Mechanical Properties of Copper-Clad Laminate Using Composite Naphthalene–Phenyl-Based Epoxy as Prepreg

Yeh-Fang Duann, Bor-Lin Chen, Teh-Hua Tsai

Department of Chemical Engineering, National Taipei University of Technology, Taipei, Taiwan, Republic of China

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ABSTRACT: A composite was prepared that contained diglycidyl ether of tetrabromobisphenol A (DGETBA) and 1,5-di(2,3-epoxypropoxy)naphthalene (A), 4,4′-bis(2,3-epoxypropoxy)benzylideneaniline (B), or 4,4′-bis(2,3-epoxypropoxy)biphenyl (C), and then was cured using different ratios of dicyandiamide (DICY). The results of DSC, TGA, coefficient of thermal expansion, dielectric constant, and dissipation factor testing of the composite epoxy resins were analyzed, and investigation of the copper-clad laminate using the composite epoxy resins as prepreg was also performed. Additionally, moisture absorption, peel strength, arc resistance, comparative tracking index, and flammability of the copper-clad laminate were examined. Clearly, some of the physical or mechanical properties of the composite and the copper-clad laminate can be improved by optimal addition of naphthalene–phenyl-based epoxy.
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Key words: resins; prepreg; copper-clad laminate; mechanical properties; differential scanning calorimetry (DSC)

INTRODUCTION

Several aromatic rigid rod moiety epoxy polymers were studied because of their thermal stability.[1–3] Naphthalene and phenyl have planar structures and thus are easily packed. Such structures increase the glass-transition temperature (T_g) of bismaleimide.[4,5] Naphthalene and phenyl trifunctional epoxy resins[6,7] cause high T_g and thermal stability.[8,9] The T_g increased with increasing epoxy functionality (di-, tetra-, penta-functionality). The phenyl-based epoxy resins[10–14] also displayed the same phenomenon, but had lower T_g values than those of naphthalene-based epoxy resins; for example, a series of polyamides and copolyamides[15] had T_g values in the range of 230–360°C, and aromatic polyimides containing bis(phenoxy)naphthalene units[16,17] display T_g values between 228 and 317°C.

Epoxy resin has been extensively used as a prepreg of copper-clad laminates because of its appropriate thermal and physical properties. Certain physical properties, such as dielectric constant, dimension stability, and brittleness, can be improved by blending the epoxy resin with thermoplastic.[18,19] In this investigation, diglycidyl ether tetrabromobisphenol A (DGETBA) epoxy resin was modified by adding 1,5-di(2,3-epoxypropoxy)naphthalene (A), 4,4′-bis(2,3-epoxypropoxy)benzylideneaniline (B), or 4,4′-bis(2,3-epoxypropoxy) biphenyl (C). Some physical properties of the composite were also examined. The composite used as prepreg of copper-clad laminate was prepared and mechanical properties were measured.

EXPERIMENTAL

Table I lists compounds used in this investigation. 1,5-Di(2,3-epoxypropoxy)naphthalene (A), 4,4′-bis-(2,3-epoxypropoxy)benzylideneaniline (B), and 4,4′-bis(2,3-epoxypropoxy) biphenyl (C) were prepared following the previously reported procedure.[20] 2-Methylimidazole (2-MI) and dicyandiamide (DICY) were obtained from Tokyo Chemical Co. (Japan). Moreover, diphenyldiaminomethane (DDM) was obtained from Acros Organics (Morris Plains, NJ). Additionally, the bromonated bisphenol A epoxy [diglycidyl ether tetrabromobisphenol A (DGETBA)] was supplied by Dow Chemical Co. (Midland, MI), and had an epoxy equivalent of 410–440 (Br: 18–19%). Solvents and reagents were reagent grade and used as received without further purification.

The thermal decomposition of epoxy resins was thermogravimetrically analyzed with a TGA, DuPont 2950 instrument (New Castle, DE) coupled to a Thermal Analyst 943 in flowing (80 mL/min) nitrogen. Samples of 0.5–0.6 mg were taken, and heating ranged from 50 to 500°C. The glass-transition temperature was measured by a differential scanning calorimeter (DuPont DSC 2010). The purge gas was dry nitrogen. Samples of around 25–35 mg were enclosed in aluminum DSC capsules. Dynamic heating experiments

Correspondence to: Y.-F. Duann (f10421@ntut.edu.tw).
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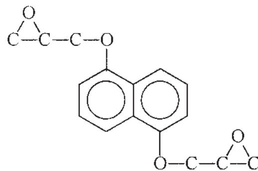
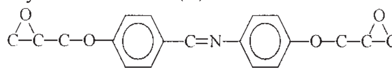
TABLE I
Names and Structures of Compounds in This Study

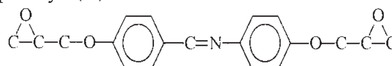
1,5-Bis(2,3-epoxypropoxy)naphthalene (**A**)



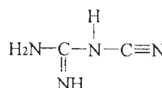
4,4′-Bis(2,3-epoxypropoxy)benzylideneaniline (**B**)



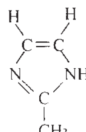
4,4′-Bis(2,3-epoxypropoxy)biphenyl (**C**)



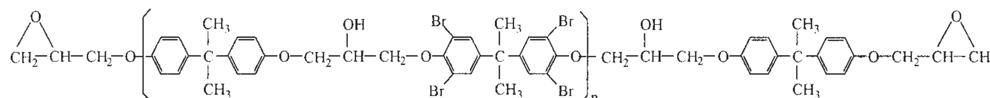
Dicyandiamide (**DICY**)



2-Methylimidazole (**2-MI**)



Diglycidal ether tetrabromobisphenol A (**DGETBA**)



were conducted with a nitrogen flow of 60 mL/min, with heating rates of 20°C/min from 50 to 200°C. Flammability was determined following the UL 94 V-0 vertical test procedure. Moisture absorption was tested following the IPC-TM-650, Method 2.6.2.1. Moreover, dielectric constant (DK) and dissipation factor (DF) were measured using a Hewlett–Packard 4291A apparatus (Palo Alto, CA) according to the IPC-TM-650, Method 2.5.5.2. Peel strength was obtained using Lloyd LR 5K following the IPC-TM-650, Method 2.4.40. Additionally, the comparative tracking index (CTI) was analyzed following the method IEC-112. Finally, arc resistance was examined using the IPC-TM-650, Method 5.1.

DGETBA and epoxy (A), (B), or (C) were mixed in various ratios, then cured with various quantities of curing agent, DICY or DDM, and small amounts of promoting agent 2-MI, over a temperature of approximately 170°C on a hot plate. The copper-clad laminate was prepared using the following procedure. The prepreg of copper-clad laminate was prepared using glass fiber (7628) and semicured epoxy resin, after which the copper foil was laid out and hot pressed. The hot press was performed under heating at 85°C for 50 min, after which the temperature was raised to 180°C for 90 min.

RESULTS AND DISCUSSION

Initially, dicyandiamide (DICY) and diphenyldiaminomethane (DDM) were selected as curing agents. The DSC of the epoxy resin that DGETBA was cured with (DICY or DDM) was measured using a nitrogen flow of 60 mL/min, at a heating rate of 20°C/min from 50 to 200°C. Figure 1 shows the T_g of the epoxy resin

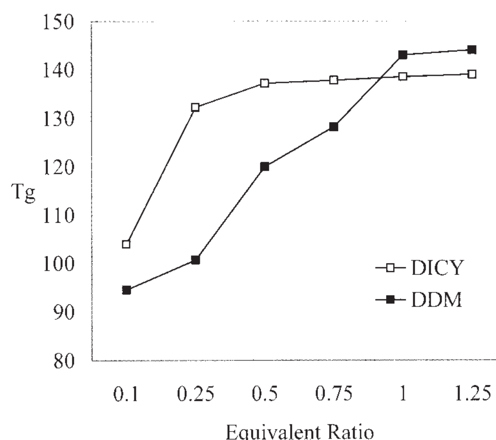


Figure 1 T_g values of the epoxy resin that DGETBA was cured with (DICY or DDM) after 2 h.

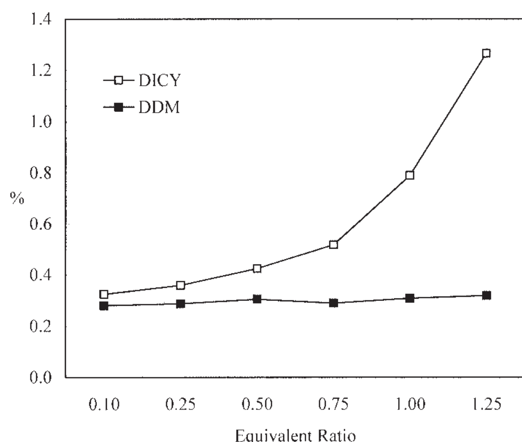


Figure 2 Moisture absorption of the epoxy resin that DGETBA was cured with (DICY or DDM) after 0.5 h.

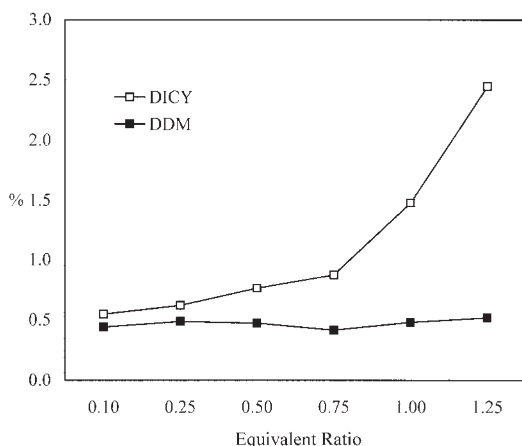


Figure 3 Moisture absorption of the epoxy resin that DGETBA was cured with (DICY or DDM) after 2 h.

based on the equivalent ratio of DGETBA and DICY, or DGETBA and DDM. The T_g shows no variation when the equivalent ratio of DGETBA:DICY is 1 : 0.5 and DGETBA : DDM is 1 : 1. Figures 2 and 3 illustrate the moisture absorption of the epoxy resin when DGETBA was cured with DICY or DDM after 0.5 or 2 h, respectively. The moisture-absorption behavior of epoxy resin cured by DGETBA with DICY exceeds that cured with DDM, although moisture absorption increased with DICY. However, the quantity of DDM does not influence the moisture-absorption ability. Moreover, DICY is cheaper than DDM, and the moisture-absorption ability and T_g of epoxy resin cured by DGETBA with DICY or DDM at an equivalent ratio of 1 : 0.5 were almost the same. The following tests were performed on composite epoxy resin in which DGETBA and epoxy (A), (B), or (C) were mixed and cured using DICY at an equivalent ratio of DGETBA : DICY, 1 : 0.5.

Table II summarizes the polymerization conditions of different simples. A0–A5, B0–B4, and C0–C5 denote different composite epoxy resins with different ratios of DGETBA and epoxy (A), (B), or (C), respectively. The amount of promoter 2-MI used in A0–A5 was decreased with increasing weight of epoxy (A) because the reactivity of the mixture was increased with increasing amount of epoxy (A). However, the weight of 2-MI in samples B0–B4 need not be changed to match the changing quantities of epoxy (B) because the mixture reactivity remained almost the same regardless of whether the quantity of epoxy (B) increased. The inverse trend was represented in samples C0–C5, which showed that the promoter weight increased with increasing weight of epoxy (C). Thus when epoxy (C) was added to DGETBA, the mixture reactivity was reduced, and more promoters are required for complete curing.

The composite

Following the formula of the reactant listed in Table II, the cured composite epoxy resins were solidified, and of about 1.5–1.6 mm thickness. Table III lists some physical properties of the composite epoxy resins.

Differential scanning calorimetry (DSC)

Table III and Figures 4–6 list the DSC results. The T_g values increased with increasing percentage of epoxy (A) or (B), but the result inversed when epoxy (C) was used. Epoxy (A), (B), or (C) was cured using DDM (20), and the T_g values of these epoxy resins were 213,

TABLE II
Composition of Different samples

Composition	Sample														
	A0	A1	A2	A3	A4	A5	B0	B1	B2	B4	C0	C1	C2	C4	C5
DGETBA (w/w)	100	90	80	70	60	50	100	90	80	60	100	90	80	60	50
(A), (B), or (C) (w/w)	0	10	20	30	40	50	0	10	20	40	0	10	20	40	50
DICY[a]	2.47	2.99	3.52	4.05	4.57	5.09	2.47	2.84	3.21	3.95	2.47	2.89	3.31	4.14	4.56
2-MI (phr[b])	0.1	0.1	0.08	0.06	0.06	0.06	0.1	0.1	0.1	0.1	0.1	0.16	0.17	0.18	0.2
Varnish GT (s)	216	191	215	218	215	210	215	216	215	218	220	198	205	215	201

[a] Equivalent number of DICY used.
[b] 1 phr (epoxy resin : 2-MI = 100 : 1).

TABLE III
Some Physical Properties of the Composite Epoxy Resin That Contains DGETBA and Epoxy Monomer (A), (B), or (C)

		Sample														
Property analysis	Unit	A0	A1	A2	A3	A4	A5	B0	B1	B2	B4	C0	C1	C2	C4	C5
DSC	°C	138	148	154	157	158	167	138	142	143	154	138	137	136	131	129
TMA	°C	124	134	143	153	166	176	124	126	130	141	124	121	119	113	112
Before T_g	μm/m°C	46	47	43	46	48	45	46	42	43	42	46	47	47	50	48
After T_g	μm/m°C	161	162	161	151	141	139	162	163	165	164	163	165	168	169	168
TGA																
5% Weight loss	°C	323	319	316	313	310	309	323	311	308	305	323	320	316	311	311
Residual weight																
At 300°C	%	100	99	99	99	99	99	100	97	96	96	100	100	98	98	98
At 350°C	%	30	31	33	36	42	43	28	30	34	41	29	29	30	34	24
At 450°C	%	18	20	22	26	30	32	18	19	22	28	18	18	18	18	19
DK	1 MHz	3.58	3.59	3.60	3.60	3.61	3.61	3.58	3.59	3.60	3.60	3.58	3.58	3.57	3.54	3.53
	1 GHz	3.10	3.12	3.13	3.14	3.15	3.16	3.10	3.10	3.11	3.10	3.10	3.09	3.08	3.04	3.00
DF	1 MHz	0.053	0.051	0.048	0.046	0.044	0.043	0.053	0.052	0.050	0.049	0.053	0.054	0.055	0.056	0.075
	1 GHz	0.017	0.016	0.015	0.015	0.014	0.014	0.017	0.006	0.015	0.015	0.017	0.018	0.018	0.019	0.019

200, and 177°C, respectively. Higher T_g appears to result from a more symmetric structure. The twisted structure of the biphenyl of epoxy resin (C) could make the epoxy resin less packed and induce lower T_g.

Coefficient of thermal expansion (CTE)

The coefficient of thermal expansion of composite epoxy resins A0–A5 was around 43–48 μm/m°C before T_g and 139–162 μm/m°C after T_g. The coefficient remained almost constant before T_g, but decreased after T_g when the percentage of epoxy (A) was increased, meaning that the dimension of the prepreg is more stable against thermal action. The B0–B4 or C0–C5 composite epoxy resins display no significant improvement at thermal expansion testing. The coefficient was in the range 42–46 μm/m°C before T_g, and 162–165 after T_g of composite epoxy resins B0–B4; and 46–50 μm/m°C before T_g, and 163–169 after T_g of composite epoxy resins C0–C5.

Thermogravimetric analysis (TGA)

The TGA measurements were performed under nitrogen atmosphere. Figures 7–9 illustrate the TGA curves for composite epoxy resin in nitrogen, at a 20°C/min heating rate. Degradation was a single-stage process in a nitrogen atmosphere. The 5% weight loss temperature of the composite epoxy resins decreased with increasing percentage of epoxy (A), (B), or (C). At 450°C, the char yield increased with increasing percentage of epoxy (A) or (B) in composite epoxy resins,

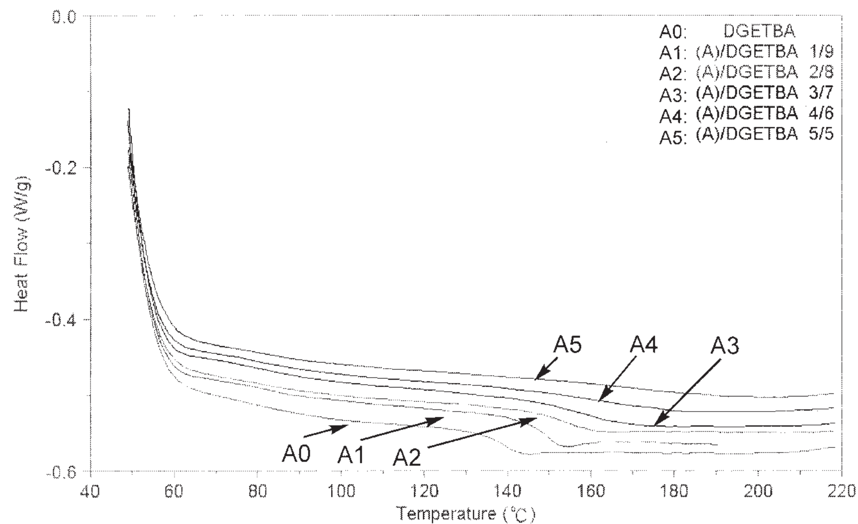


Figure 4 DSC curves of composite epoxy resins A0–A5.

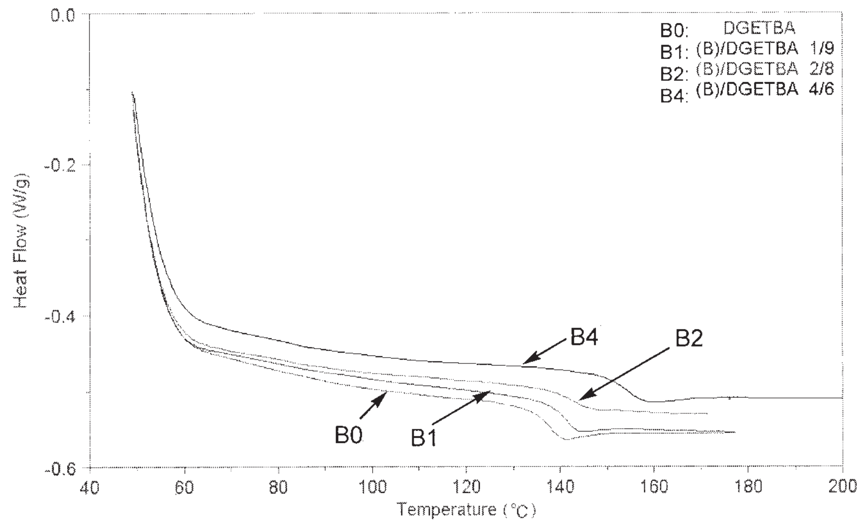


Figure 5 DSC curves of composite epoxy resins B0–B4.

but the char yield remained almost the same in composite epoxy resins C0–C5.

DK and DF

The dielectric constant (DK) and dissipation factor (DF) do not change significantly when different percentages of epoxy (A), (B), or (C) are used in the composite epoxy resins A0–A5, B0–B4, or C0–C5. Thus the composite epoxy resins A0–A5, B0–B4, or C0–C5 tested here have the same DK or DF values.

Copper-clad laminate

Finally, the prepreg of copper-clad laminates were prepared using glass fiber (7628) and semicured epoxy resins. The copper foil was laid out and hot pressed, after which the physical or mechanical properties of copper-clad laminates were examined. Table IV lists the physical or mechanical properties of the copper-clad laminates in this work.

Moisture absorption

Table IV lists the moisture-absorption ability of copper-clad laminates, and Figures 10–12 display the testing results. For copper-clad laminates A0–A5, the moisture-absorption ability decreases with increasing percentage of epoxy (A) mixed into DGETBA. Figure 10 shows this trend. However, the copper-clad laminates B0–B4 displayed different behavior. The moisture-absorption ability of copper-clad laminates B0–B4 increased with increasing percentage of epoxy (B). Possibly, the C═N structure interacts too easily

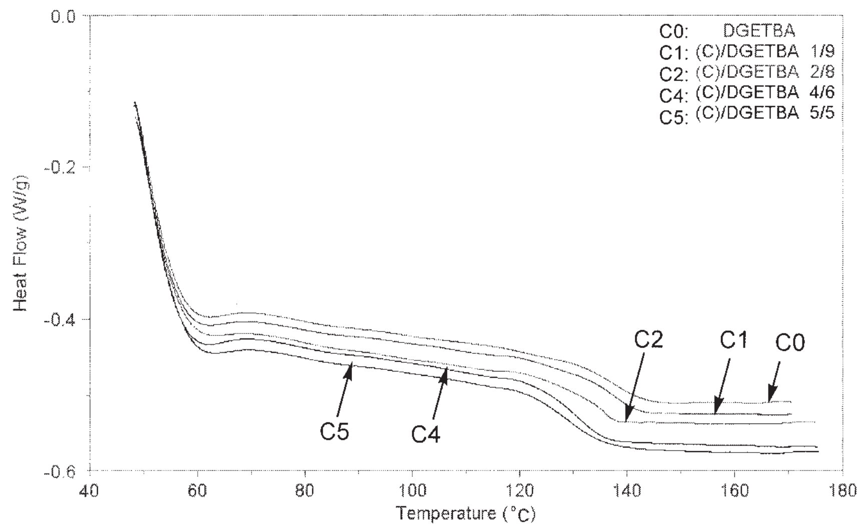


Figure 6 DSC curves of composite epoxy resins C0–C5.

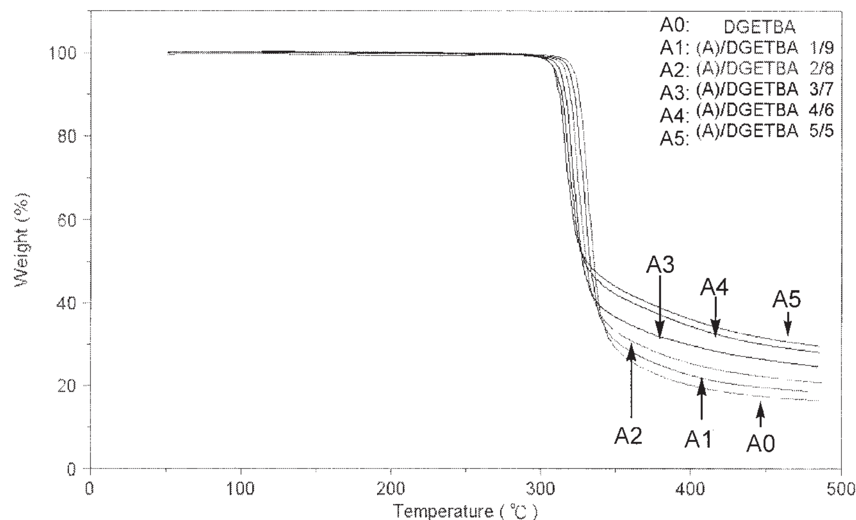


Figure 7 TGA curves of composite epoxy resins A0–A5.

with water vapor, for example, by hydrogen bonding. This problem can be overcome by extended heating, for example, by 24 h heating at 105°C. However, this solution wastes time and energy. The moisture-absorption ability of copper-clad laminates C0–C5 was the same as that of copper-clad laminates A0–A5, displaying the same trends.

Peel strength

Table IV lists the test results for peel strength of copper-clad laminates. The resulting peel strength data of copper-clad laminates C0–C5 appear unchanged despite different compositions. However, the peel strength of copper-clad laminates A0–A5 and B0–B4 decreased with increasing percentage of epoxy monomer (A) or (B). Explaining why the trend of peel strength decreased when the percentage of epoxy monomer (A) or (B) increased is difficult.

Comparative tracking index

Clearly, the data of the comparative tracking index of copper-clad laminates A1–A5, B1–B4, or C1–C5 exceeded the comparative tracking index of copper-clad laminates A0, B0, and C0. Table IV lists the data and reveals that copper-clad laminates A0, B0, and C0 performed worst.

Arc resistance

Arc resistance testing demonstrates that, regardless of the copper-clad laminates, the testing results display little variation. The copper-clad laminates A0–A5, B0–

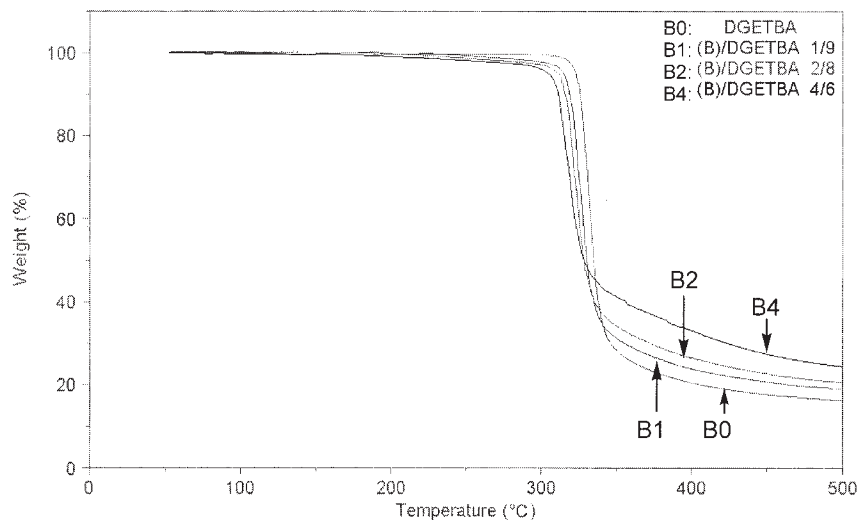


Figure 8 TGA curves of composite epoxy resins B0–B4.

Figure 9 TGA curves of composite epoxy resins C0–C5.

B4, or C0–C5 exhibit almost the same effect on arc resistance.

Flammability

Flammability measurements for copper-clad laminates A0–A5, B0–B4, or C0–C5 show that all of the copper-clad laminates passed the flammability testing UL 94 V-0.

CONCLUSIONS

The T_g values of epoxy resins A0–A5 or B0–B4 was increased with increasing percentage of epoxy resin (A) or (B), but the trend was inversed for epoxy resins C0–C5. Apparently, the structure of the epoxy resins is easy to pack, thus causing higher T_g values. Epoxy (C) exhibited the twisted structure of the biphenyl and reduced the level of packing of the epoxy resins.

The coefficient of thermal expansion of composite epoxy resins A0–A5 was almost constant before T_g, but decreased after T_g with increasing percentage of epoxy (A). The dimension of epoxy resin prepregs A0–A5 is thus more stable against thermal action. The composite epoxy resins B0–B4 or C0–C5 do not improve significantly on thermal expansion testing.

The TGA measurements of composite epoxy resins A0–A5, B0–B4, or C0–C5 were conducted under nitrogen atmosphere. Degradation is a single-stage process conducted under a nitrogen atmosphere. The 5% weight loss temperature of the composite epoxy resins A0–A5, B0–B4, or C0–C5 decreased with increasing percentage of epoxy monomer (A), (B), or (C), respectively. At 450°C, the higher percentage of epoxy (A) or (B) in composite epoxy resins A0–A5 and B0–B4 increases the char yield, although the char yield remains unchanged in composite epoxy resins C0–C5.

The dielectric constant (DK) and dissipation factor (DF) remain largely unchanged in the composite epoxy resins A0–A5, B0–B4, or C0–C5.

For composite epoxy resins A0–A5 or C0–C5, the moisture-absorption ability of copper-clad laminates A0–A5 or C0–C5 decreases with increasing weight of epoxy (A) or (C) mixing into DGETBA. However, the

TABLE IV
Some Physical Properties of the Copper-Clad Laminate Examined in This Study

Property	Unit	Sample														
		A0	A1	A2	A3	A4	A5	B0	B1	B2	B4	C0	C1	C2	C4	C5
Moisture absorption																
24-h water	%	0.178	0.177	0.174	0.173	0.162	0.160	0.182	0.185	0.188	0.195	0.175	0.171	0.165	0.159	0.158
0.5-h PCT	%	0.445	0.423	0.370	0.349	0.321	0.314	0.451	0.462	0.488	0.539	0.442	0.412	0.361	0.314	0.298
2-h PCT	%	0.684	0.665	0.597	0.525	0.477	0.458	0.686	0.721	0.769	0.884	0.680	0.625	0.575	0.443	0.418
Peel strength oz.	lb./in.	13	10.6	10.5	9.1	7.8	7.5	12.9	11.8	11	10.8	12.6	12.5	12.1	12.3	12
Arc resistance	s	124	126	127	126	127	128	124	125	124	126	124	124	125	124	125
Comparative tracking index	V	220	240	260	280	280	300	220	220	240	240	220	260	260	280	280
Flammability (UL94)	—	V-0	V-0	V-0	V-0	V-0	V-0	V-0	V-0	V-0	V-0	V-0	V-0	V-0	V-0	V-0

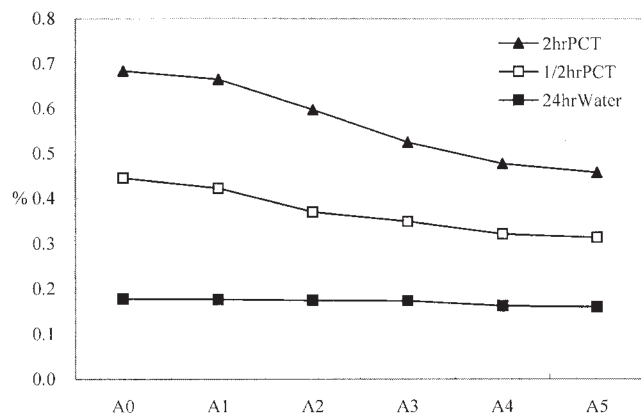


Figure 10 Moisture-absorption ability of composite epoxy resins A0–A5.

moisture-absorption ability of copper-clad laminates B0–B4 increased with increasing addition of epoxy (B).

The resulting peel strength data of copper-clad laminates C0–C5 remain constant, but data of copper-clad laminates A0–A5 and B0–B4 were reduced.

Copper-clad laminates A0, B0, and C0 performed worst on a comparative tracking index among copper-clad laminates A0–A5, B0–B4, or C0–C5.

The arc resistance testing did not show substantially different results for copper-clad laminates A0–A5, B0–B4, or C0–C5.

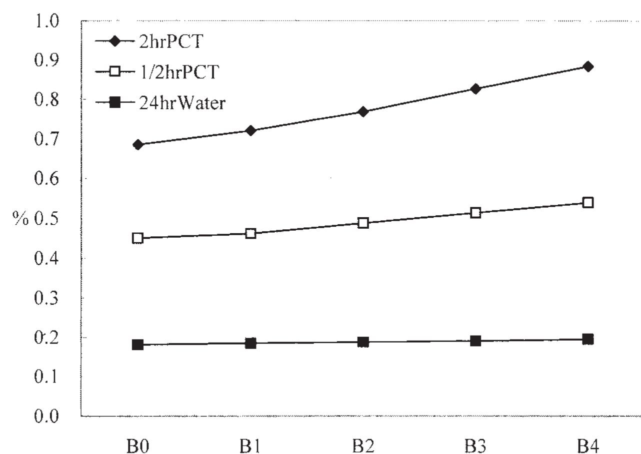


Figure 11 Moisture-absorption ability of composite epoxy resins B0–B4.

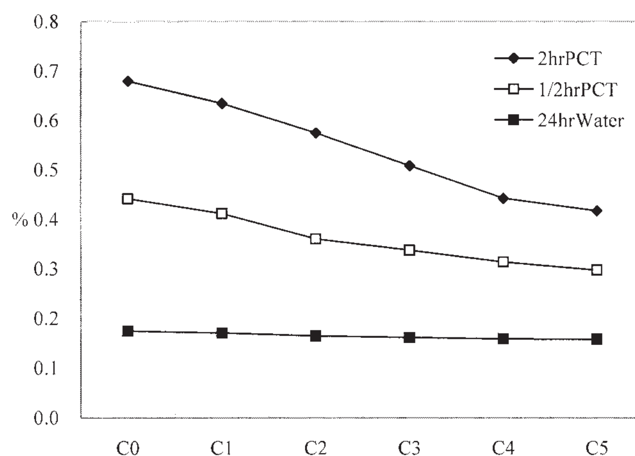


Figure 12 Moisture-absorption ability of composite epoxy resins C0–C5.

Flammability measurements indicated that all of the copper-clad laminates passed flammability testing.

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