Polyimide-Silica Hybrid Materials Based on *p*-Aminophenyltrimethoxysilane Terminated Poly(amic acid)s

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ABSTRACT: Polyimide-silica hybrid materials with covalently bound phases were prepared *via* a sol-gel process. The starting materials were *p*-aminophenyltrimethoxysilane terminated poly(amic acid)s of controlled molecular weight ranging from 5000 to 10000 g mol⁻¹ and tetramethoxysilane. Optical transparency of the final films increases with the number of bonds between phases. The dependence of the thermal and mechanical properties and morphology on the silica content and/or concentration of bonds between phases were studied.

KEY WORDS Poly(amic acid) / Polyimide-Silica Hybrid Materials / Sol-Gel Process /

Aromatic polyimides (PI) (Figure 1) exhibit outstanding dielectric and mechanical properties at elevated temperatures.¹

Nevertheless, relatively high values of water sorption (up to 3–4 wt%) and coefficients of thermal expansion ($\sim 5 \times 10^{-5} \text{ K}^{-1}$) impede (micro)electronic applications, *e.g.*, forming stress-free films on silicon substrates.² From this point of view silica (SiO₂), that exhibits very low values of water sorption (close to 0 wt%) and coefficients of thermal expansion ($\sim 5 \times 10^{-7} \text{ K}^{-1}$), would be more suited for (micro)electronic applications but dielectric properties and planarizability are inferior to polyimides.

Combined materials exhibiting favourable properties of both polyimides and silica are therefore in great demand. However, a classical combination of these materials (filling, composites) leads to heterogeneous products not applicable to some purposes (*e.g.*, optoelectronics).

In recent years increased attention has been paid to the preparation of highly homogeneous organic-inorganic hybrid materials *via* the sol-gel method. This

procedure has also been utilized for the preparation of polyimide-silica hybrid materials.

The most direct route to these materials is hydrolysis and condensation of tetraalkoxysilane in a solution of a polyimide precursor [poly(amic acid) (Figure 1)] in *N*-methyl-2-pyrrolidone or *N,N*-dimethylacetamide followed by thermal treatment.³ Due to the apparent macrophase separation, the resulting films with silica content of 5–8 wt% and above were found to be opaque and exhibit poorer mechanical properties compared to those of pure polyimides. Using the poly(amic acid) trimethylamine salt in methanol as the starting material the point of incipient opacity of the resulting films shifted to a higher level.⁴

Morikawa *et al.*⁵ prepared transparent films with high content of silica (up to 70 wt%) by introducing into the polymer backbone ethoxysilyl groups which act as bonding sites for the silica. However, this is complicated and difficult to apply to large-scale production. In the work⁶ *p*-aminophenyltrimethoxysilane was added into a solution of poly(amic acid) in *N,N*-dimethylacetamide.

Figure 1. Synthesis of polyimides.

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Figure 2. *p*-Aminophenyltrimethoxysilane terminated poly(amic acid) used in this study.

The compound undergoes hydrolysis and polycondensation along with tetraalkoxysilane while its amino groups react at high temperatures with the carboxylic acid groups in the poly(amic acid). However, the transformation of poly(amic acid) to polyimides is not complete and the properties may be inferior to those of fully imidized polyimides.

We suggest preparing polyimide-silica hybrid materials with covalently bound phases based on poly(amic acid)s terminated with commercially available *p*-aminophenyltrimethoxysilane⁷ (Figure 2). The controlled (defined) molecular weights of poly(amic acid)s govern the concentration of the bonds. In the present work we focus attention on the characterization of these materials.

EXPERIMENTAL

3,3'-Oxydiphthalic anhydride (ODPA) (Chriskev) was heated to 180°C overnight in a vacuum before use. 4,4'-Diaminodiphenylether (ODA) (Aldrich) was used as received. Tetramethoxysilane (TMOS) and *p*-aminophenyltrimethoxysilane (APTMS) (both ABCR) were used without further purification. *N*-Methyl-2-pyrrolidone (NMP) (Merck) was distilled under vacuum over phosphorus pentoxide and stored in an inert atmosphere.

p-Aminophenyltrimethoxysilane terminated poly(amic acid)s were prepared in a 250 ml three-necked flask equipped with a mechanical stirrer, nitrogen inlet, and condenser with a drying tube.

A typical example of the synthesis of terminated poly(amic acid) of this type (with theoretical molecular weight $M_n = 5000 \text{ g mol}^{-1}$) is as follows:

5 g (0.01612 mol) ODPA was dissolved in 55.3 ml NMP and 0.7353 g (0.00345 mol) of the endcapping agent (APTMS) was added (the weighing dish+funnel was rinsed with 10 ml NMP) to the reaction mixture and allowed to react with ODPA for 2 hours. 2.8823 g (0.01439 mol) ODA were then added (10 ml NMP used for rinsing) and the reaction was allowed to proceed at room temperature for 24 hours.

A calculated amount of tetramethoxysilane (TMOS) (to reach the desired silica content) was added directly to a 10 wt% solution of PAA in NMP under stirring. A stoichiometric amount of water per methoxy groups of TMOS was then added. The resulting homogeneous solution was poured onto a Teflon dish. After drying at 60°C for 24 hours, the film was heated 2 hours at 125°C,

Table I. Transparent/opaque character of the prepared hybrid films

$M_{n,theor}^a$ g mol ⁻¹	Silica content/wt%				
	10	20	30	40	50
5000	T ^b	T	T	T	O ^c
7500	T	T	O	O	O
10000	T	O	O	O	O

^a Theoretical molecular weight of *p*-aminophenyltrimethoxysilane terminated poly(amic acid). ^b Transparent. ^c Opaque.

2 hours at 200°C and, finally 5 hours at 300°C.

The density of the prepared films was determined by a pycnometer. IR spectra were taken with a NICOLET 740 spectrometer. Dynamic thermogravimetric measurements were performed in air with a Du Pont 990 Thermal Analyzer, module 951 (heating rate 5, 10, and 20°C min⁻¹, respectively), and DSC measurements with a Du Pont 2000 Thermal Analyzer, module 910 (5°C min⁻¹). Tensile properties were measured with Instron 1122 at room temperature at drawing rate of 20 mm min⁻¹. Film specimens about 50 μm thick were measured. Scanning electron micrographs (SEM) were taken on crosssections of the films covered with a thin gold layer using a JOEL 100 B (scanning mode) electron microscope.

RESULTS AND DISCUSSION

The most reactive tetraalkoxysilane—tetramethoxysilane (TMOS)—was used as the starting material for the non-catalyzed sol-gel process. The silica content in the hybrid materials was calculated assuming,

proceeded to completion.

Our experiments showed that *p*-aminophenyltrimethoxysilane terminated ODPA-ODA poly(amic acid)s (Figure 2) with molecular weight M_n lower than 10000 g mol⁻¹ are suitable for preparing transparent hybrid materials with silica content higher than 10 wt%. The optical transparency of the prepared products is given in Table I. This property improves with increasing concentration of bonds between phases. Hybrid films with silica content of 50 wt% and more were opaque but

still showed self standing.

Thermogravimetry and density measurements (quantitatively) and IR spectroscopy (qualitatively) show thermal treatment (final phase 5 h/300°C) not to be sufficient to complete the sol-gel reactions. It is apparent that prolonged heating at higher temperatures after moderate drying (see Experimental section) reduces the amounts of volatiles escaping below the decomposition temperature of the hybrid materials. Samples treated at 300°C for 5 hours contained less than 5 wt% of such volatiles. From the extrapolated dependence of the density of hybrid materials on the silica content, the density of silica was found to be about 2 g cm^{-3} (theoretically it should be 2.2 g cm^{-3}). The absorbance of the Si-O-Si asymmetric stretching vibration at $1013\text{--}1018 \text{ cm}^{-1}$ becomes more intensive during heating, while the absorbance of the Si-OH stretching vibration at $930\text{--}940 \text{ cm}^{-1}$ becomes weaker but it does not disappear fully.

The activation energies of 5 wt% thermooxidative degradation of the hybrid materials increased slightly with silica content (Table II). The residual ash (after $20\text{--}800^\circ\text{C}$ thermal exposition) was almost proportional to inorganic content. The glass transition temperature (T_g) of these samples were nearly constant up to 30 wt% silica content. The restricted movement of the polyimide

chains at the higher silica amounts was reflected in the rise in T_g (Table II).

The tensile strength and elongation at break of the hybrid films decreased with increasing silica content and the tensile modulus increased slightly (Table II).

Thermal and mechanical properties were influenced by the concentration of the bonds between phases insignificantly (for hybrid films based on poly(amic acid)s with $M_n = 5000$ and 7500 g mol^{-1} at the same content of silica).

Scanning electron micrographs of the hybrid films are shown in Figures 3a–c. A reasonably good adhesive

Table II. Thermal and mechanical properties of polyimide-silica hybrid materials (prepared from poly(amic acid) with $M_n = 5000 \text{ g mol}^{-1}$)

	Silica content/wt%					
	0	10	20	30	40	50
$E_A^a/\text{kJ mol}^{-1}$	110	156	193	215	230	240
$T_g^b/^\circ\text{C}$	190	192	188	194	219	225
Tensile strength/MPa	120 ^c	118	51	46	—	—
Elongation at break/%	8, 9 ^c	6, 7	2, 6	2, 3	—	—
Tensile modulus/GPa	2, 1 ^c	2, 4	2, 4	2, 6	—	—

^a Activation energy. ^b Glass transition temperature. ^c ODPA-ODA polyimide with uncontrolled molecular weight.

(a)

(b)

(c)

Figure 3. Scanning electron microscopic photographs of the polyimide-silica hybrid films based on: (a) *p*-aminophenyltrimethoxysilane terminated poly(amic acid) with $M_n = 5000 \text{ g mol}^{-1}$ and a silica content of 10 wt% (bar = $1 \mu\text{m}$); (b) *p*-aminophenyltrimethoxysilane terminated poly(amic acid) with $M_n = 5000 \text{ g mol}^{-1}$ and a silica content of 30 wt% (bar = $1 \mu\text{m}$); (c) poly(amic acid) with uncontrolled M_n at silica content of 10 wt% (bar = $1 \mu\text{m}$).

interface between the polyimide and silica phase (particles with diameter $0.1\ \mu\text{m}$) was observed in the hybrid films based on the terminated poly(amic acid) with $M_n = 5000\ \text{g mol}^{-1}$ (Figures 3a, b). Silica particles with diameter of $0.75\text{--}1\ \mu\text{m}$ were evidently separated from the polyimide matrix when no bonds were formed between the phases (Figure 3c).

A detailed study of the thermal expansion coefficient and water sorption of these hybrid materials is to be made.

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