

Preparation of a New Class of Polyimide–Silica Hybrid Films by Sol–Gel Process

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ABSTRACT: A new class of polyimide–silica hybrid films were successfully prepared by the sol–gel reaction starting from tetraethoxysilane (TEOS) in the solution of polyamic acid in *N,N*-dimethylacetamide. The hybrid films were obtained by the hydrolysis–polycondensation of TEOS in the polyamic acid solution, followed by heating at 270°C. Fairly flexible films were obtained up to 70 wt% of silica content. The films containing the silica less than 8 wt% were yellow and transparent, whereas the films with higher silica content were yellow and opaque. The density of the silica in the hybrid films was estimated to be 1.65 gcm^{-3} . The ^{29}Si nuclear magnetic resonance spectrum indicated that the silica in the films consisted of non-hydroxy, monohydroxy, and dihydroxy siloxane structures. Silica particles with diameter of around $5 \mu\text{m}$ were observed in the hybrid films by scanning electron microscopy. The density, decomposition temperature, and modulus of the hybrid films increased with increasing the silica content, whereas the tensile strength and elongation at break of the films decreased in this order. The glass transition temperature of the hybrid films showed the minimum at 8 wt% of silica content. The linear thermal expansion coefficient of the silica in the hybrid films was estimated to be $1.3 \times 10^{-5} \text{ K}^{-1}$.

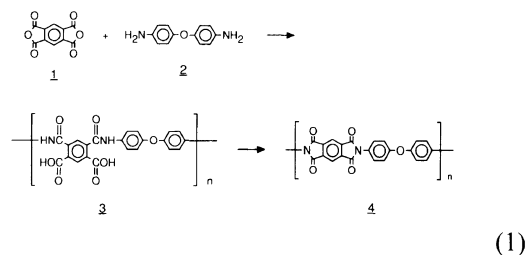
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The sol–gel process is the method for preparation of inorganic metal oxides under mild conditions starting from organic metal alkoxides. The reaction consists of hydrolysis of the metal alkoxides, followed by polycondensation of the hydrolyzed intermediates. Recently, the sol–gel reaction have been applied to the reaction in polymer matrix to prepare inorganic and organic hybrid materials. Silicon oxide (silica) and polymer hybrid materials have been synthesized from tetraethoxysilane (TEOS) and the polymers such as poly(oxytetramethylene),^{1–4} poly(oxyethylene),⁵ sodium poly(4-styrene sulfonate),⁶ perfluorosulfonic acid ionomer,^{7,8} poly(ether ketone),⁹ poly(dimethyl-siloxane),^{3,10,11} polysiloxane elastomers,^{12–17} and polyoxazoline.^{18,19}

Polyimides are known as reliable high

temperature polymers, especially in the aerospace and electronics industries. As shown in eq 1, polyimide **4**, which are usually insoluble in organic solvents, are prepared from the soluble precursor, polyamic acid **3**.²⁰ In these fields, they require new materials such as high temperature polymers possessing high modulus and strength, and, especially in microelectronics, low thermal expansion efficiency. Although polyimides–silica composites have been used in an industrial scale to improve polyimide properties, a few tens percent of inorganic silica particle can be mixed into the polymer matrix. If polyimide–silica hybrid materials with high silica content are successfully prepared, they must be accepted as new high performance materials.

In this paper, we report the first successful



preparation of the silica–polyimides hybrid materials by the hydrolysis–polycondensation of TEOS in polyamic acid solution, and by subsequent heating of the resulting film at 270°C.

EXPERIMENTAL

Measurement

IR and NMR spectra were recorded on a JASCO FT/IR-5000 spectrophotometer, and a JEOL-GSX270 spectrometer, respectively. Thermogravimetry (TG) was performed with a Shimadzu thermal analyzer TGA-40M. Dynamic mechanical analysis was performed with TOYOSEIKI Rheograph Solid. Scanning electron micrograph was obtained with JEOL-T220. Mechanical properties were measured with Toyo Baldwin Tensilon UTM-11-20 at a strain rate of 20% min⁻¹.

Materials

Tetraethoxysilane (TEOS) was obtained from Toshiba Silicone Co., and was used without further purification. Pyromellitic anhydride (PMDA) and bis(4-aminophenyl) ether (ODA) were purified by sublimation before their use. *N,N*-dimethylacetamide (DMAc) was distilled under reduced pressure.

Typical Sol–Gel Procedure

First, polyamic acid **3** was prepared from PMDA **1** and ODA **2** in DMAc as described in the literature.²⁰ Inherent viscosity of **3** was over 1.20 dl g⁻¹ which was sufficiently high molecular weight for preparation of tough polyimide films.

In a flask, 1.00 ml of tetraethoxysilane

Table 1. Preparation of polyimide–silica hybrid films

Entry	PAA ^a	H ₂ O	TEOS	Silica ^b	Remarks ^c
	g	ml	ml	wt%	
1	10.0	1.0	0	0	T
2	10.0	1.0	0.10	3	T
3	10.0	1.0	0.30	8	T
4	10.0	1.0	0.50	13	O
5	10.0	1.0	1.00	22	O
6	10.0	1.0	1.50	30	O
7	10.0	1.0	3.00	46	O
8	10.0	1.0	4.50	56	O
9	10.0	1.0	6.00	63	O
10	10.0	1.0	8.00	70	O

^a 10 wt% DMAc solution.

^b Calculated of silica content in the hybrid films.

^c T, transparent; O, opaque.

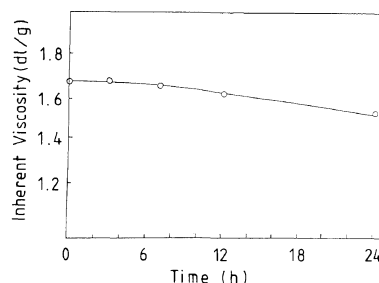


Figure 1. Influence of water on inherent viscosity of polyamic acid in DMAc.

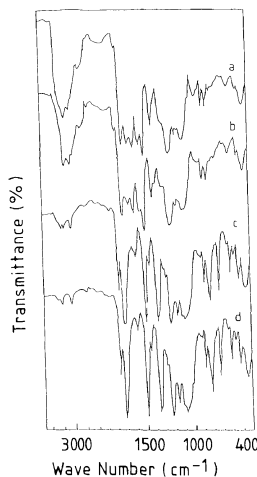


Figure 2. IR spectra of polyimide–silica hybrid films. (a) before heating; (b), (c), and (d), after heating at 100°C, 200°C, and 300°C for 1 h, respectively.

Preparation of Polyimide-Silica Hybrid Films

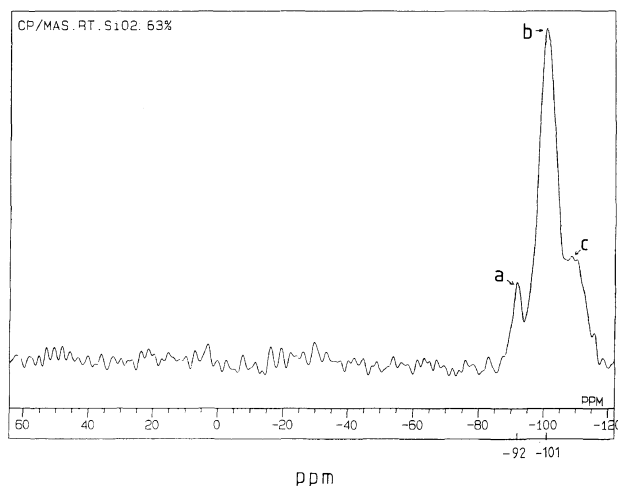


Figure 3. ^{29}Si NMR spectrum of polyimide-silica hybrid films (silica content was 63%).

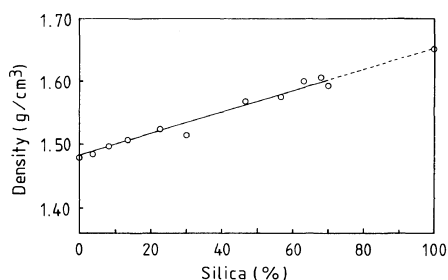


Figure 4. Density of polyimide-silica hybrid films.

(TEOS) and 1.00 ml of water were added to 10.00 g of 10 wt% solution of polyamic acid **3** in DMAc. The heterogeneous solution was stirred for 6 h until the solution became homogeneous. The film was prepared by casting the solution on a glass plate. After the film had been dried at 60°C for 12 h, the film was heated at 270°C for 3 h under nitrogen.

RESULTS AND DISCUSSION

Because polyimide **4** was insoluble in organic solvents, the sol-gel reaction was carried out in a solution of polyamic acid. Thus, polyimide-silica hybrid film was prepared as follows: first, TEOS was reacted with water in the polyamic acid solution, second, the

resulting homogeneous mixture was cast onto a glass plate to prepare the polyamic acid-silica hybrid film, and finally the polyimide-silica hybrid film was obtained by heating the precursor film at 270°C.

Since the sol-gel reaction requires water to hydrolyze TEOS, there might be a possibility that polyamic acid **3** is also susceptible to hydrolysis by water. When a solution of polyamic acid **3** in DMAc was stirred in the presence of same amount of water as in the case of the sol-gel reaction for 24 h, polyamic acid **3** retained enough high molecular weight without remarkable decrease in inherent viscosity, as shown in Figure 1.

Table I summarizes the results of the preparation of polyimide-silica hybrid films. The silica (SiO_2) content in the table denote the values calculated by assuming that the sol-gel reaction proceeded completely. All the solutions of precursor polymeric mixture before casting on a glass plate were homogeneous. The cast films were dried at 60°C on the glass plate to evaporate the solvents as well as to develop the siloxane network of silica. The polyimide-silica hybrid films having silica content up to 70 wt% were obtained as self standing form. The films of entries 1 and 2 were transparent and yellow even after the films

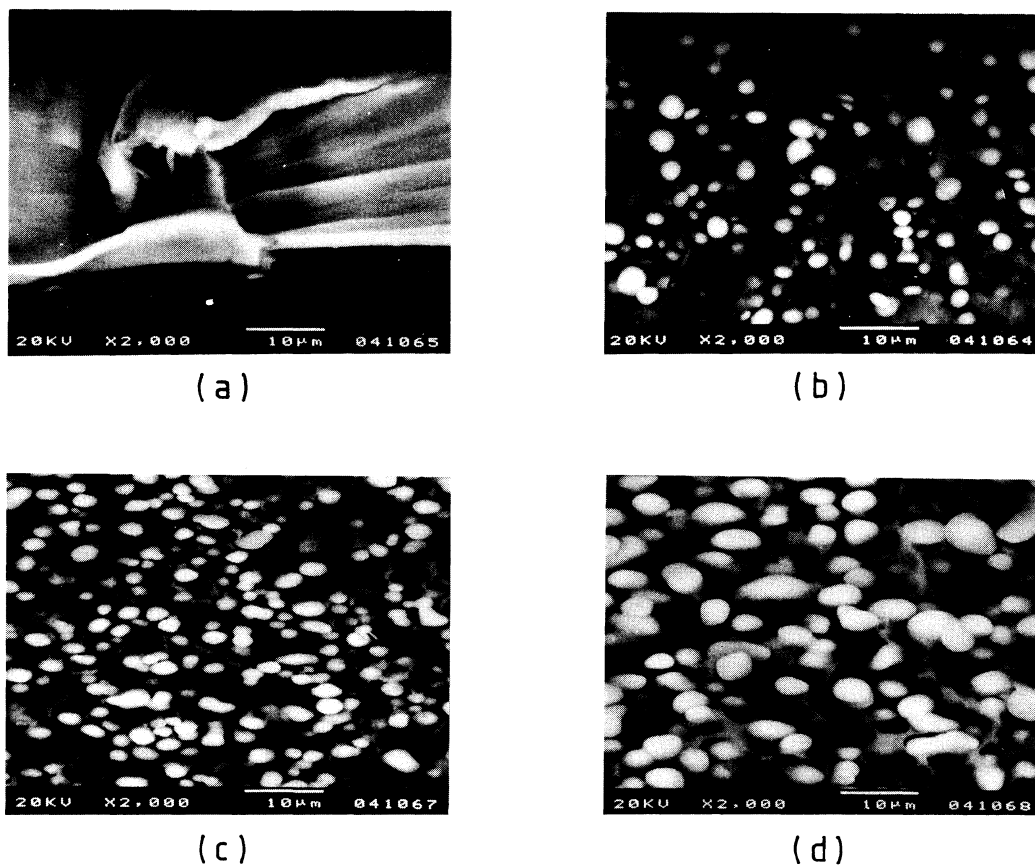


Figure 5. Photographs of scanning electron microscope of polyimide-silica hybrid films. (a), (b), (c), and (d): polyimide films containing 0, 30, 63, and 70 wt% of silica.

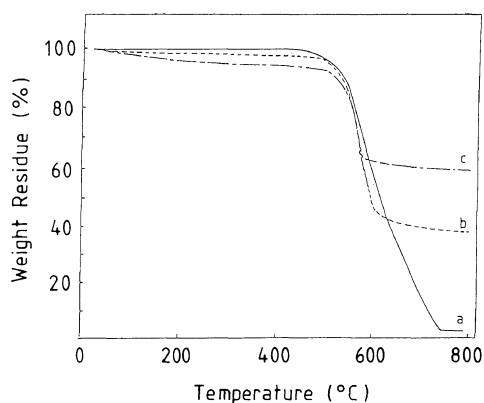


Figure 6. TG curves of polyimide-silica hybrid films at a heating rate of $10^{\circ}\text{Cmin}^{-1}$ in air. (a), (b), and (c): Polyimide films containing 0, 30, and 70 wt% of silica.

had been heated at 270°C , whereas the films containing silica more than 10 wt% were opaque and yellow. Phase separation of the opaque films caused in drying process of precursor films.

The chemical structure of the matrix polymer was confirmed by means of IR spectroscopy. Figure 2 shows the IR spectra measured after the film of entry 6 (30% SiO_2) was successively heated at a) 100°C for 30 min, b) 200°C for 30 min, and c) 300°C for 30 min. The conversion of polyamic acid **3** to polyimide **4** was elucidated by decreasing the absorption of amide carbonyl at 1650 cm^{-1} and increasing the absorptions of imide carbonyl at 1720 and 1780 cm^{-1} . In addition, the appearance of two

Table II. Thermal properties of Polyimide-silica hybrid films

Entry	Silica ^a	T_d ^b	Ash ^c	M ^d	T_g ^e
	wt%	°C	%	X10 ⁹ Pa	°C
1	0	470	3	1.9	419
2	3	475	8	1.5	410
3	8	480	12	1.6	396
4	13	477	17	2.2	403
5	22	478	26	2.0	405
6	30	492	35	1.2	412
7	46	510	49	2.2	425
8	56	513	49	4.4	412
9	63	515	58	3.0	430
10	70	505	57	6.0	419

^a Calculated silica content in hybrid films.

^b Decomposition temperature determined by TG in air at a heating rate of 10°C min⁻¹.

^c Residual ash at 800°C.

^d Storage modulus at 100°C.

^e Determined by DMA at a heating rate of 2°C min⁻¹ at 10 Hz.

absorptions at 1100 cm⁻¹ and 830 cm⁻¹ meant the formation of silicon-oxygen bonds.

As observed in the solid state ²⁹Si NMR spectrum measured with polydimethylsilane (-34 ppm) as the external standard (Figure 3), the silica in the present hybrid film had three kinds of silicon species, *i.e.*, non-hydroxy, monohydroxy, and dihydroxy species, however, which suggest that formation of developed silica-oxygen network structure like silica glass was incomplete.

The density of the hybrid films increased with increasing the silica content as shown in Figure 4. The density of silica was estimated to be 1.65 g cm⁻³ by extrapolation of the curve. This value was smaller than that of the usual silica glass (2.22 g cm⁻³). It also suggests incompleteness of polycondensation to form silica structure.

The scanning electron microscopic (SEM) photographs of the fracture surface of the hybrid films are shown in Figure 5. The dispersed silica particles could be seen as white beads having a diameter of 3–7 μm. The particle size increased with increasing the silica

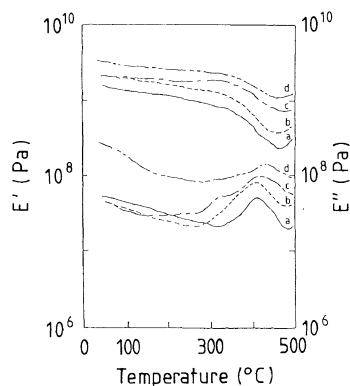


Figure 7. DMA curves of polyimide-silica hybrid films. (a), (b), (c), and (d): polyimide films containing 0, 8, 30, and 63 wt% of silica.

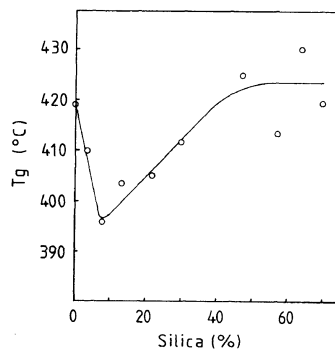


Figure 8. Relationship between T_g and content of silica in polyimide-silica hybrid films.

content.

Figure 6 shows the typical thermogravimetric curves of the hybrid films in air. The results are summarized in Table II. The decomposition temperature increased slightly with increasing silica content, and the weight residue at 800°C was almost proportional to the silica content. The dynamic mechanical behavior of the hybrid films indicated that higher silica content films exhibited higher values of storage modulus (Figure 7). The glass transition temperatures (T_g) determined by the peak temperature of the loss modulus curves are summarized in Table II. The relationship between the T_g and silica content is also shown in Figure 8. The hybrid films with lower silica

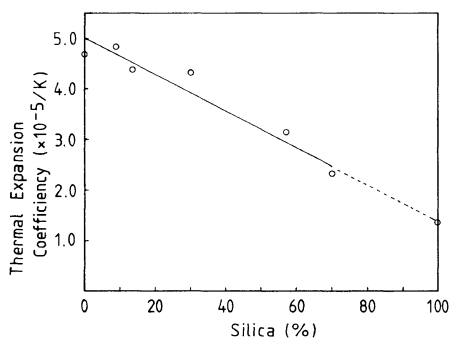


Figure 9. Relationship between thermal expansion coefficient and content of silica in polyimide-silica hybrid films.

content exhibited lower T_g than that of the original polyimide film, showing the minimum in entry 3. These phenomena may be explained by existence of low T_g substance which was compatible with polyimide matrix. Assuming that TEOS was polymerized incompletely in the polymer matrix under the low TEOS concentration, transparency of the films as well as the T_g behavior in entries 2 and 3 could be explained by the compatibility of the polyimide matrix with low molecular weight silica, which might make lower the T_g . Even in the films of entries 4, 5, and 6 in which the phase separated structure could be observed by the SEM photograph, the low molecular weight silica existed in the polyimide matrix.

Figure 9 shows the relationship between linear thermal expansion coefficient (TEC) and silica content. The TEC of silica in the hybrid films was estimated to be $1.3 \times 10^{-5} \text{ K}^{-1}$ by extrapolation of the straight line. Since the TEC of usual silica glass is known to be $5.5 \times 10^{-7} \text{ K}^{-1}$, the TEC of the present silica was larger in two orders.

Typical stress-strain curves of the hybrid films are shown in Figure 10. Although the modulus of the films increased with increasing the silica content, the tensile strength and elongation at break decreased in this order. This phenomenon was probably explained by the incorporation of the large size silica particles.

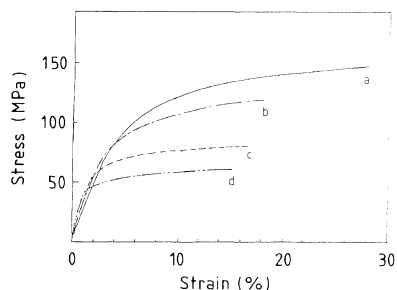


Figure 10. Stress-strain curves of polyimide-silica hybrid films. (a), (b), (c), and (d): polyimide films containing 0, 22, 30, and 46 wt% of silica.

In conclusion, polyimides-silica hybrid films, which were fairly flexible even in the case of 70 wt% of silica content, were successfully prepared by the sol-gel reaction starting from TEOS in the polyamic acid solution. Thus, the sol-gel process is very useful to prepare new high temperature polymer-inorganic hybrid materials.

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