

Increase in Flame Retardance of Glass-Epoxy Laminates without Halogen or Phosphorous Compounds by Simultaneous Use of Incombustible-Gas Generator and Charring Promoter

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ABSTRACT: Highly flame-resistant glass-epoxy laminates without flame-retarding additives such as halogen and phosphorous compounds have been developed to overcome environmental problems caused by these additives. The laminates consist mainly of a self-extinguishing epoxy-resin compound (phenol aralkyl), an incombustible-gas generator (amino-triazine-novolac hardener: ATN hardener), and inorganic materials such as a charring promoter (zinc molybdate on talc: ZMT) and a limited amount of harmless metal hydroxide (aluminum trihydroxide: ATH). They are highly flame-resistant and have other beneficial characteristics, including soldering-heat resistance, humidity resistance, electronic properties, and processing advantages. These qualities make them applicable enough to replace the FR-4 type

printed wiring boards (PWBs) that are widely used today. Simultaneously using the ATN hardener and ZMT in the laminates, including the epoxy-resin compound and ATH, greatly improved their flame retardance. We then reduced the amount of ATH to obtain even better flame retardance in the laminates. This reduction of the ATH, consequently, improved other practical characteristics such as soldering-heat resistance, humidity resistance, and electronic properties. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 3367–3375, 2006

Key words: flame retardance; glass-epoxy laminate; halogen and phosphorous additives; self-extinguishing epoxy-resin compound; inorganic materials

INTRODUCTION

Glass epoxy laminates, which generally consist of epoxy-resin compounds with halogenated flame-retarding additives and glass clothes, are used as printed wiring boards (PWBs) in electronic instruments. These flame-retarding additives, however, sometimes generate toxic gases, when the compounds containing them are burned.^{1,2} Because of these toxic effects, the replacement of halogen compounds with alternative safer compounds soon began.^{3,4} These halogen compounds were mainly replaced with phosphorous compounds, such as organic phosphorous esters. However, these compounds are not sufficiently safe, i.e., triphenyl phosphate, which is the basic unit of organic phosphorous esters, is chronically toxic.⁵ The PWBs with phosphorous flame-retarding additives also show low humidity resistance.⁶ We consider, therefore, substituting alternative safer and more practical

flame-retarding materials for the phosphorous compounds is important.

Moreover, metal hydroxides such as aluminum trihydroxide (ATH) and magnesium dihydroxide (MDH) have been suggested as being safer materials than phosphorous compounds.⁷ These hydroxides retard flames by absorbing the heat during ignition. However, they must be added in large amounts (over 60 wt %), and adversely affects important characteristics of PWBs, such as soldering-heat resistance and dielectric properties.

On the other hand, to improve flame retardance of epoxy-resin compounds, methods to increase the heat resistance of these compounds has been studied. Depression of molecular mobility in crosslinking structures has been investigated by increasing the crosslinking density of resin structures and by introducing bulky moieties in the structures.^{8,9} This method can increase the heat resistance revealed by increased glass transition temperature (T_g) of epoxy-resin compounds, however, it cannot improve the flame retardance of the compounds. Therefore, a safer and more practical flame-retarding technology for epoxy-resin compounds has been required.

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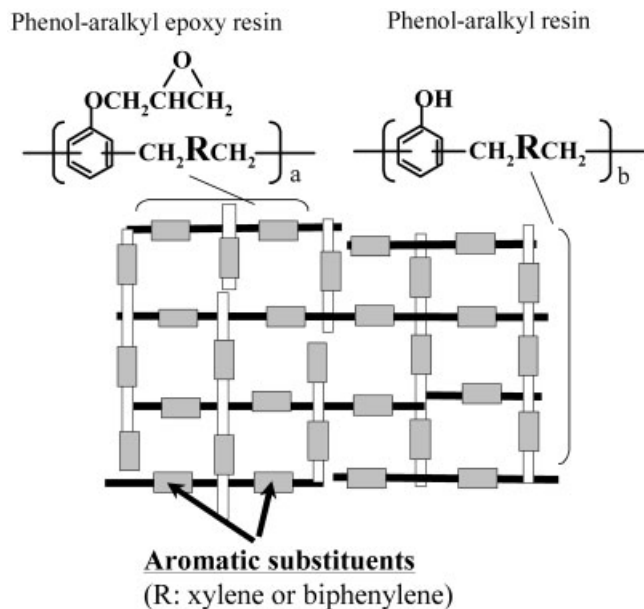


Figure 1 Network formed in phenol-aralkyl epoxy-resin compound.

To address these problems, we previously reported new flame-resistant epoxy-resin compounds without flame-retarding additives (Fig 1).¹⁰ The new compounds contain phenol aralkyl epoxy resins and phenol aralkyl resin hardeners, both of which contain aromatic moieties such as xylene and biphenylene, in the main chain of the novolac resin structure (phenol aralkyl epoxy-resin compounds). The compounds form a self-extinguishing network of structures after crosslinking reactions between the epoxy resins and the hardeners. The significant improvement in flame retardance results from a unique flame-retarding mechanism. During ignition, the resin compounds form stable foam layers consisting mainly of the compounds and volatile materials (carbon oxides, hydrocarbons) generated by pyrolysis of the compounds on their surfaces (Fig. 2). These foam layers effectively retard the transfer of heat to the insides of the compounds and the flames are thus extinguished. The foam layers are formed because of the low elasticity of the compounds at high temperatures due to the low crosslinking densities of their network structures. The high stability of the foam layers during ignitions is a result of the high pyrolysis resistance of the compounds with the aromatic moiety in their structures. We also developed a new epoxy-molding compound without any flame-retarding additives for integrated circuit (IC) packages by using the phenol-aralkyl epoxy-resin compounds, silica filler, and other additives.^{11–13}

Furthermore, a flame-resistant glass-epoxy laminate without halogen or phosphorous compounds, which shows high flame retardance and good practicality,

has been developed by using the above-mentioned phenol aralkyl epoxy-resin compounds and a limited amount of harmless ATH.^{14,15}

In this article, we report further improvement in flame retardance and other practical characteristics of the above-mentioned glass-epoxy laminate for FR-4 type PWB used most widely. Improving the flame retardance of the laminate was achieved by the simultaneous use of an incombustible-gas generator (amino-triazine-novolac hardener: ATN hardener) and a charring promoter (zinc molybdate on talc: ZMT). This laminate includes the phenol aralkyl epoxy-resin compound (phenol biphenylene epoxy-resin compound) and the ATH. This method, to achieve high flame retardance, consequently decreased the ATH content and improved other practical characteristics such as soldering-heat resistance, and humidity resistance and electronic properties.

EXPERIMENTAL

Materials

The epoxy resins and hardeners we used are listed in Table I. The epoxy resins tested were phenol biphenylene epoxy resin (PB epoxy resin, softening temperature: 57°C, epoxy equivalent: 274 g/equiv., Nippon Kayaku) used as a phenol aralkyl epoxy resin and bisphenol A epoxy resin (Bis-A epoxy resin, viscosity: 120–150 poise at 25°C, epoxy equivalent: 187 g/equiv., Japan Epoxy Resins) used as a conventional epoxy resin.

The hardeners tested were phenol biphenylene resin (PB hardener, softening temperature: 127°C, hydroxyl equivalent: 242 g/equiv., Meiwa Plastic Industries) used as a phenol aralkyl resin hardener and phenol novolac-type resin (PN hardener, softening temperature: 105°C, hydroxyl equivalent: 108 g/equiv., Meiwa Plastic Industries) used as a conventional resin hardener. The incombustible-gas generators tested consisted of 60 wt % of amino-triazine-novolac resins

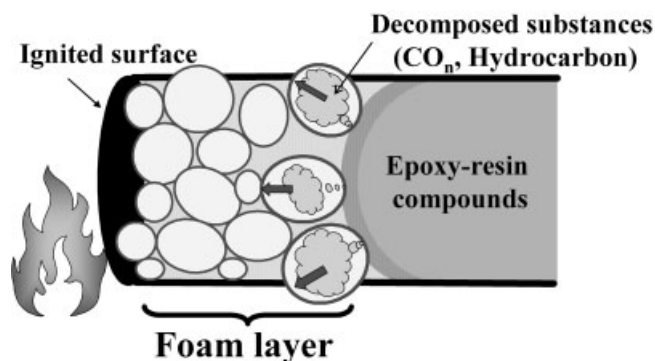


Figure 2 Self-extinguishing mechanism in phenol-aralkyl epoxy-resin compounds.

TABLE I
Structures of Tested Epoxy Resins and Hardeners

Types of resin	Chemical structures
Phenol biphenylene epoxy resin (PB epoxy resin)	
Phenol biphenylene resin (PB hardener)	
Bisphenol-A epoxy resin (Bis-A epoxy resin)	
Phenol novolac-type resin (PN hardener)	
Amino-triazine-novolac resins (ATN hardener)	

(ATN hardener) and 40 wt % of 2-butanone (nitrogen content: 12 or 19 wt % in the resin parts, hydroxyl equivalent: 125 or 146 g/equiv., Dainippon Ink and Chemicals). These hardeners and incombustible-gas generators were stoichiometrically added to the epoxy resins at the ratio of one hydroxyl moiety per one epoxy moiety (OH/Ep = 1.0).

The inorganic additives tested were aluminum trihydroxide (ATH: Higilite HP-350*, Showa Denko K. K.), zinc molybdate on talc (Kemgard 911C, Sherwin-Williams), zinc molybdate (Mitsuiwa Chemical), zinc borate (Firebrak ZB, U.S. Borax and Chemical) and hydroxyl zinc stannate (Nihon Kagaku Sangyo). The curing promoter tested was epoxy-resin adducted type imidazole (P200, Japan Epoxy Resins). An electrolytic copper foil with 18 μm thickness (IIIEC series, Mitsui Mining and Smelting) was used.

Prepregs, which consisted of a half-cured epoxy-resin compound and glass-fiber woven fabric (50 and 100 μm thickness, Arisawa Manufacturing), were produced by impregnating the fabric with a varnish containing resins and additives such as inorganic fillers and curing promoters. This fabric was dried at room temperature for 30 min, then half cured at 120°C with an applied pressure at 0.5 MPa for 5 min. Final varnish consisted of the above-mentioned epoxy resin, hard-

ener, inorganic filler, curing promoter with 2-butanone.

Glass-epoxy laminates were prepared by pressing four or six layers of prepregs at 4 MPa under curing conditions at 180°C for 90 min. Double-sided copper-clad laminates (CCLs) consisting of four layers of the prepregs between two sheets of 18 μm thickness copper foil, which were prepared by thermal pressing as described above.

Method

The flame retardance of glass-epoxy laminates was determined by using the UL94 vertical (UL94 V) method regulated by the Underwriters Laboratories. In this method, a sample material (13 mm wide, 127 mm long, and 0.5–0.8 mm thickness) is held vertically and ignited with a flame of over 98% methane gas applied to the bottom twice for 10 s each. The flame retardance of the material is classified according to how long it burns and whether particles that ignites the surgical cotton placed under the specimen fall from it. The range of burning time for a total of five samples classifies the flame retardance extent from V-0 (total flaming time is 50 s or less and maximum flaming time is 10 s or less) to V-1 (total flaming time

is 250 s or less). If the cotton is ignited, the flame retardance of the material is classified as V-2; otherwise it is "NOT" classified.

The soldering-heat resistance of the glass-epoxy laminates (4 cm × 4 cm, 0.4 mm thick) was determined by observing the defects, such as delamination and swelling of the laminates, after they had been dipped in a solder bath at 260°C for 30 s following humidity treatment (121°C, 100% relative humidity, 0.2 MPa) for 12 h. The soldering-heat resistance of the CCLs that floated on solder bath at 260 or 288 °C was determined by measuring the time when the swelling between the coppers and the laminates or among laminates occurred.

The peel strength between the laminates and coarse face of copper foil was measured by a method specified in IEC 60249. The thermal degradation behavior of the laminates was examined by using a thermogravimetric analyzer (TG/DTA 6200, Seiko Instruments) in 0.2 L/min of air at a heating rate of 20°C/min. The glass transition temperature (T_g) of laminates with 22 mm × 10 mm was determined by the bending method specified in IEC 60249 with the use of a dynamic mechanical analyzer at 1.0 Hz (DMA, TA Instruments Japan, RSAII). The laminates were heated from 25 to 250°C at the rate of 10°C/min. The chemical resistance was evaluated by observing the laminates dipped in 5 wt % NaOH solution at 40°C for 60 min, in 10 vol % H₂SO₄ solution at 30°C for 60 min, and in propylene glycol monomethyl-ether acetate (PGM-AC) at 20°C for 60 min specified in IEC 60326.

The humidity resistance of the laminates was estimated by measuring the water absorption ratio after the above humidity treatment for 12 h. The dielectric properties containing dielectric constant (ϵ_r) and dissipation factor ($\tan \delta$) of the laminates at 1 MHz were estimated by a method specified in IEC 60249-1. The reflow-soldering resistance of the laminates was estimated by the method specified in IEC 60326; heating the laminates four times at 290°C within peak temperature from 10 to 12 s.

The change in the insulation resistance of 0.35 mm-diameter drilling holes and 0.1 mm-diameter laser via holes (LVH) was determined by a method specified in IEC 60326. The insulation resistance within 10% variation satisfied the standard. The laminates were subjected to the measured insulation resistance after treating the laminates from -65 to 125°C for 30 min, and then dipping them in oil (1 cycle = heated at 260°C for 5 s, then cooled by standing air for 15 s, finally stored at 20°C for 20 s).

RESULTS AND DISCUSSION

Increase in flame retardance and other important properties of laminates

To improve the flame retardance and other properties of the glass-epoxy laminate including phenol biphe-

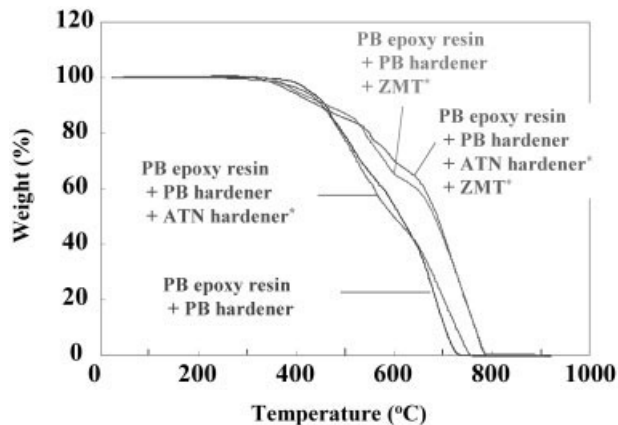


Figure 3 Thermogravimetric analysis of laminates (content: 10 wt % in the resin parts of laminates except glass clothes).

nylene (PB) epoxy-resin compound (as a self-extinguishing phenol aralkyl epoxy resin compound) and aluminum trihydroxide (ATH), we studied the single use of an amino-triazine-novolac (ATN) hardener as an incombustible-gas generator, the single use of zinc molybdate on talc (ZMT) as a charring promoter, and the simultaneous use of the ATN hardener and the ZMT.

Single use of ATN hardener

The ATN hardener generates incombustible gas mainly consisting of carbon dioxide and nitrogenous series gas. Adding the ATN hardener to the self-extinguishing epoxy-resin compounds used for integrated-circuit (IC) molding resulted in compounds with high flame retardance.^{16,17} From the results of thermogravimetric analysis (TGA) of glass-epoxy laminates with the ATN hardener (Fig. 3) in air, which shows that incombustible gas generated over 300°C (especially 300–500°C), the increase in flame retardance of the laminates with the ATN hardener was expected.

However, contrary to our expectations, single use of the ATN hardener on the glass-epoxy laminates, which included the self-extinguishing epoxy-resin compound and 35 wt % of the ATH in the resin parts of laminates excluding glass clothes, decreased the flame retardance of the laminates (Fig. 4). Furthermore, the amount of the ATN hardener showed a complicated influence on the flame retardance of the laminates. This complicated influence resulted perhaps from two major factors caused by adding the ATN hardener, which are the generation of the incombustible gas and the inhibition of the self-extinguishing epoxy-resin compound forming a flame-retarding foam layer.

The use of a small amount of the ATN hardener (10 wt % in total hardener) excessively decreased the

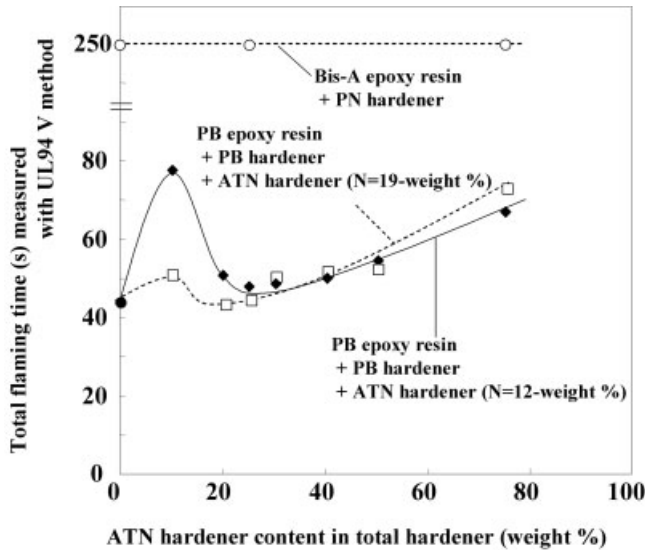


Figure 4 Flame retardance of laminates with ATN hardeners (ATH Content: 35 wt % in the resin parts of laminates except glass clothes).

flame retardance of the laminate. This decrease in the flame retardance likely resulted from the insufficient formation of the flame-retarding foam layer caused by both the small amount of incombustible-gas generated and the increase in interaction among crosslinking molecules deriving from the high polarity of the ATN hardener. Adding the ATN hardener in an amount that equaled 20–40 wt % recovered the flame retardance slightly. This most likely resulted from increasing the incombustible gas generation. However, the more the ATN hardener content increased (over 40 wt %), the worse the flame retardance of laminates was. It is assumed that the accelerated decomposition of total resin parts by increasing the ATN hardener had an adverse effect on the flame retardance of the laminates in contrast to the flame-retarding effect derived from incombustible-gas generation. Thus, it was difficult to form the stable flame-retarding foam layer.

Furthermore, single use of the ATN hardener on the conventional epoxy-resin compound, which consisted mainly of Bis-A epoxy resin and PN hardener, resulted in even lower flame retardance than that of the self-extinguishing epoxy-resin compound, and had no effect on flame retardance.

On the contrary, the single use of the ATN hardener increased the adhesive strength of laminates to copper foils (Fig. 5). High polarity of the amino moieties in the ATN hardener structure resulted in the increased adhesive strength.¹⁶ The adhesive strength of laminates with the addition of the ATN hardener to copper foils remained constant, when the ATN hardener content in total hardener was more than 20 wt %. The adhesive strength of the laminates, moreover, indicated almost the same value when the nitrogen content in the ATN hardener was changed.

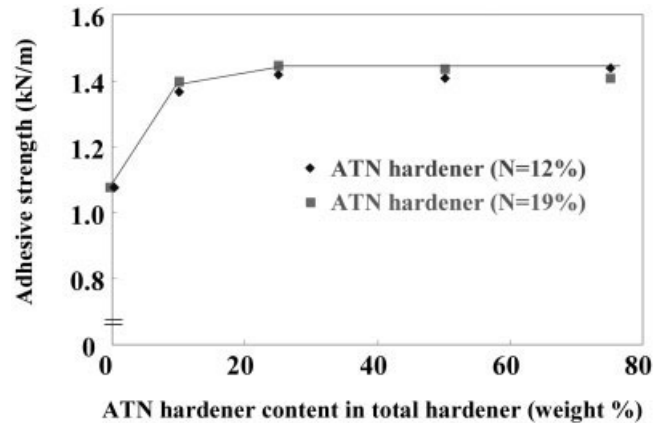


Figure 5 Peel strength between laminates (PB epoxy resin, PB hardener, ATN hardener, and 35 wt % of ATH are contained in the resin parts of laminates except glass clothes) and coarse face of copper foil.

The double-sided copper-clad laminates (CCLs) with the ATN hardener showed excellent soldering-heat resistance at 260°C for over 300 s with no defects such as delamination or swelling, when compared to that of the CCL without the ATN hardener. The soldering-heat resistance at 288°C, however, was decreased (Fig. 6). The CCLs including the ATN hardener with the lower nitrogen content (12 wt %) indicated higher soldering-heat resistance than that of the CCLs including the hardener with the higher nitrogen content (19 wt %). These results indicate that amino moieties with high basicity in the ATN hardener accelerated pyrolysis of the ATH on decreasing soldering-heat resistance of the CCLs under temperatures higher than 288°C.

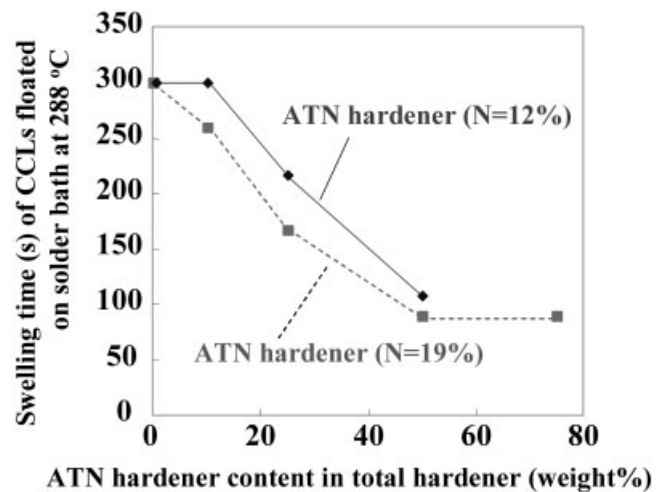


Figure 6 Soldering-heat resistance (maximum floating time on solder bath at 288 °C is 300 s) of CCLs with ATN hardeners (PB epoxy resin, PB hardener, ATN hardener, and 35 wt % of ATH are contained in the resin parts of laminates except glass clothes).

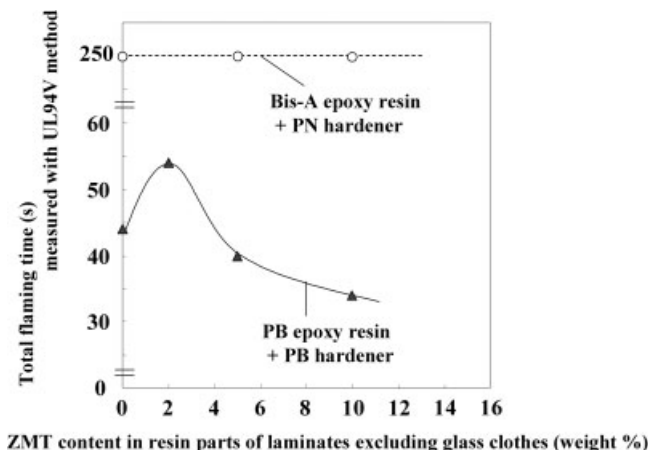


Figure 7 Flame retardance of laminates (ATH content: 35 wt % in the resin parts of laminates except glass clothes).

Single use of ZMT

We studied using zinc compounds as charring promoters, generally known as dehydrogenating catalysts,^{18,19} thus promoting the dehydrogenation of aromatic moieties such as phenol or biphenylene in resins, and consequently forming chars that retard the resins burning.

The zinc molybdate on talc (ZMT) was selected as the charring promoter for laminates due to its excellent resistance to chemical agents such as acidic and alkaline solutions used for printed wiring board (PWB) manufacture, and also due to its low specific gravity (sp. gr.). The addition of the other zinc compounds such as borates or stannates was also investigated. However, laminates including zinc borate or zinc stannate showed lower chemical resistance than that of the laminate with zinc molybdate. After dipping in 1N hydrochloric acid at 30°C for 4 h, for example, the laminates with zinc borate or zinc stannate remarkably decreased in weight and changed color. The laminate with the zinc molybdate, on the contrary, showed good chemical resistance. The molybdate with the high sp. gr. of 5.1 insufficiently dispersed in varnish solution mainly consisting of organic solvent and epoxy-resin compounds. We consequently use the ZMT with sp. gr. of 2.8 to bring laminates into uniform composition.

Single use of the ZMT showed some flame-retarding effect on the glass-epoxy laminate consisting of the self-extinguishing epoxy-resin compound and the ATH (Fig. 7). From the TGA results (Fig. 3), which showed that the laminate with the ZMT had less weight loss at high temperatures when compared with the laminate without ZMT, the increase in the flame retardance was due mainly to the high pyrolysis resistance of the laminate resulting from the acceleration of the charring reaction by the ZMT. The flame retardance of the laminate depended on the ZMT content.

The small amount of ZMT, which is less than 2 wt % in the resin parts of laminates excluding the glass clothes, decreased the flame retardance. We consider that this decrease in the flame retardance was thought to be caused by the low content of the ZMT. This resulted in inhibiting the formation of a flame-retarding layer by both the lack of the char-promoting effect and the insufficient dehydrogenation of the resin parts. More than 2 wt % of the ZMT can improve the flame retardance of this laminate. Especially, adding the ZMT more than 5 wt % achieved a relatively even better flame retardance. However, its flame retardance needs to be improved further (Fig. 7). The increase in the burning resistance of the laminate by the addition of ZMT caused the decrease in gas generation during combustion, which probably retarded the formation of the flame-retarding foam layer, thereby producing the insufficient flame retardance.

Increasing the ZMT content, which caused an increase in the molten viscosity of the epoxy-resin compounds used for the laminates, decreased their wetting-ability to copper surfaces and resulted in lower adhesive strength to the copper foils (Fig. 8). Higher content of ZMT, more than 8 wt %, was not able to satisfy the standard of build-up structure systems specified in IEC 60249 (IEC 60249 indicates that the systems must have more than 0.8 kN/m of the adhesive strength). Less than 5 wt % of the ZMT content was able to satisfy the above adhesive strength; however, it was insufficient in achieving high flame retardance, as previously mentioned.

The CCLs with the ZMT showed excellent soldering-heat resistance at 260 and 288°C with no defects such as delamination or swelling. The resistance was maintained in the CCLs with various ZMT contents tested in the study.

Simultaneous use of ATN hardener and ZMT

As above-mentioned, single use of the ATN hardener or the ZMT was insufficient to improve flame retar-

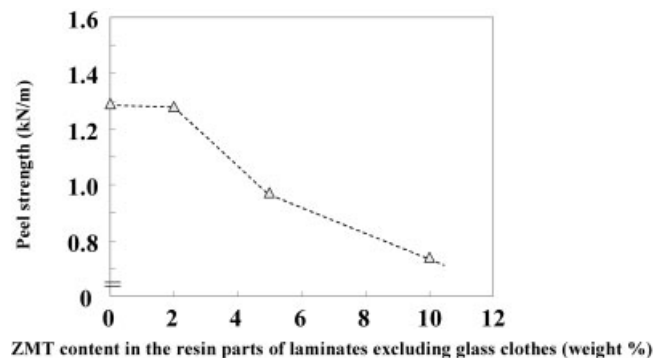


Figure 8 Peel strength between laminates (PB epoxy resin, PB hardener, and 35 wt % of ATH are contained in the resin parts of laminates except glass clothes) and coarse face of copper foil.

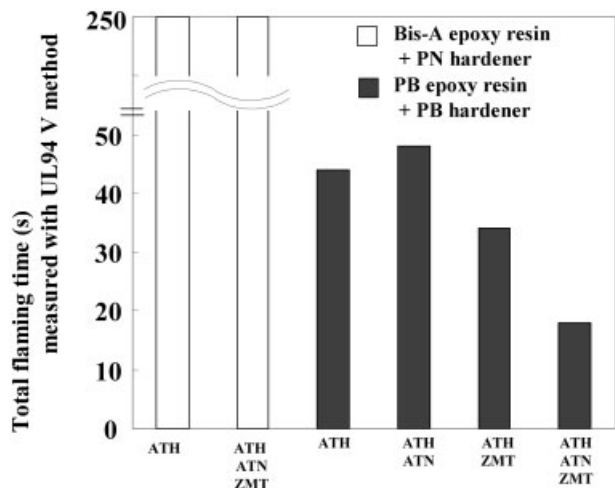


Figure 9 Flame retardance of laminates [ATH (35 wt % in the resin parts), ATN hardener (N content : 12 wt %, 25 wt % in total hardener), and ZMT (10 wt % in the resin parts) are included respectively].

dance of the glass-epoxy laminates. However, judging from the results, it's hypothesized that the simultaneous use of the ATN hardener and the ZMT may produce a stable foam layer with high flame-retarding effect due to the fact that the ZMT can reinforce the foam layer by its charring effect and the layer can then effectively catch the incombustible gas from the ATN hardener.

Significant increase in the flame retardance of the glass-epoxy laminate consisting of the self-extinguishing epoxy-resin compound and the ATH (Figs. 9 and 10) was achieved by simultaneous use of ATN hardener and ZMT.

The TGA of the laminates consisting of the self-extinguishing epoxy-resin compound (PB epoxy-resin compound), the ATN hardener, and the ZMT (Fig. 3)

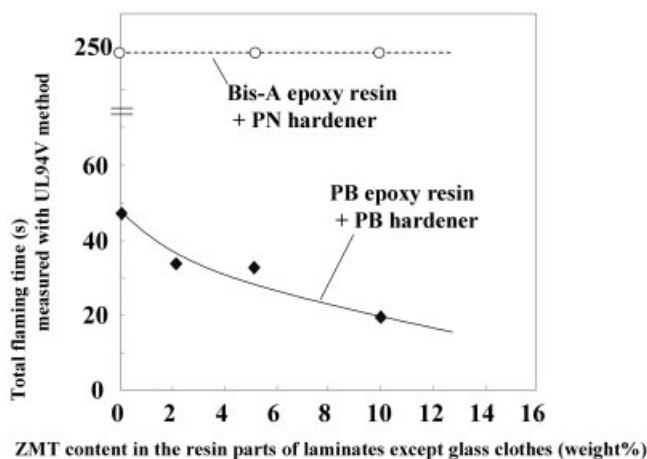


Figure 10 Flame retardance of laminates [ATH (35 wt % in the resin parts) and ATN hardener (N content : 12 wt %, 25 wt % in total hardener) are included].

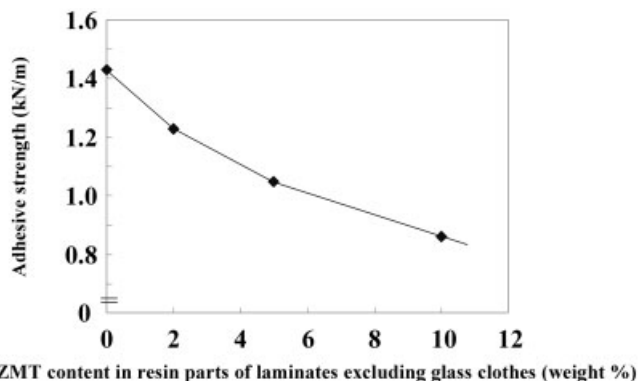


Figure 11 Adhesive strength between laminates (PB epoxy resin, PB hardener, 35 wt % of ATH in the resin parts of laminates, and 25 wt % of ATN hardener (N = 12 wt % in total hardener are contained in laminates) and coarse face of copper foil.

showed that the thermal degradation in air of the compound was accelerated from 300 to 500°C and its decomposition was retarded above 500°C. Therefore, we consider that at the beginning of combustion (300–500°C) the incombustible gas derived from the ATN hardener was generated, and afterward, during combustion (above 500 °C), the resin parts turned out to be a char by the ZMT, which can strengthen the foam layer to catch the incombustible gas effectively and produce a stable foam layer for high flame retardance.

On the other hand, the flame retardance of the conventional epoxy-resin compound consisting mainly of Bis-A epoxy resin and PN hardener does not form such a foam layer during ignition, and it cannot be improved by adding the ATN hardener and the ZMT.

Increasing the amount of the ZMT decreased the adhesive strength of the laminates with 35 wt % of the ATH to copper foils (Fig. 11). The decrease of the adhesive strength resulted from the increase in total inorganic filler contents in the laminates. The laminates that included the ZMT within 10 wt %, however, satisfied the standard of build-up structure systems, which indicates that the systems must have over 0.8 kN/m adhesive strength.

The glass-epoxy laminate with the ATN hardener and the ZMT achieved high soldering-heat resistance, can the ATH content be decreased because of the high flame retardance. This will be described later.

Characteristics of new laminate

The new laminate consisting of the self-extinguishing epoxy-resin compound (PB epoxy-resin compound), an ATN hardener, ZMT, and a limited amount of harmless ATH demonstrated excellent practical characteristics such as soldering-heat resistance, humidity resistance, good dielectric properties, and connection

TABLE II
Characteristics of New Glass-Epoxy Laminate

Characteristics	Conditions	Current halogen-containing FR-4 (Bisphenol A epoxy resin + Dicyandiamide + Brominated epoxy resin)	New laminate PB epoxy resin + PB hardener + ATH (about 40-weight % ^a) + ATN hardener (about 10-weight% ^a) + ZMT (about 5-weight % ^a)
Flame retardance	UL94V (0.5 mm–0.8 mm thickness)	V-0	V-0
Chemical resistance	Alkali: 5 wt % NaOH/40°C for 60 min Acid: 10 vol % H ₂ SO ₄ /30°C for 60 min Organic solvent: PGMAC/20°C for 60 min	Pass	Pass
Humidity resistance	Water absorption ratio after humidity treatment for 12 h (weight %)	1.59	0.55
Heat resistance	Glass transition temperature (°C) measured by DMA method	145	160
Dielectric properties	Dielectric constant (ϵ^f , at 1 MHz)	4.4	5.0
	Dissipation factor ($\tan \delta$, at 1 MHz)	0.020	0.006
Soldering-heat resistance	1. Reflow soldering \times 4 based on IEC 60326 (max. 290 °C/10s)	Failure (Delamination)	Pass (No delamination)
	2. Dipping humidity-treated laminates in solder bath at 260°C for 30 s	Failure (Delamination)	Pass (No delamination)
Adhesive property	Peel strength (kN/m) 18-mm-thick copper foil (0 mm width)	1.60	1.50
Connection reliability in inner circuit	Variations in insulation resistance within 10% (0.35 mm φ through hole)		
	1. Heat cycle test (65°C/30 min \leftrightarrow 125°C/30 min)	Failure at 400 cycles	Pass more than 500 cycles
	2. Oil dip cycle test (heated at 260°C for 5s \leftrightarrow cooled by standing air for 15s \leftrightarrow stored at 20 °C for 20 s)	Failure at 400 cycles	Pass more than 500 cycles

^a Content in the resin parts of laminates except glass clothes.

reliability in the inner circuits, in addition to flame retardance (Table II).

The flame retardance of glass-epoxy laminates consisting of PB epoxy-resin compound and ATH was increased by simultaneously using ATN hardener and the ZMT. This simultaneous use, consequently, decreased the content of the ATH, which adversely affects the soldering-heat resistance of glass-epoxy laminates. Therefore, this decrease in ATH content resulted in higher soldering-heat resistance in the new glass-epoxy laminate than that in the current FR-4 material. The new laminate also demonstrated high soldering-heat resistance, which was evaluated by floating new CCLs after humidity treatment on a hot solder bath and reflow-soldering specified by IEC 60326. It did not suffer from any defects such as delamination or swelling, while the current FR-4 material did. These resulted from the decrease in the amount of ATH and also the good resistance against humidity.

This new laminate had higher resistance against humidity than that of the current FR-4 material that contains halogenated flame-retarding additives. The water absorption ratio used to estimate the resistance to humidity was a third of the current FR-4 material.

This better humidity resistance was probably derived from the biphenylene moieties that have excellent hydrophobic properties in the structure of the resin.

The new laminate had higher T_g than that of the current FR-4 material, which can be called a limited heat-deforming material. This higher T_g for the new laminate was most likely derived from the increasing molecular weight of the PB hardener. This increase in molecular weight increased the intermolecular forces originating from intertwining molecular chains, resulting in higher T_g .

Moreover, the new laminate with its low transmission loss had good dielectric properties. The dielectric constant (ϵ_r) of the new laminate was higher than that of the current FR-4 material. Despite this higher dielectric constant, the dissipation factor ($\tan \delta$) of the new laminate was lower than that of the current FR-4 material. Thus, its transmission loss obtained from the equation, $K \times f \times \sqrt{\epsilon_r} \times \tan \delta$, was a third of the current FR-4 material. The transmission loss for the new laminate was 0.013Kf and for the current FR-4 material was 0.042Kf. The "K" above indicates constant, and "f" indicates frequency. These good dielectric properties were mainly due to the nonpolar aro-

matic moiety of the PB resins and the decreased amount of ATH.

The reliability of connections in the inner circuits of the new printed wiring board (PWB) was superior to that of a conventional PWB composed of the current FR-4 material. After adding over 500 cycles of heat shock through thermal or oil-dipping treatment, variations in the insulation resistance of holes with a diameter of 0.35 mm in the new PWB were within 10%, which satisfied the standards specified by IEC 60326. After adding only 400 cycles of heat shock, on the other hand, the variations in the conventional PWB didn't satisfy the standards specified by IEC 60326. Furthermore, the new PWB demonstrated good connection reliability in 0.1-mm diameter laser via holes (LVHs) after over 500 cycles of heat shock were applied. The good connection reliability was most likely derived from the PWB's resistance to deformation at high temperatures. The connections in the conventional PWB, on the other hand, showed lower reliability than that of the new PWB, after only 400 cycles of heat shock were applied.

Build-up materials' standard indicates that materials must have over 0.8 kN/m of adhesive strength. The new laminate, which had slightly lower adhesion to copper foils than that of the current FR-4 material, could sufficiently satisfy this standard.

CONCLUSIONS

We developed environmental-friendly and applicable glass-epoxy laminates, which have high flame retardance without the use of halogen or phosphorous flame-retarding additives. The laminates contained a phenol aralkyl epoxy-resin compound that has self-extinguishing properties, an amino-triazine-novolac (ATN) hardener that acts as an incombustible-gas generator, zinc molybdate on talc (ZMT) that performs a

charring promoter, and aluminum trihydroxide (ATH) that acts as an endothermic agent. Simultaneously using the ATN hardener and ZMT in the laminates, consisting of the epoxy-resin compound and ATH, dramatically improved the laminates' flame retardance. The PWBs consisting of these laminates were also highly applicable due to their high soldering-heat resistance, high humidity resistance, good electric properties, and reliabilities.

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