Radiation Effects on Aluminum-Epoxy Adhesive Joints

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ABSTRACT: Two epoxy adhesive types, Cole-Parmer and Devcon, were used for preparing aluminum-epoxy bondings. The adherend surfaces, of 30 mm in diameter, were prepared using grits of 120, 240, and 320 followed by a final grit of 400, according to the ASTM D897 standard. The curing was set at 72 h at room temperature. The samples were submitted to irradiation for different times in the pool of a SLOWPOKE-2 reactor which produced thermal neutrons, fast neutrons, and γ rays. The tensile properties of nonirradiated and irradiated samples were obtained with an Instron Tester, model 4206. The failure stress, about 11 MPa for nonirradiated samples, had a large decrease after a short period of irradiation and then constantly increased for longer irradiation periods. This may be explained by a predominant effect of crosslinking over chain scissions for higher irradiation doses. The density data and tensile properties of the bulk cured epoxy (Devcon) also supported the above findings. The presence of water on the bonding joints had an effect of exaggerating the irradiation effects on the strength of joints. The use of the adhesive failure modes to group the results into subgroups has permitted the reduction of the spread of the results from the tensile tests. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci **67:** 37–47, 1998

Key words: epoxy adhesives; aluminum; radiation effects; failure modes

INTRODUCTION

Adhesives based on epoxy resins are widely used for bonding metals, concrete, and a whole range of nonporous materials.[1] They established their reputation as adhesives for bonding metals in the 1950s by virtue of their ease of application and the very high strengths of the joints that they form. In addition to providing the general advantages of adhesive bonding over mechanical fastening, epoxy resin adhesives offer clear advantages over the other synthetic bonding materials, such as curing without generation of by-products and cure with negligible shrinkage. As a structural adhesive, epoxy glues have become almost indispensable, thanks to their favorable characteristics which make them especially attractive for applications such as in the aerospace and nuclear industries. The use of epoxy adhesives in radiation-intense environments requires previous knowledge of how radiation can affect the mechanical (adhesive) properties of epoxies. The organic nature of epoxies makes them particularly susceptible to radiation effects. In almost all cases, the absorbed radiation dose necessary to bring about physical changes in polymers is considerably less than that required to cause significant change in other materials such as glasses, ceramics, or metals.[2]

Radiation Effects on Polymers

The effects of radiation on polymers depend strongly on the molecular structure, for instance, the presence of tertiary or quaternary carbon as well as the presence of oxygen in the structure, the presence of additives, and the radiation environment[2] itself. When the radiation consists of

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electromagnetic photons (X-rays and γ rays), the predominant mechanisms of interaction of the photons with the matter are the Compton and photoelectric effects and the pair production.[3] The consequences of these effects are essentially the ejection of free electrons from the atoms (primary ionization) and the secondary ionization of the surrounding molecules and atoms. The positive ions and the ejected electrons can then recombine to produce highly excited molecules which undergo decay to their respective ground states, usually with the emission of radiation. They may also release part of their energy through chemical reactions by heterolytic bond cleavage, producing ions, or by homolytic bond cleavage, leading to the formation of free radicals. As a whole, the effects of radiation depend essentially on the type and cumulative dose of the incident radiation. The presence of hetero elements such as oxygen, chlorine, and sulfur complicates these reactions further.[2,3] After the formation of free radicals, polymerization is terminated by way of recombination to form a crosslink or chain scission. Both may occur simultaneously, but one is usually predominant, depending on the structure of the polymer. The presence of aromatic rings in the polymer backbone, such as phenoxy resins, has a radiation-stabilizing effect[4] on the polymer.

From a previous work[5] on the effects of high-energy electron beam radiation on the processing of epoxy, it has been speculated that the tensile strength of cured epoxy was improved to a significant extent; this improvement may be attributed to the increase of crosslinking degree which was controlled by the diffusion process during the chemical curing period. In the case of an adhesive joint, the strength of the latter is dependent on two factors—the adhesion of the adhesive to the materials being bonded and the cohesive strength of the adhesive itself. Thus, it is interesting to investigate the radiation effects on the overall strength of an aluminum-epoxy adhesive joint.

EXPERIMENTAL

Materials

In this work, two different types of epoxy adhesives are used. The first adhesive is a Cole-Parmer epoxy kit 08778-00, with the trade name Epoweld 8173. This is a two-part epoxy adhesive which sets in just 3–5 min at room temperature. The chemical compositions of both Part A (resin) and Part B (hardener) are of trade secret which cannot be disclosed, but some of their properties such as the viscosities at room temperature are shown as being 55,000 and 10,000 cps, respectively. The second adhesive used is a Devcon product consisting in a Devcon Plastic Liq Resin 10210 and a Liquid Hardener 0202. This is a long-curing adhesive type with a curing period of 24 h at room temperature. The Devcon resin is mainly composed of diglycidyl ether of bisphenol A (DGEBPA) and many additives such as carbon powder, aluminum powder, and others. The Liquid Hardener 0202 is mainly made of polyamide of C18 fatty acid dimers and tetraethylene tetramine (TETA), as well as many additives.

Aluminum-Epoxy Bonding

The preparation of the adhesive bonds and the testing procedures followed rigorously the ASTM D897 *Standard Test Method for Tensile Properties of Adhesives Bonds.*[6] Identical aluminum flanges were machined in a double-size cylindrical shape with the smaller cylinder of 30 mm in diameter used as the adhered surface and the larger cylinder used as the base for tensile testing. Before the application of epoxy adhesive, the aluminum-adhered surfaces were carefully prepared with a first grinding done with water flowing for removing the fine aluminum particles. Then, the surfaces were subsequently ground using grits of 120, 240, and 320. As per the standard procedure, a sanding grit of 400 was used for the final grinding of aluminum surfaces and their condition was verified with an optical microscope. The epoxy adhesive mixing was then prepared according to the manufacturer's instructions, which recommended essentially a ratio of 9 : 1 (by weight) between epoxy resin and hardener for the Cole-Parmer adhesive and 1 : 1 for the Devcon epoxy. The problem of producing uniform adhesive batches was solved by building and calibrating a dual syringe applicator for a precise control of the quantities used and this system produced excellent repeatability. Also, in order to ensure an uniform resin-hardener mixture, a well-defined mixing pattern using a glass rod was rigorously followed. Finally, the gluing of two adherend surfaces was done with a jig to ensure an uniform epoxy thickness for all bonded samples. This thickness was controlled to about 0.4 mm by applying a constant slight pressure (12.5 kPa) on the top of the aluminum flange with a 900-g w. The curing period was set at 72 h for both types of epoxy adhesives at room temperature. The effects of surface etching was also investigated by preparing a batch of samples ac-

cording to the DTD915B standard procedure.[7] After this, the aluminum flanges, after the sanding steps, were immersed in a 5% chromium trioxide–15% sulfuric acid solution kept at 60°C for at least 30 min. The flanges were then rinsed with distilled water and dried in blowing air. The adhesive joints prepared by this procedure are presented with the label "treated." In order to obtain the cohesive tensile strength of epoxy resins, a set of epoxy samples were cured in "dogbone" shape with molds made in Teflon with a gauge length of 25 mm, a gauge width of 6 mm, and a thickness of about 3.5 mm.

Radiation Processing

The radiation is produced by the SLOWPOKE-2 nuclear research reactor consisting in thermal and epithermal neutrons and in γ rays. The dose rates for the neutrons and γ radiations at the irradiation sites in the pool were determined from measurements and summarized as follows[8]: 600 $\pm$ 50 Gy/h for neutrons, 12 $\pm$ 4.5 Gy/h for fast neutrons, and 3600 $\pm$ 1250 Gy/h for γ rays, at full reactor power. The sample holder used for the irradiation was a plexiglas sector-shaped box designed to fit snugly against the reactor vessel wall. The holder could hold eight samples in two rows of four, which were all well covered by a waterproof tape to avoid all contact with water in the reactor pool. The holder was affixed to the "elevator," a device designed to position in the reactor pool the samples to be irradiated and maintain them exactly at the desired location. Irradiation ranged from 2 to 32 h at half reactor power. Undue personal exposure to radiation was avoided by first allowing the irradiated samples to decay radioactively for 5 days in the reactor pool, but at a position about halfway up where the neutrons and γ photons do not affect the samples. After the dose rates have dropped sufficiently, below 25 μSv/h at the surface of the samples, as monitored with a Chicago Nuclear beta/gamma survey meter, the holder was lifted up to the pool surface and the samples were removed from the elevator and placed into a lead cask for further decay for five more days before testing.

Tensile Test

The tensile tests were performed on nonirradiated and irradiated adhesive-bonded samples with an Instron Tester, model 4206, completely digitalized, where the force applied to the sample, as well as its elongation during the test, was automatically recorded by the control board of the Tester. The tensile load cell has a capacity of 500 N. A suitable cylindrical grip was used for firmly holding the circular bases of samples in place without slipping. The crosshead speed used was 1 mm/min. All experimental data were recorded at the breakpoint of samples, and the broken surfaces of samples were carefully examined in order to categorize their failure modes relative to the interfacial adhesive strength and the cohesive strength of cured epoxy. In the case of tensile tests performed on "dogbone" samples, their dimensions were well measured with a micrometer before the tests, and suitable grips were used for firmly holding the samples without slipping.

Density Measurement

It is known that the crosslinking degree of thermoset materials, such as cured epoxy, is directly proportional to its density. The density of the nonirradiated and radiated "dogbone" samples was measured by following the ASTM D792-A procedure.[9] The samples were sliced into pieces of approximately 2.5 cm in length, weighing between 2 and 5 g. A small hole was drilled at one end of each piece. A Mettler-H35AR balance was used. A wire hook was hung off of the balance hook, and a support table was assembled over the scale's platform. The scale was set at zero position with the tare knob and then was not adjusted for the remainder of the experiment. The sample was first weighed in air and then thoroughly wetted with water; air bubbles were carefully removed from its surface. The sample was then weighed in water. Its weight loss after immersion was determined, and its density was calculated by use of the following expression:

$$\text{Density} = 0.9975\left(\frac{W_o}{W_0 - W_1}\right) \qquad (1)$$

where W_0 is the apparent weight of the sample in air and W_1 is the apparent weight of the sample completely immersed in water. The measurement was carried out at 23°C. The accuracy in the reading is $\pm$0.0005 g.

RESULTS AND DISCUSSION

Curing Mechanism of Devcon and Cole-Parmer Epoxy Adhesives

Polyfunctional primary and secondary aliphatic amines give fast cures and provide overall proper-

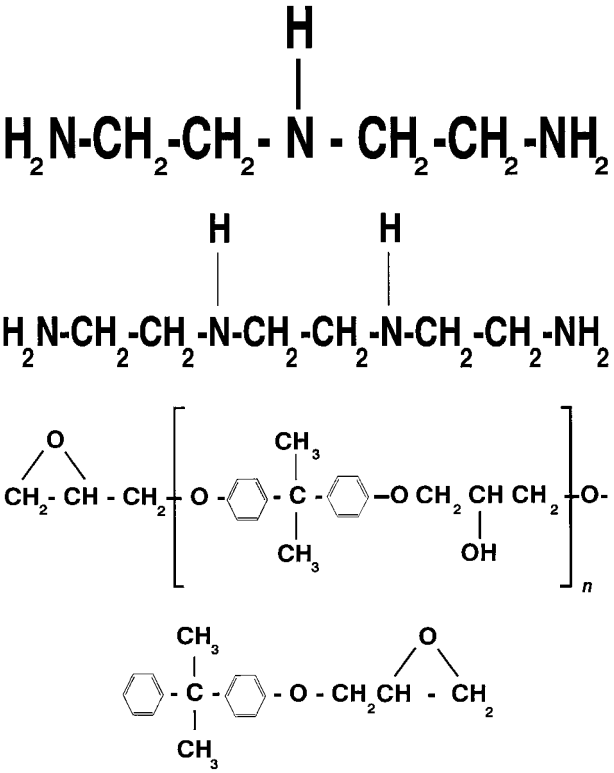

Figure 1 Chemical structure of (a) DETA, (b) TETA, and (c) DGEBPA.

ties satisfactory for a wide variety of commercial applications of epoxy.[1,10] Among these amines, diethylene triamine (DETA) and TETA are the most commonly used curing agents. Figure 1(a) and (b) present the chemical structure of DETA and TETA, respectively. DETA possesses five active hydrogens available for crosslinking, and the stoichiometric quantity between epoxy resin and hardener required is approximately 10 : 1 to 11 : 1. DETA-cured epoxy resin will gel and set hard at room temperature within a very short time. Therefore, DETA is probably the hardener used for the Cole-Parmer adhesive, while its epoxy resin, Epoweld 8173, is mainly made of DGEBPA, which is illustrated in Figure 1(c). Theoretically, each active hydrogen of DETA can react with the epoxy group of an epoxy molecule to form a secondary amine as well as one hydroxyl group in such a manner that a total of five epoxy molecules are crosslinked around one DETA molecule; similarly, the second epoxy group of each epoxy molecule can react with a hydrogen of another DETA molecule, and so on. During the early stage of cure, before the molecules are all crosslinked, semithermoplastic or B-stage resins are in existence. At this stage, the reaction has been initiated at a number of widely dispersed points in the resinous mass. With additional cure, crosslinking becomes general and the compound assumes its thermoset nature. For practical purposes, a thoroughly cured system is considered one in which the degree of crosslinking is sufficient to provide optimal physical properties for a particular application. Complete cure, requiring consumption of all reactive functions in both the resin and the hardener, is seldom if ever achieved because of the diffusion-controlled rate of these reactive groups.

In the case where TETA was used for the curing of Devcon adhesive, a total of six active hydrogens [Fig. 1(b)], four belonging to primary amine groups and two belonging to secondary amine groups, can assume crosslinking of DGEBPA resin. However, because of steric hindrance effects, the curing rate with TETA is slower than that with DETA. Another important factor governing the slow curing rate of Devcon adhesive is the presence of many additives in both liquid resin and hardener, specifically the use of C18 fatty acid dimers together with TETA. One carboxylic group of a C18 fatty acid dimer will react with one primary amine group of TETA to form one amide functional group which cannot react with the epoxy resin, leaving only four hydrogens of TETA capable of reacting and crosslinking with the epoxy resin.[1] Consequently, the crosslinking degree and the curing rate of the Devcon adhesive are assumed to be much lower than those of the Cole-Parmer adhesive. The presence of fatty acid dimers is to provide a flexibilizing effect, which increases the impact resistance and greatly lowers the stiffness of the cured epoxy systems.[1] This is confirmed by the values of the Young's modulus of cured Devcon epoxy obtained from the tensile testing, 1.1 ± 0.15 GPa, compared with the usual values of about 2.5 GPa for unmodified epoxy,[10] and the elongation at break of about 10%.

Radiation Effects on the Cohesive Properties of Cured Devcon Epoxy

Like polystyrene and because of its high aromatic content, cured epoxy has a very high radiation resistance.[10] Under an inert atmosphere, a cured epoxy novolac, a family of epoxy resins containing several OH groups in each molecule, could maintain its mechanical properties nearly unaltered at 5×10^6 Gy (or 5×10^8 rad).[10,11] Among numerous chemical bonds constituting the cured epoxy network, the one established between N and C during the curing process has a bond enthalpy[12] of 292 kJ/mol, which is susceptible to be readily dissociated by thermal neutron radiation or γ radiation

at moderate doses.[3] However, the presence of aromatic rings in the polymers exerts a strong stabilizing influence on the yield of radiation-induced crosslinking at low radiation doses such that cured epoxy could become highly radiation resistant.[3] The increase in crosslinking degree may occur on the same sites as for the curing process described above, for example, between the amine and epoxide functional groups, or on some newly created neighboring free radical sites, which can easily recombine. The tensile tests performed on "dogbone" samples made of Devcon epoxy confirmed that their tensile strength increased from 34.0 to 44.0 ± 5.0 MPa after 8 h of irradiation. It is noticed that the measured tensile strength of nonirradiated samples is a little lower than that suggested[1,10] for DGEBPA resin cured with polyamides, which falls in the range of 31 to 48 MPa depending on the type of polyamide as well as its proportion used. This difference may be mainly attributed to the presence of various additives in the Devcon adhesive epoxy resin and hardener, as well as to the straining rate of the tensile testing.[13] The possible increase in crosslinking degree as mentioned above is also supported by the results from the density measurements and is calculated from eq. (1), which shows a net increase from 2.044 ± 0.002 to 2.169 ± 0.002 g cm^{-3} for the studied samples. The obtained values for the density of cured adhesive samples are much larger than those of usual cured epoxy[10] (about 1.3 g/cm) because of the presence of carbon and metal powder in Devcon adhesive.

Properties of Nonirradiated Adhesive Joints

Stress Analysis of a Butt Joint

Practically every failure of an adhesive joint takes place within a material (cohesive failure) rather than between adhered and adhesive (adhesive failure). When this occurs, the breaking or failure stress of the joint must be related to the strength of its weakest phase, for example, the epoxy adhesive phase. This is confirmed by many observations, but unfortunately, the relation between the strength of an adhesive joint and that of the weakest material (adhesive) is complex and varies from instance to instance.[14] This relation, however, can be based on the following equation:

$$\xi = (\alpha f_m + s)\beta \qquad (2)$$

where ξ is the molecular cohesion of the adhesive, f_m is the failure stress of the adhesive joint, s is the "frozen stress," and α and β are the stress concentration factors. Factor α is different from unity because the stress at the "crucial point," that is, at the point of incipient fracture, is not the average stress and deviates from it the most when the difference in the mechanical properties of adherend and adhesive is the largest. The "frozen stress" s is referred to as shrinkage and swelling stresses caused by the curing or setting of adhesives. It has to be vectorially added to or subtracted from stress αf_m caused by external force.

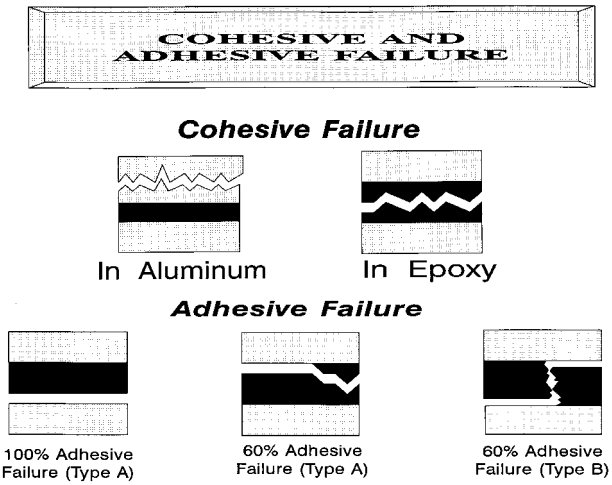

Figure 2 Failure modes.

Regarding the stress concentration factor α for a butt joint, this factor may be expressed as a function of the Poisson ratio of adhesive, v, the thickness of adhesive film, h, the strain of adhesive film due to external tensile loading, Δh, and the radius of the adherend flanges, r, as follows[14]:

$$\alpha = 1 + 8vr\Delta h/h^2 \qquad (3)$$

For a set of adhesive joints prepared under exactly the same procedure, all joints should have the same values of v, h, and Δh, leading to the same values of α for these joints. In general, the factor α can have values much greater than unity because of large values of the ratio r/h. This factor may be mainly responsible for large discrepancies between the observed cohesive strength of Devcon epoxy adhesive (about 34 MPa) as reported above and the observed failure stress of aluminum-epoxy joints presented in the following section (about 12 MPa). Furthermore, it can be seen from eqs. (2) and (3) that for a given butt joint with known values of v and r, the stress concentration factor α and then the failure stress f_m should be greatly sensitive to the thickness of adhesive film

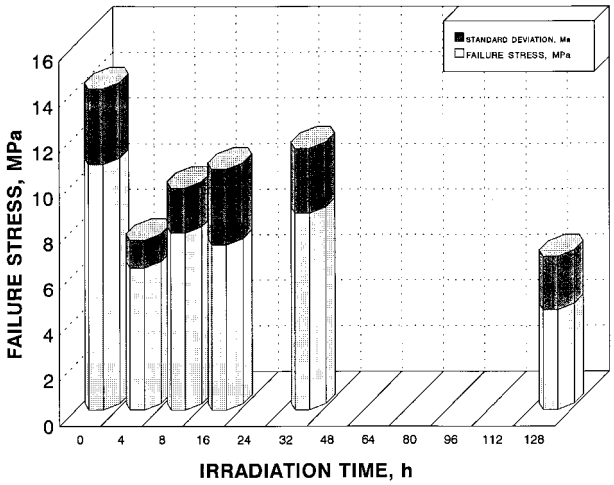

Figure 3 Average failure stress versus irradiation time, Devcon epoxy.

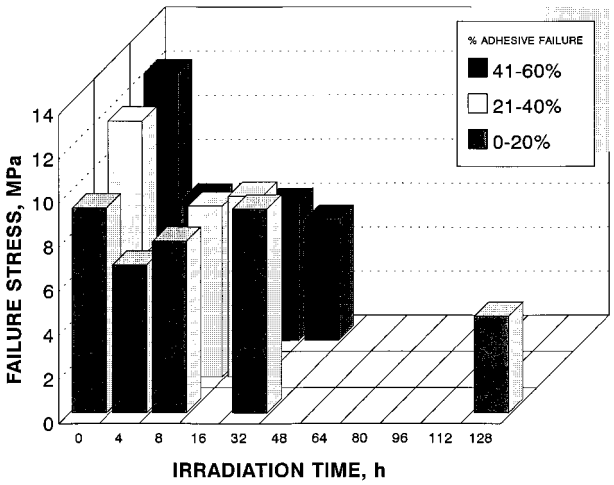

Figure 5 Failure stress regrouped in % adhesive failure, Devcon epoxy.

h. This has been shown by experimental data for butt joints glued with poly(methyl methacrylate)[15,16] or poly(vinyl acetate),[17] where the failure stress was very sensitive to the film thickness when the film was very thin.

The sum ($\alpha f_m + s$) would be equal to the molecular cohesion of the adhesive, ξ, if the adhesive were uniform down to molecular dimensions. However, this sum has to be multiplied by a second stress concentration factor β because no cured adhesive solid is truly uniform up to molecular level. This nonuniformity results from the fact that the mixing of epoxy resin and its hardener, because of their relatively high viscosity, can never yield a completely uniform mixture at the molecular level, contrary to a "usual" liquid mixture of low viscosity such as water + methanol, for example. The experimental failure stresses of adhesive solids has been accounted for by flaws or defects. It is believed that every rupture originates at a bad flaw or a particularly weak spot and that those weak spots are randomly distributed in the solid adhesive film. Consequently, the β factor may be mainly responsible for the fluctuation of the failure stresses of different adhesive joints belonging to the same set of joints, and this dependency becomes more significant for a fast-setting glue such as the Cole-Parmer adhesive.

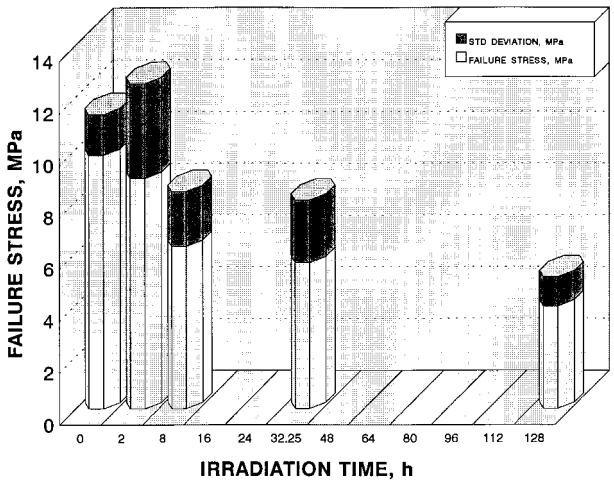

Figure 4 Average failure stress versus irradiation time, Cole-Parmer epoxy.

Failure Modes of Adhesive Joints

Figure 2 illustrates the various types of failures possible for the adhesive joints. The fully cohesive failures (or failures in cohesion) were not observed at all, and only the adhesive failures (or failures in adhesion) were noted. This is in agreement with the fact that the measured failure stresses of all joints are in the range of 6 to 14 MPa, while the cohesive strength of the cured adhesive varies between 31 and 48 MPa, as reported above. These differences were already attributed to the contributions of both stress concentration factors α and β. The 100% adhesive failure type A (Fig. 2) may be attributed to two main causes: differences in the preparation of the two aluminum surfaces of a joint and variations of the lapse of time between the deposing of adhesive on one surface and the gluing of both surfaces, producing unequal interfacial adhesive strengths on both surfaces. By definition, in this work, the 60% adhesive failure means that 60% of the area of the face of one aluminum cylinder previously in con-

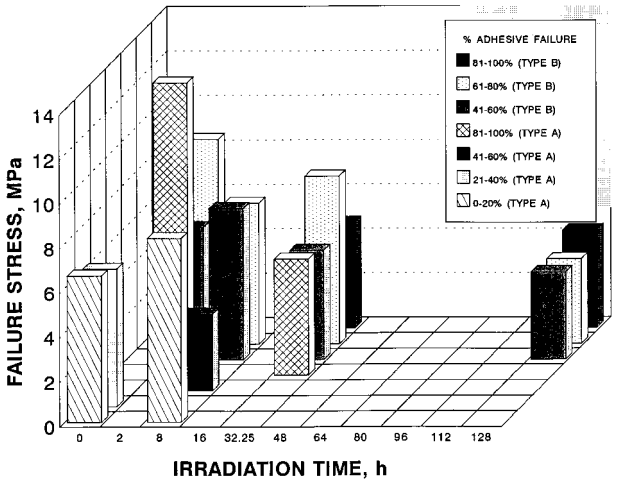

Figure 6 Failure stress regrouped in % adhesive failure, Cole-Parmer epoxy.

tact with the epoxy adhesive is left uncovered after the test, with the rest of the breakage occurring within the epoxy material. On the other hand, adhesive failure type B happens if the preparations of both surfaces are exactly the same and the gluing operation is uniform and rapidly leading to equal interfacial adhesive strengths on both sides.

Failure Stresses of Nonirradiated Adhesive Joints

The failure or breaking stresses of nonirradiated joints glued with Devcon and Cole-Parmer adhesives are illustrated in Figures 3 and 4, respectively, with values corresponding to zero irradiation time. The failure stresses for Devcon adhesive are 12.2 $\pm$ 1.5 MPa, compared with 10.5 $\pm$ 1.2 MPa for Cole-Parmer adhesive, which are all better than the values suggested by the manufacturers.[18] The difference in failure stresses between the two types of adhesives comes from differences in their chemical composition together with their curing rate. The fluctuations of data for a given set of joints are likely attributed first to differences in the uniformity of adhesive film, which lead to different values of the stress concentration factor β, as already discussed above. A second cause of fluctuation may result from a small variation in the film thickness between various joints, which greatly affects the stress concentration factor α. Both factors contribute largely to the failure stress, f_m, as illustrated by eq. (3).

In Figures 5 and 6, the results presented as averages in Figures 3 and 4 appear as separated into subgroups characterized by the failure mode, as explained above. The existence of these subgroups within a given set of joints comes directly from the effects of the factors α and β on the joint failure mechanism. This way, it is believed that the joints that failed within a given mode would have been prepared within very similar conditions. Thus, the effects of joint preparations could be somewhat minimized by this method of reporting the results. For the Devcon adhesive, Figure 5, the broken joints could be gathered into three subgroups: 0–20%, 21–40%, and 41–60% "failure in adhesion" modes (Type A); meanwhile, for the Cole-Parmer adhesive (Fig. 6), the broken joints were gathered into more subgroups due to the "Type B" failures, the statistics are poorer within each subgroup, and the interpretation of these results is more difficult. For both types of adhesives, in the case of nonirradiated joints, it is found that those joints which have broken with a very low percentage of adhesive failure ($<$20%) displayed a lower failure stress than the ones broken with a high percentage of adhesive failure. This can be interpreted in terms of the adhesive strength between the epoxy and the aluminum surface being larger than the cohesive strength of epoxy adhesives, as is generally observed in adhesive applications.[14] The existence of subgroups within a given set of broken joints comes directly from the great effects of the stress concentration factors α and β on the failure mechanism of joints. These effects are more pronounced in the case of the fast-setting Cole-Parmer adhesive, where the nonuniformity degree of the adhesive film may be large as a result of a very high curing rate.

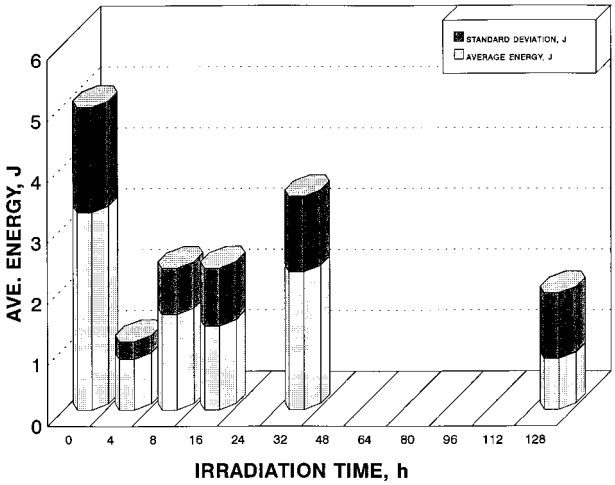

Figure 7 Average energy to break point versus irradiation time, Devcon epoxy.

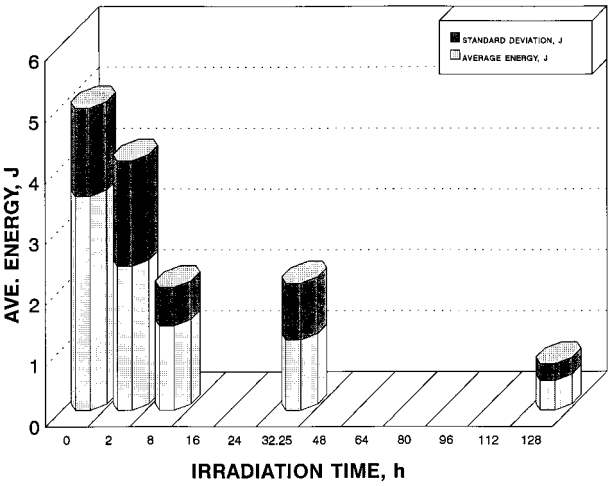

Figure 8 Average energy to break point versus irradiation time, Cole-Parmer epoxy.

Radiation Effects on Adhesive Joints

Failure Stresses and Failure Modes

Figures 3 and 4 show the average failure stresses versus the irradiation time for adhesive joints irradiated close to the reactor core, for both Devcon and Cole-Parmer adhesives, respectively. Because the reactor was operated steadily at half-maximum power, the doses absorbed by the epoxies were estimated, for the 32-h irradiations, at 9.6 kGy for the thermal neutrons, 190 Gy for the fast neutrons, and 57.6 kGy for the gammas. The failure stress of joints using the Devcon epoxy displays a nearly 50% decrease after a 4-h exposure to the radiations, and then it increases continuously until 32 h of exposure. It is known that the cured adhesive molecules at the boundary layers between the adhered surfaces and the adhesive film undergo a much higher stress than those found within the film because of the larger adhesive strength between adhered and adhesive compared with the cohesive strength of adhesive.[14] Under such a higher stress, the "interfacial molecules" or "tie molecules" are immediately affected by chain scissions[2,3] at low radiation doses, leading to a marked fall of the failure stress. However, when the irradiation lasts for larger doses, the increase in crosslinking through the whole adhesive film, as discussed above, provides the beneficial effect of bringing the failure stresses of joints up close to the original level. For the Cole-Parmer adhesive (Fig. 4), the failure stress decreases steadily, but slightly, as the irradiation proceeds, but the decrease rate is very small at the 32-h mark. The observed difference in the behavior of joints prepared with Devcon adhesive and those prepared with Cole-Parmer adhesive with irradiation may be attributed to the presence of various mineral fillers in Devcon resin which have an effect of significantly enhancing the radiation stability of cured epoxy molecules,[2] in particular, those at adhered-adhesive boundaries (or tie molecules).

Figures 5 and 6 present the failure modes gathered into subgroups. These results are similar to those corresponding to nonirradiated joints (at zero irradiation time), except that the failure stresses of different subgroups belonging to the same irradiation time vary only slightly. This may be explained by the fact that the breaking of irradiated joints was mainly determined by the resistance of tie molecules to irradiation. For the Devcon adhesive (Fig. 5), the first two subgroups display the same trend as for the averages (Fig. 3): a sharp decrease of the failure stress at 4 h of irradiation, followed by a recovery for longer exposures. The third subgroup, however, does not show the recovery trend. This may be because of the large standard deviation due to a small number of broken samples belonging to this subgroup. For the Cole-Parmer adhesive, (Fig. 5), more subgroups were observed because of the "Type B" failure modes.

Energy to Break Point and Young's Modulus

The average energy to break point, corresponding to the product of the ultimate force and the elongation at break of adhesive joints, is displayed in Figures 7 and 8 for the two types of adhesives. For the Devcon adhesive, this energy drops

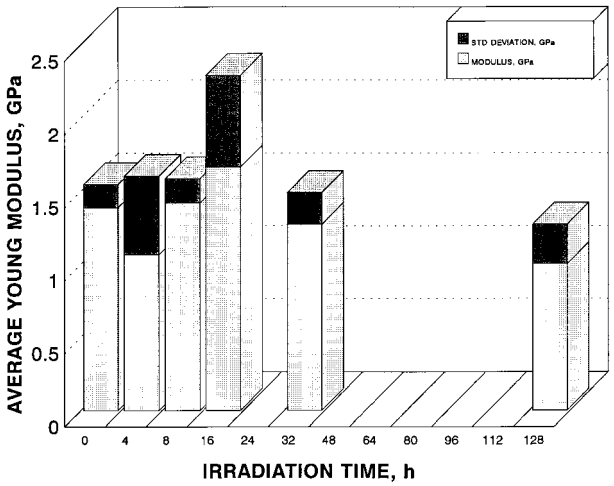

Figure 9 Average Young's modulus versus irradiation time, Devcon epoxy.

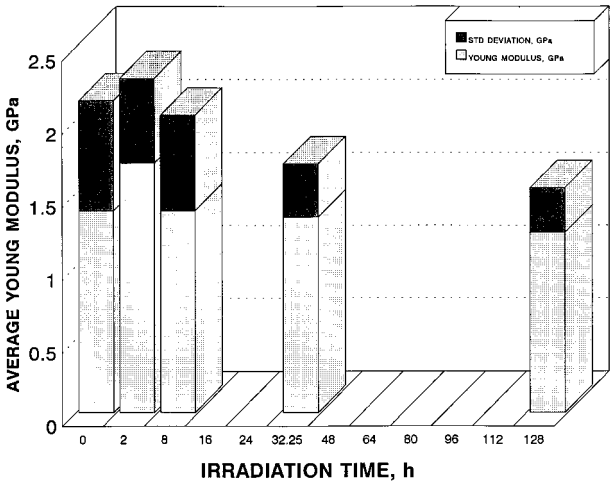

Figure 10 Average Young's modulus versus irradiation time, Cole-Parmer epoxy.

initially from an average above 3 J for the nonirradiated joints to a value below 1 J at 4 h of irradiation and then recovers to about 2 J for the 32-h exposure. Similarly, the trend for the Cole-Parmer adhesive is essentially a steady decrease from about 3.6 J to about 1 J, quite comparable to the trend of the failure stress. In general, the decrease of the energy to break point with irradiation time may result from a small decrease in the failure stress combined with a larger decrease in the elongation at break of the irradiated joints compared with the nonirradiated ones. The large decrease of the elongation at break may be directly related to the increase in the crosslinking degree due to irradiation.

Figures 9 and 10 present the graphs of the average "apparent" or "constrained" Young's modulus of adhesive joints, E', versus the irradiation time. This modulus differs from the true Young's modulus, E, of adhesive because of the radial constraint applied to the adhesive by the adherends.[19] When the butt joint is loaded in tension, the adhesive and the adherends tend to contract radially in such a manner that the radial strain in the adhesive film would be smaller than that of a bulk adhesive sample. Consequently, E' would be generally greater than E according to the following expression[19]:

$$\frac{E'}{E} = \frac{(1 - v)}{(1 + v)(1 - 2v)} \qquad (4)$$

where v is the Poisson ratio of the adhesive. In general, the Poisson ratio of polymeric adhesives has a value between 0.3 and 0.4 so that, according to eq. (4), the ratio (E'/E) varies between 1.35 and 2.15. This explains the difference between the apparent Young's modulus for Devcon adhesive joints presented in Figure 9 and the true Young's modulus of Devcon adhesive, about 1.1 GPa, obtained from the tensile testing of Devcon adhesive "dogbones," as shown earlier. For the Devcon adhesive, a minimum of E' occurs at a 4-h irradiation, followed by a maximum at 16 h. The values for the Cole-Parmer (Fig. 10) do not change significantly, except for a maximum at a 2-h irradiation. The increase in the apparent Young's modulus, especially for the Devcon adhesive, may result from a slight increase of the failure stress, while the elongation at break might remain constant or at least change by a very small amount as a result of the thermosetting characteristics of the cured epoxies. On the other hand, on the basis of the decrease of the energy to break point (or toughness) with irradiation time, it can be deduced that the elongation at break was effectively smaller than that of the nonirradiated samples. This negative change is again related to higher crosslinking degrees, such as confirmed by the density measurements of the "dogbone" samples.

Effects of Water and Surface Etching

During the experiments of irradiation performed in the pool of the SLOWPOKE-2 reactor, a certain number of samples were involuntarily put in contact with the water of the pool. Consequently, the presence of water had greatly enhanced the irradiation effects on these samples, as illustrated on

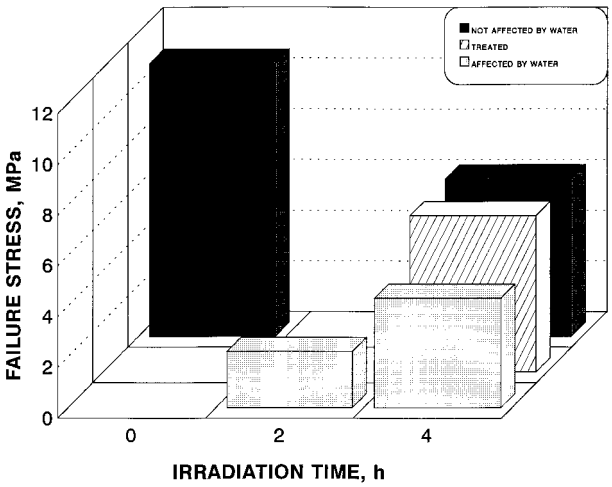

Figure 11 Water and etching effects on failure stress, Devcon epoxy.

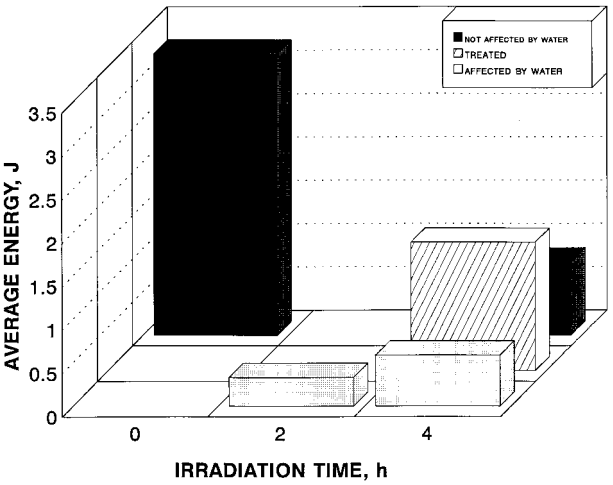

Figure 12 Water and etching effects on energy to break point, Devcon epoxy.

Figures 11–13 for the Devcon adhesive. It was found that all three tensile properties decreased by a great extent, especially the failure stress, by a factor as large as 5 for the 2-h irradiation. This significant decrease resulted from two successive effects. First, water tends to accumulate in sites near the interface, interfering with interfacial aluminum-epoxy bonds by weakening these bonds. This effect would be greatly accelerated if shrinkage stress, which is presented by the s parameter in eq. (2), is present in the joints, resulting from the curing of epoxy.[19] Then, the chemical action of the oxygen of water with adhesive molecules will cause rapid and predominant chain scissions, in particular for those at boundary layers, during the short irradiation period.[2,3] The properties seemed to recover a little after longer irradiation periods as a result of the effect of the crosslinking phenomenon; however, these effects are definitely smaller in magnitude than the ones observed with joints irradiated without the interference of water.

These last three figures also present the results obtained from the etched surfaces using the acid solution, called "treated samples." These joints were not irradiated in the presence of water. Except for a slight change of the average energy to break point, these results are very similar to those prepared following the ASTM D897 procedure. This allows the conclusion that the sanding operation of the aluminum surfaces as per the ASTM D897 standard was satisfactorily carried out.

CONCLUSIONS

The results obtained in this study, with acceptable uncertainties, confirm that the bulk properties of the Devcon adhesive, as well as the adhesive strength of aluminum-epoxy joints made from both types of adhesive, are significantly affected by the radiations produced from the SLOWPOKE-2 reactor, which consist mainly of the γ photons with a smaller thermal neutron flux component. In both cases, an initial reduction of the tensile strength is observed, followed by a recovery for the Devcon adhesive, or a stabilization for the Cole-Parmer adhesive, as irradiation progresses. At first, for short irradiation durations, the mechanical properties diminish by almost 50%, as a result of the predominance of the chain scission process, which significantly affects the tie molecules at the adherend-adhesive boundaries. Then, the crosslinking phenomenon occurs after a series of chemical reactions with overall longer irradiation durations. These effects were demonstrated as being greatly accelerated by the presence of water on the adhesive joints. The surface etching procedure using an acid solution did not significantly alter the adhesive strength compared with the sanding procedure suggested by the ASTM D897 standard.

The use of the adhesive failure modes to group the results into subgroups, believed to have similar preparation conditions, has permitted somewhat the reduction of the spread of the results and, in the case of the Devcon adhesive, confirms the trends observed for the average results, in addition to facilitating the interpretation of the test results. This research permits the assessment of the pertinence of using epoxy adhesives in applications where the polymer may be subjected for long periods to bombardment by radiations, such

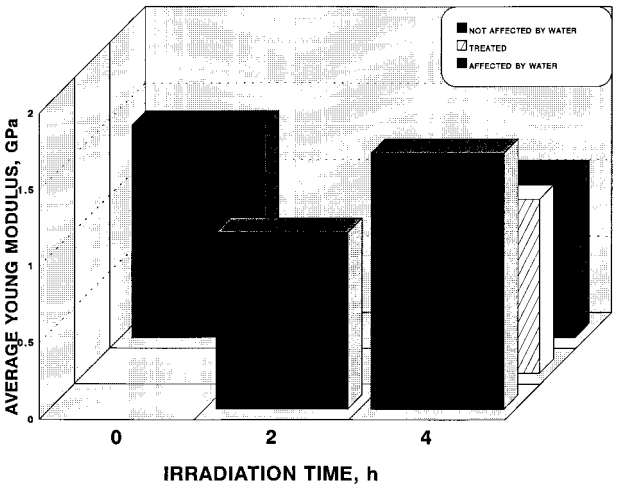

Figure 13 Water and etching effects on Young's modulus, Devcon epoxy.

as for prolonged space missions, or in spent nuclear fuel long-term disposal applications.

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