

Strategy for Improvement of Non-flammability in Functional Polyimides

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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, high temperature adhesives for their combined excellent properties, i.e., high glass transition temperature (T_g), 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 FPCs, TAB and COF assembly systems are fabricated. We have developed new types of functional PIs for FPC applications: (a) poly(ester imide)s (PEIs) as FPC base film materials showing low linear coefficients of thermal expansion (CTE) and low linear coefficients of humidity expansion (CHE), and (b) ultra-low-modulus siloxane (or long alkyl chains)-containing PIs as cover layer (CL) materials. 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. In this report, we present a strategy using phosphorus-containing monomers for improvement of non-flammability of PEIs without sacrificing already achieved other target properties. This approach was also attempted to our ultra-low-modulus cover layer materials.

Experimental Section

Ester-containing tetracarboxylic dianhydrides were obtained by the reaction of diols, i.e., hydroquinone(HQ), methylhydroquinone, and trimellitic anhydride chloride in the presence of pyridine as an HCl acceptor. On the other hand, ester-containing diamines were synthesized by catalytic reduction of the ester-containing dinitro-intermediates which were synthesized by the reaction of diols, i.e., 10-(2,5-dihydroxyphenyl)-10H-9-oxa-10-phospha-phenanthrene-10-oxide, HQ, and 4-nitrobenzoyl chloride in the presence of pyridine. PEI precursors, poly(ester amic acid)s (PEsAAs) were obtained by the equimolar polyaddition of these tetracarboxylic dianhydrides and diamines in NMP. 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 PEI 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.

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.

Results and Discussion

The structures of our PEIs are shown in Fig. 1. The film properties of PEI systems are listed in Table 1. The TAHQ/PDA PEI film shows an extremely low CTE (0.8 ppm/K), good thermo-oxidative stability ($T_d^5 = 499$ °C), and the highest level of non-flammability (UL-94, V-0). However, there is room for further improvement of water absorption, CHE, and film toughness (ϵ_b). Copolymerization using M-TAHQ, BPTP (60), and ODA (40) improved these properties (W_A , CHE, and ϵ_b) as listed in Table 1. The decreased W_A 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 PEI copolymer system. However, only the highest level of non-flammability was not retained in this PEI 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 PEI systems, the non-flammability (V-0) was plotted as a function of chemical composition in Fig.2. A V-0/NG boundary was observed around the ester content of 14 wt%. Recall that the PEI 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 (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.

Our next step is to drastically improve the non-flammability of the PEI 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. We have previously reported that the non-flammability of a series of our PEIs can be significantly improved by copolymerization with a minor fraction of a P-containing tetracarboxylic dianhydride. In the present work, we synthesized a novel P-containing diamine [ABHCAHQ, Fig.1] and applied to our various PEI systems. A typical result is shown in Table 1 and Fig.2. 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.2. The properties of the P-modified PEI copolymer are listed in Table 1. This strategy drastically enhanced non-flammability while keeping originally excellent properties; a low W_A (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 PEI 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.

In contrast to conventional film-type CL 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. 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.3. 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 ($\epsilon_b = 462\%$) 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.4 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 (< 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.4. 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.

Table 1 Properties of PEIs.

Tetracarboxylic dianhydride (mol%)	Diamine (mol%)	η_{inh} (dl/g)	T_g (°C)	CTE (ppm/K)	ϵ_b (%)	W_A (%)	CHE (ppm/RH%)	T_{50}^{air} (°C)	UL-94, V-0 (Thickness)	Content (wt%)
TAHQ (100)	PDA (100)	3.7	ND	0.8	8.8	1.25	7.40	499	Passed (20 μ m)	Imide; 26.4 Ester; 16.6
M-TAHQ (100)	BPTP (60) ODA (40)	3.8	390	12.3	41.6	0.52	4.98	445	NG (22-27 μ m)	Imide; 19.3 Ester; 19.4 Methyl; 2.1
M-TAHQ (100)	BPTP (55) ODA (40) ABHCAHQ (5)	3.6	382	15.7	37.3	0.54	5.53	444	Passed (22-25 μ m)	Imide; 19.0 Ester; 19.1 Methyl; 2.0 Phosphorus; 0.21

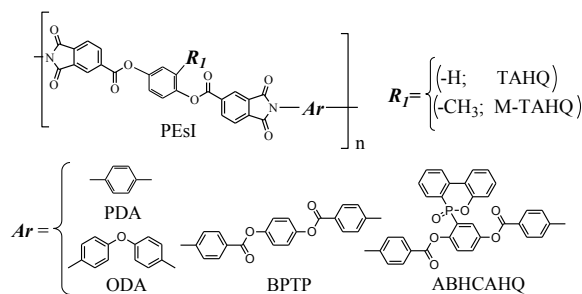


Fig.1 Structures of PEIs for base films of CCL.

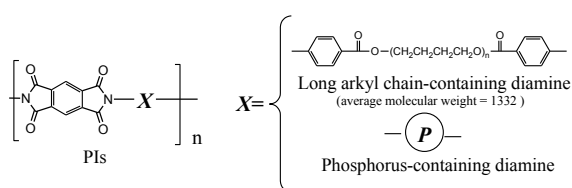


Fig.3 Structures of PIs for CL films.

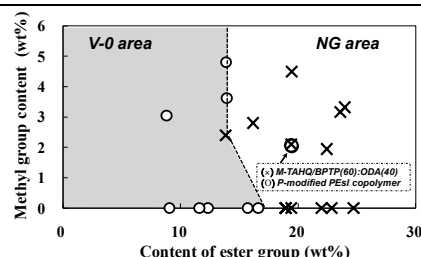


Fig.2 Effect of chemical composition of PEIs on non-flammability: (o) V-0 and (x) NG.

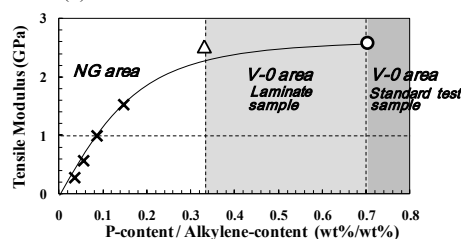


Fig.4 Relationship between the tensile modulus and non-flammability as a function of the ratio of P and alkylene contents in the films: (o) V-0, (A) V-0 at laminated sample, and (x) NG.