Synthesis and Characterization of Fluorinated Polyimide/Silica Nanocomposites with Low Water Absorption and Dielectric Constant

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A fluorine-containing polyimide(FPI) was synthesized by reacting 4,4'-(hexafluoroisopropylidene) diphthalic anhydride (6FDA) with 2,2'-bis-(trifluoromethyl)-4,4'-diaminobiphenyl (TFDB). A series of polyimide composite films with various contents of nanosilica were prepared by an *in situ* polymerization technique. The obtained composite materials were analyzed with FTIR and the results showed that the amino groups were completely imidized. The morphology of the composites was characterized with SEM and the results indicated that the nanosilica particles integral dispersed but micro-aggregated in the fluoro-contained polyimide matrix if the nanosilica content exceeded 10 wt %. The nanocomposite films were found to hold comparable thermal stability with the pure fluoro-contained polyimide film. The humidity absorption rate decreased with the increase of silica content. The dielectric constant of fluoro-contained polyimide/nanosilica films decreased with increasing the frequency and exhibited an arch curve profile with its maximum value of less than 3, indicating the excellent dielectric property.

Key Words: Polyimides, Nanosilica, Dielectric properties, Water absorption.

INTRODUCTION

Polyimides (PIs) exhibit a number of outstanding properties such as thermal stability, electrical behaviour, *etc.*^{1,2} and have found in broad applications in packaging materials, aerospace and so on^{3,4}. All the polyimides are frequently used as interlayer dielectric insulators (ILD). To achieve maximum possible running speed in a limited dimensions, insulating materials with dielectric constant as small as possible are preferred. Polyimides with increasingly low dielectric constant and humidity absorption rate have being become the focus of several recent investigations⁵⁻⁸. As reported preparation of the matrix of fluorinated polyamide (FPI) and the incorporation of inorganic micro- or nano-fillers such as silica nanoparticles are a feasible way of improving these properties. For example, fluorination can impart the resulting fluorinated polyamides with the decreased dielectric constants because of the lower polarizability of fluorine⁹⁻¹¹.

On the other hand, the polyimide/SiO₂ composites have been found to exhibit the good thermal properties^{12,13}, low humidity absorption¹⁴, decreased dielectric constant¹⁵ and improved optical properties¹⁶. More importantly, the introduction of silica into polyimide films could increase the hydrophobicity, reducing the humidity absorption with a lower dielectric constant reached¹⁷.

This paper reports a study on the new fluorinated polyamide (6FDA-TFDB)/silica nanocomposite thin films obtained by reacting 4,4'-(hexafluoroisopropylidene) diphthalic anhydride (6FDA) with 2, 2'-bis-(trifluoromethyl)-4,4'-diaminobiphenyl (TFDB). Instead of using poly(amic acid) (FPAA) to prepare the silica composite materials, a soluble fluorinated polyamide (**Scheme-I**) was prepared from 6FDA and TFDB. Its molecular, the morphology, thermal, electrical and optical properties of the resulting fluorinated polyamide/silica nanocomposite thin films were analyzed with FTIR, TGA, SEM, UV-VIS and capacitance. In addition, the effects of the nanosilica content on the structure and properties of the prepared composite films are examined.

EXPERIMENTAL

Nanosilica produced *via* vapour method were purchased from Zhonggui High-Technology Co., Ltd. (Luoyang, China) with an particle size of 15-30 nm and a specific surface area of 150 m²/g. 4, 4'-(hexafluoroisopropylidene)diphthalic anhydride and 2,2'-bis-(trifluoromethyl)- 4,4'diaminobiphenyl (Shanghai Chemical Reagent Co., China) were purified by vacuum sublimation. *N,N*-dimethylacetamide was distilled over powdered calcium hydride under reduced pressure and stored over 4 Å molecular sieves prior to use.

Preparation of fluorinated polyamide/silica nanocomposite films: The fluorinated polyamide was synthesized according to the literature¹⁸. The polymerization process of fluorinated polyamide/silica nanocomposite materials is illustrated in **Scheme-I**.

Scheme-I: Reaction scheme for fluorinated polyamide/silica nanocomposite materials (the "....." means the hydrogen bond)

To a 100 mL round-bottom flask 3.2 g (0.01 mol) of TFDB and 20 mL dimethyl acetamide were added at room temperature with the slow stirring speed until a clear solution of diamine was obtained. To this solution, a calculated weight of nanosilica was added vigorous stirring for 1 h at room temperature. Followed by the stepwise addition of 6FDA (4.573 g, 0.0103 mol) in 30 min under argon flow. A sticky and homogenous suspension fluorinated polyamic acid (FPAA)/nanosilica was obtained after stirring under an argon and at room temperature for 24 h. The FPAA/nanosilica solution was casted on a clean

glass substrate (cleaned with ultrasonic treatment, methanol and demonized water), rotated to form an even gel film and then was heated sequentially under vacuum at 50, 80, 120, 150, 200, 250, 300 and 350 °C for 3, 2, 1, 1, 1, 1, 1 and 1 h respectively. After that the composites films were immersed into deionized water for 2 h, peeled off from the substrates and heated at 120 °C for 2 h under nitrogen flow, then the fluorinated polyamide/silica nanocomposite films obtained.

Characterization: FTIR spectra were recorded on a Nicolet 6700 spectrometer with a wave number range from 4000 to 400 cm^{-1} . The morphology of composite films and nanosilica were examined with a scanning electron microscopy (SEM, FEI SIRION 200). Ultraviolet-visible optical transmittances of the films were recorded on a UV-VIS spectrophotometer (Unocal UV-4802 s). Thermal-gravimetric analysis (TG) were performed with a NETZSCH TGA 200 F3 thermal analyzer at a heating rate of 10 °C/min under argon flow. The electrical capacitance was measured with a KEITHLEY 4200-SCS semiconductor characterization system at different frequency. The dielectric constant was calculated by using the following equation¹⁹:

$$\epsilon = \frac{C \cdot d}{\epsilon_0 \cdot S} \quad (1)$$

where, C is the electrical capacitance, ϵ is the dielectric constant, ϵ_0 is the permittivity of the free space (8.85×10^{-14} F/cm), d and S are the film thickness and electrode area, respectively.

The water absorption values of the obtained films were determined at 30 °C. Before the measurement, the films were vacuum-dried for 24 h at 100 °C, for then were weighed and immersed in deionized water for 24 h. The wet films were wiped dry and quickly weighed. The humidity absorption of the films was calculated in weight per cent as follows²⁰:

$$\text{Water absorption rate} = \frac{(W_2 - W_1)}{W_1} \times 100 \% \quad (2)$$

where, W_2 is the weight of thin film after absorption water and W_1 is the weight of dry film.

RESULTS AND DISCUSSION

Structure of the fluorinated polyamide/silica nanocomposites: FTIR spectra of the prepared fluorinated polyamide/silica nanocomposite films containing 3 wt % of silica are shown in Fig. 1. Where the corresponding characteristic absorption peaks of the fluorinated polyamide matrix and the Si-O-Si stretching bands (1120 cm^{-1}) of the curve of fluorinated polyamide/SiO₂ (3 wt %) are highlighted. The imide groups or functionalities of fluorinated polyamide and FPAA are further supported. The bands observed around 1786 cm^{-1} (C=O, symmetrical stretching), 1727 cm^{-1} (C=O, asymmetrical stretching), 719 cm^{-1} (C=O bending) 1370 cm^{-1} (C-N stretching), C-NH (1540 cm^{-1} , symmetrical stretching; 1332 cm^{-1} and asymmetrical stretching) and COOH (2940 cm^{-1}). In contrast, the characteristic band of polyamic acid around 1680 cm^{-1} is not found on the curves of fluorinated polyamide and its composite. In addition, the IR absorption of the O-H group and N-H group of the FPAA have disappeared, indicating that the imidization reaction was completed *via* the heating process and the fluorinated polyamide synthesized. There are no free amine group. This conclusion can be hardly obtained from

Fig. 1. FTIR spectra of nanosilica, FPAA, fluorinated polyamide and fluorinated polyamide composite containing 3 wt % nanosilica

the absorption of N-H and OH, as shown 3500 cm^{-1} detected in the final spectra of the composite films, which indicates the successful incorporation of the nanosilica to the resulting composites films. Furthermore, the addition of nanosilica caused the absorption band of C=O slightly red shift in the fluorinated polyamide/silica nanocomposites, which can be attributed to the hydrogen-bonding between the O-H of nanosilica and the oxygen atoms in fluorinated polyamide.

The effect of the organic/inorganic interface compatibility on the mechanical properties can be estimated by observing the fracture surface of the specimen by using a SEM. Fig. 2(a) shows the typical SEM images of the nanosilica particles. The SiO_2 nanoparticles are gathered in a loose state with the average diameter of about 15 nm. The cross-sectional fractures of the nanocomposites with a nanosilica loading of 3 wt % as showed in Fig. 2(b). The SiO_2 nanoparticles can be integral dispersed at low content in the fluorinated polyamide matrix.

Fig. 2. SEM images of the nanosilica particles (a) and the broken section of fluorinated polyamide nanocomposite film containing 3 wt % nanosilica (b)

Fig. 3 is the schematic diagram of the silica nanoparticles, showing structural characteristics and linkages among Si, O and H atoms. A large number of the hydroxy groups distributed in the core and at surface of the silica particles, which could account for the H-bonding between the SiO_2 nanoparticles and the fluorinated polyamide matrix, further improving the dispersion of SiO_2 . This conclusion is supported analysis of nanosilica FTIR spectra.

Table-1 presents the thermal properties and transmittance of fluorinated polyamide nanocomposite thin films with different

Fig. 3. Ideal structure of the SiO_2 nanoparticles

contents of silica. The pure fluorinated polyamide shows the excellent thermal stability with the temperature for 5 % weight loss of 531°C . The thermal stability of the fluorinated polyamide nanocomposites with different nanosilica contents were better than that of the pure fluorinated polyamide, their T_g and temperatures for 5 % weight loss increased with adding of nanosilica and were higher than 314°C and 530°C , respectively. This performance is acceptable for polyimide-based materials in most practical applications with the thermally resistant requirement.

As shown in Table-1, the transmittance of the prepared composite thin films exceeded 88 % at 500 nm and 600 nm and showed a trend of enlarging with adding nanosilica to fluorinated polyamide, had a low cutoff wavelength with indicating excellent optical transparency. It can be said that the composite thin films have a high homogeneity because of their better transparency compared to that of pure fluorinated polyamide without nanosilica³.

TABLE-1
PHYSICAL PROPERTIES OF FLUORINE CONTAINED
POLYIMIDE COMPOSITE THIN FILMS WITH
DIFFERENT CONTENTS OF NANOSILICA

Silica content (wt %)	Transmittance		T_g ($^\circ\text{C}$)	Temperature ($^\circ\text{C}$) for 5 % weight loss
	^a (%)	^b (%)		
0.0	88.3	88.4	314	531
0.5	88.5	88.7	316	533
1.0	88.4	89.0	318	535
3.0	89.2	89.4	321	536
7.5	90.2	90.5	326	540
10.0	90.8	90.8	330	545
15.0	90.7	90.9	332	549
20.0	91.2	91.6	335	555
25.0	91.3	91.5	337	561

^aOptical transmittance at 500 nm; ^bOptical transmittance at 600 nm

Water absorption property of the fluorinated polyamide/silica nanocomposite films: A necessary consideration

for application of polyimides in microelectronics is the humidity absorption and hydrothermal resistance. Fig. 4 demonstrates water absorption as a function for the fluorinated polyamide nanocomposite films with various nanosilica particle contents. Clearly, the water absorptions of the fluorinated polyamide/nanosilica composite films are all smaller than that of the pure fluorinated polyamide film and decreased with the increased nanosilica content, indicating that it is easier for water molecules to diffuse into the fluorinated polyamide matrix without the nanosilica filler. The diffusion of water molecules becomes more difficult in the fluorinated polyamide composite films. That was attributed to the strong hydrophobicity of the SiO₂ nanoparticles though they contain hydrophilic groups (-OH). In addition, for fluorinated polyamide, its fluorine content with 31.3 %¹⁸, can be synthesized by reacting monomers 6FDA with TFDB, both of which bear two trifluoromethyl groups, thus exhibiting favourable hydrophobicity²¹.

Fig. 4. Water absorption of the films with different SiO₂ content (the average thickness of films was 8.5×10^{-5} m)

Dielectric characteristics of the fluorinated polyamide/silica nanocomposites: The dielectric constants of the prepared composite thin films at three different frequencies were listed in the Table-2. As results, the dielectric constant of pure fluorinated polyamide has the value between 2.78 and 2.81 depending on the applied frequencies. For the composites, their dielectric constants increase firstly along with the nanosilica load, reach the maximum value at the 10 wt % of nanosilica and then decrease with the nanosilica load.

TABLE-2
DIELECTRIC CONSTANT OF THE NANOSILICA/FPI COMPOSITES

Sample	Dielectric constant at different frequency		
	f = 50 KHz	f = 100 KHz	f = 500 KHz
FPI	2.812	2.800	2.780
0.5 wt % SiO ₂ /FPI	2.820	2.813	2.803
1.0 wt % SiO ₂ /FPI	2.837	2.826	2.816
3.0 wt % SiO ₂ /FPI	2.863	2.858	2.838
7.5 wt % SiO ₂ /FPI	2.980	2.948	2.920
10 wt % SiO ₂ /FPI	2.994	2.960	2.948
15 wt % SiO ₂ /FPI	2.950	2.890	2.866
20 wt % SiO ₂ /FPI	2.937	2.865	2.832
25 wt % SiO ₂ /FPI	2.790	2.780	2.760

The increase of the dielectric constant is mainly attributed to the relatively high dielectric constant of nanosilica particles (about 3.8-3.9)²² incorporated into fluorinated polyamide matrix and the strong interactive interface between the inorganic nanosilica and the organic fluorinated polyamide matrix. This effect was also corresponded to the sum property principle of polymer composites, *i.e.*, $\epsilon_{\min} < \epsilon < \epsilon_{\max}$ ¹⁹. Moreover, the flaws introduced by the incorporating of nanosilica phase, such as the electrons, cavities, vacancies, *etc.*, changed the distribution of charge in composite films and under electric field, the charges migrated to the positive and negative electrode, respectively, leading the charges accumulating in the interfacial flaws. The orientation polarization of interfacial charges, which was also called interfacial charge polarization, took place as a consequence of charge migration, bringing about the dielectric coefficient of hybrid films increasing. It also can be remarkably seen that the growth trend of ϵ towards frequency was obedient to the change trends at a low frequency forecasted by Debye relaxation theory ($\omega\pi \ll 1$ or $2\pi f \ll 1$). The ϵ decreased with the increasing of SiO₂, presumably due to the movement of chain segments and the interfacial polarization were hindered as the large and compact SiO₂ network formed with increased SiO₂ content.

Kramarenko *et al.*²² pointed out that the relationship of composition dependence of ϵ of the SiO₂ suggested a probability of a morphology change, presumably, a sort of percolation transition from small-size, individual clusters into large-size, infinite clusters and fluorinated polyamide derived nanoparticles may have a reasonably good potential as low dielectric constant materials⁶.

Conclusion

A series of fluorinated polyamide/silica nanocomposite thin films were successfully prepared *via in situ* polymerization of TFDB and 6FDA in the presence of nanosilica particles. The nanocomposite films hold the preferable thermal stability as same as the pure fluorinated polyamide. Their water absorption decreased with increasing of the silica content. The dielectric constant of fluorinated polyamide/nanosilica films decreased with the increased frequency. As the silica contents increased, the dielectric constant of composite films slightly increased gradually up to 10 wt % silica; after decreased. The films possessed the low dielectric constant for all compositions. In summary, the fluorinated polyamide/silica is a kind of nanocomposites material with to be specific properties, showing a great potential for practical applications in high performance microelectronic devices and electron packaging.

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