

A Highly Reliable Halogen-Free Dielectric for Build-up Printed Circuit Boards

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We have developed a highly reliable halogen-free (HF) flame-resistant epoxy dielectric for build-up printed circuit boards (PCBs). This material does not generate environmentally hazardous products such as polybrominated dibenzodioxins/furans or hormone disruptive agents like bisphenol-A and its derivatives. The dielectric is composed of a mixture of a reactive type oligomeric organic phosphate and $\text{Al}(\text{OH})_3$ as the flame resistant. High Cu conductor corrosion resistance under high-temperature, high-humidity bias conditions has been obtained due to a cross-linkable organic phosphate that reduces the free phosphate ion content. The newly developed dielectric has the thermal and mechanical properties required in mobile electronic devices such as hand phones and laptop PCs, for example, high flexibility and shock resistance.

1. Introduction

Recently, due to the tremendous popularity of the Internet among the general public, demand for personal computers and mobile phones has been growing explosively. This will make millions of electronic devices obsolete within a couple of years, creating a massive environmental threat. To eliminate this threat, electronic device manufacturers have focused on developing environmentally friendly products such as Pb-free solders, halogen-free resins, recyclable Mg housings, and recyclable paints.

In the printed circuit board industry, brominated compounds are widely used as flame resistants; these brominated compounds are alleged to produce toxic substances, for example, polybrominated dibenzodioxins and dibenzofurans, on combustion. The hazardous nature of the brominated compounds compelled us to search for new types of flame-resistant materials. As a result of our continuous efforts in this field, we have developed a new environmentally benign dielectric material composed of a non-toxic organic

phosphate flame resistant.¹⁾⁻³⁾ However, we felt that this material needed further improvements concerning the following points:

- The material causes conductor corrosion due to ion migration under high-temperature, high-humidity bias conditions, because of the relatively high moisture absorption of the organic phosphate. Also, we have observed that the organic phosphate, which has a low molecular weight, is slightly soluble in hot water.
- The organic phosphate is slightly soluble in aqueous alkaline solutions. As a result, the surface properties required for a satisfactory peel strength (adhesion to Cu conductor) cannot be obtained.
- The base epoxy resin produces a notable amount of bisphenol-A and its derivatives at combustion; these compounds are suspected of being potent hormone disruptive agents.

We have therefore made the following modifications:

- To prevent the organic-phosphate from leaching out from the dielectric into hot water and

alkaline aqueous solutions, we developed a reactive type organic-phosphate.

- To improve the peel strength, a polyaromatic epoxy resin that is chemically stable in alkaline/ KMnO_4 etchant was used as the main component.
- To reduce the amount of bisphenol-A derivatives generated at combustion, a non-bisphenol-A type resin was developed.

Through these modifications, we were able to develop a new halogen-free, bisphenol-A-free dielectric material that exhibits high corrosion resistance and strong adhesion to Cu conductors.

2. Experiments

2.1 Dielectric preparation

The composition of the present dielectric formulation is shown in **Table 1**. An epoxy that contains a thermally and chemically stable naphthalene ring was selected as the main resin. In order to obtain flexibility, a rubber modified epoxy resin was added as an elastomer. Also, by selecting a phenolic epoxy hardener having a flexible group, we achieved a 3-D network structure with sufficient flexibility. The flame resistant system consists of a reactive type organic phos-

phate and $\text{Al}(\text{OH})_3$, which does not generate any toxic gasses containing S or N.

The epoxy mixture was thoroughly dispersed in a bead mill and was coated to get 70 μm -thick films. The epoxy films were pre-baked at 120°C for 20 minutes and then cured at 170°C for 1 hour in an oven.

2.2 Combustion product analysis

The dielectric was burned at 400°C, 600°C, and 700°C by using a CG-77 combustion gas sampler in a pure air atmosphere. The combustion products were absorbed in Tenax-GR (Poly (2,6-diphenyl-p-phenylene oxide + 30% carbon) at 0°C. The absorbent was then placed in a gas sampler (JAS-100A) that was pre-heated to 230°C. The volatile components were then eluted by purging and reabsorbed in glass wool at -60°C. The volatile components were then re-eluted from the glass wool by heat treatment. The eluate was quantitatively analyzed by the GC/MS method.

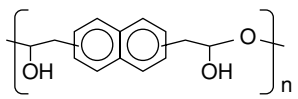
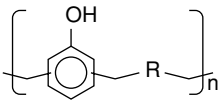
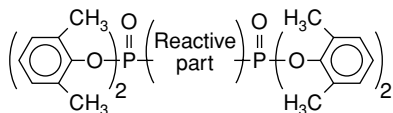
Ultra-trace analysis of polychlorinated and brominated dibenzodioxins/dibenzofurans in the combustion products of the dielectric was carried out at 600°C for 1 hour in an air atmosphere according to guidelines given by the Ministry of Health and Welfare of Japan.⁴⁾

2.3 Dielectric reliability evaluation

Test specimens were prepared as follows. A 70 μm B-stage sheet of the dielectric was laminated and cured on a 50 × 50 mm core substrate that consisted of an epoxy/glass-fabric dielectric sandwiched between two Cu foils (18 μm). On the surface of the laminated film, a Cu conductor pattern was created (thickness = 12 μm , diameter = 6 mm). These specimens were subjected to the unsaturated pressure cooker bias test (USPCBT) under the following conditions: T = 121°C, RH = 85%, P = 1.7 atm, V = 20 V, t = 100 h.

The ionic impurities in the dielectric were estimated as follows. The dielectric films were boiled in deionized water at 120°C for 48 hours in a closed Teflon bath, then qualitative and quantitative

Table 1
Components of newly developed dielectric.

Component	Chemistry
Epoxy	 <p>Rubber-modified epoxy</p>
Hardener	
Accelerator	Imidazole derivatives
Flame retardant	 <p>$\text{Al}(\text{OH})_3$</p>

analyses of the water samples were done by ion chromatography.

2.4 Peel strength

The surface of the cured dielectric was etched in an aqueous alkaline KMnO_4 solution, and the surface morphology was inspected by microscopy. A 25 μm -thick Cu foil was deposited onto the etched dielectric surface by electroless-plating followed by electro-plating using Shipley plating solutions. After drying at 120°C for 1 hour in an N_2 atmosphere, the specimens were scored to provide 10 mm-wide strips for peel testing. Testing was done in a universal tester employing electronic load cells equipped with traversing fixtures to assure a 90° pull along the length of peel.

3. Results and discussion

3.1 Combustion products

The GC patterns of the combustion products of the newly developed dielectric (naphthalene

epoxy with reactive type organic phosphate) and a previously reported dielectric (bisphenol-A epoxy with an additive type organic-phosphate) burned at 600°C are shown in **Figures 1 (a)** and **(b)**, respectively.

From these figures, it can be seen there is a drastic reduction in the amount of bisphenol-A generated when the new material is burned. However, a small amount of bisphenol-A was detected even in this sample. Because no bisphenol-A derivatives were present in the new dielectric formulation, we believe that bisphenol-A is a decomposition product of the phenolic epoxy hardener.

Toxicological data of the p-containing combustion products of the additive type phosphate are shown in **Table 2**. The LD50 (Lethal Dose, 50%) value of compound 2 is reported to be greater than 15 800 mg/kg, suggesting that this compound is non-toxic. The LD50 value of the original flame resistant is about 2000 mg/kg. This

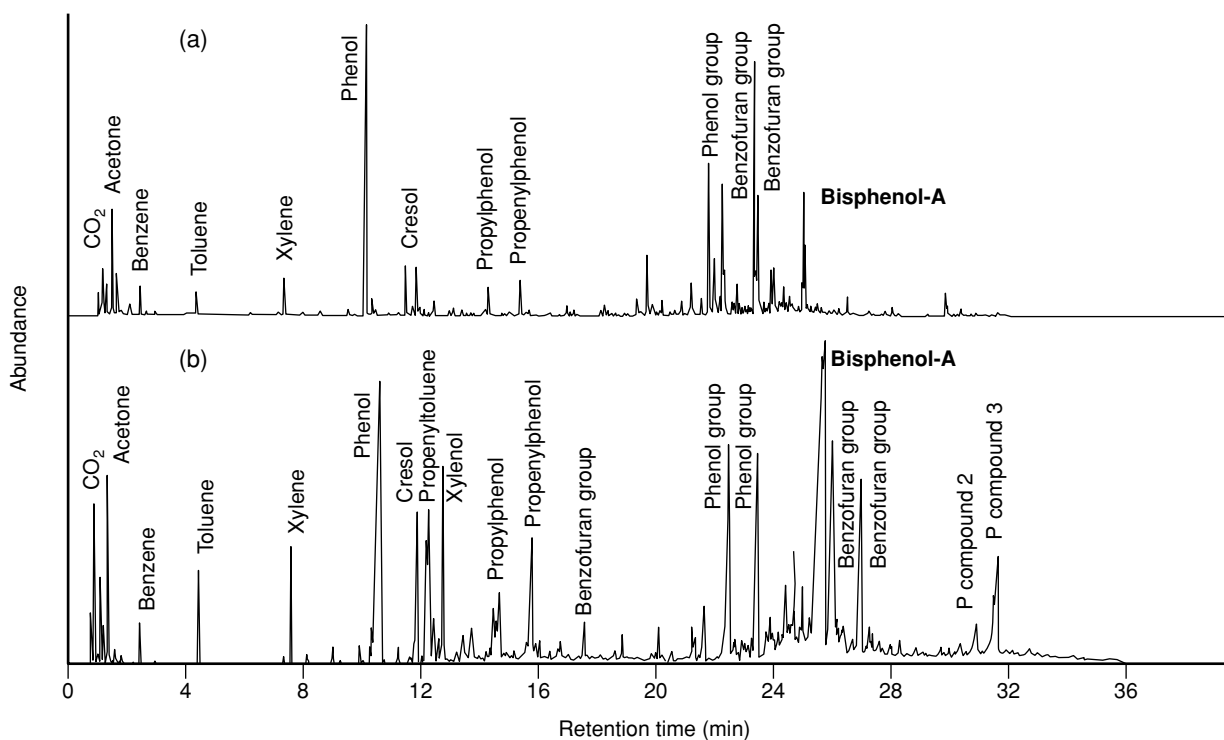
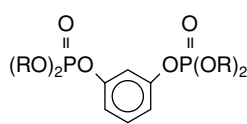
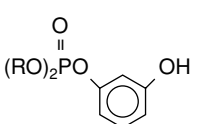


Figure 1
GC patterns of combustion products at 600°C.
(a) Naphthalene type epoxy (reactive phosphate), (b) Bisphenol-A type epoxy (additive phosphate).

Table 2
LD-50 values (oral) of P- compounds (Additive type flame retardant and its combustion products).

Compound	Oral LD-50 (mg/kg)
 (1)	>2000
Combustion products	
(RO) ₃ P = O (2)	>15800
 (3)	-
ROH	1750
R: 2,6-dimethylphenyl	

reveals that the use of this material is not a serious environmental threat. The LD50 value of compound 3 has not been reported yet.

3.2 Ultra-trace analysis of dioxins/dibenzofurans

Although no chlorinated compounds were used in the present formulation, it should be mentioned that a trace amount of chlorine (ionic and covalent form) was present at the impurity level of 300 ppm in the epoxy resins. We believe that this impurity chlorine may generate dioxins and dibenzofurans. Therefore, we measured the amounts of dioxin and dibenzofuran that are generated when the new dielectric is burned. The results are summarized in **Table 3** together with the dioxin levels generated by burning a bisphenol-A type dielectric with different Cl contents.

Table 3
Polychlorinated dibenzodioxin/furan combustion products of dielectrics.

Dioxin compound	Quantity (ng/g)			TEQ ^{note 1)} (ng-TEQ/g)		
	Naphtalene type	Bisphenol-A type		Naphtalene type	Bisphenol-A type	
	[Cl] = 360 ppm	[Cl] = 100 ppm	[Cl] = 900 ppm	[Cl] = 360 ppm	[Cl] = 100 ppm	[Cl] = 900 ppm
2,3,7,8-T ₄ CDD ^{note 2)}	ND ^{note 4)}	ND	ND	-	-	-
1,2,3,7,8-P ₅ CDD	ND	ND	ND	-	-	-
1,2,3,4,7,8-H ₆ CDD	ND	ND	ND	-	-	-
1,2,3,6,7,8-H ₆ CDD	- ^{note 5)}	ND	ND	-	-	-
1,2,3,7,8,9-H ₆ CDD	ND	ND	ND	-	-	-
1,2,3,4,6,7,8-H ₇ CDD	0.0039	ND	0.055 22	0.000 039	-	0.000 552
O ₈ CDD	-	0.015	0.0579	-	0.000 001 5	0.000 005 79
2,3,7,8-T ₄ CDF ^{note 3)}	-	ND	0.0121	-	-	0.001 21
1,2,3,7,8-P ₅ CDF	-	-	0.01052	-	-	0.000 531
2,3,4,7,8-P ₅ CDF	-	ND	0.01684	-	-	0.008 42
1,2,3,4,7,8-P ₆ CDF	ND	ND	0.03481	-	-	0.003 481
1,2,3,6,7,8-P ₆ CDF	ND	ND	0.02648	-	-	0.002 648
1,2,3,7,8,9-P ₆ CDF	ND	ND	ND	-	-	-
2,3,4,6,7,8-P ₆ CDF	-	ND	0.071 01	-	-	0.007 101
1,2,3,4,6,7,8-P ₇ CDF	0.0025	0.0025	0.074 51	0.000 025	-	0.000 745 1
1,2,3,4,7,8,9-P ₇ CDF	-	ND	0.0371	-	-	0.000 371
O ₈ CDF	-	ND	0.164 52	-	-	0.000 016 4
Total (PCDDs+PCDFs)	-	-	-	0.000 064	0.000 001 5	0.0251

note 1) TEQ: Toxic equivalents (WHO-1998), note 2) CDD: Chlorinated dibenzodioxin, note 3) CDF: Chlorinated dibenzofuran, note 4) ND: not detected, note 5) -: below the detectable limit

From the present investigation it was found that the new formulation did not generate highly toxic dioxins or dibenzofurans and generated several less-toxic substances in only very minute quantities; the total toxic equivalent was found to be 0.064 pg/g. It should be noted that two compounds, H₇CDD and P₇CDF, are more easily generated compared with the other compounds, irrespective of the dielectric formulation.

Moreover, it was understood that the toxicity level of the dielectric combustion products would increase with the amount of Cl impurity that is present. From careful analyses of the Cl impurity level and the toxicity levels, we believe that a dielectric with a Cl impurity level of less than 1000 ppm would be environmentally safe.

In addition, we have investigated some brominated dielectrics for bromodioxins and bromodibenzofuran liberation. In the case of a commercially available brominated dielectric with about 10% bromine, a high concentration (1 ng/g) of bromodioxins and bromodibenzofurans was detected. Therefore, it is important to note that if the toxicity levels of bromodioxins and bromodibenzofurans are clarified, we will be able to determine the magnitude of the environmental impact of brominated chemicals.

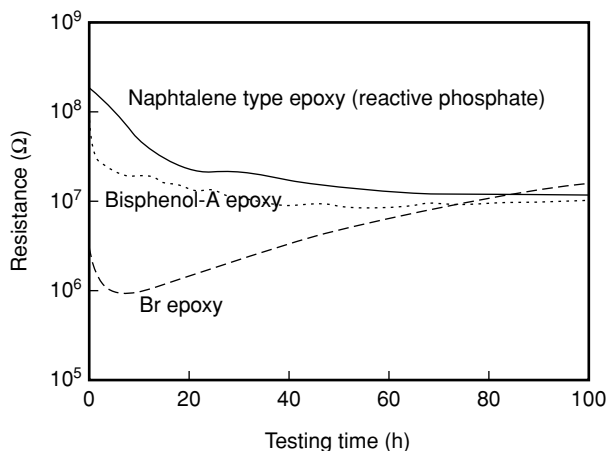


Figure 2 USPCBT reliability test results (Test conditions: 120°C, 85% RH, 1.7 atm, 20 V, 100 h).

3.3 Unsaturated pressure cooker bias test (USPCBT)

Figure 2 shows the interlayer resistance variation during the USPCBT of the newly developed dielectric ([Br] < 5 ppm, [Cl] = 880 ppm) together with that of a bromine-free bisphenol-A type dielectric ([Br] < 5 ppm, [Cl] = 130 ppm) and a conventional brominated dielectric ([Br] < 85 000 ppm, [Cl] = 230 ppm). Before the reliability test, all three samples exhibited an interlayer resistance of greater than 10¹¹ Ω. However, as can be seen from this figure, immediately after the test initiation, the resistance decreased significantly.

In the case of P-containing dielectrics (bromine-free), the interlayer resistance decreased to the 10⁷-Ω level and then remained unchanged, even after 100 hours. In the case of the brominated dielectric, after about 5 hours, the resistance decreased to the 10⁶-Ω level. It is believed that the sudden decrease in the interlayer resistance may be attributed to water absorption by the material. After the material reached the saturation level, the resistance remained constant. However, in the case of the brominated dielectric, it is believed that there is another reason for the lower resistance compared with the other two dielectrics.

Figure 3 shows cross-sectional SEM photographs of the dielectric/Cu interface after the corrosion test. In Figure 3 (a) (brominated epoxy), some white particles can be seen at the Cu/dielectric interface; this phenomena cannot be

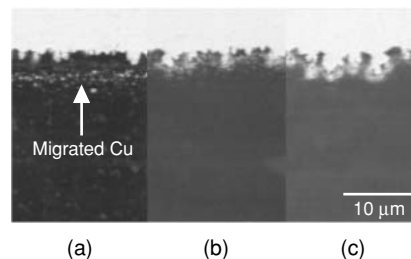


Figure 3 Cross-sectional images of the dielectric materials after USPCBT. (a) Br epoxy, (b) Bisphenol-A epoxy, (c) Naphthalene type epoxy.

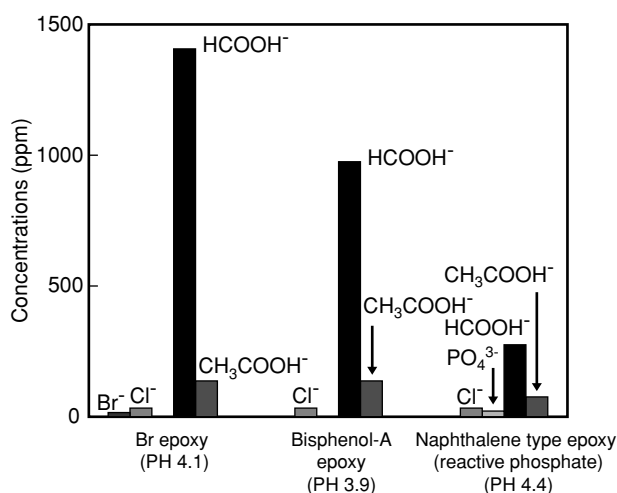


Figure 4
Extracted ion concentrations (ppm) from dielectric materials.

seen in the other samples. These particles were identified as CuO by EPMA studies. Moreover, Br distribution at the interface was also monitored, and no unusual Br accumulation was detected.

The quality and quantity of ions extracted into hot water from the dielectrics are summarized in **Figure 4**. It is important to mention that the Br⁻ and PO₄³⁻ ion contents in the water samples were found to be extremely low; this suggests that free Br⁻ and PO₄³⁻ ions were not the main causes for the weaker dielectric properties.

The striking feature of this data is the high concentrations of organic acid ions such as acetate and formate that have been detected. Particularly, in brominated dielectrics, a high concentration of formate (1400 ppm) was detected. We believe that these organic ions are mainly responsible for the lower dielectric resistance. In other words, it can be said that to achieve a high degree of corrosion resistance, the epoxy resins must be very pure.

Furthermore, it was understood that the use of reactive type organic phosphates instead of additive type phosphates prevents phosphate from leaching out from the dielectric.

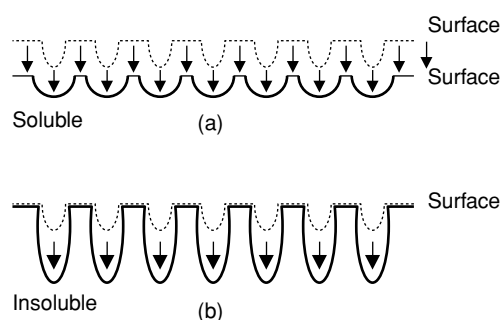


Figure 5
Mechanism for surface morphology changes of dielectrics in aqueous alkaline/KMnO₄.
(a) weak peel strength, (b) strong peel strength.

3.4 Adhesion to Cu conductor

In previous studies, we have found that brominated dielectrics exhibit quite a strong adhesion to metals, while dielectrics with organic phosphates exhibit comparatively poor adhesion.

It is well documented that in order to get a strong adhesion, micro-cavities should be created on the dielectric surface so that the Cu conductor can enter them and become anchored to the dielectric surface. In the case of brominated dielectrics, we believe that Br compounds partially retard the etching process, creating an appropriate surface morphology with sufficiently large cavities as shown in **Figure 5 (b)**. On the other hand, as shown in **Figure 5 (a)**, bromine-free dielectrics with components that are soluble in KMnO₄ solution are removed from the surface during the etching process without creating cavities, leading to poor adhesion.

Previously, we have reported that the introduction of polyfunctional epoxies in bromine-free dielectrics significantly improves the adhesion to metals. From the present study, we have found that the introduction of epoxies containing a naphthalene ring can further enhance the peel strength.

The effects of the surface morphology and cavity depth on the peel strength are shown in **Figures 6** and **7**, respectively. The figures suggest that the peel strength increases with the

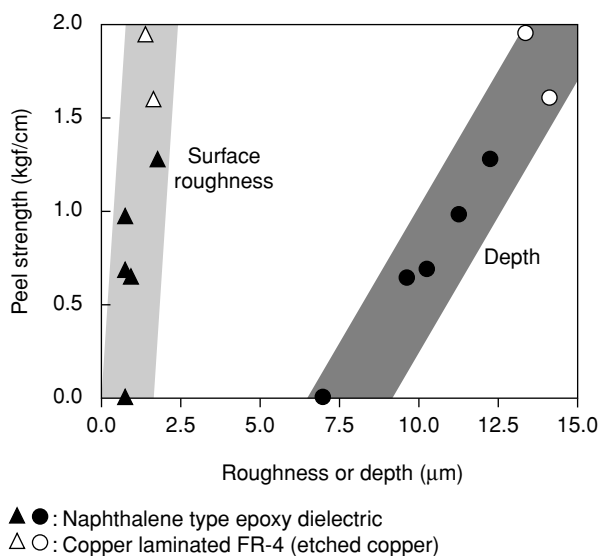


Figure 6
Effect of cavity depth on peel strength.

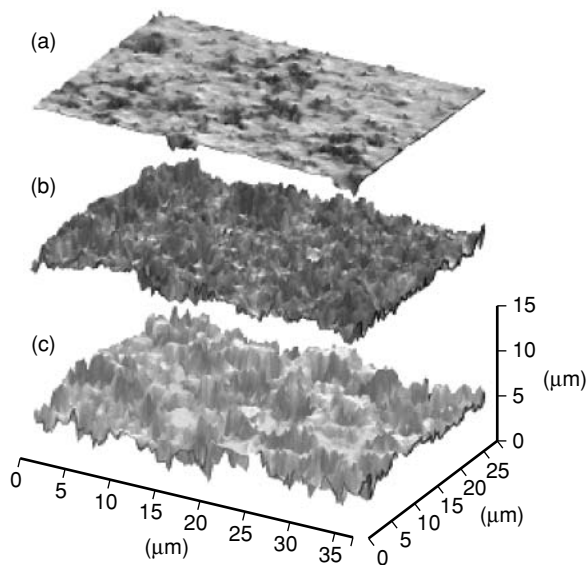


Figure 7
AFM surface images of dielectric materials after etching process.
Peel strength: (a) 0.7 kgf/cm, (b) 1.0 kgf/cm, (c) 1.3 kgf/cm.

cavity depth. In order to get a peel strength of about 1.3 kgf/cm, the cavity depth should be about 12.5 μm. However, the effect of cavity diameter on the peel strength remains unclear. Also, we found that the introduction of polyaromatic rings in the dielectric greatly reduces the susceptibility to the etching process, while giving deep cavities

Table 4
Properties of newly developed HF dielectric.

Property	Commercially available dielectric		
	New dielectric	Halogen free	Brominated
Tensile strength (MPa)	84	63	67
Elongation at break (%)	10	3.6	3.5
Decomposition temp. (°C)	290	260	260
CTE	α1 (ppm/°C)	43	76
	α2 (ppm/°C)	160	192
Tg (°C, DMA)	155	135	135
Dielectric constant (1 MHz)	3.47	3.60	3.60
Dielectric loss (1 MHz)	0.022	0.023	0.03
Water absorption (%)	0.7	1.1	1.3
Flame-proof (UL94)	(Film)	V-0	V-0
	(Peel strength (kgf/cm))	1.3	0.8
USPCBT	OK	poor	NG
(120°C, 85% RH, 20 V, 100 h)			

that result in a strong peel strength of about 1.3 kgf/cm.

The physical properties of the newly developed dielectric are summarized in **Table 4**, together with those of two commercially available dielectrics. Among these dielectrics, the new formulation provides the best mechanical and dielectric properties. Specifically, it has the highest tensile strength, elongation at break, adhesion to Cu, and decomposition onset temperature and the lowest water uptake.

4. Conclusion

We have developed a new halogen-free flame-resistant epoxy dielectric that has a non-bisphenol-A epoxy resin as the main component. The new dielectric has a high electrical reliability and peel strength and generates drastically less hormone disruptive substances during combustion than bisphenol-A type epoxies. We found that the toxic equivalent of the polychlorinated dibenzodioxins/furans generated by combustion of this material increases logarithmically with the Cl concentration. We therefore propose that the amount of chlorine content should be less than 1000 ppm.

The use of a reactive organic-phosphate

prevents phosphate ions from leaching out from the dielectric into hot water and alkaline aqueous solutions. It was found that the ion migration mainly depends on the concentration of impurity organic-acids in the dielectric. Therefore, the purity of the resin components must be high to achieve a high-reliability dielectric. Strong adhesion to Cu has been obtained by using a chemically stable naphthalene epoxy as the main component. It was observed that the peel strength was linearly dependent on the depth of surface cavities, and an average peel strength of 1.3 kgf/cm was obtained when the cavity depth was 12.5 μm .

We are now developing recycling technologies for this new material.

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