

Microstructure and Properties of New Polyimide/Polysiloxane Composite Films

Changli Lü,^{1,2} Zhen Wang,¹ Feng Liu,¹ Jingling Yan,¹ Lianxun Gao¹

¹State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, 130022, People's Republic of China

²Polymer Engineering Laboratory, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, 130022, People's Republic of China

Received 24 February 2005; accepted 24 June 2005

DOI 10.1002/app.22532

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A series of novel polyimide/polydiphenylsiloxane (PI/PDDS) composite films with different contents of DDS were prepared using sol-gel method. The non-crosslinked PI-DDS and crosslinked PIS-DDS were synthesized through cohydrolysis and condensation between DDS and polyamic acid (PAA) or aminopropyltriethoxysilane(APTES)-terminated polyamic acid (PAAS). All the composite films have high thermal stability near pure PI. Field emission scanning electron microscopy (FE-SEM) study shows that the polysiloxane from hydrolyzed DDS well dispersed in polyimide matrix, without macroscopic separation for the composite films with low content of DDS, while large domain of polysiloxane was formed in films with high DDS content. The microstructure of composite

films is in accordance with the transparency of corresponding films. X-ray study shows the PDDS is amorphous in PI matrix. The introduction of DDS into PI can improve the elongation at break and at the same time, the composite films still remained with higher modulus and tensile strength. The density and water absorption of the composite films decreased with the increasing DDS content. The composite films with DDS content below 10 wt % exhibit good solvent resistance. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 124–132, 2006

Key words: polyimide composites; diphenyldimethoxysilane; polysiloxane; properties; microstructure

INTRODUCTION

Polyimide as a high-performance polymer material has been widely used in industrial fields such as microelectronics, aerospace, and other advanced technologies because of their excellent mechanical, thermal, and dielectric properties as well as good resistance to organic solvents.^{1–4} To further improve the properties of PI materials, many polyimide composites, including silica/PI,^{5–8} TiO₂/PI,^{9,10} PI/layered silicates,^{11,12} have been developed. In particular, polysiloxane, as hybrid components, was incorporated into polyimide to fabricate PI based hybrid composites in recent years. For example, A series of poly(silsesquioxane) (PSSQ)/PI hybrid materials have been prepared from corresponding precursors such as methyltrimethoxysilane (MTMS),¹³ triethoxyvinylsilane (TEVS),¹⁴ phenyltrimethoxysilane (PTS),¹⁵ etc. These materials ex-

hibited improved thermal, mechanical, and dielectric properties. In addition, the dimethoxydimethylsilane (DMDMS), as a building block, also was introduced into PI to synthesize PI-PDMS block polymers or composite materials in which microphase separation was observed.¹⁶

One promising and general method is the sol-gel technique for preparing afore-mentioned polymer hybrids. This process consists of the hydrolysis of a metal alkoxide and polycondensation of the hydrolysis products, which allows one to easily control the composite's microstructure and interfacial properties, because the interfacial force between two phases plays an important effect on the properties of composite materials.^{17–19} The formation of the hydrogen bonding or covalent bonding between polymer and filler phase can prevent phase separation of composites and the transparent hybrid materials can be also prepared.^{20,21}

The poly(dialkylsiloxane), especially, poly(dimethylsiloxane) has been incorporated into PI by sol-gel method and the structure and properties of the resulting composites have been widely studied.^{16,22–24} However, the synthesis and property of poly(diarylsiloxane)/PI composites have not been reported up to now. These composites may exhibit excellent mechanical and thermal properties due to the introduction of diarylsiloxane. In this article, we incorporated differ-

Correspondence to: L. Gao (lxgao@ciac.jl.cn).

Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 50333030.

Contract grant sponsor: China Postdoctoral Science Foundation and Young Science Foundation of NE Normal University; contract grant number: 111494015.

ent content of DDS as precursors into the PI to prepare a series of PI composites by sol-gel process. The pure PAA and PAAS were selected as PI matrix. The mechanical, thermal, optical properties and microstructure for PI based composites with covalent and non-covalent bonds were studied in detail.

EXPERIMENTAL

Materials

Pyromellitic dianhydride (PMDA, 99%) and 4,4'-oxydianiline (ODA, 99%) were purchased from Shanghai Chemical Reagents Company and were purified by sublimation under vacuum. Diphenyldimethoxysilane (DDS, 99%, Dalian Yuanyong Organosilicon Plant, Dalian, China) and 3-aminopropyltriethoxysilane (APTES, 99%, Nanjing Shuguang Chemical Group Co., Ltd., Njing, China) were used as received. *N,N*-Dimethylacetamide (DMAc, 99.5%) was purified by distillation over phosphorus pentoxide and stored over 4 Å molecular sieves.

Synthesis of PAA and PAAS

PAA from PMDA and ODA was synthesized by one-step process in DMAc. ODA (4.00 g, 20 mmol) was dissolved in the dry DMAc with stirring and PMDA (4.36 g, 20 mmol) was added in ODA solution at room temperature. After the mixture of reaction was stirred for 24 h, a 10 wt % solution of PAA in DMAc was obtained.

PAAS with theoretical molecular weight of 5000 and 10,000 g mol^{-1} were prepared from PMDA, ODA, and APTES with the molar ratio of 1.09:1:0.18 and 1:0.959:0.082, respectively. Firstly, PMDA was added into an ODA solution in DMAc with stirring. The viscosity of mixture solution increased quickly after 0.5 h. Then, the APTES was added into the earlier mentioned reaction solution after the next 1.5 h, and the reaction was continued for 24 h at room temperature. The solid content of PAAS solution is 12 wt %.

Preparation of PI/polysiloxane composite films

DDS (19.55 g, 0.08 mol) and water (2.88 g, 0.16 mol) was added into DMAc solvent (19.33 g) and the mixture was continued for 24 h to make a clear homogeneous solution with 50 wt % of solid content. Then, the calculated quantity of DDS solutions were added to the PAA or PAAS solution and the mixture was stirred for 24 h. The composite films were prepared by casting the above solution onto glass plates. The films were cured on a hot plate at 60°C for 12 h and then a step thermal imidization process (0.5 h each at 100, 150, 200, 250°C, and finally at 300°C for 2 h) was carried out. The composite films from PAA-DDS and

PAAS-DDS, with theoretical molecular weight of 10,000 and 5000 g mol^{-1} are encoded as PI-*x*-DDS, 10,000-PIS-*x*-DDS, and 5000-PIS-*x*-DDS, respectively, where *x* is the weight percentage of DDS to the initial reaction mixtures PAA/DDS or PIS/DDS.

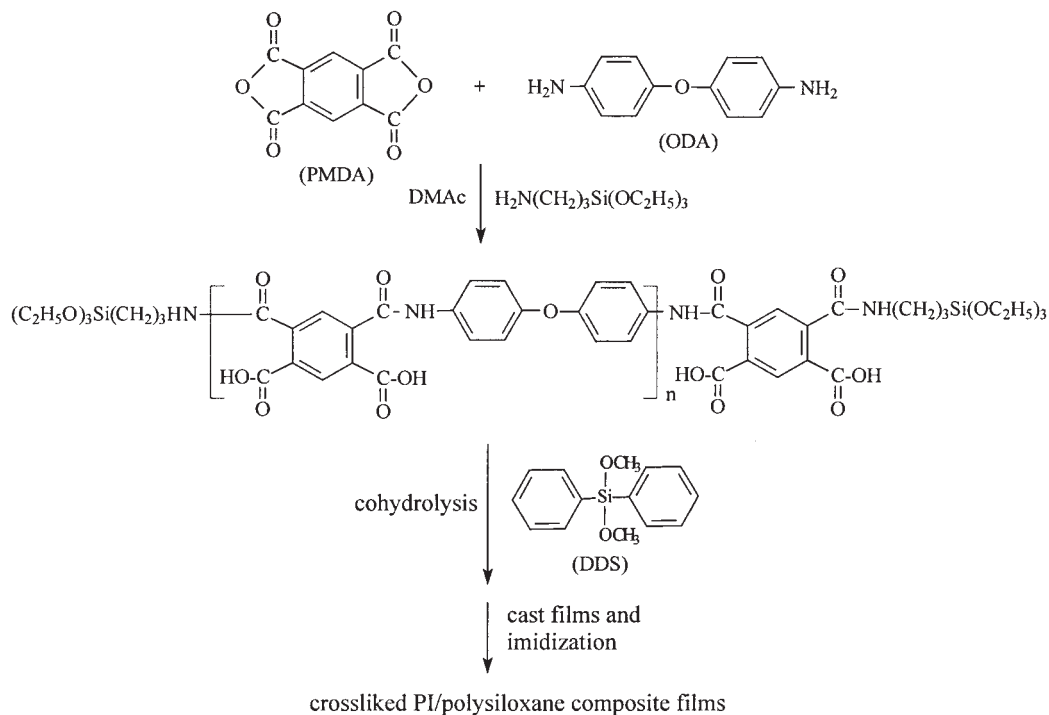
Characterization

FTIR spectra were recorded on a Nicolet AVATAR360 FTIR spectrometer. UV-vis spectra of the composite films with the thickness of about 60 μm were recorded on a Shimadzu UV3100 UV-Vis-NIR spectrometer, air as reference. Thermogravimetric analyses (TGA) were obtained at a heating rate of 20°C/min in nitrogen, with a Perkin-Elmer TGA-2 thermogravimetric analyzer. The glass transition temperature of composite films was measured on a dynamic mechanical thermal analyzer (DMTA) used film samples (length: 10 mm). The run conditions were conducted at a frequency of 1 Hz and a heating rate of 3°C/min from 40 to 500°C in a tensile mode (strain: 0.1%, initial static force: 0.2 N, static > dynamic force by 10.0%, minimum static force: 0.01 N, maximum autotension displacement: 3.0 mm). The tensile measurements were carried out on an Instron model 1122 at room temperature. The wide-angle X-ray diffraction (WAXD) measurements were undertaken on a Rigaku max 2500 V PC X-ray diffractometer with Cu K α radiation (40 kV, 200 mA) with a scanning rate of 2°/min from 5 to 50°. The morphologies of fractured surfaces of composite films were studied with an XL-30 ESEM FEG Scanning Electron Microscope (FEI COMPANY). ^{29}Si -NMR spectra for samples dissolved in chloroform-*d* were obtained through a Bruker APC 300 NMR Spectrometer. Water absorption experiments were performed on the four pieces of film samples with masses ranging from 100 to 150 mg and the films were heated at 180°C for 1 h to remove the water to get the initial weight of the film before soaking in water. The earlier treated film samples were immersed in deionized water at 25°C, and water absorption equilibrium was considered to be attained after 10 days. The weight gains were measured as percent of the water absorption. The solvent resistance of composite films in toluene, methanol, chloroform, DMAc, and *N*-methyl-2-pyrrolidone (NMP) was tested by immersing the composite films, which were dried at 180°C for 1 h, into the corresponding solvent. After 30 days, the weight decrease percent of films relative to films before immersion was determined.

RESULTS AND DISCUSSION

Preparation of polyimide/polysiloxane composite films

The hydrolyzed DDS was introduced into PAA and PAAS with controlled molecular weight M_n of 5000



Scheme 1 Synthesis process of crosslinked polyimide/polysiloxane composite films.

and $10,000 \text{ g mol}^{-1}$ to synthesize a series of PI/polysiloxane composite films with noncrosslinked and crosslinked networks. The preparation route of crosslinked polyimide/polysiloxane composite films (PIS-DDS) is shown in Scheme 1. In the sol-gel process, the acid groups of PAA, rather than an additional acid or base, were used as the catalyst to carry out self-catalyzed condensation reaction of alkoxy groups. We can successfully prepare self-standing composite films of noncrosslinked PI-DDS, with DDS content up to 50 wt %. However, for the crosslinked 5000-PIS-DDS and 10,000-PIS-DDS composite films, the DDS content in the obtained films is lower than that of noncrosslinked PI-DDS films and can only reach to 30 and 40 wt %, respectively. When the DDS content in composite films is above the upper limit, the resultant films with good mechanical properties cannot be obtained. In addition, the crosslinked 5000-PIS-DDS also can not easily be removed from the glass plate because of the strong interaction between the composite films and glass substrate. All the composite films are transparent to the eye, in which the DDS content is lower than 20 wt %, and opaque while the DDS content is beyond 30 wt % (these results will be further discussed later).

FTIR analysis

FTIR was used to confirm the conversion of polyamic acid to polyimide and to assess the chemical changes

in composite films. Figures 1 and 2 show the FTIR spectra of the PI-DDS and 5000-PIS-DDS composite films. All the composite films exhibit the characteristic absorption peaks of imide groups at near 1776 ($\text{C}=\text{O}$ symmetric stretching), 1712 ($\text{C}=\text{O}$ asymmetric stretching), 1373 ($\text{C}-\text{N}$ stretching), 1113 and 721 cm^{-1} . The characteristic absorption peak of polyamic acid at 1650 cm^{-1} disappeared, indicating that the imidization reaction was complete. The absorption peaks at 1409–1427 and 692 cm^{-1} were assigned to the

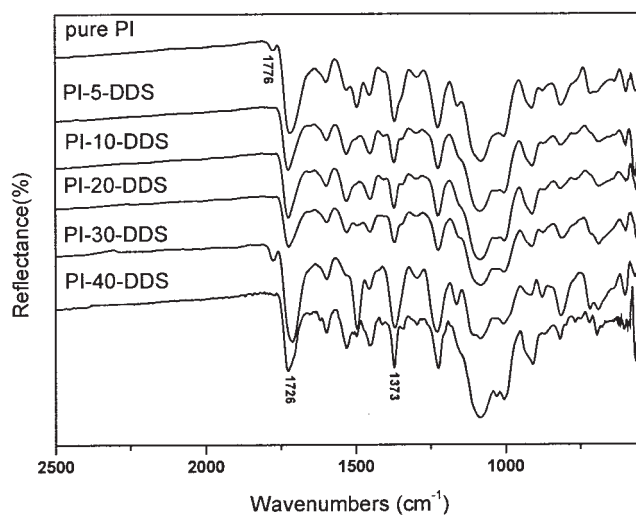


Figure 1 FTIR spectra of PI-DDS composite films.

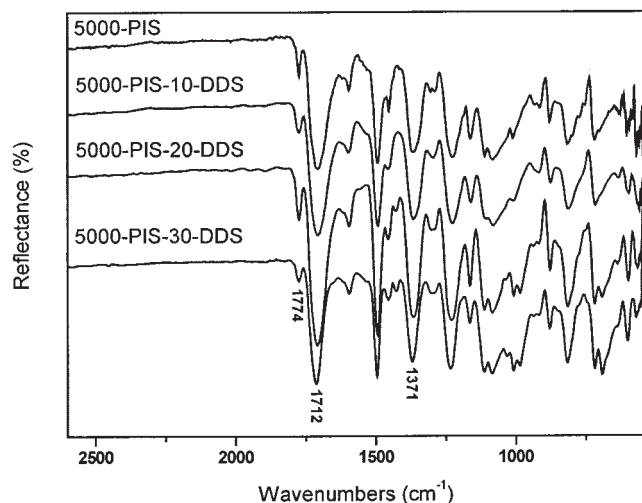


Figure 2 FTIR spectra of 5000-PIS-DDS composite films.

characteristic Si—Ph absorption, meaning that the DDS have been introduced into the polyimide matrix. The Si—O—Si stretching near 1087 cm^{-1} is associated with open chain structures.^{25,26} In the spectra of PI-DDS films (Fig. 1), the Si—O—Si stretching is overlapped by the absorption bands of polyimide. However, this absorption band in the spectra of 5000-PIS-DDS films (Fig. 2) is very clear and gradually increases in intensity with increasing content of DDS compared with the intensity of the characteristic absorption bands of imide groups at 1712 cm^{-1} . The absorption band ranging from 1010 to 1030 cm^{-1} is indicative of uncondensed Si—OH groups because of the steric hindrance of phenyl groups in DDS.

Optical transparency of the composite films

The optical properties of the obtained composite films were studied by using UV-vis spectra. The UV-vis spectra of PI-DDS and 10,000-PIS-DDS composite

films are shown in Figure 3(a,b). The transparency of the composite films with DDS contents below 20 wt % is compared with that of pure polyimide matrix. The transparency for all of the composite samples decreases with the increase of DDS contents in films. However, the introduction of coupling agent (APTES) as capping agent of polyimide chains did not play obvious effect on the improvement of transparency for composite films. So the structure of DDS containing two phenyl groups has the primary contribution to the compatibility between the two phases. We can also see that the transmittances of the PI-DDS, 10,000-PIS-DDS composite films with DDS contents below 10 wt % are higher than that of pure polyimide. In addition, the cutoff wavelengths of these films shift toward the shorter wavelength compared with that of polyimide matrix. It is well known that the fully aromatic polyimides with the coloration of pale yellow to deep brown strongly absorb visible light because of their aromatic conjugated structures and the intermolecular or intramolecular charge-transfer complexes (CTCs) formed between or within polymer chains.^{27,28} The reason for the earlier mentioned shift of cutoff wavelengths of some composite films may be that the small polysiloxane domain from hydrolyzed DDS affects the electron state of polyimide and destroys intermolecular CTCs formed between polymer chains to some extent. This result is favorable for the improvement of the optical transparencies of the composite films.

Microstructure of the composite films

Figure 4 shows the SEM photographs of the fracture surface of composite films with different DDS content. It can be seen that there is a difference in microstructure for the different composites. The composites with low DDS content, PI-10-DDS and 10,000-PIS-10-DDS exhibit uniform phase structure without phase separation, indicating that there is good compatibility be-

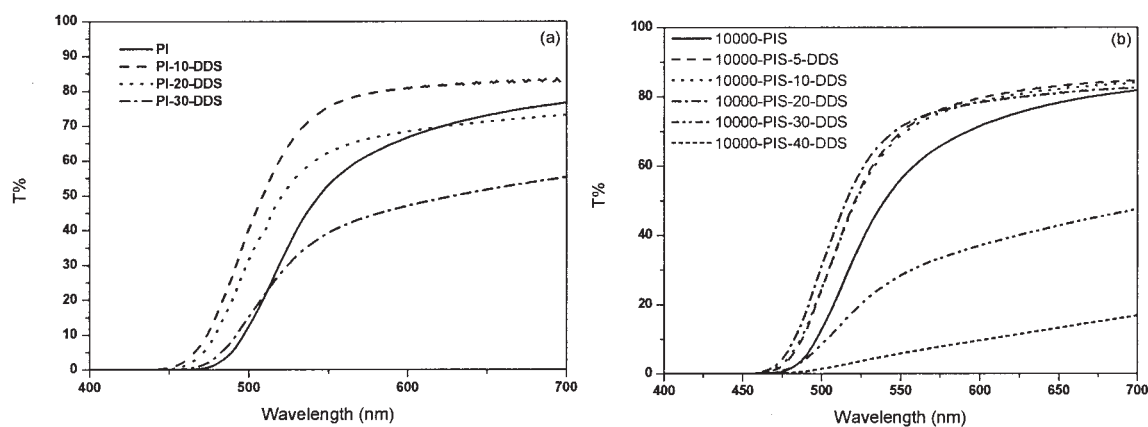


Figure 3 UV-vis spectra of PI-DDS and 10,000-PIS-DDS composite films.

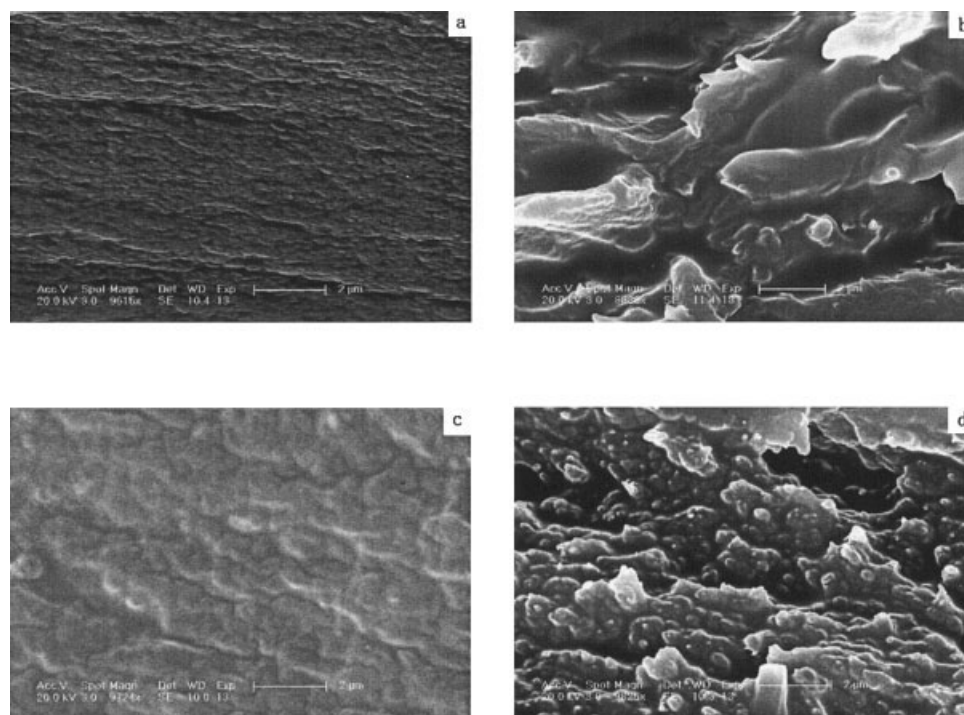


Figure 4 SEM images of the fracture surface of composite films with different DDS contents (a) PI-10-DDS, (b) PI-40-DDS, (c) 10,000-PIS-10-DDS, (d) 10,000-PIS-40-DDS.

tween the two phases. However, when the DDS content reached to 40 wt %, large domain (>200 nm) of siloxane structure was observed in composites, especially in 10,000-PIS-40-DDS films. These large domain sizes can result in high light scattering of composite films,²⁹ so the composites with high DDS contents are opaque. These results are in accordance with that of UV-vis spectra of composite films with different DDS contents.

Thermal characteristics

TGA was used to study the thermal properties of the three series of composite films PI-DDS, 5000-PI-DDS

and 10,000-PIS-DDS. The weight residues above 750°C and 5 wt % decomposition temperatures (T_d) of prepared composite films are listed in Tables I and II. TGA curves of 10,000-PIS-DDS series of composite films are also illustrated in Figure 5. It can be seen that the residues above 750°C for each series of composite films, especially for composite with high DDS content, increase with increasing DDS content. This result indirectly indicates that the DDS linkages were successfully incorporated into polyimide films. The three series of composite films exhibit good thermal stability and their T_d 's are all above 529°C.

The glass transition temperature (T_g) of composite films PI-DDS and 10,000-PIS-DDS were determined

TABLE I
Properties of PI-DDS Composite Films

Sample	Modulus (MPa)	Tensile strength (MPa)	Elongation (%)	Density (g/cm ³)	Rwa ^a (wt %)	T_d^b (°C)	T_g^c (°C)	Residue ^d (wt %)	Degree of condensation ^e
PI	1300	110	56	1.4573	3.0	548	—	0	—
PI-5-DDS	1537	122	80	1.4380	2.04	529	82	375	100
PI-10-DDS	1340	116	77	1.4248	1.75	529	79	386	90
PI-20-DDS	1250	115	76	1.3953	1.70	533	82	384	2.27
PI-30-DDS	1010	115	65	1.3539	1.67	549	82	381	5.8
PI-40-DDS	890	91	64	1.3485	1.65	550	83	385	5.86

^a Water absorption of composite films.

^b 5 wt % decomposition temperature.

^c Glass transition temperature of composite films obtained by DTMA.

^d Char yield of composite films at 750°C based on the experimental results from TGA.

^e Degree of condensation of DDS in PI matrix calculated based on the chloroform extraction results.

TABLE II
Properties of 10000-PIS-DDS and 5000-PIS-DDS Composite Films

Sample	Modulus (MPa)	Tensile strength (MPa)	Elongation (%)	Density (g/cm ³)	Rwa (wt %)	T_d (°C)	T_g (°C)	Residue (wt %)	
10,000-PIS	1417	108	28	1.4771	3.11	553	—	400	1.25
10,000-PIS-5-DDS	1373	105	37	1.4640	2.5	548	88	388	1.33
10,000-PIS-10-DDS	1410	114	54	1.4294	2.10	534	85	397	1.94
10,000-PIS-20-DDS	1430	107	52	1.4142	2.09	532	84	368	4.9
10,000-PIS-30-DDS	1127	92	55	1.3896	1.44	540	79	374	9.07
10,000-PIS-40-DDS	1014	77	41	1.3831	1.33	539	82	376	11.62
5,000-PIS	1460	116	37	1.4344	3.6	546	—	—	4.31
5,000-PIS-10-DDS	1403	111	37	1.4086	2.12	536	—	—	4.32
5,000-PIS-20-DDS	1380	99	33	1.4027	1.58	529	—	—	5.48
5,000-PIS-30-DDS	1097	85	33	1.3985	1.37	532	—	—	11.37

by DMTA, and the results are listed in Tables I and II. The DTMA curves are also shown in Figure 6 (inset is the partially amplificatory figure for Fig. 6). It can be seen that as the DDS was incorporated into PI matrix, two primary T_g 's for both noncrosslinked and crosslinked composite films was observed. The T_g at 79–88°C corresponds to PDDS, the higher T_g at 374–405°C corresponds to PI matrix. The higher T_g is shifted to lower temperatures in comparison with pure PI or PIS films (about 400°C) and the T_g of PDDS is higher than that reported in literatures.^{30–32} This result indicates that the flexible siloxane domains have well compatibility at a certain extent and can present the plasticizing effect on the rigid polyimide chains. However, in our composite system, the second transition, the crystal to mesophase transition at $\sim 265^\circ\text{C}$,³² was not observed clearly in Figure 6. This result shows that the PDDS in composites may mainly remain an amorphous structure and the crystallization may be

restrained. X-ray diffraction analysis supports this result. The X-ray pattern of PI, PI-20-DDS and PI-40-DDS films are shown in Figure 7. Although the PI has small crystalline regions because of a small portion of the crystalline peaks, PI films are mainly amorphous. For the composite films PI-20-DDS and PI-40-DDS, the broad halo diffraction patterns of PDDS are observed at around $2\theta = 9^\circ$ and $2\theta = 19^\circ$. So we can deduce that the formed PDDS phase in PI matrix is an amorphous structure.^{31,32}

Mechanical properties

The mechanical properties of the composite films were examined and the results are listed in Tables I and II, respectively. For the noncrosslinked PI-DDS, it can be seen from Table I that there is a maximum at 5 wt % of DDS content for the modulus and the tensile strength. The elongation at break has the same trend and in-

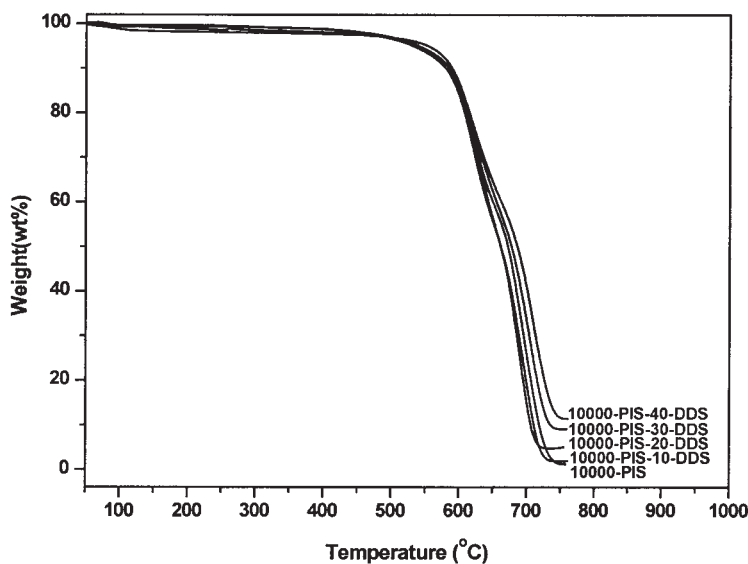


Figure 5 TGA curves of 10,000-PIS-DDS series of composite films.

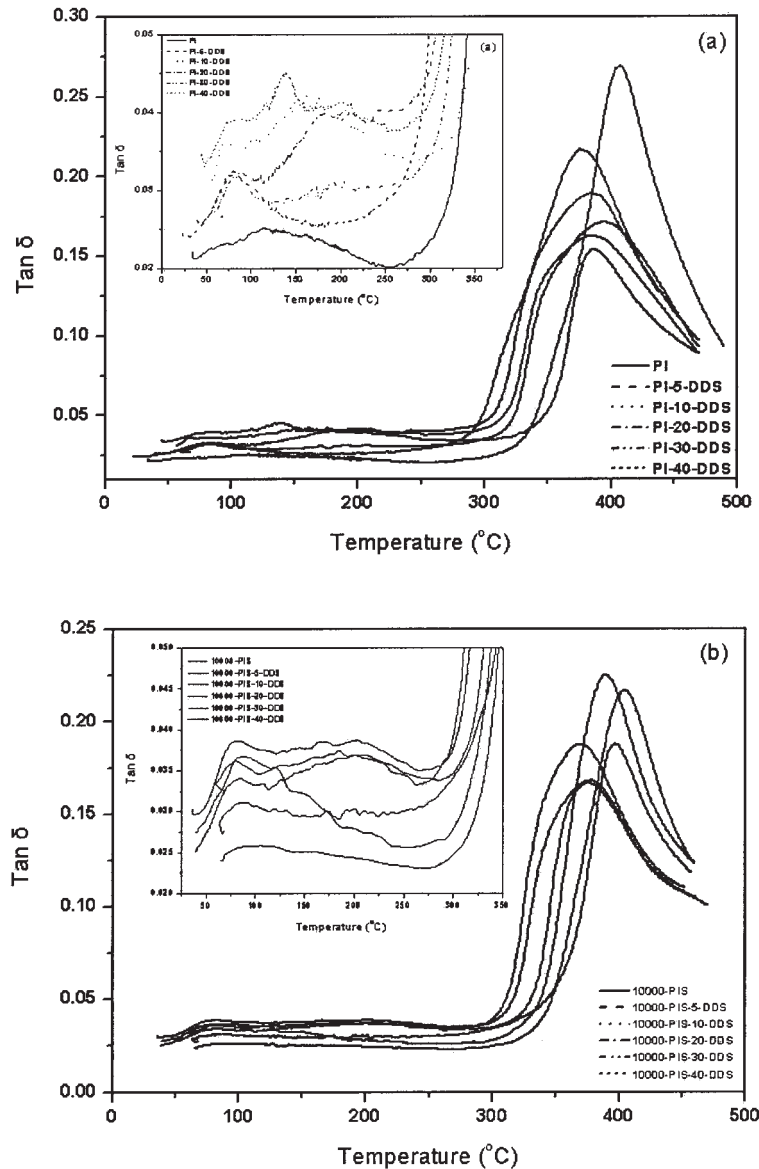


Figure 6 DTMA curves ($\tan\delta$) of (a) PI-DDS and (b) 10,000-PIS-DDS composite films.

creases compared with that of the pure PI films. The improvement of mechanical properties of PI-DDS composite films with low DDS contents can be explained by the result of the better interfacial interaction between PI and the siloxane domains as well as the development of fine morphology in composite films. However, as the DDS content exceeds 10 wt %, the slow reduction in mechanical properties may be attributed to the formation of larger domain of siloxane domains (see SEM images in Fig. 3) and the increase of flexible polysiloxane linkages in composite films. For the two series of the crosslinked composite films, Table II shows that the modulus and the tensile strength of composite films changed slightly, except the films with higher DDS contents. While in comparison with pure PIS, the elongation at break also in-

creases sharply. The elongation at break of the crosslinked composite films is lower than that of pure PI because of the increasing crosslinking density of polymers and the decreasing molecular weight, especially for the 5000-PIS composite films. When the low content of DDS (10–20 wt %) was introduced into the PIS films, the elongation at break for 10,000-PIS-DDS composite films just reached to similar level with that of the pure PI films (Table I), while the modulus and tensile strength increased slightly. So the flexible organic siloxane phase from DDS plays a significant role in the improvement of mechanical properties of composite films because of its interfacial adhesion and compatibility with PI matrix. However, when the DDS content exceeds 20 wt %, the modulus and tensile strength of 10,000-PIS-DDS films decrease because of

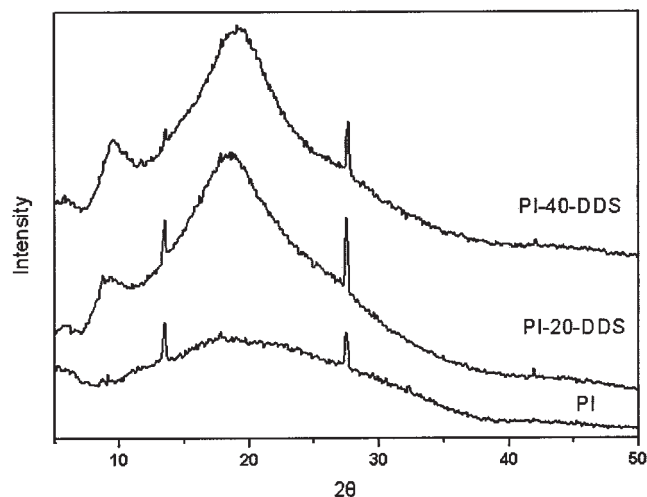


Figure 7 X-ray diffraction patterns of PI, PI-20-DDS and PI-40-DDS composite films.

the formation of larger domains of siloxane domains [Fig. 3(d)] and the poor interfacial adhesion, although the films still have higher elongation at break. For the 5000-PIS-DDS composite films, the introduction of DDS reduced the mechanical properties of composite films because of the higher crosslinking density and lower molecular weight of 5000-PIS polymer.

Other properties

The densities and water absorption of the composite films were measured and the results are listed in Tables I and II. It can be seen that densities of the composite films gradually decreased with the increasing DDS content for each series of composite films

because of the increasing free volume and domain sizes of polysiloxane domains. In addition, the crosslinked composite films have higher density than noncrosslinked composite films, on the whole. This is a result of the increase of crosslinking degree of polymer networks.

The data of the water absorption indicate that pure polyimide, 10,000-PIS and 5000-PIS, films have high water uptake (3.0–3.6 wt %), while introducing DDS into the films decreases the water absorption of composite films with increasing DDS content. When the DDS content reaches to 30 wt %, the water uptake of composite films decreases by about 50 wt % compared with the initial matrix films. This result indicates that the polysiloxane has a higher hydrophobicity than PI materials.

Resistance of the composite films to selected solvents (toluene, methanol, chloroform, DMAc, NMP) was evaluated by the weight change after immersion into these solvents for 30 days (Table III). The lowest weight change was found in toluene and methanol (<1 wt %) for all composite films, regardless of composition. All samples with the DDS content lower than 10 wt % exhibit a good resistance to chemical solvent including all earlier mentioned solvents. However, when the DDS content in composite films is higher than 20 wt %, the higher weight change was found in chloroform, DMAc, and NMP, and the highest value reaches to 20 wt % for composite films with 40 wt % DDS. We analyze the soluble material of PI-40-DDS after chloroform extraction using ^{29}Si -NMR (Fig. 8). There is a signal peak at 33.7 ppm in ^{29}Si -NMR spectra, indicating that the soluble materials mainly are cyclic trimer monomers of DDS (hexaphenylcyclotrisiloxane).^{30,32} It can be seen that condensation of hydro-

TABLE III
The Results of Solvent Resistance of Composite Films^a

Sample	Toluene	Methanol	Chloroform	DMAc	NMP
PI	0.23	0.87	0	0	0.17
PI-5-DDS	0	0.55	0	0	0.82
PI-10-DDS	0.44	0.54	0.91	0.67	0.97
PI-20-DDS	0.13	0.95	6.59	5.93	7.65
PI-30-DDS	0.74	0.88	18.81	17.62	16.52
PI-40-DDS	0.38	0.74	19.64	18.05	20.44
10,000-PIS	0.38	0.79	0	0	0
10,000-PIS-5-DDS	0.34	0.79	0.97	0	0
10,000-PIS-10-DDS	0.34	0.12	0.80	0.96	0
10,000-PIS-20-DDS	0.50	0.95	9.01	8.27	9.17
10,000-PIS-30-DDS	0.92	0.97	16.43	16.84	17.07
10,000-PIS-40-DDS	0.98	0.32	18.23	19.05	20.86
5,000-PIS	0	0	0	0	0
5,000-PIS-10-DDS	0.44	0.67	0	0.28	0
5,000-PIS-20-DDS	0.56	0.49	9.93	9.56	8.33
5,000-PIS-30-DDS	5.88	0.63	14.11	16.14	14.26

^a The solvent resistance of composite films was tested by immersing the composite films into the corresponding solvent. After 30 days the relative weight change percent (wt %) was determined as the solvent resistance of corresponding sample to some solvent.

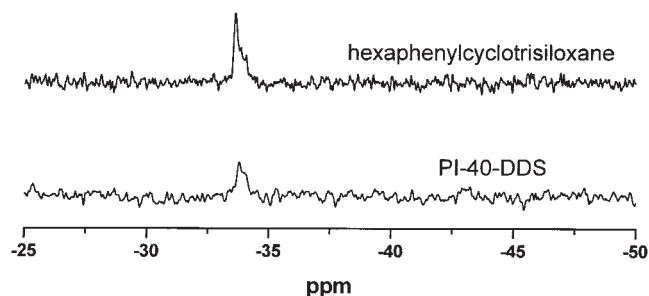


Figure 8 ^{29}Si -NMR spectra of hexaphenylcyclotrisiloxane and soluble material of PI-40-DDS composite film after chloroform extraction.

lyzed diphenylsilanediol form cyclotrisiloxanes to a high degree for composite system with high DDS content.³³ In experiment, we also found that the high concentration of hydrolyzed DDS solution in DMAc (>50 wt %) can form white crystal (hexaphenylcyclotrisiloxane) after aging for a month. From the solvent extraction results, we can calculate the degree of condensation of DDS in noncrosslinked composites (Table I). The higher the DDS content, the lower the degree of condensation of DDS in the composite films.

CONCLUSIONS

To improve the properties of PI materials, for the first time the diarylsiloxane DDS was incorporated into polyimide matrix to prepare a series of no-crosslinked and crosslinked composite films by sol-gel process. The composite films remain transparent up to 20 wt % of DDS because of the good compatibility between the two phases. The composite films with low DDS contents exhibit good flexibility and still have excellent mechanical properties and thermal stability compared with that of the pure PI matrix. The polydiphenylsiloxane phase shows amorphous structure and the composite films exhibit two glass transitions of polysiloxane and PI, respectively. The detailed structure of the formed polydiphenylsiloxane in PI need to be further studied. In addition, we also expect that the properties of the PI/polysiloxane composite films can

be further improved by introduction of inorganic silica.

References

1. Ghosh, M. K.; Mittal, K. L., Eds.; *Polyimides: Fundamentals and Applications*; Dekker: New York, 1996.
2. Sroog, C. E. *Prog Polym Sci* 1991, 16, 561.
3. Hasegawa, M.; Horie, K. *Prog Polym Sci* 2001, 26, 259.
4. Feger, C., Ed.; *Polyimide: Trends in Materials and Applications*; Society of Plastic Engineers: New York, 1996.
5. Morikawa, A.; Iyoku, Y.; Kakimoto, M.; Imai, Y. *Polym J* 1992, 24, 107.
6. Ahmad, Z.; Mark, J. E. *Chem Mater* 2001, 13, 3320.
7. Wang, H.; Zhong, W.; Xu, P.; Du, Q. *Macromol Mater Eng* 2004, 289, 793.
8. Park, H. B.; Kim, J. H.; Kim, J. K.; Lee, Y. M. *Macromol Rapid Commun* 2002, 23, 544.
9. Tong, Y.; Li, Y.; Xie, F.; Ding, M. *Polym Int* 2000, 49, 1543.
10. Chiang, P. C.; Whang, W. T. *Polymer* 2003, 44, 2249.
11. Lan, T.; Kaviratna, P. D.; Pinnavaia, T. J. *Chem Mater* 1994, 6, 573.
12. Jiang, L. Y.; Leu, C. M.; Wei, K. H. *Adv Mater* 2002, 14, 426.
13. Lin, W. J.; Chen, W. C. *Polym Int* 2004, 53, 1245.
14. Wahab, M. A.; Kim, I.; Ha, C. S. *Polymer* 2003, 44, 4705.
15. Tsai, M. H.; Whang, W. T. *Polymer* 2001, 42, 4197.
16. Sysel, P.; Hobzová, R.; Šindelář, V.; Brus, J. *Polymer* 2001, 42, 10079.
17. Sanchez, C.; Ribot, F.; Lebeau, B. *J Mater Chem* 1999, 9, 35.
18. Novak, B. M. *Adv Mater* 1993, 5, 422.
19. Park, Y. W.; Lee, D. S.; Kim, S. H. *J Appl Polym Sci* 2004, 91, 1774.
20. Beecroft, L. L.; Johnen, N. A.; Ober, C. K. *Polym Adv Technol* 1997, 8, 289.
21. Chen, Y.; Iroh, J. O. *Chem Mater* 1999, 11, 1218.
22. Kriptou, S.; Pissis, P.; Bershtein, V. A.; Sysel, P.; Hobzová, R. *Polymer* 2003, 44, 2781.
23. McGrath, J. E.; Dunson, D. L.; Mecham, S. J.; Hedrick, J. L. *Adv Polym Sci* 1999, 140, 61.
24. Brus, J.; Dybal, J.; Sysel, P.; Hobzová, R. *Macromolecules* 2002, 35, 1253.
25. Huang, X. Y.; Zhu, Z. K.; Yin, J.; Ma, X. D. *Chem Mater* 1989, 1, 269.
26. Chang, C. C.; Chen, W. C. *Chem Mater* 2002, 14, 4242.
27. Dine-Hart, R. A.; Wright, W. W. *Makromol Chem* 1971, 143, 189.
28. Hiroshi, S.; Takeshi, S.; Amne, M. *High Perform Polym* 1999, 11, 255.
29. Beecroft, L. L.; Ober, C. K. *Chem Mater* 1997, 9, 1302.
30. Lee, M. K.; Meier, D. J. *Polymer* 1993, 34, 4882.
31. Harkness, B. R.; Tachikawa, M.; Mita, I. *Macromolecules* 1995, 28, 8136.
32. Harkness, B. R.; Tachikawa, M.; Yue, H.; Mita, I. *Chem Mater* 1998, 10, 1700.
33. Yang, M. H. *J Chin Chem Soc* 1995, 42, 923.