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FATIGUE AGING OF ADHESIVE BONDS*

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ABSTRACT

A year long study has been made of the effect of fatigue on the bond between two epoxy encapsulant formulations and a fused alumina disc. The variables studied included isothermal aging at temperatures up to and including the cure temperature and cyclic thermal aging from +74°C to -54°C. The encapsulants were glass microballoon filled epoxies differing only in curing agents. One was cured with an aromatic amine eutectic (Shell Curing Agent Z). The other was cured with diethanolamine. The Z cured encapsulant bond failed completely at the bond interface with little or no aging; infrared evidence indicated a soluble interlayer as a possible cause of failure. The diethanolamine cured encapsulant survived a year of isothermal aging with little or no evidence of bond degradation. Cyclic thermal aging resulted in gradual bond failure with time. An extrapolation of the cyclic aging data indicates that the stresses induced by thermal cycling would result in complete bond failure in about 1200 days.

MASTER

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INTRODUCTION

Electrical/electronic assemblies which include resin encapsulants usually require good adhesion at the encapsulant/dielectric interfaces to minimize electrical breakdowns. Those bonds are also required to be stable for the lifetime of the assembly.

A bonded interface is a discontinuity, and, when the bonded adherends have different coefficients of expansion, built in stress exists at this interface or discontinuity. The problem posed by this condition is whether the built in stress at this interface would eventually result in bond failure and electrical breakdown.

Representative Sandia electronic assemblies quite often include encapsulant bonds to fused alumina insulators and this combination of materials has resulted in concern as to the stability of the bond at the interface. A year long study was initiated to investigate the effect of isothermal and cyclic thermal aging on the stability of that bond.

MATERIALS

The materials evaluated in this investigation are listed in Table I. These include two similar epoxy encapsulants which differ only in the type of amine used as a curing agent. Formulation A is cured with Shell Curing Agent Z, an aromatic amine eutectic (See note Table I). Formulation B is cured with diethanolamine. In the Review of Earlier Work the formulation used in the first reference was an unmodified epoxy cured with curing agent Z. The formulation reported on in the second reference was identical with Formulation A in Table I.

SPECIMENS

The test specimens were prepared by casting and curing the encapsulant up against a fused alumina disc. The encapsulant thus became both the adherend and the bonding agent. The fused alumina discs were 0.1 inch thick by one inch in diameter. The encapsulant was cast in place to a depth of 0.2 inch to more nearly represent an encapsulant rather than a thin bond. The alumina surface was sandblasted and exposed in an argon activated gas plasma immediately prior to bonding.

Since changes in bond strength might be due to changes in the encapsulant, Flexbars per ASTM D790 were prepared for isothermal aging with the bonded specimens. These were cast as bars 10 x ½ x ½ inches and tested in flexure at the same intervals as the bonded specimens.

AGING SCHEDULE

The aging schedule as shown in Table II included isothermal aging at four temperatures including the cure temperature for formulation A cured with Shell Curing Agent Z and at three temperatures including the cure temperature for formulation B cured with diethanolamine. In addition, the schedule included specimens for thermal cycling from -55°C to + 74°C. These were cycled both dry and wet. Dry cycling consisted of placing the specimens in a closed jar with a desiccant. Wet cycling consisted of simply placing the specimens in the cycling chamber where they were exposed to water condensation and freezing. The specimens were removed for testing at intervals of 7, 30, 180 and 365 days. The thermal cycling chamber includes three cycles per 24 hours with a transition time of one hour between temperature extremes.

PROCESSING

After aging, the alumina/encapsulant specimens were first bonded to aluminum plugs with a room temperature curing epoxy adhesive (Hysol EA934) to minimize any effect due to elevated temperature cure and to stress build up in the bond on cooling to room temperature. However, these assemblies tended to fail outside of the alumina/encapsulant bond area and the resulting bond values are listed in the result tables as greater than the measured values. In order to get more valid results, subsequent alumina encapsulant specimens were bonded with a high temperature cure (93°C) tougher adhesive (3M's EC2214R). Coefficients of expansion were matched as closely as possible by bonding Kovar tensile plugs to the alumina discs while aluminum tensile plugs were bonded to the encapsulant surface. The surfaces to be bonded were prepared by sandblasting immediately prior to bonding. A sketch of the bonded assembly is shown in Figure 1. The specimens were all tested in tension at 0.05 inch per minute of head travel. All testing was done at room temperature.

EXPERIMENTAL RESULTS

Encapsulant A Using Shell Curing Agent Z

Specimens using encapsulant A with curing agent Z were all cured as described in the materials section at 93°C and then placed in the various isothermal and cyclic thermal environments as described in Table II. The controls were tested and failed at values of 44 psi or less with failure occurring completely in adhesion. Subsequent inspection of the bond of other untested specimens at 16 power magnification revealed the existence of a fine crack at the edge of the bond interface for all of the Z cured encapsulant/alumina specimens. Specimens selected at random all cleaved cleanly at the bond interface with little or no evidence of cohesive failure. Infrared absorption curves of washings taken from the bond interfaces indicated the presence of a soluble carbonyl containing material at the interface possibly from the CTBN carboxy terminated Butadiene/Nitrile Rubber modifier. Similar tests with different lots of Curing Agent Z with modified and unmodified epoxies resulted in the same failure in adhesion to the fused alumina. Indications were that the failures were peculiar to Curing Agent Z rather than the epoxy resins. A more comprehensive investigation is being initiated to resolve this point.

Encapsulant Using Diethanolamine

The diethanolamine cured encapsulant specimens were cured at 65°C and survived the isothermal aging with very little or no loss in strength. The results are shown in Table IV. The seven and thirty day specimens, which were bonded to the aluminum tensile plugs with the room temperature cured EA934, failed at the EA934 interfaces and did not test the encapsulant/alumina assembly. The assembly strength is therefore greater than the observed value. The 180 and 360 day specimens were bonded with a 93°C cure system 3M's EC2214R. These failed almost completely cohesively in the encapsulant. the 180 day results vary from 3566 psi to 3711 psi. The 360 day results were lower and exhibited more scatter. Evidence of the beginnings of failure in adhesion can be seen in the fracture surfaces shown in Figure 2.

The results of the thermal cycled specimens show a uniform bond degradation with time (Table V). A schematic diagram illustrating how the bond degradation took place in adhesion advancing from the edge toward the center is also shown in Table V. Figure 2 shows the failed surfaces after the full year of exposure to both the isothermal and cyclic thermal aging. While there may be some effect due to wet cycling, the bond degradation is probably due primarily to bond fatigue regardless of the humidity which was present under ambient conditions.

In Figure 3 the bond strength of the thermally cycled specimens was plotted on a semi-log scale against aging time. The initial strength was estimated at about 3000 psi. This gives straight line extrapolations to zero strength in about 1200 days for both the wet and dry cycle test results. This indicates that there is little or no accelerating effect due to moisture.

Table VI gives the flexural moduli of the diethanolamine cured encapsulant. These moduli have not changed appreciably with aging as evidenced by an average value of 472,000 psi compared to the final value of 471,000 psi for the flexbars aged at 66°C. Thus, changes in encapsulant properties as typified by flexural modulus should not be a significant factor in the results.

REVIEW OF EARLIER WORK

Because of these results, earlier bonding studies of similar encapsulants using Shell Curing Agent Z were reviewed. The first study[1] included an alumina filled unmodified epoxy resin cured with Z and bonded to aluminum and Kovar substrates. These bonds were cured at 93°C. The bonds to aluminum survived one year of isothermal aging both wet and dry at temperatures from -55°C to 74°C. Testing was done at the exposure temperature. The failures were primarily cohesive at 3000 to 4000 psi. The bonds to Kovar reflected the bond line stresses due to cooling from the cure temperature of 93°C. The failing stresses at -55°C were primarily in adhesion at about 1000 psi. Room temperature aging and testing exhibited both cohesive and adhesive failure at about 2000 psi. Those specimens aged and tested at 74°C failed cohesively at about 3000 psi.

The second study[2] was similar to the study reported in this paper in that the encapsulant formulations were similar and the bond was to fused alumina. The bond strength of the Z cured encapsulant after curing was about 50 percent (1424 psi) of the bond strength of the diethanolamine cured encapsulant (2973 psi) with failure of the Z cured encapsulant bond being primarily in adhesion. After three thermal cycles (-45°C to +71°C), the bond of the Z cured encapsulant tended to fall apart with the average bond strength of five survivors of twelve bonds being 378 psi. The author implies the presence of a weak interlayer as being responsible for the poor results. No attempt was made to identify any interlayer. The specimens used in this second study were one half inch in diameter and would develop lower stresses than would the one inch diameter specimens evaluated in this investigation. This would account for the higher test values.

These two investigations indicated that the stress sensitive nature of Z cured epoxy systems in not an isolated phenomena and is worthy of further study.

STRESS FACTORS

Stress inducing factors for the materials combinations evaluated in this report are defined by the properties listed in Table III. These are the lower modulus (see Table III) of the two adherends forming the test specimen, the difference in the thermal expansions of the two adherends (α) and the thermal excursions (see Table III) of the two assemblies from the zero stress level. In this case the cure temperature of the two formulations (see Table II) are assumed to be the zero stress levels. For the Shell Z cured assembly the thermal excursion was cooling from the cure temperature (93°C) to room temperature

(24°C) where failure was first noticed. The temperature excursion for the DEA cured assembly is from the cure temperature 65°C to the thermal cycle extreme of -55°C, i.e., 120 centigrade degrees. When these are combined in the expression $\alpha E \Delta T$, the DEA cured assembly has twice the stress factor (1695) as the Z cured assembly (850). In spite of this, it took repeated thermal cycling of the DEA cured specimens to initiate failure in adhesion. This would support the evidence that a contributory factor in the form of migratory interlayer is present and is the reason for a completely adhesive failure at the interface.

The results plotted in Figure 3 are valid for the specimen design as evaluated (Figure 1) and are not to be construed as being valid for other specimen designs using the same adherend and encapsulant. However the results do show that under the isothermal and thermal cycling aging conditions reported in this investigation the diethanolamine cured encapsulant bond to alumina is far more durable than the Shell Z cured encapsulant.

SUMMATION

1. The evaluation of bond fatigue for the Shell Z cured encapsulant to fused alumina was rather inconclusive in that all the specimens failed at the encapsulant/alumina interface with no extended aging. There was evidence, using infrared absorption techniques, of a soluble carbonyl containing material at the interface. A more comprehensive investigation of the reason for these failures has been initiated.

2. The DEA cured encapsulant bond to fused alumina seems to have little or no bond weakening effect due to isothermal aging at temperatures up to 66°C for the full year of the investigations.

3. The DEA cured encapsulant bond to fused alumina does exhibit adhesion failure when subjected to thermal cycling fatigue for periods up to one year. The failure in adhesion progresses gradually from the outside edge toward the center.

4. There is no significant degradation of the encapsulant when aged isothermally at temperatures up to 66°C for 432 days as evidenced by flexural moduli measurements.

REFERENCES

1. Quant, A. J., "Adhesion of Encapsulants," Sandia Report, SC-DR-67-332, May 1967.

2. Creed, K. E., "Alumina Ceramic Surface Cleaning for Optimum Bonding of Resin Encapsulant," General Electric Report, GEPP-301A, July 1977.

TABLE I

Encapsulant Formulations

A	CTBN Modified Epoxy	75 pbw
	Shell Curing Agent Z	15 pbw
	3M GMB B=40	25 pbw
	Cure 4 hrs RT + 4 hrs 54°C + 16 hrs 93°C	
B	CTBN Modified Epoxy	75 pbw
	Diethanolamine	9 pbw
	3M GMB B-40	25 pbw
	Cure 16 hrs 65°C	

NOTE: CTBN means Carboxy Terminated Butadiene Nitrile rubber.
3M GMB B-40 = Minnesota Mining and Manufacturing Glass Microballoons.
Shell Curing Agent Z = An Aromatic Amine Eutectic including Methylene Dianaline, Metaphenylene Diamine and Phenyl Glycidyl Ether.

TABLE II

AGING SCHEDULE

1. Isothermal

Adhesive A (2)

Aging temp °C	No. of Specimens per Sample Sampling Schedule Days				
	0	7	30	180	360
93	3	3	3	3	3
82		3	3	3	3
71		3	3	3	3
23		3	3	3	3

Adhesive B (DEA)

Aging temp °C	0	7	30	180	360
65	3	3	3	3	3
54		3	3	3	3
23		3	3	3	3

2. Thermal Cycling

Thermal Cycle	Condition	Sampling Schedule Days				
		0	7	30	180	360
74°C to -54°C	Dry[a]	3	3	3	3	3
Every 8 hours	Wet[b]		3	3	3	3

(a) Dry cycle consists of placing specimens in chamber in desiccated jar.

(b) Wet cycle consists of placing specimens directly in chamber where specimens are subject to water condensation and freezing.

TABLE III

STRESS FACTORS

	FUSED ALUMINA	828/Z/GMB	828/DEA/GMB
Zero Stress Level (Cure Temp)		93°C	65°C
Coefficient of Expansion (in/m x 10^{-6}/°C)	8.6	36.0	40.0
Modulus of Elasticity (E) psi	53×10^6	0.45×10^6	0.45×10^6
Difference in Coefficient of Expansion (α)		27.4	31.4
Maximum Temperature Excursion (ΔT)		69°C	120°C
Stress Factor ($\alpha E \Delta T$) psi		850	1695

TABLE IV

ISOTHERMAL AGING OF DEA CURED ENCAPSULANT BOND TO Al_2O_3 TENSILE ADHESION (PSI)[a]

Aging Temp. °C	Aging Time Days 7	30	180	360
24	---	> 2203[b]	3590[c] (3745-3312)[d]	2611[c] (3407-1783)[d]
54	> 2780[b]	> 1830[b]	3566[c] (4191-2942)	3265[c] (4172-2343)
66	> 2715[b]	> 1850[b]	3711[c] (4191-3057)	2919[c] (3790-2165)

(a) Each value is average of 3 specimens.

(b) Greater than 50% failure in EA934 bond to tensile plugs or to encapsulant with little failure in encapsulant/Al_2O_3/bond.

(c) 100% cohesive failure in encapsulant.

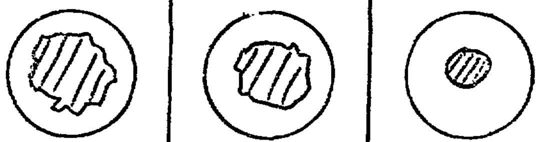
(d) Figures in parentheses are high and low test values.

TABLE V

THERMAL CYCLING AGING OF DEA CURED ENCAPSULANT BOND TO Al_2O_3 TENSILE ADHESION (PSI)

No. of Days (3 cycles per day) (+74°C to -55°C)

7		30		180		360	
Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry
> 1046 (a)	> 773 (a)	1670 (b)	2073 (b)	925 (c) (1133-668)	1046 (c) 1140-923	515 (d) (573-439)	728 (d) (815-637)



FAILURE IN ADHESION

FAILURE IN COHESION

(a) Primarily failure of EA934 to aluminum.

(b) About 80% cohesive failure in encapsulant.

(c) About 50% cohesive failure in encapsulant.

(d) 10 to 20% cohesive failure in encapsulant.

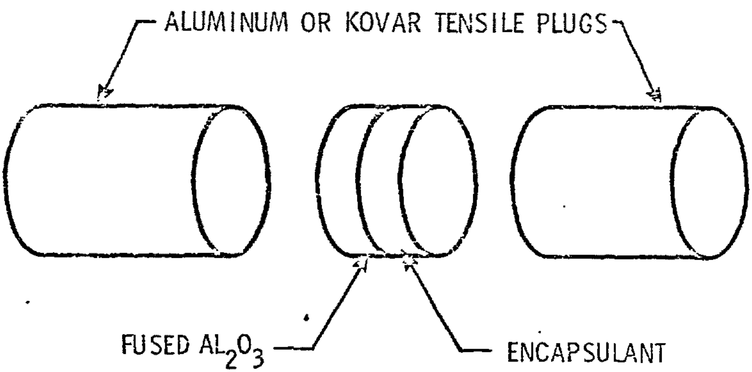
TABLE VI

FLEXURAL MODULI OF ENCAPSULANT (828/DEA/GMB)

WITH ISOTHERMAL AGING

Aging Days	Temp. °C	Flexural Modulus per ASTM
0	24	471,000
7	"	471,000
30	"	492,000
90	"	492,000
180	"	492,000
432	"	451,000
0	55	451,000
7	"	471,000
30	"	492,000
90	"	492,000
180	"	492,000
432	"	470,000
0	66	451,000
7	"	471,000
30	"	481,000
90	"	481,000
180	"	481,000
432	"	471,000

FIGURE I



EA934 (RT CURE) OR EC2214R (200°F CURE)
USED TO BOND AL_2O_3 ENCAPSULANT
ASSEMBLY AFTER AGING AND PRIOR TO TEST.

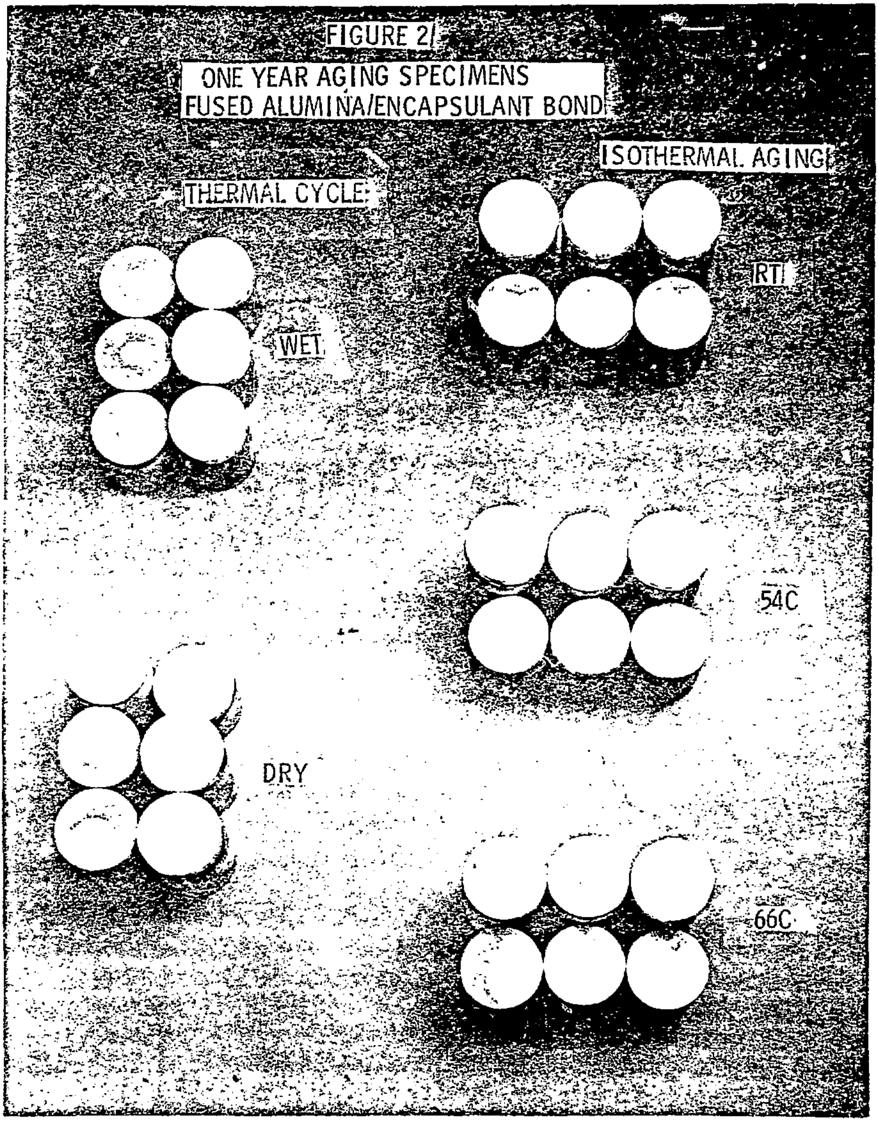


FIGURE 2
ONE YEAR AGING SPECIMENS
FUSED ALUMINA/ENCAPSULANT BOND
ISOTHERMAL AGING
THERMAL CYCLE
RT
WET
54C
DRY
66C

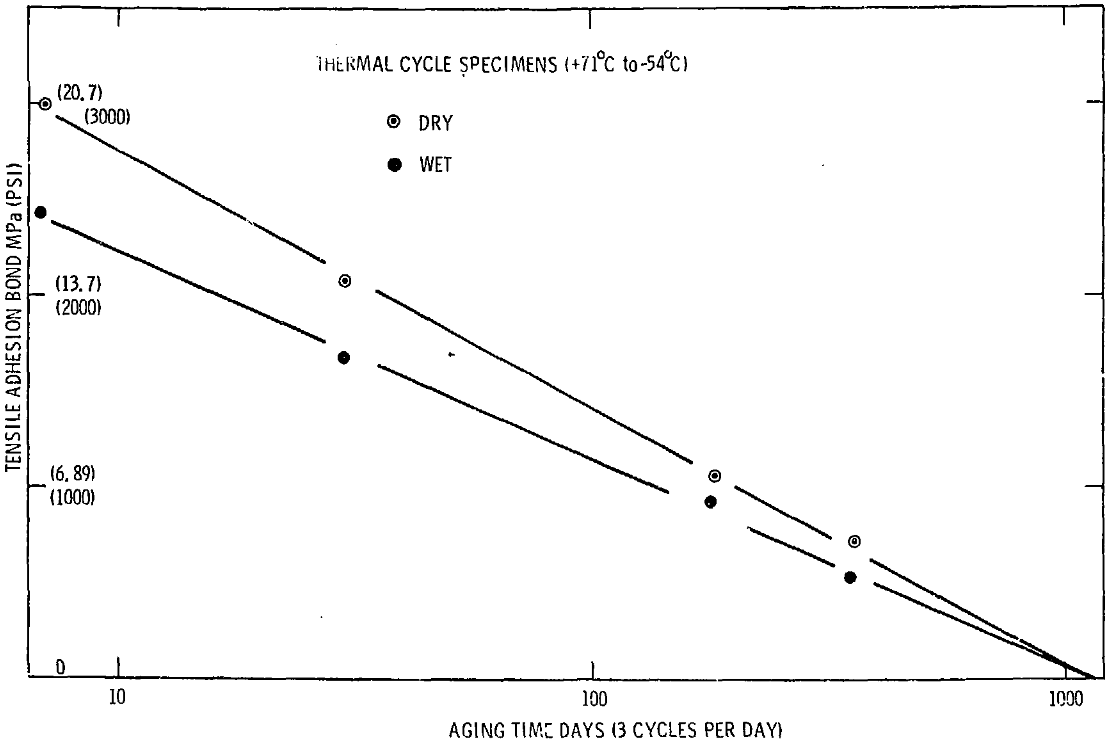


FIGURE 3. AGING TIME vs BOND STRENGTH FOR THERMAL CYCLED SPECIMENS USING DEA CURED ENCAPSULANT