

# Physical and mechanical properties of polyimide/titania hybrid films

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## Abstract

Titania-containing polyimide (PI) hybrid films with homogeneous and flexible properties have been fabricated via sol–gel process. Various contents of titania are added to three different PI systems by using acetylacetone to reduce the reaction rate and to prohibit gelation. The thermal, electrical and mechanical properties of the hybrid films will be measured and compared to pure PI. Results indicate that the metal-containing PI possesses lower thermal expansion and resistivity than pure PI. Incorporation of small amount of titania enhances mechanical properties of the hybrid films at both low and elevated temperature. The relationship between the effect of titania concentration, structure and properties will also be discussed.

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**Keywords:** Polymers; Titanium oxide; Metal

## 1. Introduction

Metal-containing polymers (MCPs) have been widely studied in recent years due to the unique combination of advantageous properties from each component [1–4]. Polyimide (PI) is a promising candidate for the matrix, because of its outstanding electrical, mechanical properties and high thermal stability [5–7]. Metal-containing PI was first reported by Angelo, who added organometallic complexes to several types of PI [8]. Taylor and co-workers have studied PI films containing in-situ generated metal/metal oxide particles [9–11]. The main goal of these production techniques is the formation of small aggregate and the control of their size to tailor their properties. Specific modified PI would improve their properties, such as enhanced electrical, magnetic, thermal and adhesive properties [12,13]. Because of its high refractive index, titania has been attracted much attention to be used as interference filters, antireflective coatings, protective layers and optical waveguides [14–17].

In this study, a polyamic acid (PAA) was used as a matrix, because it transforms into PI at a curing temperature that is compatible with the titania formation temperature. Three PI systems were chosen for modifi-

cation by the titania precursor. PI/metal hybrid films used in this study are listed in Table 1. The primary aim of the work reported here will attempt to describe the structure/properties relationships of metal-containing PI. The effect of titania concentration upon film properties will be demonstrated. Elevated temperature, mechanical properties and electrical data of hybrid films will also be discussed.

## 2. Experiment

### 2.1. Materials

4,4'-diaminodiphenylether (ODA, 98%) was obtained from Aldrich Chemical Co. and vacuum dried overnight at 70 °C prior to use. The monomers and modifiers used are shown in Fig. 1. 3,3',4,4'-benzophenonetetracarboxylic acid dianhydride (BTDA) which was obtained from TCI, recrystallized from acetic anhydride and vacuum dried at 120 °C for 24 h. Pyromellitic dianhydride (PMDA) and 3,3',4,4'-biphenyl tetracarboxylic dianhydride (BPDA) were obtained from TCI and Lancaster, respectively, and used as received. Dimethyl sulfoxide (DMSO) and 1-methyl-2-pyrrolidinone (NMP) were obtained from Aldrich Chemical Co. and stored over molecular sieves prior to use. The titania additive was tetraethyl orthotitanate (Ti(OEt)<sub>4</sub>), obtained from TCI.

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Table 1  
Physical, thermal and mechanical properties of PI-TiO<sub>2</sub> hybrid films

TiO <sub>2</sub> content	Color			Flexibility			CTE (ppm/K) <sup>c</sup>			T <sub>g</sub> (°C) <sup>e</sup> from tanδ			T <sub>d</sub> (°C) <sup>f</sup>			Stress (MPa) <sup>g</sup>			Elongation (%) <sup>h</sup>			Modulus (GPa) <sup>i</sup>		
	PM <sup>a</sup>	BP <sup>a</sup>	BT <sup>a</sup>	PM	BP	BT	PM	BP	BT	PM	BP	BT	PM	BP	BT	PM	BP	BT	PM	BP	BT	PM	BP	BT
0 wt.%	Yellow			C <sup>b</sup>	C	C	32.5 (52.0) <sup>c</sup>	43.4 (80.5)	45.6 (71.1)	368.1	276.1	305.4	569	590	570	129.1 (70.4)	207.9 (82.4)	134.4 (77.5)	29.4 (37.8)	39.2 (55.4)	25.2 (47.3)	2.1 (1.5)	2.9 (1.5)	2.8 (1.8)
1 wt.%	Pale brown			C	C	C	27.9 (42.5)	37.8 (68.3)	42.6 (65.4)	388.3	279.3 (397.5)	307.5 (390.1)	564	589	573	132.3 (73.1)	221.0 (110.7)	151.3 (79.1)	18.5 (12.2)	34.1 (51.6)	23.7 (31.5)	2.5 (1.7)	3.1 (1.7)	3.2 (1.8)
3 wt.%	Brown			C	C	C	20.2 (40.5)	28.6 (57.4)	38.3 (62.1)	429.4	313.4 (411.0)	312.1 (414.1)	547	585	574	103.4 (59.0)	150.7 (77.1)	150.5 (86.3)	3.2 (1.7)	16.4 (14.7)	18.4 (27.9)	2.7 (1.7)	3.2 (1.9)	3.3 (2.1)
5 wt.%	Deep brown			B <sup>b</sup>	C	C	17.3 (34.1)	24.7 (48.7)	33.7 (54.1)	<sup>d</sup>	332.41 (412.8)	327.6 (415.5)	523	566	560	39.5 (21.6)	112.0 (69.6)	118.4 (48.6)	1.4 (0.7)	2.5 (7.8)	4.5 (3.2)	2.8 (2.3)	3.5 (2.3)	3.5 (2.7)
7 wt.%	Deep brown			B	B	C	<sup>d</sup>	21.0 (45.6)	29.3 (46.3)	<sup>d</sup>	350.92 (414.2)	342.3 (416.9)	508	542	551	<sup>d</sup>	23.1 (38.2)	69.4 (45.3)	<sup>d</sup>	1.1 (1.6)	1.9 (2.3)	<sup>d</sup>	3.6 (2.4)	3.9 (3.1)
9 wt.%	Deep brown			B	B	C	<sup>d</sup>	<sup>d</sup>	26.1 (44.5)	<sup>d</sup>	<sup>d</sup>	363.4 (419.3)	490	513	530	<sup>d</sup>	<sup>d</sup>	51.2 (42.1)	<sup>d</sup>	<sup>d</sup>	1.5 (2.1)	<sup>d</sup>	<sup>d</sup>	4.2 (3.3)

<sup>a</sup>PM: PMDA/ODA; BP: BPDA/ODA; BT: BTDA/ODA.

<sup>b</sup>C is abbreviated from creasible refers to films that can be folded and creased twice in a perpendicular fashion without fracturing; B is abbreviated from bendable refers to films that can be folded but not creased without fracturing.

<sup>c</sup>The first entry was determined over a 50–200 °C range; the entry in parentheses was determined over a 200–300 °C range.

<sup>d</sup>The film was too brittle and fragile to obtain satisfactory for measurement.

<sup>e</sup>The maxima in tanδ curve obtained from DMA measurement is used as the definition of glass transition temperature.

<sup>f</sup>Temperature at which 5% weight loss recorded by thermogravimetry at a heating rate of 20 °C/min in nitrogen.

<sup>g</sup>The first entry was corresponding to load at break at 30 °C; the entry in parentheses was measured at 200 °C.

<sup>h</sup>The first entry was corresponding to elongation at a break point at 30 °C; the entry in parentheses was measured at 200 °C.

<sup>i</sup>The first entry was corresponding to initial modulus at 30 °C; the entry in parentheses was measured at 200 °C.

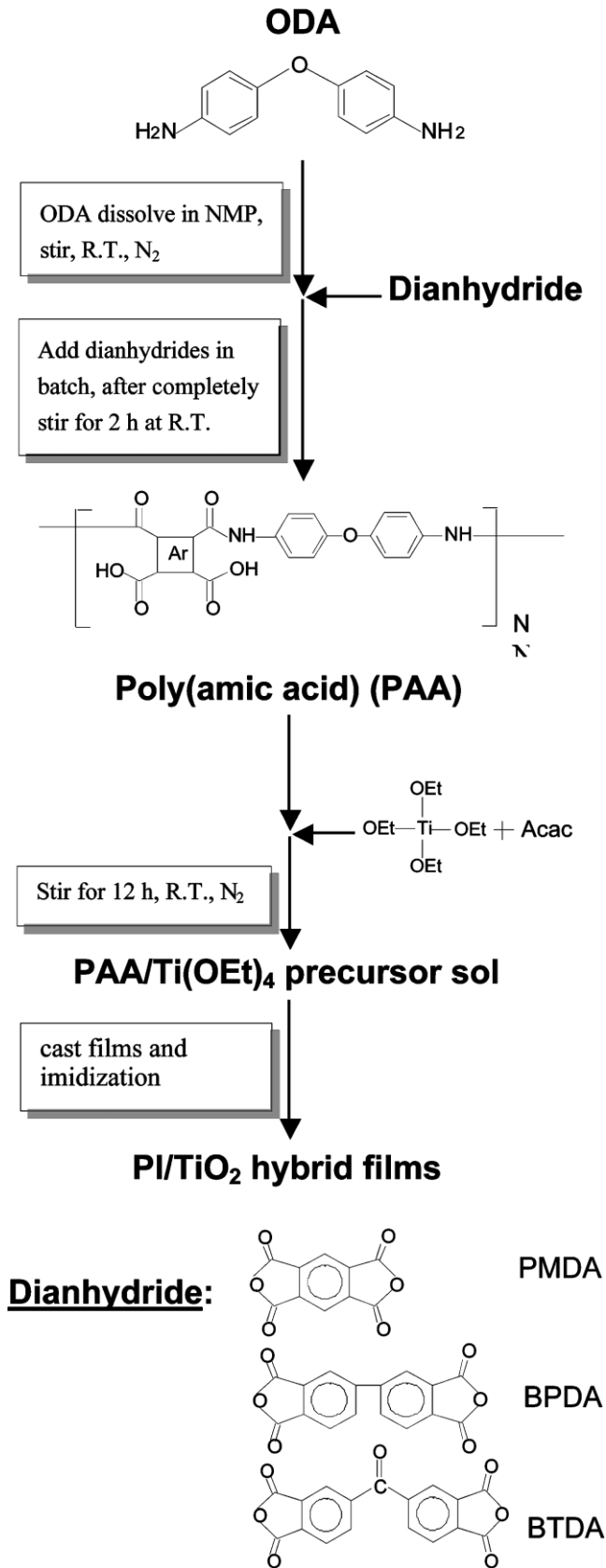


Fig. 1. Flow chart of the procedures to prepare the PI/TiO<sub>2</sub> hybrid films.

Other additive includes acetylacetone (acac) was available from Fluka.

## 2.2. Synthesis

Poly(amic acid) (PAA) solutions were made by reacting equal molar amounts of diamine and dianhydride in solution (15% solids for PMDA in DMSO, 15% solids for BPDA in NMP and 22% solids for BTDA in NMP) under a nitrogen atmosphere. Dianhydride was added into the solution by five portions and after the dissolution of all dianhydride, the PAA mixture was further stirred for 2 h. After this period, modified PAA solutions were made by adding the mixture of Ti(OEt)<sub>4</sub> and acac (molar ratio of Ti(OEt)<sub>4</sub> to acac was fixed to 1:4) and stirring for at least 12 h. The metal concentration were approximately 1, 3, 5, 7, 9 wt.%, assuming complete imidization, complete conversion of the Ti(OEt)<sub>4</sub> to the titania, and no residual solvent.

The freestanding films were made by casting the modified and unmodified PAA solutions onto a dust free glass plate with a doctor blade. The film was then cured under a dynamic air atmosphere at 100, 150 and 200 °C for 1 h each and 300 °C for 12 h. Upon cooling, the films were removed from the glass plate using a razor blade to lift off the film. The hybrid films have an average final thickness of 35–40 μm.

## 2.3. Measurements

The coefficients of thermal expansion (CTE) measurement of the films were carried out by using a DuPont TMA 2940 at a heating rate of 10 °C/min. Thermogravimetric analyses (TGA) were obtained with a DuPont TGA 2050 and at a heating rate of 20 °C/min under a nitrogen atmosphere. The dynamic mechanical analysis was carried out from 50 °C to 450 °C with a DuPont DMA 2980 at a heating rate of 2 °C/min, at 1 Hz frequency. The dielectric constants were measured by the Agilent 4294A at 1 MHz frequency, after coating gold on two surfaces 300 Å thick and 5.5 mm diameter. The dielectric constant ( $k$ ) can be calculated from the following formula  $k = Cd/A\epsilon_0$ , where  $C$ ;  $d$ ;  $A$  and  $\epsilon_0$  represent the observed capacitance; film thickness; gold area and free permittivity, respectively. Surface and volume resistivities were measured by employing an Agilent 4339B at a voltage of 500 V.

## 3. Results and discussion

Table 1 presents the films that were synthesized and characterized in this study. The expectation is that the inorganic phase, formed via sol–gel process, would uniformly disperse in polyimide (PI) matrix and result in a tailored effect of the hybrid films without compromising other essential PI properties. In this study, tetra-

ethyl orthotitanate ( $\text{Ti}(\text{OEt})_4$ ) was used as a precursor to titania in hybridization. To prevent gelation occurring, acetylacetone (acac) was used to reduce the reaction rate through the formation of a complex [18–20]. During thermal treatment of the hybrid films, no phase separation of inorganic component is visually apparent. The color of the hybrid films becomes darker with increase of titania. In the series of PMDA/ODA, the films containing titania of 5 wt.% or more are brittle. However, the hybrid films of BPDA/ODA and BTDA/ODA series are still flexible with titania content up to 5 wt.% or more. The results imply that the flexibility of hybrid films have an order of  $\text{BTDA/ODA} > \text{BPDA/ODA} > \text{PMDA/ODA}$ .

From the data in Table 1, there is a marked lowering of the coefficient of thermal expansion (CTE) in hybrid films with small amount of titania. This dramatic decrease in CTE could be due to metals and inorganic materials having lower CTE values. The polyamic acid (PAA) reacting with the alkoxy group of the sol–gel precursor would form a bond between the PI and the inorganic phase. The titania domains served as cross-link points could lead to a decrease in the segmental mobility of the PI chain. That is why the CTE of the hybrid films will be changed [21,22]. The CTE of these hybrid films have been measured at both ranges of 50–200 °C and 200–300 °C. For these two conditions, there is a similar tendency of CTE lowering with increasing the content of titania. The decrease of CTE at elevated temperature is more remarkable, that enhances the reliability for applications at high temperature. CTE data for additional hybrid films prepared from BPDA/ODA and BTDA/ODA are also shown in Table 1. All metal-containing PI have lower CTE relative to the pure PI. It is interesting to note that the PMDA/ODA series have much lower CTE than the other two series at elevated temperature. This could result from the glass transition temperature ( $T_g$ ) of BPDA/ODA and BTDA/ODA series of approximately 300 °C. Thus, the increase in CTE of the latter two series could be due to the rise of chain mobility at elevated temperature.

The dynamic mechanical properties of PMDA/ODA hybrid films are presented in Fig. 2. From Fig. 2a, the storage modulus ( $E'$ ) of hybrid films increases with increasing the amount of titania. Specifically, at lower temperature (50 °C), the storage modulus of hybrid films is larger than that of pure PI. At elevated temperature (400 °C), the hybrid films have remarkable increase of modulus compared to the pure PI. However, the loss modulus ( $E''$ ) of the hybrid films decreases with increasing the amount of titania as shown in Fig. 2b. The decrease of loss modulus could be due to the network structure of the hybrid films, which make the lower interaction force between molecular chains [21]. Therefore, lower loss modulus and lower  $\tan\delta$  are obtained.

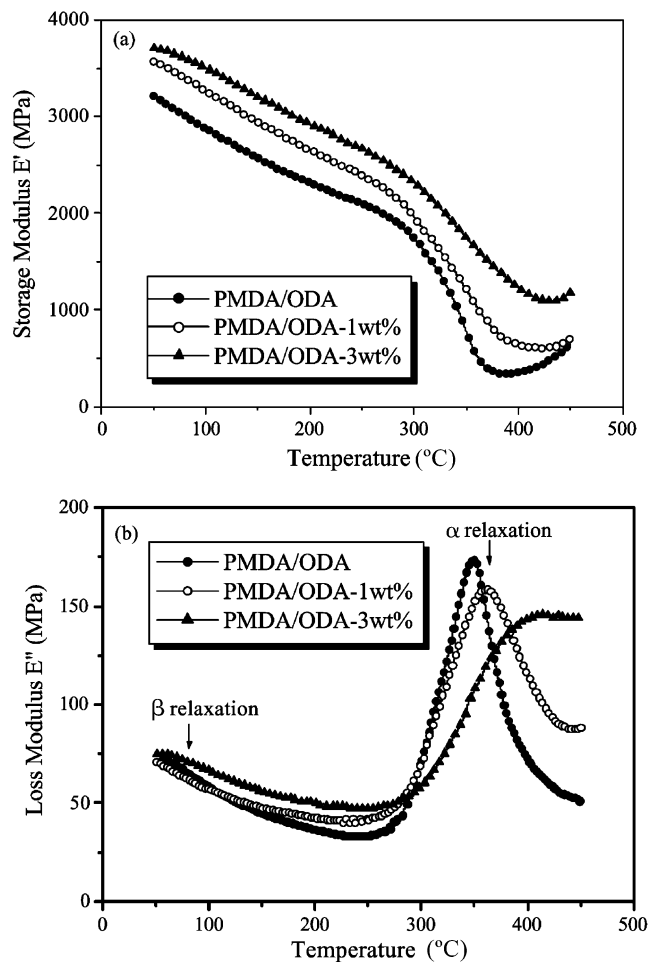


Fig. 2. (a) the storage modulus and (b) the loss modulus of PMDA-ODA/TiO<sub>2</sub> hybrid films of at different temperatures.

For the three series of hybrid films, the maximum  $\tan\delta$  ( $E''/E'$ ) is defined as glass transition temperature ( $T_g$ ).  $T_g$ s of all metal-containing PI are higher than the pure PI. This increase may be due to the filler effect of the titania, thereby affording a stiffer hybrid film. However, the cross-linking reaction between PI chains and metal alkoxide would be expected to increase  $T_g$ . According to Fig. 3 and Fig. 4, the series of BPDA/ODA and BTDA/ODA hybrid films exhibit two obvious transition peaks in the  $\tan\delta$  curves, the first peak near 280–350 °C and the second peak in the range of 400–420 °C. The peaks of  $\tan\delta_1$  ( $T_{g1}$ ) and  $\tan\delta_2$  ( $T_{g2}$ ) are related to PI matrix and inorganic domains, respectively. From Fig. 3 and Fig. 4, both  $T_{g1}$  and  $T_{g2}$  shift to high temperature with increasing the content of titania. The shift is resulted from higher cross-linking density leading to a higher hindrance from chain movement, so that the chain movement occurs at higher temperature [21]. However, the extent of representative shifts of  $T_{g1}$  and  $T_{g2}$  is different. Based on our experiment, the shift of  $T_{g1}$  is larger than the shift of  $T_{g2}$ . Thus, it can be

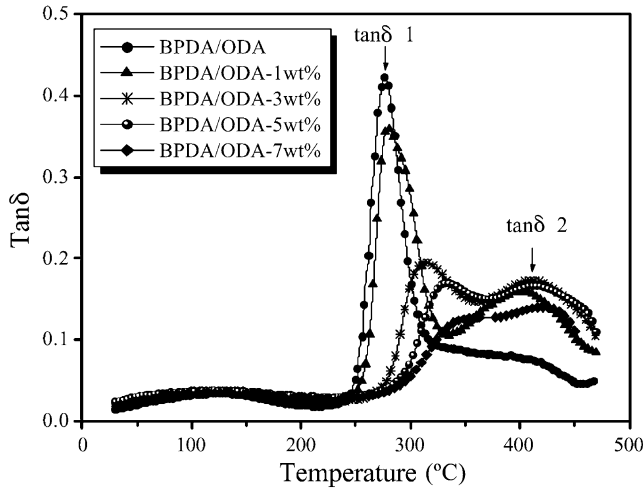


Fig. 3. The  $\tan\delta$  curves of series of BPDA-ODA/TiO<sub>2</sub> hybrid films at different temperatures.

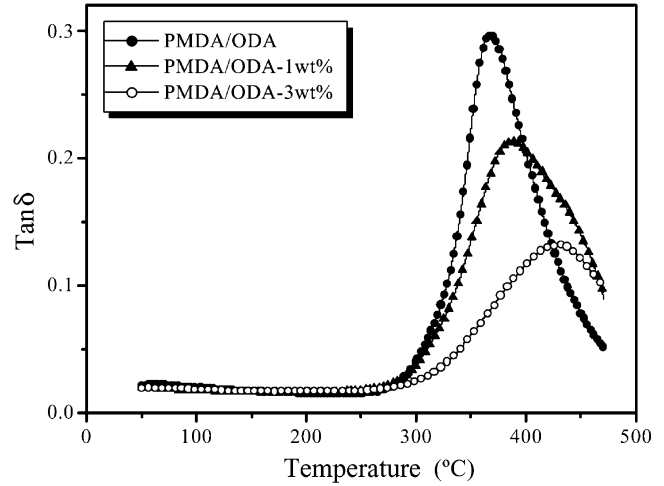


Fig. 5. The  $\tan\delta$  curves of series of PMDA-ODA/TiO<sub>2</sub> hybrid films at different temperatures.

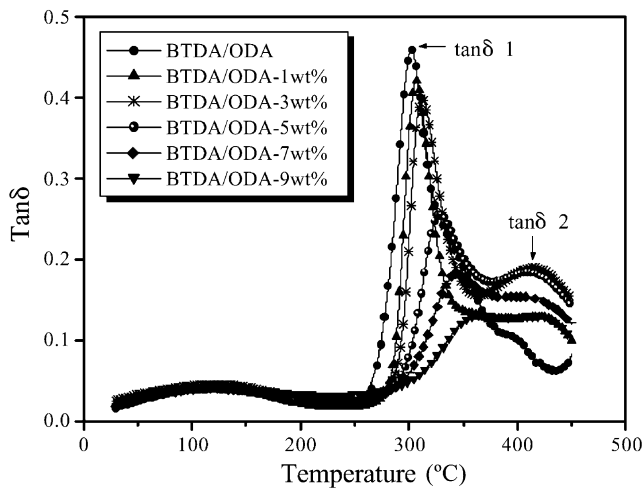


Fig. 4. The  $\tan\delta$  curves of series of BTDA-ODA/TiO<sub>2</sub> hybrid films at different temperatures.

predicted that the two peaks would merge into a broad one in a certain range of titania content. Moreover, there is also a reduction in the  $\tan\delta_1$  peak, when the amount of titania increases. This is presumably due to higher cross-linking density making lower damping of PI chains that depress  $\tan\delta_1$  value. The lower damping means the network structure decreases the chain friction and chain interaction during chain movement. For the series of PMDA/ODA in Fig. 5, there is only one broad  $\tan\delta$  peak. It can be explained that the two  $\tan\delta$  signals overlap into a broad one, because PMDA/ODA has higher  $T_g$  compared to BPDA/ODA and BTDA/ODA.

The network structure of hybrid films reinforces the pure PI. From Table 1, the stress, elongation at break and initial modulus of these hybrid films are in the range 23–220 MPa, 1.1–39% and 2.1–4.2 GPa at 30

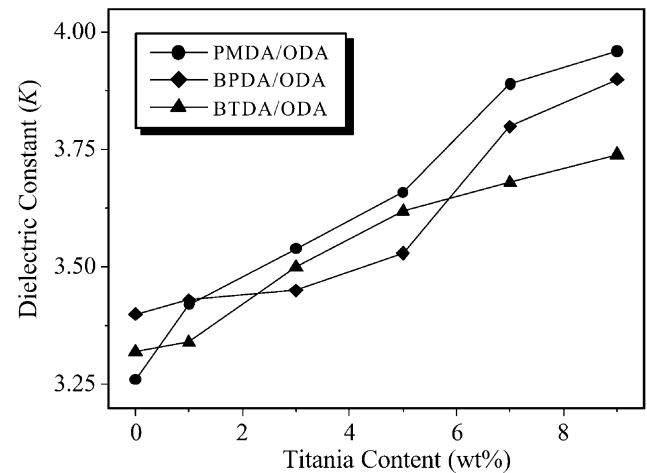


Fig. 6. Variation of dielectric constants of hybrid films as a function of titania content (wt%).

°C. At elevated temperature, the hybrid films also have enhanced improvement relative to the pure PI. The variation in maximum stress at break initially increases with titania content at 1–3 wt.%. However, further addition of titania decreases the stress because of increasing brittleness of hybrid film. Values of the modulus, calculated from the initial slopes of the stress–strain curves show increase with increasing titania content. The elongation at break is found to decrease with titania content.

The thermal stability of the hybrid films are listed in Table 1. The introduction of titania causes a decrease in thermal stability of hybrid films. However, the hybrid films still possess good thermal property for the practical application. The decrease in thermal stability of hybrid films could be attributed to the metallic compounds, which can oxidatively degrade polyimide films [23–26].

Table 2  
Surface and volume resistivity of hybrid films

TiO <sub>2</sub> content wt. %	PMDA/ODA		BPDA/ODA		BTDA/ODA	
	Rv (Ω-cm)	Rs (Ω)	Rv (Ω-cm)	Rs (Ω)	Rv (Ω-cm)	Rs (Ω)
0	$5.6 \times 10^{16}$	$9.1 \times 10^{15}$	$1.6 \times 10^{17}$	$4.4 \times 10^{16}$	$3.2 \times 10^{17}$	$7.3 \times 10^{16}$
1	$2.5 \times 10^{16}$	$5.3 \times 10^{15}$	$1.4 \times 10^{17}$	$1.7 \times 10^{16}$	$2.7 \times 10^{17}$	$5.8 \times 10^{16}$
3	$8.9 \times 10^{15}$	$2.1 \times 10^{14}$	$5.8 \times 10^{16}$	$9.0 \times 10^{15}$	$6.8 \times 10^{16}$	$8.3 \times 10^{15}$
5	$1.7 \times 10^{15}$	$1.6 \times 10^{14}$	$1.7 \times 10^{16}$	$8.7 \times 10^{15}$	$2.5 \times 10^{16}$	$7.3 \times 10^{15}$
7	<sup>a</sup>	<sup>a</sup>	$1.4 \times 10^{16}$	$4.7 \times 10^{15}$	$2.2 \times 10^{16}$	$5.1 \times 10^{15}$
9	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	<sup>a</sup>	$1.8 \times 10^{16}$	$4.3 \times 10^{15}$

<sup>a</sup>The film was too brittle to be measured.

The dielectric constants of each hybrid films are plotted with titania content as shown in Fig. 6. For each series, the dielectric constant increases with increasing the titania content. The hybrid films possess dielectric constants in the range of 3.2–3.9. Surface and volume resistivities of hybrid films list in Table 2. The series of PMDA/ODA exhibit lower resistivities relative to other two series. Furthermore, work needs to be carried out of how the dopants affect electrical properties for applications as conductive space films, industrial films and coatings.

#### 4. Conclusion

Polyimide containing titania have been prepared by sol–gel method. Most films are homogeneous and each exhibits good thermal stability. There is an obvious decrease of thermal expansion of the hybrid films at both low and elevated temperatures. Dynamic mechanical thermal analysis shows a systematic increase in the glass transition temperature with an increase of titania content. This indicates that the mobility of the polyimide chain was diminished by the inorganic phase and the network structure. At high concentration of titania,  $T_{g1}$  and  $T_{g2}$  will shift to high temperature and gradually merge into a broad one. However, there is only one  $\tan\delta$  peak in PMDA/ODA series. Because of its higher  $T_g$  than two other series, the peak related to the  $T_{g1}$  has been overlapped on  $T_{g2}$ . Incorporating titania would cause the surface and volume resistivities to decrease, but the dielectric constant displays the reverse trend.

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