Effect of Gamma Radiation on the Adhesion of Metals to Epoxy Resin

INTRODUCTION

As part of a comprehensive program of research on the utilization of ^{60}Co gamma radiation, the effect of irradiating epoxy resin casts containing embedded metal inserts is under study. Our interest in this particular system stems in part from earlier work in this laboratory on the effect of inductive heating on similar composites.[1–3] Results of our current study show that the strength of joints between stainless steel or copper and an epoxy resin can be increased up to 300% by gamma irradiation.

EXPERIMENTAL

Tensile test specimens were cast from an epoxy resin (Epon 828 of Shell Chemical Company) and metaphenylenediamine, with 1 cm^2 metal inserts, about 0.04 cm thick, embedded in the center. Curing of the specimens, while still in the molds, was completed by heating at 85–90°C for $^1/_2$ hr after they had remained overnight at room temperature. In some cases, postcuring was done at 180°C for 1.5 hr.

The metal inserts were machined from stainless steel (Type 304) obtained from Washington Steel Corporation, Washington, Pennsylvania, or Cominco Electronic Company, Spokane, Washington, and copper (Grade 59) which was obtained from Cominco Electronic Company, Spokane, Washington. Prior to being embedded in the resin, they were vapor degreased with trichloroethylene and etched with the appropriate solutions. Two methods were adopted for stainless steel. In one,[4] etching was done for 30–40 sec at room temperature in a solution made up of $FeCl_3$ (20 wt-%) in HCl (75 vol-%)–HNO_3 (5 vol-%)–H_2O (20 vol-%). In the other method,[5] the inserts were first subjected to alkaline cleaning with a solution of 3% each of trisodium phosphate and sodium carbonate for 5 min at 80°C. The inserts were then rinsed and immersed in a solution of 50 g KBr per liter of a 1:1 mixture of concentrated H_3PO_4 and water, for 2 to 10 min at 95 ± 10°C. The metal pieces were dried at 20–70°C after rinsing in deionized water. The surface preparation of copper involved the following steps[6]: (i) vapor degreasing, (ii) acid etching for $^1/_2$ min in a mixture of concentrated H_3PO_4, concentrated HNO_3, and H_2O (75:10:15 by volume), (iii) rinsing with water, (iv) immersing in a solution of 1% each of potassium permanganate and sodium hydroxide at 95°C for 5 min, (v) rinsing with deionized water, and (vi) air drying. In one set, the copper inserts were subject to acid etching only according to steps (i), (ii), (v), and (vi) above.

The cast specimens were exposed to gamma radiation from a ^{60}Co source at a dose rate close to 1 Mrad/hr.

The thin layer of epoxy resin, less than 0.5 mm thick, surrounding the edges of the metal inserts in the specimens was carefully filed away so that each specimen consisted of two blocks of resin adhering to opposite faces of the metal insert fixed in between the two. The strength of the joints was measured in an Instron Universal Testing Instrument, Model TTCML, and calculated from the recorded load at break and the area of the exposed face of the metal insert. Five specimens were used for each test set. In all cases, boundary failure was observed.

RESULTS AND DISCUSSION

It is known that surface treatments before bonding can improve the strength and durability of joints. For example, the immersion of stainless steel in KBr–H_3PO_4 is reported to result in the formation of a continuous layer of epsilon-Fe_2O_3 and hence to give strong and durable adhesive joints.[5] On copper, an alkaline permanganate treatment has been shown[6] to produce a mechanically strong and continuous oxide layer of about 500-Å thickness. Therefore, various metal surface treatments were applied in our study of the effect of gamma radiation on metal–epoxide resin joint strength. Indeed, Table I shows that the initial values of the joint strength of the irradiated composites depend on the surface treatment of the metals as well as on the degree of thermal cure.

Thus, for stainless steel obtained from the Washington Steel Corporation, after postcure at 180°C for 1.5 hr, the unirradiated joint strength was 10 kg/cm^2 when the metal surface had been treated with $FeCl_3$–HCl–HNO_3, but 19 kg/cm^2 when KBr–H_3PO_4 was used. Without postcure, the latter treatment gave a value of 16 kg/cm^2. For a stainless steel sample from the Cominco Electronic Company, which was also of type 304 but with a different finish, the unirradiated joint strength, after KBr–H_3PO_4 treatment and without postcure, was 8.4 kg/cm^2.

TABLE I
Dependence of Joint Strengths Between Metals and an Epoxy Polymer on Radiation Dose

Metal	Surface treatment	Thermal cure	Strength,[a] kg/cm^2 0 rads	2.0×10^7 rads	4.0×10^7 rads	6.0×10^7 rads
Stainless steel[b]	$FeCl_3$–HCl–HNO_3	90°C/0.5 hr 180°C/1.5 hr	10(2)	12(4)	29(9)	17(5)
Stainless steel[b]	KBr–H_3PO_4	90°C/0.5 hr	16(5)	16(7)	21(5)	18(6)
Stainless steel[b]	KBr–H_3PO_4	90°C/0.5 hr 180°C/1.5 hr	19(5)	—	24(6)	24(8)
Stainless steel[c]	KBr–H_3PO_4	90°C/0.5 hr	8.4(4)	8.0(2)	21(8)	15(3)
Copper	(i) HNO_3–H_3PO_4 (ii) NaOH–$KMnO_4$	90°C/0.5 hr	15(6)	19(6)	18(6)	22(6)
Copper	HNO_3–H_3PO_4	90°C/0.5 hr	11(2)	5.7(2)	6.3(2)	32(2)

[a] Standard deviation in parentheses.
[b] Type 304, Washington Steel Corporation, Washington, Pa.
[c] Type 304, Cominco Electronic Co., Spokane, Wa.

The subsequent increases in joint strength caused by irradiation were different in all cases. Moreover, when copper was subjected only to acid etching to remove surface oxides, the joint strength decreased initially with the irradiation dose before showing a drastic increase at 6.0×10^7 rads; when treated with alkaline permanganate, the initial joint strength was not only higher but increased steadily on irradiation.

Though changes in the mechanical properties of the polymer and metal are bound to influence the joint strength between the two adherends, such changes must be considered negligible[7,8] at the radiation doses used in this study. It remains to be investigated whether these complex phenomena can be analyzed in a manner similar to that applied earlier to metal–epoxy resin composites which had been subjected to inductive heating.[1–3] It could now be assumed that changes in the metal–polymer interfaces are caused by internal bombardment by the Compton electrons generated by the gamma irradiation, leading to atom displacements in the metals and free radicals in the polymer.[9–11]

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