Strategy for Improvement of Non-flammability in Functional Polyimides

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A phosphorus (P)-containing diamine was synthesized and used as a comonomer at a minor fraction to improve insufficient non-flammability of a poly(ester imide) system as a promising candidate of base film materials in flexible printed circuit boards (FPC). The P-modified PEI copolymer film displayed the highest level of non-flammability (UL-94, V-0) comparable to commercially available conventional aromatic PI films in addition to original excellent properties, i.e., a very high $T_g$, a low linear coefficient of thermal expansion (15.7 ppm/K) close to copper foils, a low water absorption (0.54 %), a low linear coefficient of humidity expansion (5.53 ppm/RH%), and sufficient toughness (elongation at break = ca. 40%). This approach was also attempted for a very flammable low-modulus PI system for aiming at an application as a coating-type cover layer material in FPC.

Keywords: Non-flammability, Poly(ester imide)s, Low-modulus polyimides, Phosphorus-containing monomers, Copper clad laminates, Cover layers, Flexible printed circuit boards

1. Introduction
Polyimides (PIs) have been widely utilized in a variety of microelectronic applications, for example, as the base films for flexible printed circuit boards (FPC) and the tape-automated bonding (TAB), the chip-on-film (COF) assembly systems, the buffer-coating films and interlayer dielectrics for LSI chips, high temperature adhesives for their combined excellent properties, i.e., high glass transition temperature ($T_g$), high resistance to chemicals and radiation, relatively low dielectric constants, and good mechanical properties. One of the most important applications of PIs is a use as dielectric layers (base film materials) in copper clad laminates (CCL), from which flexible printed circuit boards (FPC), tape-automated bonding and chip-on-film assembly systems are fabricated. A schematic structure of FPC is depicted in Fig.1. CCL is classified into three types: (1) conventional three-layered CCL where a non-thermoplastic PI base film is laminated with a copper foil through thermally less stable conventional adhesives (for example, epoxy resin/acyrlic rubber and epoxy resin/nitrile-butadiene rubber), (2) adhesive-free two-layered CCL which is fabricated by solution-casting of PI precursor [poly(amic acid) (PAA)] solutions onto a roughened surface of copper foil and successive thermal imidization or by a metalizing technique based on Cu-plating process after the formation of a Ni-Cr seed layer sputtered on the base film, and (3) three-layered CCL using conventional or thermoplastic PI adhesives.

![Fig.1 Illustration of FPC for cellular phones: (a) The schematic diagram of FPC for LCD module, (b) Cross-sectional image of FPC.](image-url)

We have developed new types of functional PIs for FPC applications: (a) mellophanic dianhydride-based PIs as high-temperature adhesives in three-layered CCL, which simultaneously possess excellent thermo- and solution-processability, and very high $T_g'$s...
approximate to 300 °C [1], (b) poly(ester imide)s (PEsIs) as FPC base film materials showing low linear coefficients of thermal expansion (CTE) and low linear coefficients of humidity expansion (CHE) [2-5], and (c) ultra-low-modulus siloxane (or long alkyl chains)-containing PIs as cover layer (CL) materials [6-8]. However, in some cases, the molecular designs addressed to the addition of these new functions (low CHE for dimensional stability against moisture absorption and ultra-low-modulus for inhibition of FPC curling, etc.) caused a serious problem: a decrease in non-flammability. Almost no attention has been so far paid to the non-flammability of functional PIs in the literature because of a “stereotype” that PI systems should be commonly non-flammable as observed in conventional commercially available aromatic PI films. In this paper, we present a strategy using phosphorus-containing monomers for improvement of non-flammability of PEsIs without sacrificing already achieved other target properties. This approach was also attempted to our ultra-low-modulus cover layer materials. The present work also discusses the structure-non-flammability relationship in our pristine (phosphorus-free) PEsI systems.

2. Experimental Section

2.1. Monomer synthesis

Ester-containing tetracarboxylic dianhydrides were obtained by the reaction of diols (40 mmol), i.e., hydroquinone (HQ), methylhydroquinone (M-HQ), and trimellitic anhydride chloride (TMAC, 80 mmol) in the presence of pyridine as an HCl acceptor as shown in Fig. 2 (a).

First, ester-containing dinitro-intermediates were synthesized by the reaction of diols (20 mmol), i.e., 10-(2,5-dihydroxyphenyl)-10H-9-oxa-10-phosphaphenanthrene-10-oxide (HCA-HQ), HQ, and 4-nitrobenzoyl chloride (4-NBC, 45 mmol) in the presence of pyridine, followed by catalytic reduction of the dinitro compounds in a hydrogen atmosphere in the presence of Pd/C.

The molecular structures of the products were confirmed by FT-IR, 1H-NMR spectroscopy, and the elemental analysis. All the products showed very sharp endothermic peaks at each melting point in the DSC thermograms, indicating their considerably high purity suitable for polymerization of PEsIs.

2.2. Polymerization of PEsIs precursor and PEsI film preparation

PEsI precursors, poly(ester amic acid)s (PEsAAs) were prepared as follows: tetracarboxylic dianhydride powder (5 mmol) was added into a N-methyl-2-pyrrolidone (NMP) solution of diamines (5 mmol) with continuous stirring at room temperature for a prolonged period until the reaction mixture turned to a viscous/homogeneous solution and the solution viscosities were stabilized. The PEsAA solutions were coated on a glass substrate and dried at 80 °C for 3 h in an air-convection oven. The PEsAA films obtained were thermally imidized as fixed on a glass substrate at established temperatures (typically 250 °C/1 h + 300 °C/1 h) in vacuum. The PEsI films obtained were removed from the substrate and successively annealed at an established temperature (typically at 350 °C/1 h) in vacuum to eliminate residual stress.

As discussed later, we revealed that the non-flammability depends strongly on the backbone structures of PEsIs. In the present work, we selected a methyl-substituted PEsI system (Fig.3) possessing insufficient non-flammability to investigate the effect of the incorporation of a phosphorus-containing unit.

Fig. 2 Synthetic route of ester-containing monomers used in this work: (a) Tetracarboxylic dianhydrides, (b) Diamines.

Fig. 2 (b) shows a reaction pathway for ester-containing diamines used in the present work.
2.3. Polymerization of low-modulus PI precursors and thermal imidization

Low-modulus PIs were prepared using pyromellitic dianhydride (PMDA) and very flexible diamines containing long alkyl chains or a siloxane block via the conventional two-step process. A phosphorus-containing diamine was also used as a comonomer to improve non-flammability. The structures of the copolyimides are shown in Fig.4.

![Fig.4 Structures of PIs for CL films.](image)

3. Measurements

The inherent viscosities (ηinh) of PI precursors were measured at 0.5 wt% in NMP at 30 °C using an Ostwald viscometer.

CTEs of films (20 mm long, 5 mm wide and typically 15 µm thick) were measured at a heating rate of 5 °C/min as an average within 100–200 °C for the film plane direction on a thermomechanical analyzer (Bruker AXS TMA 4000) with a constant load (0.5 g per film thickness in µm) in a nitrogen atmosphere. In this case, the data were collected from the second heating run with a continuous dry nitrogen flow after pre-heating up to 120 °C from the second heating run with a continuous dry atmosphere. In this case, the data were collected from the second heating run with a continuous dry nitrogen flow after pre-heating up to 120 °C to eliminate the adsorbed water since the first run occasionally shows an abnormal TMA curve.

Dimensional changes of the PEsI specimens were also monitored at fixed temperature at 25 °C in a wet air atmosphere with a relative humidity (80 RH%) on the same TMA system being connected with a precise humidity generator (Shinyei Technology, SRG-1R-1). In order to avoid moisture condensation in the sample chamber, the relative humidity was increased very slowly from 50 to 80 % and maintained at 80 % for 15–20 h until the specimen length was stabilized.

Storage modulus (E’) and loss energy (E”) were measured as a function of temperature to determine Tg from the peak temperatures in the E” curve on the same TMA system at a heating rate of 5 K/min with a sinusoidal load frequency of 0.1 Hz in a nitrogen atmosphere.

Thermal stability of PEsI films was estimated from the 5 % weight loss temperatures (T5 %) by thermogravimetric analysis (Bruker-AXS, TG-DTA2000) at a heating rate of 10 K/min in an air atmosphere.

The extent of water absorption (WA) for PEsI films was determined from the relation:

\[ W_A = \frac{W - W_0}{W_0} \times 100 \quad (\%) \]  

where \( W_0 \) is the weight of the samples vacuum-dried at 50 °C for 24 h, and \( W \) is the weight of the samples immersed in water at 23 °C for 24 h and subsequently wiped well with a tissue paper.

The imide, ester, methyl, and phosphorus contents were calculated from the relation:

\[ F_W(\text{unit}) = \frac{W_{(A)} - W_{(F)}}{W_{(F)}} \times 100 \quad (\text{wt}\%) \]

where \( F_W(\text{unit}) \) denote the repeating units (O=C–N–C=O), ester (COO), methyl groups (CH3), and phosphorus atom (P), respectively. \( W_{(A)} \) and \( W_{(F)} \) denote the formula weights of imide, ester, and phosphorus atom (P), respectively.

Non-flammability of PEsI films was evaluated according to UL-94 V-0 standard test (five sample specimens: 125 mm long, 13 mm wide). For the long alkyl chain-containing PI systems, the sample specimens were prepared as follows: the PAA solution was coated on both sides of a glass paper.

Tensile modulus (E) and the elongation at break (εb) of the PI specimens (3 mm wide and 30 mm long, sample numbers > 15) were measured on a stretching testing machine (A & D, Tensilon UTM-II) at a crosshead speed of 8 mm/min.

4. Results and Discussion

4.1. PEsIs as novel FPC base films

4.1.1. Basic properties and non-flammability of pristine and P-containing PEsI films

The film properties of PEsI systems are listed in Table 1. The TAHQ/PDA PEsI film shows an extremely low CTE (0.8 ppm/K), good thermo-oxidative stability (Tg = 499 °C), and the highest level of non-flammability (UL-94, V-0 class) [2]. However, there is room for further improvement of water absorption, CHE, and film toughness (εb). Copolymerization using M-TAHQ, BPPT (60), and ODA (40) allowed drastic improvement of these properties (WA, CHE, and εb) while keeping low CTE characteristics are listed in Table 1 [4]. The decreased WA and CHE are closely related to a relative decrease in the content...
of highly polarized imide group in the structure, which was caused by a further increase in the aromatic ester units: imide content = 26.4 wt% for TAHQ/PDA and 19.3 wt% for the PEsI copolymer system. However, only the highest level of non-flammability was not retained in this PEsI copolymer. The results suggest that both of the incorporated methyl group and the increased ester group probably contribute to the decreased non-flammability. Then we investigated the structure–non-flammability relationship. For our various PEsI systems, the non-flammability (V-0) was plotted as a function of chemical composition in Fig.5. A V-0/NG boundary was observed around the ester content of 14 wt%. Recall that the PEsI copolymer listed in Table 1, i.e., M-TAHQ/BPTP(60);ODA(40) system (ester content = 19.4 wt%, methyl group content = 2.1 wt%) does not achieve non-flammability (UL-94, V-0) when 22–27 µm thick specimens were used. This diagram may suggest that the ester groups are somewhat flammable compared with ether linkages.

Fig.5 Effect of chemical composition of PEsIs on non-flammability: (o) V-0 and (×) NG.

4.1.2. Effect of P-containing monomer

Our next step is to drastically improve the non-flammability of the PEsI systems without sacrificing other excellent properties. As a common approach, some fire-retardant low-molecular weight additives are often physically dispersed into the resins. However, migration of the additives causes some serious troubles such as deterioration of electric insulation properties. In order to avoid such a migration problem, in the present work, we adopted a copolymerization approach using a bifunctional fire-retardant monomer. It is known well that halogenated (particularly Br-substituted) aromatic compounds are very effective for enhancing non-flammability. However, a serious problem of environmental pollution arising from the use of halogenated fire-retardants is pointed out as controlled by “RoHS” directive in electronic applications. Therefore, we aimed at an outstanding fire-retardant effect of phosphorus (P) compounds, which are believed to be based on a radical-trapping action in combustion processes [9].

We have previously reported that the non-flammability of a series of our PEsIs can be significantly improved by copolymerization with a minor fraction of a P-containing tetracarboxylic dianhydride [5,10]. In the present work, we synthesized a novel P-containing diamine [ABHCAHQ, Fig.2(b)] and applied to our various PEsI systems. A typical result is shown in Table 1 and Fig.5. A minor content (only 5 mol% in the whole diamine components) of this P-containing diamine was copolymerized into the M-TAHQ/BPTP(60);ODA(40) copolymer system, which is originally positioned in NG area as shown in Fig.5. The properties of the P-modified PEsI copolymer are listed in Table 1. This strategy drastically enhanced non-flammability while keeping originally excellent properties; a low WA (0.54 %), a low CHE (5.53 ppm/RH%), and a low CTE (15.7 ppm/K) as listed in Table 1. It should be noted that the phosphorus content was only 0.21 wt% in the PEsI copolymer. A porous char layer was observed in a scorched portion of the specimens by SEM. The formation of such char layers probably plays a great role for suppressing heat conduction during combustion.

Table 1 Properties of PEsIs.

<table>
<thead>
<tr>
<th>Tetraacarboxylic dianhydride (mol%)</th>
<th>Diamine (mol%)</th>
<th>ƞinh (dL/g)</th>
<th>Tg (°C)</th>
<th>CTE (ppm/K)</th>
<th>εb (%)</th>
<th>Wa (%)</th>
<th>CHE (ppm/RH%)</th>
<th>Td5 (°C)</th>
<th>UL-94, V-0* (Thickness)</th>
<th>Content (wt%)</th>
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</thead>
<tbody>
<tr>
<td>TAHQ (100)</td>
<td>PDA (100)</td>
<td>3.7</td>
<td>ND</td>
<td>0.8</td>
<td>8.8</td>
<td>1.25</td>
<td>7.40</td>
<td>499</td>
<td>Passed (20 µm)</td>
<td>Imide; 26.4</td>
</tr>
<tr>
<td>M-TAHQ (100)</td>
<td>BPTP (60)</td>
<td>3.8</td>
<td>390</td>
<td>12.3</td>
<td>41.6</td>
<td>0.52</td>
<td>4.98</td>
<td>445</td>
<td>NG (22-27 µm)</td>
<td>Imide; 19.3</td>
</tr>
<tr>
<td></td>
<td>ODA (40)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ester; 19.4</td>
<td>Methyl; 2.1</td>
</tr>
<tr>
<td>M-TAHQ (100)</td>
<td>BPTP (55)</td>
<td>3.6</td>
<td>382</td>
<td>15.7</td>
<td>37.3</td>
<td>0.54</td>
<td>5.53</td>
<td>444</td>
<td>Passed (22-25 µm)</td>
<td>Phosphorus; 0.21</td>
</tr>
<tr>
<td></td>
<td>ODA (40)</td>
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<td></td>
<td>ABHCAHQ (5)</td>
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</table>

* Standard test sample
4.2. Low modulus PIs for CL films

In contrast to conventional film-type cover layer materials where epoxy-type adhesives are coated on commercially available Kapton®H films, casting-type ones need to show a very low modulus (< ∼ 0.3 GPa) after coating/drying on printed circuits. Otherwise, significant curling occurs by a CTE mismatch in the laminates. This is a main reason why we have challenged the development of ultra-low-modulus PIs [6-8]. However, the molecular designs addressed to ultra-low modulus also give rise to an inevitable serious problem due to a decrease in the content of aromatic units, i.e., a drastic decrease in non-flammability. It is very difficult to solve this problem particularly when long alkyl chains were chosen as a flexible unit.

The structures of our low-modulus PIs are shown in Fig.4. In this case, we used another P-containing diamine with high hydrolytic stability. The copolyimide film prepared from PMDA with the alkylene-containing diamine (50) and P-containing diamine (50) showed an excellent toughness (εb= 462 %) and an extremely low-modulus (E = 0.28 GPa), which is sufficiently low to avoid curling of FPC.

However, this copolyimide film showed no fire-retardance, indicating that the flammable alkyl chain content is too high compared to the P content in the film. Fig.6 shows the tensile modulus and non-flammability as a function of the ratio of P and alkylene contents (wt%/wt%) in the films. At a low relative P content (< 0.1 (wt%/wt%)), the PI films possess comparatively low modulus (E < 1 GPa). However, these PI films were flammable. On the other hand, above 0.33 (wt%/wt%), the PI films became fire-resistant as shown in Fig.6. However, the modulus significantly increased up to the values approximate to conventional PI films. Thus, it was very difficult to achieve non-flammability and low modulus (< 1 GPa) at the same time, as far as the long alkyl chain-based PI systems are selected as a basic backbone structure and the present P-containing diamine with a low P content is used. On the other hand, to choose siloxane-containing PI systems as an alternative basic polymer is much more advantageous from the viewpoints of non-flammability. This project is in progress.

4. Conclusions

Copolymerization with a minor fraction (only 5 mol%) of the P-containing diamine (ABHCAHQ) drastically improved the non-flammability of PEI copolymer while retaining excellent combined properties, i.e., a very high Tg, a low CTE, a low Wα, low CHE, and sufficient toughness.

The copolymerization approach using a P-containing diamine was also applied to improve the non-flammability of long alkyl chain-based low-modulus PI system. However, the results are quite far from the present goal because of its originally high flammability.

References