Effects of Various Fillers on CEM-1 Laminate Punchability

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 primary objective of this study is to emphasize the modification of the epoxy resin formulation by implementing falling weight test to discuss reduction of impact energy and apply the thesis to improve the punchability on the CEM-1 copper clad laminate. Experimental results demonstrate that the core structure can be modified with different phenolic resin; when phenolic resin PF-440 of a smaller molecular weight is used as the modified agent, the impact energy can be lowered by 17%. In addition, three kinds of inorganic fillers, such as TiO_2, $Al(OH)_3$, SiO_2, are added and the core and face structure were modified separately. Adding these fillers has a small effect on lowering the impact energy and no clear evidence of tendency, while the phenolic resin has significant effect. When 10 phr TiO_2 is added to face, the impact energy can be lowered around 60% and has a visible effect on improving the punchability improvement of CEM-1 copper clad laminate. J Appl Polym Sci 101: 3381–3386, 2006

Key words: impact energy; cracking; propagation; falling weight; CEM-1; punchability

INTRODUCTION

Short and small, light and thin seems to be the common development trend of most electronic products, hence the technology and manufacturing of Print Circuit Boards has become more and more stringent and secretive. Also Different laminates will result from different processes in manufacturing; however, selection can primarily be based on quality and characteristic of the materials and the scope of suitability.

Using Print Circuit Board holes' processing as an example, FR-4 laminate were used to form through hole[1] by CNC drilling, HDI laminate using laser drilling,[2]and plasma technology for micro-via, and FR-1 CEM-1 laminate using punch etc. NEMA grade CEM-1 laminate is composed of a cellulose paper core, sandwiched between two plies of continuous woven glass fabric, infiltrated with an epoxy resin binder. The primary objective of this study is to reduce or lower the impact energy of this kind of sandwich composition of the CEM-1 composite materials, which separately modifies the composition formula, using the falling weight[3,4] impact as the evaluation method to understand the modified effect and trend of the formula. This study analyzes the application of additional filler and resin modification on the improvement of the punchability of CEM-1 laminate.

Correspondence to: H.-T. Chiu (marvin.cheng1@msa.hinet.net).

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The primary purposes of studying the effect of inorganic filler on CEM-1 laminate are to lower the cost and to increase the flame retardant effect. Aside from these, the relationship between the addition of inorganic filler and punchability has rarely been studied. There is an evident difference in the effect of the particle shape[5] of different inorganic fillers on the reduction of impact energy and on the punchability of CEM-1; the higher toughness of materials, having higher impact energy, result in the reduction of machine punch life, beside increasing the manufacturing cost. In addition, it will destroy the quality of the punch hole, with too much burr on the surface; the residual smear will result in a Tin tainted negative effect.[6]

Figure 1 shows the falling weight testing result for etched CEM-1 laminate with 1.6 mm thickness. The illustration demonstrates the change in the impact energy during testing process and the accumulated energy curve. Figure 2 is the illustration of the destruction process of the material, wherein point 0 is the initial point with fixed striker altitude, zero time, and impact energy. When striker hits the specimen, the impact energy continues to increase with time until it reaches point 1, where the energy was absorbed by the crack that was caused by the striker impact. The slope becomes smaller. The energy accumulated in this action is called Energy of crack (E_c), also known as Initial Energy. Figure 1 is a plot of force versus time; using the formula stated elsewhere[3] the area underneath the curve can be calculated. The computed area is the Energy of crack resulted from the impact. Point 2 of

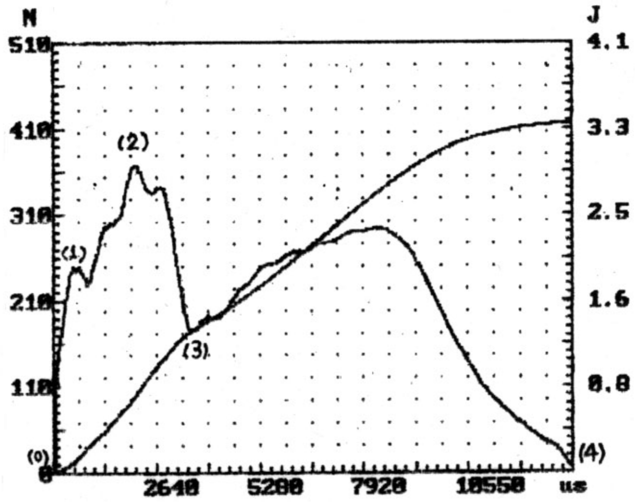


Figure 1 Illustration of falling weight testing for 1.6-mm thick CEM-1 laminate.

Figure 1 demonstrates the maximum impact force on the material, and at this point the total demolition of the specimen took place; the demolition has counteracted the impact energy, which encourages the descending of the curve of force. This act is closely followed by upward of the curve of force to Point 3. Such phenomenon is mainly attributed to the rebounded characteristic of the material. The motion will continue until the material has completely broken and fell off from the striker and reaches Point 4 (rest state). The accumulated energy from time of cracking (t_c) till time of finishing (t_f) is called energy of propagation as shown in formula.[4] The ductility of the material is based on the ratio of E_p to E_c (E_p/E_c). E_p/E_c is defined as the Ductile Index (DI); the lower the DI value means the more brittle the material is and vice versa. The sum of E_c and E_p is the impact energy, and its value can be defined by the punchability index of the CEM-1 material.

$$E = \int_0^s F dS = \int_0^t F d(Vt) \tag{1}$$

where F is the impact force; S, Displacement of impact head; V, Velocity of impact head; and E, impact energy.

Assume V is constant, thus

$$E = V \int_0^t F dt \tag{2}$$

$$E_c = V \int_0^{t_c} F(t) dt \tag{3}$$

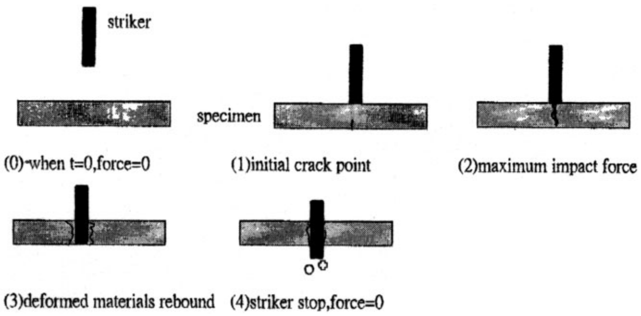


Figure 2 Illustration of specimen fracture by falling weight testing.

$$E_p = V \int_0^{t_f} F(t) dt \tag{4}$$

$$E_t = E_c + F_p \tag{5}$$

E_c: Energy of crack, E_p: Energy of propagation, E_t: Energy of total, t_c : time of crack, and t_f : time of finishing.

EXPERIMENTAL

Materials

The epoxy resins used in this experiment are products of Nan Ya Plastics Corp. These are Brominated Epoxy Resin NPEB 450 and Basic NPEL128. The phenolics products are of Chang Chun PF-5110 and PF-440, and the other phenolic product is Bakelite 9721–1z. The Curing Agents used are Cyanoguanidine (1-Cyanoguanidine), and Dicyandiamide Dicy (DCD; CAS no. 461–58-5 $H_2NC(=NH)NHCN$), and 2-Methyl Imidazole ($C_4H_4N_2$ CAS no.69–39-81) was used as a catalyst. The solvent used is DMF (Dimethyl formamide). Varieties of inorganic filler aluminum hydroxide $Al(OH)_3$ is made from Showa Denko H-32M while Titanium oxide TiO_2 is made from DuPont Ti-pure. The Silica is made from MIN-U-SIL (U.S. SILICA Company). For reinforcements we used E-glass fabric type 7628 (Taiwan Glass Ind. Corp.) on face structure and used Bukye 220 g/M^2 cotton liter paper on core structure.

TABLE I
Comparison of Various Phenolic Molecular Weights

Phenolic resin			
Manufacturer	Product designation	M_n	M_w
Chang Chun	PF-5110	1366	3648
Bakelite	9720–1Z	1257	3828
Chang Chun	PF-440	890	2401

TABLE II
Comparison of the Modification of Core Composition Formula Table and Falling Weight Testing Impact Energy

Sample no. of Epoxy:phr	unmodified	A	B	C	D	E	F
PF-5110		26.9			26.9	26.9	70
9720–1Z			26.9	26.9			
PF-440						5.92	
TiO_2		5.92	5.92	5.92	5.92		5.92
Silica		29.58	29.58	29.58	15	15	15
$Al(OH)_3$							
FW (J)	3.167	3.14	3.13	2.64	2.85	3.2	2.96

Sample preparation

In the face preparation, to produce impregnation, resin, curing agent, catalyst, filler, and solvent were all weighed according to their proportion and were mixed evenly for 8 h. The mixture was impregnated in the glass fabric 7628 with ready mixed varnish (control resin content at (43 ± 0.5)%), and the gel time was tested (control the gel time within 110 ± 5 s).

In the core preparation, using IPC4101 TM650, the varnish of core formula was placed in a temperature controlled oven (which was set at 175°C) to produce impregnation, with resin flow testing control ranging from 2 to 5% to ply-up the sandwich contracture. After which, 1 ply of face preparation and 3 plies of core preparation were placed one above the other. Then the stack was held in a top–bottom manner to release film, which was then laminated using smooth steel plate. The press cycle time is around 2.5 h and the heating rate and pressure were controlled. Subsequently, the samples were cut into 65×65 mm^2 pieces.

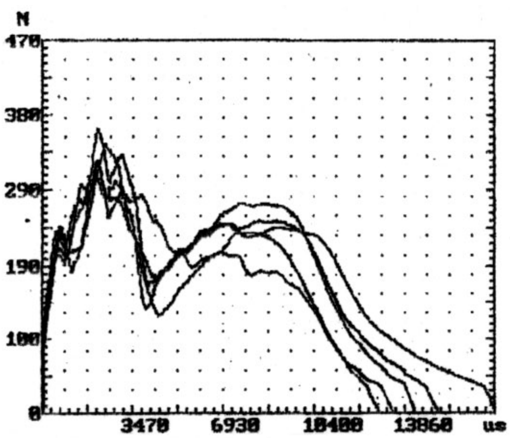
Measurements

Falling weight testing was based on ASTM D3029. Mold 208, the experiment equipment manufactured by Hung Sun Engineering CO., had the following features: drop height, 17 cm; striker weight, 3.65 kg m; diameter, 0.5 in.

DISCUSSION

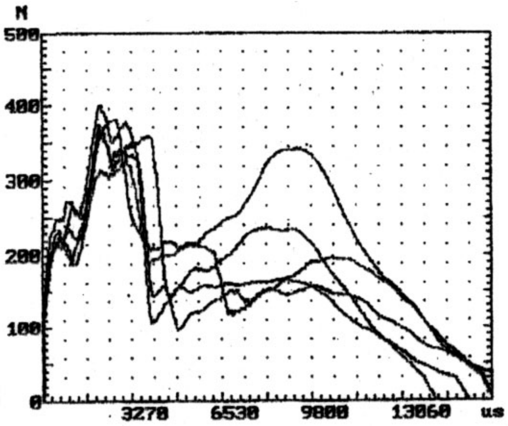
The effect of the core resin modified on the falling weight result

Generally after the cotton linter paper impregnation, the ductility of object will be increased and consequently, impact energy is enhanced. Such outcome is not desired by print circuit board user. On the core composition formula, a more brittle phenolic resin was used as a modifier. Table I shows the details of different types of phenolic resins[7] and their molecular weights, the addition of different amounts of phenolic resin and various fillers on the core resin formula. As the primary modified formula ratio, sample A, B, C uses different phenolic resin addition as basis for comparison (Table II); the result shows that the phenolic resin type added to sample C has the smallest molecular weight, while the impact energy of the falling weight testing is also the smallest impact energy. This is primarily because it is easier for small molecules to be impregnated, and effectively lowering the ductility of the material. Compared with impact energy, it was lowered by 15% of the impact energy from nonmodi-



sample	F	Ec	Ep	Et
1	391	0.856	2.601	3.457
2	369	0.756	2.493	3.249
3	348	0.658	2.483	3.141
4	380	0.723	2.203	2.926
5	424	0.781	2.279	3.061
AVG	382	0.755	2.412	3.167
STD DEV	23	0.065	0.148	0.18
COEF VEF	6.58	8.66	6.12	5.67

Figure 3 Unmodified force falling weight testing.



sample	F	Ec	Ep	Et
1	413	0.766	3.138	3.904
2	424	0.846	2.297	3.143
3	445	0.844	2.433	3.278
4	456	0.929	2.399	3.328
5	369	1.138	2.137	3.275
AVG	421	0.905	2.481	3.386
STD DEV	30	0.127	0.344	0.266
COEF VEF	7.18	14.08	13.87	7.87

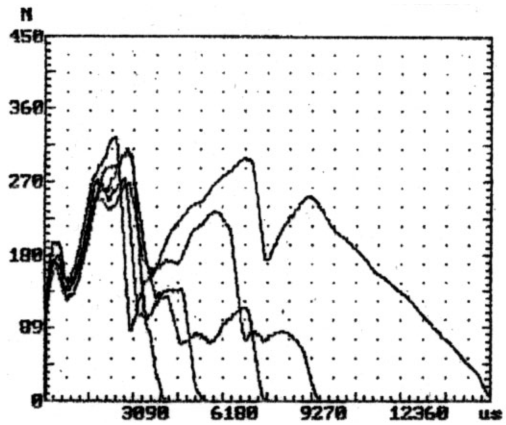
Figure 4 Falling weight testing of force with the addition of modified $Al(OH)_3$ filler.

fied sample. On the other hand, similar to sample F, the phenolic amount in sample D phenolic is increased, Although these results have smaller impact energy when compared with that of nonmodified ones; the level of its effect is smaller than the molecular weight factor. The effect of the filler on modified core composition can be seen in the comparison between samples A and D; lowering $Al(OH)_3$ addition amount, its impact energy decreases from 3.14 to 2.85 J. Comparing sample D (containing silica) with sample E (containing TiO_2), the desired effect on the falling weight was not obtained. Core structure filler addition has an effect on impact energy reduction. This effect is still incomparable with that obtained using smaller molecular phenolic resin, which has been more effective.

Effect of face resin modified on falling weight result

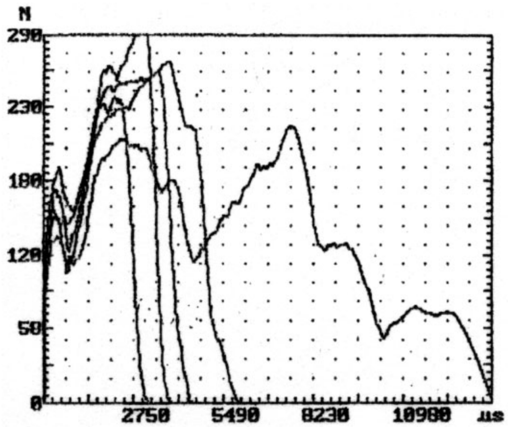
In face prepreg production, primary phenolic resin[8,9] cannot generally be used under conditions of DMF solvent system. Hence, evaluation was limited to the effect of filler on impact energy. In the selection of fillers, considerations were made as regards added quantity, shape, size,[10] size distribution, or surface treatment on CEM-1 in the modified application of inorganic filler; moreover, commercial product particle size of 10–30 μm were also important considerations for selection.

Face composition is made up of epoxy resin, impregnated with woven glass fabric as the primary impregnation. Figure 3 shows unmodified face materials without addition of fillers modified. Figures 4, 5, and 6 illustrate the test drawing of the falling weight of fix addition 10 phr of three kinds of fillers face materials. As discussed earlier, the impact energy can be gleaned from impact force, ductile index, and total impact energy. These three indices are the basis for judging the degree of difficulty and easiness for CEM-1 punchability. In each illustration test value of 5 specimens are showed. The Curve drawing demonstrates the force of striker changes with time, and the final results are arranged as seen in Table III. The result showed the effect of three kinds of fillers. Con-



sample	F	Ec	Ep	Et
1	369	0.804	2.585	3.388
2	337	0.581	0.503	1.084
3	293	0.82	1.265	2.085
4	337	0.902	0.657	1.559
5	326	0.85	0.553	1.403
AVG	332	0.791	1.112	1.904
STD DEV	24	0.11	0.785	0.81
COEF VEF	7.34	13.95	70.59	42.54

Figure 5 Falling weight testing of force with the addition of modified SiO_2 filler.



sample	F	Ec	Ep	Et
1	239	1.611	0.665	2.326
2	326	0.566	0.555	1.121
3	293	1.074	0.456	1.53
4	282	0.429	0.334	0.763
5	282	0.851	0.288	1.139
AVG	285	0.755	0.46	1.376
STD DEV	28	0.065	0.139	0.534
COEF VEF	9.78	8.66	30.23	38.78

Figure 6 Falling weight testing of force with the addition of TiO_2 modified filler.

trary to expectations, with $Al(OH)_3$ the impact energy did not decrease but increase; the impact force of 421 N is greater than the impact force of 382 N before modification, and the total impact energy was also bigger than the impact energy before modification. The other two kinds of fillers had a remarkable decrease in the impact energy, most evidently with the TiO_2 filler to face resin to increase the hardness of the material and also increase the stress needed to create cracks on the material. Hence the energy of cracking is higher when compared with that at prior-addition stage, while the particle shape in energy of propagation clearly creates a big disparity, Using $Al(OH)_3$ filler particle shape with octahedral-like crystal structure, where the six hydroxyl are positioned in the six intersecting points of the octahedral structure, and two aluminum ions positioned in the middle, each distributed with three hydroxyls. Therefore, the crystal is composed of the middle plane between the top and low level of hydroxyl and aluminum ions. Crystal pattern belongs to Monolinic type, the big granule is usually composed of the flat surface or the diamond-shaped crystals accumulation. The flat shape can assist the dispersion of impact stress, but also has an opposite effect on the application of the modified ductility.

The crystallographic pattern of TiO_2 filler particle seems to be spherical or needle-like, whereas TiO_2 powder is tetragonal, which assists in the centralization of stress and swift stress propagation. This result proves the relationship between the geometric shape of particle and the impact fracture behavior of the material.

Figure 7 showed that with the further increase in the amount of TiO_2, corresponding impact energy decreases, with a lower impact energy shown at 10 phr of $TiO_{2.}$ Beyond this value and up to15 phr, the energy of propagation, on the contrary, increases. The result under a modified lowering of impact energy explains the restriction on the right amount of inorganic filler addition that is impregnated; too much filler addition leads to an increase in the viscosity of the varnish, which enables the decrease in glass fabric wetting. Hence it is unable to effectively make the material brittle.

CONCLUSIONS

1. Through the use of the falling weight test to observe the impact process of CEM-1 combined with the material, from the relationship of the impact energy with the change in time, the material characteristic is clearly understood and the formulation to improve the goal of punchability can be adjusted.

2. In the core structure, using phenolic resin of different molecular weights (to modify the characteristic) and adding different kinds of inorganic fillers, the modified effect of using a smaller molecular

TABLE III
Summary for Impact Energy for Various Filler Types In Face Addition

Filler type	Force (N)	Energy of cracking (J)	Energy of propagation (J)	Ductile index (E_p/E_c)	Energy of total (J)
Non Filler	382	0.755	2.412	3.19	3.167
TiO_2	285	0.916	0.46	0.5	1.376
$Al(OH)_3$	421	0.905	2.481	2.74	3.386
SiO_2	332	0.761	1.112	1.46	1.904

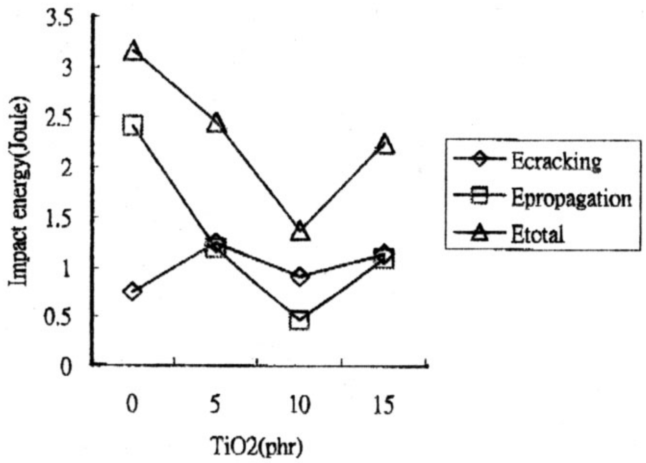


Figure 7 Falling weight testing of force with addition of different ratios of modified TiO_2 filler.

weight phenolic resin is more evident and can lower the impact energy by 17%.

3. As regards the changes characteristic of face structure, the crystal morphology of inorganic filler particles had a visible effect on the impact energy. The flat-shaped $Al(OH)_3$ had a dispersion function on impact stress, resulting in a larger E_p and E_t values. Addition of spherical or needle-like TiO_2 and SiO_2 helped stress concentration and stress propagation, and hence gave a lower E_p and E_t values. TiO_2 was more effective in lowering the impact energy E_t; when 10 phr TiO_2 was added to face structure, it could lower the impact energy by 60%.

References

1. David, A.; Hazlebeck, J.; Talbot, B. AIChE J, 2004, 36, 1145.
2. Takamori, K.; Furukawa, H.; Morikawa, Y.; Katayama, T.; Watanabe, S. Lasers Surg Med 2003, 32, 25.
3. Golovoy, A. Polym Eng Sci 2004, 25, 903.
4. Alexander, A.; Bibeau. Polym Eng Sci 1975, 15, 294.
5. Iwasaki, N.; Takahashi, H.; Aoyagi, Y.; Jin, J. Y.; Tonami, K.; Nishimuras F. J. J Dent Mate 2003, 22, 194.
6. Hillman, C.; Rogers, K.; Dasgupa, A.; Pecht, M. Circuit World 1999, 25, 28.
7. Chiu, H. T.; Cheng, M. F. J Appl Polym Sci, to appear.
8. Lee, S. M.; Hwang, T. R.; Song, Y. S.; Lee, J. W. Polym Eng Sci 2004, 44, 1170.
9. Duann, Y.-F.; Chen, B.-L.; Tsai, T.-H. J Appl Polym Sci 2005, 95, 1485.
10. Bose, S.; Mahanwar, P. A. J Mater Mater Charact Eng 2004, 3, 23.