

Studies of Dielectric Characteristics and Surface Energies of Spin-Coated Polyimide Films

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ABSTRACT: A two-step method, that is, polyamic acid formation with subsequent curing, was used to synthesize six kinds of polyimides. Dielectric constants and surface energies were investigated to determine the nature of the fluorinated and nonfluorinated polyimides. The dielectric constant decreased from 3.3 (at 100 kHz) for PMDA/ODA to 2.6 (at 100 kHz) for 6FDA/4,4'-6F when the fluorine content increased from 0 to 30.7 wt %. Simultaneously, the water contact angle increased from 65° for PMDA/ODA to 78° for 6FDA/4,4'-6F. Experimental results indicated that fluorinated polyimides contained a lower dielectric constant with improved water resistance. The surface energy values obtained from experiments agreed well with Holmes' correlation between surface energy and dielectric constant. The surface energies and dielectric constants were significantly affected by the polymer backbone structures, especially by the fluorination effect. Therefore, by choosing the appropriate monomers, polyimides of low dielectric constants with hydrophobic surfaces could be obtained. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 1642–1652, 2001

Key words: polyimide; dielectric properties; surface energy; contact angle

INTRODUCTION

Polyimide films spin-coated from polyamic acid solutions have become increasingly important as interlevel dielectrics for multilevel interconnections in microchips and electronic packaging structures because of their unique features, such as thermal stability, chemical resistance, low dielectric constant, and ability to planarize underlying structures.¹ Polyimide films, which possess good electrical properties such as low dielectric constants and dissipation factors over a wide range of temperatures and frequencies, provide electrical insulation between conduction paths

with low capacitance and cross talk. This is attributed to the signal propagation speed in the devices, which is inversely proportional to the square root of the dielectric constant of the dielectric material.² Therefore, they can allow dense wiring of metal conductors and result in smaller devices with high-speed signal propagation.

As electronic devices are miniaturized, the requirements for the materials become much more stringent. Polyimides provide low dielectric constant and good surface properties. Fluorination is one of the methods to decrease the dielectric constant of polyimides. Because the incorporation of fluorine increases the fractional free volume, the electronic polarizability decreases, providing that it is a symmetric substitution of the fluorine groups.³ It has been shown that a dielectric constant of 2.5–3.3 and a moisture absorption con-

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tent of 0.05–1.9 wt % may be achieved, by fluorinating both of the dianhydride and diamine units.⁴ For nonfluorinated polyimides, the dielectric and moisture absorption content are higher and are in the ranges of 3.0–3.5 and 1.4–3.5 wt %, respectively. In addition, 4,4'-hexafluoroisopropylidenediphthalic anhydride/4,4'-oxydiphenylene diamine (6FDA/ODA) has been commercialized since the 1990s. Because fluorine substitution affects many properties, it is very difficult to isolate specific property dependencies on fluorine replacement. For example, the increased hydrophobicity caused by fluorine substitution will both decrease the ambient moisture absorption and lower the dielectric constant.

To incorporate the polyimides as the low-*k* dielectrics in microelectronic devices requires good metal–polymer adhesion and high stability of all interfaces. Adhesion strength depends on interfacial bonding through various interactions, such as mechanical interlocking, polar interactions, van der Waals interactions, chemical bonding, and surface properties including surface energy and surface roughness, as well as bulk properties such as thermal expansion coefficients of the interfacial layers. A few theories, based on the assumption of the additivity of different molecular interactions, such as dispersion forces, dipole and induced dipole interactions, and hydrogen bonding, have been proposed to evaluate the solid surface energy.⁵ The surface free energy measured by the contact angle method can be used to evaluate the chemical structural effects on the surface properties of the polymer. It is based on the contact angle measurements of various liquids on a solid polymer surface and use of appropriate theory to estimate the surface energy. However, the study of surface energy for polyimide surfaces, especially fluorinated surfaces, has not been investigated extensively by using the three-liquid goniometry.

In this study, several kinds of polyimides were synthesized, and the dielectric properties of these polyimide films were measured as functions of time, frequency, and temperature to observe the effects of fluorination and chemical structures on the dielectric properties. Also, the surface energy of the fluorinated polyimide films was evaluated by using the three-liquid goniometry to explain the fluorination effect on moisture uptake, which would inversely influence the dielectric properties. It is hoped that this research would provide important information of dielectric properties and surface energy of polyimides for the microelectronic industry, for example, the optimum fluo-

rine contents for low dielectric constants while not decreasing the reliability of all surfaces and the surface energy of polyimides suitable for the interfaces in microelectronic devices.

EXPERIMENTAL

Polymer Syntheses

The diamine and dianhydride monomers used were pyromellitic dianhydride (PMDA), 4,4'-hexafluoroisopropylidenediphthalic anhydride (6FDA), 4,4'-(hexafluoroisopropylidene) dianiline (4,4'-6F), 3,3'-(hexafluoroisopropylidene) dianiline (3,3'-6F), 4'',4''-(hexafluoroisopropylidene)bis(4-phenoxyaniline) (4-BDAF), and 4,4'-oxydianiline (ODA). All monomers were obtained from the Aldrich Chemical Co. (Milwaukee, WI) and were purified by recrystallization before use. Also, the solvents, *N*-methyl-2-pyrrolidinone (NMP; obtained from Merck, Darmstadt, Germany), acetic anhydride, and ethanol were distilled before use.

A two-step synthetic method was used to prepare the polymers. First, 15 wt % of the diamine was dissolved in NMP in a flask under nitrogen purging. Second, a stoichiometric amount of the dianhydride in powder form was slowly added to the diamine solution with a stirrer to obtain a poly(amic acid) solution, called PAA. Third, the PAA solution was spin-coated onto glass slides and then thermally converted into polyimides by heating in a forced-air oven at 100, 200, and 300°C with a ramping rate of 2.0°C/min for 1 h at each temperature. The synthesized polyimides are listed in Table I.

Fourier Transform Infrared Spectroscopy

The degree of imidization was monitored as a function of curing temperature by a Perkin–Elmer FT-IR Spectrometer Spectrum 2000 (Perkin Elmer Cetus, Norwalk, CT). The absorption band at 1780 cm⁻¹ was used to follow the appearance of the imide moiety.

Coefficient of Thermal Expansion

A TA Instruments TMA 2940 Thermomechanical Analyzer (TA Instruments, New Castle, DE) was used to obtain the linear coefficient of thermal expansion (CTE). The polyimide films were cut into 2-mm × 22-mm pieces and mounted between two vertical clamps in tension under a force of 0.05 N. The samples were heated from room temperature to 350°C at a heating rate of 5°C/min.

Table I Abbreviations and Structures of Polyimide Repeat Units

Polyimides	Structures
PMDA/ODA	
PMDA/4-BDAF	
PMDA/3,3'-6F	
6FDA/4-BDAF	
6FDA/3,3'-6F	
6FDA/4,4'-6F	

CTE values of the polyimides in the film plane were obtained over the temperature range of 100–200°C by averaging three test results.

Moisture Absorption

The amount of weight loss measured by a Perkin-Elmer TGA 7 Thermogravimetric Analyzer (TGA) at 100°C was used to determine the moisture uptake. First, the polyimide film of 40 μm thickness was put into a vacuum oven at 100°C for 1 day to obtain a dry film. Then, the film was put in an environmental chamber at 70% relative humidity and room temperature for 15 days. Afterward, the film was analyzed by TGA at a heating rate of 20°C/min and the weight loss at 100°C was taken as the moisture uptake.

Dielectric Properties

The dielectric properties were measured using a TA Instruments DEA 2970 Dielectric Analyzer. To ensure good electrical contact between the

electrodes and the samples, polyimide films around 20 μm thick were sputter-coated beforehand with a thin layer of gold for 40 s on both sides.⁶ The main parameters of interest were the dielectric constant ϵ' , dielectric loss ϵ'' , and loss factor $\tan \delta$, which were determined over the frequency range of 1–10⁵ Hz at temperatures between 30 and 300°C at a heating rate of 3°C/min in a nitrogen gas environment. The ram force applied on the sample was 500 N. The calculation of the dielectric constants was based on the film thickness at 100°C and 1 kHz.

Contact Angle

The contact angles of the polyimide films after being cleaned by a mildly alkaline solution were obtained by a contact angle goniometer (Model 100-22; Ramé-Hart, Mountain Lakes, NJ) at 25°C using the sessile drop method. Three liquids [deionized water (W, prepared in this laboratory), glycerol (GL, from BDH, Toronto, Canada), and diiodomethane (DIM, from Nacalai Tesque, Kyoto,

Table II Surface Energy Components (mJ/m^2) of Testing Liquids

Testing Liquids	γ^+ (mJ/m^2)	γ^- (mJ/m^2)	γ^{AB} (mJ/m^2)	γ^{LW} (mJ/m^2)	γ (mJ/m^2)
Water	25.5	25.5	51.0	21.8	72.8
Glycerol	3.92	57.4	30.0	34.0	64.0
Diiodomethane	0	0	0	50.8	50.8

Japan)], two polar and one apolar, were chosen as the probing liquids for measuring the contact angles.^{7,8} All probing liquids were reagent grade and used as received. Table II tabulates their basic surface tension parameters.

Liquid droplets (about $10 \mu\text{L}$) were introduced by a Gilmont microsyringe onto the polymer surfaces. Four to five droplets were deposited at different locations of the same polyimide film. Two pieces of polyimide films were used to obtain 10 reliable contact angle data. The contact angle was obtained by averaging the 10 data for each kind of testing liquid. A built-in image system could transmit the image obtained to a computer for image analysis. Advancing and receding contact angles were obtained through a tilting base.⁹ Because the advancing contact angles represent the equilibrium contact angles more closely than the

receding angles,^{7,10-13} only advancing contact angles were used to calculate the surface free energy.

RESULTS AND DISCUSSION

Fourier Transform Infrared Spectra

Fourier transform infrared spectroscopy (FTIR) was used to identify the degree of imidization. Figure 1 shows the FTIR spectra of PMDA/3,3'-6F cured at 100, 200, and 300°C. The spectrum of the uncured PMDA/3,3'-6F exhibited characteristic absorption amide peaks at around 1660, 1520, and 1300 cm^{-1} . The band around 3300 cm^{-1} represented the N—H linkage stretching. The IR absorption band around 2400–3200

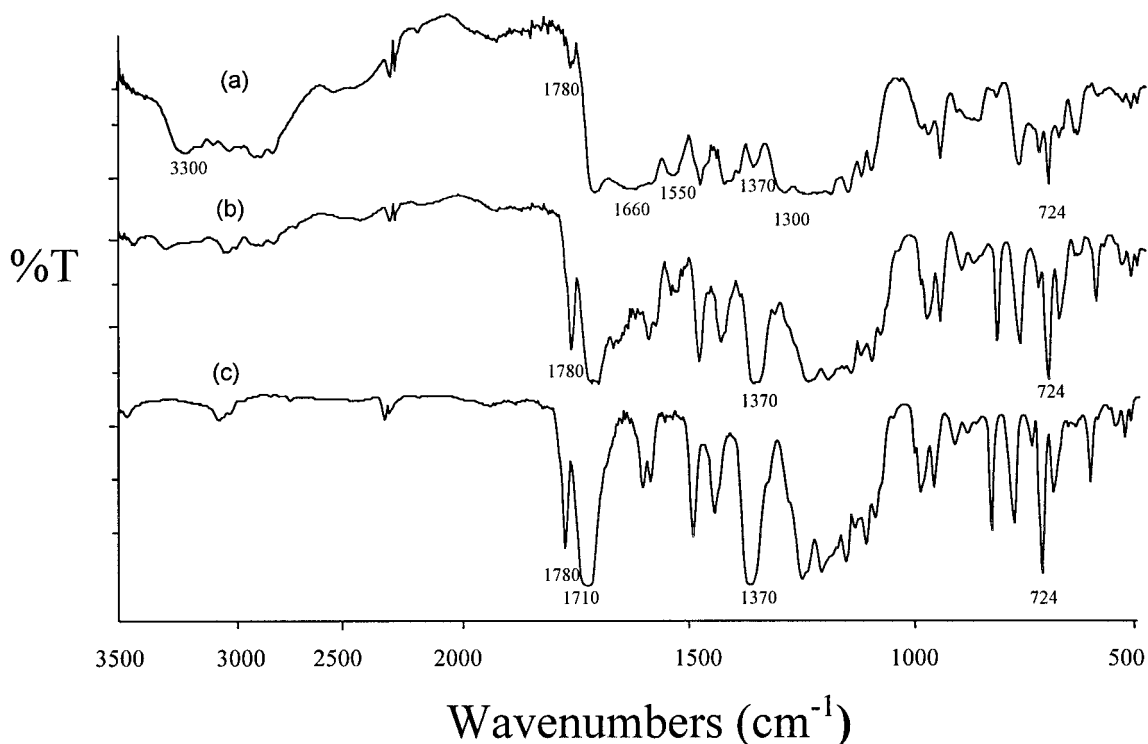


Figure 1 FTIR spectra of PMDA/3,3'-6F cured at (a) 100°C, (b) 200°C, and (c) 300°C.

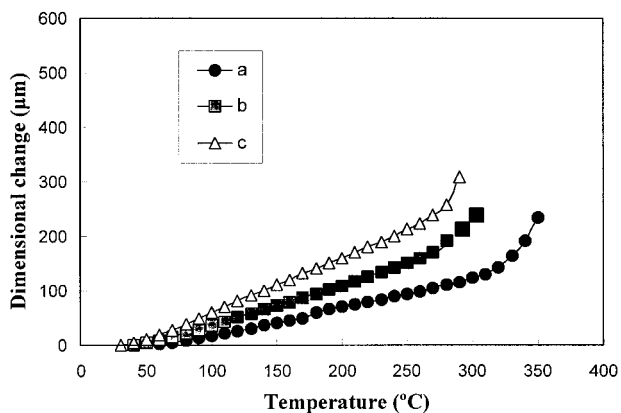


Figure 2 Dimensional changes of PMDA-based polyimides: (a) PMDA/ODA, (b) PMDA/3,3'-6F, (c) PMDA/4-BDAF.

cm^{-1} was attributed to the stretching of the —O—H groups in the carboxylic acid. As the temperature increased, the intensity of these characteristic poly(amic acid) (PAA) absorption peaks gradually decreased and finally disappeared at above 300°C . New absorption peaks appeared at 1780 , 1710 , 1370 , and 724 cm^{-1} . The peaks at 1780 and 1710 cm^{-1} were ascribed to the vibrations of the C=O linkages in the imide rings, and the peaks at 1370 and 724 cm^{-1} were attributed to the vibrations of the C—N cyclic imide groups. The IR spectrum indicated that the final product cured at 300°C was almost completely imidized into polyimide.

Coefficient of Thermal Expansion

The coefficient of thermal expansion (CTE) is strongly related to the chemical and geometrical structure of the molecule. Numata and coworkers¹⁴ found that rodlike polyimides without side groups exhibited larger packing density and lower CTEs than those of other polyimides. The chain orientation significantly influences film properties such as the dielectric constant, CTE, and modulus.¹⁵ A polymer containing disorientated molecular chains usually gives a high CTE, whereas a polymer containing highly orientated molecular chains gives a low CTE. Thus, there is a relation between structure and properties of polyimides. The experimental results are summarized in Table III.

One group of polyimides is PMDA with different diamines and the other group is 6FDA with different diamines. Their CTE values were obtained in the temperature range of $100\text{--}200^\circ\text{C}$. Figure 2 is used to calculate the CTE values of

PMDA-based polyimides in the tensile mode under a force of 0.05 N . The dimensions increased almost linearly with temperature at temperatures below 250°C . Then, the dimensions increased abruptly as a result of the onset of glass-transition temperatures. The averaged CTE values, in ascending order, were $42.0 \times 10^{-6}/^\circ\text{C}$ for PMDA/ODA, $57.7 \times 10^{-6}/^\circ\text{C}$ for PMDA/3,3'-6F, and $69.9 \times 10^{-6}/^\circ\text{C}$ for PMDA/4-BDAF. The results clearly indicated that the diamine chain rigidity directly affected the CTE. The more flexible of the diamine chains gave rise to higher CTEs. In the other group, the CTEs of 6FDA/4,4'-6F, 6FDA/3,3'-6F, and 6FDA/4-BDAF were $59.9 \times 10^{-6}/^\circ\text{C}$, $57.6 \times 10^{-6}/^\circ\text{C}$, and $71.8 \times 10^{-6}/^\circ\text{C}$, respectively. 6FDA/4-BDAF, with the most flexible chains, exhibited the highest CTE because of the free rotations of oxy-bridges in the imide chains. 6FDA/4,4'-6F and 6FDA/3,3'-6F had only slightly different CTEs because they contained the same hexafluoroisopropylidene groups in their diamine backbones with similar bond angles and bond lengths from molecular modeling results.¹⁶

Table III also shows that the CTEs of 3,3'-6F-based and 4-BDAF-based polyimides containing either PMDA or 6FDA dianhydrides were almost the same, respectively. This indicated that the dianhydride structures had less effect on the CTEs.

Relationship of Fluorine Content with Moisture

Moisture uptake is dependent on both physical and chemical interactions of the film with water vapor. The diffusion rate of water vapor into a film is related directly to the flexibility of the polymer chain and inversely to the film density and film orientation. The higher degree of molecular in-plane orientation and packing order gives rise to a lower diffusion coefficient and water uptake.¹⁷ The presence of residual solvents in-

Table III CTE Values of Polyimides

Polyimides	CTE ^a ($\mu\text{m m}^{-1} \text{ }^\circ\text{C}^{-1}$)
PMDA/ODA	42.0
PMDA/3,3'-6F	57.7
PMDA/4-BDAF	69.9
6FDA/4-BDAF	71.8
6FDA/3,3'-6F	57.6
6FDA/4,4'-6F	59.9

^a CTE was tested by TMA at a heating rate of $5^\circ\text{C}/\text{min}$. The CTE value was obtained from the temperature range of $100\text{--}200^\circ\text{C}$.

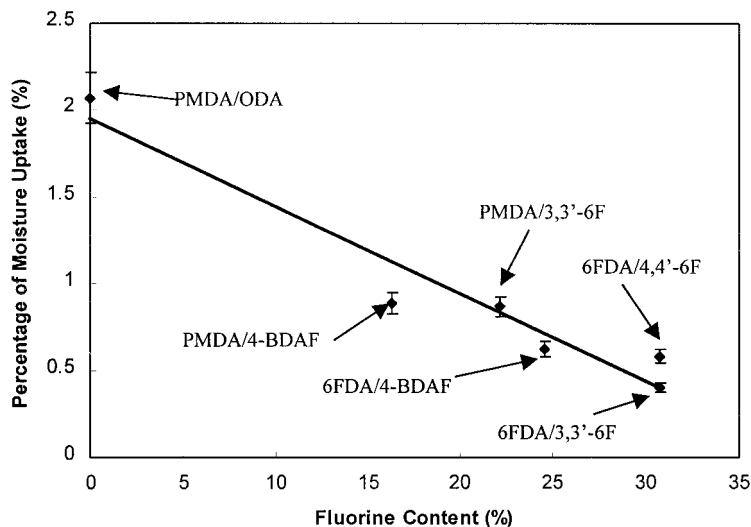


Figure 3 Relationship of moisture uptake with fluorine content of polyimides.

increases the rate of water vapor diffusion in polymers.¹⁸ The moisture uptake of nonfluorinated and fluorinated polyimide films was obtained by measuring the TGA weight loss at 100°C. Figure 3 shows that the water vapor uptake decreases linearly with increasing fluorine content because of the hydrophobic effects of the fluorine atoms. With increasing fluorine content in the polyimide repeat unit, hydrophobic strength increased, leading to a decrease in moisture uptake. In addition, the bulky $-\text{CF}_3$ groups reduced the molecular packing density and increased the free volume of the polyimides. Given that polyimides with high free volume would have low density, the

diffusion rate of water vapor into the film was inversely related to the film density. In this study, 6FDA/3,3'-6F absorbed 0.4 wt % moisture compared to the conventional PMDA/ODA, which absorbed 2.1 wt % moisture in 15 days at room temperature. The low moisture uptake level of 6FDA/3,3'-6F was attributed to its high fluorine level. Therefore, increasing fluorine content was an effective way to reduce moisture absorption.

Dielectric Properties

Figure 4 shows the dielectric constants of polyimides measured from 40 to 260°C at four decades of

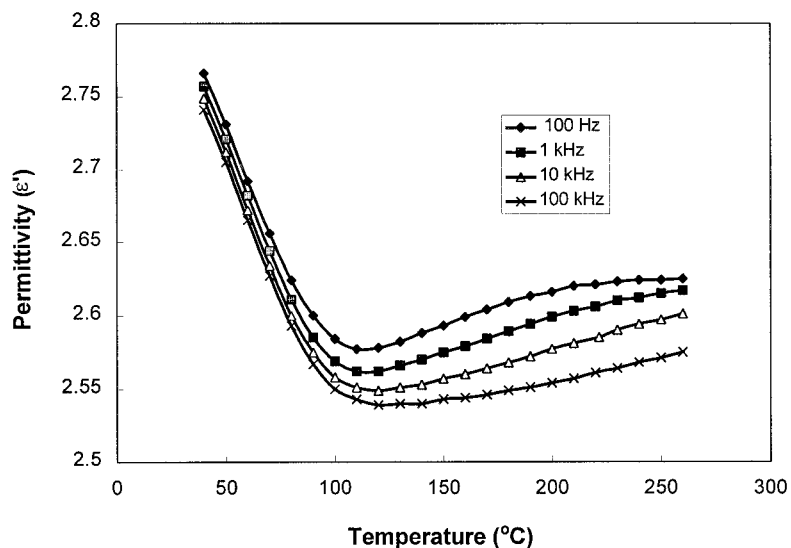


Figure 4 Variation of the dielectric constant (ϵ') of 6FDA/4,4'-6F with temperature at four decades of frequencies.

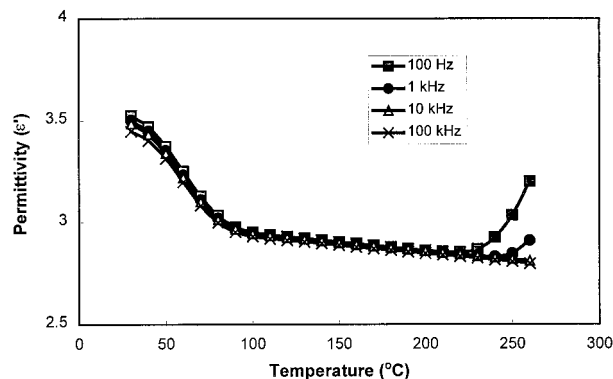


Figure 5 Variation of the dielectric constant (ϵ') of PMDA/ODA with temperature at four decades of frequencies.

frequencies, that is, 0.1–100 kHz. At 100°C, 6FDA/4,4'-6F films showed permittivities (ϵ') of 2.584, 2.569, 2.558, and 2.550 at 0.1, 1, 10, and 100 kHz, respectively. The dielectric constant decreased slightly from 40 to 100°C and remained almost constant up to about 250°C. Afterward, a gradual increase of ϵ' was observed with further increase of temperature attributed to an increase in molecular motion and hence free volume. Fluorinated and nonfluorinated polyimide films exhibited similar dependencies on temperatures and frequencies (Fig. 5).

Figures 6–8 show the dependencies of loss factor (ϵ'') and dissipation factor ($\tan \delta$) on temperatures and frequencies. The loss factor consists of dipole loss factor and ionic conductance. At temperatures below T_g , the values of the loss factor were comparatively small as a result of the small

amounts of energy dissipation by the limited molecular motions or small dipole loss factor. With increasing temperature, the molecular motions increased and hence the increased free volume led to enhanced alignments of the dipoles to the external electric field with increased energy dissipation; thus the loss factors were higher at high temperatures. The dissipation factor ($\tan \delta$) indicated a sharp increase at the high frequency of 100 kHz (Fig. 7). This rapid increase in the dissipation factor was ascribed to the high ionic conductance contribution to the loss factor (ϵ''). Therefore, the loss factor in the out-of-plane direction as measured by parallel plate sensor was largely contributed by the electron mobility of polyimides at high temperatures.

Figure 8 shows similar behavior for nonfluorinated polyimide films. The relaxation process could be explained by the concept of electric loss modulus M'' , which is defined as $\epsilon''/(\epsilon'^2 + \epsilon''^2)$,^{19–21} because the dielectric loss modulus offered some advantages over the loss factor at high temperatures under conditions where ϵ' was increasing with temperature.¹⁹ Because ϵ' increases much faster than ϵ'' as a result of increasing ionic conductance with temperature, the contribution from ϵ'' is overshadowed by ϵ' in M'' . A plot of logarithmic M'' versus temperature for 6FDA/4,4'-6F polyimide at three frequencies is shown in Figure 9. The maxima in M'' occurred at about the same temperatures as the maxima in ϵ'' and $\tan \delta$ in Figures 6 and 7. Moreover, both M'' and ϵ'' relaxation peaks occurred at around 100°C at 0.1 kHz. Therefore, the permittivity and electric loss mod-

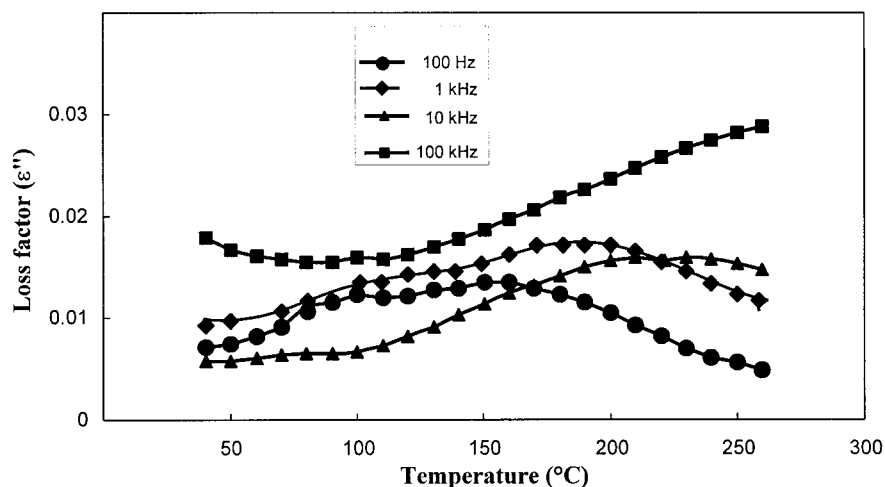


Figure 6 Variation of loss factor (ϵ'') with temperature of 6FDA/4,4'-6F at four decades of frequencies.

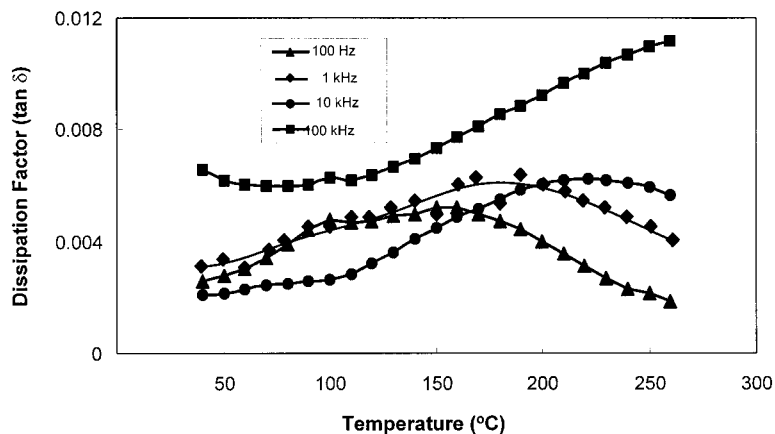


Figure 7 Variation of dissipation factor ($\tan \delta$) of 6FDA/4,4'-6F with temperature at four decades of frequencies.

ulus contained the same information for the fluorinated polyimides studied in this investigation.

The dielectric constant is composed of electronic, atomic, and dipole orientational contributions. At frequencies below 100 MHz, all three kinds of polarizations contribute to the dielectric constant. The dielectric constant is thus related to the polarizability of a material and is strongly dependent on its chemical structure.²² The structural effects of diamines on the dielectric properties were examined with PMDA/ODA, PMDA/3,3'-6F, and PMDA/4-BDAF. Among the three kinds of diamines, ODA contained an oxy-bridge, 3,3'-6F contained a bulky $-\text{C}(\text{CF}_3)_2$ bridge, and 4-BDAF contained two oxy-bridges and a

$-\text{C}(\text{CF}_3)_2$ bridge in the main chain. The oxy-bridge decreased the chain rotational energy and consequently the chain became more flexible. The bulky $-\text{CF}_3$ groups on the $-\text{C}(\text{CF}_3)_2$ bridge reduced the chain packing density and the inter-chain charge transfer of the polar dianhydride groups. In addition, the large fluorine atoms also increased the free volume fraction in the polymer and, as a result, reduced the number of polarizable groups per unit volume. Hence, PMDA/4-BDAF showed the lowest dielectric constant.

In Group B, 6FDA dianhydride was reacted with three kinds of diamines to form 6FDA/4-BDAF, 6FDA/3,3'-6F, and 6FDA/4,4'-6F polyimides. Among the three kinds of polyimides, 6FDA/

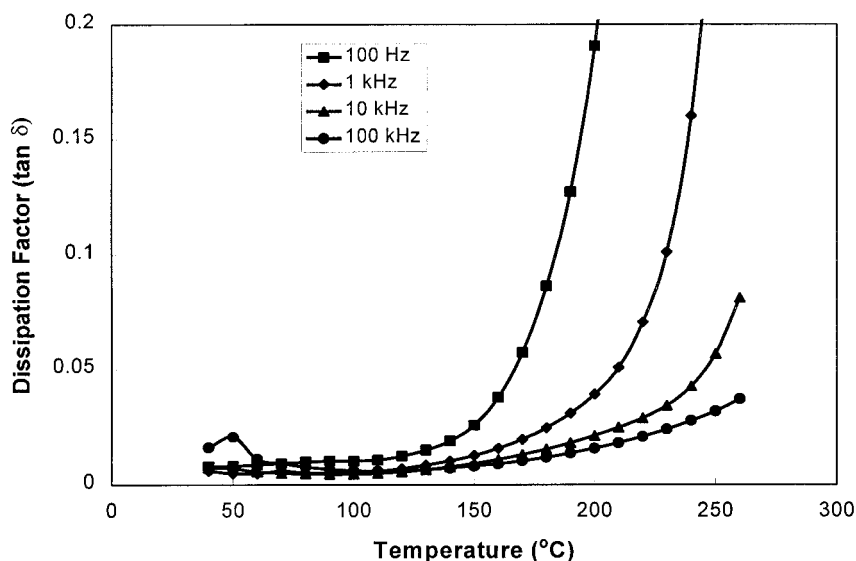


Figure 8 Variation of dissipation factor ($\tan \delta$) of PMDA/ODA with temperature at four decades of frequencies.

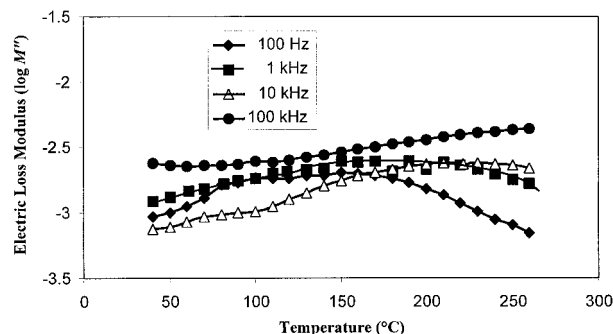


Figure 9 Relationship between electric loss modulus ($\log M''$) of 6FDA/4,4'-6F and temperature at four decades of frequencies.

4-BDAF contained the lowest number density of F-atoms per repeating polymer chain unit and therefore the highest density of polarizable groups per unit volume. As a result, the dielectric constant of 6FDA/4-BDAF was higher than that of either 6FDA/3,3'-6F or 6FDA/4,4'-6F. Figure 10 shows that the dielectric constants were 2.383 for 6FDA/3,3'-6F and 2.569 for 6FDA/4,4'-6F at 1 kHz and 100°C, even though they contained the same amounts of fluorine. The different structural incorporations of the trifluoromethyl ($-\text{CF}_3$) groups into the polymer backbones caused significant effects to the dielectric properties. In 6FDA/3,3'-6F, the $-\text{CF}_3$ pendant groups were attached to the *m*-linkages of the diamine, whereas the $-\text{CF}_3$ groups were attached to the *p*-linkages in 6FDA/4,4'-6F. Consequently, the free volume in 6FDA/3,3'-6F was larger and the chain packing density was lower. Because of the lower electronic polarizability and larger free volume in 6FDA/3,3'-6F, its dielectric constant was lower than

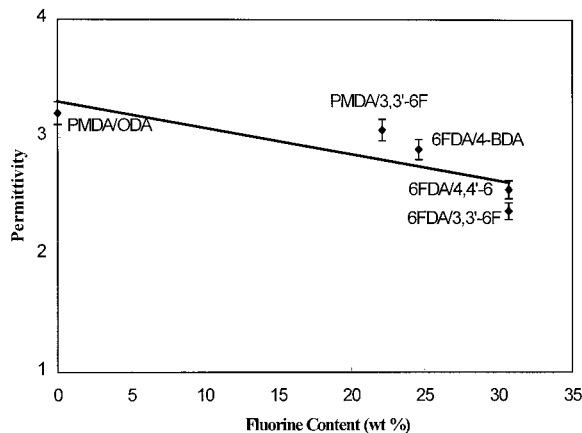


Figure 10 Dielectric constant (or permittivity, ϵ') versus fluorine content of polyimides.

Table IV Contact Angles of Nonfluorinated and Fluorinated Polyimides

Polyimides	Water Contact Angle (°)	Glycerol Contact Angle (°)	Diiodomethane Contact Angle (°)
PMDA/ODA	65.28	57.36	42.14
PMDA/4-BDAF	66.22	62.18	46.16
6FDA/4-BDAF	71.80	32.40	50.70
6FDA/3,3'-6F	74.73	62.30	49.00
6FDA/4,4'-6F	78.36	64.68	46.84

that of the *p*-isomer 6FDA/4,4'-6F. Therefore, incorporating some “kinks” in the polymer backbones might reduce the dielectric constant.

The results obtained suggest that the dielectric properties of the polyimides were affected by four factors: (1) the temperature and frequency applied to the material, (2) the structural difference of *meta* and *para* groups in the polyimides' backbones, (3) the orientational effects induced during spin-coating and the temperature effects in the subsequent curing step, and (4) the moisture content of the material. The CTE values were in good agreement with the dielectric constants obtained. Compared to nonfluorinated polyimides such as PMDA/ODA, fluorinated polyimides contained a lower degree of orientation because of the bulky $-\text{CF}_3$ group in the main chain. As a result, they had higher thermal expansion coefficients and lower dielectric constants.

Surface Energy

Lee et al.²³ reported the advancing contact angles were 87, 79, and 85° for 6FDA/ODA, BPDA/PDA, and PMDA/ODA, respectively. Moreover, 6FDA/ODA had a greater water receding contact angle than that of BPDA/PDA and PMDA/ODA because 6FDA/ODA contained the nonpolar $=\text{C}(\text{CF}_3)_2$ units. To examine the effects of fluorine on the surface free energy and water resistance, contact angles of various polyimide films were measured with water, a polar liquid; glycerol, a moderately polar liquid; and diiodomethane, an apolar liquid. Table IV shows the contact angle measurements on PMDA/ODA, PMDA/4-BDAF, 6FDA/4-BDAF, 6FDA/3,3'-6F, and 6FDA/4,4'-6F film surfaces. The water contact angle increased with increasing fluorine content from 65.28° for nonfluorinated PMDA/ODA to 78.36° for 6FDA/4,4'-6F containing 30.7 wt % fluorine. The relatively large advancing angle may be ascribed to the nonpolar

Table V Comparison of Surface Energies of PMDA/ODA and Fluorinated Polyimides

Polyimides	F-Content (wt %)	γ^+ (mJ/m ²)	γ^- (mJ/m ²)	γ^{AB} (mJ/m ²)	γ^{LW} (mJ/m ²)	γ_s (mJ/m ²)
PMDA/ODA	0	0.56	13.95	5.60	38.52	44.12
PMDA/4-BDAF	16.3	0.25	16.33	4.01	36.39	40.40
6FDA/4-BDAF	24.6	1.08	9.23	6.31	33.88	40.20
6FDA/3,3'-6F	30.7	0.88	7.38	5.08	34.83	39.91
6FDA/4,4'-6F	30.7	0.65	5.31	3.73	36.02	39.75

hexafluoroisopropylidene =C(CF₃)₂ moiety. This is consistent with the findings that 6FDA/ODA has a greater advancing contact angle than that of PMDA/ODA because it contains the nonpolar C(CF₃)₂ unit.²³

Fowkes suggested that surface energy (γ_s) could be divided into an apolar component (γ^{LW}) and a Lewis acid–base interaction component (γ^{AB}) as follows:

$$\gamma_s = \gamma^{LW} + \gamma^{AB} \quad (1)$$

Moreover, Van Oss et al.^{12–13} proposed two additional parameters to describe the strength of the Lewis acid–base interactions:

$$\gamma^{AB} = 2\sqrt{\gamma^+\gamma^-} \quad (2)$$

where γ^+ is the Lewis acid parameter of surface free energy and γ^- is the Lewis base parameter of surface free energy.

To obtain surface free energies of fluorinated polyimide and PMDA/ODA films, the three-liquid equations of Van Oss and Good were used:

$$\gamma_{l_1}(1 + \cos \theta_1) = 2(\sqrt{\gamma_s^{LW}\gamma_{l_1}^{LW}} + \sqrt{\gamma_s^+\gamma_{l_1}^-} + \sqrt{\gamma_s^-\gamma_{l_1}^+}) \quad (3)$$

$$\gamma_{l_2}(1 + \cos \theta_2) = 2(\sqrt{\gamma_s^{LW}\gamma_{l_2}^{LW}} + \sqrt{\gamma_s^+\gamma_{l_2}^-} + \sqrt{\gamma_s^-\gamma_{l_2}^+}) \quad (4)$$

$$\gamma_{l_3}(1 + \cos \theta_3) = 2(\sqrt{\gamma_s^{LW}\gamma_{l_3}^{LW}} + \sqrt{\gamma_s^+\gamma_{l_3}^-} + \sqrt{\gamma_s^-\gamma_{l_3}^+}) \quad (5)$$

The surface energies (γ_s) and components (γ^+ , γ^- , γ^{AB} , and γ^{LW}), calculated by using eqs. (3)–(5) for various polyimide films with different fluorine contents, are shown in Table V. The surface energy γ_s is made up of both the Lifshitz–van der Waals component (γ^{LW}) and the acid–base interaction component (γ^{AB}). The Lewis acid parameters (γ^+) of all polyimides were small, varying from 0.25 to 1.08 mJ/m², resulting in small acid–base parameters (γ^{AB}). The Lifshitz–van der Waals component (γ^{LW}) was in the range of 33.88–36.39 mJ/m² for the fluorinated polyimide films containing 16.3–30.7 wt % of fluorine, and it increased to 38.52 mJ/m² for the nonfluorinated PMDA/ODA films. Thus, values of the Lifshitz–van der Waals components were much greater than those of the Lewis acid–base interaction components ($\gamma^{LW} > \gamma^{AB}$). The higher polymer surface energy gave rise to lower contact angles or greater surface wettability. Moreover, polyimide films with higher surface energy would have poor water uptake resistance. Therefore, it further suggested that the fluorine atoms did improve the hydrophobicity and increased the water uptake resistance, resulting in a decrease of the dielectric constant.

A simple empirical relation between the surface energy and the dielectric constant was proposed by Holmes, as follows²⁴:

$$\gamma_s = 20.9\varepsilon' - 20.5 \quad (6)$$

Table VI Comparison of Surface Energies of Three Selected Polyimides

Polyimides	ε' (30°C, 1 kHz)	γ_s (Experimental) (mJ/m ²)	γ_s (Calculated) (mJ/m ²)
PMDA/ODA	3.30	44.12	48.07
6FDA/4-BDAF	3.04	40.20	43.08
6FDA/4,4'-6F	2.78	39.75	37.60

The experimental results of the surface energies of three polyimides were examined by this linear correlation and are listed in Table VI. The data show that the calculated surface energy increased with increasing dielectric constant. The percentage difference between the calculated and experimental surface energies was in the range of 5–9%.

CONCLUSIONS

In this study, one nonfluorinated polyimide (PMDA/ODA) and five fluorinated polyimides (PMDA/3,3'-6F, PMDA/4-BDAF, 6FDA/4,4'-6F, 6FDA/3,3'-6F, and 6FDA/4-BDAF) were synthesized and their dielectric properties and surface energies were investigated in detail. The dielectric properties of the polyimides were dependent on temperature and frequency. The loss factor and the electric loss modulus gave similar information on the dielectric relaxation peaks for the six types of polyimide studies. The same dielectric behavior was observed for the fluorinated and nonfluorinated polyimides. The dielectric constant decreased with increasing fluorine content. It increased from 2.4 for 6FDA/4,4'-6F (with 30.7 wt % F) to 3.3 for PMDA/ODA (with no F) when measured at 100 kHz and 100°C. Among the six polyimide films, the surface energy of the nonfluorinated polyimide (PMDA/ODA) was higher than that of the fluorinated polyimides. Experimental results indicated that the fluorine atoms improved the hydrophobicity, increased the water uptake resistance, and eventually led to a low dielectric constant of the polyimides.

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