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# Synthesis and characteristics of polyimide/titania nano hybrid films

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**Abstract**

Polyimide/titania (PI/$TiO_2$) nano hybrid films are synthesized by sol–gel technology. [4,4′-(4,4′-Isopropylidenediphenoxy) bis (phthalic anhydride)] (IDPA), 4,4′-diaminodiphenyl ether (ODA) and 3-aminopropyltrimethoxysilane (APrTMOS) mixed entirely and reacted at room temperature to form the polyamic acid (PAA). Tetraethyl orthotitanate ($Ti(OEt)_4$) and actylacetone, the latter one is used as chelating agent, are then added to the polyamic acid. After imidization at high temperature, PI/$TiO_2$ hybrid films with different block chain length, 5000 of PAA and 15000 g $mol^{-1}$, and a cross-linked structure are formed. The resulting hybrid films, containing relatively small amounts of titania, exhibit higher transparency and flexibility. Moreover, as compared with pure PI, the hybrid film formed from APrTMOS has better ability to form a film with a higher titania content. Due to the high and low refractive index (RI) of $TiO_2$ and APrTMOS, their introduction may lead to the change of the RI of hybrid films. From the transmission electron microscope (TEM) images; the particle size of titania decreases with increasing APrTMOS content. Thermal decomposition temperatures ($T_d$), with a 5% weight loss, are in the range of 400–540 °C. The dynamic mechanical thermal analysis showed a systematic increase of glass transition temperature, along with a broader and weaker tan $\delta$ peak with increasing titania content.


*Keywords:* Polyimide/titania; Nano; Hybrid film; Morphology; Optical

## 1. Introduction

Organic/inorganic hybrid materials have become a popular topic in material science because of their unique properties. Polyimides (PI), which can be prepared from a variety of starting materials, by a variety of synthesis routes, and possess high thermal stability, high chemical resistance and excellent mechanical properties, are a promising matrix candidate for hybrid materials.

A new range of material properties can be produced by combining the features of the inorganic sol–gel alkoxide moieties with those of oligomeric/polymeric species[1,2]. The resulting composites can vary from soft to hard, flexible to brittle, materials depending on the chemical structure of the organic components and the overall composition ratio of organic to inorganic. In addition, ultrafine particles have become a popular topic because of the novel properties, which greatly differ from the bulk properties. Due to the expected properties of $TiO_2$ (high-refractive-index, catalytic etc.), considerable attention has been devoted to the manufacture of high-content and well-dispersed $TiO_2$ in a PI matrix for potential uses as interference filter, as antireflective coating, and as optical waveguides [3–5]. When metal alkoxides were added into the PI matrix, the gelation and phase separation easily occurred due to the relatively fast hydrolysis rate of metal alkoxides. Therefore, the use of acetylacetone (acac) chelating agent is necessary in order to be able to control the reactivity of the metal alkoxides and to tailor the structure of the resulting hybrid materials.

In this study, the titanium alkoxide is incorporated into PI matrix through a simpler process and good quality and well-dispersed polyimide/titania hybrid films with relatively high titania content and APrTMOS are prepared. Moreover, the characteristics of morphology, optical, mechanical, and thermal properties for the hybrid films are also investigated.

## 2. Experimental

### 2.1. Materials

4,4′-Diaminodiphenylether (ODA, 98%) from Lancaster was dried in a vacuum oven at 125 °C for 24 h prior to use.

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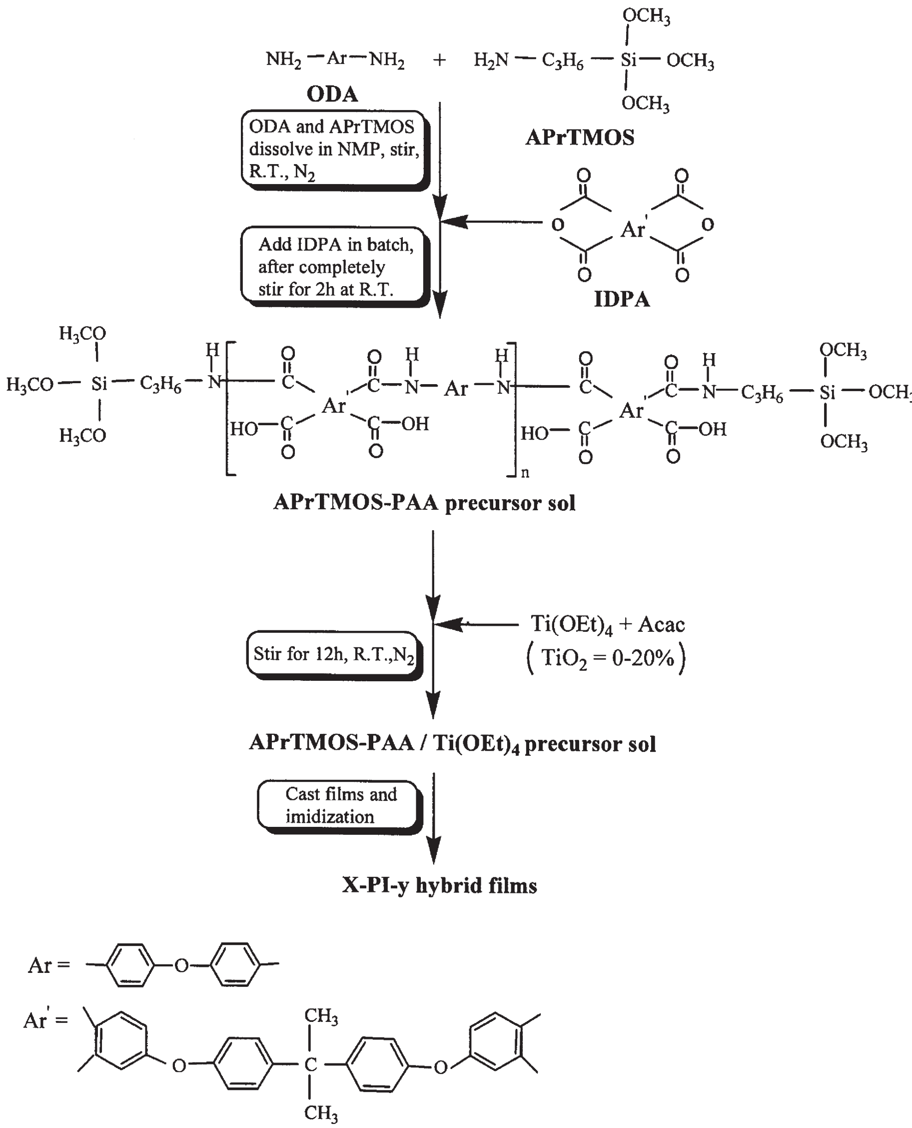


Fig. 1. The flow chart of the procedures to prepare the *X*-PI-*y* hybrid films.

4,4′-(4,4′-Isopropylidenediphenoxy) bis (phthalic anhydride) (IDPA, 97%) from Aldrich Chemical Company was purified by recrystallization from acetic anhydride and then dried in a vacuum oven at 125 °C overnight. 3-Aminopropyltrimethoxysilane (APrTMOS) was obtained from Tokyo Chemical Industry. *N*-methyl-2-pyrrolidone (NMP) from Tedia Company was dehydrated with molecular sieves. The titania additive of tetraethyl orthotitanate ($Ti(OEt)_4$) and acetylacetone (acac) were acquired from Tokyo Chemical Industry.

## 2.2. Synthesis

The flow chart of the procedures to prepare the X-PI-y hybrid films is shown in Fig. 1. The polycondensation reaction is carried out in the flask by adding diamine (ODA), monoamine (APrTMOS), and dianhydride (IDPA) in NMP under a nitrogen stream at room temperature. The addition of APrTMOS is used to control the chain length, ODA-IDPA, of the trimethoxysilane-terminated polyamic acid (PAA). In the preparation of the APrTMOS-terminated PAA with an ODA-IDPA block chain length of 5000 g $mol^{-1}$, 0.03439 mol of IDPA is added into the solution containing 0.02939 mol of ODA and 0.01 mol of APrTMOS in 16.4 g of NMP. Meanwhile, the IDPA is introduced into the solution by three portions. It is better to ensure the complete dissolution of the prior portion before adding a fresh portion. After the dissolution of all IDPA, the reaction

Table 1
Preparation and inherent viscosities of pure PAA and *X*-PAAs precursors

| *X*[a] | IDPA:ODA:APrTMOS[b] | Inherent viscosities[c] |
|---|---|---|
| 5000-PAA | 5.88: 6.88:2 | 0.42 |
| 15,000-PAA | 20.08:21.08:2 | 0.62 |
| Pure PAA | 1.00: 1.00:0 | 0.85 |

[a] Theoretical molecular weight of APrTMOS-terminated polyamic acid.
[b] Mole ratio.
[c] The inherent viscosities are determined at a concentration of 0.5 g/dL of pure PAA and APrTMOS-PAA in NMP at 25 °C.

Table 2
Physical, optical, thermal and mechanical properties of pure PI, PI-*y*, 5000-PI-*y* and 15,000-PI-*y* series hybrid films

| Compound code[a] | Film | | Transmittances (%)[d] | Refractive index | | Decomposition temperature $T_d$ (°C)[e] | Storage modulus (MPa)[f] | Glass transition temperatures $T_g$ (°C)[g] |
|---|---|---|---|---|---|---|---|---|
| | Color[b] | Quality[c] | | 540 nm | 589 nm | | | |
| Pure PI | PY | − | 84.88 | 1.6695 | 1.6610 | 535.0 | 2014 | 233.1 |
| PI-2 | PB | − | 65.26 | 1.7076 | 1.7017 | 530.4 | 1821 | 243.5 |
| PI-4 | B | − | 44.89 | h | h | 523.9 | 2222 | 256.9 |
| PI-6 | DB | − | 32.63 | h | h | 513.1 | 2231 | 271.0 |
| PI-8 | DB | + | i | i | i | 494.2 | i | i |
| PI-10 | DB | + | i | i | i | 470.6 | i | i |
| 5000-PI | PY | − | 87.87 | 1.3840 | 1.3797 | 537.6 | 1089 | 235.3 |
| 5000-PI-2 | Y | − | 83.01 | 1.3865 | 1.3875 | 523.5 | 1198 | 241.4 |
| 5000-PI-4 | Y | − | 77.65 | 1.3953 | 1.3875 | 516.9 | 1874 | 247.5 |
| 5000-PI-6 | B | − | 68.15 | 1.4013 | 1.3982 | 513.8 | 2209 | 258.0 |
| 5000-PI-8 | B | − | 47.89 | h | h | 500.8 | 2994 | 273.5 |
| 5000-PI-10 | DB | − | 30.45 | h | h | 491.1 | 3015 | 275.1 |
| 5000-PI-15 | DB | + | i | i | i | 430.0 | i | i |
| 5000-PI-20 | DB | + | i | i | i | 404.1 | i | i |
| 15,000-PI | PY | − | 86.26 | 1.3940 | 1.3898 | 536.4 | 1637 | 234.8 |
| 15,000-PI-2 | Y | − | 80.21 | 1.3942 | 1.3989 | 531.5 | 1813 | 241.2 |
| 15,000-PI-4 | B | − | 65.88 | 1.4032 | 1.3996 | 519.7 | 2313 | 249.6 |
| 15,000-PI-6 | B | − | 55.25 | h | h | 515.4 | 2343 | 258.8 |
| 15,000-PI-8 | DB | − | 45.01 | h | h | 506.5 | 2842 | 268.4 |
| 15,000-PI-10 | DB | + | i | i | i | 487.8 | i | i |

[a] *X*-PI-*y*: "*x*", polyimide block chain length; "*y*", $TiO_2$ wt.%.
[b] PY: Pale yellow; PB: pale brown; B: brown; DB: deep brown; Y: yellow.
[c] "−", flexible; "+", brittle.
[d] Using visible light at 638 nm, and air as reference (thickness of film about 40 μm).
[e] Temperature at 5% weight loss.
[f] Storage modulus of hybrid films are measured at 60 °C.
[g] The maximum in tan $\delta$ curve is designated as glass transition temperature.
[h] The hybrid film is too deep colored to obtain satisfactory measurement.
[i] The hybrid film is too brittle and fragile to obtain satisfactory measurement.

mixture is further stirred for 2 h at room temperature. The APrTMOS-PAA solution has 18% of solid content (w/w). Moreover, the APrTMOS-PAA with 15,000 g mol$^{-1}$ block chain length is also prepared through the same procedures. The mole ratios of IDPA/ODA/APrTMOS are shown in Table 1. After this step, the desired amount of $Ti(OEt)_4$ and acac are completely mixed and added dropwise into the PAA solution with vigorous stirring to avoid local inhomogeneity. The mixture proceeded with continuous stirring for another 12 h. The theoretically calculated content of $TiO_2$ in the hybrid films follows from an assumption that all the $Ti(OEt)_4$ and PAA precursors are converted to $TiO_2$ and PI completely and there is no residual solvent after imidization process. The molar ratio of $Ti(OEt)_4$ to acac is fixed at 1:4. The theoretically calculated content of $TiO_2$ in the hybrid films ranges from 2 wt.% to 20 wt.% in this study.

The freestanding hybrid films are made by casting the pure PAA without APrTMOS. The APrTMOS-PAA and APrTMOS-PAA/$Ti(OEt)_4$ solution was poured onto a glass plate and then cured in an air-circulating oven at 60, 100, 150, 200, or 300 °C for 1 h at each temperature. In this paper, the sample code is presented by *X*-PI-*y*, *X* denotes the block chain length of polyimide and *y* implies the weight percentage of $TiO_2$ within PI matrix. Three series of PI/$TiO_2$ hybrid films, based on IDPA, ODA and controlling the block chain length to be either 5000 or 15,000 g mol$^{-1}$ for IDPA-ODA oligomer, are synthesized.

### 2.3. Measurements

The inherent viscosities ($\eta_{inh}$) of pure PAA and APrTMOS-PAA were determined at a concentration of 0.5 g/dl in NMP and thermostated at 25 °C by an Ubbelohde viscometer with the flow time of pure NMP solvent greater than 120 s. Fourier transfer infrared spectrophotometer (FT-IR) absorption spectra were recorded between 4000 and 400 cm$^{-1}$ by Nicolet PROTEGE-

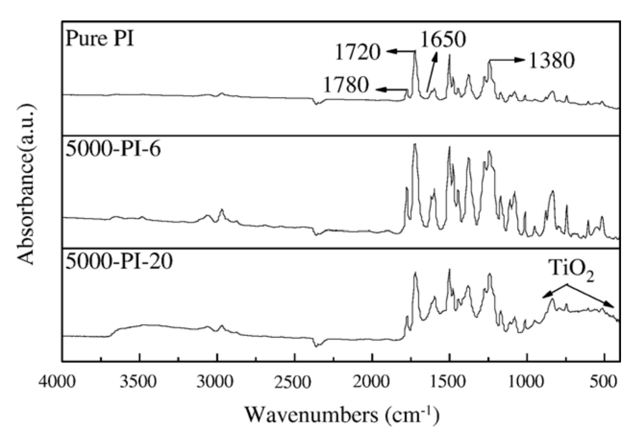


Fig. 2. Fourier transfer infrared spectrophotometer spectra of pure PI, 5000-PI-6 and 5000-PI-20 hybrid films.

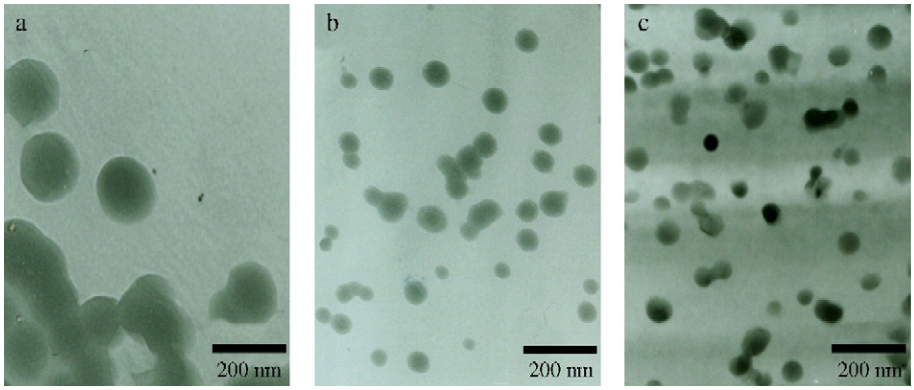


Fig. 3. Transmission electron microscope photographs of the hybrid films (a) PI-8 (b) 5000-PI-8 (c) 15,000-PI-8.

460. UV-visible absorbance spectra are collected by a Shimuza UV-160A spectrophotometer with transparency mode. The dynamic mechanical analysis (DMA) was carried out by means of thermal analyzer DMA-2980 from 60 °C to 300 °C, at a frequency of 1 Hz and heating rate of 3 °C/min. Thermogravimetric analysis (TGA) was performed with a Du Pont TGA-950 at a heating rate of 20 °C/min from 50 °C to 800 °C under nitrogen. Transmission electron microscope (TEM) data was obtained by JEOL-2000FX. Abbe Refractometer was inspected by ATAGO-dr-m2 at room temperature.

## 3. Results and discussion

Polyimide/titania (PI/$TiO_2$) nano hybrid films were prepared by the sol–gel method. The monomer composition and inherent viscosity of pure polyamic acid (PAA) and APrTMOS-PAA oligomers are shown in Table 1. The inherent viscosities of pure PAA and PAA with block chain length of 5000, 15,000 g $mol^{-1}$ are 0.42, 0.62 and 0.85 dl/g, respectively. According to our results, it is indicated that the more APrTMOS contained in the film, the shorter the PI chain length that is formed and thus the lower the inherent viscosity of the precursor that is obtained. From Table 1, it is assured that the amount of APrTMOS could control PI chain length. Hybrid films with $TiO_2$ incorporated were brown in color. Table 2 shows that for more $TiO_2$ incorporated, into the films, less flexibility and deeper color are obtained. Moreover, the transparency, flexibility and even the ability to form a film with higher titania content can be enhanced by incorporating APrTMOS into PI matrix.

Fourier transform infrared spectrophotometer spectra of pure PI, 5000-PI-6 and 5000-PI-20 hybrid films are shown in Fig. 2. The characteristic peaks of symmetric and asymmetric C=O stretching and C–N stretching of the imide group at 1720, 1780, and 1380 $cm^{-1}$ are apparent in Fig. 2 [6]. After the introduction of inorganic components, the absorption bands in the range between 400–850 $cm^{-1}$ corresponding to Ti–O–Ti network are clearly present. There is no absorption near 1650 $cm^{-1}$ for the carbonyl group of PAA which appeared in the spectra of all the hybrid films. This result indicates the complete imidization of hybrid films and ensures the imidization process has not been impeded by inorganic moieties [7].

A Shimadzu UV-160A spectrometer was used to examine UV-visible transmission spectra of the PI/$TiO_2$ hybrid films. The transparency of pure PI, PI-*y*, 5000-PI-*y* and 15000-PI-*y* series are shown in Table 2. In the series of PI-*y*, the hybrid film with 2 wt.% titania exhibits 65.26% VIS-transmittance. However, in the series of 5000-PI-*y* and 15,000-PI-*y*, the VIS-transmittance of hybrid films with 2 wt.% titania are 83.01% and 80.21%, respectively. The hybrid films with APrTMOS

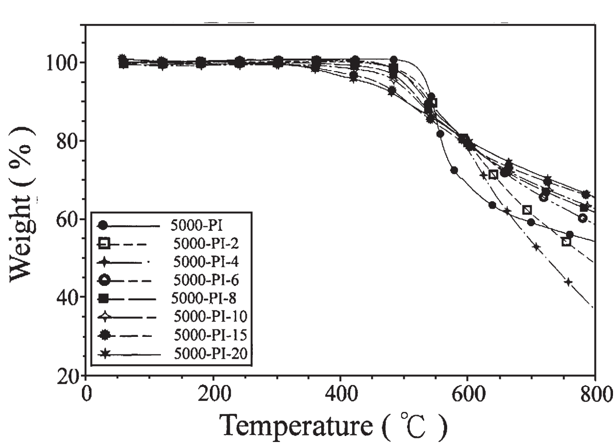


Fig. 4. Thermogravimetric profiles of the 5000-PI-*y* series hybrid films.

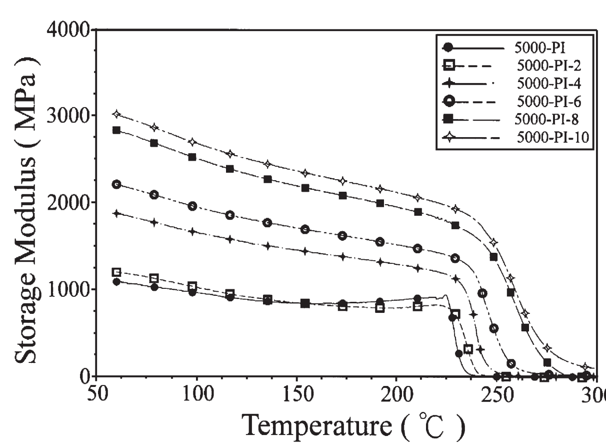


Fig. 5. The storage modulus of dynamic mechanical analysis for 5000-PI-*y* series hybrid films.

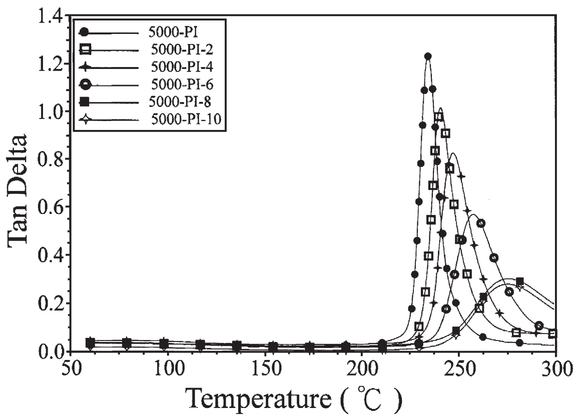


Fig. 6. The tan $\delta$ of dynamic mechanical analysis for 5000-PI-$y$ series hybrid films.

incorporated have better transparency as compared with hybrid films without APrTMOS.

Optical devices such as photonic integrated circuits generally require the control of refractive index (RI) and other optical properties of the thin film as well as the dimension of the waveguide structure. Due to the high RI of $TiO_2$, its introduction may lead to the change of the RI of the hybrid material [8]. The RI of pure PI, PI-$y$, 5000-PI-$y$ and 15,000-PI-$y$ series are shown in Table 2. It can be seen that the RI decreases with increasing inspection wavelength and APrTMOS content. In addition, the more titania in the films, the higher the RI. Therefore, a hybrid film with a specific RI can be prepared by controlling the amount of APrTMOS and titania.

Transmission electron microscope micrographs of the fractured hybrid films are shown in Fig. 3. Some discrete $TiO_2$ domains dispersed in PI matrices may be clearly observed. The particle size of $TiO_2$ is in the range of 150–180, 10–70, 30–80 nm for PI-8, 5000-PI-8, 15,000-PI-8, respectively. It has been noted that the hybrid films with APrTMOS have both smaller titania particle sizes and a better titania distribution within the PI matrix. It is suggested that APrTMOS could provide, covalent bonding between the PI and $TiO_2$ phases. Moreover, the incorporation of APrTMOS also facilitates $TiO_2$ to distribute within the PI matrix [9].

The thermal stability of pure PI, PI-$y$, 5000-PI-$y$ and 15,000-PI-$y$ hybrid films are measured under a nitrogen atmosphere at a heating rate of 20 °C/min. The thermogravimetric profile of 5000-PI-$y$ series are shown in Fig. 4. The decomposition temperatures ($T_d$), at 5% weight loss, are given in Table 2. The results indicate that hybrid films begin to decompose around or above 400 °C and typically exhibit weight losses of 5% weight between 404 and 537 °C. The introduction of $TiO_2$ causes a decrease in thermal stability, as shown by lower decomposition temperatures. The decrease in thermal stability could be attributed to the presence of metallic compounds which can oxidatively degrade polyimide films [10].

Fig. 5 shows the storage modulus as a function of temperature for 5000-PI-$y$ series. It can be seen that the storage modulus decreases with increasing temperature. The increase of storage modulus with the level of $TiO_2$ doping is ascribed to the formation of a network structure and an increase in the rigidity of the hybrid films [11–15].

For the pure PI, PI-$y$, 5000-PI-$y$ and 15,000-PI-$y$ series hybrid films, the glass transition temperature ($T_g$) is taken at the maximum tan $\delta$. Fig. 6 shows the tan $\delta$ as a function of temperature for 5000-PI-$y$ series. As illustrated in Fig. 6, the results are summarized in Table 2. Each hybrid film has a higher $T_g$ as compared with the pure polyimide and the $T_g$ increases with increasing $TiO_2$ content. This increase in $T_g$ may be related to the higher stiffness of the hybrid films. The cross-linking reaction between polyimide and titanium ethoxide would be expected to increase the value of $T_g$ [16–18].

## 4. Conclusion

Polyimide/titania ($PI/TiO_2$) nano hybrid films have been prepared by the sol–gel method. The higher the level of APrTMOS in the film, the shorter the PI chain length that is formed and thus the lower the inherent viscosity that may be obtained. By incorporating APrTMOS into the $PI/TiO_2$ mixture, the properties of transmittance and flexibility of the resulting films can be improved. The addition of APrTMOS appears to facilitate the dispersal of titania within the polyimide matrix. From transmission electron microscope images, the particle sizes of $TiO_2$ in PI-8, 5000-PI-8 and 15,000-PI-8 are 150–180, 10–70 and 30–80 nm, respectively. Less flexibility, less transparency and a deeper color are apparent in all hybrid films with added titania as compared with pure PI. The mechanical properties of hybrid films have been enhanced with an increasing titania content. Hybrid films with higher titania content exhibit higher glass transition temperatures ($T_g$) and a higher storage modulus than pure PI. As expected, the $T_g$ and refractive index (RI) are increased with increasing titania content. Therefore, a hybrid film with some specific RI can be achieved by adjusting the amount of titania in the PI matrix. Although the thermal stability of the hybrid films is decreased by the introduction of $TiO_2$, the hybrid films still exhibit good thermal resistance for practical applications.

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