Study of Comparative Tracking Index on Brominated Epoxy and Its Application in Copper Clad Laminates

Hsien-Tang Chiu, Ming-Feng Cheng

Graduate School of Polymer Engineering, National Taiwan University of Science and Technology, Taipei 10672, Taiwan, Republic of China

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ABSTRACT: The study mainly investigates the improvement of the comparative tracking index (CTI) on brominated epoxy resins in a copper clad laminate. We compare the effects of the differences in structures of various epoxy resins on the CTI. In addition, on the basis of the proportion of inorganic fillers and type, we use Pauling's electronegativity theory to find inorganic materials that affect CTI. Experimental results show that the laminate surface CTI increases as the brominated epoxy resin content decreases. When looked at structurally, epoxys modified by phenolic resin systems had lower CTI values than those modified by bisphenol A type epoxy resin systems. Analyzing the effects of inorganic filler types, we found that the ideal bromide epoxy resin proportion and the CTI value of $Al(OH)_3$ could exceed 600 V. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 2814–2818, 2006

Key words: comparative tracking index; brominated epoxy; copper clad laminate

INTRODUCTION

Comparative tracking index (CTI) is often used for electronic insulation materials. This index pin-points the voltage at which tracking occurs. Tracking is a process wherein there is a partial reduction in conductive path on the surface of the insulation material. This is caused by the electric charge emission on or near the electronic insulation material. Under certain circumstances, surface tarnish can accelerate tracking. Hence the CTI indicates the voltage at which tracking occurs after 50 drops of dirt fluids. CTI is used to indicate the quality of single- or double-sided material boards used on consumer electronic appliances, or other high voltage (110 V/220 V) electronic objects. Since it does not belong to the domain of computer information and communications, it is not included in IPC-4101, but the International Electrician Committee (IEC) has included it in IEC-STD-112.[1–4]* Simulation studies have been done on circuit boards polluted in the environment that had leaks in their electrical conductance pathways, resulting in a heating and scorching effect.

The merit of using brominated epoxy resin on copper clad laminated series FR-4[5] is that it is of low cost, it improves the nature of electric appliances' insulated material, it has dimensional stability, and it has some chemical tolerance. However, after bromination, the flame tolerance nature of FR-4 must pass UL 94 V1[6]. FR-4 board using brominated epoxy resin, available in the market under CTI special nature, can meet UL third grade standard,[6] with a CTI value of 175–249 V. Although high CTI value laminates have been produced by many CCL manufacturers, there has been no report, till date, of FR-4 laminate boards with high CTI value. This research specially focuses on the effects of brominated epoxy resin on copper clad laminates, using different factors and comparisons.

EXPERIMENTAL

Materials

The epoxy resins used in this experiment were products of Nan Ya Plastics Corporation. The brominated epoxy resin NPEB 454, the series of nonbrominated epoxy resins of different epoxy (bisphenol A) content, and the nonbrominated phenolic type epoxy resin NPPN 638 used in this study, as well as their epoxy equivalents and molecular weights are listed in Table I, while their structures are shown in Figure 1. Curing agents used were cyanoguanidine, 1-cyanoguanidine, and dicyandiamide dicy (DCD; $H_2NC({=}NH)NHCN$, CAS no. 461–58-5). The catalyst used was 2-methyl imidazole ($C_4H_4N_2$, CAS no.69–39-81). The solvent used was DMF (dimethyl formamide). The various inorganic fillers used were $Al(OH)_3$, TiO_2, and Sb_2O_3.

Correspondence to: H.-T. Chiu (hchiu@tx.ntust.edu.tw).

*M. A. Lamothe, PE, is the president of M. A. Lamothe & Associates (Georgetown, ON, Canada).

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TABLE I
Series of Epoxy Resin

Epoxy resin	EEW[a] (g/mol)	MW (g/mol)	Bromine content
Bisphenol A type			
NPEL 128	390	380	Nonbrominated
NPES 901	460	2600	Nonbrominated
NPES 902	630	4300	Nonbrominated
μNPES 903	720	5500	Nonbrominated
μNPES 904	810	6300	Nonbrominated
μNPEB 454	430	2800	18–22%
Phenolic type			
NPPN 638	178	1300	Nonbrominated

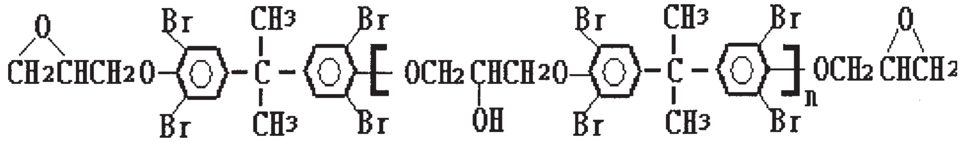
[a] Epoxy equivalent weight.

Clay reinforcements used were of E-glass fabric type 7628.

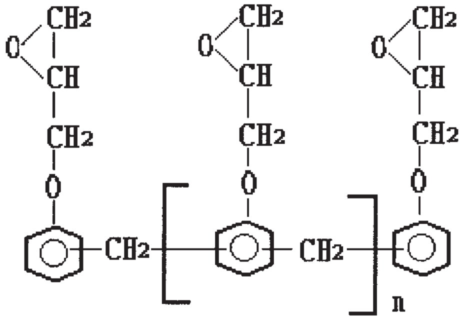
Sampling production

Weighting resin, curing agent, catalyst, filler, and solvent according to its proportion were mixed evenly for 8 h, and then impregnated in glass fabric 7628 with ready-mixed varnish. Control resin content was kept at (41 ± 0.5)%. Impregnated product was kept in a temperature-controlled oven, maintained at 180°C and control gel time within 110 ± 5s, get 8 plies prepreg ply-up, put on its top and bottom release film and smooth steel plate proceed to lamination cycle time 2.5 h, control temperature heating rate and pressure. After formation, the laminates were cut to 100 × 100 mm^2 samples.

Bisphenol A type Epoxy Resin



Brominated Epoxy Resin



Phenol Novolac Epoxy Resin

Figure 1 Chemical structure of epoxy series.

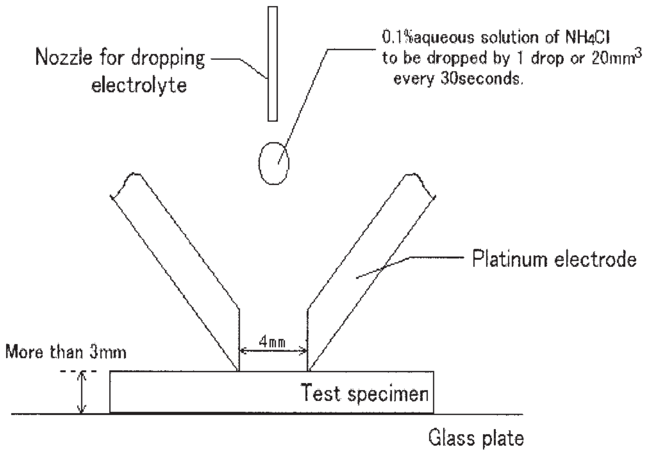


Figure 2 Scheme of CTI test for specimen.

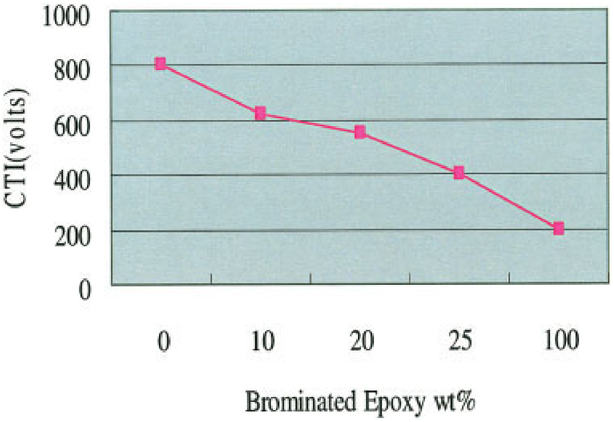


Figure 3 Brominated epoxy (NPEB 454) content versus CTI value. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Measurement

The thickness of the test specimens was 3 mm and the required area for each test was more than 15 × 15 mm^2. Test apparatus (type Tsc11 of CTI tester) was from Tokyo Seiden Co. Per the IEC 112 standard requirements, the electrode was made of platinum (Fig. 2) and its cross-sectional area was 5 × 2 mm^2, with one end in the form of a chisel (and the chisel angle is 30°). A-type electrolyte was 0.1% aqueous solution of NH_4Cl (395 Ω cm resistivity at room temperature.) added dropwise once every 30 s, the size of each drop being 20 mm^3. Each test was continued at an arbitrary level of voltage until the addition of 50 drops (or failure, if tracking happened earlier). Then the test was repeated at either higher or lower voltage on the same specimen but at a different position from the previous test, until the maximum voltage at which the failure did not occur up to 50 drops on all the five different test positions. CTI was the maximum endurable voltage for a certain insulator without causing tracking up to 50 drops of the electrolyte in each of the five tests.

RESULTS AND DISCUSSIONS

Effects of bromine content on CTI

With nonbrominated resin NPES 901 as matrix, different weight ratios (0, 10, 20, 25, and 100 wt %) of brominated epoxy resin NPEB 454 were added to produce base boards to test CTI. Figure 3 shows that the CTI value decreased as brominated epoxy resin content increased.

Halogens are generally good flame retardants. But with NH_4Cl electrolyte and the heat produced by the high voltage, there could have been a decomposition of the highly active bromine, thus causing the production of Br^- on the surface of the insulated material. Br^-, being a donor, could have provided electrons, thereby accelerating the destruction of the surface insulation material as well as accelerating tracking. High bromine content can thus account for the low CTI value.

Chemical structure and effect of epoxy equivalent on CTI

To better understand CTI value in relation to chemical structure, Table II provides a comparison of the effects of nonbrominated bisphenol A type (NPES 902) epoxy and phenolic type (NPPN 638) epoxy on CTI value for a fixed proportion of EEW (epoxy equivalent weight). The results show that NPPN 638 did not increase the CTI value in spite of its lack of bromine content. From the chemical structure, however, it may be inferred that the small molecular phenolic novolac epoxy, under repetitive phenolic contractions (because of the presence of benzene rings on either side), could have easily produced a conjugation structure, which in turn could have provided a pathway for the donor to destroy the surface of the insulated material, thereby causing an acceleration of tracking.

NPES 638 has a smaller EEW but a higher DCD content. But because the ratio of EEW and DCD is a constant, if DCD cannot completely react, it can absorb water and decrease the insulation. Thus, to ascertain its effect on CTI, a comparison was made by fixing

TABLE II
Comparison of Nonbrominated Epoxy Bisphenol A Type and Phenolic Type on CTI Value

Resin type	Bisphenol A	Phenolic
Resin	902(EEW63O)	638(EEWI78)
Curing agent	DCD	DCD
Catalyst	2MI	2MI
Filler	$Al(OH)_3$	$Al(OH)_3$
CTI (V)	400	225

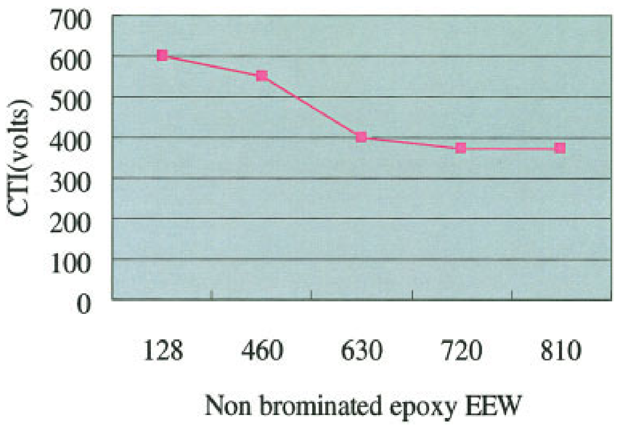


Figure 4 CTI value of NPES 90l resin within different DCD (2,3, and 5 phr).[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

NPES 901 with a changing DCD content (2, 3, and 5 phr). The results (Fig. 4) show that the effect on CTI was not significantly different. Figure 5 shows that chemical structure (various EEW) has different effects on CTI. Tests using different epoxy content as well as fixed, nonbrominated epoxy and DCD proportions showed that the CTI value decreased as the molecular content increased, possibly because the crosslinking density decreases when the molecule weight increases. The glass transition temperature (T_g) and heat tolerance nature also decreased. In terms of the impregnation process, the longer the molecular chain (higher EEW), the worse the wetting result in improving the CTI value. One needs to consider not only the effect of chemical contractions but also their additive effects.

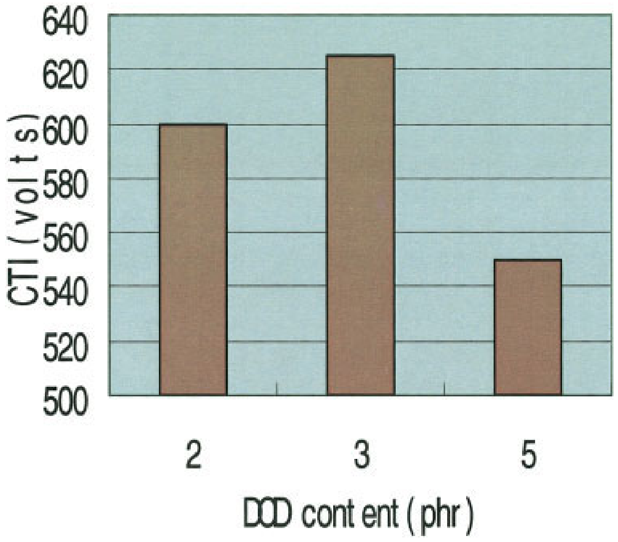


Figure 5 Effect of chemical structure (various EEW) on CTI Value.[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

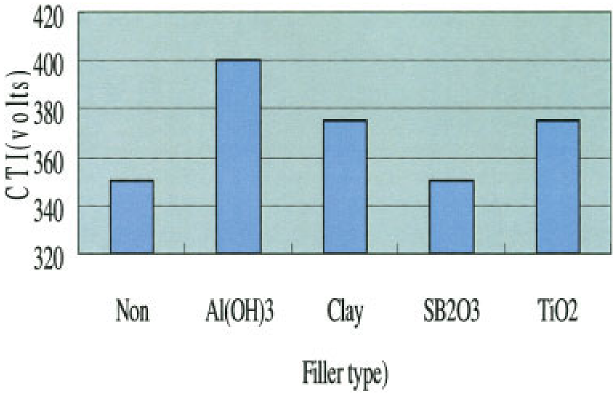


Figure 6 CTI outcome with different fillers.[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Effect of different inorganic additives on CTI

A large variety of inorganic fillers affect the CTI value. Figure 6 shows a comparison of different inorganic fillers and their effects on CTI value. The addition of inorganic fillers decreases the matrix resin content and the probability of tracking, but there can still be different conclusions on the effects of different inorganic filler additive proportions on CTI value. According to Pauling's electronegativity theory, the power of an atom in a molecule is to attract electrons to itself. Table III shows the electronegativities of some elements. The higher the difference between the electronegativity value of a metal and that of oxygen, the higher would be the relative polarities of the molecules of the inorganic filler. Consequently, electronegativity and the molecular polarity of the filler may be considered as parameters that have an influence on the CTI value. Tests showed that among the different inorganic fillers, $Al(OH)_3$ was the best, thus confirming our theoretical deductions. $Al(OH)_3$, in the process of burning, probably emits crystal water, thereby decreasing the thermal feedback to the insulated material; this in turn may decrease the damaging effect on the material, thereby promoting CTI value.

CONCLUSIONS

1. CTI value on laminate boards decreases as the bromine content increases.

TABLE III
Electronegativities of the Elements[7]

Element	Pauling's electronegativities	Filler
O	3.44	—
Al	1.61	$Al(OH)_3$
Si	1.9	SiO_2
Ti	1.54	TiO_2
Sb	2.05	Sb_2O_3

2. In a comparison of halogen free epoxy resins, the CTI value of phenolic epoxy type was found to be lower than that of bisphenol A type epoxy.
3. Overuse of DCD will cause the laminate board to absorb water, thus reducing its heat tolerance nature; but this has no sufficient effect on CTI value.
4. Effect of EEW on CTI value: As the EEW value increases, the CTI decreases.
5. The effect of filler on improving CTI value: With increases in the addition of filler, the CTI value increases. Tests showed that among the different inorganic fillers, 20–30% $Al(OH)_3$ mixed with non-brominated epoxy resin can improve the CTI value to above 600 volts.

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