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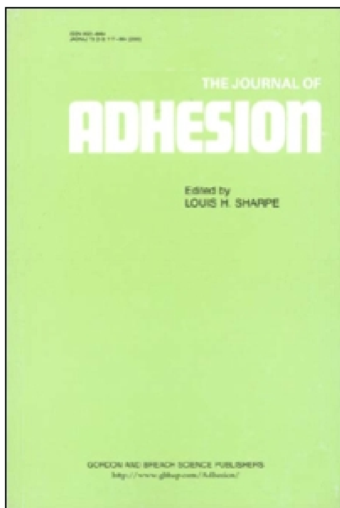

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Thermal Shock Failure in Thick Epoxy Coatings

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In this paper we describe an apparatus for reproducibly measuring thermal shock resistance of thick polymer layers bonded to metals. The thermal shock behavior is discussed in terms of epoxy samples bonded to an aluminum substrate. It was found that both high resin toughness and low resin thermal expansion coefficient improved thermal shock resistance of thick coatings, but only a sample containing 60 wt.% glass beads did not develop a failure crack. Effects of sample thickness, temperature gradient, and resin composition on thermal shock behavior are discussed.

KEY WORDS Thermal shock; epoxy coatings; thermal stress; epoxy adhesives; stress cracking; failure.

INTRODUCTION

Thermal stress for present purposes may be defined as the internal polymer stress generated during heating or cooling of a polymer sample which is attached to a substrate of different thermal expansion coefficient, or is otherwise constrained from normal thermal expansion and contraction. Thermal shock is a failure process in which such a constrained polymer sample is rapidly cooled or heated, leading to crack development when the polymer internal stress exceeds the polymer or interface strength. The present report attempts to relate the thermal stress development in

an epoxy resin to its resistance to thermal shock failure. Effects of resin composition, filler content, thickness, and temperature gradient on thermal shock and thermal stress were studied. A new method for thermal shock resistance determination was developed for use in this study.

The development of thermal stress in thick (>0.127 cm) epoxy coatings bonded onto aluminum was shown in a recent study[1] to deviate from that found in thin coating studies,[2,3] particularly as the Tg and elastic modulus of the epoxy increase. Equation (1) has been shown to describe *thin* coating stress levels at a given $T < Tg$.[2-4]

$$\text{Stress } (T < Tg) = \int_{T}^{Tg} (\alpha_E - \alpha_S)\, dT \qquad (1)$$

Where α_E is the expansion coefficient of the epoxy resin below Tg and α_S is the thermal expansion coefficient of the metal substrate. Thicker coatings (>0.127 cm) exhibit thermal stresses that do not fit Eq. (1) as well. The observed deviation in measured *vs.* calculated stress for thick coatings was found to be a result of the extensive crosslinking in the high Tg epoxy samples; they resisted stress relaxation above Tg. Also, a significant thermal gradient developed within the thick coatings.[1]

Thermal shock behavior is usually examined on a comparative basis. The most universally used test is the Olyphant washer,[5] where the resin is placed in a high thermal stress environment; the number of cycles of a given temperature gradient withstood without resin cracking is taken as an indication of the thermal shock resistance. The most recent work in thermal shock by McCoy[6,7] and Rahut[8] uses a different test configuration but the results still are qualitative, with no indication of the stress levels achieved. A quantitative approach to thermal shock determination is needed to determine the stress levels obtained and to show how the polymer properties interact to control thermal shock resistance. A thermal shock apparatus is presented in this study, allowing a more quantitative analysis of thermal shock and a direct comparison with the corresponding thermal stress analysis. This leads to better understanding of the factors controlling thermal shock resistance.

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EXPERIMENTAL

A Materials and sample preparation

The first sample series was prepared by varying the ratio of a standard diglycidylether of bisphenol A type epoxy (Epon 828†) to an aliphatic epoxy resin (diglycidylether of butanediol, Araldite‡ RD-2) with methylene dianiline (MDA) as the curing agent. These resins were selected because they are simple in chemical structure, and when cured with methylene diamiline under the conditions used here the curing reaction between epoxy groups and primary and secondary amino groups goes to completion, without appreciable side reactions.[9–13] No strong tertiary amines are present to promote the etherification side reaction. The cured systems can be regarded as being chemically at equilibrium. The stress developed because of the curing reaction of similar systems has been shown to be negligible relative to the stress developed because of the thermal expansion coefficient mismatch between polymer and metal substrate.[13] Care was taken to provide uniform curing mass, the temperatures cycles and times, etc., for both thermal stress and thermal shock samples. The resin-curing agent batch size was approximately 150 gms in all tests. The Epon 828, because of its backbone aromatic rings, is a more rigid molecule and gives a much higher *Tg* upon curing than the RD-2, which contains only CH_2 units, without aromatic rings. RD-2/MDA has $Tg < 100°C$, whereas Epon 828/MDA gave $Tg = 170°C$ for the curing conditions used. The MDA was added in stoichiometric amounts, and the compositions tested contained 10 mole percent and 30 mole percent of RD-2 resin. The MDA and diepoxide materials were heated to 100°C and were mixed and cured for 2 hrs at 80°C, 2 hrs at 150°C and 2 hrs at 180°C. Adding the more flexible Araldite RD-2 to Epon 828 gave lower *Tg* and higher ductility, but a poorer thermal expansion coefficient match than the standard Epon 828-MDA composition.

The second sample series involved the addition of glass beads to an Epon 828 and stoichiometric (26 phr) MDA mixture. The compositions tested contained 20% and 60% by weight glass

† Trade name of Shell Chemical Co.
‡ Trade name of Ciba-Geigy Chemical Co.

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beads,† of diameter range 0.00051–0.0061 cm. Addition of the glass beads resulted in a better thermal expansion coefficient match of the polymer-glass mixture to the aluminum metal. The MDA and Epon 828 were heated to 100°C and mixed. The glass beads were added to this mixture and the mixture was continuously stirred at 80°C on a hot plate for thirty minutes before pouring into the mold. This allowed the viscosity of the epoxy mixture to increase to a level that prevented the glass beads from settling after pouring into the mold. The curing schedule after pouring was the same as that for the first sample series except that the time at 80°C was reduced to 1.5 hrs. The difference between preparation conditions for the glass-bead materials and the other samples is that the glass bead materials were stirred on a hot plate at 80°C for 0.5 hrs., whereas the other samples were placed in an oven at 80°C during the same period. The authors believe this difference is not significant, especially since cure is taken to completion in both cases.

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B Thermal measurements

The glass transition temperatures were determined by thermal analysis on an Omnitherm Q.C. 25 apparatus at a heating rate of 20°C/min. For thermal expansion coefficients, a DuPont 941 thermomechanical analyzer was used at a heating rate of 5°C/min; three measurements were made on each sample.

For thermal stress determination a bending beam technique applied by Dannenberg[2] and others[3,4] was used. The principle involved is the same as that for a bimetallic strip in a thermostat; heating causes one material to try to expand more than the other, causing beam curvature to develop. The interfacial stress can be calculated from the moduli and curvature, by Eqs (2) and (3) below:

$$S = P/(bh_1) = E_2 h_2^3/12h_1^* 8d/lH^* F(m, n) \tag{2}$$

$$F(m, n) = ((1 - mn^2)^3(1 - m))/(1 + mn^3) + ((mn(n+2)+1)^3 + m(mn^2 + 2n + 1)^3)/(1 + mn)^3 \tag{3}$$

where S is the stress through the resin cross sectional area, P is the total force required to bend the beam, b is the width, E_2 is Young's

† Ferro Corp. Cataphote Division of Jackson, MS. Product No. PR-11R.

modulus of the metal (6.96×10^{10} Pa), h_1 is the thickness of the resin, h_2 is the thickness of the metal (0.013 cm), H is the thickness of the resin plus the metal, l is the length of the beam between supports (5 cm), d is the deflection of the beam center, m is E_1/E_2, and n is h_1/h_2. $F(m, n)$ is a modulus/thickness ratio parameter of Inoue and Kobatake,[2b] defined by Eq. (3).

Each of the physical measurements of the previous paragraph has been described in greater detail elsewhere.[1]

C Thermal shock analysis

Figure 1 shows the thermal shock apparatus. The epoxy-aluminum sample A̰ was clamped to the heat sink B̰, (also heated to 180°C) by the use of C-clamps. The polymer surface and aluminum plate thermocouples were put in place as shown in Figure 1, with a highly thermally conductive silicone paste C̰ for good heat transfer. A chart recorder was turned on and the heat sink-sample assembly was inverted, resting on the two long-screw ends of the C-clamps. This procedure provided maximum gravitational contact of the coolant with the hot metal surface. Air cooling was permitted until the interface thermocouple reached 126°C. This arbitrarily selected temperature was that reached by the first sample in the transfer

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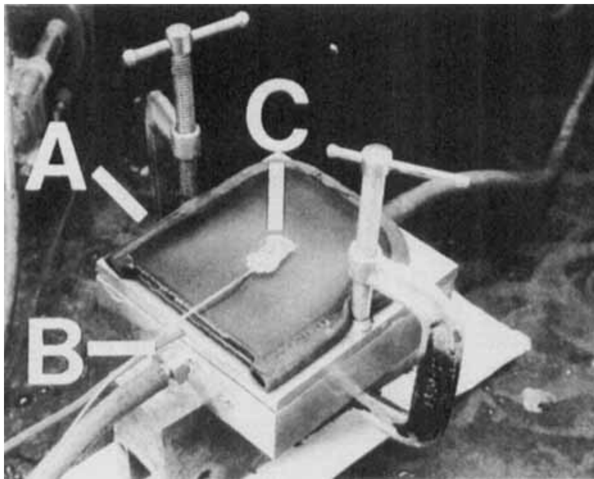

FIGURE 1 Thermal shock apparatus.

process from the oven to the heat sink, and thus this same temperature for the start of rapid cooling was maintained as a constant for later samples. When the temperature of the epoxy-metal interface reached 126°C, a pump was turned on to circulate ice water at a defined rate through the heat sink and over the aluminum plate. The temperature of the epoxy-metal interface and the outside epoxy surface were recorded as a function of time until the epoxy coating failed, which could be detected visually (and often audibly).

The sample compositions tested in the thermal shock analysis were the same as those tested in the thermal stress analyses in this study and in the previous work.[1] The samples were prepared by curing a 0.635 cm thick coating of each of the epoxy compositions onto one side of an aluminum plate 10.16 cm × 10.16 cm × 0.635 cm. To prepare the aluminum plate for bonding, the surface was abraded with 3M #240 emory cloth to remove the oxide layer and was degreased with trichloroethylene solvent. After the curing cycle, the epoxy coated aluminum was retained at 180°C until testing.

The aluminum plate contained a 0.32 cm diameter hole drilled 0.16 cm from the epoxy bonded surface and 5.08 cm deep (Figure 1). This provided for insertion of a thermocouple (0.254 cm outside diam., 0.08 cm tip diam.) during testing.

Two other samples of Epon 828 and a stoichiometric amount of MDA were prepared, one 0.635 cm thick and the other 0.32 cm thick. The 0.32 cm thick sample was tested at the same cooling rate as described above and illustrated the effect of coating thickness upon the thermal shock resistance. In another test, a 0.635 cm thick sample was also tested at a lower circulating pump rate than the previous samples. This was intended to determine the effect of cooling rate upon the thermal shock resistance, but the interface temperature was found to be the same; in both cases the water flow rate was sufficient to maintain the boundary layer at 0°C.

The reproducibility of the thermal shock data was examined by testing five samples of the stoichiometric Epon 828/MDA composition. Standard deviations for the five were calculated for the time of failure, epoxy-metal interface temperature and the epoxy surface temperature at failure.

The temperature gradient developed through the thickness of the

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epoxy coating during cooling was measured. A stoichiometric Epon 828/MDA sample was cured with three thermocouples (0.08 cm tip diam.) placed at locations of one-quarter, one-half and three-quarters of the coating thickness. After complete cure, the 180°C sample was placed into the heated thermal shock apparatus with the two normal thermocouples (epoxy surface and epoxy-metal interface) and the three thermocouples in the epoxy coating connected to the chart recorder. The temperature at each thermocouple location was measured as the sample was cooled to 0°C by the circulating ice water.

D Tensile properties

Tensile strength and modulus were measured using an Instron TM-S 1130 tensile tester according to ASTM D638–68, with dog-bone shape samples 3.18 mm thick and a crosshead speed of 0.5 mm/min.

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RESULTS AND DISCUSSION

A Thermal stress analysis

The glass transition temperature (*Tg*) and the coefficients of expansion below and above the *Tg* were determined for each of the samples containing an amount of flexible aliphatic epoxy or of glass beads. These results are presented in Table I with standard deviations ($N = 5$) in parentheses.

The RD-2 resin has more backbone CH_2 groups, thus on curing

TABLE I
Tg and coefficients of expansion

Sample	*Tg* (°C)	Expans. coeff. $\times 10^6$, °C^{-1} $<Tg$	$>Tg$
Epon 828-MDA Control	170	62.3 (1.7)	158 (3.0)
10 mole % RD-2†	165	74.6 (3.3)	148 (7)
30 mole % RD-2†	146	46.5 (4.5)	132 (5)
20 wt.% glass†	169	46.5 (4.4)	139 (6)
60 wt.% glass†	171	29.2 (1.6)	83.2 (1.0)

† Added to Epon 828-MDA

TABLE II
Elastic moduli. Modulus × 10^9 (Pa)

Sample	−30°C	0°C	22°C	50°C	80°C	100°C	130°C
10 mol. percent RD-2	2.48	2.23	2.08	1.77	1.57	1.21	1.30
30 mol. percent RD-2	2.50	2.18	2.23	1.79	1.50	1.39	0.965
20 wt. percent Glass	2.90	2.74	2.42	2.13	1.93	1.96	1.78
60 wt. percent Glass	5.10	4.27	4.08	4.07	3.70	3.43	3.20

gives a lower *Tg* than the Epon 828 resin. One would expect the *Tg* of a combined system to decrease as more of the RD-2 resin is added. This expected effect is observed in the *Tg* decrease between the control, 10 mole percent and 30 mole percent RD-2 compositions. Adding RD-2 resin would also be expected to increase the coefficients of expansion, but the data in Table I are not clear on this point; perhaps the expansion data for the 30% RD-2 sample are in error.

Non-polymeric fillers have a predictable additive effect upon the coefficient of expansion of the epoxy matrix. The literature value of the coefficient of expansion for the glass beads is 84.7×10^{-7} (K^{-1}).[14] By a simple addition rule, the system coefficients of expansion should decrease to $42.4 \times 10^{-6} K^{-1}$ and $25.4 \times 10^{-6} K^{-1}$, respectively, as more of the glass beads are added. In Table I, the results for 20 wt.% and 60 wt.% glass beads are only slightly higher than these estimates.

The elastic moduli for each of the samples were determined from the stress-strain curves of the tensile experiments and are presented in Table II.

The modulus data were fitted with a second-degree polynomial equation and these functions, along with the values in Table I, were used in the calculations of the thermal stresses from Eqs (1) through (3). The polynomial coefficients and the correlation coefficient for each sample are given in Table III.

Figure 2 shows the deflection of the epoxy-coated aluminum strips as a function of temperature. As previously found,[1] all curves show a change in slope, corresponding to the change in the coefficient of expansion, at the *Tg* of each sample. The deflection is a indication of the amount of strain, which is determined by the sample coefficient of expansion. Any change in the coefficient of expansion therefore results in a change in the deflection.

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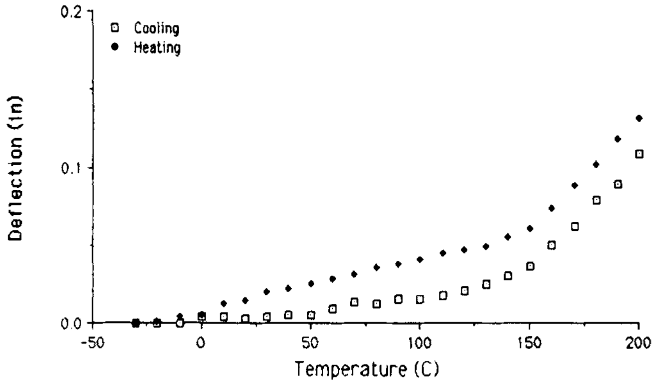
TABLE III
Elastic modulus functions. $E(\text{Pa}) = A0 + A1^*T + A2^*T^2$ $T = (°\text{C})$

Sample	A0	A1	A2	Corr.
10 mol. percent RD-2	2.218×10^9	-0.972×10^7	0.151	0.982
30 mol. percent RD-2	2.212×10^9	-0.531×10^7	-0.337	0.988
20 wt. percent Glass	2.629×10^9	-1.02×10^7	0.286	0.987
60 wt. percent Glass	4.497×10^9	-1.39×10^7	0.334	0.969



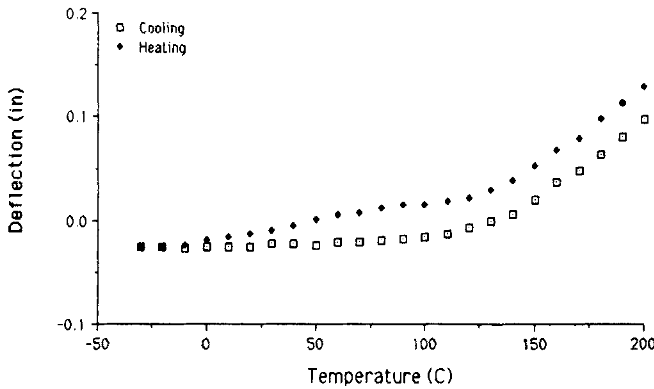


FIGURE 2 Epoxy-metal strip deflection *vs*. temperature. a) 10 mole % RD-2 in Epon 828/MDA, b) 30 mole % RD-2 Epon 828/MDA.

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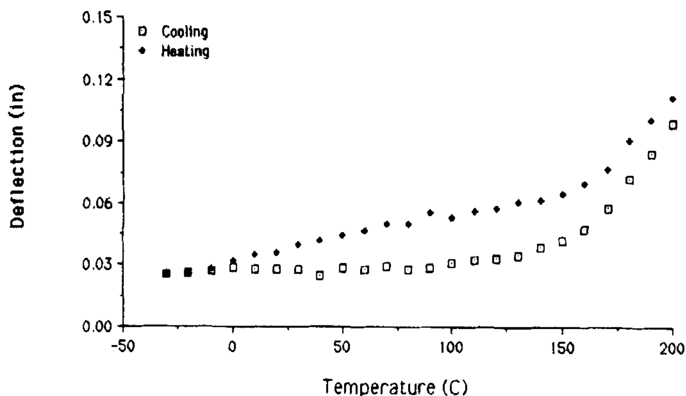
All of the curves show positive deflections, *i.e.*, expansive stresses, except for the 30 mole percent RD-2 sample. The 30 mole % RD-2 sample behavior is similar to that of the 100% excess MDA sample of the previous work.[1] Both have relatively lower *Tg* and elastic moduli, and so behave more like the samples in thin coating studies[2,3] in that contractive stresses begin to appear. The



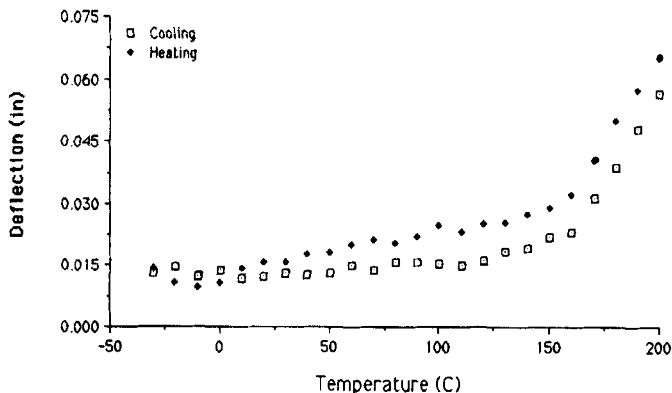


FIGURE 3 Epoxy-metal strip deflection *vs.* temperature. a) 20 wt.% glass beads in Epon 828/MDA, b) 60 wt.% glass beads in Epon 828/MDA.

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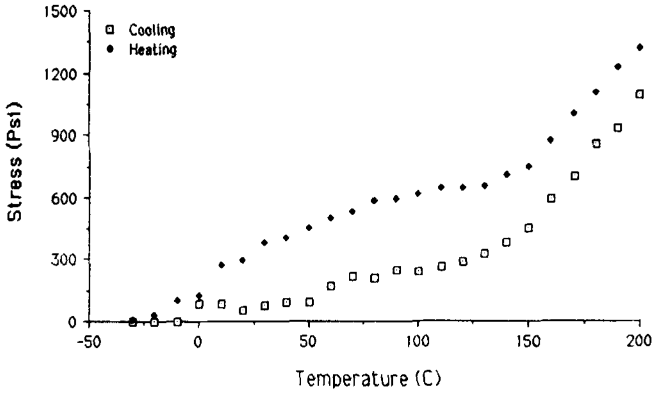
samples show various degrees of irreversible stress development, as in the earlier work.

The deflection of Figures 2 and 3 were converted into stress levels by the use of Eqs (2) and (3); stress *vs*. temperature curves are shown in Figures 4 and 5. The stress curves are affected both by the coefficient of expansion and by the elastic modulus of the epoxy.



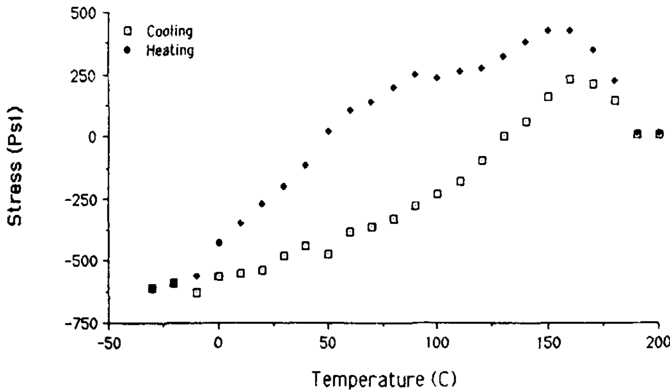


FIGURE 4 Epoxy coating stress *vs*. temperature. a) 10 mole % RD-2 in Epon 828/MDA, b) 30 mole % RD-2 in Epon 828/MDA.

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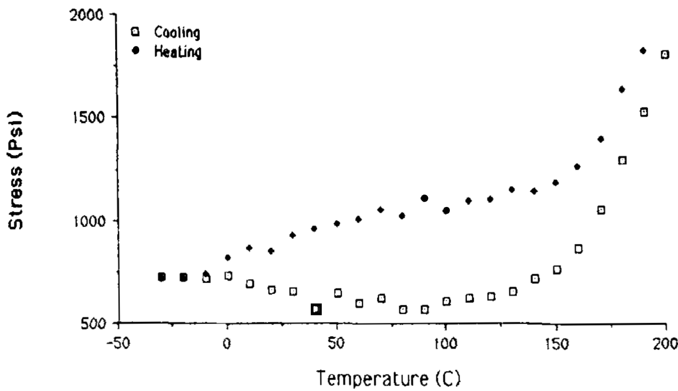

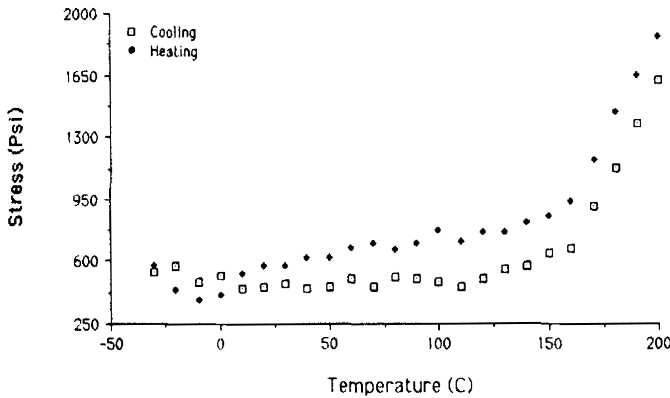

FIGURE 5 Epoxy coating stress *vs*. temperature. a) 20 wt.% glass beads in Epon 828/MDA, b) 60 wt.% glass beads in Epon 828/MDA.

The change in the coefficient of expansion at the *Tg* causes an abrupt change in the slope of the stress curves. The elastic modulus steadily decreases with an increase in temperature and causes the stress level to decrease with temperature. For the low modulus and *Tg* sample (30 mol percent Rd-2), where the modulus goes to zero in the higher range of temperatures, the stress level will also go to

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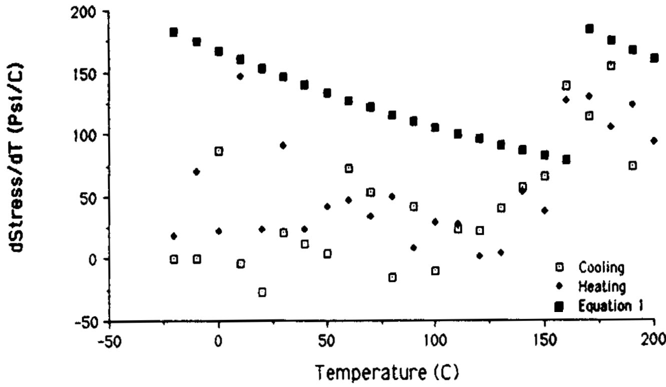
zero and will distort the coefficient of expansion effect. This sample is also the only one with contractive (negative) stresses present.

The difference between the stress development found experimentally and that predicted by Eq. (1) is shown by comparison of the derivative of Eq. (1) with the corresponding derivative of the curves in Figures 4 and 5. These results are shown in Figures 6 and 7. The



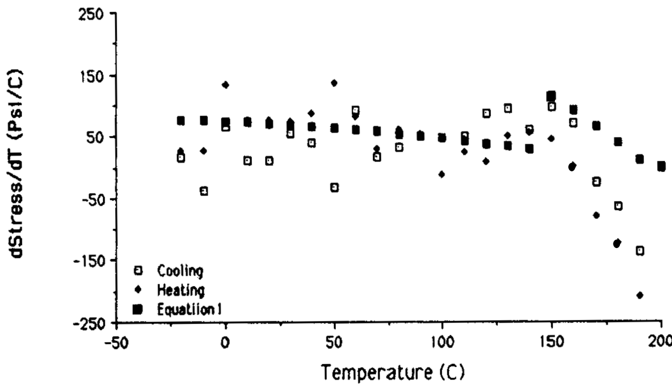


FIGURE 6 Comparison of Eq. (1) with experimental results. a) 10 mole % RD-2 in Epon 828/MDA, b) 30 mole % RD-2 in Epon 828/MDA.

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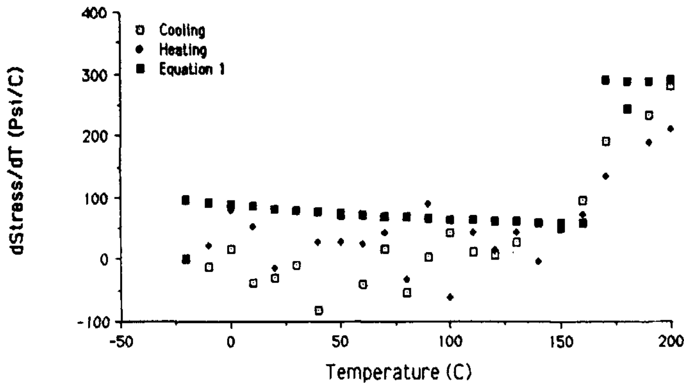

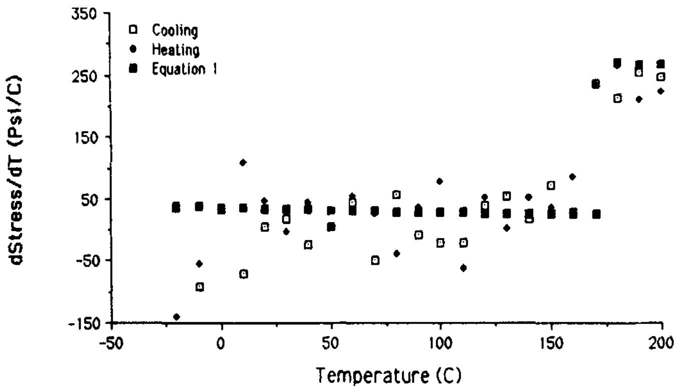

FIGURE 7 Comparison of Eq. (1) with experimental results. a) 20 wt.% glass beads in Epon 828/MDA, b) 60 wt.% glass beads in Epon 828/MDA.

experimental results have approximately the same shape but are generally lower in value than the results obtained from Eq. (1). Again, it is the 30 mol percent RD-2 sample that shows the best agreement with Eq. (1). The good fit of the samples with glass beads is a result of the high volume of the sample matrix being glass. Any deviation from the equation that might be caused by the

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epoxy resin is lessened with increasing amounts of glass beads in the sample.

B Thermal shock analysis

All of the samples tested in thermal shock failed by crack development upon cooling from 180°C to 0°C, except for the composition with 60 weight % glass beads. Thermal shock results, given in Table IV, show the time for each sample to fail after the cooling water was turned on, the epoxy-metal interfacial temperature at failure and the epoxy free surface temperature at failure. "Percent excess" refers to stoichiometric excess of MDA; greater excess means greater flexibility, fewer crosslinks, and lower *Tg*; the crosslink density and *Tg* can be quantitatively predicted.[10]

The reproducibility of the experimental results was determined by testing five samples of the Epon 828-MDA stoichiometric (0% excess) composition, Table V. The standard deviations calculated show good reliability of the data in Table IV and comparisons can be made between the different samples presented in Table IV.

The thinner epoxy coating (0.32 cm thick) showed better resistance to thermal shock and longer failure time (5.68 min) than the thicker coating (0.635 cm thick, 1.97 min). This is believed to be the result of a larger thermal gradient being formed in thicker

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TABLE IV
Thermal shock results

Sample	Cooling rate	Time to fail (min)	Interfacial temp. (°C)	Surface temp. (°C)
0% Excess MDA, 0.635 cm thick	1	1.97	3	72
0% Excess MDA, 0.32 cm thick	1	5.68	1	10
0% Excess MDA, 0.635 cm thick	2	2.10	8	57
23.1% Excess MDA	1	1.27	8	79
50.0% Excess MDA	1	2.39	2	52
100% Excess MDA	1	4.76	1	30
10 mol. percent RD-2	1	2.62	0	52
30 mol. percent RD-2	1	2.49	2	42
20 wt. percent Glass	1	1.80	2	81
60 wt. percent Glass	1	————	No failure	————

TABLE V
Thermal shock data reproducibility

Trial	Time to fail (min)	Interfacial temp. (°C)	Surface temp. (°C)
1	1.97	3	72
2	2.25	2	60
3	1.85	3	70
4	2.44	2	57
5	2.36	2	57
Avg.	2.17	2	63
Std. Dev.	0.25	1	7

coatings during the cooling process. In the presence of a thermal gradient in the epoxy coating, the epoxy layer close to the aluminum plate feels tensile stresses from both sides. The tensile stress on the aluminum side is a result of the coefficient of expansion mismatch between the epoxy and the aluminum. The tensile stress on the other side of the epoxy layer is a result of the adjacent epoxy layer at a different temperature and therefore at a different state of thermal expansion. The difference in expansion states causes a tensile stress between the two epoxy layers. The total tensile stress exerted on the epoxy layer is the combined effect of these two stresses.

The cooling rate was changed by cutting the flow rate of the cooling water in half, Rate 2. This was found to have little effect on the thermal shock resistance of the coating. The cooling rate would be expected to have an effect only if it changed the development of the thermal gradient through the epoxy coating. The second cooling rate used in this study gave an interfacial temperature of 8°C as compared with 3°C for the control at the same thickness. This difference was not sufficient to change the thermal gradient development significantly, and therefore did not change the measured thermal shock resistance of the system. It did, however, illustrate that exact reproduction of the higher cooling rate was not essential for reproducibility. As long as the coolant flow rate was sufficient to maintain the water-metal boundary layer less than 8°C, no measurable effect of coolant flow rate was found.

The best indication of the thermal shock resistance for this test configuration is the time of failure. The thermal shock resistance

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was improved with a large excess of MDA curing agent which has the effect of lowering *Tg* and decreasing crosslink density.[10] The time of failure increased from about 2 minutes at 0% excess to 4.8 minutes at 100% excess MDA. The addition of the more flexible RD-2 resin (compare with 0°C excess control) also appeared to increase the thermal shock resistance slightly. The addition of glass beads increases the thermal shock resistance to a point where failure no longer occurred, at 60 wt.% glass beads, even after 13 minutes of cooling to 0°C. It is interesting that addition of a small amount of glass beads, 20% weight percent, gave marginal or no improvement. In general, increased thermal shock resistance occurred when the epoxy coating was toughened or when the coefficient of expansion was substantially decreased.

The stress development at the epoxy-metal interface predicted by Eq. (1) was calculated from two initial states: 1) from stress-development beginning at a temperature of 180°C and 2) beginning from the *Tg* of each of the samples. These stresses are compared with the separately measured tensile stress required to break the sample at 0°C (Table VI). There is a large difference between these calculated results and the experimental strength values obtained at

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TABLE VI
Comparison of stress at failure

Sample	Interfacial stress, (Pa) × 10^7		Measured tensile strength at 0°C, (Pa) × 10^7
	Calculated from 180°C	Calculated from *Tg*	
0% Excess MDA, 0.635 cm thick	2.013	1.302	5.295
0% Excess MDA, 0.3175 cm thick	2.023	1.311	5.295
0% Excess MDA, 0.635 cm thick Rate 2	1.945	1.234	5.295
23.1% Excess MDA	1.845	1.479	7.170
50.0% Excess MDA	1.381	1.373	7.377
100% Excess MDA	1.131	0.920	7.446
10% RD-2†	2.588	2.389	5.923
30% RD-2†	1.083	0.7591	7.240
20% Glass beads†	1.370	1.132	6.309
60% Glass beads†	1.198	1.001	6.826

† The balance is Epon 828/MDA (0% excess).

0°C. Two explanations of the deviation appear: Either Eq. (1) is not a true indication of the stress level obtained at failure or the mode of failure is not purely tensile.

Equation (1) does not give a true indication of the stress in thick epoxy coatings. This is seen both from the thermal stress analysis presented earlier in this paper and also in our previous work.[1] If the stress development is influenced by the development of a thermal gradient during cooling, as discussed earlier, then the stress calculated from Eq. (1) would be expected to be lower than the actual stress for thick coatings. It is logical that the deviation is in the application of Eq. (1) and not with the mode of failure.

To give an indication of the thermal gradient developed in the epoxy coating during cooling, the temperature at five different locations of the epoxy-metal system was measured as a function of time, as shown in Figure 8.

The thermal profile changes in a coating during the cooling process are shown schematically in Figure 9. The first profile (Figure 9–I) represents time before the cooling water was turned

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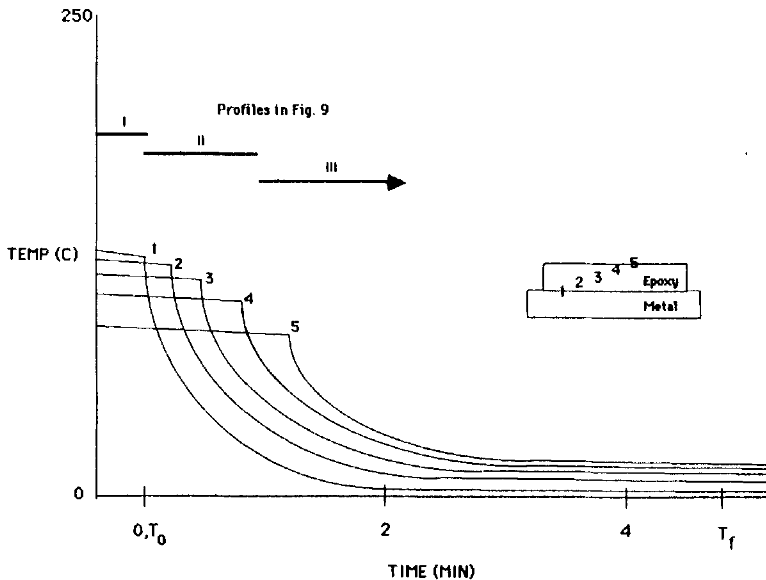

FIGURE 8 Thermal gradient in epoxy coating during cooling.

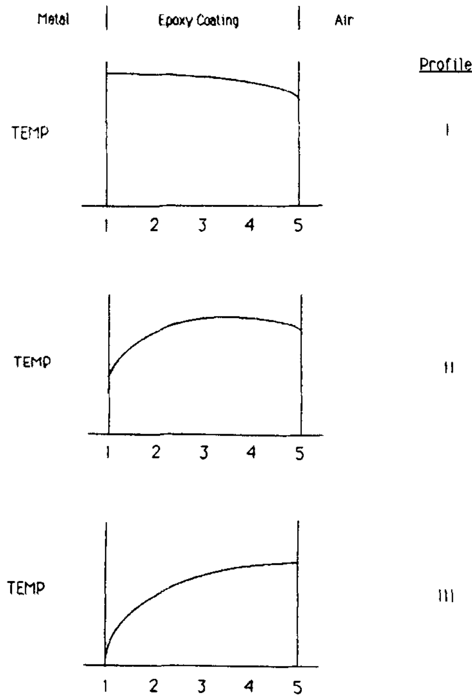

FIGURE 9 Thermal gradient profiles in epoxy coating during cooling.

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on. Because the heat sink was also heated to 180°C, the cooling rate at the exposed epoxy surface was greatest, with little heat transfer occurring at the epoxy-metal interface. The profile steadily decreases in temperature toward the exposed epoxy surface.

When the cooling water is turned on, the heat transfer at the epoxy-metal interface becomes much greater than the exposed epoxy surface rate. Profile 2 (Figure 9-II) is transitional with a maximum in the temperature profile somewhere in the interior of the epoxy coating. This maximum shifts toward the exposed epoxy surface with time until the third profile (Figure 9-III) is achieved.

Failure within the epoxy coating occurs during the third gradient profile. As the cooling process continues, the profile tends to flatten out, but the steepest gradient is near the interface. The expansion coefficient mismatch and the thermal gradient near the surface combine to give a higher stress than predicted from Eq. (1).

Theoretically, these profiles are expected from heat transfer derivations such as these presented for simple slabs by Carslaw and Jaeger.[15] The equations obtained are infinite series, however, and direct numerical application would not be helpful. The temperature profile charts which they do provide as a function of time and position within the slab show qualitative agreement between the expected and observed results.

CONCLUSIONS

A thermal shock testing apparatus was designed and gave effective results. The standard deviation of the time-to-fail data was found to be approximately 10%. Interfacial and surface temperatures were also measured. The apparatus is suitable for bondable polymeric systems on metals.

The addition of a high concentration of glass beads in the epoxy resin improved the thermal shock resistance more than any other system studied. Thermal shock failure did not occur when sufficient glass beads were added to lower the coefficient of expansion to a level where only small levels of strain developed during cooling. Increasing the amount of curing agent in the epoxy system, which lowers *Tg* and increases separation of crosslinks, also resulted in improved thermal shock resistance. With a large excess of MDA, the time to fail by thermal shock increased. The blending of the second, lower *Tg* resin also appeared to improve the thermal shock resistance, but only slightly relative to the glass bead and excess curing agent systems.

Thermal stress development of thick epoxy coatings on a metal substrate deviates from that found with thinner coatings. This deviation was greatest for high *Tg*, rigid epoxy systems. As the *Tg* or thickness of epoxy resin decreased, the development corresponded more to that found with thin coatings. The stress levels predicted by the equation for thin coatings were much lower than the separately determined ultimate tensile stress required for the epoxy systems to fail. The equation for thin coatings does not properly indicate the level of stress in the thick epoxy coating because: 1) The curing schedule affects the zero stress temperature, 2) The *Tg* and rigidity of the epoxy have an effect upon the stress

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relaxation, and 3) A thermal gradient within the epoxy coating is developed during cooling.

The thermal gradient development in the thick epoxy coating is represented by three different profiles. Failure occurs in profile III, where the temperatures of the epoxy layers closest to the aluminum are lower than the subsequent adjacent layers; the warmer upper epoxy layer inhibits the lower layer (against the metal) from contracting, resulting in a tensile stress. Failure appears to occur at or near the epoxy layer adjacent to the metal surface, where the sum of the two stresses being applied on the epoxy is the greatest. The two stresses result from the coefficient of expansion mismatch between the epoxy and the metal on one side and the different expansive state of the adjacent epoxy layer on the other side. Thinner coatings have a greater thermal shock resistance because of the decrease in magnitude of the thermal gradient through the epoxy coating.

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