

Weathering of Fiber-Reinforced Epoxy Composites

DAVID ROYLANCE

*Department of Materials Science and Engineering
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139*

and

MARGARET ROYLANCE

*Organic Materials Laboratory
Army Materials and Mechanics Research Center
Watertown, Massachusetts 02139*

Unless suitably stabilized and coated, fiber-reinforced composites are subject to photoinitiated oxidation which results in a degradation of the resin surface and an eventual reduction in the composite's mechanical properties. The photo-oxidation, which is initiated by UV-absorbing oxidation products created during cure, is relatively amenable to detection by techniques of analytical chemistry. Mechanical test results, which reflect a wide range of material properties, are more subject to variability and misinterpretation.

INTRODUCTION

Since their large-scale introduction as radome materials during the Second World War, fiber-reinforced composite materials have enjoyed a remarkable growth market, and are now being used in a wide variety of military and commercial applications. Excellent toughness, high strength, low density, microwave transparency, and many other attributes not present in more traditional materials provided much of the impetus for this growth. However, one must also include the excellent environmental resistance of composites as a factor sought by many designers. As will be detailed below, composites are not totally immune to the outdoor environment, but they are less susceptible to corrosion than many other materials, and they are in many cases easier to stabilize against it.

Even though the vast majority of commercial items employing composites consists of chopped glass fibers in polyester matrices, applications requiring excellent performance usually specify epoxy resins and often more exotic fibers (aramid, graphite, boron). While this review will deal in detail only with epoxy composites, many of the comments to be made will be germane to the polyester composites as well.

The composites industry has been diligent in recognizing adverse weathering effects, and in developing means of combating them. As a result, one often hears the claim that a "well-built" material—containing a minimum of voids and other internal defects, and suitably stabilized and coated—will exhibit excellent weathering resistance. Many successful applications attest to this fact. Nevertheless, most stabilization methods have been developed empirically, and many designers of high-performance systems have expressed a lack of

confidence as to the long-term corrosion resistance of these relatively new materials. In order to provide a more rational basis for prediction and stabilization, attention has turned in recent years to means of elucidating the chemical mechanisms operative during corrosion of composites, and in seeking mechanical property tests which provide reliable measures of deterioration.

MECHANISMS OF ENVIRONMENTAL DETERIORATION IN COMPOSITES

Solar Radiation

The photon energy in solar radiation is the most damaging component of the outdoor environment, serving to initiate a wide variety of chemical changes in polymeric materials (1). According to the Planck-Einstein law $E = h\nu = hc/\lambda$ (where E , h , ν , c and λ are energy, Planck's constant, frequency, wavespeed, wavelength, respectively), the energy contained in a photon rises as the wavelength decreases. Although the sun emits radiation over a wide range of wavelengths extending from below 100 nm to over 3000 nm, the earth's atmosphere prevents radiation of wavelength less than approximately 290 nm from reaching the surface. *Figure 1* shows the spectral distribution of surface sunlight in the ultraviolet range, and compares the solar spectrum with the energy received from an S-1 mercury sunlamp at a distance of 22 cm. The energy of ultraviolet photons is comparable with that of the dissociation energies of polymeric covalent bonds, which lie in the range of approximately 290-460 kJ/mole. Such photons have the capability of altering the polymer's chemical structure.

In order to induce chemical change, the photon must first be absorbed by the material, and a material totally

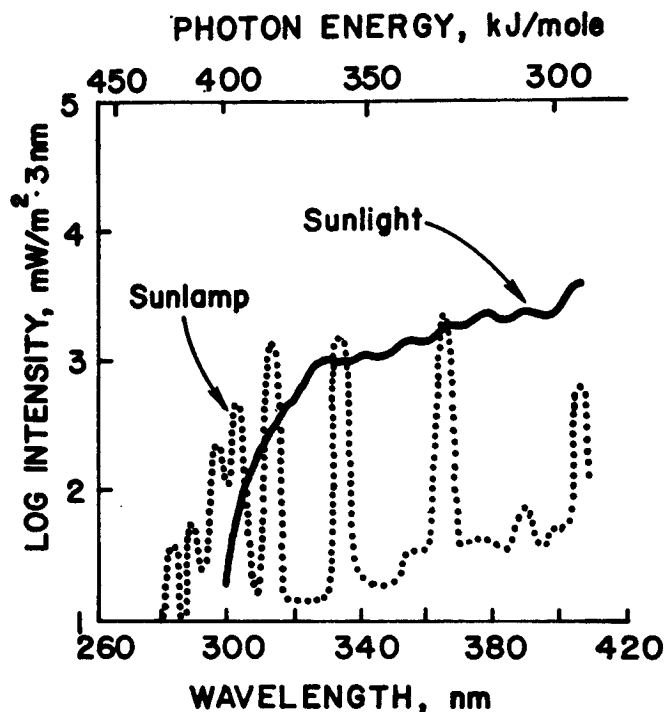


Fig. 1. Typical spectrum of surface solar intensity and emission spectrum from S-1 mercury sunlamp (2).

transparent in the UV range will not exhibit photo-initiated corrosion. Many chemical entities often found in polymers, however, have characteristic ultraviolet absorptions. The carbonyl group, for instance, has a broad absorption peak at approximately 300 nm due to the excitation of a nonbonding electron into the π^* molecular orbital. UV-absorbing groups may be present naturally in the polymer; or they may be introduced adventitiously by any of several means, such as oxidation during fabrication, polymerization anomalies, introduction of various additives, etc. The energy contained in photon-excited high-energy orbitals may be dissipated harmlessly in the form of heat, but a certain fraction of these excited states may relax by initiating chemical change. It is this latter process that produces deterioration.

The deterioration process is frequently some form of photoinitiated oxidation. Typically, the process is initiated when a sufficiently energetic photon strips away a labile proton from the polymer, leaving behind a free radical:



The radical is highly unstable, and reacts easily with atmospheric oxygen to form a peroxy radical:



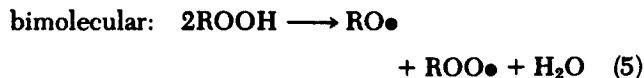
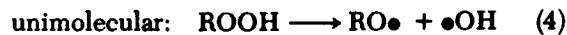
(This process may be limited by oxygen diffusion in thick specimens.) The peroxy radical also seeks to complete its unsatisfied valence, which it may do by abstracting a proton from a nearby molecule to form a hydroperoxide and a new chain radical:



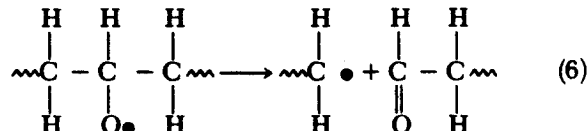
The oxidation process of Eq 2 may now be repeated, so

that the initial abstraction by the photon serves to set up a chain reaction which may include thousands of steps.

The hydroperoxides formed in Eq 3 are generally felt to be the direct cause of degradation in polymer properties, as they decompose via mechanisms which cause polymer chain scission and/or crosslinking. Hydroperoxides may decompose by either unimolecular or bimolecular dissociation to produce alkoxy radicals:



Chain scission may occur by disproportionation of the alkoxy radical to produce a new chain radical and a carbonyl group:



Relatively few such scissions are sufficient to lower markedly the molecular weight of the polymer. In crosslinked systems, this effectively reduces the crosslink density, which may be observed as a reduction in the material's softening temperature.

Another deleterious result may be the production of chromophoric chemical species. Such groups may impart an unacceptable discoloration to the polymer if they absorb in the visible range of light, and an autocatalytic UV degradation may be established if UV-absorbing chromophores are produced, which in turn serve to capture more UV photons. The carbonyl formed in Eq 6 constitutes such a group. These groups, however, may also serve as convenient means of monitoring the extent of the deterioration process, since they are often amenable to quantitative analysis by suitable spectroscopic techniques.

Crosslinking may also occur as a result of chain radical coupling:



Scission and crosslinking may be regarded as competitive mechanisms, with one or the other dominating in a particular situation. Crosslinking may also be deleterious, in that it reduces molecular mobility and leads to the sort of brittleness often seen in elastomers which have been exposed to sunlight.

Physical or chemical stabilization against corrosion may be achieved by blocking any of the above steps in the deterioration process. UV radiation may be excluded by various coatings or screening agents (such as carbon black), or may be absorbed harmlessly by chemical agents which dissipate the photon energy without chemical change. Radical scavengers may be employed to terminate chain radicals and halt the propagation steps, and various deactivators are available which serve to stabilize the hydroperoxide groups. The

reader is referred elsewhere (e.g., Ref. 3) for a more complete treatment of stabilization.

Moisture

Absorbed water is generally not so damaging to polymeric materials as is sunlight, but its effects may be important in certain cases. Its role is usually to act as a plasticizer leading to increased flexibility in semirigid polymers and a reduced softening temperature in glassy polymers. This latter effect has caused concern for composites employed in advanced aircraft, where absorbed moisture may lower the resin's softening temperature to the point that the material is unable to withstand the severe aerothermal loadings encountered (4). Cases in which water causes permanent degradation by hydrolysis of chemical bonds is not common, and the plasticizing effects can generally be reversed upon drying the material. Rainfall, however, may act in concert with photo-initiated oxidation to produce erosion of the material, serving to wash away the embrittled surface layer so as to expose new material to direct sunlight.

Water is of special concern in the case of glass-fiber reinforced composites, since glass is known to be subject to permanent hydrolytic damage, especially when simultaneously exposed to stress. Water causes significant reductions in the strengths of fiberglass composites, and it has been common practice in the marine industry to design to "wet" rather than dry strength limits. The nature of the water-induced damage is not well understood, since its effect is often but not always reversible on drying (5). The difference between wet and dry values has been reduced by the development of surface treatments applied to the fibers before impregnation. These surface treatments are considered by many to stabilize fiber-matrix adhesion by forming chemical bonds between the glass fibers and organic resin, although others argue that the treatment acts primarily to shield locally defective regions of the fiber from the corrosive effects of the water.

Miscellaneous

In addition to sunlight and moisture, one may encounter cases where mechanical, chemical, thermal, irradiative, or other sources of degradation may be considerable or even dominant. Even brief discussions of these other phenomena cannot be included here due to space limitations, although data to be presented later will indicate the influence of mechanical stress acting simultaneously with environmental factors. For more thorough treatments the reader is referred elsewhere (e.g., Ref. 6).

EXPOSURE STUDIES

The general principles of corrosion in composites will be illustrated by means of results obtained in weathering studies of a typical composite system, 3M 1009-26 Scotchply laminate. This material is typical of that used in many applications, and is also attractive for basic studies since it is relatively free of proprietary restrictions as to disclosure of its composition. The laminates consisted of seven crossed plies containing 27 weight

percent resin. The fibers were Dow Corning 801-E glass with 0.8 percent aminosilane coupling agent on the surface. The epoxy system consisted of two parts Dow DEN438 (an epoxidized novolac) to one part of Shell EPON 828 (a diglycidyl ether of Bisphenol A), cured with a boron trifluoride-monoethylamine complex.

Commercially prepared laminates, without any coating or other protective preparations, were exposed to natural and accelerated outdoor climates at various test sites around the world, to include: Panama Canal Zone (two open field sites, one rain forest, one breakwater site), Puerto Rico, Arizona, Massachusetts, Australia, and the accelerated outdoor site operated by Desert Sunshine, Inc., in Arizona. The laminates were approximately 46 by 46 by 0.32 cm in size and were exposed in an unloaded state, facing south and inclined 45 deg to the vertical.

Chemical Analyses

Laminates in the as-fabricated and exposed states were subjected to a variety of chemical investigative techniques in an attempt to ascertain the micromechanisms responsible for environmental deterioration. These techniques included Fourier transform infrared spectroscopy, electron spectroscopy for chemical analysis (ESCA), laser Raman spectroscopy, differential scanning calorimetry, laser pyrolysis—gas chromatography—mass spectroscopy, and liquid chromatography. All of these methods are made considerably more difficult by the rather intractable nature of the material: its opacity, the presence of the reinforcement, and the inability to swell or dissolve the resin. Nevertheless, innovative techniques have succeeded in overcoming many of these obstacles and producing a great deal of insight as to the deterioration mechanism.

A particularly valuable contribution made by chemical analysis has been the elucidation of the means by which the oxidative degradation may be initiated (7). Figure 2 shows the absorption spectra of cured and uncured resin as determined by UV spectrophotometry, and compares them with the short-wavelength edge of

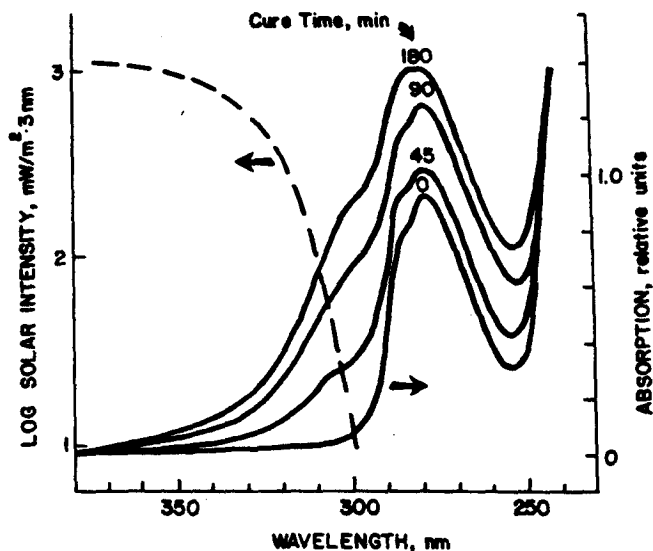


Fig. 2. Development of chromophore during cure of 1009 resin (7).

the solar spectrum. Before cure, the resin is almost transparent in the UV, so that few damaging photons can be absorbed. As the cure of the resin progresses, however, a chromophore is developed whose absorption reaches into the range of solar UV radiation. Fourier transform infrared spectroscopy shows this chromophore to be an aromatic carbonyl, formed by oxidation during cure of methylene bridges in the novolac constituent of the resin. Significant improvements in weathering properties can be obtained by preventing this oxidation during cure, for instance, by vacuum curing, although incorporation of a UV-screening agent such as benzophenone is still recommended.

Surface washings of the laminates exposed to ultraviolet radiation exhibit an increasing concentration of oxidation products (notably aliphatic carbonyl) which may be detected by infrared spectroscopy (7). As mentioned earlier, however, the intractable nature of the cured laminates renders IR spectroscopy somewhat difficult. An interesting technique which can be applied directly to the laminates was developed by Merritt, *et al.* (8). These workers employed a slightly defocused laser beam to pyrolyze the surface layer of the composite, and the products of this pyrolysis were then swept directly into a combination gas chromatograph—mass spectrometer for separation and identification.

When the laser pyrolysis GC-MS analysis is applied to the unexposed control specimens, only water and carbon dioxide are yielded as pyrolysis products. Several additional compounds are detected in the exposed specimens, however, including methane, ethane, benzene, toluene, ethylbenzene, 2-phenylpropane, methanol, ethanol, acetone, phenol, acetophenone, and phenyl ethyl ether. The total concentration of all these pyrolysis products is shown in Fig. 3 as a function of exposure time and for several different test sites. Note the close agreement of the values for the various sites in spite of significant differences in the climates there. These results may be interpreted qualitatively by surmising that terminal groups created by photo-oxidative scission are pyrolyzed more easily than groups in a

three-dimensional crosslinked system, and that the pyrolysis products are the result of the cleavage by the laser of these terminal groups.

Mechanical Properties

As portions of the sample population were returned from the test sites at six month intervals for analysis, an increasing degradation of outer surfaces—especially that facing the sun—was clearly visible. Resin was markedly yellowed and was actually lost from the surface, leaving behind exposed fibers. Figure 4, however, shows the difficulty in obtaining mechanical property data which correlate with this obvious deterioration. This figure shows the tensile and flexural strengths for specimens which had been exposed for various times at the Panama open site (sunny, hot, humid). The brackets on the values indicate standard deviations of the replications for a given exposure time, and the lines represent linear regression fits to the data. The values are given as percentages of the strengths of "control" specimens which had not seen outdoor exposure. Although the trend indicated by the regression lines is downward, the data are too scattered around these lines to be of much use for design purposes. This variability, in which actual improvement in mechanical properties is sometimes observed, is typical of that often found in environmental deterioration studies of composites. It may be due to a number of sources, postcuring or transient plasticization of the resin, inapplicability of standard mechanical test procedures to eroded and unbalanced laminates, etc., but the effect is not fully explained, and is a source of considerable concern in such studies.

Analysis of the variability seen in Fig. 4 is made difficult by the inherently complex nature of the tensile and flexural tests, whose results reflect a wide variety of material properties: fiber-matrix bonding, interply bonding, resin flexibility, internal defect distribution, fiber strengths, etc. Less variability is observed in numerical-property tests which reflect a smaller number of materials properties. Such a test is dynamic mechanical spectroscopy, in which the material's ability to store and dissipate energy during cyclic loading is monitored as a function of temperature.

Laminates obtained from the test sites were split into three sections to demonstrate the effect of weathering

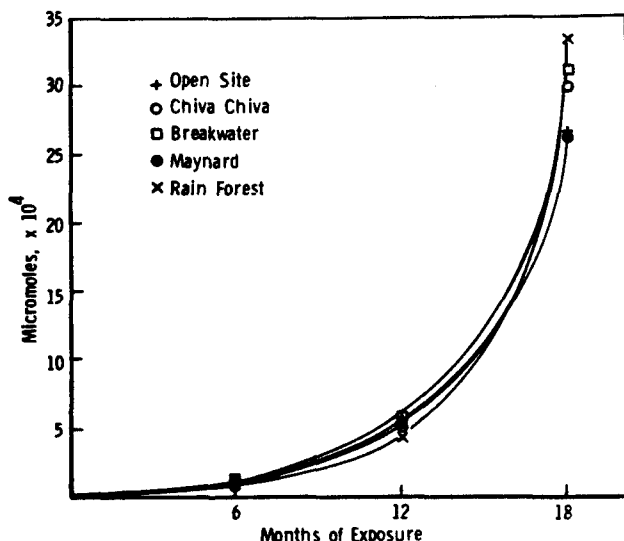


Fig. 3. Total gas evolution from laser pyrolysis of exposed 1009 laminate (8).

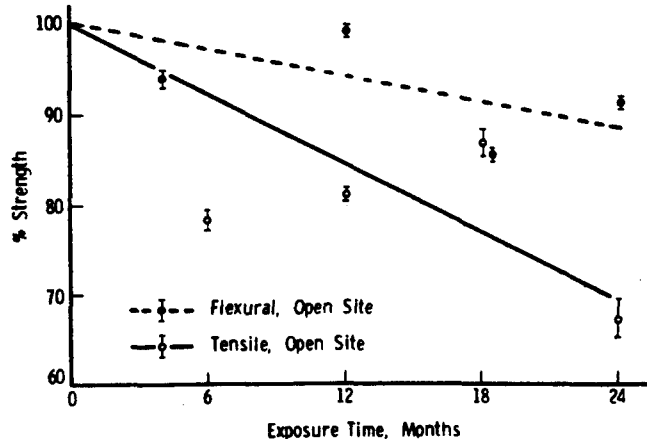


Fig. 4. Influence of outdoor weathering on mechanical properties of unstabilized and unprotected 1009 laminate (9).

on the top (sun-facing), bottom and interior regions, then submitted to torsional pendulum analysis to determine the dynamic mechanical spectrum of the three sections as functions of exposure time. The torsional pendulum test obtains a measure of resin flexibility at a given temperature, and among other things may be used to determine the softening (glass transition) temperature of the resin. Figure 5 shows how the glass transition temperature is affected by exposure. The outer plies suffer the worst deterioration, but the bottom surface is almost as seriously degraded by reflected light. The interior ply is relatively unchanged. The reduced glass transition temperature is a result of photolysis among the network of chemical bonds in the resin, which renders it less resistant to thermally-induced molecular motions. The shape of the curves in Fig. 5 are similar to that of the laser pyrolysis-GC-MS data in Fig. 3, and it can be reasonably argued that both reflect a decrease in the resin crosslink density due to oxidative chain scission.

Laboratory Environment/Fatigue Testing

In an effort to avoid the variability of actual weathering conditions, and to shorten the long times needed to obtain outdoor weathering results, investigators have sought laboratory tests which simulate the effect of outdoor exposure in an accelerated and controllable manner. Such laboratory tests are often a useful and economical means of obtaining a measure of weatherability, but must be viewed with caution. Their results are valid only when the mechanism of deterioration actually present outdoors is induced by the test, and there is no general means of assuring this. An example is the use of such radiant UV sources as xenon or carbon arcs or mercury-vapor sunlamps to simulate the effects of sunlight. As seen in Fig. 1, these sources may contain significant UV energy but are not necessarily a good match of the solar spectrum. Depending on the activa-

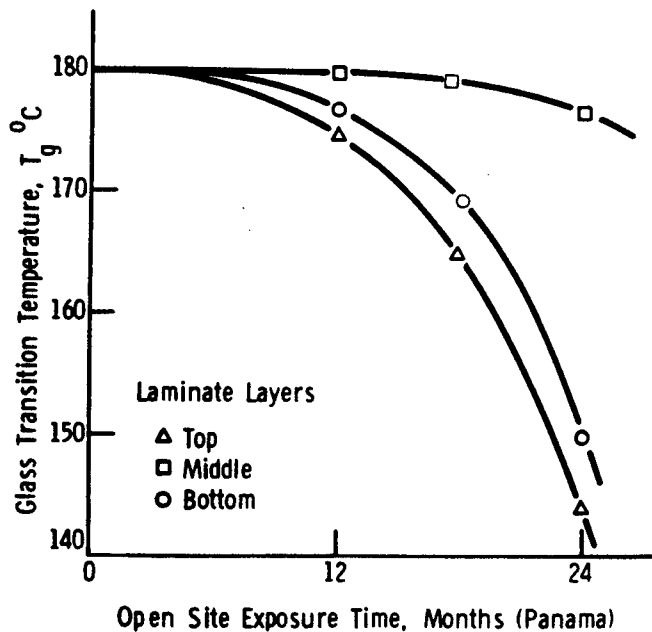


Fig. 5. Influence of outdoor exposure on glass transition temperature of 1009 laminate (9).

tion spectrum of the material, artificial sources may induce deterioration mechanisms which are not present outdoors, or may fail to induce the mechanism which is present outdoors. In such cases, poor correlation between laboratory and outdoor test results must be expected.

Laboratory testing may be indicated when one seeks experimental data which would be overly cumbersome or expensive if obtained outdoors. An example is the study of interactions between exposure effects and simultaneously applied fatigue loading. Such studies are relevant to such structures as helicopter rotor blades, which experience such loading. One might expect an interaction between exposure and fatigue loading which produces more drastic deterioration than the sum of both effects acting alone. Fatigue damage may serve to open pathways which facilitate the entry of moisture into the interior of the material, or fatigue loading may assist in the flaking away of surface resin so as to expose new material to solar radiation.

In order to simulate combined environment/fatigue loading on composites, a cyclic fatigue machine was outfitted with laboratory weathering devices which operated during the course of the fatigue experiment. These included mercury-vapor lamps for UV radiation, radiant heaters and liquid nitrogen cooling for temperature control, and spray devices for moisture application. At the time of this writing, this facility has been used primarily to explore the response of aramid/epoxy composite (aerospace grade Kevlar 49 in Fiberite 934 resin). Figure 6 shows the fatigue response of unexposed laminate obtained by fatigue lifetime testing of over fifty specimens. Also indicated on this figure are the limited fatigue exposure data obtained to date. Although not enough exposure tests have been completed to permit a statistically sound assessment of environment/fatigue response, it does appear that exposure serves to degrade the fatigue resistance of the material.

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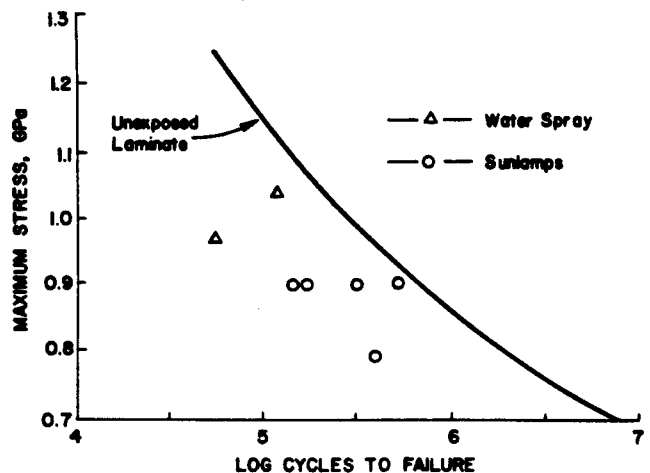


Fig. 6. Influence of simulated exposure on fatigue resistance of aramid/epoxy laminate.

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