Preparation and Properties of Glass Cloth-Reinforced Polyimide Composites with Improved Impact Toughness for Microelectronics Packaging Substrates

Hong-Yan Xu, Hai-Xia Yang, Li-Ming Tao, Lin Fan, Shi-Yong Yang

Laboratory of Advanced Polymer Materials, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

Received 28 December 2008; accepted 2 December 2009
DOI 10.1002/app.31914
Published online 26 March 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A series of glass cloth-reinforced thermosetting polyimide composites (EG/HTPI) were prepared from E-glass cloth (EG) and polyimide matrix resins. The polyimide resins were derived from 1,4-bis(4-amino-2-trifluoromethyl-phenoxy)benzene, *p*-phenylenediamine, diethyl ester of 3,3′,4,4′-benzophenonetetracarboxylic acid, and monoethyl ester of cis-5-norbornene-endo-2,3-dicarboxylic acid. Based on the rheological properties of the B-staged polyimide resins, the optimized molding cycles were designed to fabricate the EG/HTPI laminates and the copper-clad laminates (Cu/EG/HTPI). Experimental results indicated that the EG/HTPI composites exhibited high thermal stability and outstanding mechanical properties. They had flexural strength of >534 MPa, flexural modulus of >20.0 GPa, and impact toughness of >46.9 kJ/m^2. The EG/HTPI composites also showed good electrical and dielectric properties. Moreover, the EG/HTPI laminates exhibited peel strength of $\sim$ 1.2 N/mm and great isothermal stability at 288°C for 60 min, showing good potential for application in high density packaging substrates. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 1173–1183, 2010

Key words: thermosetting polyimide; glass cloth-reinforced composite; mechanical properties; isothermal stability; packaging substrates

INTRODUCTION

To meet the requirement of advanced microelectronic packaging technology, System-in-Package (SiP) technology has been considered as the most effective packaging pathway, which could meet the predictable and challenging market-defined needs due to its area grid array and flip-chip attach features.[1] However, one of the big technological challenges for SiP that packaging engineers have to deal with is how to design and fabricate a high density multilayer packaging substrate that could provide high I/O density, high operation frequencies, and high thermal stability. The desirable features for the high density packaging substrates include (1) high thermal stability, (2) fine-pitch lines (<30 μm), (3) fine via-hole diameters (<30 μm), (4) high operation frequency (>3 GHz), (5) excellent flip-chip mounting reliability, and (6) low production costs.[2]

Conventional packaging substrates are usually build-up printed circuit boards in which the substrate cores are made of multifunctional epoxy (FR-4)[3] or BT[4] resins. The limited thermal stability[5,6] of epoxy and BT resins usually results in the conventional packaging substrates with some critical disadvantages for high density IC packaging application, including (1) the distribution multilayers must be built up on both sides of the core laminate due to its deficient stiffness, resulting in higher production costs; (2) the curvature and unevenness of the core laminates at elevated temperature become the limiting factor in achieving high density packaging;[7] (3) the through-holes drilled in the core laminates could result in impedance mismatching, hampering for the high-speed and high-frequency applications. Hence, built-up multilayer packaging substrate with high thermal resistance become the key issue for advanced microelectronics packaging technology.[3,4]

Aromatic polyimides, because of their excellent thermal stabilities, good dielectric and electrical insulating properties, high thermomechanical properties and dimensional stability, as well as low coefficient of thermal expansion (CTE), have been extensively used in flexible substrates.[8–13] At present, flexible substrates in high-end applications are generally made from polyimide films such as Kapton® and Upilex®. However, the insufficient melt processability of aromatic polyimides has hampered their application as the matrix resin of core laminate,

Correspondence to: H.-X. Yang (Yanghx@iccas.ac.cn) or S.-Y. Yang (Shiyang@iccas.ac.cn).

Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 50903087.

© 2010 Wiley Periodicals, Inc.

probably caused by the inherent rigid backbones and strong interchain interaction. Thus, few commercial polyimide rigid core laminates have been reported nowadays. This work takes the initiative to develop core laminates using novel polyimide resin system.

PMR-type (*In situ* Polymerization of Monomer Reactants) thermosetting polyimides, such as commercial PMR-15 (theoretically calculated molecular weight of 1500 g/mol, developed at the NASA Lewis Research Center), are regarded as state-of-the-art high temperature polymeric resins for carbon or glass fiber-reinforced matrix composites because of their excellent thermal and processing properties.[14–19] Hence, PMR-type thermosetting polyimides are the preferred resins for developing rigid substrate laminates. However, there are two problems that are not crucial to common composite use but must be solved before the thermosetting polyimides could be used as the core laminates for the microelectronics packaging substrates: (1) thermosetting polyimides are intrinsically brittle; (2) voids and defects are probably formed in core laminate due to the evolving of organic volatiles and/or high melt viscosity. Hence, developing thermosetting polyimide resins with good processability which could be melt processed at relatively low temperature to produce laminate with high thermal stability improved impact toughness and void or defect-free has been a scientific and technological challenge.

Recently, a novel PMR-type polyimide matrix resin was developed in the authors' laboratory to improve the processability and enhance the impact toughness of PMR-15.[20] The monomer 1,4-bis (4-amino-2-trifluorornethy-phenoxy)benzene (1,4,4–6FAPB), which has a flexible ether-bridges and trifluoromethyl groups in the chemical structure, was used in place of the 4,4′-methylenediamine (MDA), a carcinogen in PMR-15. The polyimides obtained herein exhibited good processability and a significant improvement in toughness.

In this study, the polyimides based on aforementioned chemical structure were adopted to prepare high density substrate core. A rigid aromatic diamine *p*-phenylenediamine (*p*-PDA) was inserted in the polymer backbone to ensure that the fully cured resin would have high thermal stability and a high cured glass transition temperature (T_g). In addition, it is known that for a given thermosetting resin, if the prepolymer has a relatively high molecular weight then the resin typically has high toughness but also a low T_g and high melt viscosity.[21] The prepolymer's calculated molecular weight was fixed at 2500 g/mol based on previous research, which assured a balance of T_g, toughness and processability.[20] Moreover, the trifluoromethyl groups in polyimide backbones were expected to decrease the dielectric constant and water uptake of polyimide resins,[22,23] which are important properties to packaging substrates. The polyimides using the molecular architectonic technique were synthesized to fabricate glass cloth (EG) reinforced composite laminates. Effects of the chemical structures of the thermosetting polyimides on their melt processability as well as the thermal, mechanical, and electrical properties of laminates were systematically investigated. The potential of the laminates used in high density packaging substrate core was also evaluated.

EXPERIMENTAL

Materials

1,4-Bis(4-amino-2-trifluoromethy-phenoxy)benzene (1,4,4–6FAPB) was synthesized according to the reported method in our laboratory.[24] *p*-Phenylenediamine (*p*-PDA; Beihua Fine Chemicals, Beijing, China) was purified by vacuum sublimation before use. 4,4′-Methylenedianiline (MDA) was recrystallized in anhydrous ethanol before use (Chemical Reagents Corporation of Beijing, China). 3,3′,4,4′-Benzophenone-tetracarboxylic dianhydride (BTDA) was purchased from Sigma–Aldrich Corp. and dried in a vacuum oven at 180°C for 12 h before use. Cis-5-norbornene-endo-2,3-dicarboxylic anhydride (NA; Nanxiang Chemical Reagents Co. of Shanghai, China) was vacuum sublimed before use. Anhydrous ethyl alcohol (Beijing Fine Chemicals, China) was dried over molecular sieves and freshly distilled before use. E-glass cloth 1080 (EG) was purchased from Wuxi First Special-type fiberglass, China and used as received. Copper foil (Cu), which was 35 μm in thickness, was obtained from Hubei Research Institute of Chemistry, China, and used as received.

Preparation of the thermosetting polyimide resins

Diethyl ester of 3,3′,4,4′-benzophenone-tetracarboxylic acid (BTDE) solution was prepared by refluxing a suspension of BTDA (341.56 g) in dry ethyl alcohol (549 mL) for 2 h. Monoethyl ester of cis-5-norbornene-endo-2,3-dicarboxylic acid (NE) solution was synthesized by refluxing a mixture of NA (131.33 g) and ethyl alcohol (230 mL) for 3 h. Then, BTDE and NE solution were mixed together and added to the solution of 1,4,4–6FAPB (562.83 g) and *p*-PDA (15.79 g) in anhydrous ethyl alcohol (1097 mL) in a 3000 mL three-necked flask fitted with a mechanical stirrer, N_2 inlet and outlet. The monomer mixture was mechanically stirred for 8 h at room temperature to yield a homogeneous polyimide resin solution (HTPI-1, 2550 g). The mole ratio of reactants NE: BTDE: (1,4,4–6FAPB + *p*-PDA) was 2: n: (n+1) in which *p*-PDA/(1,4,4–6FAPB + *p*-PDA) was 0 for

HTPI-0, 0.1 for HTPI-1, 0.2 for HTPI-2 and 0.5 for HTPI-5, respectively. All of the thermosetting polyimide resins were designed to have theoretically calculated molecular weight of 2500 g/mol and the resin solutions for glass cloth impregnation had solid concentration of 40 wt %.

B-Staged polyimide molding resins

The thermosetting polyimide resin solution was evaporated using a rotary-evaporator at 60°C to remove most of the solvents. The viscous material obtained was then dried at 60°C for 4–6 h in vacuum to give an A-staged solid resin with yellow to red brown in color depending on the content of *p*-PDA. The B-staged polyimide molding resin was prepared by thermally baking the A-staged solid resin at 150°C for 2 h, 200°C for 1 h, 220°C for 1 h, and 240°C for 0.5 h, successively.

Preparation of EG/HTPI prepregs

The E-glass cloth-reinforced polyimide prepreg (EG/HTPI) was prepared by impregnating the EG cloth with the thermosetting polyimide resin solution by brushing, followed by drying in the air at room temperature, and then thermally baking in the following schedule to give the B-staged EG/HTPI prepregs: 150°C/2 h, 200°C/1 h, 220°C/1 h, and then 240°C/0.5 h, respectively.

Fabrication of EG/HTPI and Cu/EG/HTPI composite laminates

The B-staged prepregs were plied up in a mold at room temperature and then placed into a press preheated at 200°C. When the mold temperature reached 290°C, a pressure of 0.5–3.0 MPa was applied in 10–20 min. The temperature was subsequently increased to 320°C and held for 2 h under the applied pressure. After thermally cured for 2 h at 320°C, the mold was cooled to 100°C and the applied pressure was released. The thermally cured EG/HTPI composite laminate was removed from the mold at room temperature and then cut into desired sizes for thermal, mechanical, and electrical testing. The dual-side copper-clad EG/HTPI (Cu/EG/HTPI) composite laminates were fabricated in a similar method. The weight fractions of the polyimide resin in the composite laminates determined according to GB/T 2577-2005 were in the range of 55–60 wt %.

Measurements

Fourier transform infrared spectra were obtained on a PerkinElmer 782 FTIR spectrophotometer.

^{1}H-NMR spectra were performed on a Bruker Avance 400 spectrometer operating at 400 MHz in acetone-d_6.

Complex viscosity (η*) were measured on a TA AR2000 rheometer. The specimens were prepared by pressing the B-staged polyimide resin powder into disks with 25 mm in diameter and 1.2 mm in thickness at room temperature. The measurements were performed using a parallel-plate fixture by oscillation mode at a fixed strain of 0.1% and a fixed angular frequency of 10 rad/s. In the temperature ramp procedure, an initial temperature was set and the parallel plates with testing sample were equilibrated at this temperature for 10 min. Then, the complex viscosity (η*) was measured at a rate of 4°C/min. Meanwhile, the dynamic rheology was also used to imitate the resin viscosity of the EG/HTPI prepregs in the melt processing.

Differential scanning calorimetry (DSC) was performed on a TA Q100 thermal analysis system in nitrogen atmosphere at a flow rate of 50 cm^3/min and the scanning range was from 50 to 400°C. The glass transition temperature (T_g) was determined by the inflection point of the heat flow versus temperature curve.

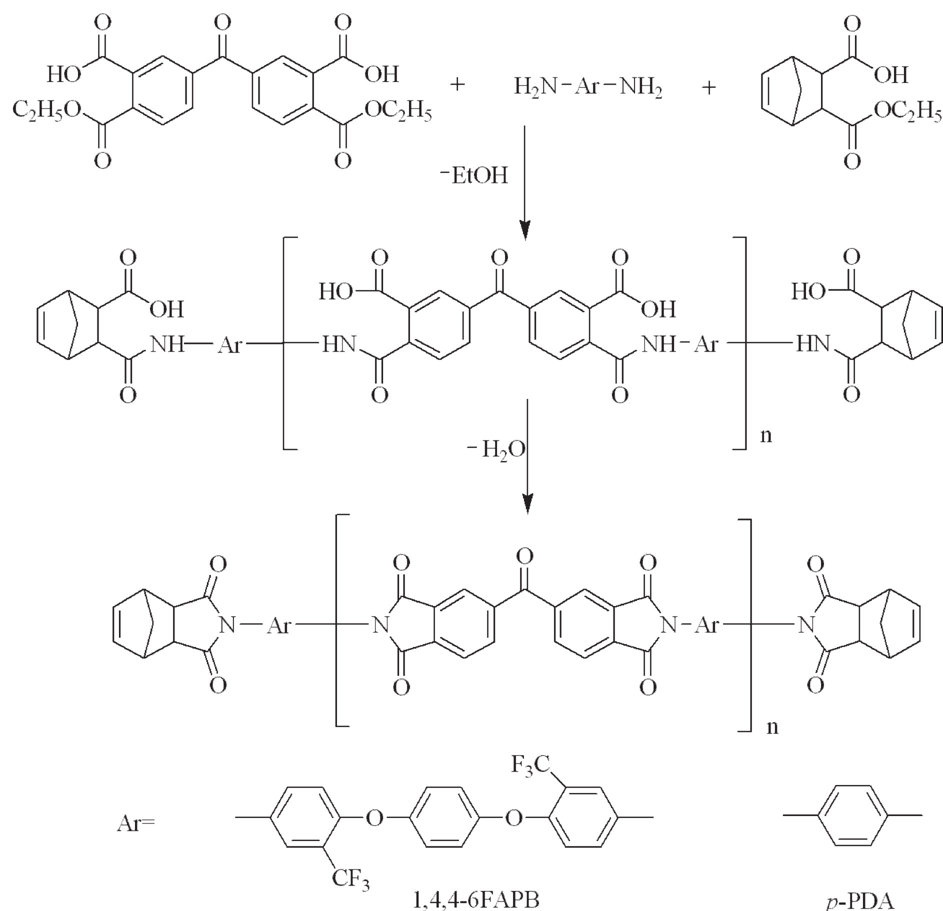
Thermal gravimetric analysis (TGA) was performed on a Perkin-Elmer 7 Series thermal analysis system at a heating rate of 20°C/min in nitrogen atmosphere at a flow rate of 20 cm^3/min.

Dynamic mechanical analysis (DMA) was performed on a Perkin-Elmer 7 Series thermal analysis system with a heating rate of 5°C/min and a frequency of 1 Hz. A three-point bending mode was used and the specimen size was 18.0 mm × 3.0 mm × 1.2 mm. The storage modulus (G'), loss modulus (G''), and tangent of loss angle (tan δ) were determined as the function of scanning temperature.

Thermal mechanical analysis (TMA) was carried out using a Perkin-Elmer 7 Series thermal analysis system. The samples were scanned twice from 30 to 350°C at a heating rate of 10°C/min under a force of 20 mN. The CTEs of samples were calculated according to the second scanning curves.

The time to delamination of EG/HTPI laminates and Cu/EG/HTPI laminates were also conducted with a TMA instrument according to IPC-TM-650. Both of the tests were performed from temperature ramp at a heating rate of 40°C/min and then an isothermal process to observe failure coming up.

The tensile properties were measured on an Instron-3365 Tensile Apparatus in agreement with GB 1447–2005 at a drawing rate of 2.0 mm/min. The flexural strength and modulus of laminates were obtained at a span to depth ratio of 16 according to GB/T 1449–2005, and the test speed was of 1.0 mm/min. The test of nonnotched impact was performed according to GB/T1451-2005. The peel strength, electrical and dielectric properties of laminates was tested in accordance with IPC-TM-650.



Scheme 1 Synthesis of the thermosetting polyimide resins.

RESULTS AND DISCUSSION

Preparation and characterization of the thermosetting polyimides

The thermosetting polyimide solutions with solid content of 40 wt % in anhydrous alcohol were prepared by reacting the ethyl alcohol solutions of NE, BTDE, 1,4,4–6FAPB, and *p*-PDA at room temperature by the polymerization of monomer reactants process according to the PMR method previously reported (Scheme 1).[25] The homogeneous resin solutions, with absolute viscosity of 5–20 mPa s at 30°C, showed

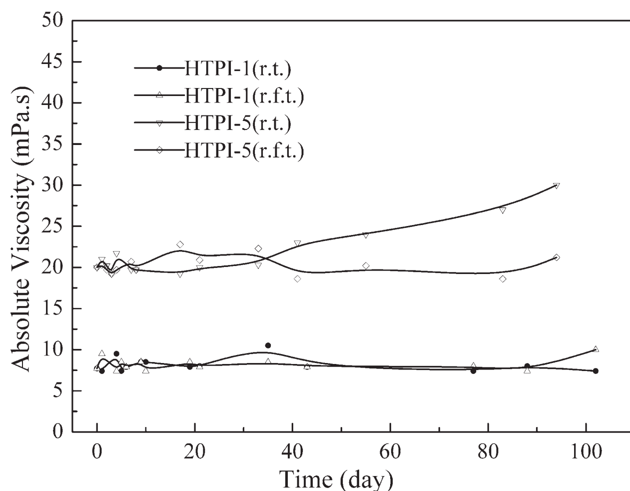


Figure 1 Effect of storage time on the absolute viscosity of HTPI solution.

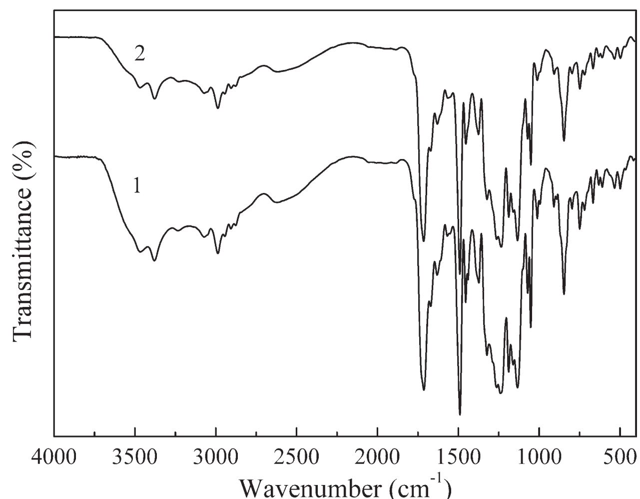


Figure 2 The FTIR spectra of HTPI-2 solution before (1) and after (2) storage for 3 weeks at room temperature.

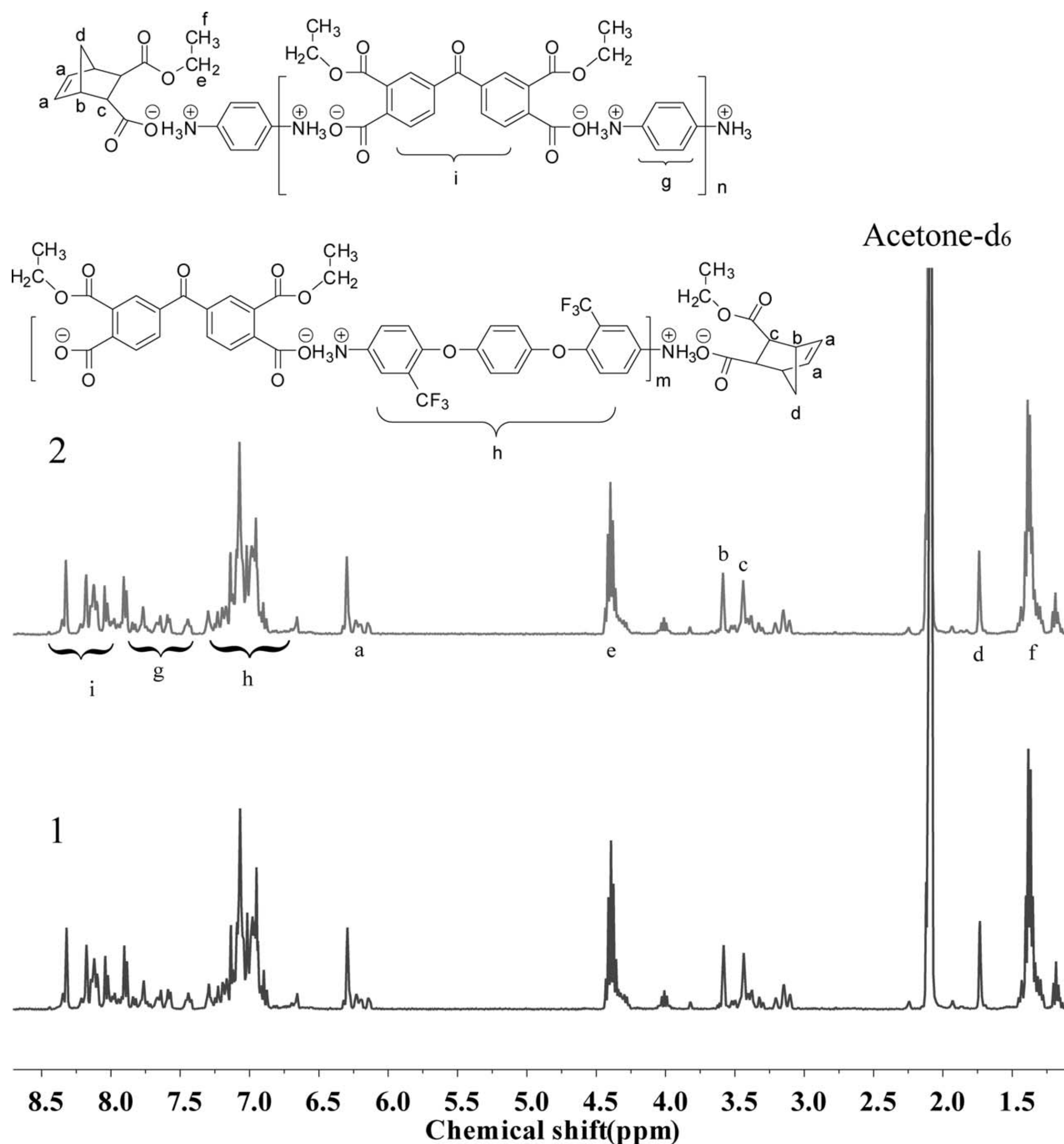


Figure 3 The ^{1}H-NMR spectra of HTPI-2 solution before (1) and after (2) storage for 3 weeks at room temperature.

colors changed from yellow to red brown depending on the *p*-PDA's concentration, and they were all stable both in viscosity and in color after storing for more than 3 weeks at room temperature) (25°C) and more than 3 months in a refrigerator (4°C). Figure 1 depicts the absolute viscosity changes of representative HTPI resin solutions along with storage time. It can be seen that the HTPI resin with higher *p*-PDA mole ratio was a little more unstable, probably due to the high reactivity of *p*-PDA. In addition, no apparent changes were observed in FTIR and ^{1}H-NMR spectrum after the resin solutions were stored for 3 weeks at room temperature (Figs. 2 and 3). The resin solutions could be used to impregnate EG cloth to give high quality prepregs.

Preparation of the EG/HTPI prepregs

The EG/HTPI prepregs were baked up to 240°C before composite melt processing to remove the organic volatiles as completely as possible. The low volatiles of the B-staged prepregs could reduce the possibility of voids and defects formation in the composite processing. Generally, the PMR-type polyimide prepregs are treated at temperature of lower than 200°C to avoid the B-staged resin with too high

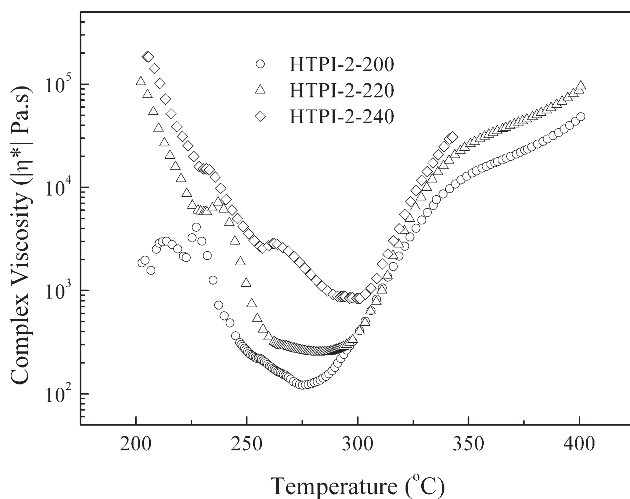


Figure 4 The melt viscosities versus temperature for HTPI-2 resin baked at different temperature.

melt viscosity.[16,18] After baking at the same procedure, the B-staged resins had almost the same volatile content. Figure 4 depicts the melt viscosities of typical HTPI-2 resin baked at different temperature. The result shows clearly that when the baking temperature was raised from 200 to 240°C, the minimum resin melt viscosities increased from 121 to 839 Pa s, but it is still low enough for composite processing. The low melt viscosities of the B-staged resins are probably attributed to the flexible ether segments and the trifluoromethyl groups in the polymer backbone.[18,26] Moreover, the total weight loss in air (50–300°C) of the B-staged resin treated at 240°C was only 1.3 wt % (Fig. 5) compared to 5.5 wt % for the B-staged resin treated at 200°C. It should be noted that the low volatile outlet was critical for the B-staged prepregs to fabricate void-free copper-clad composite laminates.

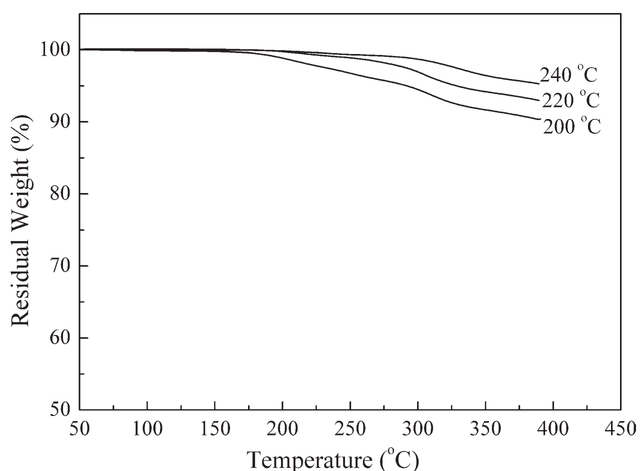


Figure 5 TGA of the B-staged HTPI-2 resin thermally baked at different temperature.

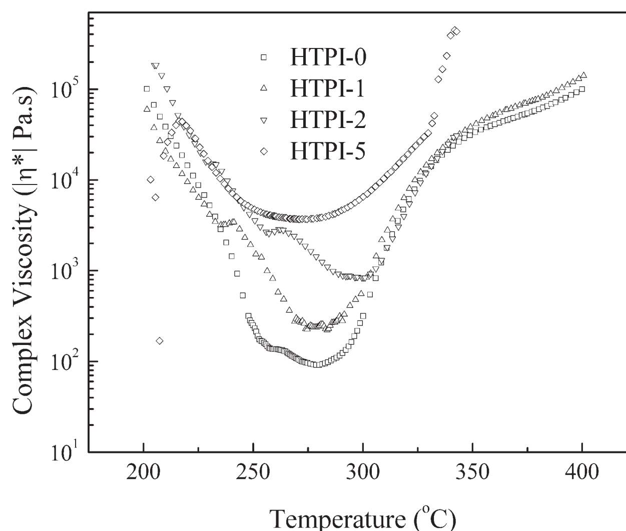


Figure 6 The melt viscosities versus temperature for the B-staged polyimide resins.

Rheological properties of the B-staged polyimides

Dynamic rheology was used to investigate the melt processability of the B-staged polyimides, which were thermally baked in the same schedule as EG/HTPI prepregs, so that the polyimide resin viscosity could be used to imitate the resin viscosity of the EG/HTPI prepregs. Figure 6 compares the melt viscosities of the B-staged thermosetting polyimide resins with different *p*-PDA concentrations at different temperature, and the data are summarized in Table I. It can be seen that the molten resin viscosities decreased with the temperature increasing at the beginning stage and then started to increase after a specific temperature. The first decreasing in the molten resin viscosity was primarily attributed to the melting of the B-staged polyimide resin, and then the increasing in molten resin viscosity was due to the crosslinking reaction of nadic endcapping groups. The temperatures, at which the resin had the minimum melt viscosity, increased from 279°C (91 Pa s) for HTPI-0 to 284°C (223 Pa s) for HTPI-1 and 301°C (839 Pa s) for HTPI-2, respectively. Obviously, the increases in the minimum melt viscosities were attributed to the increasing of *p*-PDA

TABLE I
Melt Viscosities of the Thermosetting Polyimide Resins at Elevated Temperatures

	Complex melt viscosities (Pa s) at		Minimum melt viscosities (Pa s/°C)
	270°C	290°C	
HTPI-0	109	117	91 at 279°C
HTPI-1	298	299	223 at 284°C
HTPI-2	2135	881	839 at 301°C
HTPI-5	3710	4424	3728 at 267°C

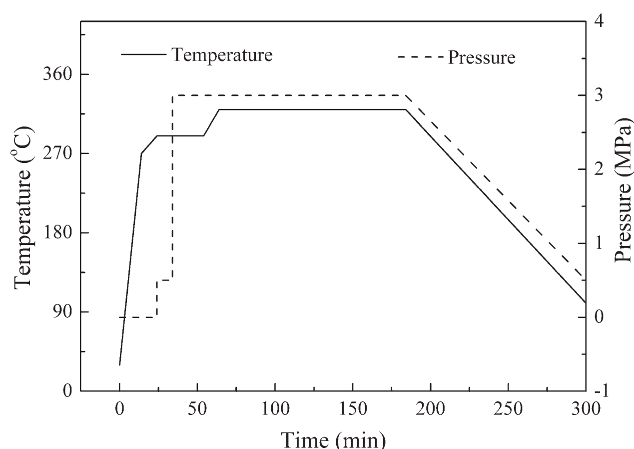


Figure 7 The thermal curing diagram of the EG/HTPI and Cu/EG/HTPI composite laminates.

concentration in diamines, resulting in more rigid chemical structure. In comparison, HTPI-5 had remarkably higher melt viscosity than other resins, showing the minimum melt viscosity of 3728 Pa s at 267°C. Therefore, the melt processability of the thermosetting polyimide resins could be controlled by adjusting the molar ratios of the rigid phenyl groups to the flexible ether segments in the resin chemical backbone.

Melt processing of EG/HTPI and Cu/EG/HTPI composites

EG/HTPI composite laminates and copper-clad Cu/EG/HTPI laminates were fabricated by melt processing of the EG/HTPI prepregs or copper foil-covered EG/HTPI prepregs. The prepregs were first baked at 240°C for 0.5 h to remove most of the organic volatiles that could cause voids in the melt processing of the composite. Figure 7 is the representative melt process diagram of the EG/HTPI composite laminates designed according to Figure 6. At the beginning of the process, the EG/HTPI prepregs were

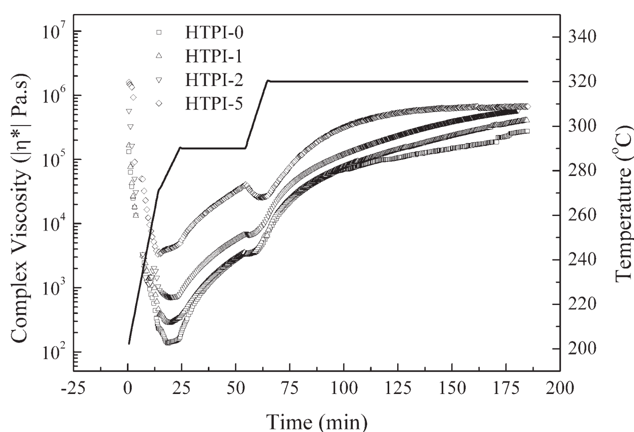


Figure 8 Changes in melt viscosities of HTPI resins in the simulated curing process of composites.

TABLE II
Thermal Properties of the EG/HTPI Composite Laminates Thermally Cured at 320°C for 2 h

	T_g (°C)[a]	T_d (°C)[b]	T_5 (°C)[c]	T_{10} (°C)[d]
EG/HTPI-0	264	454	511	637
EG/HTPI-1	274	457	488	615
EG/HTPI-2	282	445	503	615
EG/HTPI-5	_[e]	449	561	638

[a] T_g: Obtained from DSC curves.
[b] T_d: Initial decomposition temperature.
[c] T_5: Temperature at 5 wt % loss.
[d] T_{10}: Temperature at 10 wt % loss.
[e] _: Not detected.

heated gradually from 200 to 290°C and kept for 30 min, ensuring that the B-staged polyimide resins was completely molten to give high flowing fluid and further remove the residual volatiles. Then, under the applied pressure of 3 MPa, the mold was kept at 320°C for 2 h. At this stage, the molten resin underwent chain extension and crosslinking to produce the thermoset materials.

Dynamic rheology was also used to monitor the viscosity changes of the B-staged resins in the thermal processing of laminates. The heating diagram of the monitoring tests was same to the curing process of the EG/HTPI composite laminates as shown in Figure 8. As the temperature ramped from 200 to 270°C, dramatic viscosity drops were observed due to the softening and melting of the B-staged polyimide resins. When the temperature ramped slowly from 270°C to 290°C and held at 290°C, the melt viscosities increased slowly. The experimental results indicated that the HTPI-0, HTPI-1, and HTPI-2 resins possessed low viscosities with minimum melt viscosities of 138 Pa s, 283 Pa s, and 720 Pa s, respectively. Moreover, the time during which the viscosities were lower than 1000 Pa s for HTPI-0, 1, 2 was

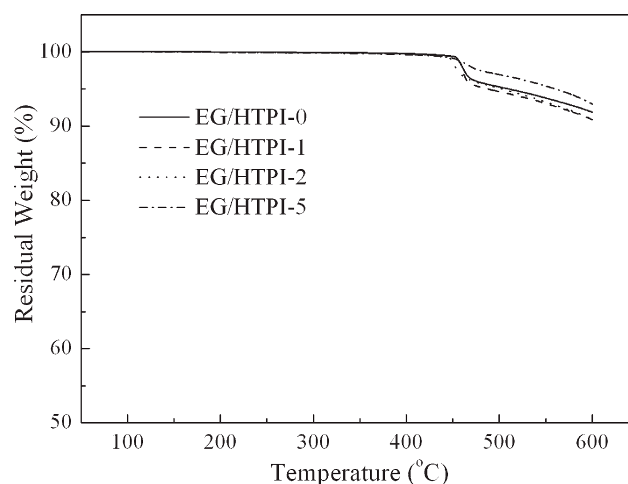


Figure 9 TGA of the EG/HTPI composite laminates thermally cured at 320°C for 2 h.

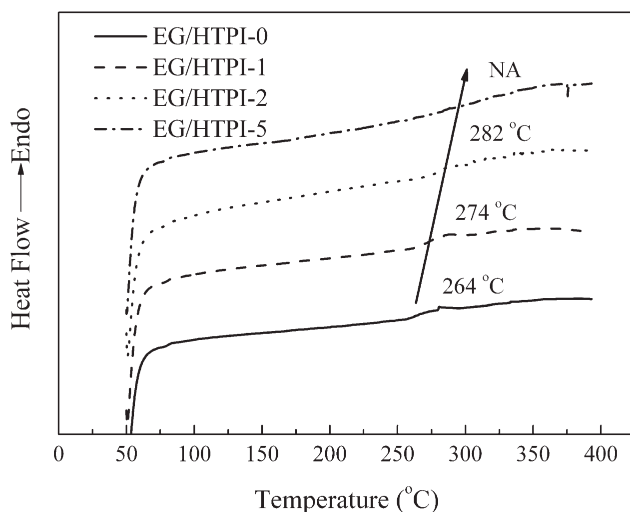


Figure 10 DSC of the EG/HTPI composite laminates thermally cured at 320°C for 2 h.

25.3 min, 23.4 min, and 10.8 min, respectively. Many experiments indicate that when the minimum melt viscosity is lower than 1000 Pa s, the obtained composites have acceptable combined properties. The results demonstrate that the molten resins have good proc essability, ensuring that the melt processing of composites could be conducted smoothly. It should be noted that the HTPI-0 with larger calculated molecular weight of 2500 possess comparable viscosity with PMR-15, indicating that the novel structure of HTPI have achieved the success of improving processability. It is not unexpected that HTPI-5 exhibited too high melt viscosity to melt processing of the composites with high quality.

Thermal properties of the EG/HTPI composites

The thermal properties of the EG/HTPI composites evaluated by DSC and TGA are summarized in Table II. Figure 9 depicts the TGA curves of the EG/HTPI composites from which we can see that the EG/HTPI composites showed excellent thermal stability with T_d of >445°C, T_5 of >488°C, and T_{10} of >615°C, respectively. Figure 10 shows DSC curves of the EG/HTPI composites in which the composite T_gs increased from 264°C for EG/HTPI-0 to 282°C for EG/HTPI-2. It is clear that the increases in T_g values are attributed to the increases in rigidity of the polymer chemical backbones. However, EG/HTPI-5 composite did not show obvious glass transition in DSC, probably due to the too rigid polymer backbone of the polyimide.

TABLE III
DMA Data for the EG/HTPI Composite Laminates Thermally Cured at 320°C for 2 h

	G' (°C)[a]	G'' (°C)[b]	Tan δ (°C)[c]
EG/HTPI-0	269	275	284
EG/HTPI-1	266	280	288
EG/HTPI-2	277	287	294
EG/HTPI-5	294	310	322

[a] G': The onset temperature in the storage modulus curve;
[b] G'': The peak temperature in the loss modulus curve;
[c] Tan δ: The peak temperature in the Tan δ curve.

Figure 11 illustrates DMA curves of a representative EG/HTPI composite (EG/HTPI-1) and the DMA data for all of the composites are summarized in Table III. The T_g values increased from 284°C for EG/HTPI-0 to 322°C for EG/HTPI-5 and an increase of 38°C was observed, which was attributed to the increasing of *p*-PDA loadings in the composite. For instance, EG/HTPI-1 composite showed T_g of 288°C and its storage modulus did not go down until the temperature was scanned to 266°C, implying that the thermally cured polyimides possess outstanding thermomechanical properties.

Figure 12 shows the TMA curves of a representative composite (EG/HTPI-1) including the coefficient

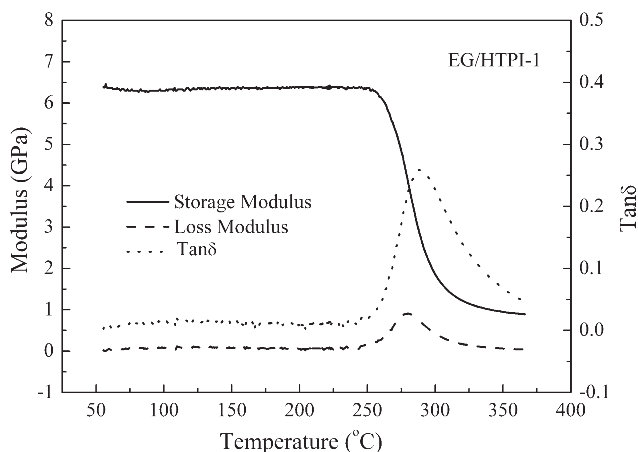


Figure 11 DMA of the EG/HTPI-1 composite laminates thermally cured at 320°C for 2 h.

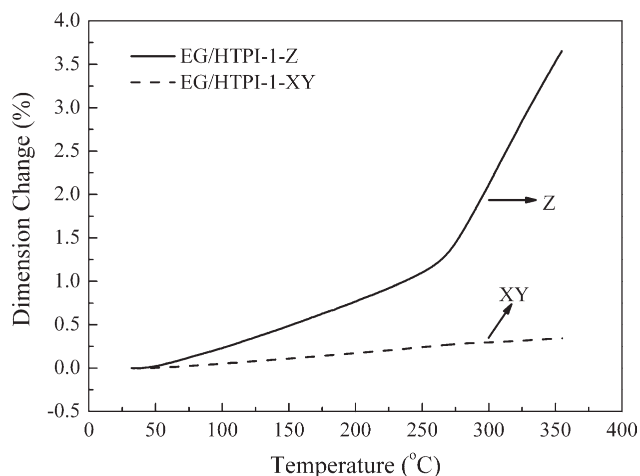


Figure 12 TMA of the EG/HTPI-1 composite laminates thermally cured at 320°C for 2 h.

TABLE IV
TMA Data for the EG/HTPI Composite Laminates Thermally Cured at 320°C for 2 h

	CTE_{XY} (ppm/°C)	CTE_Z (ppm/°C)	T_g (°C)[b]
EG/HTPI-0	12.9	51.9	257
EG/HTPI-1	11.2	49.7	271
EG/HTPI-2	12.9	48.1	281
EG/HTPI-5	_[a]	_[a]	_[a]

[a] _: Not available due to delamination.
[b] T_g: Temperatures of inflection point in TMA curves.

of thermal expansion (CTE) in *XY* and *Z* directions and the CTE and T_g data for all the composites were summarized in Table IV. The T_g values showed an expected increase from 257 to 281°C. The CTEs of the composites (EG/HTPI-0, EG/HTPI-1, and EG/HTPI-2) were measured in the range of 11.2–12.9 ppm/°C in *XY* direction and 48.1–51.9 ppm/°C in *Z* direction, respectively, implying the excellent dimension stability for high density packaging. In contrast, EG/HTPI-5 composite could not give fine TMA curve to determine the CTE due to the delamination of composite occurred in the thermal testing.

Mechanical properties of the EG/HTPI and Cu/EG/HTPI composites

Table V compares the mechanical properties of the EG/HTPI composites and EG/PMR-15 composite. It can be seen that the EG/HTPI composites possess the tensile strength in the range of 253–270 MPa, tensile modulus of 10.9–11.7 GPa, flexural strength of 534–730 MPa, and flexural modulus of 20.0–24.2 GPa, a little higher than EG/PMR-15 composite in all above properties. Moreover, the composites showed high impact strength in the range of 46.9–53.5 kJ/m^2, more than 23% higher than PMR-15 composite. We can conclude that the impact toughness of EG/HTPI composites are improved without sacrificing the flexural and tensile strength, primarily attributing to significantly improvement of matrix[27] resulted from the distribution of soft-rigid segments in the polymer backbone. It is important to note that the EG/HTPI-5 composite could not give good mechanical properties and valid data in impact strength because of its poor quality derived from the high *p*-PDA loading. It can be concluded that the mole ratio of *p*-PDA in diamines could not exceed 0.2, otherwise the composite should have the deteriorated mechanical properties. The thermosetting polyimide laminates with high impact strength and high temperature can be obtained by adjusting the mole ratio between 1,4,4–6FAPB with flexible structure and *p*-PDA with rigid structure. The peel strength of copper foil from the composite surface in Cu/EG/HTPI laminates was measured in the range of 1.18–1.24 N/mm, demonstrating that the composite surface have good adhesion to copper foil, ensuring the processing and working stability of the electrical signal patterns in packaging substrate.

Electrical and dielectric properties of EG/HTPI and Cu/EG/HTPI composites

Table VI shows the electrical and dielectric properties of the EG/HTPI composite laminates in which it can be seen that EG/HTPI composite laminate showed good electric insulating properties with volume resistivity of 7.0–7.7 $\times$ 10^{16} Ω cm and surface resistivity of 2.9–8.5 $\times$ 10^{16} Ω, respectively. The dielectric constants were measured in the range of 4.2–4.3 and dielectric dissipation factor in the range of 6.1–7.3$\times$ 10^{-3} at 1 MHz, better than BT resin based laminates.[28] The dielectric breakdown was determined in the range of 20.4–28.9 kV/mm and low water uptake (0.48–0.71%) were measured for EG/HTPI-0, EG/HTPI-1, and EG/HTPI-2. Not surprisingly, EG/HTPI-5 showed the water uptake of 1.30%, presumably due to the more defects in the composite laminate.

Thermal reliability of the EG/HTPI and Cu/EG/HTPI composite laminates

Time to delamination determined by the thermo-mechanical analyzer is one of the standard methods to identify the EG/HTPI laminate reliability for the microelectronics packaging substrates. Figure 13

TABLE V
Mechanical Properties of the EG/HTPI Composite Laminates Thermally Cured at 320°C for 2 h

	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation (%)	Flexural strength (MPa)	Flexural modulus (GPa)	Impact strength (kJ/m^2)	Peel strength (N/mm)
EG/HTPI-0	253	10.9	4.2	724	23.5	47.9	1.24
EG/HTPI-1	270	11.2	4.2	730	24.2	53.5	1.23
EG/HTPI-2	266	11.7	3.3	534	20.0	46.9	1.18
EG/HTPI-5	235	10.4	3.2	419	16.9	_[a]	_[b]
EG/PMR-15	269	10.5	3.3	570	17.9	38.0	NA

[a] _: No valid data.
[b] _: No specimens available.

TABLE VI
Electrical and Dielectric Properties of the EG/HTPI Composite Laminates Thermally Cured at 320°C for 2 h

	Dielectric constant (1 MHz)	Dissipation factor (1 MHz)	Volume resistivity (Ω cm)	Surface resistivity (Ω)	Dielectric breakdown (kV/mm)	Water uptake (%)
EG/HTPI-0	4.2	6.1×10^{-3}	7.3×10^{16}	8.5×10^{16}	22.4	0.48
EG/HTPI-1	4.3	6.9×10^{-3}	7.7×10^{16}	7.6×10^{16}	28.9	0.60
EG/HTPI-2	4.3	7.3×10^{-3}	7.0×10^{16}	2.9×10^{16}	20.4	0.71
EG/HTPI-5	4.3	7.1×10^{-3}	8.6×10^{16}	4.5×10^{16}	_[a]	1.30

[a] _: No valid data.

depicts the dimension changes versus time in a fast temperature ramp and isothermal process at 288°C for the EG/HTPI composite laminates except for EG/HTPI-5. No delamination in laminates was observed after isothermal aging for 60 min at 288°C. Then, one of Cu/EG/HTPI laminates (Cu/EG/HTPI-1) was selected to investigate its failure time at different temperature (Fig. 14). The results show that the laminates expanded rapidly as the temperature increased at the heating rate of 40°C/min. The higher the temperature, the larger the expansion was detected. When the Cu/EG/HTPI-1 laminates were isothermally aged at different temperatures, the failure times were drastically changed. When the laminate was isothermally aged at 260°C, no obvious failure was detected after 60 min aging. However, when the isothermal aging temperature was increased to 288°C, the "popcorning" phenomenon was observed in 16 min. Moreover, the Cu/EG/HTPI-1 laminate could stand for 4 min at 300°C, indicating that the composite laminates could withstand the harsh environments in lead-free microelectronics packaging production lines where the temperature could ramped to 260°C in short time. Hence, the EG/HTPI and Cu/EG/HTPI laminates have outstanding thermal reliability, showing good potential for application in high density packaging substrates.

CONCLUSIONS

Based on the results of this study, several conclusions can be drawn.

1. The introduction of flexible ether-bridges and trifluoromethyl groups into the polymer backbone lowered the resin viscosity and thus improved the processability.
2. The increasing of *p*-PDA concentration in the backbone increased the T_g values of polyimides obviously, meanwhile resulted in higher viscosity. Finally, the processability was deteriorated when the viscosity was extremely high and so were the mechanical properties of the laminates. In summary, the HTPI laminates with high impact strength and high temperature can be obtained by adjusting the mole ratio between 1,4,4–6FAPB with flexible structure and *p*-PDA with rigid structure.
3. The EG/HTPI composites exhibited high thermal stability with the glass transition temperature (T_g) of >284°C, the temperatures at 5% loss of the original weight (T_5) of > 488°C and outstanding mechanical properties with flexural strength of >534 MPa, flexural modulus of

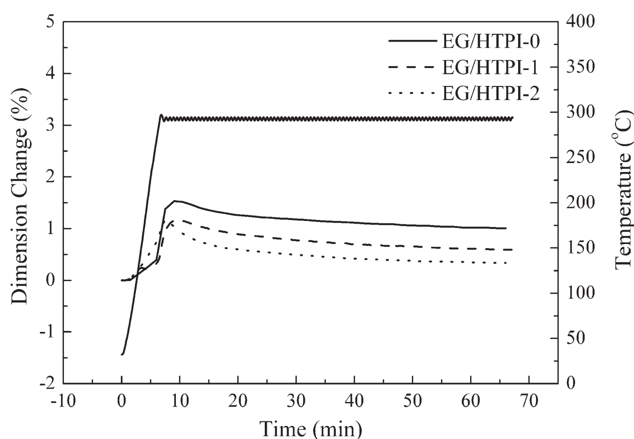


Figure 13 Dimension changes versus time at 288°C for the EG/HTPI composite laminates.

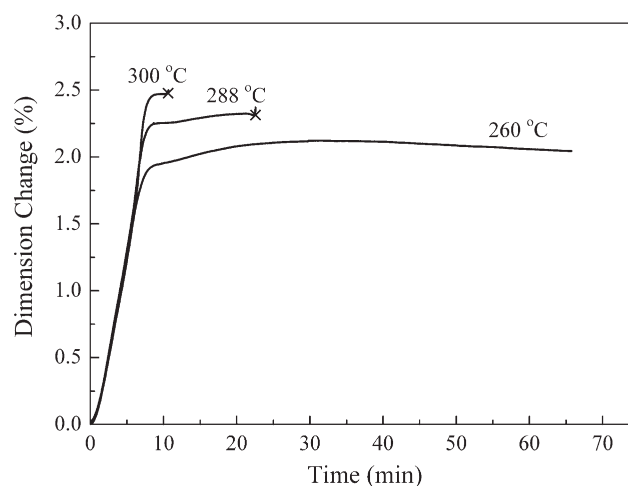


Figure 14 Failure time at different temperature for the Cu/EG/HTPI-1 composite laminates.

>20.0 GPa and impact strength of >46.9 kJ/m^2, respectively. The EG/HTPI composites also showed good electrical and dielectric properties. In addition, the EG/HTPI laminate exhibited peel strength of ~ 1.2 N/mm and great isothermal stability at 288°C for 60 min, showing good potential for applications in high density packaging substrates.

The author thank Dr. Xiaojuan Zhao of Institute of Chemistry Chinese Academy of Sciences for her kind help.

References

1. Song, Y. H.; Kim, S. G.; Lee, S. B.; Rhee, K. J.; Kim, T. S. Microelectron Reliab 2003, 43, 1405.
2. Shimoto, T.; Baba, K.; Matsui, K.; Tsukano, J.; Maeda, T.; Oyachi, K. Microelectron Reliab 2005, 45, 567.
3. Mcgregor, D. R.; Cox, G. S.; Lantzer, T. D. Proceedings of 2nd Inernational Conference on Embedded Passives, Sab Jose, CA, June 15–17, 2004.
4. Chong, D. Y. R.; Lim, B. K.; Rebibis, K. J.; Pan, S. J.; Krishnamoorthi, S.; Kapoor, R.; Sun, A. Y. S.; Tan, H. B. Proc 2004 Electron Compon Technol Conf 2004, 2, 1174.
5. Mccluskey, F. P.; Condra, L.; Torri, T.; Fink, J. Microelectron Int 1996, 13, 23.
6. Tummala, R.; Raj, P. M.; Sundaram, V. Adv Packag 2004, 13, 26.
7. Ho, P. S.; Wang, G.; Ding, M.; Zhao, J.; Dai, X. Microelectron Reliab 2004, 44, 719.
8. Mittal, K. L., Ed. Polyimide: Synthesis, Characterization, and Application; Halsted Press: New York, 1984.
9. Numata, S.; Oohara, S.; Fujisaki, K.; Imaizumi, J.; Kinjo, N. J Appl Polym Sci 1985, 31, 101.
10. Lupinski, J. L.; Moore, R. S. Polymeric Materials for Electronic Packaging and Interconnection; American Chemical Society: Washington, DC, 1989.
11. Electronics: Kapton® Polyimide Film. Available at: http://www2.dupont.com/Kapton/en_US/(Accessed, August 5, 2008).
12. Xiao, S. Y.; Che, L. F.; Li, X. X.; Wang, Y. L. Microelectron Eng 2008, 85, 452.
13. Tsutsumi, M.; Maeda, S.; Kawahara, K.; Oya, K.; Shimizu, Y.; Kurahara, S. Jpn. Pat. JP2008038083 (2008).
14. Wilson, D. Brit Polym J 1988, 20, 405.
15. Milhourat-Hammadi, A.; Gaudemer, F.; Merienne, C.; Gaudemer, A. J Polym Sci, Part A Polym Chem 1994, 32, 1593.
16. Hao, J. Y.; Hu, A. J.; Yang, S. Y. High Perform Polym 2002, 14, 325.
17. Wang, J.; Yi, X. S. J Appl Polym Sci 2003, 89, 3913.
18. Chen, J.; Yang, S.; Tao, Z.; Hu, A.; Fan, L. High Perform Polym 2006, 18, 377.
19. Chen, J.; Yang, S.; Tao, Z.; Hu, A.; Gao, S.; Fan, L. High Perform Polym 2006, 18, 265.
20. Yang, H. X.; Liu, J. G.; Chen, J. S.; Fan, L.; Yang, S. Y. J Aeronaut Mater 2006, 26, 172.
21. Zhou, J.; Zhang, J.; Liu, W. L.; Ding, M. X.; He, T. B. J Mater Sci 1996, 31, 5119.
22. Qu, W. L.; Ko, T. M. J Appl Polym Sci 2001, 82, 1642.
23. Maier, G. Prog Polym Sci 2001, 26, 3.
24. Xie, K.; Zhang, S. Y.; Liu, J. G.; He, M. H.; Yang, S. Y. J Polym Sci Part A Polym Chem 2001, 39, 2581.
25. Xiao, T. J.; Gao, S. Q.; Hu, A. J.; Wang, X. C.; Yang, S. Y. High Perform Polym 2001, 13, 287.
26. De Abajo, J.; De La Campa, J. G. Prog Polyimide Chem I 1999, 140, 23.
27. Bagwell, R. M.; Wetherhold, R. C. Compos Part A Appl S 2005, 36, 683.
28. Electronics: BT Materials for Chip-On-Board, Burn-In-Board and Multi-layered PWB. Available at: http://www.mgc.co.jp/eng/products/lm/btprint/lineup/cob.html (Accessed, November 7, 2009).