

## Adhesion of Metals to Polymers.

### I. Study of Interfaces Modified by Inductive Heating

R. A. V. RAFF and A. M. SHARAN, *Department of Metallurgy, College of Engineering, Washington State University, Pullman, Washington 99163*

#### Synopsis

The objective of the work reported in this paper is to explain theoretically the observations made in an earlier study that castings of an epoxide resin reinforced by electrically conductive inserts, after having been postcured by inductive heating, had strength properties superior to those achieved by a purely thermal postcure. A search of the literature on adhesion suggested that among the theories presented, those dealing with electrical double layer formation, interdiffusion, and mixed polymer grafting on the insert-polymer interface deserve to be considered. Experiments were then planned in such a manner as to permit a choice between these theories. Epoxide resin specimens reinforced with various metals (pure silver, silver with an oxide layer, pure copper, copper with an oxide layer, aluminum, and stainless steel) were prepared. They were then either postcured in a heated oven, or postcured in an induction furnace for various lengths of time. Bonding strength was determined by a knife-edge method, and the exposed insert and resin surfaces were tested for electrical potential and surface wettability (angle-of-contact). Most strikingly, the curves obtained with increasing induction heating times for bonding strength, electrical potential, and wettability were all sinusoidal in shape, and their maxima and minima generally were found to coincide. For oven-postcured specimens, bonding between different metal inserts and an epoxide resin is explained by double electrical layer formation (insert positive, resin negative), with bonding strength increasing as the stability of the oxide forming the surface layer of the metal decreases. Metals with no oxide surface layer thus have the highest bonding strengths. For inductively postcured specimens, bonding is effected by both electrical double layer formation and mixed polymer grafting through the oxygen atoms in the metal surfaces, with the more stable metal oxide giving the stronger bonding in grafting. Where the insert does not carry an oxygen surface layer, bonding takes place through electrical forces only. Alternating build-up and internal discharge of electrical double layers are the direct cause of the sinusoidal shape of the electrical potential curves and the indirect cause of the comparable shape of the wettability curves. Their combination results in the observed periodicity of the breaking load curves.

#### INTRODUCTION

A previous study<sup>1</sup> had shown that specimens of precured thermosetting resins reinforced by inserts of stainless steel, graphite, or carbon cloth, after having been subjected to inductive heating, had superior strength over that obtained by a purely thermal postcure. The samples were made of an epichlorohydrin bisphenol-A type epoxide resin (Epon 828, Shell) as the matrix (with *m*-phenylenediamine as the curing agent) and five

TABLE I  
 Comparison of Tensile, Flexural, and Compressive Strengths of Oven-Postcured and Inductively Postcured Specimens<sup>a</sup>

Curing cycle	Postcure	Mechanical properties					
		Tensile		Flexural		Compressive	
		Strength, psi	Modulus, psi $\times 10^{-5}$	Strength, psi	Modulus, psi $\times 10^{-5}$	Strength, psi	Modulus, psi $\times 10^{-5}$
Oven, 6 hr at 50°C	Oven, 4 hr at 150°C	3770	6.9	11900	5.8	14600	3.0
+2 hr at 85°C	Induction,						
Oven, 6 hr at 50°C	10-13 sec	5750	8.6	17900	5.8	16600	5.1
+2 hr at 85°C							

<sup>a</sup> Data of Raff et al.<sup>1</sup>

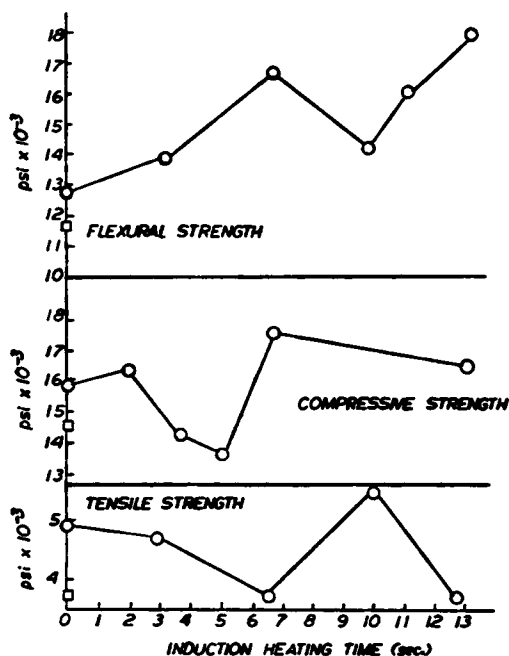


Fig. 1. Change of flexural, compressive, and tensile strengths with induction heating time: (○) inductively postcured; (□) oven-postcured. Data of Raff et al.<sup>2</sup>

layers of stainless steel cloth as the insert. The results obtained in this prior study are summarized in Table I, wherein the strength data given are the peak values shown by specimens just prior to incipient overall softening and degradation. These peaks had not been reached by steady increase in strength in proportion to the time of exposure in the induction coil. Rather the strength, with increasing time of exposure of the samples, generally went through an initial first maximum, followed by a minimum, to reach a second and final maximum<sup>2</sup> as is shown in Figure 1. Separate experiments had indicated that the strength properties of the resin itself are not affected by inductive heating, in that resin specimens without insert did not change in strength on inductive heating.

The observed increase in mechanical strength had been explained tentatively by assuming the following sequence of events. The internal heating produced by intense electrical induction losses in the metallic insert causes degradation of the resin along the polymer-metal interface with the subsequent formation of free radicals, while the relatively cold outer shell of the resinous structure keeps the decomposition product confined under considerable pressure. On cooling the specimen after removal from the induction coil, rearrangement and recombination reactions take place in the resin, and bonding of the rearranged and reformed polymer to both the resin matrix and the metallic insert may occur. The establishment of such interfacial bonds could then explain the observed superiority

in bonding strength of these inductively postcured structures over similar structures where postcuring was done thermally, namely in an oven or in a heated press. These views are substantiated by the results reported by Keenan and Smith,<sup>3</sup> who have done studies on the thermal nonoxidative degradation of epoxide resins. These authors investigated, by gas chromatography, the hot wire pyrolysis of a purified epoxide resin of a composition very similar to that used by Raff et al.<sup>1,2</sup> Keenan and Smith<sup>3</sup> conclude that the first step in the thermal degradation of epoxide resins consists of an homolytic rupture of bonds to produce resonance-stabilized free radicals, for which there is evidence both from electron spin resonance measurements and from reactions with 2,2-diphenyl-1-picrylhydrazyl. These free radicals undergo further reactions of a complex nature, and the products formed thereby are themselves likely to undergo more secondary reactions. The extent of degradation is believed to be related to the proximity to the hot wire, and a spectrum of products varying from small molecules of the phenol or cresol type through to compounds not greatly differing from the parent matrix was identified.

These are also essentially the requirements for the postulated formation of free radicals and an interface consisting of reformed polymer in the case of a resin being heated inductively through an imbedded insert. The interface away from the insert is bound to approach gradually the composition of the resin matrix and eventually to merge with it.

## THEORETICAL CONSIDERATIONS

### Objective

The objective of this study was then to determine the cause for the observed superiority in bonding of metal and resin as it may be achieved by inductive heating. Under the assumption that bonding of the reformed polymer to the metal insert is taking place on the interface, several mechanisms may be visualized. These may range from mere adhesion caused by secondary bonds to true mixed polymer-to-metal grafting by primary bonds. Worthy of particular consideration are the following concepts found in the literature:<sup>4</sup> (a) the electrical theory of adhesion of high polymers to metals by Deryagin and Krotova, (b) the diffusion theory of adhesion which assumes gross intermixing and molecular interdiffusion of two phases of the interfacial region, and (c) the theory of mixed polymer grafting, which may involve an activated metal oxide layer or events on a freshly formed surface. These possibilities will now be discussed.

### The Electrical Theory

The energy bands in metals and insulators are shown in Figure 2.<sup>5,6</sup> In metals, the Fermi level lies in the conduction band; in insulators, it is between conduction and inner valence band. For insulators, the energy gap between the conduction and the inner valence bands is quite large, with the result that no electronic transition can take place between these

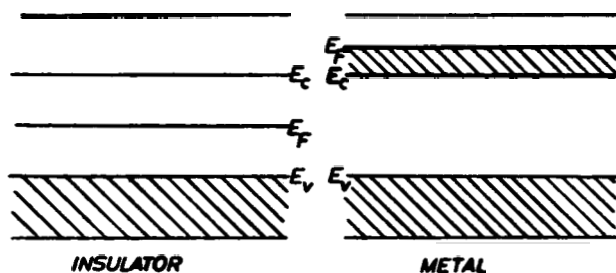


Fig. 2. Energy levels in insulators and in metals (energy band diagram).  $E_v$  = top of valence band;  $E_c$  = bottom of conduction band;  $E_f$  = Fermi level.<sup>5,6</sup>

two levels. In case of metals, however, such transitions are possible, and as a matter of fact, the conduction band itself is partially filled at ordinary temperatures. At low electrical fields, current can flow in metals but not in insulators. Here, the electrons can be promoted to the conduction band from the valence band by providing them with thermal energy from outside. Since the gap is quite large, a very considerable amount of thermal energy is required for their promotion.

Although there are some electrons in metals which are found in the conduction band, a still very large amount of energy is required to remove these from the conduction band to infinity owing to the very high barrier which prevents electrons from leaving the metals. There is finite probability that some electrons might leave the metal on being heated, and the amount of electrons leaving the metal surface is then given by the Richardson-Dushman equation<sup>5</sup> as

$$\ln (J/T^2) = \ln A_0 - (E_w/k) (1/T) \quad (1)$$

where  $A_0$  is a universal constant,  $E_w$  is the work function,  $T$  is the absolute temperature, and  $k$  is the Boltzmann constant.

Under the conditions of experiments, it is likely that some electrons leave the metal surface and enter the epoxide resin which is considered to be deficient in electrons, with the result that the metal surface acquires a net positive, and the opposing epoxide resin surface a net negative charge.<sup>7</sup> This opposing nature of charges is then considered responsible for the force of attraction between the metal and the resin.

### The Diffusion Theory

Measurements have shown<sup>8</sup> that the surface diffusion obeys activation or Arrhenius-type laws so that it is possible to write the temperature dependence in the form.

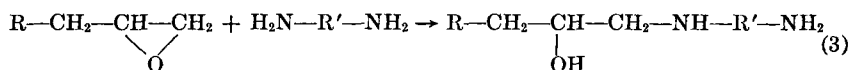
$$D_s = D_{s0} e^{-\theta_s/RT} \quad (2)$$

where  $D_s$  is diffusivity,  $D_{s0}$  is a frequency factor,  $\theta_s$  is the experimental activation energy for surface diffusion,  $T$  is absolute temperature, and  $R$  is the universal gas constant.

There is evidence that surface diffusion is the fastest of the three possible ways of diffusion, which may also be lattice or grain boundary, as is understandable in view of the open structure found on the exterior surfaces. The possibility thus exists that on induction heating, the metal could diffuse into the epoxide resin by a surface diffusion mechanism to establish a diffusion bond. However, the time involved for diffusion of an appreciable fraction of metal is not known, and it may be longer than the induction heating times used in experiments.

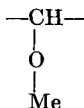
### The Mixed Polymer Grafting Theory

The hardening reaction with polyamines consists of opening the epoxide groups of the resin to form an alcohol according to eq. (3):

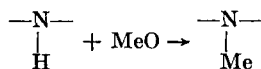


Actually, the "cure" produces first linear and then crosslinked chains through the active hydroxyl groups until the molecular structure of the resin is quite complex.

It can be visualized that, in the course of the curing reaction, epoxide or hydroxyl groups may form bonds with contacting metals, e.g.,



Or, amino groups on the polymer may connect with oxide groups in the metal surface, e.g.,



These possibilities are enhanced if the metal surface or oxide groups on the metal surface are in contact with the polymer while it undergoes heat degradation and reformation, thereby generating free radicals, as is the case in the course of inductive heating.

As is shown in a recent review by Raff,<sup>9</sup> the concept of grafting by primary bonds of polymers onto inorganics and metals ("mixed grafting") is well established. An extension of this concept as it applies to this project has been published recently by Raff and Sharan.<sup>10</sup>

The objective of this study has now become more specific, namely to demonstrate which, if any, of the above discussed theories is best suited to interpret the results observed in the inductive postcuring of a metal-reinforced epoxide resin.

## EXPERIMENTAL TECHNIQUES

## General

The overall procedure consisted in casting a metal disk into the epoxide resin which in all cases was Epon 828 (Shell). The casting mixture was prepared by heating 15 parts by weight of Epon 828 to 66°C, mixing with 14 parts of molten (66°C) *m*-phenylenediamine, the curing agent, and then blending with 85 parts of Epon 828 at room temperature. After a precuring period of 2 hr at 85°C, some of the cylindrical samples were given a conventional thermal postcure for 4 hr at 150°C, whereas others were postcured by inductive heating for various lengths of time in a Leco induction furnace. The details of these procedure steps are the same as those used by Raff et al.<sup>2</sup> in an earlier study.

No measurements were made of the temperatures reached in the course of inductive heating by the inserts imbedded in the resin. A temperature of about 600°C was noted by means of the color change observed with temperature-indicating crayons on an isolated disk of silver exposed to inductive heating for 50 sec.

The three types of samples (precured, oven-postcured, and inductively postcured) were then tested for bonding strengths and for the wettabilities of the opposing polymer and metal surfaces. Also, the electrical potentials of the split specimens were determined, and some x-ray diffraction tests were carried out. These measurements which will be subsequently discussed in more detail were thus designed to allow for making a decision among the theories outlined in the previous section.

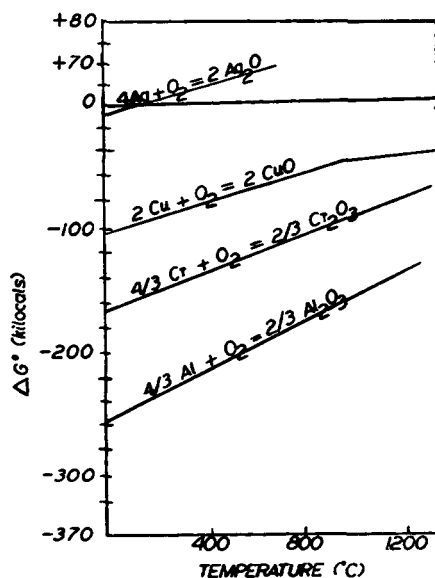


Fig. 3. Standard free energy of formation of oxides versus temperature.<sup>11</sup>

Similar considerations led to the choice of the metals used as inserts. Thus, the study had to include metals with unoxidized and oxidized surfaces, considering the different degree of stability of these oxides (Fig. 3). Consequently, the following metals were studied: pure silver (Ag); silver with an (unstable) oxide layer (Ag-Ag<sub>2</sub>O); pure copper (Cu); copper with a (medium stable) oxide layer (Cu-CuO); stainless steel with its surface layer of Cr<sub>2</sub>O<sub>3</sub> (stainless steel); and aluminum with its very stable oxide layer (Al-Al<sub>2</sub>O<sub>3</sub>). The abbreviated designations given in parentheses for the particular metal specimens will be used in the subsequent and more specific discussion of sample preparation and testing. The metal disks were obtained from Cominco American Inc., Spokane, Washington.

### Specimens with Inserts of Stainless Steel

The disks were 1.5 cm in diameter and 0.0051 cm in thickness. Their composition was as follows: C, 0.15%; Cr, 17-19%; Si, 1%; Mn, 2%; P, 0.04% (max); S, 0.03% (max); and Fe, balance.

The castings were made first by heating a glass ring (diameter, 3 cm; height, 1 cm) over a flame and pressing it slightly into a sheet of polyethylene. This gave a tightly sealed bottom but allowed for easy removal after completion of the casting. Into the center of the bottom of the resultant cup, a rod of polyethylene (diameter, 0.1 cm; height, 0.4 cm) was glued vertically with an epoxy cement; then the metal disk (rinsed with a mixture of alcohol and ether) was glued on the top of the polyethylene cylinder. Finally, the inside rim of the glass ring was lined with a strip of polypropylene to facilitate removal of the finished casting. The catalyzed epoxide resin was then poured in an amount sufficient to fill the cup. The total assembly is shown in Figure 4.

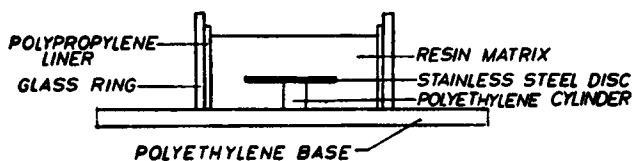


Fig. 4. Casting of disk of stainless steel in epoxide resin.

All castings were precured in an oven for 6 hr at 50°C and 2 hr at 85°C. Some castings were removed from the rings and kept as such. Other castings were postcured in an oven for 4 hr at 150°C and then removed from the rings. Still others, after removal from the rings, were inductively postcured for various lengths of time by vertical insertion into the coil of a Leco induction furnace (27 meps). Prior to testing, surplus resin along the rim of the specimen was taken off by machining so that the final specimens had remained the same in height but their diameter was that of the metal disk.



### Testing for Bonding Strength (Breaking Load)

Testing for the bonding strength of the top side of the metal disk to the resin matrix was carried out by equipping the upper portion of the compression cell of an Instron testing machine with a knife edge and determining the force required to split the disk along the metal surface (knife-edge breaking strength). In all cases, clear separation was achieved, and no resin could be detected visually in the metal surface, nor could it be observed under natural or ultraviolet illumination.

### Testing for Surface Wettability

The testing for water wettability of the opposing but separated metal and resin surfaces was then carried out by angle-of-contact measurements.<sup>12</sup> Small drops of distilled water were deposited along the periphery of the surfaces of the metal or resin disks and the contact angle read through a microscope aimed at the base of the droplet. Absence of wettability would be read as a contact angle of 180°, maximum wettability as 0°. Thus, lower angle readings denote increased wettability. The metal surfaces were retested for wettability after having been rinsed with a polar (acetone) and a nonpolar (benzene) solvent. In all cases, the absence of any electric charge on surfaces was ascertained by means of an oscilloscope prior to the testing for wettability.

No voltage measurements were made on any of the specimens containing stainless steel disks.

### Specimens with Inserts of Silver with Oxide Layer (Ag-Ag<sub>2</sub>O)

The silver disks as obtained from the supplier had the following composition: Mg, 0.1 ppm; Si, 0.1 ppm; Ca, 0.1 ppm; Pb, 0.2 ppm; Bi, 0.1 ppm; V, 0.2 ppm; and Ag, balance. They were 1.875 cm in diameter and 0.036 cm in thickness.

For preparations of the castings, a glass rod (diameter, 0.5 cm; height, 2.4 cm) was glued at the center of a polyethylene cylinder (diameter, 3.5 cm; height, 4.5 cm) as shown in Figure 5. The silver disk was glued to the top of the glass rod and then kept at 100°C for 1 hr to ensure the formation of a uniform surface layer of silver oxide, after which the epoxide resin was poured inside the cylinder so as to fill it completely. After about 15 hr at room temperature, the specimens were moved into an oven which was maintained at 50°C. After 6 hr, all the specimens were transferred to another oven and kept at 85°C for 2 hr. Some specimens were then tested as such, others were postcured at 150°C for 4 hr, while still others were inductively heated for various lengths of time. During induction heating of these specimens, the axis of the cylindrical specimen coincided with the axis of the coil, so that the metal insert could generate the maximum amount of heat. After induction heating, the cylinders were allowed to condition at room temperature for 15 hr. They were then machined on a lathe to be tested in the Instron tester.

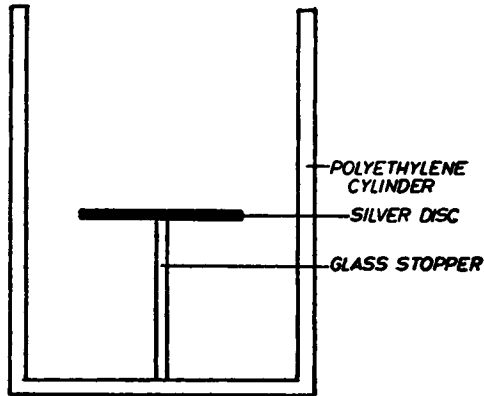


Fig. 5. Casting of silver disk in epoxide resin.

### Testing for Interfacial Electrical Potential

While measuring contact angles on specimens of stainless steel and epoxide resin, it was observed that the droplets were attracted towards the center of the disks. This and other electric phenomena such as sparking noted on separating the metal insert from the resin base led us to suspect that electric forces may also play an important role in the bonding. Therefore, for this and all subsequent composites, an oscilloscope was used to measure voltage on the metal-resin boundary.

After having tested the specimens in the compression cell of the Instron machine (as described above for the stainless steel samples), the split specimens were immediately taken to an oscilloscope for measurement of voltage.

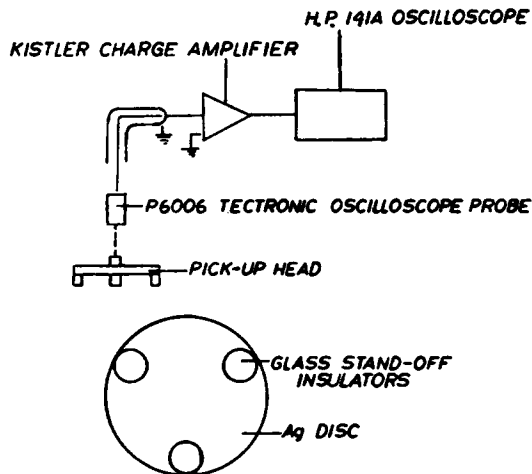


Fig. 6. Circuit for measuring the electrical surface potential, and pick-up head shown from top.

For this, an H.P. 141 oscilloscope was connected to the output of a Kistler charge amplifier (Fig. 6). The input of the Kistler charge amplifier was connected to a P6006 Tectronic oscilloscope probe. In the measurement of voltage, it was important that the distance of separation between the pick-up head and the surface, whose charge was to be measured, remained constant. A silver disk was used as a pick-up head, and three stand-off insulators (height, 0.1 cm) were cemented onto the disk. The stand-off insulators were placed at an angle of  $120^\circ$  to each other to give stability to the silver disk used as the pick-up head. Figure 6 shows the view from the top, indicating the location of the three stand-off insulators on the silver disk.

It must be pointed out that considerable difficulties were encountered in these measurements, since preliminary discharge of the separated surfaces could not always be prevented and many specimens had to be discarded.

#### **Specimens with Inserts of Pure Silver (Ag), Copper (Cu), and of Copper and Aluminum with Oxide Layer (Cu-CuO; Al-Al<sub>2</sub>O<sub>3</sub>)**

The copper disks as obtained from the supplier had the following compositions: Ag, 0.5 ppm; Mg, 0.1 ppm; Si, 0.5 ppm; Cu, balance. The aluminum disks had the composition: Cu, 0.2 ppm; Mg, 0.1 ppm; Al, balance. All disks were 1.875 cm in diameter and 0.036 cm in thickness.

The methods of preparation and testing of the specimens made with inserts Ag, Cu, Cu-CuO, and Al-Al<sub>2</sub>O<sub>3</sub> were the same as those described above for Ag-Ag<sub>2</sub>O samples. The only difference was in the pretreatment of the metal disks. The pure Cu disks were prepared by heating the commercial copper disks in the oxidizing flame of a gas burner and then immediately quenching them in methyl alcohol so as to reduce any surface oxide completely. The Cu-CuO disks were made by heating the commercial copper disks in an oxidizing flame and allowing them to cool in air. The Ag and the Al-Al<sub>2</sub>O<sub>3</sub> disks were used as supplied, after rinsing with methyl alcohol.

### **ACCURACY OF MEASUREMENTS**

#### **Load Measurements**

The mean of two samples was taken. The variation between the readings of two samples was larger than the possible error from the instruments. All the readings were within an error of 10%. This error can be justified by the following facts.

(1) The samples were machined on lathe. The bonding could have been weakened by "jerks" experienced by the samples in the lathe.

(2) The split may not have been occurring always exactly across the metal epoxide interface.

(3) There might have been differences in the nature of different disks.

(4) The difference in bonding could also have been caused by minute gas bubbles entrapped in the specimens.

### Electrical Potential Measurements

The mean of five readings was taken. The instrument had exact reproducibility, and all the readings were within 10% experimental error. This can be justified in view of the following sources of errors.

- (1) The surfaces may not have been uniform throughout.
- (2) The charge may have leaked at different rates at different points of the sample surface.
- (3) The sample surface itself may not have been isotropic to develop equal charge density on all the points of the surface.
- (4) During splitting on the Instron tester, different points on the surface may have been stressed differently, thereby affecting the electrical nature of the surface.
- (5) The inductive heating may not have been uniform along the periphery of the metal insert (end effects). This could have given rise to the difference in charge on the epoxide surface, especially on the points which are in contact with the periphery of the metal surface.

### Angle-of-Contact Measurements (Wettability)

In the microscope,  $1^\circ$  was the minimum angle difference which could be read. Standard deviations were of the order of  $1.0$ – $1.5^\circ$ , which may be explained by several facts.

- (1) The nature of different points across the surface may have been different.
- (2) The nature of the surface could have been changed by the compressive and tensile stresses induced in the specimens.
- (3) The nature of the surface could have been changed during the machining on the lathe.
- (4) Discrepancies could also have been caused by differences in heating of several points across the interface, since points in contact with the periphery of the metallic insert might be heated at a different rate.

## EXPERIMENTAL RESULTS

### Specimens with Inserts of Aluminum with Oxide Layer (Al–Al<sub>2</sub>O<sub>3</sub>)

The experimental results obtained on the precured (0 sec induction time), on the inductively postcured (5–50 sec induction time), and on the oven-postcured samples are summarized in Table II and plotted in Figure 7.

Interpretation of the results in this and the subsequent series of experiments is primarily based on the similarities in the shapes of the load, interfacial potential, and wettability curves versus induction times, and on similarities in the spacings of the peak values. Further points of reference and comparison are the values obtained on the samples which had precure only (induction heating time = 0) and on those which had undergone oven postcure.

The load curve (Fig. 7) starts at a very low value for both the precured and the oven-postcured samples but rises to a moderate maximum after an induction heating time of 5 sec. The potential as well as the wettability curves also have a maximum at the same induction heating time. After that, the wettability as well as the potential curves have steeper slopes than does the load curve. The potential curve and possibly the load curve have their next maxima at 30 sec of induction heating time, whereas the wettability curve has its second maximum after 25 sec of induction heating.

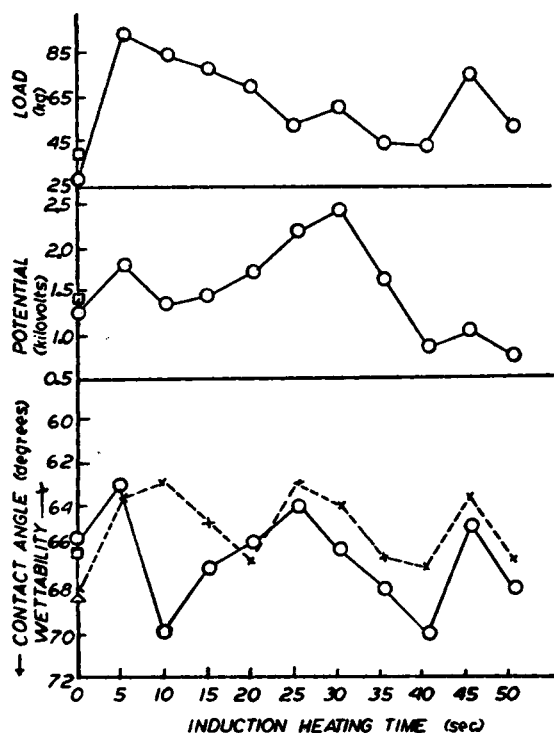


Fig. 7. Change of load, potential, and wettability of Al-Al<sub>2</sub>O<sub>3</sub> and epoxide resin surfaces with induction heating time: (O) inductively postcured values for Al-Al<sub>2</sub>O<sub>3</sub>; (X) inductively postcured values for the resin; (□) oven-postcured values for Al-Al<sub>2</sub>O<sub>3</sub>; (Δ) oven-postcured values for the resin.

The maxima of the load and wettability curves are lower than the corresponding first maxima, but the second maximum of the potential curve is higher than its first and third. All three curves have their third maxima at 45 sec, where potential and wettability appear to add up to result in a corresponding maximum in the load curve. The potential and the wettability values of the oven postcured samples almost equal those shown by the precured specimens. The considerable strength improvement by induction postcure is to be noted.

TABLE II  
Effect of Induction Heating on Specimens with Inserts of Al-Al<sub>2</sub>O<sub>3</sub>

Induction heating time, sec	Load, kg	Aluminum with oxide layer surface		Epoxide resin surface	
		Potential, kV	Contact angle, deg	Potential, kV	Contact angle, deg
0	25.0	1.25	66.0	-1.25	68.2
5	93.0	1.75	63.0	-1.75	63.7
10	83.0	1.30	70.0	-1.30	63.0
15	77.0	1.40	67.0	-1.40	64.7
20	68.0	1.65	66.0	-1.65	66.5
25	50.5	2.15	64.0	-2.15	63.0
30	59.0	2.40	66.0	-2.40	64.0
35	42.0	1.60	68.0	-1.60	66.5
40	40.0	0.80	70.0	-0.80	66.8
45	74.0	1.00	65.0	-1.00	63.7
50	50.0	0.70	68.0	-0.70	66.5
Oven-postcured	38.0	1.30	66.2	-1.30	68.5

### Specimens with Inserts of Stainless Steel

The experimental results obtained on the precured (0 sec induction time), on the inductively postcured (5-70 sec induction time), and on the oven-postcured samples are summarized in Table III and plotted in Figure 8. In interpreting the results, it is to be remembered that stainless steel has

TABLE III  
Effect of Induction Heating on Specimens with Inserts of Stainless Steel

Induction heating time, sec	Load, kg	Contact angle, deg	
		Stainless steel surface	Epoxide resin surface
0	11.0	72.0	74.5
5	24.0	64.2	71.0
10	41.0	63.0	63.0
15	36.0	67.1	65.0
20	28.0	70.0	67.0
25	22.0	70.4	68.1
30	23.0	70.6	69.2
35	24.0	70.8	70.2
40	26.0	71.0	70.8
45	36.0	71.5	71.0
50	46.0	72.0	71.2
55	50.0	72.5	71.3
60	54.0	73.0	71.4
65	68.0	69.0	71.4
70	78.0	67.0	70.0
Oven-postcured	11.0	71.6	74.5

a surface layer of  $\text{Cr}_2\text{O}_3$ . No interfacial potentials were measured in this series.

As can be seen, the breaking strength of the laminate reaches its first maximum at the same induction heating time as do the wettabilities of the separated metal and resin surfaces. Strength and wettability then decrease, but the minima do not coincide as well as did the first maxima. The breaking strength rises again, and a similar trend is shown by the wettability curve, but the rate of increase is much greater in the load curve. Higher breaking strength is apparently connected with an increase in wettability.

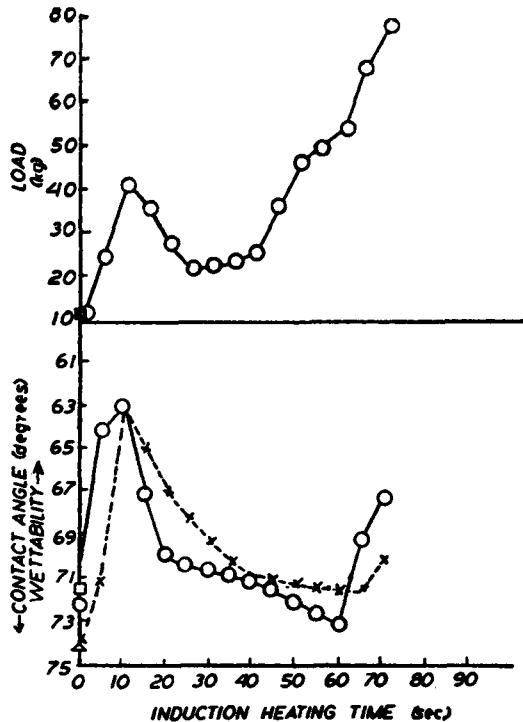


Fig. 8. Change of load and wettability of stainless steel and epoxide resin surfaces with induction heating time: (○) inductively postcured values for stainless steel; (×) inductively postcured values for the resin; (□) oven-postcured values for stainless steel; (△) oven-postcured values for the resin.

Assuming that a change in chemical structure denotes a change in wettability, it appears that the presence of the metal insert, in the course of the precuring stage, had somewhat changed the curing mechanism of the resin immediately surrounding the insert (some metal compounds are known to be curing accelerators<sup>13</sup>), so that the chemical structure of the resin close to the metal surface became different from that of the resin matrix. However, subsequent oven postcuring caused no further change in either surface.

### Specimens with Inserts of Copper with Oxide Layer (Cu-CuO)

The experimental results obtained on the precured (0 sec induction time), on the inductively postcured (5-50 sec induction times), and on oven-postcured samples are summarized in Table IV and plotted in Figure 9.

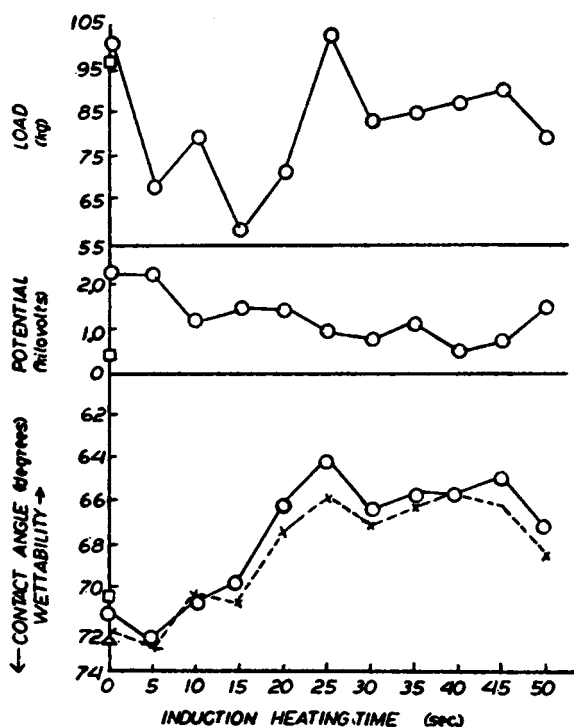


Fig. 9. Change of load, potential, and wettability of Cu-CuO and epoxide resin surfaces with induction heating time: (O) inductively postcured values for Cu-CuO; (X) inductively postcured values for the resin; (□) oven-postcured values for Cu-CuO; (Δ) oven postcured values for the resin.

The load curve has an unusual behavior. Strength and wettability decrease at first and then rise again. The potential curve runs horizontally in the region where strength declines, but it shows a decrease when the load curve rises. The load curve is quite closely followed by the wettability curve. The difference between the potentials obtained on the precured and on the oven postcured specimens is quite large; in fact, the potential by thermal postcuring in the oven is smaller than that obtained by induction heating. This unusual behavior is perhaps caused by any differences in the thickness of the oxide layers of the metal disks.



TABLE IV  
Effect of Induction Heating on Specimens with Inserts of Cu-CuO

Induction heating time, sec	Load, kg	Copper with oxide layer surface		Epoxide resin surface	
		Potential, kV	Contact angle, deg	Potential, kV	Contact angle, deg
0	101.0	2.25	71.0	-2.25	72.0
5	68.0	2.25	72.5	-2.25	72.7
10	80.0	1.20	70.4	-1.20	70.2
15	58.0	1.50	69.7	-1.50	70.5
20	72.0	1.50	66.2	-1.50	67.2
25	104.0	1.00	64.0	-1.00	65.7
30	84.5	0.85	66.3	-0.85	67.0
35	86.0	1.20	65.5	-1.20	66.0
40	88.0	0.55	65.5	-0.55	65.5
45	91.0	0.75	64.8	-0.75	66.0
50	63.0	1.57	67.0	-1.57	68.2
Oven-postcured	92.0	0.40	70.6	-0.40	72.5

**Specimens with Inserts of Silver with Oxide Layer  
(Ag-Ag<sub>2</sub>O)**

The experimental results obtained on the precured (0 sec induction time), on the inductively heated (5-50 sec induction times), and on the oven-postcured samples are summarized in Table V and plotted in Figure 10.

The interfacial potential reaches a maximum at 5 sec induction time and then decreases. A similar trend is shown by the wettability curve, and both curves have two minima and three maxima. The wettability and the potential curves reinforce each other at these three maxima and thus give rise to corresponding maxima in the load curve.

TABLE V  
Effect of Induction Heating on Specimens with Inserts of Ag-Ag<sub>2</sub>O

Induction heating time, sec	Load, kg	Silver with oxide layer surface		Epoxide resin surface	
		Potential, kV	Contact angle, deg	Potential, kV	Contact angle, deg
0	25.0	1.00	69.0	-1.00	66.0
5	160.0	2.25	64.2	-2.25	61.6
10	93.0	1.00	69.0	-1.00	64.8
15	82.0	2.00	66.8	-2.00	62.0
20	87.5	0.75	65.8	-0.75	59.4
25	125.0	1.05	65.0	-1.05	60.6
30	97.0	0.75	67.0	-0.75	63.0
35	75.0	1.00	68.0	-1.00	61.4
40	76.0	1.53	67.0	-1.53	59.2
45	106.0	1.75	65.0	-1.75	60.1
50	108.0	1.68	68.5	-1.68	61.6
Oven-postcured	150.0	1.00	68.4	-1.00	66.2

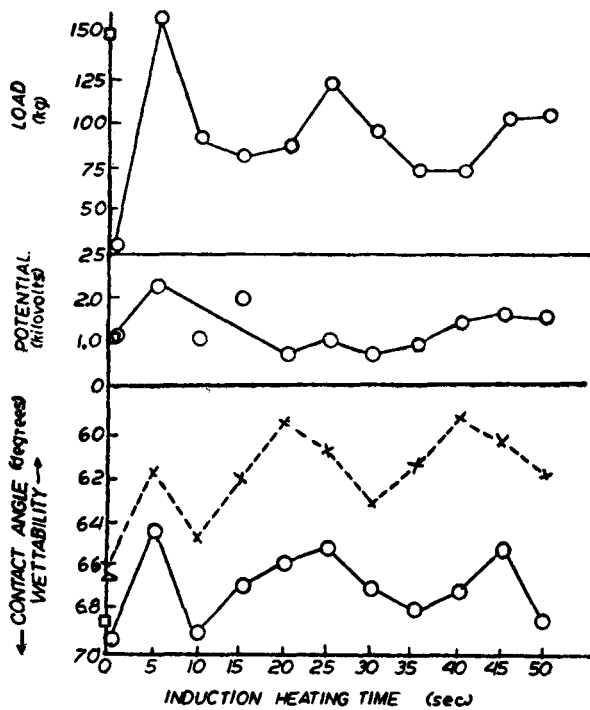


Fig. 10. Change of load, potential, and wettability of Ag-Ag<sub>2</sub>O and epoxide resin surfaces with induction heating time: (O) inductively postcured values for Ag-Ag<sub>2</sub>O; (X) inductively postcured values for the resin; (□) oven-postcured values for Ag-Ag<sub>2</sub>O; (Δ) oven-postcured values for the resin.

### X-Ray Fluorescent Analysis of Ag-Ag<sub>2</sub>O Specimens

On being inductively heated, the metal atoms acquire thermal energy so that the amplitude of vibration increases; if sufficient thermal energy is given to the atoms, they can leave their position in the crystals. In our case, the atoms may enter the epoxide resin. This migration will depend upon the diffusivity as well as upon the concentration gradient. The longer the heating time, the greater is the thermal energy input into the system; therefore, the better are the chances for diffusion. Whether or not the metal atoms diffuse into the epoxide resin can be ascertained by various measurements. One of these is x-ray fluorescent analysis.

Specimens having Ag-Ag<sub>2</sub>O as inserts and which had been inductively heated for 45 or 50 sec were used to investigate whether Ag was present in the epoxide resin. At first, a dime coin, known to contain silver, was used as a standard. Then, epoxide resin, obtained from splitting the inductively heated specimens, was subjected to analysis. Since the  $K\alpha$  emission lines of Ag were not observed, it was concluded that Ag had not diffused into the epoxide resin in the course of the inductive heating. This excludes the

diffusion theory of adhesion as an explanation of the observed superiority in bonding as acquired by inductive heating.

### Specimens with Inserts of Silver (Ag)

The experimental results obtained on the precured (0 sec induction time), on the inductively heated (5–50 sec induction time), and on the oven-postcured samples are summarized in Table VI and plotted in Figure 11.

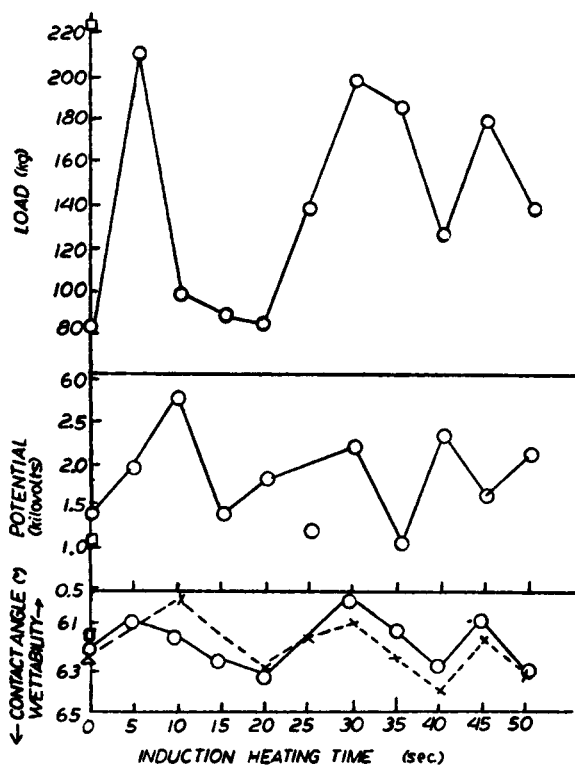


Fig. 11. Change of load, potential, and wettability on Ag and epoxide resin surfaces with induction heating time: (O) inductively postcured values for Ag; (X) inductively postcured values for the resin; (□) oven postcured values for Ag; (Δ) oven postcured values for the resin.

The load, potential, and wettability curves have corresponding trends with three maxima and two minima. At 5 and 45 sec of induction heating, the wettability and load curves have their maxima occurring together, but they are out of phase at 25 sec, where there is a maximum in the load curve. The wettability curve lags by 5 sec. The maxima in the potential and the load curves never coincide, having either a lead or a lag of 5 sec. The bonding strength improves quite considerably by induction heating of 5 sec, in comparison to the precured strength. In all cases, however, the strength obtained by induction heating is below that shown by the postcured

TABLE VI  
Effect of Induction Heating on Specimens with Inserts of Ag

Induction heating time, sec	Load, kg	Silver surface		Epoxide resin surface	
		Potential, kV	Contact angle, deg	Potential, kV	Contact angle, deg
0	82.5	1.40	62.2	-1.40	62.5
5	213.0	2.00	61.0	-2.00	61.7
10	99.0	2.80	62.0	-2.80	60.0
15	90.0	1.40	62.8	-1.40	61.5
20	86.0	1.80	63.5	-1.80	63.0
25	140.0	1.20	61.8	-1.20	62.0
30	200.0	2.20	60.0	-2.20	61.0
35	186.0	1.00	61.4	-1.00	62.7
40	126.0	2.35	63.0	-2.35	64.2
45	180.0	1.60	61.0	-1.60	62.0
50	140.0	2.10	63.3	-2.10	63.5
Oven-postcured	225.0	1.09	62.0	-1.09	62.3

specimens. The difference between the strength maxima and minima in the induction heating is exceptionally large, and the bonding strength is thus very sensitive to inductive heating time when inserts of pure silver are used.

#### Specimens with Inserts of Copper (Cu)

The experimental results obtained on the precured (0 sec induction time), the inductively heated (5-50 sec induction time), and the oven-postcured samples are summarized in Table VII and plotted in Figure 12.

The load curve may have three maxima, namely at 5, 25, and 45 sec. The first and the second maxima are quite weak, but the third maximum is

TABLE VII  
Effect of Induction Heating on Specimens with Inserts of Cu

Induction heating time, sec	Load, kg	Copper surface		Epoxide resin surface	
		Potential, kV	Contact angle, deg	Potential, kV	Contact angle, deg
0	70.0	1.00	67.0	-1.00	68.2
5	88.0	1.20	63.0	-1.20	64.0
10	72.5	1.80	63.7	-1.80	63.5
15	72.5	1.45	65.0	-1.45	65.2
20	68.0	1.00	68.0	-1.00	67.2
25	77.5	1.35	65.0	-1.35	64.0
30	60.0	0.40	63.5	-0.40	65.5
35	68.0	0.80	65.5	-0.80	67.5
40	77.0	0.90	67.0	-0.90	68.0
45	90.0	1.06	64.5	-1.06	65.0
50	60.0	0.60	66.0	-0.60	67.0
Oven-postcured	99.0	0.60	66.4	-0.60	68.4

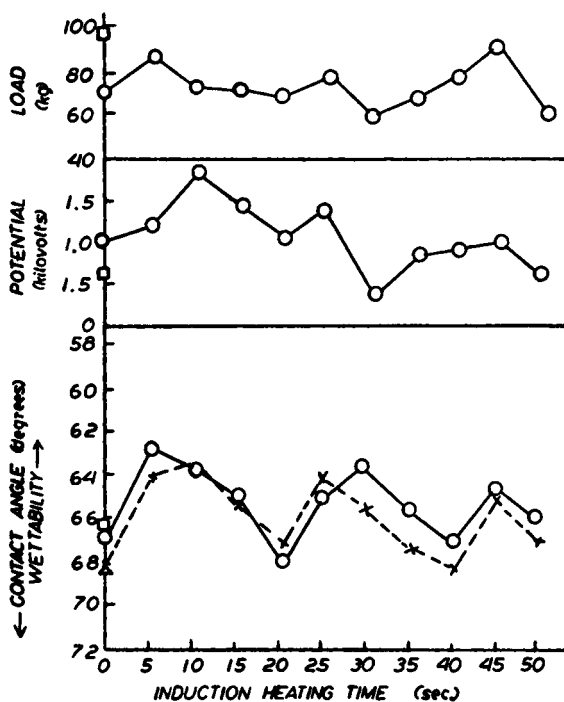


Fig. 12. Change of load, potential, and wettability on Cu and epoxide resin surfaces with induction heating time: (O) inductively postcured values for Cu; (X) inductively postcured values for the resin; (□) oven-postcured values for Cu; (Δ) oven-postcured values for the resin.

higher and almost equal to the strength obtained by postcuring in the oven. As with pure silver, the postcured strength obtained by oven postcuring is higher than that obtainable by any amount of induction heating. The wettability and potential curves have similar shapes. The maxima in the potential curve coincide with the maxima in the load curve at 25 and 45 sec but not at 5 sec. Similarly, the maxima in the wettability and the load curves coincide at 5 and 45 sec but not at 25 sec.

## DISCUSSION

It has been stated earlier that the objective of this study was to determine the cause for the observed superiority in bonding of metal and resin as it may be achieved by inductive heating. More specifically, and after theoretical considerations, the objective had become to decide among the electrical, the diffusion, and the mixed polymer grafting theories of adhesion. The results of x-ray fluorescent analysis appear to have eliminated the diffusion theory.

A choice between the two remaining theories must then be based on a comparison of breaking loads, interfacial electrical potential values, and

TABLE VIII  
Summary of Data

	Stainless steel	Al-Al <sub>2</sub> O <sub>3</sub>	Cu-CuO	Ag-Ag <sub>2</sub> O	Ag	Cu
Breaking load, kg						
Precured sample (a)	11	25	101	25	83	70
Oven-postcured sample (b)	11	38	92	150	225	99
Increase of (b) over (a), %	0	52	-9	500	171	41
Inductively postcured, maximum (c)	78	93	104	160	213	90
Increase (or decrease) of (c) over (b), %	+609	+145	+13	+7	-5	-9
Angle of contact, degrees <sup>a</sup>						
Original insert surface (a)	74.0	73.1	74.0	75.0	70.0	72.0
Precured sample (b)	72.0 (74.5)	66.0 (68.2)	71.0 (72.0)	69.0 (66.0)	62.2 (62.5)	67.0 (68.2)
Difference, a-b	2.4	6.9	3.4	6.6	8.0	5.6
Oven postcured sample (c)	71.6 (74.5)	66.2 (68.5)	70.6 (72.5)	68.4 (66.2)	62.0 (62.3)	66.4 (68.4)
Difference, b-c	0.4 (0.0)	-0.2 (-0.3)	0.4 (-0.5)	0.6 (-0.2)	0.2 (0.2)	0.6 (-0.2)
Difference, a-c	2.4	6.9	3.4	6.6	8.0	5.6
Inductively postcured, at maximum load (d)	67.0 (70.0)	63.0 (63.7)	64.0 (65.7)	64.2 (61.6)	61.0 (61.4)	64.5 (65.0)
Difference, a-d	7.0	10.1	10.0	10.8	9.0	7.5
Electrical potential, kV						
Precured sample	no data	1.3	2.3	1.0	1.4	1.0
Oven postcured sample	no data	1.3	0.4	1.0	1.1	0.6
Inductively postcured, maximum	no data	2.4	2.3	2.3	2.8	1.8
Inductively postcured, at maximum load	no data	1.8	1.0	2.3	2.0	1.1

<sup>a</sup> Values in parentheses refer to resin surfaces, the others to metal surfaces.

wettability data for an oven-postcured specimen with the corresponding values obtained on the same specimen after varying induction heating times and on the changes in these relationships as they depend on the kind of metal used as the insert.

In the following, reference is made to Figures 7–12 and to the summary of the data in Table VIII. First, a summary of these results will be given.

### **Bonding Strength (Breaking Load)**

The bonding strength of the oven-postcured specimens increases in the order: stainless steel, Al–Al<sub>2</sub>O<sub>3</sub>, Cu–CuO, Ag–Ag<sub>2</sub>O, and Ag; it then decreases somewhat for Cu. Thus, bonding strength increases as the stability of the surface oxides decreases, so that metals with no oxide layer have the highest bonding strength. According to Figure 3, the order between stainless steel (Cr<sub>2</sub>O<sub>3</sub> surface) and Al–Al<sub>2</sub>O<sub>3</sub> should be reversed. However, the data given there are for the formation of Cr<sub>2</sub>O<sub>3</sub> from Cr and need not necessarily apply for Cr<sub>2</sub>O<sub>3</sub> backed by Fe, as in stainless steel.

In the case of inductive heating, all load curves have a sinusoidal shape in that the breaking load increases after a relatively short induction heating time and then goes through several minima and maxima.

In order to ascertain the contribution made to the bonding strength by inductive heating, in comparison to the bonding strength shown by the oven-postcured specimens, the breaking load at the highest peak of the induction postcure breaking load curve is compared with the breaking load achieved by oven postcure and expressed as percentage change.

Drastic differences are observed in the specimens with various metal inserts. There are increases in bonding strength by 609% for stainless steel, by 145% for Al–Al<sub>2</sub>O<sub>3</sub>, by 13% for Cu–CuO, and by 7% for Ag–Ag<sub>2</sub>O; but there are decreases by 5% for Ag and by 10% for Cu. Here, the relative percentage improvement in bonding strength which can be achieved by inductive heating increases for the various metals in about the same order as the stability of their surface oxides increases. With reference to Figure 3, reversal of the order between stainless steel (Cr<sub>2</sub>O<sub>3</sub>) with Al–Al<sub>2</sub>O<sub>3</sub> is again observed, and the comments to this effect made earlier apply here also.

### **Surface Wettability**

By definition, higher angle-of-contact values denote decreased wettability, and vice versa.

The observed angle-of-contact (wettability) curves for matching metal and resin surfaces resemble each other and, furthermore, follow the load curves quite consistently in shape. Although occasionally advancing or lagging, the maxima and the minima in the wettability curves usually correspond quite well to the maxima and minima observed on the load curves after the same times of inductive heating.

The wettability of the metal surface facing the precured resin is always greater than that of the original metal, but oven-postcuring does not further increase wettability. Changes in wettability are, however observed on

inductive heating, capable of going above or below the values for the precured or oven-postcured samples, thus paralleling the load curves as above discussed.

The highest peak in the wettability curve corresponds to the highest peak in the load curve. The increase in wettability at this point is of about the same value for all inserts tested, i.e., the differences in the angle-of-contact values observed at the load curve peak and on the original surface of the insert range between 7.0 and 10.8.

### Interfacial Electrical Potential

After separation, all specimens showed an electrical potential on the matching surfaces. Usually, the surface of the insert carries a positive, that of the resin a corresponding negative charge. The charges on the precured and on the oven-postcured samples are of about the same magnitude.

In the case of inductive heating, sinusoidal potential curves are obtained. The potentials at their highest peaks are about the same for the various inserts and considerably higher than the potentials observed on the precured and oven-postcured samples.

Although at times somewhat out of phase, the maxima and minima of the potential curves correspond to the coinciding maxima and minima of the load and wettability curves.

Based on the above experimental results, an attempt will now be made at an explanation of the observed phenomena and thus at meeting the objective of this study.

### Precuring and Oven Postcuring

As was discussed earlier, precuring (done at 50°C for 6 hr and at 85°C for 2 hr) causes the formation of long polymer chains by opening the epoxide groups of the prepolymer and the joining of the shorter prepolymer chains through the bifunctional molecules of the diamine. The oven-postcuring (done at 150°C for 4 hr) then introduces crosslinks between these linear chains to yield the "cured" epoxide resin.

No mixed polymer grafting of the epoxide resin to the insert is likely to take place at the low temperature of 50°C, nor is it likely to occur at 150°C at which the resin is known to be entirely stable. This is further substantiated by the observation that there is no significant difference in the angles of contact between the precured and the oven-postcured specimens.

Thus, the observed bonding strength of the precured and the oven-postcured specimens is not likely to be caused by mixed polymer grafting, and it has now to be investigated whether the electrical theory offers a likely explanation.

According to this theory, the formation of a double electric layer at the opposing surfaces of insert and resin is the prerequisite for adhesion. This double electric layer is the result of the transition of electrons into the dielectric, assuming<sup>7</sup> that at the contact of metal and polymer, the electrical



barrier at the metal surface is decreased and electrons pass from metal to dielectric.

Interfacial electrical potentials were observed on all precured and oven-postcured samples, with the metal surfaces carrying the positive charge. Furthermore, the breaking loads of the oven-postcured samples differ with the type of insert, increasing in the order: stainless steel, Al-Al<sub>2</sub>O<sub>3</sub>, Cu-CuO, Cu, Ag-Ag<sub>2</sub>O, Ag. Now, if the electrical theory of adhesion does apply to this system, the differences in bonding strength observed for the various inserts should be caused by differences in the amount of electrons transferred to the resin.

For oven-postcured specimens, bonding between different metal inserts and the epoxide resin may then be explained by double electrical layer formation, with bonding strength depending on the stability of the oxide forming the surface of the metal. The less stable the oxide, the fewer electrons will be tied up in its bonding and the more electrons will be free and mobile and therefore available for the formation of a double electrical layer, resulting in an increased breaking load. Metals with no oxide surface layer will thus have the highest bonding strength.

The above argument has one weakness, in that the electrical potentials at the interfaces should then show an increasing trend, which they do not. However, the inherent difficulties of potential measurements where the samples have to be cleaved prior to measurement have been mentioned earlier, with other reservations summarized by Parkman,<sup>14</sup> so that only limited credence can be given to the actual values.

All in all, it is reasonable to conclude that the bonding strength observed on the oven-postcured specimens may essentially be explained by the electrical theory of adhesion.

### Inductive Postcuring

There is good reason to assume that electrical forces also play a role in causing the bonding of the inductively postcured specimens. Whether other bonding forces are also involved can therefore only be detected by relating the data obtained on the inductively heated samples with those of the oven precured samples. Since breaking load, wettability, and electrical potential all go through maxima and minima, depending on the inductive heating time, comparison will be limited in this section in each instance to the highest breaking load and to the corresponding angle-of-contact and electrical potential values.

When one looks at the data in Table VIII, he finds that the inductively obtained highest breaking load maximum with the stainless steel insert is 609% above that shown by the oven-precured sample; for Al-Al<sub>2</sub>O<sub>3</sub>, 145%; for Cu-CuO, 13%; and for Ag-Ag<sub>2</sub>O, 7%; for the Ag and Cu inserts, on the other hand, the highest inductive load maxima are -5 and -10%, respectively, below those shown by oven postcure.

This order of decreasing breaking strength increment for the various inserts is also about the order of decreasing stability of the oxides of the

particular metals. One may then conclude that, in addition to electrical bonding, another type of bonding is taking place under the intense energy (heat) input, which involves the oxide layer of the insert and leads to mixed polymer grafting. While it will require more energy to break the bonds of the more stable oxides and establish oxygen links between metal and polymer, the newly formed primary bonds with groups in the resin molecules will also be more stable, hence the observed increase in bonding strength. This might then explain the situation prevailing for the inserts of stainless steel, Al-Al<sub>2</sub>O<sub>3</sub>, Cu-CuO, and Ag-Ag<sub>2</sub>O.

Where there is no oxide layer, namely in the cases of Ag and Cu, no mixed polymer grafting through oxygen can take place. There could still be chemical bonding other than through oxygen; one could, for example, visualize the formation of metal-carbon bonds. However, the fact that the peak breaking strength values for the inductively postcured samples with Ag and Cu inserts are not above those of the corresponding oven-postcured samples makes it likely that the bonding of these two oxygen surface-free inserts is based solely on electrical forces. The actually observed negative increments may possibly be explained by presence or formation of a weakly adhering oxide layer.

There are still more unexplained observations. For example, it cannot be understood why all inserts show about the same difference in the angle-of-contact values between the oven-postcured samples and the inductively treated samples at peak maximum breaking load.

Also, the electrical peak potentials of the inductively cured samples are all higher than those observed on the oven post-cured specimens, but no trend is observed for the different inserts. While higher potentials could be expected in the inductively heated samples in view of more electrons being released by the metal surfaces at higher temperatures, this should then also lead to generally increased bonding strength values with a certain trend, none of which has been observed.

With these uncertainties still remaining, it appears nevertheless likely that (a) the bonding of the oven-postcured samples is essentially through an electrical double-layer formation, with bonding strength increasing as the stability of the oxides forming the surface layer of the metal decreases; (b) the bonding of the inductively heated samples is both electrical and by mixed polymer grafting through the oxygen layer of the insert, with the more stable metal oxides giving the stronger bonding in grafting; and (c) where the insert does not carry an oxygen surface layer, bonding takes place through electrical forces only.

### **The Coinciding Sinusoidal Shapes of the Inductive Load, Wettability, and Potential Curves**

The discussion has so far been limited to establishing relationships based on the peak maxima in the breaking load curves and the corresponding values of angle-of-contact and electrical potential and to relating them to

the observations made on the oven-postcured samples. The most striking feature of this study, that on inductive heating for increasing lengths of time, breaking strength, wettability, and electrical potential go through more or less coinciding maxima and minima, has yet to be explained.

The periodicities of the load and the wettability curves are bound to be a consequence of the periodicities of the electrical potential curves, and it is thus the latter which should be discussed first.

It is reasonable to assume that on induction heating, electrons are emitted from the metal insert and accepted by the electron-deficient epoxide resin, leading to the observed electrical charges on the opposing surfaces, positive for the metal and negative for the resin. As the induction heating time is increased, more electrons are emitted, and the magnitude of the charges increases. However, after the charges have built up to a certain amount, they can no longer remain separated, and internal discharge will occur. The maximum in the potential curve thus corresponds to the maximum charge build-up, the minimum to the condition prevailing after the discharge has taken place. If the induction heating time is extended further, renewed charging and discharging will take place. This process can be repeated several times as has been observed, up to the point where the resin begins to soften and then to degrade by the accumulated intense heat generated by the insert.

Finer details of the potential curves and differences between them are likely to depend upon such factors as the nature and surface of the insert, the medium separating the charges, the distribution ratio of electrons consumed by the resin, and the amount of electrons taking part in the complex reactions between the free radicals formed by the resin decomposing along the surface of the insert.

The explanation for the observation that the wettability curves for matching insert and resin surfaces resemble each other has already been given earlier, with particular reference to the paper by Raff and Sharan.<sup>10</sup> In analogy to work done by others,<sup>3</sup> it was assumed that partial degradation of the resin will take place along the surface of the inductively heated insert. The products of this degradation cannot escape but will recombine when induction heating ceases and the specimen cools to structures different from that of the original polymer. The products of degradation will be different for various induction heating times<sup>3</sup> and so will the products of recombination formed on cooling. Thus, as the intensity of heating is increased with increased induction heating times, sequences of destruction and reformation reactions of polymeric structures will take place, expressing themselves as changes in surface wettability.

It is during these periods of breaking and making of primary bonds that the fractured, free-radical-type polymer chains will graft onto the metal through the activated oxygen atoms on the metal surface.

The observation that the maxima and minima in wettability match those in the electrical potential might then be explained by assuming that the internal electrical discharges which cause the drastic decreases in the po-

tential curves also periodically break the primary bonds connecting resin and insert and possibly even damage the newly formed polymeric structures. This is not an *ad hoc* assumption, since evidence has been reported<sup>14</sup> that electric discharges cause primary bond scission in dielectrics.

One can thus arrive at the following overall picture.

As induction heating is started, electron transfer sets in, and the electrical potential on the opposing surfaces of insert and resin increases. Also, partial destruction of the resin surface opposing the insert begins under the formation of free radicals, and oxygen atoms in the metal surface (where such exist) become activated. If at this stage induction heating is stopped and the sample allowed to cool, the newly formed polymeric structures, partially grafted to the insert by oxygen, will become stabilized. The result of this is an increase in the wettability of the opposing metal and resin surfaces and consequently an increase in the interfacial breaking strength.

Longer induction heating causes more electrons to transfer, thus further increasing the electrical potential. It also causes more oxygen bonds and more bonds in the resin to break, new polymeric structures to form, and grafting to become more pronounced. All this causes a further increase in wettability and consequently in breaking strength.

This goes on to a maximum point where internal electrical discharge takes place, effecting a sudden break of the primary bonds causing the grafting. This then results in the observed coinciding minima for potential, wettability, and breaking strength. On further inductive heating, the opposing metal and resin surfaces become charged again, create another set of maxima, followed again by minima, and so forth.

As pointed out earlier, the maximum breaking strength obtained on inductive heating minus that shown by the oven-precured sample is considered a measure of the contribution by the mixed grafting to the overall bonding strength, a contribution which increases with the stability of the metal oxide deposited on the surface of the insert.

In dealing with inserts which have no oxide layer (Ag, Cu), the above picture is only changed in that no mixed grafting can take place so that the inductively obtained breaking strength does not exceed the breaking strength of the oven postcured specimen. Periodic breaking of polymer molecules and reforming into new polymeric structures, and consequently periodic wettability changes, can still be expected to take place and to lead to the observed coincidental and sinusoidal curves for electrical potential, wettability, and breaking strength.

## CONCLUSIONS

For oven-postcured specimens, bonding between different metal inserts and an epoxide resin is explained by formation of a double electrical layer (insert positive, resin negative), with bonding strength increasing as the stability of the oxide forming the surface layer of the metal decreases. Metals with no oxide surface layer thus have the highest bonding strength.

For inductively postcured specimens, bonding is effected by both electrical double-layer formation and mixed polymer grafting through the oxygen atoms in the metal surfaces, with the more stable metal oxide giving the stronger bonding in grafting. Where the insert does not carry an oxide surface layer, bonding takes place through electrical forces only.

Alternating build-up and internal discharge of electrical double layers are the direct cause of the sinusoidal shape of the electrical potential curves and the indirect cause of the comparable shape of the wettability curves. Their combination results in the observed periodicity of the breaking load curves.

The authors wish to thank Drs. S. A. Duran, M. F. Adams, and D. B. Masson for their assistance and Mr. Robert Bureau for help in the interfacial electrical potential measurements.

### References

1. R. A. V. Raff, I. W. Herrick, and M. F. Adams, *Mod. Plastics*, **44**, No. 2, 130 (1966).
2. R. A. V. Raff, I. W. Herrick, and M. F. Adams, unpublished data.
3. M. A. Keenan and D. A. Smith, *J. Appl. Polym. Sci.*, **11**, 1009 (1967).
4. S. S. Voyutskii, *Autohesion and Adhesion of High Polymers*, Interscience, New York, 1963, pp. 134-140, 224-225.
5. L. V. Azaroff and J. J. Brophy, *Electronic Processes in Materials*, McGraw-Hill, New York, 1963, pp. 78, 305, 316.
6. A. J. Dekker, *Solid State Physics*, Prentice-Hall, New Jersey, 1961, p. 306.
7. S. M. Skinner, R. L. Savage, and J. E. Rutzler, *J. Appl. Phys.*, **24**, 458 (1953).
8. D. A. Turnbull, *Atom Movements*, American Society of Metallurgy, Cleveland, Ohio, 1951, p. 129.
9. R. A. V. Raff, *The Grafting of Organic Polymers onto Inorganic Substances*, USAEC Report RLO-2043-2, January 30, 1968.
10. R. A. V. Raff and A. M. Sharan, *J. Polym. Sci. A-1*, **6**, 1035 (1968).
11. C. J. Smithells, Ed., *Metals Reference Book*, 2nd ed., Interscience, New York, 1955, Vol. II, p. 592.
12. F. E. Bartell and B. R. Ray, *J. Amer. Chem. Soc.*, **74**, 778 (1952).
13. H. Lee and K. Neville, *Handbook of Epoxy Resins*, McGraw-Hill, New York, 1967, chapter 11, p. 11; chapter 12, p. 3.
14. N. Parkman, in *Physics of Plastics*, P. D. Ritchie, Ed., Iliffe, London, 1965, pp. 303-308, 314-316.

Received August 23, 1968