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Synthesis of Low Dielectric Constant Polyetherimide Films

Bor-Kuan Chen, Yu-Ting Fang, Jing-Ru Cheng*

Summary: As the demand for downsizing in microelectronics is increasing, devices require material with lower dielectric constant accordingly. The dielectric constants for most polyimide (PI), including polyetherimide (PEI), films are ~3.5. In this study, we modified the PEI by incorporating various monomers (fluorinated dianhydride 6FDA and phenylene ether diamines) to reduce the dielectric constant. The dielectric constants of synthesized PEIs decreased with increasing amounts of 6FDA content and phenylene ether units. The T_g decreased gradually with PEI containing longer phenylene ether units, but increased with the content of 6FDA. The thermal decomposition temperatures at 10% weight loss were ~550 °C, indicating that these PEIs have high thermal stability. Both the tensile strength and the modulus decreased with the PEI containing longer phenylene ether units. The PEI synthesized with 40% 6FDA dianhydride and 1,4-bis(4-aminophenoxy)benzene (*p*BAB) diamine has the lowest dielectric constant of 2.78 at 1 MHz.

Keywords: 6FDA; dielectric properties; phenylene ether diamines; polyetherimide; polyimides

Introduction

As integrated circuit (IC) dimensions continue to decrease, the device packing densities increase accordingly. However, the demand for high performance is also increasing. Within the next generation of IC production, devices may require materials to have dielectric constants approaching or below 2.0 as the dimensions of devices approach 100 nm.[1] Materials that possess low dielectric constants are being developed to replace silicon dioxide (SiO_2) as the inter-level dielectric substance. While polyimide (PI) is one of the most suitable materials, it is difficult to fabricate due to its high softening temperature and insolubility. One successful approach to increase the solubility of polyimides was to introduce flexible linkages into the polymer backbone. Ultem 1000 is an example of the important commercialized products that contains flexible ether and isopropylidene groups. An amorphous polyetherimide (PEI) introduced by General Electric Co. that is synthesized *via* the polycondensation of a dianhydride, 4,4′-(4,4′-isopropylidene diphenoxy) bis (phthalic anhydride) [BPADA], with *m*-phenylene diamine (*m*PDA), Ultem 1000 exhibits good thermal stability and mechanical properties.[2] To improve the chemical resistance of Ultem 1000, General Electric substituted *m*PDA with *para*-phenylene diamine (*p*PDA) and produced a PEI, Ultem 5000, with better dielectric properties.[3]

The dielectric constants for most PI (including PEI) films are ~3.5.[4] To reduce the dielectric constant, many researchers employed fluorine-containing compounds [5,6] or prepared hybrid nanocomposites by adding silica.[7,8] In addition, aromatic non-fluorinated PIs that have low dielectric constants have been developed from aromatic dianhydrides and diamine containing phenylene ether units.[9] In this study, we modified the PEI by incorporating various monomers (fluorinated dianhydride and phenylene ether diamines) to reduce the

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Department of Polymer Materials, Kun Shan University, Tainan, Taiwan 71003
E-mail: chenbk@seed.net.tw

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dielectric constant of PEI—thus resulting in PEIs with dielectric constant below 3.0, along with good thermal and mechanical properties.

Experimental

Materials

High purity chemicals were purchased from various commercial sources, including 4,4′-(4,4′-isopropylidene diphenoxy) bis-(phthalic anhydride) [BPADA] (Aldrich), 4,4′-(hexa fluoroisopropylidene)diphthalic dianhydride [6FDA] (Chriskev), *p*-phenylene diamine (Acros), and 4,4′-oxydianiline [ODA] (Acros). 1,4-Bis(4-aminophenoxy)-benzene [*p*BAB] was prepared by the catalytic reduction of 1,4-bis(4-nitro- phenoxy)-benzene (*p*BNB) with hydrazine hydrate and Pd/C catalyst in refluxing ethanol.[10]*p*BNB was synthesized from 1,4- hydroquinone and coupled with 4-chloronitrobenzene in the presence of K_2CO_3 in DMAc. BPADA and 6FDA were recrystallized from acetic anhydride and vacuum dried before use. *N*-methyl-2-pyrrolidone [NMP] was purchased from Tedia and purified by distillation under reduced pressure and stored over 4Å molecular sieves. The other reagents were used as received.

Synthesis of Polyetherimide

Poly(amic acid) (PAA) was first synthesized from dianhydride and diamines. A typical example of polymerization was executed as follows: *p*PDA 1.10 g (0.01 mol, 99%) and NMP 29.4 g were placed into a 250-mL three-neck flask under nitrogen purge. The mixture was stirred until the solution was clear. Equal molar amounts of dianhydride solid were added to the *p*PDA solution through an addition funnel to make a solution with a solid content of 18%. Various mole ratios of BPADA and 6FDA dianhydrides were charged (the mole ratios used are listed in the Table 1). For BPADA/6FDA = 60/40, 3.19 g BPADA (0.006 mole, 98%) was used with 1.80 g 6FDA (0.004mole, 99%). The reaction mixture was stirred for 2 h at 60 °C and resulted in a transparent yellow viscous solution of PAA. The polymer solutions were spread on a glass plate using a spin-coater to control the film thickness. The films were thermally dried at 60 °C for 6–8 h to remove most of the solvent in a forced air oven. They were subsequently heated at 100 °C, 150 °C for 2 h each, and at 250 °C for 3 h in a nitrogen atmosphere to achieve fully imidization. The films were then cooled to room temperature and stripped from the glass. Other PEIs in this study (with diamine ODA and *p*BAB) were prepared by similar procedure (see Scheme 1).

For PEI (**g**), BPADA with *p*BAB diamine: $(C_{49}H_{32}O_8N_2)_n$, $(776.77)_n$, Calcd (%) C, 75.76; H, 4.15; N, 3.61; Found (%) C, 75.23; H, 4.20; N, 3.57.

Characterization

Fourier transfer infrared (FT-IR) spectra were recorded on a Bio-Rad Digilab FTS-40 spectrometer. Elemental analyses were carried out on a Heraus CHN rapid

Table 1.
Thermal and mechanical properties of PEI nanocomposites

Code	Dianhydride BPADA/6FDA (mole ratio)	Diamine	T_g[a] (°C)	$T_{d,10\%}$ (°C)	Char yield[b]
a	100/0	*p*PDA	225	549	60.5
b	80/20	*p*PDA	240	551	60.7
c	60/40	*p*PDA	255	559	62.5
d	100/0	ODA	217	532	56.4
e	80/20	ODA	230	558	58.3
f	60/40	ODA	246	568	63.0
g	100/0	*p*BAB	205	545	53.0
h	80/20	*p*BAB	214	549	57.0
i	60/40	*p*BAB	222	564	60.2

[a] Measured by DSC.
[b] Residual wt % in nitrogen at 800 °C.

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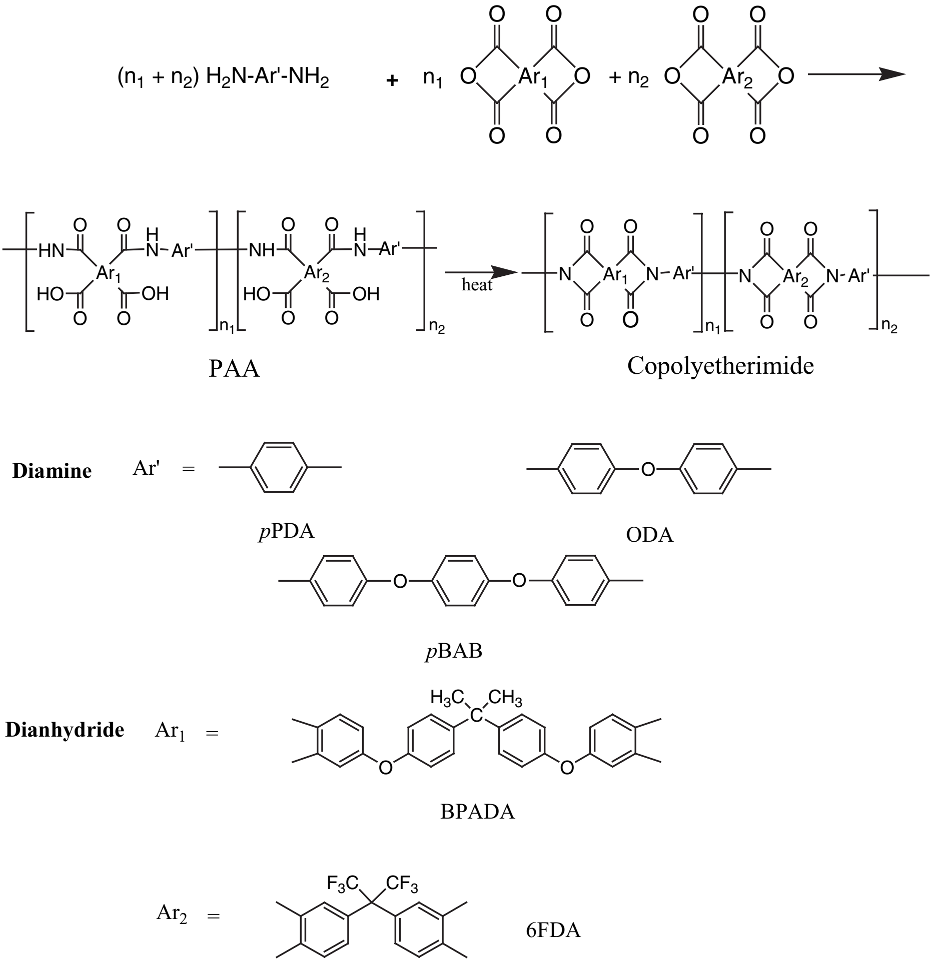

Scheme 1.
Synthesis of copolyetherimide.

elemental analyzer. Thermogravimetric analysis (TGA) was performed with a Perkin-Elmer Pyris 1 TGA at a heating rate of 20 °C/min in N_2. Differential scanning calorimetry (DSC) data were obtained from a Perkin-Elmer Pyris Diamond DSC. Samples were scanned at a heating rate of 10 °C /min under N_2. X-ray diffractograms (XRD) were obtained at room temperature on a Rigaku RINT 2000 instrument, using Ni-filtered CuK_{α} radiation (40 kV, 100 mA). An Instron universal tester model 4467 was used to study the stress-strain behavior of the samples. The load cell used was 5 Kg and the crosshead rate was 5 mm/min. Measurements were performed with film specimens (1.35 cm wide, 6 cm long and 50–60 μm thick). The dielectric property of the polymer films was tested by the Agilent 4284A LCR meter with 16451B dielectric test fixture at a frequency of 1 MHz.

Results and Discussion

Synthesis of Polymers

Polycondensation of diamines with aromatic dianhydrides were performed in NMP. Polymerizations proceeded smoothly. The FT-IR

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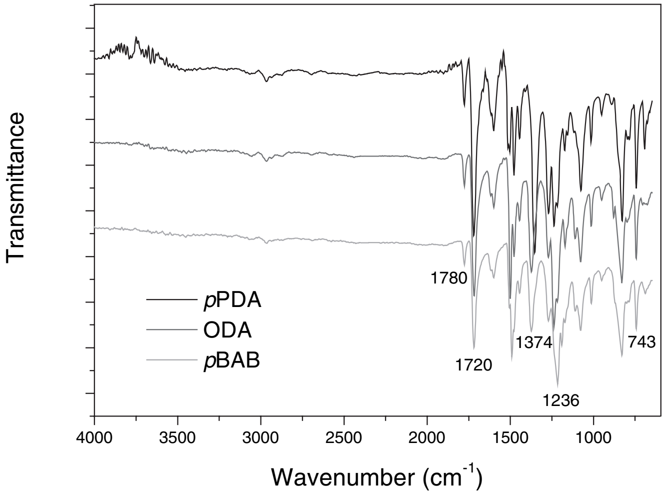

Figure 1.
FT-IR spectra of PEIs with BPADA as dianhydride.

spectra of the PEIs with BPADA dianhydride are shown in Figure 1. It exhibits characteristic imide group absorptions at 1780 and 1720 cm^{-1} (imide carbonyl asymmetrical and symmetrical stretch), at 1374 and 743 cm^{-1} (C–N stretching and bending), and 1236 cm^{-1} (aromatic ether C–O–C). The results of elemental analysis were in good agreement with the chemical structures.

Thermal Properties

The glass transition temperatures (T_g) measured by DSC are listed in Table 1. T_g increased as the content of 6FDA increased, because the introduction of fluorine groups enhanced thermal stability.[6] T_g decreased gradually with PEI containing longer phenylene ether units. The decrease in the T_gs can be attributed to the flexibility of the polymer chains.[11] The thermal decomposition temperature (T_d) at 10% weight loss in nitrogen stayed in the range of 532–568 °C. The char yields in nitrogen at 800 °C were 53–63%. The T_d values and char yields increased with increasing 6FDA content. The TGA data indicate that these PEIs have fairly high thermal stability.

Mechanical Properties

The synthesized PEIs possess good mechanical properties. Both the tensile strength and the modulus decreased with the PEI containing longer phenylene ether units as shown in Figure 2. This could be attributed to the increase of flexibility in the polymer chain.

XRD

As expected, all the PEIs failed to show any crystallinity. The XRD spectra (Figure 3) were broad and without any significant or obvious peaks, indicating that the PEIs were amorphous polymer structures.

Dielectric Constant

The dielectric strength is an important parameter for selecting an appropriate electrical insulation material.[12] Dielectric constants of polyimides, in general, are known to decrease gradually with increasing frequency.[13] The measurement results of the dielectric constants of PEI films at 1 MHz are shown in Figure 3. The dielectric constant of PEI decreased with increasing amounts of 6FDA content as well as the phenylene ether units. The decreased dielectric constants may be partly attributable to the bulky CF_3 groups in 6FDA, which resulted in less efficient chain packing and increased free volume. The strong electronegativity of fluorine also resulted in permanent dipole moments of

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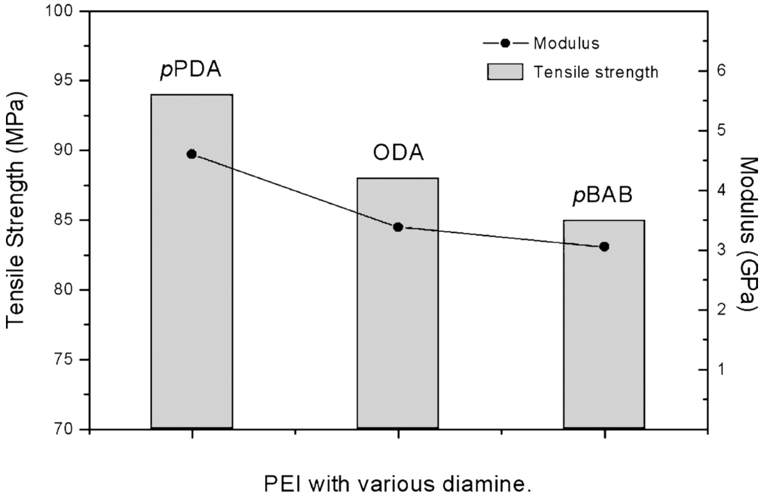

Figure 2.
Mechanical properties of polyetherimides with various diamines.

the CF_3 groups, thus decreasing the dielectric constant.[14] In addition, the phenylene ethers unit in diamine that induced the dilution effect of the polar imide ring may have contributed to the decrease in the dielectric constants.[9] The PEI (**i**) synthesized with high 6FDA-containing (40%) dianhydride and *p*BAB diamine exhibited the lowest dielectric constant of 2.78 at 1 MHz. Studies are currently underway to incorporate other diamines to reduce the dielectric constants of PEI further to below 2.5.

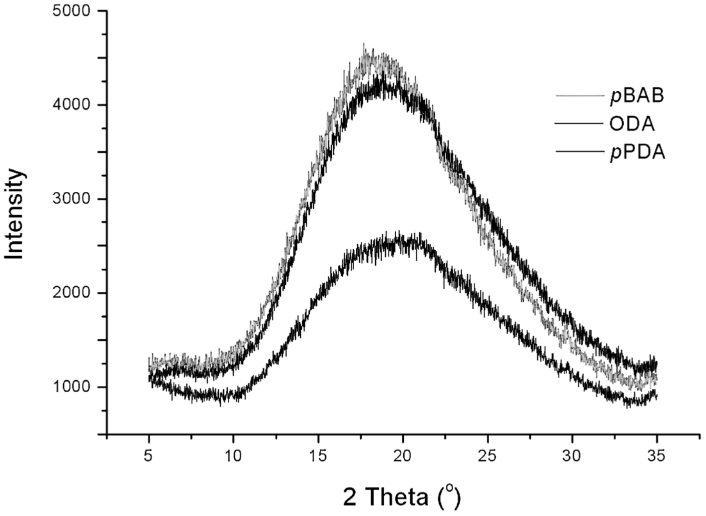

Figure 3.
X-ray diffractograms of polyetherimides with various diamines.

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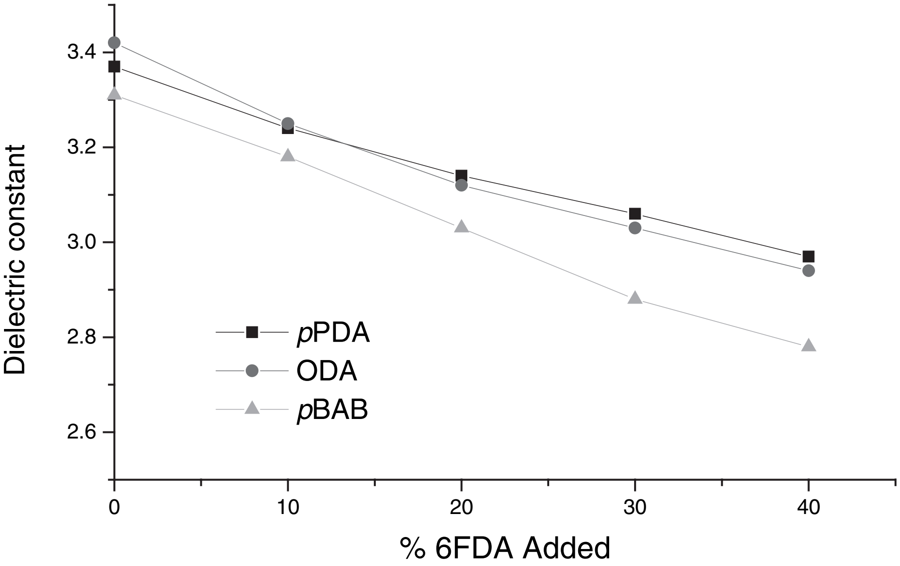

Figure 4.
Dielectric constants of PEIs measured at 1 MHz.

Conclusion

Polyetherimide films with low dielectric constant have been synthesized by incorporating fluorinated dianhydride and phenylene ether diamines. The dielectric constant of PEI decreased with increasing amounts of 6FDA content and the phenylene ether units. T_g decreased gradually with PEI containing longer phenylene ether units, but increased with the content of 6FDA. The synthesized PEI films have high thermal stability and good mechanical properties. Thus, these polymers may be the candidates for high-performance microelectronic applications.

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