Reactive & Functional Polymers 71 (2011) 85-94



Reactive & Functional Polymers

journal homepage: www.elsevier.com/locate/react

Preparation and properties of polyimide–silica hybrid films with conjugation of the polyimide and silica by a sol–gel process using 3-(triethoxysilyl)propyl succinic anhydride

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ARTICLE INFO

Article history: Received 21 September 2010 Received in revised form 10 November 2010 Accepted 11 November 2010 Available online 16 November 2010

Keywords: Polyimide-silica hybrid Sol-gel reaction A₂A'-type tri-functional amine 3-(Triethoxysilyl)propyl succinic anhydride Conjugation site

ABSTRACT

New polyimide–silica hybrid materials were prepared using the polyamic acid synthesized by copolymerization of 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA), 4,4'-oxydianiline (ODA) and an A₂A'-type tri-functional amine, 1,1-bis(4-(aminophenoxy)phenyl)-1-(4-(4-amino-2-trifluoromethylphenoxy)phenyl)ethane (1) (BTDA:ODA:1 = 7:6:1 in the molar). 3-(Triethoxysilyl)propyl succinic anhydride(TESSA) was reacted with amino groups in polyamic acid to introduce ethoxysilyl moiety which act as conjugation site for silica. The polyimide–silica hybrid films were prepared by a sol–gel reaction of tetraethoxysilane (TEOS) in a solution of the polyamic acid, followed by thermal imidation. Self-standing films were obtained with up to 50 wt.% silica, and transparent films were obtained at up to 40 wt.% silica. Dynamic-mechanical and mechanical analyses were carried out to examine the properties of hybrid films.

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1. Introduction

Polyimides are known to be reliable at high temperature polymers that exhibit superior mechanical and electrical properties [1]. Because of these excellent characteristic, polyimide have been used in aerospace, electronic and high-tech industries [2,3].

Organic-inorganic hybrids are attractive materials because they generally possess desirable characteristics that are associated with organic and inorganic compounds, such as heat, mechanical and electrical advantage. In particular, thermal stability of organic compound is enhanced through the incorporation of inorganic moiety in the hybrid material. In this regard, hybridizations of organic materials with inorganic compounds have also focused on the modification of polyimides to improve their properties [4-11]. One attractive method for hybridization with inorganic compounds is the sol-gel process [12-15]. Polyimide-silica hybrid materials were prepared by the hydrolysis and polycondensation of tetraalkoxysilane in a polyamic acid solution, followed by thermal treatment [16-23]. Preparation using polyamic acids without conjugation for silica, resulted in films with high silica content that were opaque due to the phase separation; additionally, these hybrid films exhibited poorer mechanical properties relative to pristine polyimide [18]. Transparent and tough hybrid films with high silica contents were prepared by a sol-gel reaction using polyamic acids with the alkoxysilyl group, which acted as conjugation site for silica [16,17,19,22,23]. These polyamic acids with the alkoxysilyl groups were prepared by the reaction of diamines having alkoxysilyl groups with dianhydrides and the reaction of polyamic acid with commercially available coupling agents. As the synthesis of diamines having ethoxysilyl group is complicated due to the necessity of multi-step reactions [19], polyamic acids having the alkoxysilyl group have been more frequently prepared with commercially available coupling agents, such as 3-aminopropyltrimethoxysilane(APrTMS), 3-aminopropyltriethoxysilane(APrTEOS) and *p*-aminophenyltrimethoxysilane(APTMS) [16,17,22,23]. The polyimide-silica hybrid materials with conjugation between the polyimide and the silica were prepared by a sol-gel reaction in a solution of polyamic acid terminated with APTMS and APrTEOS [16,17] and hyperbranched polyamic acid modified with APrTEOS [22,23].

In this study, polyimide–silica hybrid films were prepared using polyamic acid from BTDA, ODA and the A_2A' -type tri-functional amine 1 (BTDA:ODA:1 = 7:6:1 in the molar). As the ratio between anhydride and amino groups in the monomers was 14/15, free amino groups existed in the polyamic acids. The A_2A' -type tri-functional amine 1 was used to avoid gelation during polycondensation. Triethoxysilyl groups, which acted as conjugation site for silica, were introduced into the polyamic acid by reaction of the amino groups with TESSA. Polyimide–silica hybrid films were prepared by a sol–gel reaction with TEOS in the polyamic acid solution, and by heating the resulting film at 300 °C. The polyimide





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^{1381-5148/\$ -} see front matter @ 2010 Elsevier Ltd. All rights reserved. doi:10.1016/j.reactfunctpolym.2010.11.015

based on BTDA–ODA has five carbonyl groups in the repeating units, and was thought to be suitable for hybridization with hydrophilic silica.

2. Experimental

2.1. Materials

1,1,1-tris(4-hydroxyphenly)ethane (2), 4-fluoro-nitrobenzene (3) and 2-fluoro-5-nitrobenzotrifluoride (5) were purchased from Tokyo Kasei Kogyo and used without purification. TESSA was purchased from AZmax Co., and used without purification. Potassium carbonate, *N*,*N*-dimethylformamide (DMF) and *N*-Methyl-2-pyrrolidone (NMP) were purchased from Kanto Kagaku Co., (Japan). Potassium carbonate and DMF were used without purification and NMP was purified by vacuum distillation over calcium hydride. BTDA and ODA were obtained commercially and purified by sublimation under reduced pressure. Tetrahydrofuran, ethanol and tetraethoxysilane (TEOS) were purchased from Kanto Kagaku Co., (Japan) and used without purification.

2.2. Monomer synthesis

2.2.1. 1,1-bis[4-(4-nitrophenoxy)phenyl]-1-(4-hydroxyphenyl)ethane (4)

In a flask, a mixture of 12.25 g (40 mmol) of 1,1,1-tris(4-hydroxyphenly)ethane (2), 11.29 g (80 mmol) of *p*-fluoronitrobenzene (3), 11.04 g (80 mmol) of potassium carbonate, and 150 ml of DMF was stirred at 130 °C for 12 h. The reaction mixture was cooled to 80 °C, and the solvent was evaporated under a reduced pressure of 15– 25 torr. After 250 ml of water was added to the residue, the mixture was extracted twice with 200 ml of dichloromethane. The combined extract was dried over anhydrous magnesium sulfate, and the solvent was evaporated. After the residue was purified by silica gel chromatography with dichloromethane as the eluent, pure **4** was obtained as an amorphous compound. Yield: 9.87 g (45%).

The IR spectrum exhibited absorption bands at 3650– 3150 cm^{-1} (OH), 1520 cm^{-1} (NO₂), 1340 cm^{-1} (NO₂) and 1250 cm^{-1} (Ar–O–Ar).



The ¹H NMR spectrum [δ in CDCl₃] showed signals at 2.21 (s, 3H, CH₃-), 6.71 (d, 2H, *J* = 8.4 Hz, 6), 6.95 (d, 2H, *J* = 8.4 Hz, 5), 7.00 (d, 2H, *J* = 8.8 Hz, 2), 7.04 (d, 4H, *J* = 8.8 Hz, 3), 7.16 (4H, *J* = 8.8 Hz, 4) and 8.21 (d, 4H, *J* = 8.8 Hz, 1) ppm. The ¹³C NMR spectrum [δ in CDCl₃] showed signals at 30.78, 51.22, 114.20, 117.06, 119.90, 125.80, 127.34, 130.26, 136.80, 140.55, 146.07, 152.68, 157.07 and 162.98 ppm.

Anal. Calcd for $C_{32}H_{24}N_2O_7$: C, 70.07%; H, 4.41%; N, 5.11%. Found: C, 69.82%; H, 4.67%; N, 4.95%.

2.2.2. 1,1-bis(4-(nitrophenoxy)phenyl)-1-(4-(4-nitro-2-trifluoromethylphenoxy)phenyl)ethane(6)

In a flask, a mixture of 8.23 g (15 mmol) of **4**, 3.14 g (15 mmol) of 2-fluoro-5nitrobenzotrifluoride (5), 2.07 g (15 mmol) of potassium carbonate, and 80 ml of DMF was stirred at 130 °C for 12 h. The reaction mixture was cooled to 80 °C, and the solvent was

evaporated under a reduced pressure of 15–25 torr. After 150 ml of water was added to the residue, the mixture was extracted twice with 160 ml of dichloromethane. The combined extract was dried over anhydrous magnesium sulfate, and the solvent was evaporated. After the residue was purified by silica gel chromatography with dichloromethane as the eluent, pure **6** was obtained as an amorphous compound. Yield: 9.40 g (85%).

The IR spectrum exhibited absorption bands at $1520\ cm^{-1}$ (NO_2), $1340\ cm^{-1}$ (NO_2), $1250\ cm^{-1}$ (Ar–O–Ar) and $1210\ cm^{-1}$ (C–F).



The ¹H NMR spectrum [δ in CDCl₃] showed signals at 2.21 (s, 3H, CH₃-), 7.02 (d, 1H, *J* = 8.8 Hz, 7), 7.04 (d, 4H, *J* = 8.8 Hz, 3), 7.05 (d, 4H, *J* = 8.8 Hz, 2 and 6), 7.18 (d, 2H, *J* = 8.8 Hz, 4), 7.23 (d, 4H, *J* = 8.8 Hz, 5), 8.20 (d, 4H, *J* = 8.8 Hz, 1), 8.30 (dd, 4H, *J* = 8.8 Hz, *J* = 2.1 Hz, 8), and 8.60 (d, 4H, *J* = 2.1 Hz, 9) ppm. The ¹³C NMR spectrum [δ in CDCl₃] showed signals at 30.78, 51.21, 114.21, 117.06, 119.80, 119.90, 121.40 (q, *J* = 273 Hz), 123.26 (q, *J* = 33.5 Hz), 124.13 (q, *J* = 4.8 Hz), 125.82, 127.33, 129.08, 130.28, 136.80, 140.55, 143.88, 146.09, 152.70, 157.08, 157.09 and 162.96 ppm.

Anal. Calcd for $C_{39}H_{26}N_3O_9F_3$: C, 63.50%; H, 3.55%; N, 5.70%. Found: C, 63.31%; H, 3.61%; N, 5.58%.

2.2.3. 1,1-bis(4-(aminophenoxy)phenyl)-1-(4-(4-amino-2trifluoromethylphenoxy)phenyl)ethane (1)

A mixture of 7.38 g (10 mmol) of **6** and 0.3 g of 10% Pd/C in 60 ml of tetrahydrofuran and 40 ml of ethanol was stirred at room temperature for 15 h under a hydrogen atmosphere. After the Pd/C was removed by filtration, the solvent was evaporated under a reduced pressure of 15–20 torr. After the residue was purified by silica gel chromatography with dichloromethane as the eluent, pure **1** was obtained as an amorphous compound. Yield: 5.96 g (92%).

The IR spectrum exhibited absorption bands at 3460 cm^{-1} (NH₂), 3370 cm^{-1} (NH₂), 1230 cm^{-1} (Ar–O–Ar) and 1210 cm^{-1} .



The ¹H NMR spectrum [δ in DMSO-*d*6] showed signals at 2.20 (s, 3H, CH₃-), 4.95 (broad s, 4H, -NH₂), 5.41 (broad s, 2H, -NH₂), 6.57 (d, 4H, *J* = 8.8 Hz, 1), 6.75 (d, 4H, *J* = 8.8 Hz, 2), 6.76 (d, 4H, *J* = 8.8 Hz, 3), 6.78 (d, 4H, *J* = 8.8 Hz, 6), 6.80 (dd, 1H, *J* = 8.8 Hz, *J* = 2.9 Hz, 8), 6.87 (d, 1H, *J* = 8.8 Hz, 7), 6.90 (d, 1H, *J* = 2.9 Hz, 9), 6.94 (d, 4H, *J* = 8.8 Hz, 4) and 6.97 (d, 2H, *J* = 8.8 Hz, 5) ppm. The ¹³C NMR spectrum [δ in DMSO-*d*6] showed signals at 30.86,

50.74, 100.08, 112.89 (q, *J* = 4.8 Hz), 114.46, 116.18, 119.12, 120.49, 121.15, 121.96 (q, *J* = 33.5 Hz), 123.04 (q, *J* = 272.5 Hz), 129.61, 129.77, 141.60, 141.82, 142.47, 142.96, 145.68, 145.88, 153.44 and 156.76 ppm.

Anal. Calcd for $C_{39}H_{32}N_3O_3F_3$: C, 72.32%; H, 4.98%; N, 6.49%. Found: C, 72.08%; H, 5.10%; N, 6.34%.

2.2.4. 1,1,1-tris[4-(4-nitrophenoxy)phenyl]ethane(7)

In a flask, a mixture of 3.06 g (10 mmol) of 1,1,1-tris(4-hydroxyphenly)ethane (2), 4.23 g (30 mmol) of *p*-fluoronitrobenzene (3), 4.14 g (30 mmol) of potassium carbonate and 100 ml of DMF was stirred at 130 °C for 12 h. The reaction mixture was cooled to 80 °C, and the solvent was evaporated under a reduced pressure of 15–25 torr. After 150 ml of water was added to the residue, the mixture was extracted twice with 100 ml of dichloromethane. The combined extract was dried over anhydrous magnesium sulfate, and the solvent was evaporated. Pure **7** was obtained by crystallization from acetic acid. Yield: 5.94 g (82%).

The IR spectrum exhibited absorption bands at 1520 cm^{-1} (NO₂), 1340 cm^{-1} (NO₂) and 1250 cm^{-1} (Ar–O–Ar).



The ¹H NMR spectrum [δ in CDCl₃] showed signals at 2.21 (s, 3H, CH₃-), 7.03 (d, 6H, *J* = 8.8 Hz, 3), 7.06 (d, 6H, *J* = 8.8 Hz, 3), 7.19 (6H, *J* = 8.8 Hz, 4) and 8.22 (d, 6H, *J* = 8.8 Hz, 1) ppm. The ¹³C NMR spectrum [δ in CDCl₃] showed signals at 30.78, 51.22, 117.03, 119.90, 125.78, 130.24, 142.55, 146.07, 152.65, and 162.96 ppm.

Anal. Calcd for $C_{38}H_{27}N_3O_9$: C, 68.16%; H, 4.06%; N, 6.28%. Found: C, 68.01%; H, 3.95%; N, 6.12%.

2.2.5. 1,1, 1-tris(4-(aminophenoxy)phenyl)ethane (8)

A mixture of 5.36 g (8 mmol) of **7** and 0.3 g of 10% Pd/C in 40 ml of tetrahydrofuran and 27 ml of ethanol was stirred at room temperature for 15 h under a hydrogen atmosphere. After the Pd/C was removed by filtration, the solvent was evaporated under reduced pressure of 15–20 torr. Pure **1** was obtained by crystallization from toluene. Yield: 3.85 g (83%).

The IR spectrum exhibited absorption bands at 3460 cm^{-1} (NH₂), 3370 cm^{-1} (NH₂) and 1230 cm^{-1} (Ar–O–Ar).



The ¹H NMR spectrum [δ in DMSO-*d*6] showed signals at 2.20 (s, 3H, CH₃-), 4.95 (broad s, 6H, -NH₂), 6.57 (d, 6H, *J* = 8.8 Hz, 1), 6.75

(d, 12H, *J* = 8.8 Hz, 2 and 3) and 6.94 (d, 4H, *J* = 8.8 Hz, 4) ppm. The ¹³C NMR spectrum [δ in DMSO-*d*6] showed signals at 30.84, 50.72, 100.08, 114.45, 116.20, 121.14, 129.62, 141.81, 145.84 and 156.73 ppm.

Anal. Calcd for $C_{38}H_{33}N_3O_3$: C, 78.73%; H, 5.74%; N, 7.25%. Found: C, 78.55%; H, 5.61%; N, 7.17%.

2.3. Preparation of polyimide-silica hybrid films

In a three necked flask, 0.563 g (1.75 mmol) of **BTDA** was added to a solution of 0.161 g (0.25 mmol) of **1** and 0.300 g (1.5 mmol) of ODA in 15.0 ml of NMP at 0 °C. The mixture was stirred at 0 °C for 6 h under nitrogen until a viscous solution of polyamic acid formed. The inherent viscosity was approximately 0.95 dlg⁻¹.

A polyimide–silica hybrid film containing 20 wt.% silica is described below. To the polyamic acid solution, 0.076 g (0.25 mmol) of TESSA was added and stirred at room temperature for 1 h. Subsequently, 0.861 g (4.14 mmol) of TEOS and 0.312 g (17.3 mmol) of water were added to the polyamic acid solution, which was stirred at room temperature until the mixture was homogeneous (\sim 1 h). After stirring the resulting homogeneous solution for an additional 24 h, the solution was cast onto a glass plate and dried at 80 °C. The thermal cyclodehydration of the polyamic acid was performed by successive heating 100 °C for 1 h, 200 °C for 1 h and 300 °C for 1 h under vacuum.

IR spectrum exhibited absorption bands at 1780 cm⁻¹ (C=O), 1720 cm⁻¹ (C=O), 1375 cm⁻¹ (C–N), 1100–1000 cm⁻¹ (Si–O) and 830 cm⁻¹ (Si–O).

2.4. Measurement

¹H and ¹³C NMR were recorded on a JNM-GSX400 FT NMR spectrometer, and IR spectra were recorded on a SHIMADZU spectrophotometer IR 435. For thermogravimetry (TG), a Rigaku thermal analysis station TG 8110 was used and measurements were made at a heating rate of 10 °C min⁻¹ in air. Scanning electron microscopy (SEM) studies were performed using a JEOL JSM-5600LV. Fractured surfaces of hybrid films were fixed by carbon tape, and





Scheme 1. Synthesis of polyamic acid from tri-functional amine.

sputter-coated with Au under an electric current of 20 mA at 6 Pa for 60 s. Dynamic mechanical analysis (DMA) was performed with the Advanced Rheometric Expansion System at 1.0 Hz at 5 °C min⁻¹. Mechanical properties were measured with Shimadzu AUTOGRAPH at a strain rate 10% min⁻¹.

3. Results and discussion

3.1. Synthesis of A_2A' -type tri-functional amine (1)

1,1-bis(4-(aminophenoxy)phenyl)-1-(4-(4-amino-2-trifluoromethylphenoxy)phenyl)ethane (1), an A_2A' -type tri-functional amine, was synthesized in three steps from 1,1,1-tris(4-hydroxyphenyl)ethane (2). The reaction of 2 with 4-fluoronitrobenzene (3) yielded 1,1-bis[4-(4-nitrophenoxy)phenyl]-1-(4-hydroxyphenyl) ethane (4), and the subsequent reaction of 4 with 2-fluoro-5nitrobenzotrifluoride (5) afforded 1,1-bis(4-(nitrophenoxy)phenyl)-1-(4-(4-nitro-2-trifluoromethylphenoxy)phenyl)ethane (6). 1 was obtained by the hydrogenation of 6 using Pd/C as a catalyst.

Chemical structures were confirmed by IR and NMR spectra. Compound 1 showed IR absorption at 3380 cm⁻¹ and 3360 cm⁻¹, characteristic of amino groups and 1340 cm⁻¹, which was characteristic of trifluoromethyl groups. The ¹H NMR spectrum of 1 was assigned in Fig. 1. The signal of protons in amino group A2 was observed in downfield (5.41 ppm) of that of A1 (4.95 ppm). The signals of protons H8 and H9 on the ortho-position of the amino group A2 were also observed in downfield (6.80 ppm and 6.90 ppm, respectively) of those of H1 on the ortho-position of amino group A1 (6.57 ppm). The effect of the electron withdrawing trifluoromethyl group caused the differences in these chemical shifts in ¹H NMR spectrum.

In the ¹³C NMR spectrum, spin–spin coupling with fluorine atoms was observed, and the signals were complicated. However, the signals were classified into 21 groups, all of which indicate the formation of the postulated diamine.

3.2. Synthesis of polyamic acid using A_2A' -type tri-functional amine (1)

Polycondensation using tri-functional compounds yields polymers with a greater ratio of cross-linking units if the reactivity of the functional groups is equal. In such a polycondensation reaction, the polymer solution shows large inherent viscosity and eventually undergoes gelation. Hence, the preparation of hybrid materials from such a solution is difficult. The amino group A2 was expected



Scheme 2. Preparation of polyimide-silica hybrid films.

to react slower with anhydride than amine A1 in polycondensation due to the electron-withdrawing effect of the trifluoromethyl group on amino group A2, leading to reduction of the formation of cross-linking sites.

Table 1
Preparation of polyimide-silica hybrid films.

Code	Polyamic acid/g	TESSA/g (mmol)	H ₂ O/g (mmol)	TEOS/g (mmol)	Silica/wt.%	Remarks
PI	16.0	-	-	-	-	Т
PIS-0	16.0	0.0761 (0.25)	0.0135 (0.75)	-	-	Т
PIS-10	16.0	0.0761 (0.25)	0.146 (8.12)	0.383 (1.84)	10	Т
PIS-20	16.0	0.0761 (0.25)	0.312 (17.3)	0.861 (4.14)	20	Т
PIS-30	16.0	0.0761 (0.25)	0.525 (29.2)	1.477 (7.10)	30	Т
PIS-40	16.0	0.0761 (0.25)	0.809 (44.9)	2.297 (11.0)	40	Т
PIS-50	16.0	0.0761 (0.25)	1.206 (67.0)	3.445 (16.6)	50	0
PIS-60	16.0	0.0761 (0.25)	1.800 (100)	5.169 (24.9)	60	0
PIS-20'	16.0	,	0.289 (16.0)	0.835 (4.01)	20	0

(a) 6.4 wt.% NMP solution. (b) Calculated silica content in the hybrid films. (c) T: Transparent, O: Opaque.

Polyamic acid was prepared from BTDA, ODA and 1 (BTDA:O-DA:1 = 7:6:1 M equivalents) as shown in Scheme 1. BTDA was added to a solution of ODA and 1 in NMP at 0 °C, and the solution was then stirred. The viscous polyamic acid solution was obtained without gelation. For comparison, a polyamic acid was prepared from 1,1,1-tris(4-(aminophenoxy)phenyl)ethane (8) instead of 1. Hyperbranched polyimides were reported to be prepared from an A₃-type triamine and a tetracarboxylic dianhydride without gelation [24–27]; however, gelation could not be avoided in the polycondensation using 8 when attempting to recreate those literature results.

3.3. Preparation of polyimide-silica hybrid films by sol-gel process

Polyimide–silica hybrid films were prepared as shown in Scheme 2. First, 3-(triethoxysilyl)propyl succinic anhydride was reacted with the amino group in the polyamic acid that was synthesized from 1 to introduce triethoxysilyl groups. Second, TEOS and water were added to the polyamic acid solution, which was then stirred to form a homogeneous solution. The resulting homogeneous mixture was additionally stirred for 24 h to advance the sol–gel reaction. The solution was cast onto a glass plate and dried to reach final product of silica-containing polyamic acid films. Finally, polyimide–silica hybrid films were obtained by heating the silica-containing polyamic acid films at 100 °C for 1 h, 200 °C for 1 h, and 300 °C for 1 h under vacuum. For comparison, hybrid film (PIS-20') containing 20 wt.% silica was prepared without using TESSA.

Table 1 summarizes the results of the preparation of polyimidesilica hybrid films. The silica content in the Table 1 denotes the value calculated under the assumption that the sol-gel reaction proceeded completely. Sample codes are abbreviated using silica content. For example, PIS-30 stands for the hybrid films containing 30 wt.% of silica. The hybrid films containing up to 50 wt.% silica were obtained as free standing. Fig. 2 shows UV-Vis spectra of the hybrid films. The hybrid films containing up to 40 wt.% silica showed good transparency with transmittance higher than 70% at 700 nm, while the hybrid film containing 50 wt.% silica content was opaque. The transparent-opaque barrier was approximately the same as that of the films prepared from triethoxysilane-terminated polyamic acid [16]. The film PIS-20' prepared without using TESSA was opaque, and significant improvements in the optical transparency could be achieved by the introduction of ethoxysilyl groups in the matrix polyimides.

The chemical structure of polyimide–silica hybrid film was confirmed by IR spectroscopy. Absorptions at 1780 cm⁻¹ (C=O), 1725 cm⁻¹ (C=O) and 1375 cm⁻¹ (C–N) are characteristic of imide group confirmed the formation of polyimide. In addition, absorptions at 1100–1000 cm⁻¹ (Si–O) and 830 cm⁻¹ (Si–O) were observed in PIS-20, and indicated that silica had formed the polyimide matrix. Fig. 3 shows of the thermogravimetric curves of PI and the hybrid films under an atmosphere of air. The onset of weight loss was observed at 410 °C for PI, and at approximately 395 °C for the hybrid films. As the weight loss at 440 °C was larger with increasing silica contents, and the weight loss near 395 °C in the hybrid films was thought to be due to the loss of ethanol and water by continuation of the sol–gel reaction during heating. The weight of the residues at 800 °C was almost proportional to the silica contents.



Fig. 2. UV-Vis spectra of PI, and the hybrid films (PIS-20, PIS-40, PIS-50 and PIS-20').



Fig. 3. Thermogravimetric curves of PI, and the hybrid films with various silica contents under an atmosphere of air at a heating rate of $10 \, ^\circ C/min$.



Fig. 4. SEM photograph of PI, and the hybrid films (PIS-20, PIS-40, PIS-50, PIS-60 and PIS-20').

3.4. Morphology of silica in the polyimide-silica hybrid films

PI

PIS-40

PIS-60

The fractured surfaces of the hybrid films were observed directly by SEM (Fig. 4). The fracture morphology of the hybrid films containing up to 40 wt.% silica showed smooth surfaces. In the films with larger silica contents (PIS-50 and PIS-60), spherical phases were observed as agglomerates formed by being covered with polyimide. The diameters of the particles were approximately $0.50 \pm 0.20 \,\mu\text{m}$ and $0.8 \pm 0.20 \,\mu\text{m}$ in PIS-50 and PIS-60, respectively. This result indicated that phase separation at submicrometer-scale occurred in the hybrids. Such particles were not observed in hybrid films having less than 40 wt.% silica. On the other hand,

the silica particles were clearly observed as beads having diameter 1.0–2.0 μm in the hybrid film PIS-20' that was prepared without TESSA.

3.5. Dynamic-mechanical and mechanical properties of the polyimidesilica hybrid films

Dynamic mechanical analysis (DMA) was carried out to examine the effect of the silica contents and the introduction of ethoxysilyl group on the dynamic mechanical properties of hybrid films. In tan δ curves, single peaks corresponding to the *T*g of the polyimides were observed around 280–322 °C.



Fig. 5. DMA results of PI, PIS-0, and the hybrid films (PIS-20 and PIS-20').

Fig. 5 shows DMA curves of pristine PI, PIS-0, and the hybrid films (PIS-20 and PIS-20'). The *T*g values of PI and PIS-0 were 280 °C and 320 °C, respectively. The higher *T*g of PIS-0 suggested the formation of cross-linking by sol–gel reaction among trieth-oxysilyl groups introduced in the polyimide matrix. Despite the same silica content, for PIS-20, the *T*g value was higher, the intensity of tan δ maximum was less, and the decrement in the storage modulus at the glass transition was lower than those of PIS-20'. These results indicated that the movement of polyimide chain in the hybrid films was restricted by the conjugation between the polyimide and the silica.

Fig. 6 shows DMA curves of PIS-10, PIS-20, PIS-30, PIS-4 and PIS-50. The values of the storage modulus were greater and the decrements in the storage modulus at the glass transition were lower with increasing silica content due to the increased stiffness. *Tg* values of the hybrid films were higher with increasing silica content, and the data support the hypothesis that the degree of conjugation between polyimide chains and silica increased with silica content.

The tensile properties of the hybrid films were examined, and results are summarized in Table 2. The elongation at the break decreased and the tensile modulus increased with increasing silica content. As the content of silica increased up to 40 wt.%, the tensile strength did not decreased significantly, and for PIS-40, the tensile strength and the tensile modulus were 100 MPa and 5.3 GPa, respectively. The tensile strength and the tensile modulus of PIS-20 were higher than those of PIS-20', and the conjugation between

the polyimide and the silica had an influence on the mechanical properties. The hybrid films in the present study showed higher tensile strengths and moduli than those of the films prepared from triethoxysilane-terminated polyamic acid [16] when the silica content was constant. However, PI-50 was brittle due to the phase separation.

4. Conclusions

New polyimide-silica hybrid films with conjugation of the polyimide chains and the silica particles were successfully prepared by a sol-gel process using 3-(triethoxysilyl)propyl succinic anhydride (TESSA) as the coupling agent. The polyamic acid, which contains free amino groups, was synthesized by the copolymerization of 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA), 4,4'oxydianiline (ODA) and the tri-functional amine, 1,1-bis(4-(aminophenoxy)phenyl)-1-(4-(4-amino-2-trifluoromethylphenoxy)phenyl) ethane (1) (BTDA:ODA:1 = 7:6:1 M equivalents). The A_2A' -type triamine (1) was used to avoid cross-linking during polycondensation. TESSA was reacted with the amino group in the polyamic acid to introduce ethoxysilyl moieties that allow for conjugation to silica. The polyimide-silica hybrid films were prepared by solgel reaction with tetraethoxysilane in the polyamic acid solution, and thermal imidation. The prepared hybrid films were transparent with silica contents up to 40 wt.%, whereas the hybrid films



Fig. 6. DMA results of PI, and the hybrid films (PIS-10, PIS-20, PIS-30, PIS-40 and PIS-50).

Table 2

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Code	Silica/wt.%	Strength (MPa)	Elongation at break (%)	Modulus (GPa)
PI	0	120	11	2.5
PIS-10	10	112	8	3.3
PIS-20	20	118	6.1	3.9
PIS-30	30	113	4	4.5
PIS-40	40	100	3.2	5.3
PIS-50	50	75	1.7	5.8
PIS-20′	20	95	7	3.1

prepared without TESSA, which contained 20 wt.% silica, was opaque. Agglomerates formed by polymer coverage of silica particles (0.2-1.0 µm in diameter) were observed in the hybrid films containing 50 and 60 wt.% silica by scanning electron microscopy. The glass transition temperatures (*Tg*) of polyimides in the hybrid

film was higher than that in the hybrid prepared without TESSA. The values of Tg increased with increasing silica contents in hybrid films and indicated that movement of polyimide chains were restricted by conjugation of the polyimide and silica.

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