Preparation and Properties of Elastic Polyimide-Silica Composites using Silanol Sol from Water Glass

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ABSTRACT: A new approach for obtaining elastic polyimide-silica composites using a silanol sol prepared from water glass and the imide-containing elastic polymers (IEPs) with polytetramethyleneoxide (PTMO) soft-segment was investigated. Methods of increasing the degree of compatibility between the silica phase prepared from a silanol sol and IEPs obtained via elastic polyureas were examined. Elastic polyimide-silica composites were obtained by the thermal treatment at 200°C for 4 h *in vacuo* after *N*-methyl-2-pyrrolidone was evaporated from the IEP precursor solutions to which the silanol tetrahydrofuran solution and Bis(trimethoxysilylpropyl)amine (BisA) were added. The use of BisA possessing a reaction site with a carboxylic acid group on the IEP precursors improved the degree of compatibility between the IEPs and silica. Transparent composites were obtained when the concentration of SiO_2 was below 22 wt %. FT-IR analyses confirmed that the composite was a segmented hybrid material composed of the PTMO segment, the imide segment, and SiO_2. The silica matrix obtained via silanol sol from water glass and the silica matrix obtained by the conventional sol-gel process with an alkoxysilane were essentially the same, and there was no significant loss of silicon due to incomplete hydrolysis of the alkoxides when preparing composites via the water glass route, in contrast to the situation that can occur in the case of the sol-gel route. Dynamic mechanical and thermal analyses suggested that microphase separation between the imide segment and the PTMO segment occurred in the composites and that there was a substantial amount of phase mixing at the same time. The formation of the silica composite had a great influence on the mobility of the segmnets in the phase-mixing domain. TGA analyses indicated that the formation of the 10 wt % silica hybrid gave a composite with a 50°C higher degradation temperature. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 2211–2219, 2004

Key words: composites; silicas; polyimides; elastic polymers; water glass

INTRODUCTION

Polyimides have been widely used in the aerospace and electronic industries due to their reliable high-performance stability, chemical resistance, dielectric properties, and good mechanical strength since they were developed in 1960s. Numerous attempts have been made to introduce a polyimide unit with high-performance properties into polymeric materials to prepare a new class of block copolymers. For example, various imide-containing elastic polymers (IEPs) have been developed as high-performance polymers that can be applied in microelectronics and in specialty coatings. IEPs with a polysiloxane soft-segment are the most widely studied as oxygen plasma resistance materials, high-performance adhesives, and gas separation membranes.[1] IEPs with a polyoxyalkylene soft-segment have been investigated for application to pervaporation membranes[2] and biomaterials.[3] We recently reported a new approach for obtaining IEPs via elastic and high-molecular-weight polyurea and pyromellitic dianhydride.[4,5] Elastic polyureas are easily prepared from amino-terminated oligomers and conventional diisocyanates, which are used as raw materials for polyurethanes and high-performance polymers such as polyisocyanurates, polycarbodiimides, and polyamide-imides.

Many studies have been also carried out on polyimide-silica composites to obtain a new class of imide-containing polymeric materials. In recent years, various investigations into polyimide-silica composites have been carried out to examine changes in the thermal stability of composites,[6] to study hybrid materials with increased rigidity and mechanical strength for nanoporous membranes used for gas separation,[7] to prepare nanoporous composites with increased fracture toughness,[8] to develop hybrid materials with a low coefficient of thermal expansion,[9–11] to create an inorganically modified polyimide with a low-dielectric constant value,[12] and to prepare crack- and defect-free composites.[13] Recent investigations suggest that there are several possible routes to obtaining polyimide-silica composites. The routes investigated so far are summarized in Table I to clarify the purpose of this study.

The various techniques can be classified into three types according to the process used to prepare the

TABLE I
Methods of Preparing Polyimde-Silica Composites

| Classification | Silica | | Polyimide | | Connecting agent | Optimum silica content | Reference |
	Starting Material	Functionali-zation	M_W and monomer				
(a)	Fumed silica	No	EL-5512 (National Starch)		Not used	9 vol %	14
	Porous silica	No	SuperImide800		Not used	25 wt %	8
	Colloidal silica	No	PMDA[a]/ODA[b]		APTEOS[c]	20 wt %	15
(b)	Poly-(silsesquioxane)	End-capped	M_n = 8,900 PMDA/3FDA[d]		APhTMOS[e] capped	77 wt %	13
(c)							
i	TEOS[f]	No	PMDA/ODA		Not used	32 wt %	16
	TEOS	No	η_{red} = 1.2 PMDA/ODA		Not used	8 wt %	17
ii	TEOS	No	Ultem 1000		APTEOS	24 wt %	18
	TEOS	No	Pyre ML RK692		GOTMS[g]	Not described	19
iii	TMOS[h]	End-capped	Nadimide end-group oligomer		Trimethoxy-silane capped	Not described	20
	TMOS	Monomer	M_W = 80000 6FDA[i]/6FpDA[j]		APhTMOS modified	22.5 wt %	7
	TEOS F-TEOS[k]	End-capped	4 repeat unit 6FDA/6F$_p$DA		APhTMOS capped	40 wt %	12
	TEOS DMES[m]	Monomer	η_{red} = 0.8–1.7		Ethoxysilyl[l] diamine	70 wt %	21
(d)	Water glass	No	η_{red} = 0.5–0.8 IEP		Examined in this study	Examined in this study	This study

[a] Pyromellitic dianhydride.
[b] Oxydianiline.
[c] γ-Aminopropyltriethoxysilane.
[d] 1,1-Bis(4-aminophenyl)-1-phenyl-2,2,2-trifluproethane.
[e] (p-Aminophenyl)-trimethoxysilane.
[f] Tetraethoxysilane.
[g] γ-Glycidyloxytrimethoxysilane.
[h] Tetramethoxysilane.
[i] 4,4'-(hexafluoroisopropylidene)-dianiline.
[j] 4,4'-(hexafluoroisopropylidene)-diphthallic anhydride.
[k] (Tridecafluoro-1,1,2,2-tetrahydrooctyl)triethoxysilane.
[l] Dimethyldiethoxysilane.
[m] m-Phenylenediamine possessing directly substituted ethoxysilyl group.

silica matrix in the composite (Table I). Routes that obtain composites using silica nanoparticles are classified as Type (a). The silica matrix is formed without any reaction taking place when preparing the composites, so no volume contraction upon condensation occurs as it does in sol-gel chemistry. The Type (b) route uses poly(silsesquioxane) to obtain the composite. There is significantly less volume contraction in Type (b) than in sol-gel–based routes. Routes that prepare composites via the *in situ* polymerization of an alkoxide utilizing a sol-gel process are classified as Type (c). In this paper, a novel route using a silanol sol obtained from water glass is studied. This method of forming the silica matrix is completely different from any of the other routes, so it is classified separately as Type (d). Dehydration and hydrolysis play a role in forming the silica matrix in Type (d), but esterification, alcohol condensation, and alcoholysis that are featured in Type (c) are absent in Type (d).

The routes can be further classified according to the method by which the silica is connected with the polyimide, because the degree of compatibility between the inorganic and organic components has great influence on the properties of the composites. The degree of compatibility is increased using functionalized monomers, end-capped low-molecular-weight polyimides, and connecting agents. Herein, we examine methods of increasing the degree of compatibility between the silica phase prepared from a silanol sol and IEPs obtained via elastic polyureas.

This study uses water glass as a raw material for producing silica hybrid composites. Water glass is widely used as a grouting material in civil engineering, a detergent, a cement for glass, etc., so it is readily available at relatively low cost. Accordingly, a new route derived from water glass is expected to be more advantageous in terms of cost than the conventional sol-gel route.
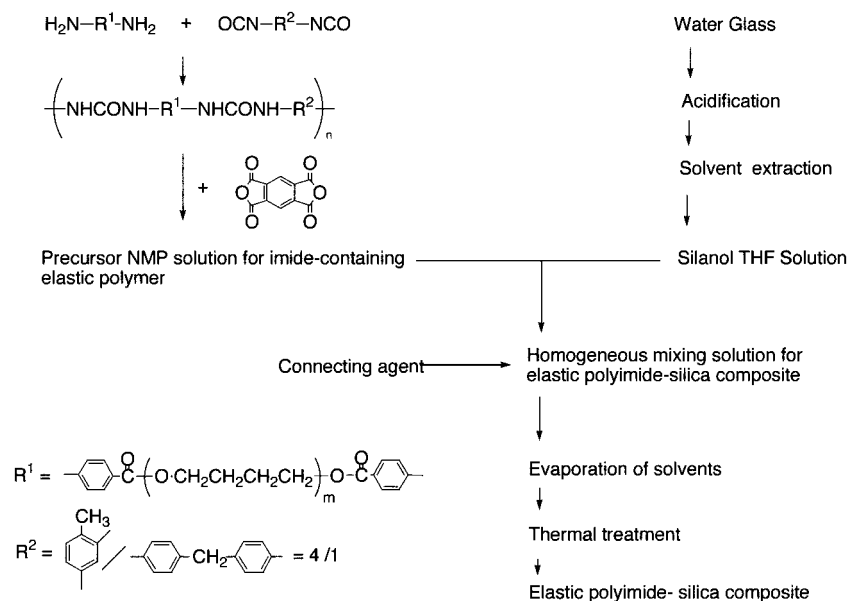
Scheme 1 Preparative procedure for elastic polyimide-silica composites using silanol sol from water glass.

EXPERIMENTAL

Materials

α-(4-Aminobenzoyl)-ω-[(4-aminobenzoyl)oxy]-poly-(oxytetramethylene) (PTMODA1000) (amine content in KOH; 90.4) and PTMODA2000 (amine content in KOH; 52.7) were supplied by Ihara Chemical Industry Co., Ltd. The PTMODA was dehydrated *in vacuo* at 80°C for about 15 h before use. 4,4′-Diphenylmethane diisocyanate (MDI) was purified by distillation under reduced pressure. Tolylene-2,4-diisocyanate (2,4-TDI, Mitsui Chem. Co.) and pyromellitic dianhydride (PMDA, Nacalai Tesque, Inc.) were used without further purification. *N*-Methyl-2-pyrrolidone (NMP, Nacalai Tesque, Inc.) was kept over a 3Å molecular sieve. Bis(trimethoxysilylpropyl)amine (BisA), γ-aminopropyltriethoxysilane (APTEOS), γ-glycidyloxypropyltrimethoxysilane (GOTMS), diphenyldimethoxysilane (DPhDMOS), and vinyltriethoxysilane (VTEOS) were supplied by Nippon Unicar Co. and were used as received. Water glass (sodium silicate No. 3; Na_2O $3.23SiO_2$, nonvolatile = 40.2 wt %) was supplied by Fuji Chemical Co. and was used as received.

Measurements

Reduced viscosity was measured at a concentration of 0.5 g/dL of polymer in NMP at 30°C with a Ubbelohde dilution viscometer. Solvent resistance was estimated from the gel fraction of each sample after immersion in NMP at 60°C for 7 days. The samples were dried at 80°C for about 15 h and at 150°C for 40 h after immersion, and the gel fraction was obtained from the residual weight of each sample. FT-IR spectra were recorded on a JASCO FT/IR-5300 with ATR-500/M. Thermal gravimetric analysis (TGA) measurements were performed on a Seiko Instruments TG/DTA6200 at a heating rate of 10°C/min under air. Differential scanning calorimetry (DSC) measurements were performed on a Rigaku Thermo plus DSC 8230 at a heating rate of 20°C/min under air. Dynamic mechanical analysis (DMA) was performed on a Seiko Instruments DMS 6100 at a heating rate of 5.0°C/min and at a frequency of 10 Hz. The tensile properties were investigated using an Orientec RTC-1225A Model U-4310 at room temperature.

Preparation of elastic polyimide-silica composites via elastic polyureas

Scheme 1 shows the preparative procedure for making the elastic polyimide-silica composites via elastic polyureas. The elastic polyurea was prepared by the bulk polymerization of PTMODA and the mixed diisocyanate (2,4-TDI : MDI molar ratio = 4 : 1) and the IEP solutions were prepared by the reaction of the polyurea with PMDA in NMP at 165°C for 3 h, as reported in the previous paper.[5] The polymer concentration in the resulting solution was adjusted to 20 wt % in NMP. PTMODA1000 and PTMODA2000 contain a type of poly(tetramethyleneoxide) (M_n of PTMO: 1000 and 2000) segment that is known as a soft-segment. The reduced viscosity of the resulting PTMODA1000-based IEP solution was 0.49 dL/g and that of the PTMODA2000-based IEP was 0.80 dL/g at a concentration of 0.5 g/dL of polymer in NMP at 30°C. The resulting PTMODA-based IEP solutions are the precursor solutions for IEPs. The precursor possesses a carboxylic acid group as reported in our recent paper.[4] Films of IEP were obtained through thermal treatment at 200°C for 2 h after the NMP was

TABLE II
Recipe and Composition of Elastic Imide-Silica Composites

No.	Recipe (g)					Composition (weight ratio)				
	IEP Solution		Silanol Solution[c]	Connecting agent		IEP			Connecting Agent	
	1k[a]	2k[b]		BisA[d]	APTEOS[e]	1k	2k	SiO$_2$	BisA	APTEOS
1k-0-0-N	20	0	0	0	0	100	0	0	0	0
1k-0-3.9-BisA	20	0	0	0.15	0	100	0	0	0	0
1k-2.5-3.9-BisA	20	0	0.88	0.15	0	100	0	2.5	3.9	0
1k-5.0-3.9-BisA	20	0	1.76	0.15	0	100	0	5.0	3.9	0
1k-10-3.9-BisA	20	0	3.52	0.15	0	100	0	10	3.9	0
1k-2.5-5.1-APTEOS	20	0	0.88	0	0.19	100	0	2.5	0	5.1
1k-5.0-5.1-APTEOS	20	0	1.76	0	0.19	100	0	5.0	0	5.1
1k-10-5.1-APTEOS	20	0	3.52	0	0.19	100	0	10	0	5.1
2k-0-0-N	0	20	0	0	0	0	100	0	0	0
2k-0-3.9-BisA	0	20	0	0.15	0	0	100	0	3.9	0
2k-10-3.9-BisA	0	20	3.62	0.15	0	0	100	10	3.9	0

[a] NMP solution of PTMODA1000-based IEP, Polymer concentration = 18.5 wt %.
[b] NMP solution of PTMODA2000-based IEP, Polymer concentration = 19.0 wt %.
[c] THF solution of silanol, SiO$_2$ concentration = 10.5 wt %.
[d] Bis(trimethoxysilylpropyl)amine, M_W = 341.6. SiO$_2$ content = 35.1 wt %.
[e] γ-Aminopropyltriethoxysilane, M_W = 221.4, SiO$_2$ content = 27.1 wt %.

evaporated at 150°C for 1 h from the precursor solutions in a spin coater.

Silanol sol obtained from water glass and a connecting agent (if required) were added to the precursor solutions at room temperature. Elastic polyimide-silica composites were obtained in films with a thickness of about 100 μm from the resulting silanol sol-IEP solution by using the same method as described for IEP.

Table II shows the recipes and compositions of the elastic polyimide-silica composites. Each sample of the elastic polyimide-silica composite was given a designation in the form of xk-y-z-Z, where 1k is PTMODA1000-based IEP, 2k is PTMODA2000-based IEP, y is the relative weight of SiO$_2$ derived from silanol with 100 weight parts of IEP, z is the relative weight of the connecting agent, Z is the name of the connecting agent, and Z is N if a connecting agent is not used.

Preparation of silanol sol from water glass

Water glass (30 mL) with a SiO$_2$ content of 3.2 mol/L was added to a precooled 2N-H$_2$SO$_4$ aqueous solution (30 mL) in a 200-mL round-bottomed flask, which was held below 5°C by cooling with iced water. The solution was vigorously stirred during the addition of the water glass. After the addition, the pH value of the solution was measured and was confirmed to be below 2.0. The solution was moved into a 300-mL separating funnel. Tetrahydrofuran (THF) (40 mL) and NaCl (16 g) were added to the solution in the funnel. The solution was vigorously shaken in the funnel and maintained below 5°C for 30 min in order for salting-out to take place. The solution was separated into two layers. The upper layer contained the silanol THF solution, and a total of 38.7 g of the silanol THF solution was obtained. As the SiO$_2$

content of the silanol THF solution was 11.8 wt %, the yield of SiO$_2$ was 79.3%. The SiO$_2$ content was derived from the residue obtained after heating the silanol THF solution up to 850°C in air.

RESULTS AND DISCUSSION

Characterization of elastic polyimide-silica composite

Figure 1 shows the IR spectra of the PTMODA1000-based IEP (1k-0–0-N) and the elastic polyimide-silica
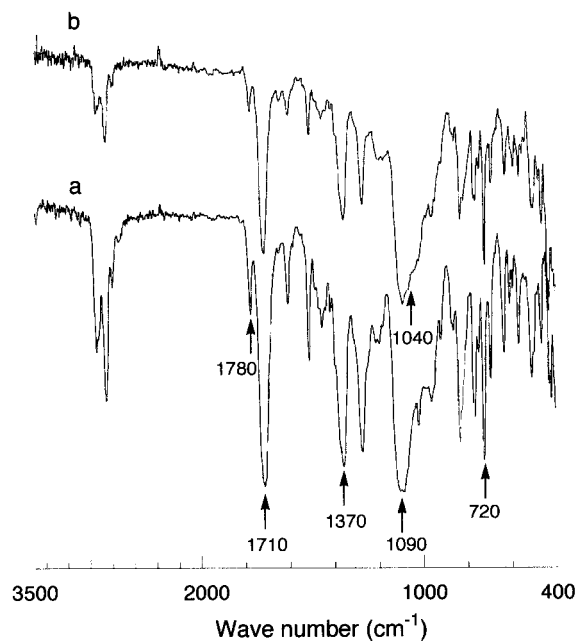

Figure 1 IR spectra of 1k-0–0-N (a) and 1k-10–3.9-BisA (b).

TABLE III
SiO$_2$ Content of Composites

No.	SiO$_2$ content (wt %)	
	Calc.[a]	Obs.[b]
1k-0-0-N	0	0
1k-0-3.9-BlsA	1.40	1.3
1k-10-3.9-BisA	10.2	9.2
2k-0-0-N	0	0
2k-0-3.9-BisA	1.37	1.7
2k-10-3.9-BisA	10.2	9.5

[a] SiO$_2$ wt % calculated from silanol and connecting agent.
[b] Final wt % residue obtained after heating at 850°C in air.

composite (1k-10–3.9-BisA) prepared from the precursor solution of 1k-0–0N, silanol and BisA. Takekoshi[22] reported that the characteristic IR absorption bands of the imide group appear at 1,780 and 1,720 ($\nu_{C=O}$), 1,380 (ν_{C-N}), and 725 cm^{-1} ($\delta_{C=O}$). As shown in Figure 1, these bands are observed in 1k-0–0-N (a) and 1k-10–3.9-BisA (b). The band ascribable to the ether group in PTMO is observed at 1,090 cm^{-1} (ν_{C-O-C}) in (a) and (b). A band due to the Si–O–Si group in SiO$_2$ is observed at 1,000 to 1,110 cm^{-1} ($\nu_{Si-O-Si}$), which overlaps with the band of the ether group, such that the assignment of the band for the Si–O–Si group is generally difficult in 1k-10-1-BisA (b). However, the band at 1,000–1,090 cm^{-1} in (b) becomes considerably broader and the band of the Si–O–Si group is clearly observed as a shoulder peak at around 1,040 cm^{-1} in (b) compared with (a) (Fig. 1). Mauritz and Warren[23] assigned the absorption band at 1,020–1,040 cm^{-1} to the linear Si–O–Si asymmetric stretching vibration. FT-IR analyses confirm that 1k-10-1-BisA is an elastic polyimide-silica composite that contains a hard imide segment, a PTMO soft-segment, and a SiO$_2$ matrix.

Table III shows the observed SiO$_2$ content in the composite derived from the residue obtained after heating the composite up to 850°C in air. The measured values agree well with the theoretical values. This indicates that there is no significant loss of silicon

through volatilization during the thermal curing step due to incomplete hydrolysis of the alkoxysilane when preparing composites via the water glass route, in contrast to the situation that can occur in the case of the sol-gel route.[16,24]

Compatibility between IEPs and silica

Table IV shows the influence of connecting agents and silica content on the degree of compatibility between PTMODA-based IEPs and silica. Transparent films of elastic polyimide-silica composites were obtained using BisA, APTEOS, and GOTMS. The use of connecting agents possessing a reaction site with a carboxylic acid group on the IEP precursors improved the degree of compatibility between the IEPs and silica. However, films prepared from DPhDMOS and VTEOS were opaque because they contained no suitable reaction site.

The results of measuring the gel fraction of the composites are shown in Figure 2. The gel fraction decreases in the following order: APTEOS > BisA > GOTMS > VTEOS > DPhDMOS. These results indicate that the crosslinking density of the hybrid IEP prepared from APTEOS is higher than that of the other IEPs and that the composites prepared from VTEOS and DPhDMOS are not crosslinked. As the amine concentration of APTEOS is higher than that of BisA for the same Si content and the reactivity of the amino group with carboxylic acid is greater than that of the glycidyl group, the compatibility between IEP and silica is considered to depend upon the reactivity of the agent with the carboxylic acid group on the IEP precursor and the concentration of the reaction site. Transparent composites are not obtained when the concentration of SiO$_2$ is over 28 wt %.

Tensile properties

Table V shows the influence of the silica content on the tensile properties of the composites prepared from

TABLE IV
Influence of Connecting Agents and SiO$_2$ Content on Appearance of Composites (weight ratio)

No.	IEP		Connecting agent					Appearance
	1k	SiO$_2$	BisA	APTEOS	GOTMS[a]	VTEOS[b]	DPhDMOS[c]	
1k-0-0-N	100	0	0	0	0	0	0	Transparent
1k-5.0-3.9-BisA	100	5.0	3.9	0	0	0	0	Transparent
1k-22-7.8-BisA	100	22	7.8	0	0	0	0	Transparent
1k-28-16-BisA	100	28	16	0	0	0	0	Translucent
1k-5.0-5.1-APTEOS	100	5.0	0	5.1	0	0	0	Transparent
1k-5.0-5.4-GOTMS	100	5.0	0	0	5.4	0	0	Transparent
1k-5.0-4.3-VTEOS	100	5.0	0	0	0	4.3	0	Opaque
1k-5.0-5.6-DPhDMOS	100	5.0	0	0	0	0	5.6	Opaque

[a] γ-Glycidyloxypropyltrimethoxysilane, M_W = 236.3, SiO$_2$ content = 25.4 wt %.
[b] Vinyltriethoxysilane, M_W = 190.3, SiO$_2$ content = 31.6 wt %.
[c] Diphenydiethoxysilane, M_W = 244.4, SiO$_2$ content = 24.6 wt %.
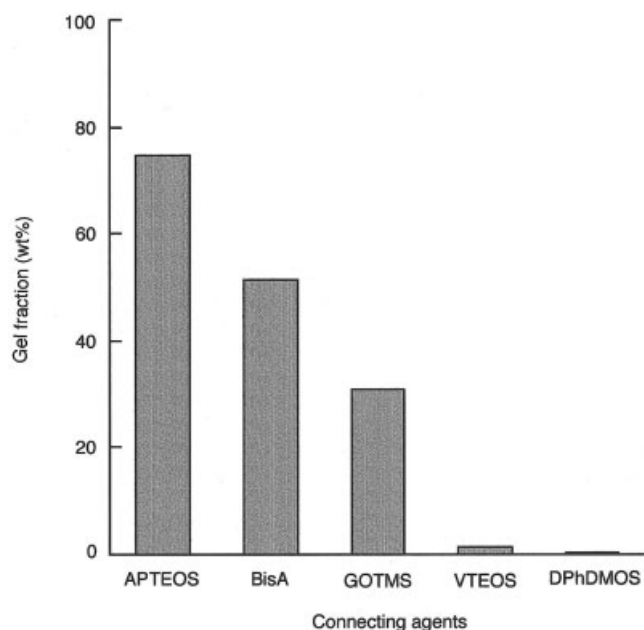
Figure 2 Influence of connecting agents on gel fraction of 1k-based composites with 5% SiO_2 content. APTEOS, γ-aminopropyltriethoxysilane; BisA, bis(trimethoxysilyl-propyl)amine; GOTMS, γ-glycidyloxytrimethoxysilane; VTEOS, vinyltriethoxysilane; DPhDMOS, diphenyldime-thoxysilane.

BisA and APTEOS. The tensile strength and elongation at breaking point decrease and the tensile modulus increases with increasing silica content in the composites. This is consistent with the results of earlier studies on polyimide-silica composites obtained by the sol-gel process with connecting agents and tetraethoxysilane.[19,25]

We also examined the influence of the molecular weight of the soft segment on the tensile properties of the composites based on 1k and 2k, as shown in Table V. The reinforcement due to the silica matrix in the 2k-based composite is larger than that in the 1k-based composite because the tensile strength at breaking point of the 2k-based composite with a SiO_2 content of 10 wt % is over 40 MPa and the increase in the tensile modulus of the 2k-based composite is much larger than that of the 1k-based composite for the same SiO_2 content.

Table V summarizes the tensile modulus and the PTMO content. The tensile modulus between 50 and 200% strains for 2k-10-3.9-BisA is higher than that for 1k-0-0N, although the PTMO content of the former is higher than that of the latter. The results suggest that if we wish to obtain an elastic material with a high tensile modulus, this method of forming the silica-composite is rather better than the method that relies on decreasing the content of the soft-segment.

Thermal and dynamic mechanical properties

The results of DSC analyses for the 1k- and 2k-based composites are shown in Figures 3 and 4. Two main transitions for the 1k-based composite and the three main transitions for the 2k-based composite can be observed, suggesting microphase-separated morphologies. The transition ($T_g{}^s$) appearing below 0°C is attributed to a relaxation of the PTMO segment and the other transition ($T_g{}^h$) appearing above 200°C is attributed to the relaxation of the imide segment. The transition ($T_m{}^s$) around 5°C for the 2k-based composite is the crystalline melting point of the PTMO segment as cited in our recent paper.[26] The value of $T_g{}^s$ derived from the DSC curve was taken as the midpoint of the change in slope of the base line (Fig. 3) and $T_g{}^h$ was taken as the initial point of the change (Fig. 4). $T_g{}^s$ values for 1k-0-0-N and 1k-10-3.9-BisA are −55 and −53°C, and $T_g{}^s$ for 2k-0-0-N and 2k-10-3.9-Bis are −69 and −69°C, respectively. Figure 5 shows the results of DMA analyses for 1k-0-0-N and 1k-10-3.9-

TABLE V
Tensile Properties[a] of 1k- and 2k-Based Imide-Silica Composites

No.	M_{50} (MPa)	M_{100} (MPa)	$M_{200}{}^b$ (MPa)	TS^c (MPa)	EL^d (%)	PTMO content[e] (wt %)
1k-0-0-N	14.2	15.4	18.1	45.4	460	57
1k-2.5-3.9-BisA	17.3	19.1	24.6	49.5	400	54
1k-5.0-3.9-BisA	19.2	21.2	27.2	37.0	290	53
1k-10-3.9-BisA	21.6	23.6	29.9	35.4	260	50
1k-2.5-5.1-APTEOS	15.6	17.8	23.2	29.9	270	53
1k-5.0-5.1-APTEOS	16.6	19.9	—	22.4	140	52
1k-10-5.1-APTEOS	20.7	—	—	22.5	70	50
2k-0-0-N	6.3	7.9	9.7	46.6	750	76
2k-10-3.9-BisA	16.5	18.8	23.3	42.1	490	67

[a] Tensile properties are measured at room temperature with strain speed of 50 mm / min.
[b] M_x is the tensile strength at a strain of X %.
[c] Tensile strength at breaking point.
[d] Elongation at breaking point.
[e] Polytetramethyleneoxide content, which is a soft-segment in the composite.
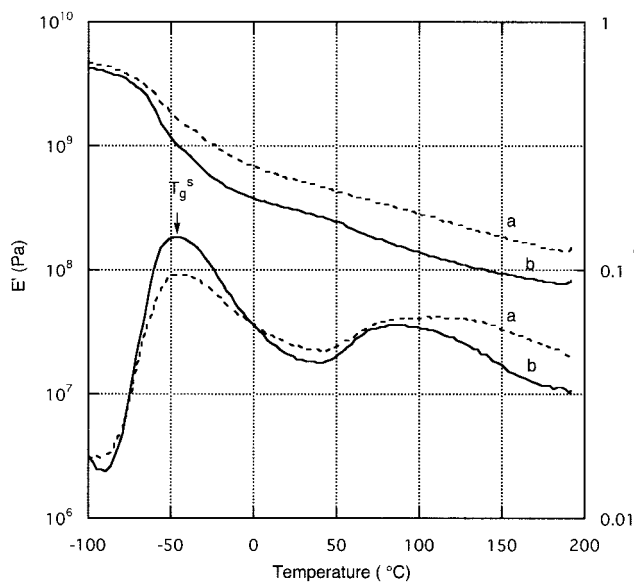
Figure 3 Temperature dependence of storage modulus (E′) and tan δ of 1k-10–3.9-BisA (a) (dotted line) and 1k-0–0-N (b) (solid line).

BisA. On the basis of the tan δ peak in Figure 5, T_g^s values for 1k-0–0-N and 1k-10–3.9-BisA are −50 and −48°C, respectively. Accordingly, the results for T_g^s suggest that the formation of the silica composite has a little influence on the mobility of the PTMO segment.

As shown in Figure 5, the storage modulus of 1k-0–0-N drops significantly above 50°C and another transition appears at 84°C. The transition at 84°C may be attributed to a relaxation of the segments in the phase-mixing domain. This transition shifts to 111°C in 1k10–3.9-BisA. This result means that the formation of the silica composite has a great influence on the mobility of the segments in the phase-mixing domain.

Figure 4 shows that T_g^h values for 1k-0–0N and 1k-10–3.9-BisA are 230 and 233°C, and T_g^h for 2k-0–0-N and 2k-10–3.9-BisA are 197 and 197°C, respectively. The degree of influence of the formation of the composite on the mobility of the hard domain is therefore very small.

Thermal gravimetric analyses

A study of the thermal degradation of the material was carried out using TGA. Figure 6 shows TGA curves under air for 1k-based composites. The 10% weight loss temperatures (T_{10}) for 1k-0–0-N and 1k-10–3.9-BisA are 320 and 370°C, respectively. T_{10} therefore probably depends upon the oxidative degradation of the PTMO segment (the unstable segment in the polymer) because T_{10} for polyimides is above 400°C in air.[27,28] The formation of the silica composite mainly reduces the mobility of the PTMO segment in the phase-mixing domain, so that the thermal degradation temperature of the composite shifts to a higher
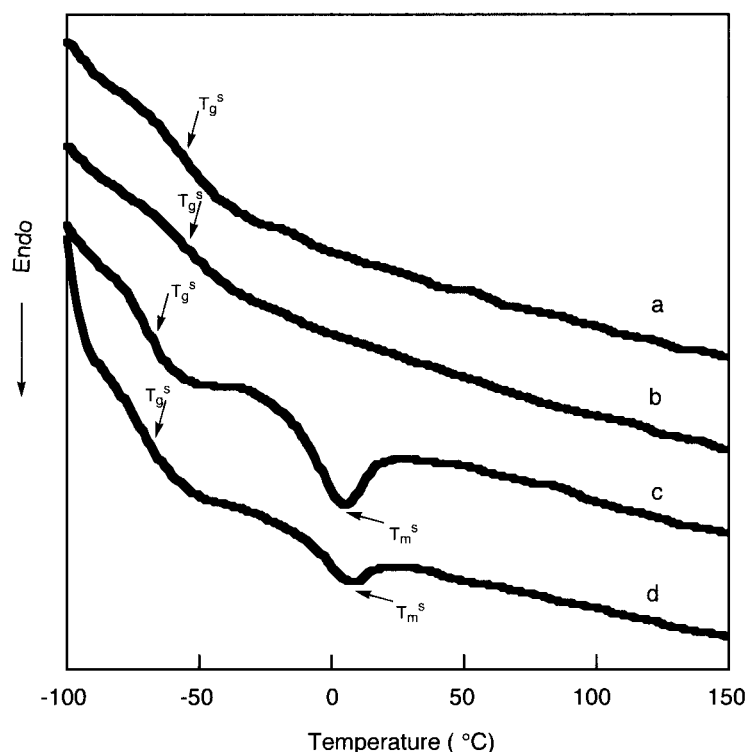

Figure 4 DSC thermograms of 1k-0–0-N (a), 1k10–3.9-BisA (b), 2k-0–0-N (c), and 2k-10–3.9-BisA (d) at the low temperature range below 100°C under air at 20°C/min.
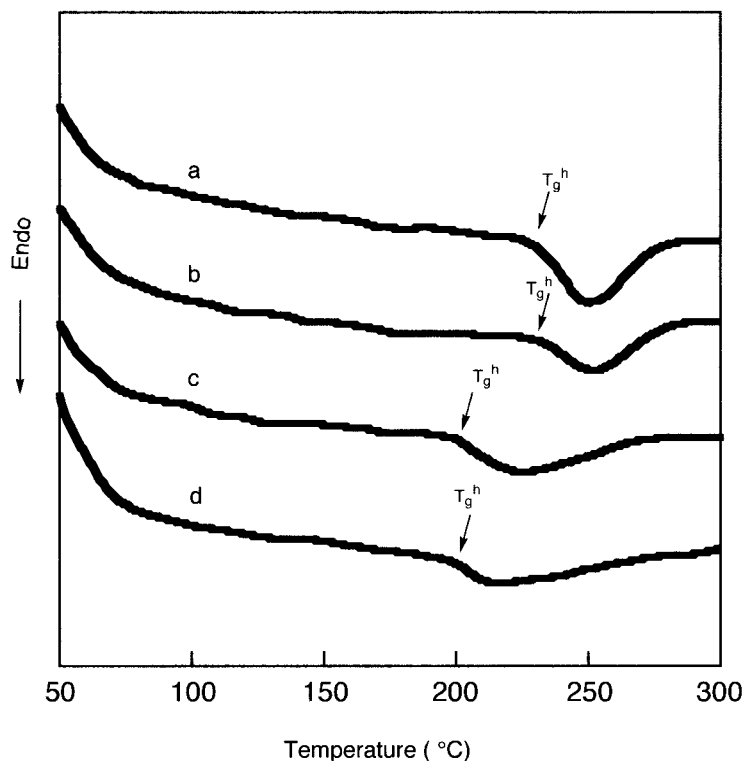
Figure 5 DSC thermograms of1k-0–0-N (a), 1k-10–3.9-BisA (b), 2k-0–0-N (c), and 2k-10–3.9-BisA (d) at the high temperature range above 100°C under air at 20°C/min.

temperature. The formation of the 10 wt % silica hybrid gives a composite with a 50°C higher degradation temperature.

CONCLUSION

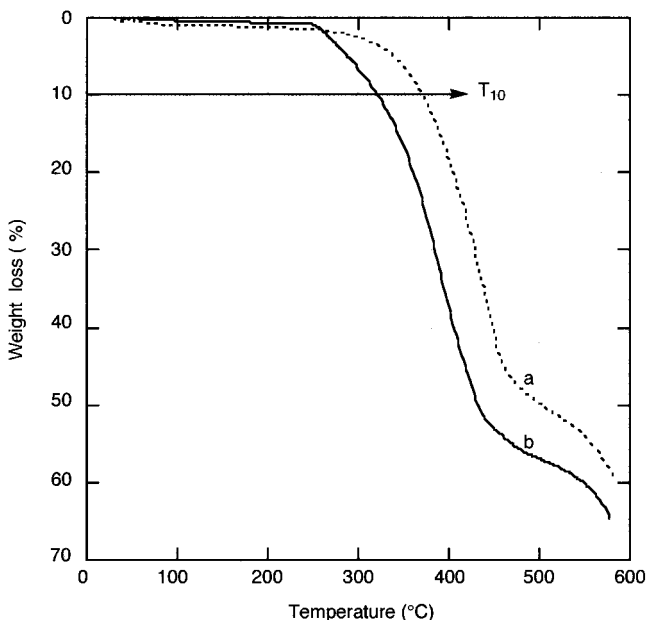Elastic polyimide-silica composites were successfully prepared, using a silanol sol from water glass and the

Figure 6 TGA curves of 1k-10–3.9-BisA (a) (dotted line) and 1k-0–0-N (b) (solid line) under air at 10°C/min.

IEPs with PTMO soft-segment. We examined methods of increasing the degree of compatibility between the silica phase prepared from a silanol sol and IEPs obtained via elastic polyureas. Their mechanical and thermal properties were investigated.

Elastic polyimide-silica composites were obtained by the thermal treatment at 200°C for 4 h *in vacuo* after NMP was evaporated from the IEP precursor solutions to which the silanol THF solution and BisA were added. FT-IR analyses confirmed that the elastic polyimide-silica composite had the PTMO segment, the imide segment, and SiO_2. The use of BisA possessing a reaction site with a carboxylic acid group on the IEP precursor improved the degree of compatibility between the IEPs and silica. Transparent composites were obtained when the concentration of SiO_2 was below 22 wt %. The measured values of the SiO_2 content in the composite agreed well with the theoretical values. The tensile strength and elongation at breaking point decreased and the tensile modulus increased with increasing silica content in the composite. These results clarified that the silica matrix obtained via silanol sol from water glass and the silica matrix obtained by the conventional sol-gel process with alkoxysilanes were essentially the same and that there was no significant loss of silicon due to incomplete hydrolysis of the alkoxysilanes when preparing composites via the water glass route, in contrast to the situation that can occur in the case of the sol-gel route.

Dynamic mechanical and thermal analyses suggested that microphase separation between imide segment and PTMO segment occurred in the composites and that there was a substantial amount of phase mixing at the same time. The formation of the silica composite had a great influence on the mobility of the segments in the phase-mixing domain. TGA analyses indicated that the formation of the 10 wt % silica hybrid gave a composite with a 50°C higher degradation temperature.

The new route from water glass for preparing the polyimide-silica composite is expected to be more advantageous in cost than the conventional sol-gel route.

References

1. McGrath, J. E.; Dunson, D. L.; Mecham, S. J.; Hedrick, J. L. Adv Polym Sci 1999, 140, 61.
2. Jonquieres, A.; Roizard, D.; Cuny, J.; Lochon, P. J Membr Sci 1996, 121, 117.
3. Masiulanis, B.; Calusinski, G. M.; Haponiuk, J. T. J Biomater Appl 1997, 11, 296.
4. Asai, K.; Inoue, S.; Okamoto, H. J Polym Sci Polym Chem 2000, 38, 715.
5. Asai, K.; Onouchi, Y.; Inoue, S.; Okamoto, H. Chem Lett 1998, 93, 227–228.
6. Bershtein, V. A.; Egorova, L. M.; Yakushev, P. N.; Pissis, P.; Sysel, P.; Brozova, L. J Polym Sci Polym Phys 2002, 40, 1056.
7. Cornelius, C. J.; Marand, E. Polymer 2002, 43, 2385.
8. Ruan, S.; Lannutti, J. J.; Prybyia, S.; Seghi, R. R. J Mater Res 2001, 16 1975.
9. Hung, J.; Zhu, Z.; Yin, J.; Zhang, D.; Qian, X. J Appl Polym Sci 2001, 79, 794.
10. Hsiue, G.; Chen, J.; Liu, Y. J Appl Polym Sci 2000, 76, 1609.
11. Zhu, Z.; Yang, Y.; Yin, J.; Qi, Z. J Appl Polym Sci 1999, 73, 2977.
12. Taylor-Smith, R. E.; Durazo, A.; Schilling, F. C. Proc ACS Polym Mater Sci Eng 1999, 81, 69.
13. Hedrick, J. L.; Cha, H.-J.; Miller, R. D.; Yoon, D. Y.; Brown, H. R.; Srinivasan, S.; Di Pietro, R.; Cook, R. F.; Hummel, J. P.; Klaus, D. P.; Liniger, E. G.; Simonyi, E. E. Macromolecules 1997, 30, 8512.
14. Breval, E.; Mulvihill, M. L.; Dougherty, J. P.; Newnham, R. E. J Mater Sci 1992, 27, 3297.
15. Yamamoto, H.; Doi, T.; Ozawa, S. Japan. Patent 63 172741A, 1988.
16. Nandi, M.; Conklin, J. A.; Salvati, Jr., L.; Sen, A. Chem Mater 1991, 3, 201.
17. Morikawa, A.; Iyoku, Y.; Kakimoto, M.; Imai, Y. Polym J 1992, 24, 107.
18. Nunes, S. P.; Peinemann, K. V.; Ohlrogge, K.; Alpers, A.; Keller, M.; Pires, A. T. N. J Membr Sci 1999, 157, 219.
19. Kioul, A.; Mascia, L. J Non-Cryst Solids 1994, 175, 169.
20. Spinu, M.; Brennan, A.; Rancourt, J.; Wikes, G. L.; McGrath, J. E. Mater Res Soc Symp Proc 1990, 175, 179.
21. Morikawa, A.; Iyoku, Y.; Kakimoto, M.; Imai, Y. J Mater Chem 1992, 2, 679.
22. Takekoshi, T. In Polyimides; Ghosh, M. K.; Mittal, K. L. M., Eds.; Marcel Dekker: New York, 1996; Chap 2, p 18.
23. Mauritz, K. A.; Warren, R. M. Macromolecules 1989, 22, 1730.
24. Joly, C.; Goizet, S.; Schrotter, J. C.; Sanchez, J.; Escoubes, M. J Membr Sci 2000, 130, 63.
25. Wang, S.; Ahmad, Z.; Mark, J. E. Macromolecular Rep 1994, A31(Suppl. 3&4), 411–419.
26. Shirasaka, H.; Inoue, S.; Asai, K.; Okamoto, H. Macromolecules 2000, 33, 2776.
27. Meyers, R. A. J Polym Sci Part A1 1969, 7, 2757.
28. Mosher, W. A.; Chlystek, S. J. J Heterocycl Chem 1972, 9, 319–324.