Soldering Deterioration of Epoxy-Molded IC Packages After Moisture Absorption

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SYNOPSIS

Molding compounds for surface-mount devices were studied by using various kinds of epoxy resins in a practical model compound with phenol resins as curing agents. The physical properties of the cured compounds were studied at 215°C to simulate the condition that they encounter during the soldering process that can relate to package cracks. The compounds that have low modulus at soldering temperature, low equilibrium water concentration, and good adhesion toward the die pad developed few cracks after soldering. The compounds from difunctional epoxy resins showed good durability, resisting this phenomenon. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The deterioration of the surface-mount epoxy resin-molded IC packages after the explosive evaporation of absorbed water during soldering, a process called the "popcorn phenomenon," is a big problem in the semiconductor industry. It has a tendency to occur with thinner package geometry and with increasing chip size. Many studies have been done to solve this problem, but it still remains significant even today.

Today, more than 90% of semiconductors are molded with epoxy- molding compounds and almost 50% of them are encapsulated as surface-mount packages like QFP, SOP, and PLCC. In contrast with insertion-mount packages that are soldered by dipping only their pins into solder, the surface-mount packages meet vigorous heat during soldering processes. The soldering processes adopted for the surface mount packages are infrared soldering, vapor-phase soldering, and solder dipping. In these processes, the temperatures of the packages rise to 215–260°C. The packages, after being left in the air to absorb moisture, develop package cracks or swelling by evaporating their absorbed moisture explosively in these soldering processes.

Many practical experimental studies and simulations have been done regarding this problem. It was first introduced by Fukuzawa et al. and the relation between the absorbed moisture and the package cracks after soldering was clearly explained. They further introduced a package having a vent hole to aid moisture vapor removal while soldering.[1]

The improvement of the adhesion between the die pad and the molding compound was proposed by Fujita et al. and a polyimid treatment of die pads was introduced to solve this problem.[2] Some approaches by changing molding compounds were also done. Kuroki and Ota studied the compounds and they suggested that cured compounds with high modulus and high tensile strength at the soldering temperature did not always give a good result but, rather, that compounds with low modulus having good adhesion to the die did give good results.[3]

Ohizumi et al. recently made some interesting conclusions. They conducted a simulation of the soldering deterioration relating to the molding compounds and stated the following: The flexural modulus at soldering temperature, the moisture solubility coefficient at the moisture absorbing temperature, and the moisture diffusion coefficient at the soldering temperature govern the deterioration.[4]

More recently, Harada et al. examined packages using X-rays at the soldering temperature and introduced a new mechanism in which the crack starts

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Table I Structures of Epoxy Resins Used

No.	Chemical Name	Structure
1	*Ortho*-cresol novolac epoxy resin (Nihon Kayaku EOCN-1020)	
2	Tetramethyl biphenyl diglycidyl ether (Yuka-Shell YX-4000H)	
3	Dihydroxynaphthyl cresol triglycidyl ether (Dainihon Inki EXA-4300)	
4	Alkyl phenol-modified phenol novolac epoxy resin (Dainihon Inki EXA-4506)	
5	Xylene-modified phenol novolac epoxy resin (Dainihon Inki EXA-1857T)	$n, m > 2$
6	Tris(hydroxyphenyl)methane triglycidyl ether (Yuka-Shell E-1032H)	
7	Triglycidyl ether of dinaphthyl triol (Dainihon Inki EXA-4750)	

Table I (*Continued from previous page*)

No.	Chemical Name	Structure
8	Tetrakis(4-hydroxyphenyl)ethane tetraglycidyl ether (Yuka-Shell E-1031S)	
9	*p*-Glycidyl phenyl dimethyl tolyl bisphenol AD (Mitsui Petrochemical VG-3101L)	
10	Limonen phenol novolac epoxy resin (Yuka-Shell YL-6241)	
11	Dihydroxynaphthalene diglycidyl ether (Dainihon Inki HP-4032H)	
12	Low molecular weight *ortho*-cresol novolac epoxy resin (Nihon Kayaku EOCN-4400)	$n = 2$
13	Triglycidyl ether of tris(methyl)-*tert*-butyl hydroxyphenyl methane (Sumitomo Kagaku ESX-221)	$R_1 = CH_3$, $R_2 = C(CH_3)_3$

Table I (*Continued from previous page*)

No.	Chemical Name	Structure
14	The same as **13**	
15	9,9′-Bis(4-hydroxyphenyl)fluorene diglycidyl ether (Shin'Nittetu Kagaku ESF-300)	
16	3 : 7 (weight) mixture of phenol novolac epoxy resin and **2**	
17	Poly(glycidyl ether) of phenol-2-hydroxy-benzaldehyde novolac (Nihon Kayaku EPPN-502H)	
18	4,4′-Oxybis(1,4-phenyl ethyl)tetra-cresol glycidyl ether (Dainihon Inki EXA-610)	R = CH_3
19	4,4′-Oxybis(1,4-phenyl ethyl)phenyl glycidyl ether (Dainihon Inki EXA-700)	

Table I *(Continued from previous page)*

No.	Chemical Name	Structure
20	Bis(dihydroxynaphthalene)tetra-glycidyl ether (Dainihon Inki EXA-4700)	
21	Naphthol-modified cresol novolac epoxy resin (Nihon Kayaku EOCN-7000)	
22	1 : 1 (weight) mixture of **1** and **2**	
23	1 : 1 (weight) mixture of **2** and **10**	

from between a chip and a die pad and the delamination starts from the die-bonding adhesive.[5] Concerning this problem, Nishioka et al. proposed a newly developed compound, in which the reduction of the absolute moisture content in the package was effective for this type of delamination.[6]

A die-bonding adhesive with poor adhesion at the soldering temperature and high equilibrium water concentration after moisture absorption may generate this problem, but the improvement of the die-bonding resin may reduce the problem to the starting point, though it will still be a problem on a much improved level.

Today, most of these surface-mount packages are still packed in moisture-proof packages or baked to dry before soldering, and the complete elimination of such an inconvenient process remains as the major target for improvement from the viewpoint of making a complete molding compound.

As the formulations of these compounds are not disclosed, the new compounds that are said to have succeeded in eliminating the "popcorn phenomenon" are tested/introduced/used without knowing the change/progress of detailed formulation.

In this article, many kinds of epoxy resins were formulated into practical compounds to study their physical properties relating to the popcorn phenomenon.

EXPERIMENTAL

Formulation of Epoxy Compounds

Epoxy resins (*Table I*) and phenol resins (*Table II*) used here are shown with their structures. Producers' names with their product numbers are also shown in these tables. These resins were selected to formulate "epoxy-molding compounds" by mixing with other materials, as shown in Table III. Epoxy and phenol resins selected to formulate each epoxy molding compound are in Table IV.

These formulations do not contain rubber, which is usually mixed to reduce the internal stress of the compounds, because the rubber modification sometimes obscures the nature of the resulting compound's performance against moisture. After selecting a certain pair of resins, the final compound is usually modified with about 2 wt % of silicone or other rubbers and that improves the total performance of the compounds. But, this time, that is not included in this study.

The materials were mixed in a paddle mixer for 2 min at room temperature, then mixed on a double-roll mixer for 5 min at 100°C. The mixtures were cooled and crushed into powder with a pin crusher. Each 40 g of powder was then pressed in a mold cylinder with 40 mm diameter under 50 kg/cm^2 to form a tablet.

Table II Structures of Phenol Resins Used

No.	Chemical Name	Structure
1	Phenol novolac resin (Gunei Kagaku PSM-4261)	OH, OH, OH, CH_2, CH_2, n
2	Limonen phenol novolac resin (Yuka-Shell YLH-402)	OH, CH_2, $H_3C-C-CH_3$, n, CH_3, OH
3	Tri(hydroxyphenyl)methane (Yuka-Shell YL-6065)	CH, HO, OH, OH
4	Dicyclopentadiene-modified cresol novolac resin (Mitui Toatsu Kagaku DPR-5000)	OH, OH, OH, CH_3, CH_3, n, CH_3
5	p-Xylene-modified phenol novolac resin (Mitui Toatsu Kagaku XL-225LL)	OH, CH_2, CH_2, n

Transfer Mold

The tablets were then transfer-molded into test pieces at 175°C for 90 s. The test pieces, after being taken out from the mold, were after-cured 12 h at 175°C.

QFP (14 mm wide [w] × 20 mm long [l] × 2.05 mm thick [t]) packages on a silver-plated 42 alloy lead frame (partially plated: only a part of each bonding lead on the lead frame) with five pieces of 80 pins QFP patterns having die pads (7 mm w × 7 mm l × 0.15 mm t) mounted with silicon chips (6 mm w × 6 mm l × 0.35 mm t) were molded at the same condition, and after-cured in the same manner.

The adhesion between die pads and chips was done with the use of Ag-epoxy (Epinal EN-4000 Hitachi Kasei Co.) at 150° for 3 h.

Table III Formulation of Epoxy Compound

Materials	Weight %
Epoxy resin Phenol resin	Total 22.8[a]
Brominated epoxy resin (brominated bisphenol A epoxy resin Dainihon Ink Epiclon-153 with 49 wt % of bromide)	
Fused silica[b] (Denka, mixture of FS-881C/FB-01 = 95/5 weight ratio)	75
Catalyst (triphenylphosphine)	0.19
Wax (Hoechst Japan, mixture of OP/S = 2/1 weight ratio)	0.3
Antimony trioxide	0.9
Carbon black (acetylene black: Denka, Ryu-AB)	0.36
Silane coupling agent[c]	0.45

[a] Amount was adjusted to give 1/0.9 mol ratio to total epoxy/phenol, while the amount of brominated epoxy resin was kept constant at 2.04 wt %.

[b] FS-881C: irregular-shaped, mean particle size is 11 microns. FB-01: spherical-shaped, mean particle size is 2.2 microns.

[c] 0.4/0.05 weight ratio mixture of γ-ureido(propyltrimethoxysilane) coupling agent (Nippon Unicar A-1160) and r-(mercaptopropyl)triethoxysilane coupling agent (Shinetsu KBM-803) were used.

Measurement

Dynamic viscoelastic properties of the cured compound were measured with a Rheovibron DDV-III-EP (Orientic Co.) at 3.5 Hz, the temperature was raised at a rate of 2°C/min, and the dimension of the test pieces was 3 mm w × 60 mm l × 1 mm t.

Bending strength, bending modulus, and bending deflection at break were measured with a Tensilon UTM-5T (Orientic Co.) universal tensile strength tester at 215°C; the test pieces used were 10 mm w × 100 mm l × 4 mm t.

The glass transition temperature was measured with a thermomechanical analyzer TMC-30 (Shimazu Co.) using a 10 mm w × 10 mm l × 5 mm t test piece. The load applied to the sample was 0.5 g, and the temperature was raised at a rate of 2°C/min. Equilibrium water concentration was measured by the increase of the weight of a test piece having 50 mm diameter(d) × 3 mm t after 168 h of water absorption at 85°C and 85% relative humidity (RH).

Soldering Test

The packages were placed in a vapor-phase soldering (VPS) apparatus at 215°C for 5 min after 168 h of water absorption at 85°C, 85% RH. The packages were then observed for external cracks with a microscope (×40) to give the percentage of cracked packages.

The internal cracks and the delamination of die pads were observed with a scanning acoustic tomograph (SAT) (AT-5000 Hitachi- kenki Co.) using 25 MHz acoustic emission. Some of the packages were further examined via their cross sections with a microscope.

The area of adhesion between lead frames and molding compounds was examined, giving an index number (0–5) to each of the samples with a corresponding picture obtained by the SAT examination: 0 is complete delamination; 1, a small area of adhesion; 2, a wider area of delamination; 3, more than a half-area of adhesion; 4, a small area of delamination; and 5, complete adhesion, giving higher index numbers to those that have a wider area of adhesion. A typical example of SAT pictures is in Figure 1 with corresponding index numbers.

The index numbers of eight packages from the same compound were accumulated, and the accumulated value was given as a "die pad adhesion index" to the sample. Therefore, if there are no delaminations observed, the value is 40 (8 × 5).

RESULTS AND DISCUSSION

Dynamic Viscoelastic Properties

Dynamic viscoelastic properties of the cured compounds were studied. Some of the typical plots obtained from difunctional, multifunctional, and other epoxy compounds are shown in Figure 2. The compounds from three- to four-functional epoxies, which were introduced intending to increase the strength of the compounds at the soldering temperature, showed a high glass transition temperature, more than 180°C, and a high dynamic modulus above 215°C. On the other hand, the compound from difunctional epoxy had less than a 150°C glass transition temperature and a low dynamic modulus value above 215°C, although their moduli were almost the same below their glass transition temperatures.

Figure 1 Typical SAT pictures of QFP packages with corresponding index numbers.

Mechanical Properties and Moisture Absorption

Figure 3 shows the bending strength of the cured compounds measured at 215°C vs. the glass transition temperature. The numbers in the figure correspond to the compounds formulated after Table IV. Those that have more than 180°C T_g (made from epoxy resins **6**, **8**, **17**, **19**, **20**) showed more than three times the strength of the compound from cresol novolac epoxy resin (**1**), which is still most popular in molding compounds.

Figure 4 shows the bending modulus measured at 215°C vs. glass transition temperature. Higher values of modulus were observed as the glass transition temperature of the compound increased. This corresponds to the fact that compounds with higher numbers of functional groups show a high viscoelastic modulus at high temperature. Those having a glass transition temperature over 190°C and made from multifunctional epoxy resin (**8**, **17**, **20**) showed more than a 200 kg/mm^2 modulus, which is two times higher than the compound from cresol novolac epoxy resin (**1**).

Figure 5 shows the equilibrium water concentrations of cured epoxy compounds vs. the glass transition temperature. This shows that those compounds having a high glass transition temperature absorb more water, and it also relates to the functionality of the epoxy resins.

Epoxy resins with high reactivity and high functionalities produce compounds having high crosslink densities with high free volumes.[7-10] In addition, they produce more hydroxy groups than do the other epoxy compounds with low functionalities when they react. Hence, the compounds tend to absorb more water than the compounds from other low functional epoxy resins.

Relation Between Physical Properties and Package Cracks

Figure 6 shows the relation between the package cracks and equilibrium water concentration of the corresponding compounds. Packages from difunctional epoxy resin and with low equilibrium water concentration show no package cracks. But the other compounds in the figure showed no definite correlation between cracking tendency and water concentration. Lower values (less than 0.3%) of equilibrium water concentration of the compound seems to be required to obtain good durability against soldering. Figure 7 shows the relation between the package cracking and the bending strength of the cured compounds at 215°C.

Table IV Combination of Epoxy and Phenol Resins Used at Each Formulation

No.	Epoxy Resin	Phenol Resin
1	*Ortho*-cresol novolac epoxy	Phenol novolac (**1**)
2	Biphenyl epoxy	"
3	Beta-naphthol-type epoxy	"
4	Modified phenol novolac	"
5	Xylene-modified cresol novolac	"
6	3 functional	"
7	3 functional naphthalene type	"
8	4 functional	"
9	3 functional	Limonen phenol (**2**)
10	Limonen phenol novolac	"
11	Difunctional naphthalene	Phenol novolac (**1**)
12	Cresol novolac (LMW)	"
13	Alkyl 3 functional	"
14	Alkyl 3 functional (the same as **13**)	3 functional (**3**)
15	Fluorene type	Phenol novolac (**1**)
16	Mixture (phenol novolac epoxy + **2**)	"
17	Modified novolac	"
18	4 functional	"
19	4 functional	"
20	4 functional naphthalene	"
21	Naphthol-modified cresol novolac	"
22	Mixture (**1** + **2**)	Dicyclopentadiene type (**4**)
23	Mixture (**2** + **10**)	Xylene modified (**5**)

The formulation numbers are correspond to the epoxy numbers in Table I and the numbers after the name of phenol resins correspond to the phenol resins in Table II.

Apparently there are three groups of compounds:

1. A group with high bending strength from multifunctional epoxy resins.
2. A group with low bending strength from difunctional epoxy resins.
3. A third group from other epoxy resins including cresol novolac epoxy (**1**).

It is shown that all the above groups have a tendency in which the package crack decreases as the bending strength of the compound increases. However, in the group with high bending strength from multifunctional epoxy resins, even the packages from the compounds (**8**, **20**) with bending strength more than 3 kg/mm^2 at 215°C showed cracks. To the contrary, the compounds from epoxy resins (**22**, **23**) with bending strength less than 1.5 kg/mm^2 showed no crack.

Figure 8 shows the package cracks vs. the bending moduli of the cured compounds at 215°C. The package crack increases as the bending modulus increases, but there are some exceptions for those from multifunctional epoxy resin.

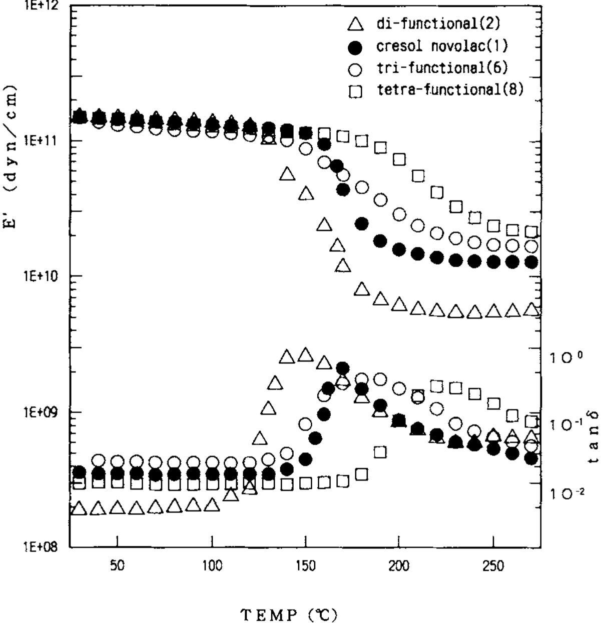

Figure 2 Dynamic viscoelastic property of cured compounds. The numbers after the name of epoxy resin correspond to the formulation numbers in Table IV.

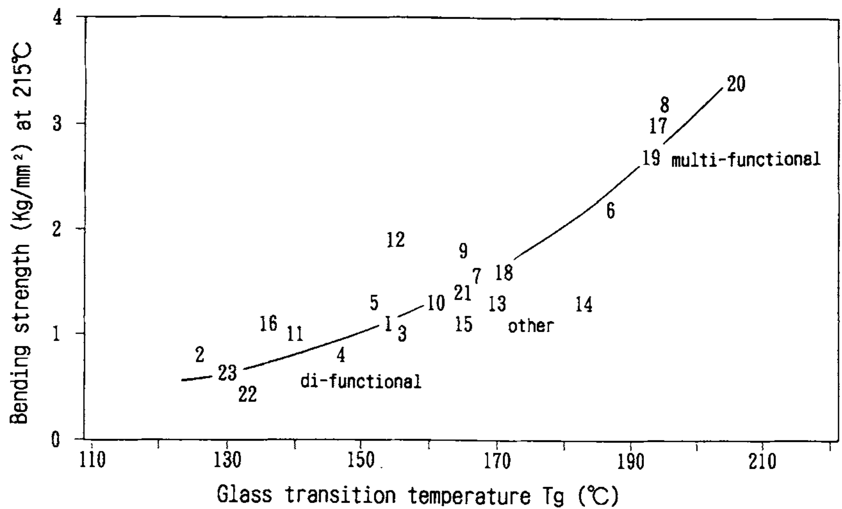

Figure 3 Bending strength at 215°C vs. glass transition temperature for cured compounds.

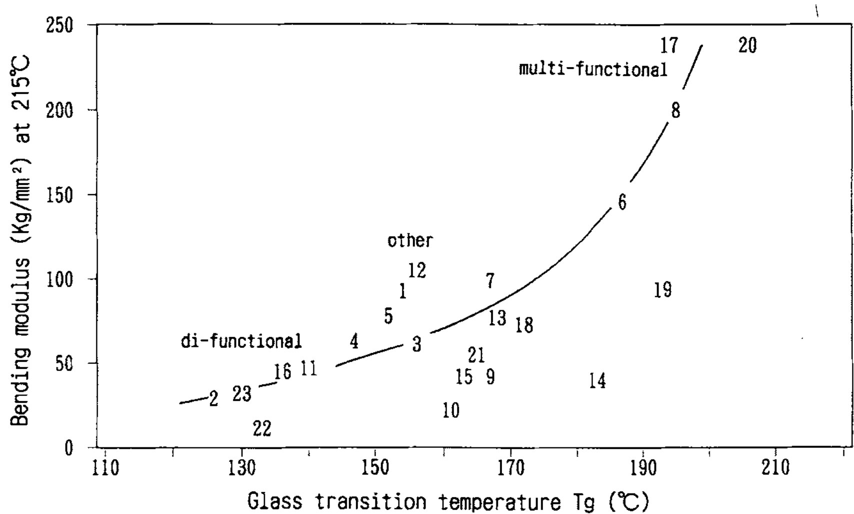

Figure 4 Bending modulus of cured compounds at 215°C vs. glass transition temperature.

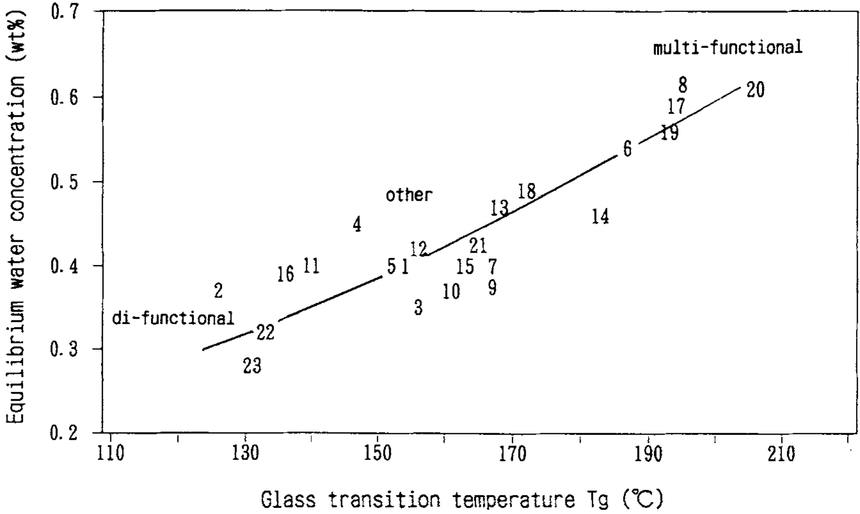

Figure 5 Equilibrium water concentrations of cured epoxy compounds obtained after 168 h water absorption at 85°C/85% RH vs. glass transition temperature.

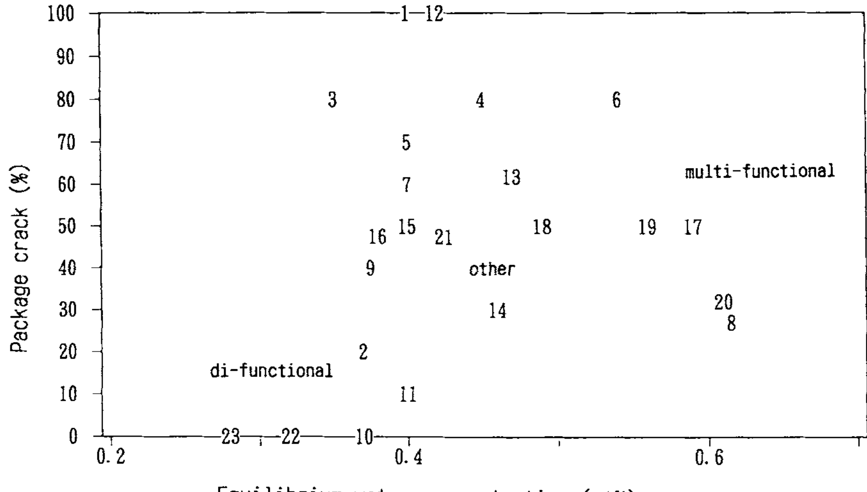

Figure 6 Package crack vs. equilibrium water concentration of the corresponding cured compounds.

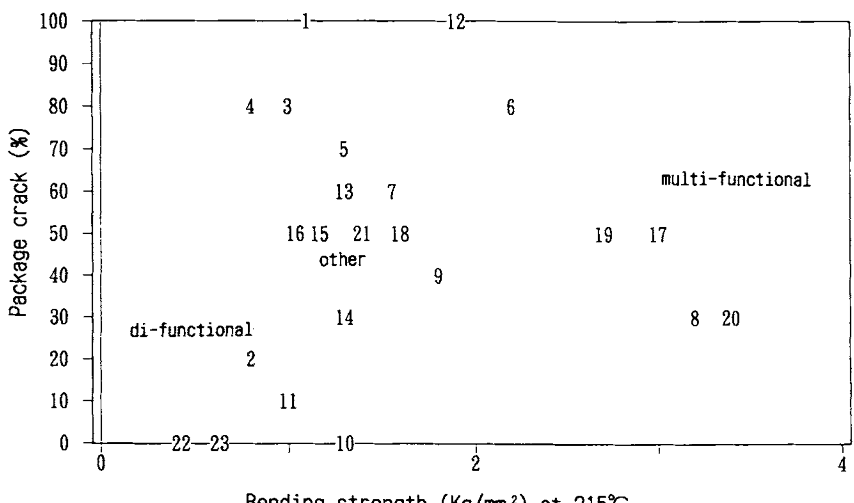

Figure 7 Package crack vs. bending strength of the corresponding cured compounds at 215°C.

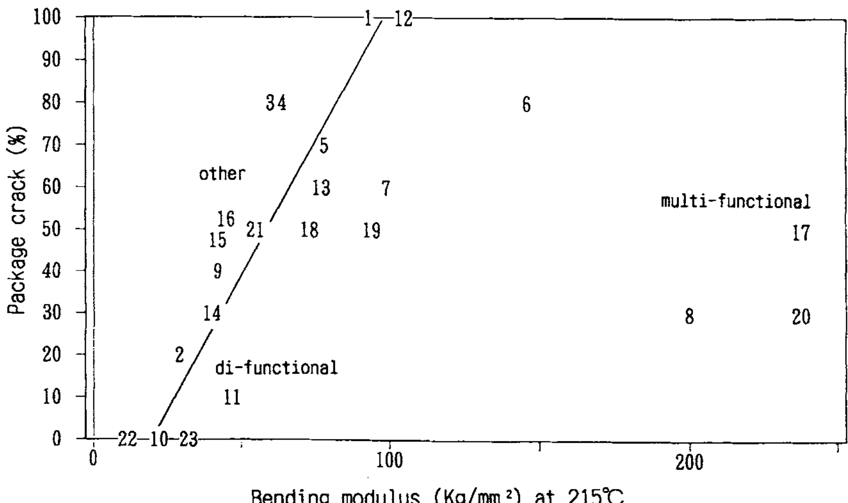

Figure 8 Package crack vs. bending modulus of the corresponding cured compounds at 215°C.

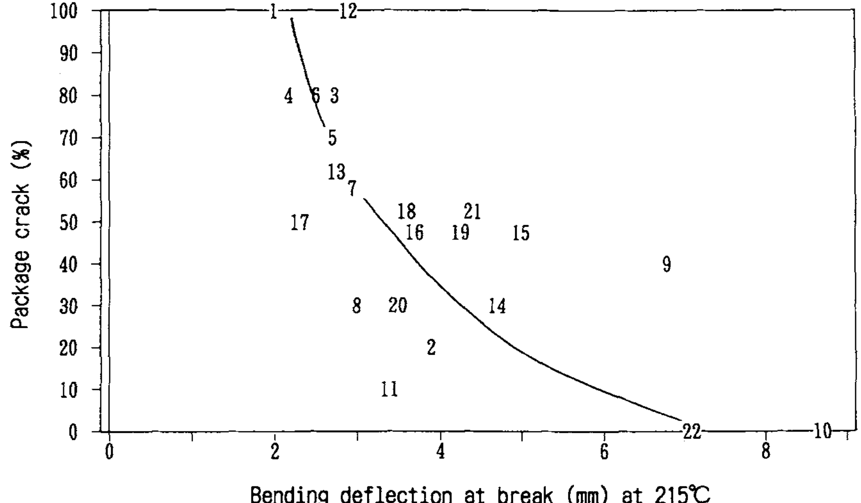

Figure 9 Package crack vs. bending deflection at break of the corresponding cured compounds at 215°C.

Figure 9 shows the package cracks vs. the bending deflection at break of the cured compounds at the same temperature. They decrease as bending deflection value at break increases. The packages from multifunctional epoxy resins absorb more water than do the packages from difunctional or other epoxy resins, and the internal vapor pressure of the water at soldering temperature is consequently higher. Therefore, the packages crack, because this vapor pressure causes higher internal stress than the strength of the epoxy compounds.

The packages from difunctional epoxy resins (**2**, **10**, **11**) with low modulus and high deflection at break showed good durability to soldering. They absorb less water than those having high moduli and from multifunctional epoxy resins. They also have good flexibility to absorb distortion occurring in the soldering process.

Figure 10 shows the package crack appearing on the surface vs. the die pad adhesion index of the compound. These two values correspond quite well with each other for compounds from difunctional and the "other" groups of epoxy. On the other hand, all the compounds from the "multifunctional" group show poor adhesion, but some show fairly low values of package cracks.

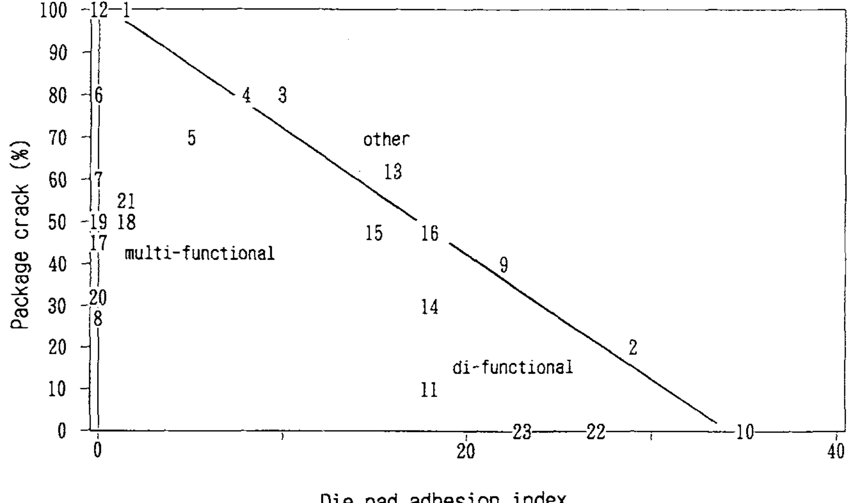

Figure 10 Package crack vs. the die pad adhesion index of the compounds.

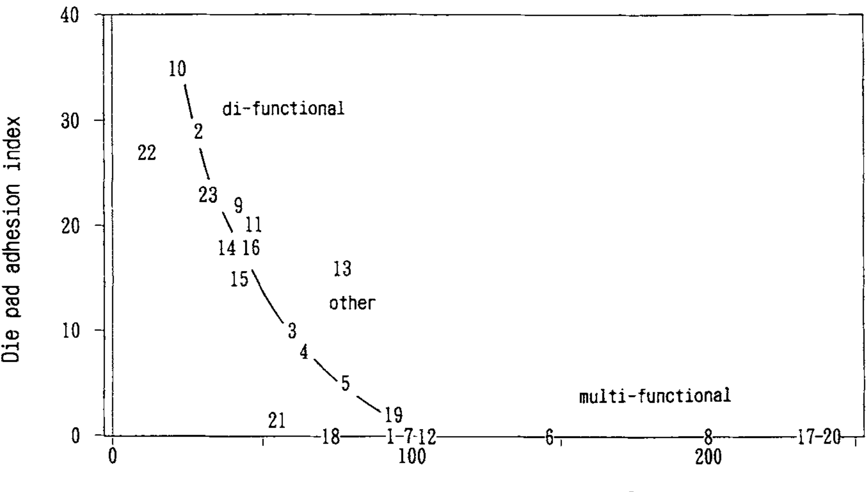

Figure 11 Adhesion index vs. bending modulus of the compounds at 215°C.

Figure 11 shows the adhesion index vs. the bending modulus of the compound at 215°C. These two values show good correlation with each other. Above 100 kg/mm^2 of the bending modulus, there is no adhesion of compounds to the lead frame.

The compounds with low bending modulus from difunctional epoxy resins have good adhesion toward the die pad and require great energy dissipation while delaminating at the soldering temperature. Even after delaminating from the die pad, they seem to be able to deform their shape more easily to reduce the internal pressure by making temporary room to entrap the moisture vapor.

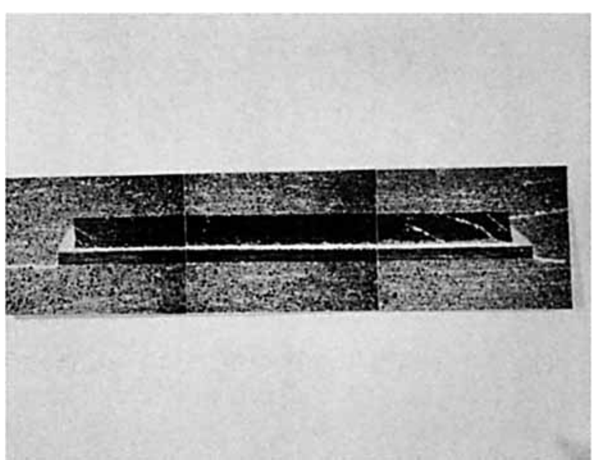

Figure 12a Cross sectional view of a package where delamination has occurred between a die pad and a chip. This also shows hair cracks extending from the die pad into resin.

Some Considerations About Die-Bonding Adhesives

Our study has been focused on the external package cracks as well as the internal delamination between die pads and compounds. The delamination that occurs between a die pad and a chip has not been discussed here. Figure 12 shows typical cross-sectional views of delamination occurring between a die pad and a chip.

Our recent study of adhesive materials shows the same tendency as in the case of the molding compounds against delamination. The adhesive that has low equilibrium water concentration, low modulus,

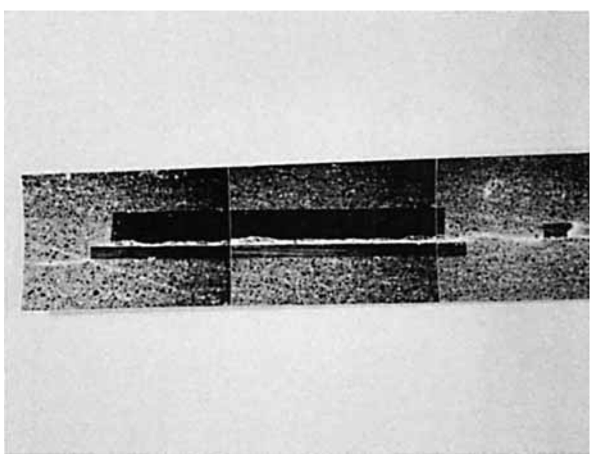

Figure 12b Cross-sectional view of another delamination.

and a high bending deflection value at break shows good results. Indeed, a die-bonding adhesive formulated with the same difunctional epoxy used in the compounds improves the cracking of the packages. The die-bonding adhesives, unlike the molding compounds that face free air to evaporate the moisture or deform to absorb energy cause severe problems when they evaporate their moisture rapidly. Those, like silicone adhesives that do not absorb water like epoxy and have a low modulus, show good results. The other way of solving this problem is to introduce a metal die-bonding material like Pb–solder. A die pad with some slits that was originally introduced to decrease the internal stress of a chip also might be another countermeasure to the problem.

CONCLUSIONS

Many kinds of epoxy resins with phenolic curing agents were formulated into molding compounds. The physical properties of the cured compounds were examined, relating the durability to soldering after moisture absorption. The compounds having a low modulus at high temperature and good adhesion to the die pad had good durability. The compounds from difunctional epoxy—limonen cresol novolac epoxy, tetra-methylbiphenyl epoxy, and naphthalen epoxy— showed especially good durability.

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