pendant hydroxyl groups on the PI backbone had positive affection on the interaction between organic and inorganic components. In this study, three hybrid films using hydrolyzed TEOS under acidic condition, polyamic acid with pendant hydroxyl groups, and silane coupling agent were prepared by sol–gel process. To improve hybrid compatibility and obtain the hybrid films with good integrated properties by controlling different interactions between PI and SiO₂ components, the effects of different interactions on the morphologies and mechanical properties of the hybrid films were discussed.

EXPERIMENTAL

Materials

4,4′-Diamino-4′-hydroxyltriiphenylmethane (DHTM) was synthesized in our laboratory.[5] 3,4,3′,4′-Benzophenone dianhydride (BTDA, ACROSOGANICS) was used after drying at 180°C under vacuum for 5 h. 4,4′-Oxydianilline (ODA, Shanghai research Institute of Synthetic Resins), tetraethoxysilane (TEOS, Shanghai Chemical Reagent), γ-glycidyloxypropyltrimethoxysilane (GOTMS, Guangdong Daoning Chemical, Guangdong, China) were used as received. N-methyl-2-pyrrolidinone (NMP, Qunli Chemical Reagents, Shanghai, China) was purified by vacuum-distillation over phosphorus pentoxide and stored over 4-Å molecular sieves.

Preparation of the CPI-OH/GOTMS/SiO₂ hybrids

BTDA was added to the NMP solution containing equimolar amount of diamine in ice bath. The solid content of the solution was 15 wt %. The mixture was stirred in ice bath for 12 h to get a viscous polyamic acid solution.

A mixed solution composed of a calculated quantity of TEOS and GOTMS (molar ratio, TEOS/GOTMS = 9/1) in NMP and deionized water with pH value 1.5 adjusted by oxalic acid was stirred at 50°C for 1.5 h, and was added into the polyamic acid solution by droplets under stirring. Then, the new mixture was stirred at room temperature for 6 h. A CPI-OH/SiO₂ hybrid film was obtained by spinning the transparent mixed solution onto a glass plate 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. This process is shown in Scheme 1. The component and abbreviation of samples are shown in Table I.

Characterization techniques

Fourier transformed infrared spectra (FTIR) of CPI-OH and hybrid films were recorded on a Nicolet 560 FTIR spectra photometer. The transmittance was tested by the UV–vis spectra with Perkin–Elmer Lambda 20 UV–vis spectrophotometer. The morphology was investigated by scanning electron microscopy (SEM) using a Hitachi X-650 operating at 20 kV. Atomic force microscopy (AFM) analysis of the surface of the hybrid film was carried out on a Digital Instruments Nano III atomic force microscope (USA) in air. The tensile strain–stress test of CPI-OH/SiO₂ hybrid films was determined on a XLL-50 tester at room temperature with a drawing rate of 5 mm/min. Thermogravimetric analysis (TGA, USA) was performed on a TGA-2950 under nitrogen at a heating rate of 10°C/min. Dynamic mechanical spectra were obtained with a TA Instruments DMA 983. The experiment was performed at a heating rate of 10°C/min from 150°C to maximal temperature of 400°C using frequency 10 Hz.

RESULTS AND DISCUSSION

FTIR characterization of the CPI-OH/SiO₂ hybrids

Figure 1 shows the FTIR spectra of the prepared BOD, BODT, and BODTG samples. The characteristic absorption bands of the imido groups were observed at 1778, 1724, 1378, and 723 cm^{-1} in FTIR spectra. The characteristic absorption band of the amide carbonyl round 1650–1660 cm^{-1} does not appear in the spectra, suggesting a higher imidization degree of PI. The major difference between the BOD and BODT samples is the absorption band at 1000–1100 cm^{-1}. The characteristic absorption band of Si—O—Si asymmetric stretching at 1093 cm^{-12} becomes stronger and broader with addition of SiO₂. The characteristic absorption band of epoxy group in GOTMS
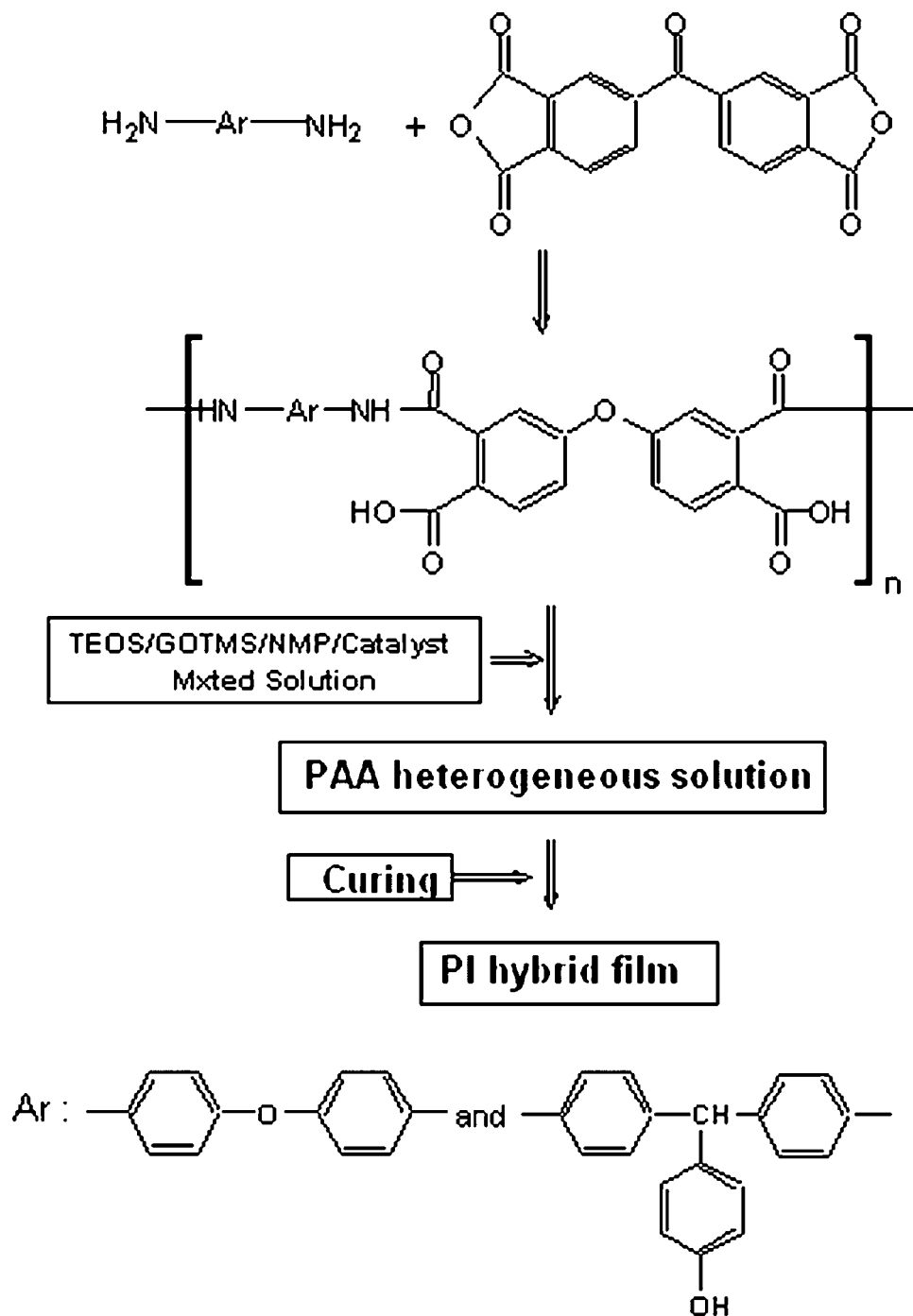
Scheme 1

TABLE I
The Formulation of the PI/SiO$_2$ Hybrids and Abbreviation

Dianhydride	Diamine	GOTMS	SiO$_2$ content (wt %)	Abbreviation
BTDA	ODA/DHTM (4 : 1)	Yes	X	BODTGX
BTDA	ODA/DHTM (4 : 1)	No	X	BODTX
BTDA	ODA	No	X	BOTX
BTDA	ODA/DHTM (4 : 1)	No	0	BOD

X is SiO$_2$ content, such as BODTG16 denote the SiO$_2$ content is 16 wt %.
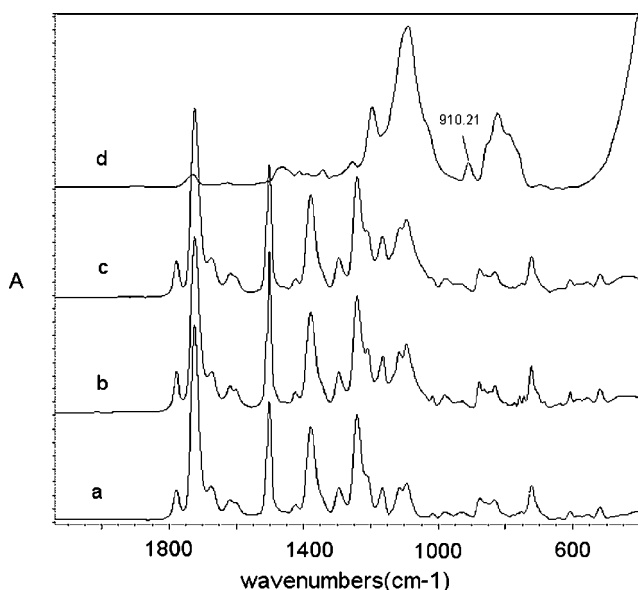
Figure 1 FTIR spectra of the CPI-OH, CPI-OH/SiO₂ hybrids and GOTMS (a) pure CPI-OH; (b) without GOTMS(7 wt % SiO₂); (c) with TEOS/GOTMS = 9/1(11 wt % SiO₂); (d) GOTMS.

Figure 2 UV–vis spectra of the BOD, BODT, and BODTG samples (11 wt % SiO₂).

is shown at 910 cm^{-1} in Figure 1(d). However, this characteristic absorption band in BODTG sample disappears in Figure 1(c), which indicates that the chemical reaction linking organic and inorganic takes place through the ring-opening reaction of epoxy group with hydroxyl group in DHTM.

Morphology of the CPI-OH/GOTMS/SiO₂ hybrids

The appearances of the PI/SiO₂ hybrid films with different components are listed in Table II. It can be seen that the transparency of the PI/SiO₂ hybrid films decreases with the SiO₂ contents increasing. It also shows that the transparency of the PI/SiO₂ hybrid films is greatly improved by the hydroxyl group and GOTMS. The hybrid films of BOT sample become opaque when the SiO₂ content is more than 8 wt %.[20] However, this critical point moves to 11 and 16 wt % by the addition of hydroxyl group and GOTMS, respectively. When the silica content is 11 wt %, the effects of hydroxyl group and GOTMS on the transparency is investigated by UV–vis spectra

of BOD, BODT, and BODTG samples, shown in Figure 2. The transparency of the hybrid film increases evidently, as a result of the addition of the coupling agent. In Figure 2, it can be seen that at the wavelength of 500 nm, transmittance of BODTG sample is 50.5%; however, transmittance of the sample without GOTMS is 13.6%, which has sufficiently indicated the evident difference of the transparency.

SEM is used to study the different morphologies of the hybrid films. The tensile fractured cross sections of BODT and BODTG samples observed by SEM are shown in Figure 3. The size of SiO₂ particles in BODTG samples increase when increasing SiO₂ content. The SiO₂ particle size is below 100 nm when the SiO₂ content is 7 wt % [Fig. 3(b)]. An increase in the SiO₂ content to 16 and to 30 wt %, as shown in Figure 3(d,f), leads to a larger SiO₂ particle size, whose average size is 450 nm and 1.3 μm, respectively. Figure 3(a,c,e) show that average size of SiO₂ particles in BODTG sample is from 150 nm to 1.8 μm, while the SiO₂ content is from 7 to 30 wt %. By comparing BODT with BODTG samples, it shows that the SiO₂ particle size in the hybrids decreases with the addition of GOTMS. The indistinct interphase of BODTG sample can also be observed, demonstrating that there is an interphase region in the hybrid film.

Figure 4 shows the scanning electron microphotograph from the tensile fractured cross sections of BOT sample with 16 wt % SiO₂, whose SiO₂ particle size is bigger than that in Figure 3(c,d) at the same silica content. Comparing Figure 3(c,d) and Figure 4, an obvious difference is observed in the interfacial region between PI and SiO₂. Figure 4 shows that there is a fractured cross section with lots of spherical SiO₂ particles and holes, but no interfacial region between PI and SiO₂. It also shows that the surface of SiO₂ particles is very smooth and separated from PI matrix phase. However, the fractured cross sec-
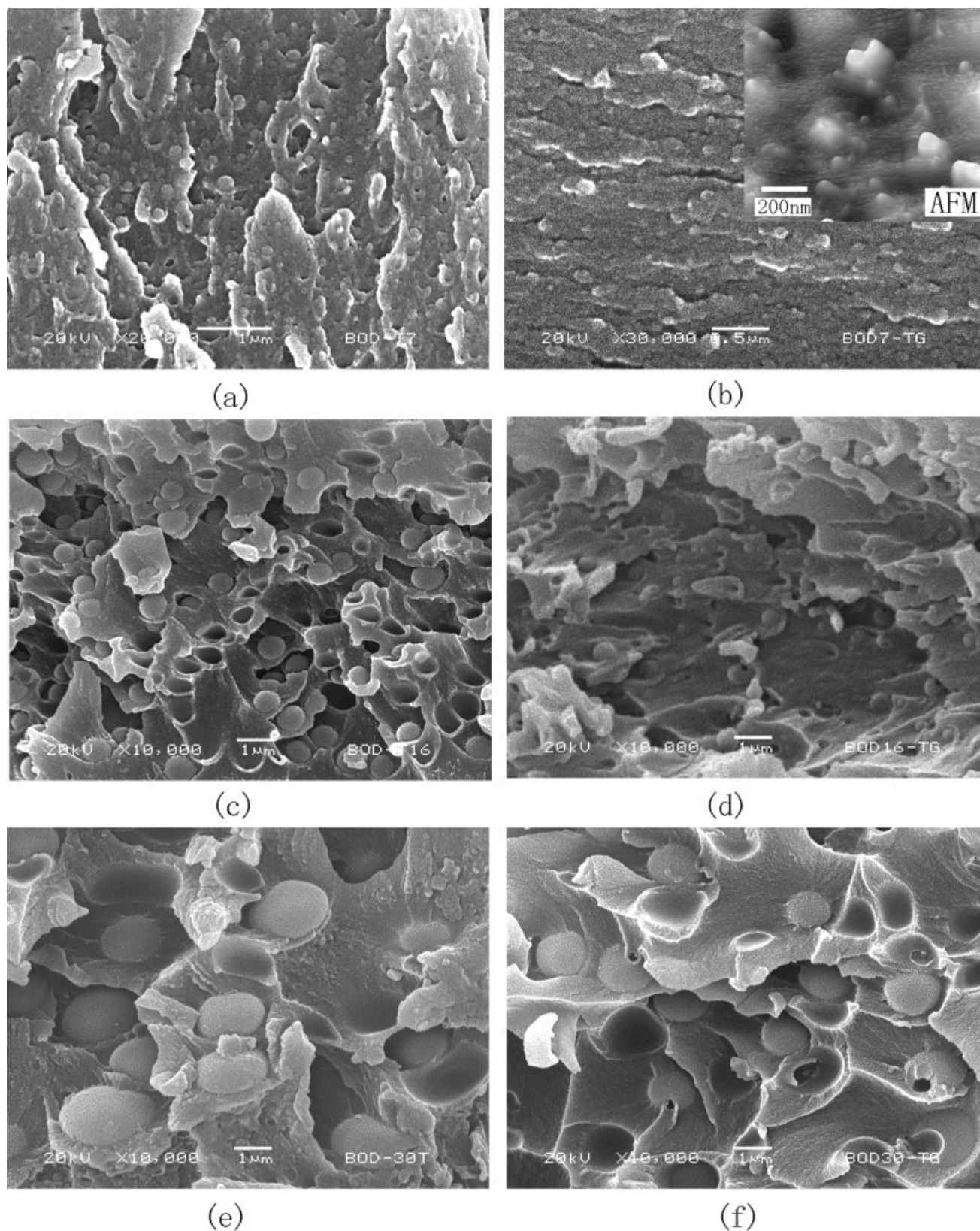
TABLE II
The Transparency of Hybrid Films

Sample	Silica content (wt %)						
	0	3	7	11	16	22	30
BOT	T	T	T	O	O	O	O
BODT	T	T	T	Ta	O	O	O
BODTG	T	T	T	T	Ta	O	O

T, transparent; Ta, almost transparent; O, opaque.

Figure 3 Scanning electron microphotographs of the BODT and BODTG samples. SiO$_2$ content: (a) (b) 7 wt %; (c, d) 16 wt %; (e, f) 30 wt % (a, c, e): BODT; (b, d, f): BODTG.
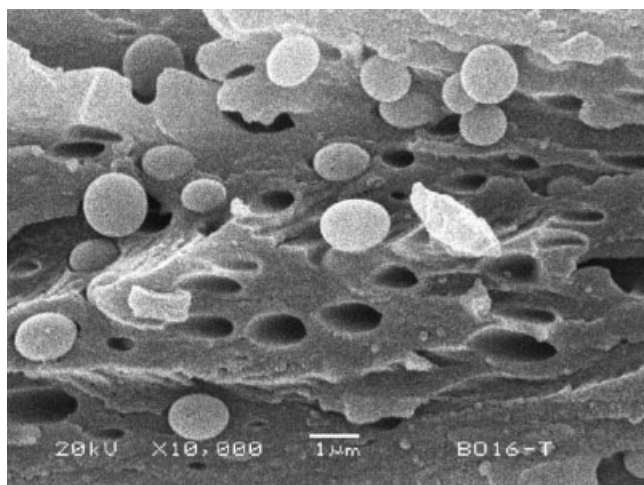
Figure 4 Scanning electron microphotographs of the BOT sample (16 wt % SiO₂).

tions in Figure 3(c,d) are very rough and contain lots of spherical SiO₂ particles in the PI matrix. It should be noted that the surfaces of these particles covered by PI component are rough. This indicates that the chemical bonds between hydroxyl groups of PI and coupling agent GOTMS can remarkably improve the compatibility between the PI and SiO₂.

Tensile mechanical properties of the CPI-OH/GOTMS/SiO₂ hybrids

Influence of the SiO₂ contents and GOTMS on the tensile mechanical properties of the hybrid films is shown in Figure 5. It can be seen that, below 16 wt %, both the tensile strength and the elongation at break of BODTG increase with increasing SiO₂ content. However, this critical point is only 11 wt % for BODT. When the silica content exceeds 16%, both

the tensile strength and the elongation at break decrease. Most data of the tensile strength and elongation at break are higher in BODTG than those without GOTMS. These can be explained by the chemical reaction between epoxy group and the hydroxyl group of CPI-OH, which strengthened interaction between PI matrix and SiO₂ particle and reduced SiO₂ particle size, shown in Scheme 2. GOTMS, as the coupling agent, plays the role of joint: on one side, it hydrolyzes and forms silanol groups that can condense with the hydrolyzed products of TEOS; on the other side, chemical reaction takes place between epoxy group of GOTMS and hydroxyl group of PI (Scheme 2, BODTG). Without GOTMS, only a weak interfacial adhesion derived from physical interaction could be formed (Scheme 2, BODT). These are consistent with the SEM results.

Figure 5 shows the tensile strength (1) and elongation at break (2) of BODT and BODTG. The tensile moduli of BODT and BODTG detected by the tensile stress–strain test are shown in Figure 6(a,b). The moduli of two samples increase when increasing the SiO₂ contents. At low SiO₂ contents (<7 wt %), the moduli of BODTG are bigger than that of BODT. However, it can be obviously seen from Figure 6 that, when increasing silica content, the moduli of BODT increase with linear trend, whereas the moduli of BODTG have no such linear increasing relationship, and the moduli of BODTG sample are lower than that of BODT sample at high SiO₂ contents. This result may be attributed to the excessive GOTMS in the hybrid films with higher SiO₂ content. Because the GOTMS content increased when increasing the SiO₂ content, the molar ratio of GOTMS/DHTM is unstable and GOTMS content is excessive. To make sure that such a phenomenon is caused by the excessive GOTMS, the tensile modulus experiments of hybrid with a stable molar ratio of
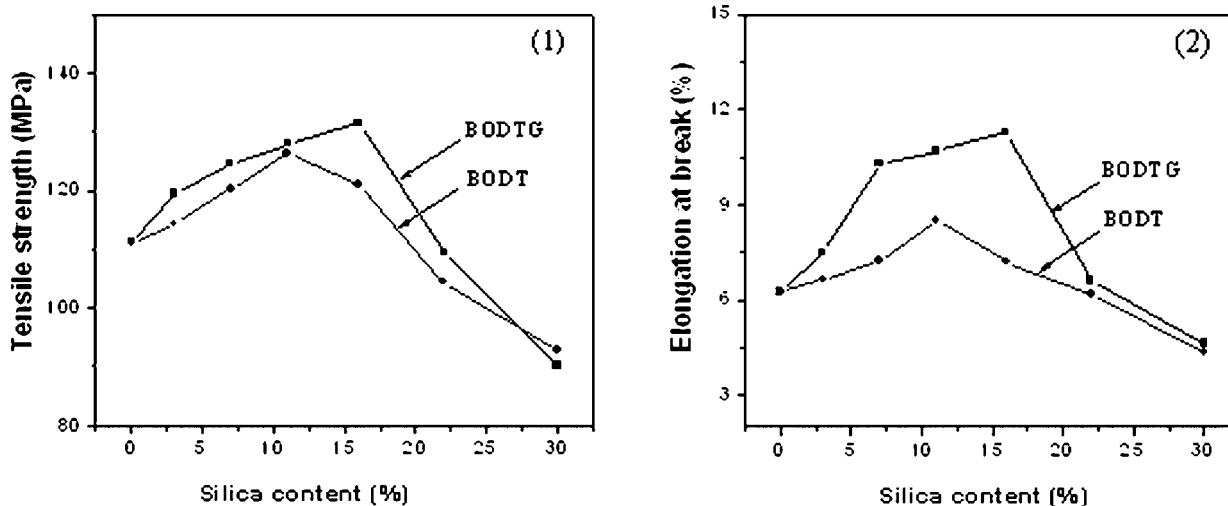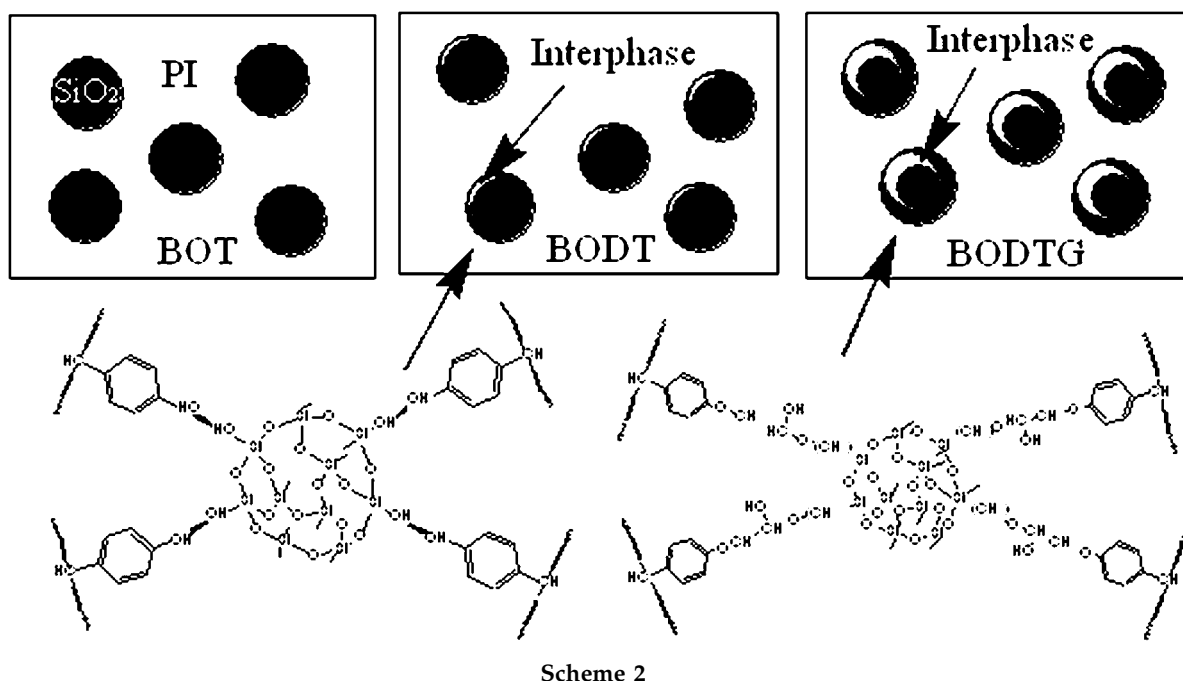

Figure 5 The tensile strength (1) and elongation at break (2) of BODT and BODTG.

Scheme 2

GOTMS/DHTM were carried out. The result in Figure 6(c) shows that the moduli of BODTG have linear trend under the stable mole ratio of GOTMS/DHTM and its slope is larger than the sample without GOTMS. It suggests clearly that the excessive GOTMS will lower the modulus of PI/SiO$_2$ hybrid films relatively.

Thermal and dynamic thermal mechanical properties of hybrid films

The thermogravimetric curves of CPI-OH/SiO$_2$ hybrid films are shown in Figure 7. The result shows that the CPI-OH/SiO$_2$ hybrid films have excellent

thermal stability and the thermal stability of hybrid without GOTMS is lower than that with GOTMS. It suggests that the thermal stability increases because the PI and SiO$_2$ components are linked by the stable chemical interaction.

To further understand whether the chemical bond between the PI matrix and SiO$_2$ is formed, dynamic mechanical experiments were performed. The results are shown in Figure 8. In Figure 8(a), a plateau region with a magnitude of $\sim10^9$ Pa is observed at the temperature ranged from 150 to 260°C. Above 260°C, the storage modulus decreases sharply until it reaches a minimum amount at the order of 10^8 Pa. Observations of two stages at different temperatures deserve an attention. First, the storage modulus (E')
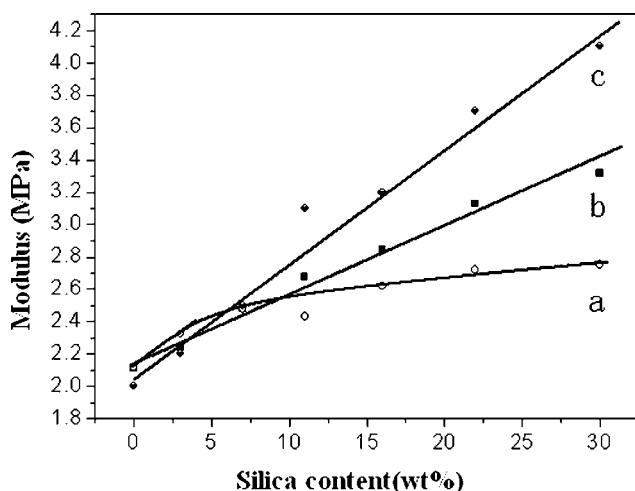

Figure 6 The moduli of the BODT and BODTG. (a) With TEOS/GOTMS = 9/1; (b) without GOTMS; (c) with 10% mol GOTMS to DHTM).
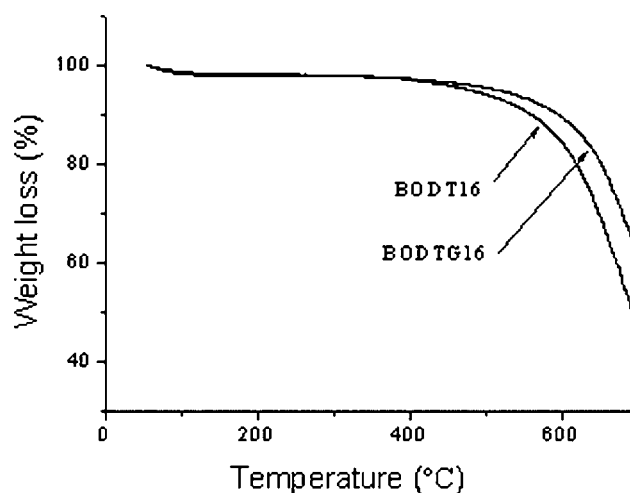

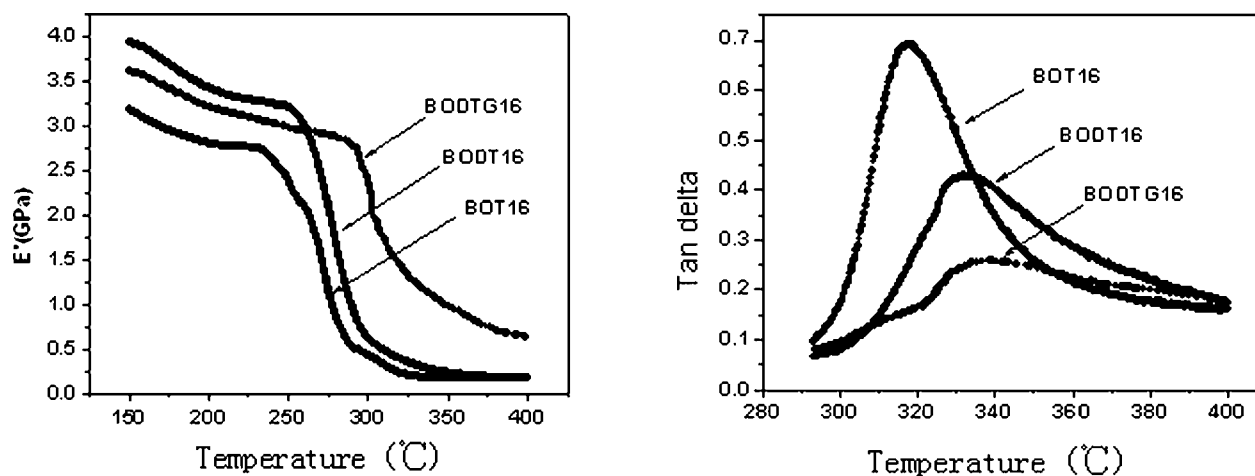**Figure 7** TGA curves of BODT and BODTG.

Figure 8 Storage modulus E' (a) and tan δ (b) versus temperature curves of three kinds of PI/SiO$_2$ hybrid films.

of BODTG16 is smaller than those without GOTMS below 260°C, which had been explained by the tensile modulus of strain–stress test. Second, E' shows an opposite result from 260 to 400°C, which indicates the PI molecular with GOTMS were restrained more than two hybrids without GOTMS at high temperature. The excessive GOTMS in hybrid films make the hybrid modulus lower at low temperature; but the modulus of BODTG16 are higher than those without GOTMS at high temperature, which shows the interfacial strength of BODTG16 is bigger than that without GOTMS. This result further suggests that, in the samples with GOTMS, chemical interactions between the PI molecular chain and SiO$_2$ (Scheme 2, BODTG) exist through the coupling agent. It also demonstrated that the hydrogen bond (Scheme 2, BODT) is a weak physical bond, therefore leading to an easier molecular mobility.

To obtain further insight into the transition behavior of these films, the tan δ spectra were examined [Fig. 8(b)]. A single maximum peak is observed in these samples. The maximum temperature increases from 317 to 337°C as interaction between PI matrix and SiO$_2$ becomes stronger. Specifically, for the sample with weak interaction (BOT), the maximum temperature is 317°C. This is about 20°C weaker than the transition temperature of BODTG with chemical interaction. Another important point is that the overall intensity of the tan δ maximum decreases with increasing interfacial adhesion, similar to the Huang's result,[24] which clearly indicates interaction intensity between organic and inorganic affect the PI mobility. The stronger the intensity is, the more the PI molecular is restricted.

CONCLUSIONS

Three kinds of PI/SiO$_2$ hybrid films were prepared successfully by sol–gel process. Morphologies and mechanical properties of hybrid films were studied by introducing the GOTMS and hydroxyl group in PI chain, which were measured by SEM and mechanical property tests. The interaction between PI and SiO$_2$ components, which includes physical and chemical interaction, affects the SiO$_2$ particle size and interphase, confirmed by UV–vis and scanning electron microphotographs. The transparency of the hybrid films with chemical interaction between PI and SiO$_2$ components is better than that of those with physical interaction. The results from scanning electron microphotographs show that the chemical interaction increases the interphase and the SiO$_2$ particle size decreases, which suggests that the morphology of hybrid films can be controlled by changing the interaction between PI and SiO$_2$ components. The tensile strength and elongation at break of hybrid films with chemical interaction are larger than those of with physical interaction. The critical point of maximum tensile strength and elongation at break moves from 11 to 16 wt %. The excessive GOTMS could decrease the modulus of hybrid films relatively. TGA and the thermal mechanical test results of hybrid films further reveal that the modulus and thermal property were affected by the interaction types between the PI and SiO$_2$. On the whole, the technique of introducing chemical interaction between PI and SiO$_2$ is an important and useful method to improve the properties of hybrid films.

References

1. Eckert, H.; Ward, M. Special Issue on Organic–Inorganic Hybrid Nanocomposites on Functional Materials. Chem Mater 2001, 13, 3059.

2. Nandi, M.; Conklin, J. A.; Salvati, L. J.; Sen, A. Chem Mater 1991, 3, 201.
3. Ahmad, Z.; Mark, J. E. Chem Mater 2001, 13, 3320.
4. Chiang, P.; Whang, W. Polymer 2003, 44, 2249.
5. Huang, Y.; Qin, J.; Gu, Y. J Appl Polym Sci 2004, 93, 1198.
6. Al-Kandary, Sh.; Ali, A. A. M.; Ahmad, Z. J Appl Polym Sci 2005, 98, 2521.
7. Morikawa, A.; Iyoku, Y.; Kakimoto, M.; Imai, Y. J Mater Chem 1992, 2, 679.
8. Zhu, Z.; Cao, J.; Shang, X.; Lu, Q. Adv Mater 2000, 12, 1055.
9. Iler, P. K. The chemistry of Silica; Wiley: New York, 1979.
10. Kripotou, S.; Pissis, P.; Bershtein, V. A.; Sysel, P.; Hobzova, R. Polymer 2003, 44, 2781.
11. Yamame, M.; Inoue, S.; Yasumoori, A. J Non Cryst Solids 1984, 63, 13.
12. Sviderskii, V. A.; Voronkov, M. G.; Klimenko, V. S.; Klimenko, S. V. Russ J Appl Chem 1996, 69, 842.
13. Vollet, D. R.; Donatti, D. A.; Ruiz, A. I.; de Castro, W. C. Phys Rev B: Solid State 2003, 67, 184207.
14. Kim, D. S.; Park, H. B.; Rhim, J. W.; Lee, Y. M. J Membr Sci 2004, 240, 37.
15. Yeh, J.; Weng, C.; Huang, K.; Lin, C. J Appl Polym Sci 2006, 102, 1151.
16. Liu, Y.; Wu, C.; Chiu, Y.; Ho, W. J Polym Sci Part A: Polym Chem 2003, 41, 2354.
17. Morikawa, A.; Iyoku, Y.; Kakimoto, M.; Imai, Y. Polym J 1992, 24, 107.
18. Park, C.; Smith, J. G., Jr.; Connell, J.; Lowther, S. E.; Working, D. C.; Siochi, E. J. Polymer 2005, 46, 9694.
19. Beecroft, L. L.; Johnen, N. A.; Ober, C. K. Polym Adv Technol 1997, 8, 289.
20. Shang, X.; Zhu, Z.; Yin, J.; Ma, X. Chem Mater 2002, 14, 71.
21. Kioul, A.; Mascia, L. J Non Cryst Solids 1994, 175, 169.
22. Schrotter, J. C.; Smaihi, M.; Guizard, C. J Appl Polym Sci 1996, 61, 2137.
23. Huang, Y.; Gu, Y. J Appl Polym Sci 2003, 88, 2210.
24. Huang, H. H.; Wilkes, G. L. Polymer 1989, 30, 2001.