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Some Fundamental Properties of the Interface of Glass–Epoxy Composites*

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Summary

A fundamental study of phenomena occurring at the interface of glass–resin composites is carried out. The role of water at the interface is examined by utilizing E-glass rods drawn from a melt in an anhydrous atmosphere as a base-line material with which to compare E-glass rods subject to aging, treatments with A-1100 silane, water, and roasting.

Model glass–epoxide composites were constructed and examined gravimetrically and radiographically for diffusion of water through them. The influence of the variables mentioned above are also examined by modulus of rupture tests and by scintillation counting, following treatment with tritiated water.

Generally, it has not been possible for the engineer to design so as to utilize the ultimate theoretical strengths of materials, as most materials fail at stress values which are a small fraction of their theoretical strengths. Failure apparently can occur by any of several mechanisms, depending upon the nature of the materials and their environments. The theory of Griffith (*1*), advanced in the early 1920's, postulates that failure is initiated at a flaw where stress is concentrated. When these flaws can be minimized by taking a very small sample such as a crystalline "whisker," which contains no internal phase boundaries, strengths approaching the theoretical maximum can be measured. However, there is considerable evidence that flaws may develop or enlarge when a sample is under stress, and water may well be a principal active agent in causing stress corrosion. Hence means of following the function of water

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on a surface are extremely important in the study of strengths of materials. We are examining several methods with the purpose of elucidating the role of water at the glass–resin interface failing under stress.

Considerable data have been amassed by a large number of investigators with respect to the properties of the glass and its interfaces (2). Frequently it is impossible to make meaningful comparisons of data obtained from different sources, since the conditions under which they were obtained are not exactly comparable. Glass research is as much an art as it is a science. We are attempting to elucidate the role of many of the variables of glass testing in order that meaningful base lines may be established to which the effect of variables may be compared.

The importance of obtaining base-line values cannot be minimized. The requirements for utilizing freshly drawn, truly virgin glass under conditions where the water-vapor content is controlled as closely as possible presents the opportunity for examining glass of completely known history. This well-defined glass serves as a starting point for all our experiments and allows the investigator to consider anhydrous glass, the same material saturated, anhydrous glass treated with anhydrous silane, the saturated glass treated with anhydrous silane, and the saturated glass treated with aqueous silane. In this manner the investigation of the glass surface under known conditions can be carried out. The work reported in this paper is concerned with the strength of glass rod as a function of the surface treatment and the effect of the surface treatment on the interfacial diffusion of water in model composite systems.

TECHNIQUES OF ROD FORMATION

It is absolutely essential that surfaces of glass be completely clean and free of defects to establish a base line for measurement. Tests of glass are notoriously sensitive to the prior history of the surface. To eliminate as many of these variables as possible, we decided to use E-glass rods drawn in anhydrous nitrogen atmosphere for testing.

A 30-ft^3 glovebox was fabricated in which was placed a resistance-heated platinum crucible. Glass was drawn by means of a remote-controlled dragout mechanism. Subsequently, glass was drawn by hand in the glovebox when it became apparent that a superior

product could thus be obtained. The water-vapor level was maintained at approximately 5 ppm by continuously flushing the interior of the drybox with anhydrous nitrogen obtained by evaporation of bulk liquid nitrogen. This assures an essentially anhydrous surface on the freshly drawn glass. The water vapor was monitored by means of a Beckman Hygromite.

Early experiments indicated that the measured MOR is highly sensitive to the method of sample preparation and the design of the MOR apparatus itself. This being the case, it is absolutely necessary to have close control over a wide range of variables for different sets of data to be comparable. Accordingly, we have taken certain arbitrary practices as our standard whenever possible. These are are follows:

1. Glass is cooked out long enough for visible bubbles and other inhomogeneities to rise to the surface, where they are skimmed off. If the glass is cooked out at 2450°F or higher, skimming may be unnecessary.
2. Temperature gradients within the melt are minimized as far as possible by the use of crucible covers, etc.
3. The crucible is made of a nonreactive substance (platinum–iridium) to minimize contamination from this source.
4. Sources of dust or other contaminants which might fall into the crucible are minimized as far as possible. Cutting of the glass above the crucible is done only while the glass is still plastic.
5. The surface of the glass is not touched on that portion of the length to be tested.
6. Glass is tested at a fixed time after drawing.
7. Work is done in an anhydrous nitrogen atmosphere with water vapor held at not more than 5 ppm.
8. The MOR test cell utilizes four-point loading and has movable bearing points.
9. A fast-response chart recorder is used as the MOR readout device.

DIFFUSION PATTERN ALONG AN INTERFACE

A central problem in the understanding of the structural behavior of glass–resin composites is the behavior at the interface. Failure can occur in either of the two solid phases or in the interacting zone between them. It is highly desirable to obtain an understand-

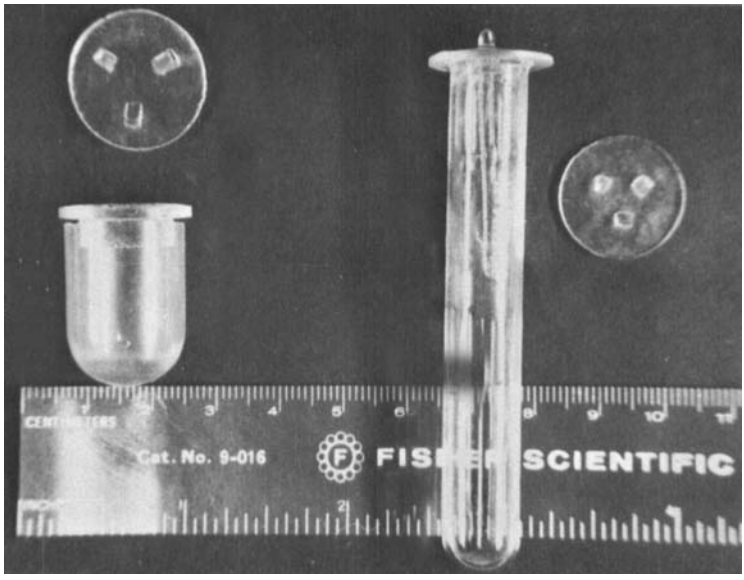

FIG. 1. Upper left: Epoxy cap for all-epoxy cell. Center left: All-epoxy cell and cap. Middle right: Glass–epoxy cell with a glass rod sealed through its cap. Far right: Three-lugged cap for glass–epoxy cell.

ing of the behavior of water in the interface. To this end a model composite cell was designed in which the properties of the glass–resin interface could be observed (see Fig. 1). This cell consists of an E-glass rod molded into an epoxy cap [50 parts by weight Dow Epoxide Resin 332, 35 parts hexahydrophthalic anhydride (Ciba 907), and 1 part Rohm and Haas DMP 30], which was in turn sealed to a glass test tube or an epoxy tube shaped like a glass test tube. Water was placed in the cell before sealing with a quick-setting epoxide resin (2 parts Genepoxy 190 to 1 part Ciba DP-116).

The seals were tested by storing the cells in a desiccator over anhydrous calcium sulfate (Drierite). A set of six cells, made with glass test tube bodies and glass microscope slide covers for caps, showed no weight loss (to the nearest milligram) for three of the cells while two had massive leaks. This test showed that the seal can be considered to be leak-free when well made, although it is difficult to get all cells of a set to be leak-free.

When epoxy caps were sealed onto glass tubes with quick-set

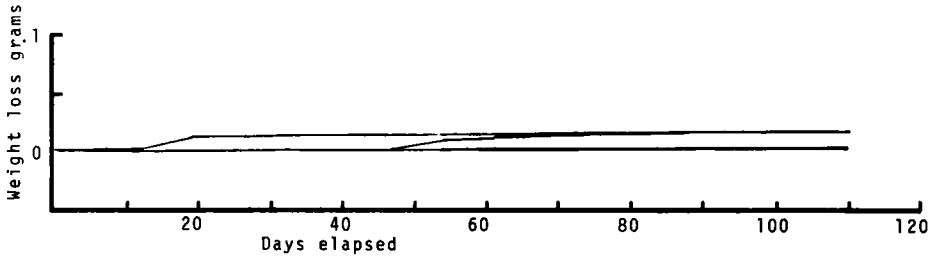

FIG. 2. Weight loss of 14 glass–epoxy cells with E-glass rods sealed through their caps sealed with quick-set epoxy.

resin, three of six cells showed weight losses of 3 mg after 120 days. The other three cells failed. The behavior of similar seals cited above suggests that the loss of weight shown here is almost entirely through the caps, at the rate of 2.5×10^{-5} g/day.

When epoxy caps with saturated glass rods sealed into them were made into cells sealed with quick-set, 3 of the 14 showed a loss of 1 mg after 110 days, 7 of the 14 lost 2 mg in 110 days, and 2 of the 14 lost 3 mg in 110 days, for an average loss rate of 2 mg/110 days, or 1.8×10^{-5} g/day. This value is less than, although comparable to, that of similar cells without glass rods, indicating that gross leakage does not occur due to the presence of the rod (see Fig. 2). Cells made as above, except that the rods were epoxy-coated while still in the anhydrous state, showed a loss rate averaging 3 mg/109 days in five of the six cells, or 2.8×10^{-5} g/day. This figure is comparable to results obtained with other cells (see Fig. 3).

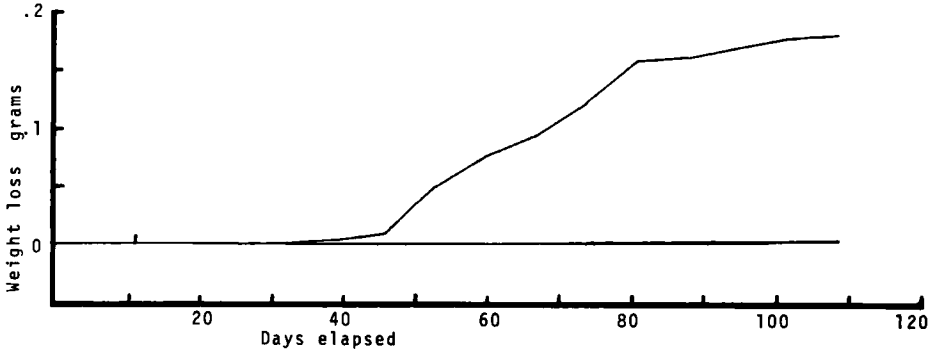

FIG. 3. Weight loss of six glass–epoxy cells with epoxy-coated E-glass rods sealed through their caps. Sealed with quick-set.

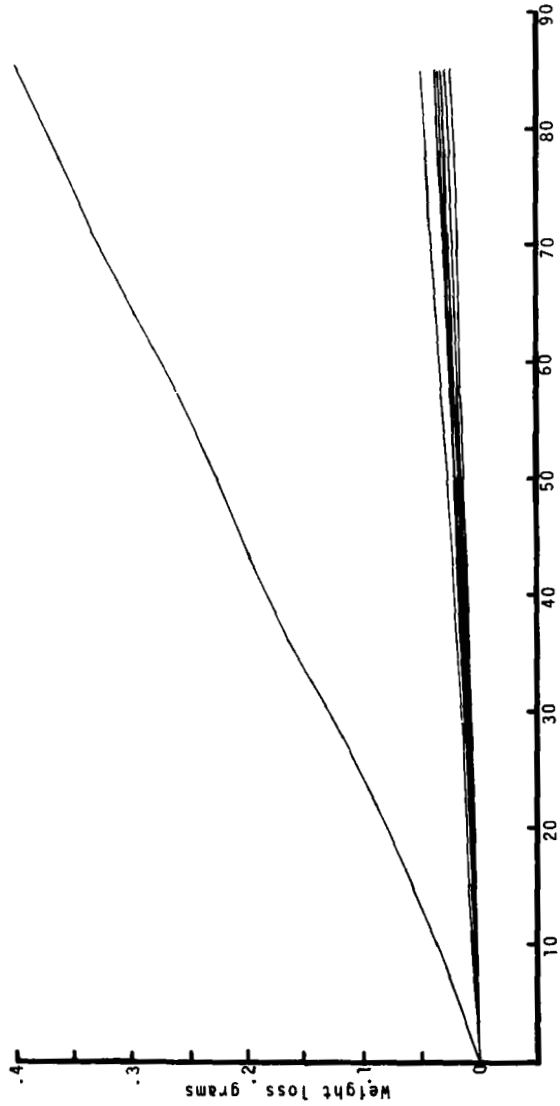

FIG. 4. Weight loss of 12 all-epoxy cells approximately 2.5 cm high, sealed with beeswax and stored in a desiccator.

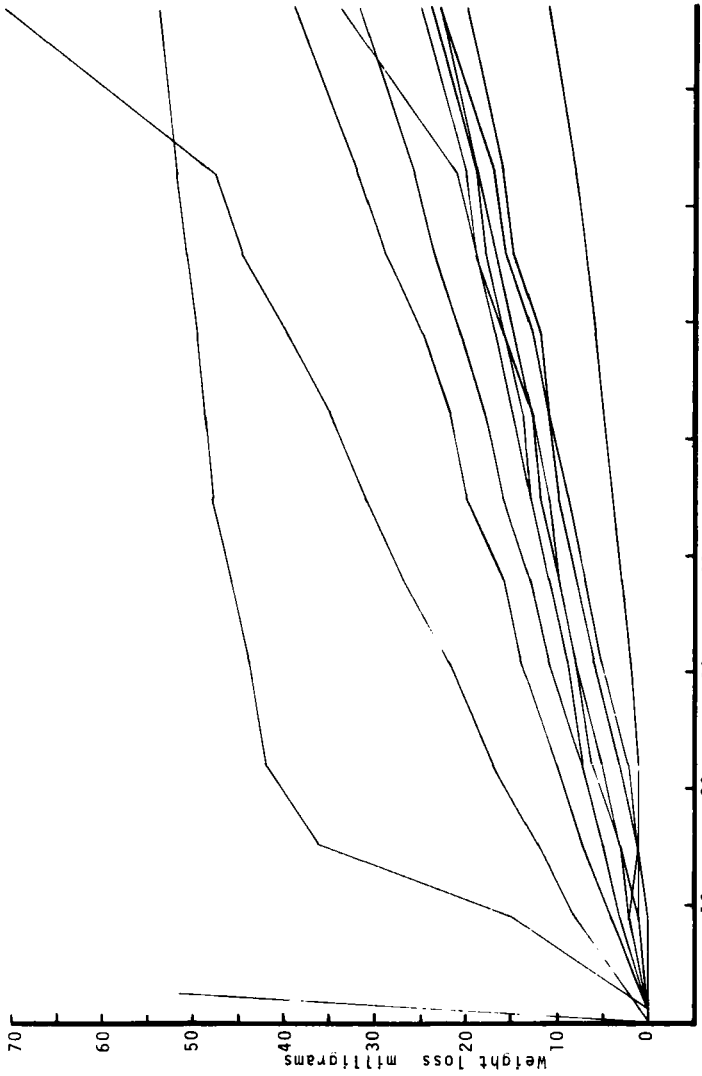

FIG. 5. Weight loss of 12 all-epoxy cells approximately 1.6 cm high, sealed with beeswax and stored in a desiccator.

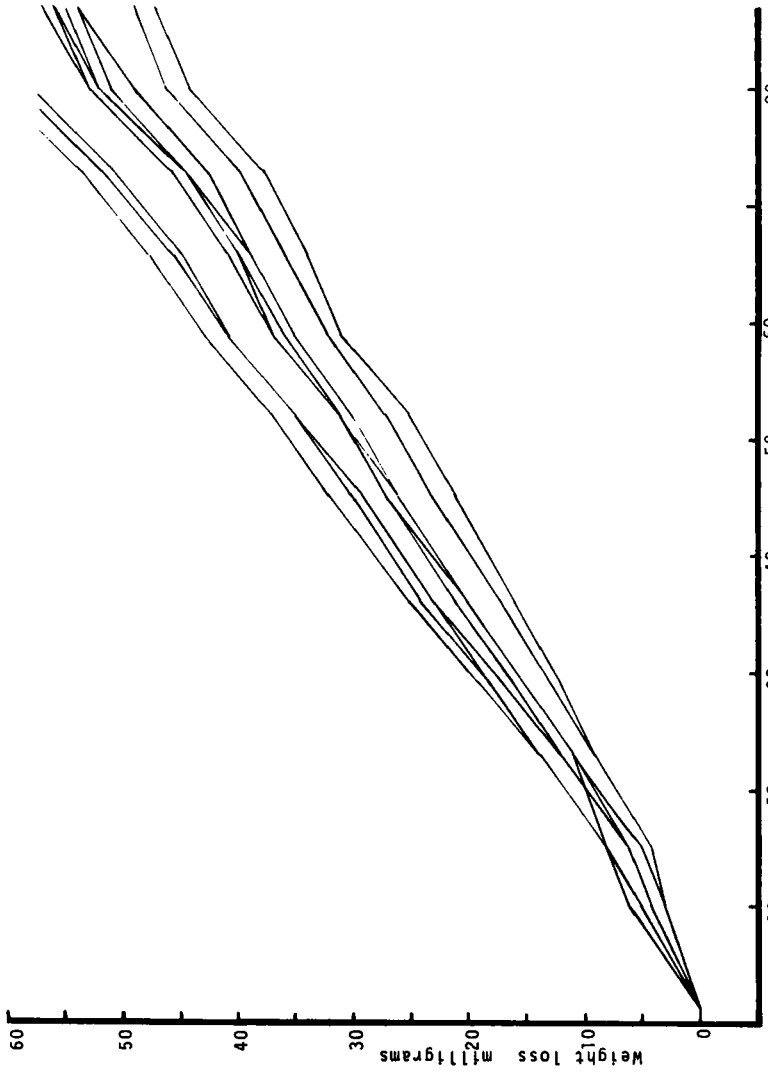

FIG. 6. Weight loss of 12 all-epoxy cells approximately 5.0 cm high, sealed with beeswax and stored in a desiccator.

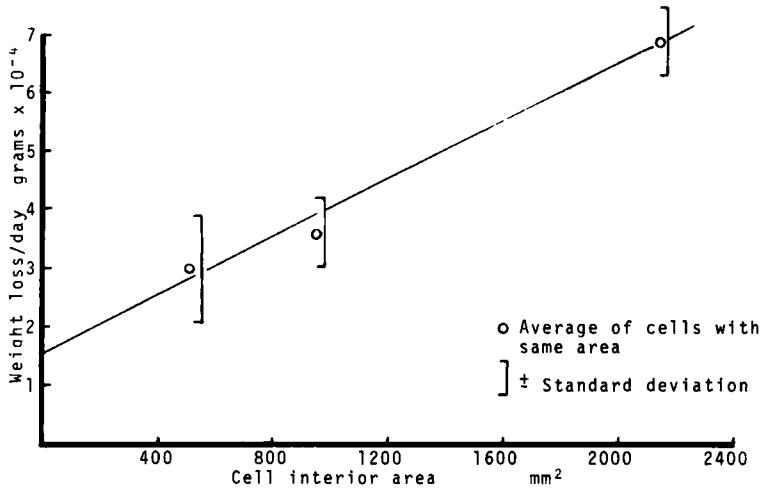

FIG. 7. Weight loss of all-epoxy cells sealed with beeswax.

A set of all-epoxy cells stored within a desiccator showed losses of 12 to 21 mg in 9 of 11 cells. This corresponds to an average loss of 17.5 mg/50 days or 0.35 mg/day (see Fig 4). To rule out the possibility that the geometry of the cap and the rounded end of the epoxy body might be influencing the results, a series of all-epoxy bodies of lengths of 16, 25, and 50 mm were prepared. One milliliter of water was introduced and an epoxy cap was sealed onto each cell with beeswax while the cell was hot. These cells were stored over anhydrous calcium chloride in a desiccator and were periodically weighed. Nine short cells had weight losses of 11 to 39 mg in 87 days, which corresponds to an average loss of 3.0×10^{-4} g/day. Long cells exhibited a range of losses from 58 to 80 mg in 101 days dropping three high values), or an average of 6.8×10^{-4} g/day (see Figs. 5 and 6). The average weight losses per day are plotted vs. cell interior areas in Fig. 7.

The fact that the best line plot does not pass through the intercept indicates an end effect not otherwise accounted for, and the slope of the line is indicative of a diffusion rate of 2.5×10^{-7} g/mm²/day. These tests definitely indicated that water can pass through the body of the epoxide apart from the seal. Left unanswered was the question of how the water passes through the epoxide. Up to this point we have used the word diffusion in a loose manner which is not intended to imply a mechanism. We then turned to the use of

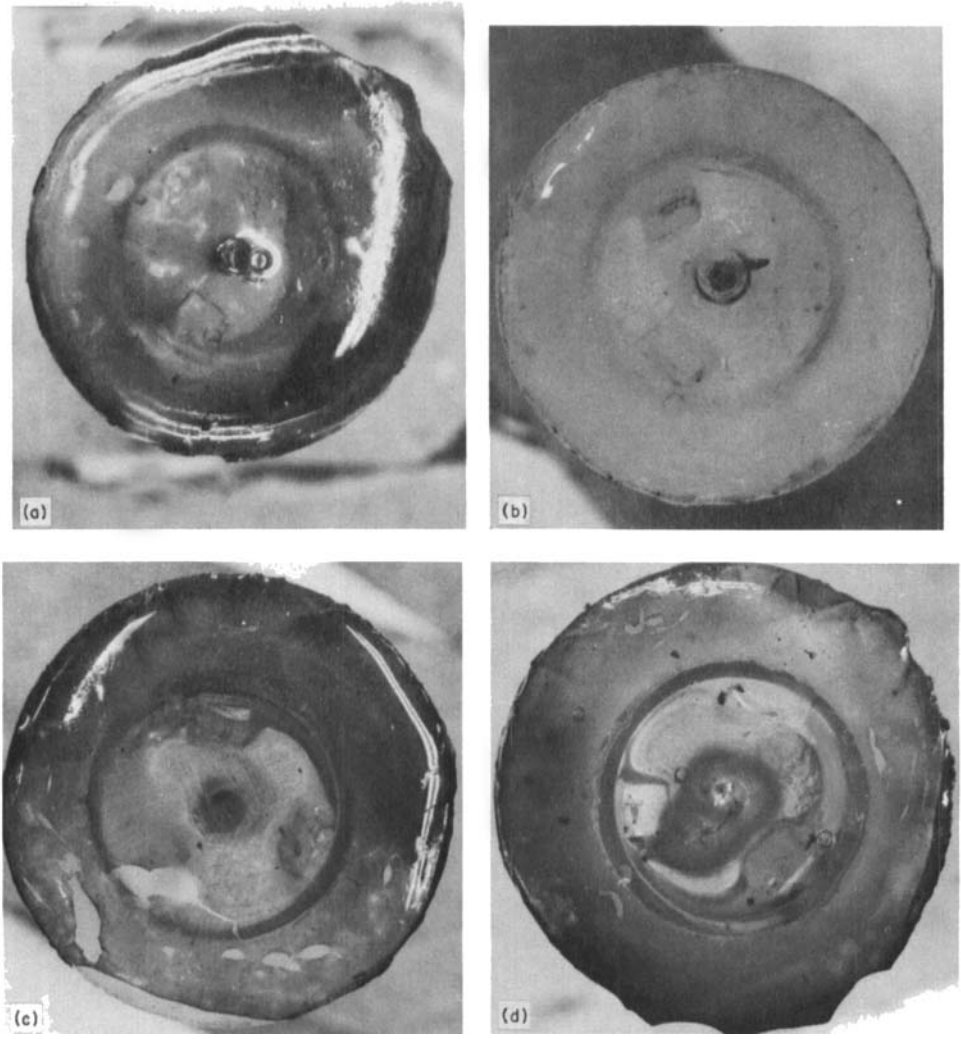

FIG. 8a. Exposure time 6 days. The rod was exposed to water but not to silane. Leakage occurs around the rod and around the beeswax seal.

FIG. 8b. Exposure time 5 days. The crescent around the rod is due to the angle of viewing and does not indicate exposure.

FIG. 8c. This cell shows a little darkening after 7 days exposure due to overall leakage.

FIG. 8d. Exposure time 8 days. Overall exposure and exposure around the rod are indicated.

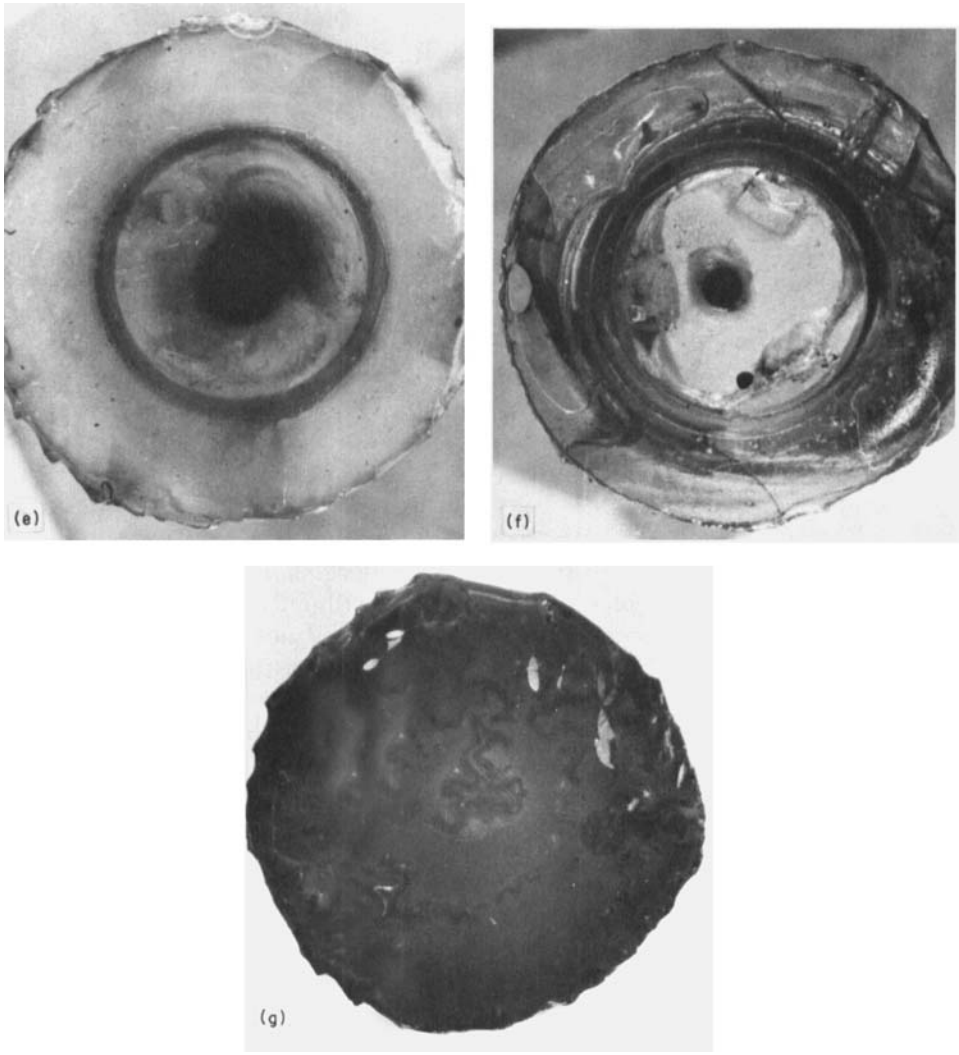

FIG. 8 (*Continued*)

FIG. 8e. Exposure time 5 days. A large smear around the rod end indicates water loss around the rod.

FIG. 8f. Exposure time 8 days. Exposure over the end of the rod is indicated, and also a spot indicates exposure through an invisible pore.

FIG. 8g. Complete exposure due to overall leakage.

the photographic emulsion to inquire as to the possible loci of diffusion.

RADIOGRAPHIC TESTS

Cell Preparation

Transferral of photographic emulsion to the cells previously described was accomplished by first dipping the cell caps into a 2% aqueous solution of gelatin. The gelatin serves to bond the emulsion to the surface. After the gelatin was thoroughly dry, a suitable piece of Kodak AR-10 photographic emulsion was stripped from its backing plate, floated on the surface of the water, and the gelatin-coated cell was brought up through the water under the floating emulsion. The emulsion was gently smoothed into place and allowed to dry. The dried cells were stored individually in screw-cap, wide-mouth bottles in a light-tight safe. Development was with Eastman Kodak DK-20 for periods of ½ hr. The radiographic emulsions were found not to undergo simulated exposure when mounted on blank cells, with or without contained water. Likewise, a rod mounted through the cap did not cause exposure to be simulated. However, our previous work did indicate that amine curing agents used in an epoxide can cause exposure to be simulated in an adjacent photographic emulsion. This aspect will be treated in detail in another article to be published in the near future.

Testing of Cells

A number of cells were prepared as above except that 0.2 ml of THO (53 mc/ml) was placed in each cell prior to sealing. Prior to coating with photographic emulsion, they were inverted for 24 hr to test for gross leakage. These were developed at varying times after sealing and the exposure patterns were noted.

Sets of cells were prepared and tested in which the variables of treatment of the rod with Union Carbide A-1100 (γ-aminopropyltrimethoxysilane), water, air exposure, and exposure time were examined.

Preliminary tests indicated the method was practical for studying losses of water. At first, the shotgun method was tried, with a number of cells of varying treatments and exposure times being prepared. The cells responded with a variety of exposure patterns.

Other expected exposure patterns were totally absent. Figure 8 shows some typical patterns. The end of the test tube can be clearly seen as a circle about half the diameter of the cell cap. Just within the test tube circumferences are three positioning lugs on the lower side of the cap. Many of the cells also show the rod, which is in the center. If the tip of the rod was ground off, this too is clearly visible, as in Fig. 8c. Exposure is indicated by darkening of the surface.

Some cells showed no exposure, as in Fig. 8b. Others showed heavy exposure preponderantly on one side, indicating leaking of the seal, as in Fig. 8a. Others were completely exposed, as in Fig. 8g. Between these extremes were many cells showing exposure in varying degrees over and around the rod, as in Figs. 8d, 8e, and 8f. Surprisingly, no cells were found with exposure confined to the area of the circumference of the test tube. This indicates that the losses of water observed gravimetrically were not due to true diffusion through the body of the epoxide, but were highly localized losses. Precisely this type of pattern is shown in Figure 8f, where a dot is observed under the rod. Subsequent examination of other cells has shown this type of localized loss turning up many times.

In addition to examination with the unaided eye, significant data are available from microscopic examination of the developed emulsions on the caps. Many cells were examined microscopically under 100× magnification and any unusual features were noted and photographed.

Figure 9a (the same rod at lower magnification is shown as Fig. 8d) shows a portion of the end of the rod. Surrounding and over the end of the rod are a number of blister-like eruptions which appeared to be firm when touched with the point of a needle, although the emulsion was easily scraped off in this manner. The eruption is clearly shown in Fig. 9b, where the tip of the rod was ground flush with the cap before application of the emulsion. The grinding marks are clearly shown as lateral grooves over which the eruption is superimposed. This eruption roughly follows the outline of the end of the glass rod. Figure 9c shows the loss of tritiated water close to the interface between the glass rod and the epoxy. Here the loss appears to be occurring through a channel or channels near the interface. Other samples showing this behavior well removed from the interface have been observed (see Fig. 9d). All the above types of behavior appear to be typical of this type of cell. Figure 9e illustrates a crack in the end of a glass rod which was probably formed when the rod was cut to length. There is reason to believe that in

FIG. 9a. Sample 8, 100× magnification. Silver grains over the end of the rod are visible, also eruptions around the rod.

FIG. 9b. Sample 17, 100×. Lateral lines are grinding scratches. Eruptions over the end of the rod are superimposed.

FIG. 9c. Sample 3, 100×, exposure around rod. The tip of the rod was ground off prior to adding emulsion.

FIG. 9d. Sample 21, 100×. An exposed spot which may result from a pore or channel in the epoxy.

FIG. 9e. Sample 37. Exposure over a crack at the end of a rod.

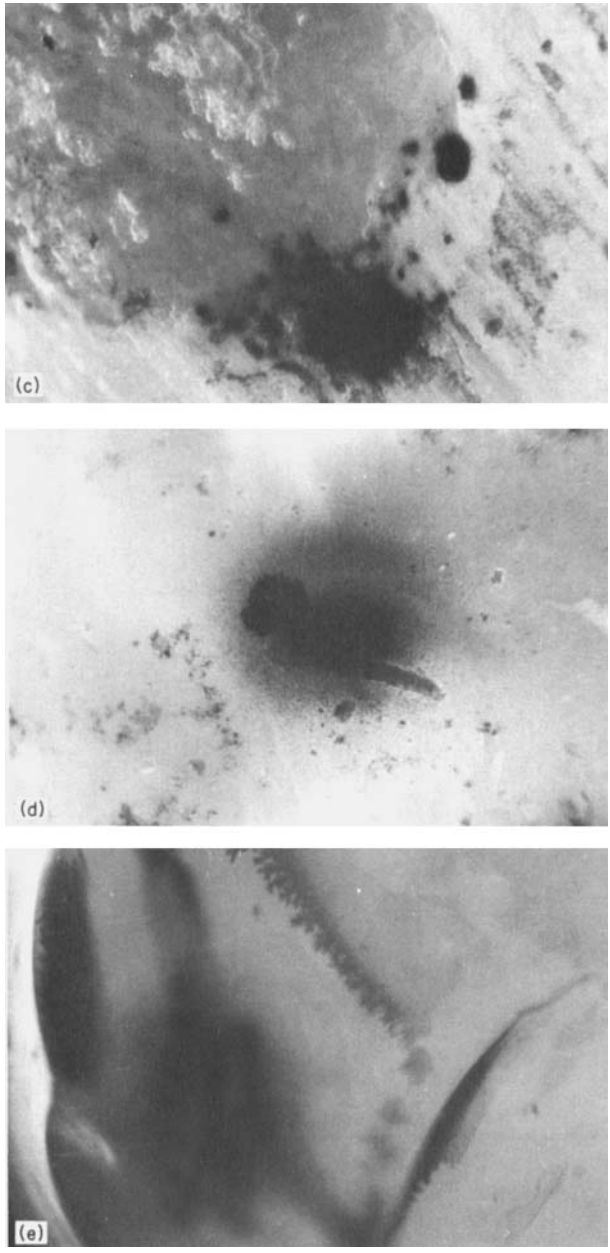

FIG. 9 (*Continued*)

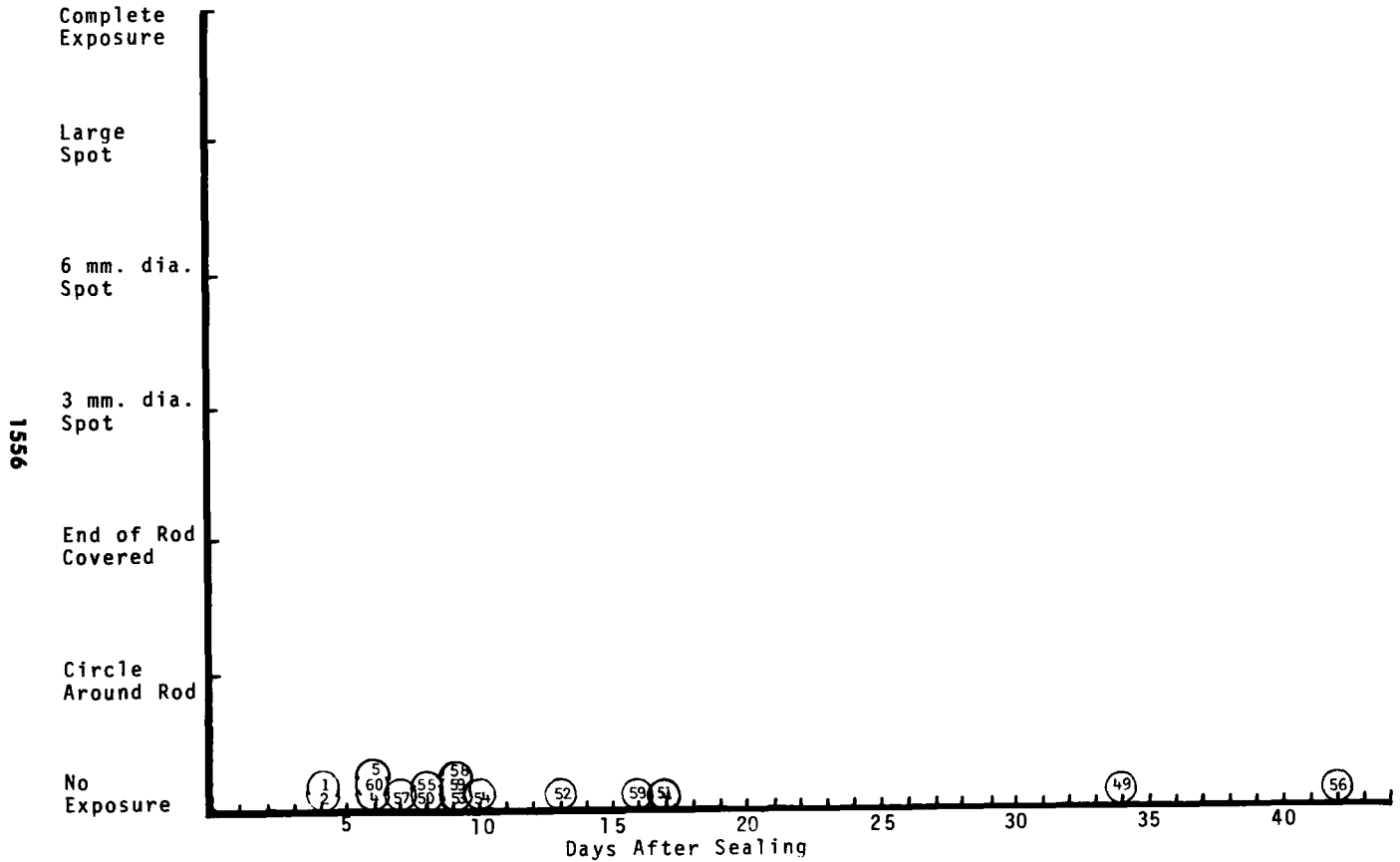

FIG. 10. No silane treatment; rod treated with water and dried.

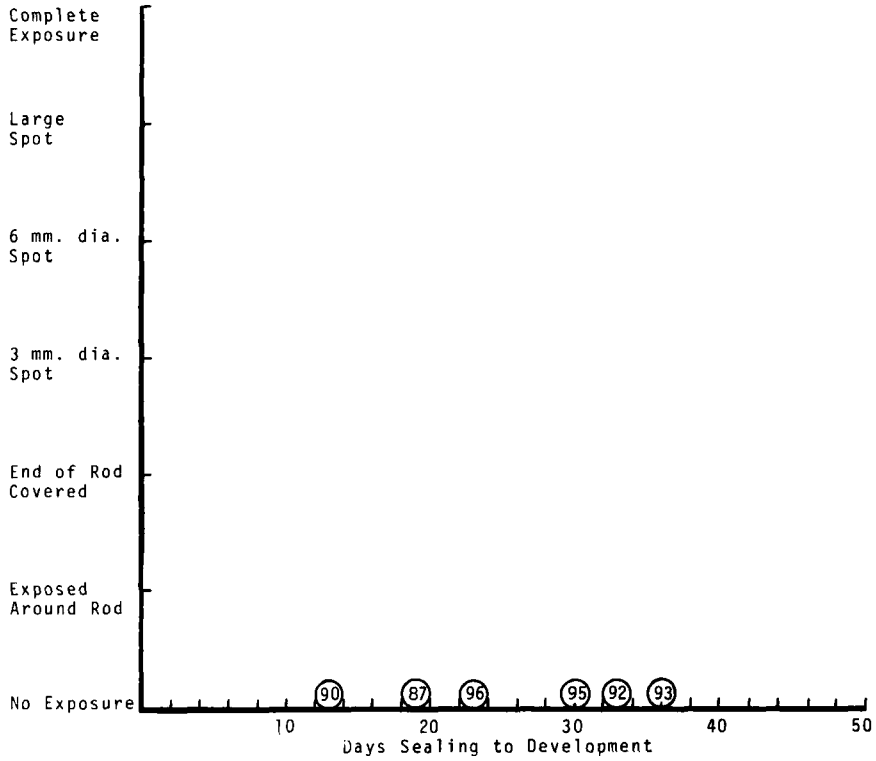

FIG. 11. Diffusion losses of cells made with untreated, anhydrous, freshly drawn E-glass rods.

some instances such cracks are the channels by which losses of water around the rod occur.

Nevertheless, exposure patterns around the rod remain our primary interest. These cells appear to conform to the following pattern. Upon developing, approximately 1 week after sealing the cell, a small circle of dots on the photoemulsion may be observed surrounding the end of the glass rod. This indicates that the tritiated water is diffusing through discrete channels adjacent to the surface of the rod. This circle of dots eventually overlaps, forming a circle surrounding the end of the rod. The circle spreads, covering the end of the rod and forming a dot which enlarges steadily until it covers the whole end of the cap, resulting in complete exposure.

To study the relationship of time of exposure to intensity of exposure, an arbitrary scale of 7 degrees of exposure was assumed and the extent of exposure of a number of samples was plotted vs.

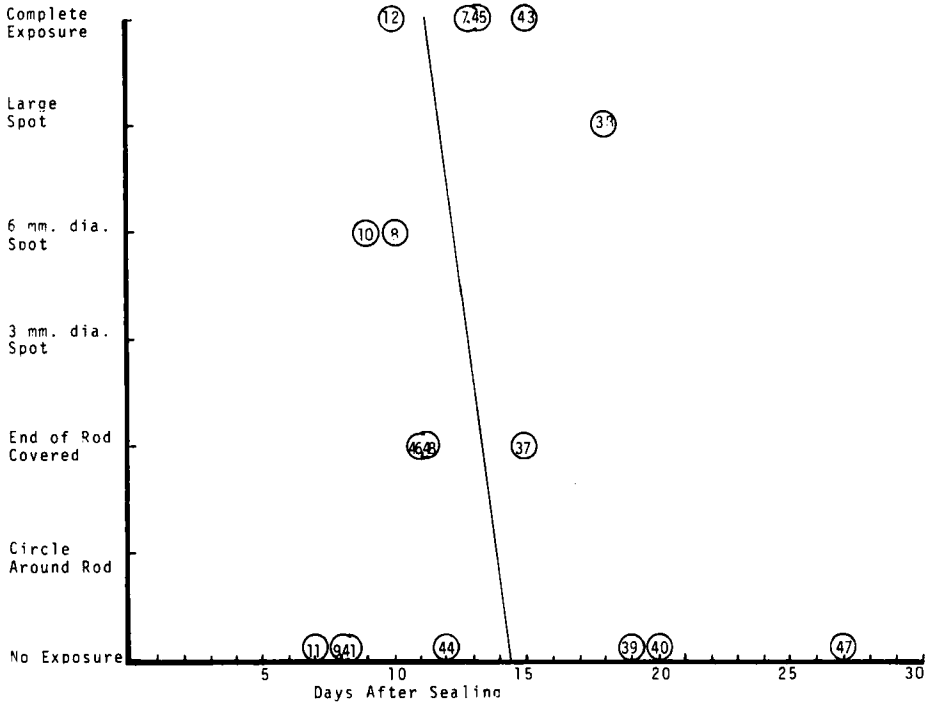

FIG. 12. 1% silane treatment, water exposed.

exposure time. Then plots were made for the following categories of rod treatment; (1) rods water-treated, dried, but without silane treatment; (2) rods water-treated, dried, and treated with A-1100 1% silane in hexane; (3) rods water-treated, dried, and treated with ½% A-1100 silane in hexane; (4) air-exposed glass without treatment; and (5) anhydrous glass with no treatment. In addition, a few cells were prepared without rods (see Figs. 10 to 16).

A consistent pattern emerges from this study; cells made from rods treated with A-1100 permit THO passage at the interface region; cells made from rods without A-1100 do not. Water treatment of the rod appears not to influence greatly whether or not water is lost around the rod. With silane-treated rods, every degree of exposure around the rod is observed, but with non-silane-treated rods, allowed 15 or more days exposure, only nonexposed or completely exposed patterns are found. The latter are in most, if not all, cases, due to leakage of the cell seal and are, therefore, not pertinent to this discussion.

MECHANICALLY STRESSED MODEL LAMINATES

Mechanically stressed model composites were obtained by placing the standard glass-epoxy cell in a specially designed cell holder (see Fig. 17). It was designed so that it could be fabricated almost enitrely from standard plumbing hardware items. A body consists of a ¾-in. threaded pipe nipple and two ¾-in. threaded pipe caps. A small hole was drilled in the end of one of the caps to allow the insertion of a steel pin by which a force is applied to test cells. The pin bears on the head of a metal screw. The screw is inserted into the center of a fiber disc which bears on a rubber washer. The washer transfers the load to the periphery of the cell cap, allowing a bending stress to be applied to the cap. The bottom of the cell rests on a tapered nylon washer. The composite cell may be

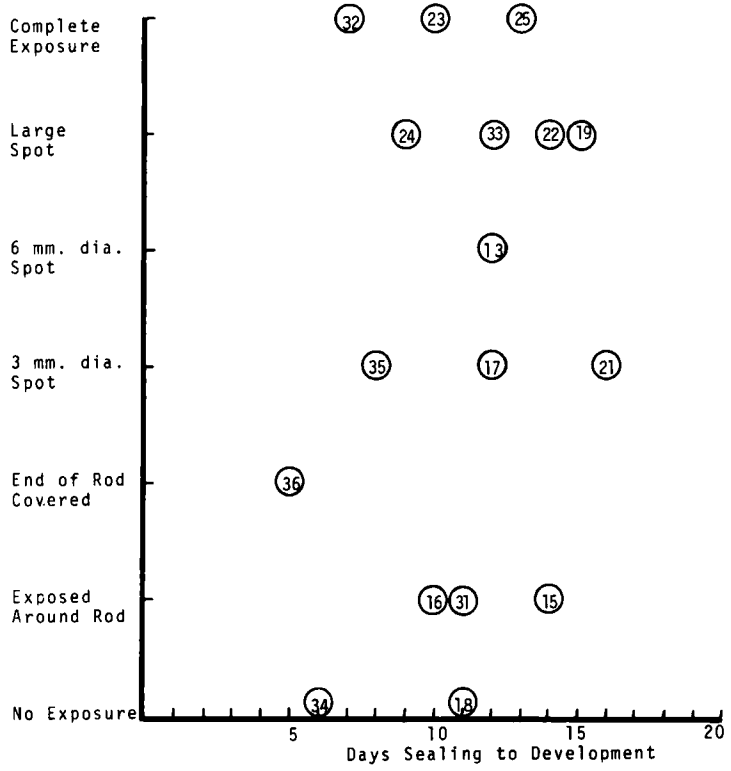

FIG. 13. Rods treated with water, dried, then treated with ½% A-1100 in hexane.

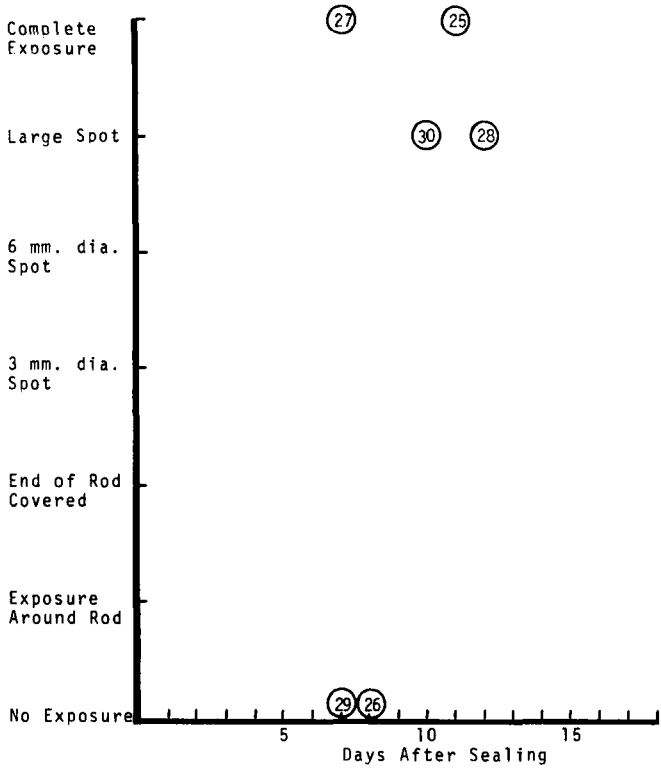

FIG. 14. Losses of diffusion cells made without rods.

mounted in an inverted position by making a simple modification of the internal arrangement.

A test frame was designed and fabricated in which seven cell holders can be mounted, and a constant mechanical load was applied to each (see Fig. 18). Tests with this apparatus are currently in progress.

TECHNIQUES OF MODULUS OF RUPTURE TESTS

It follows directly from Griffith's theory that the strength of the specimen must be a function of type and size of flaws existing in or on the surface; consequently the strength of the specimen is a measure of the flaws present. A convenient measure of the strength of glass rods is the modulus of rupture (MOR), which can be measured by observing the force necessary to break a rod in flexure in a test cell. To this end we fabricated test cells in which the bearing

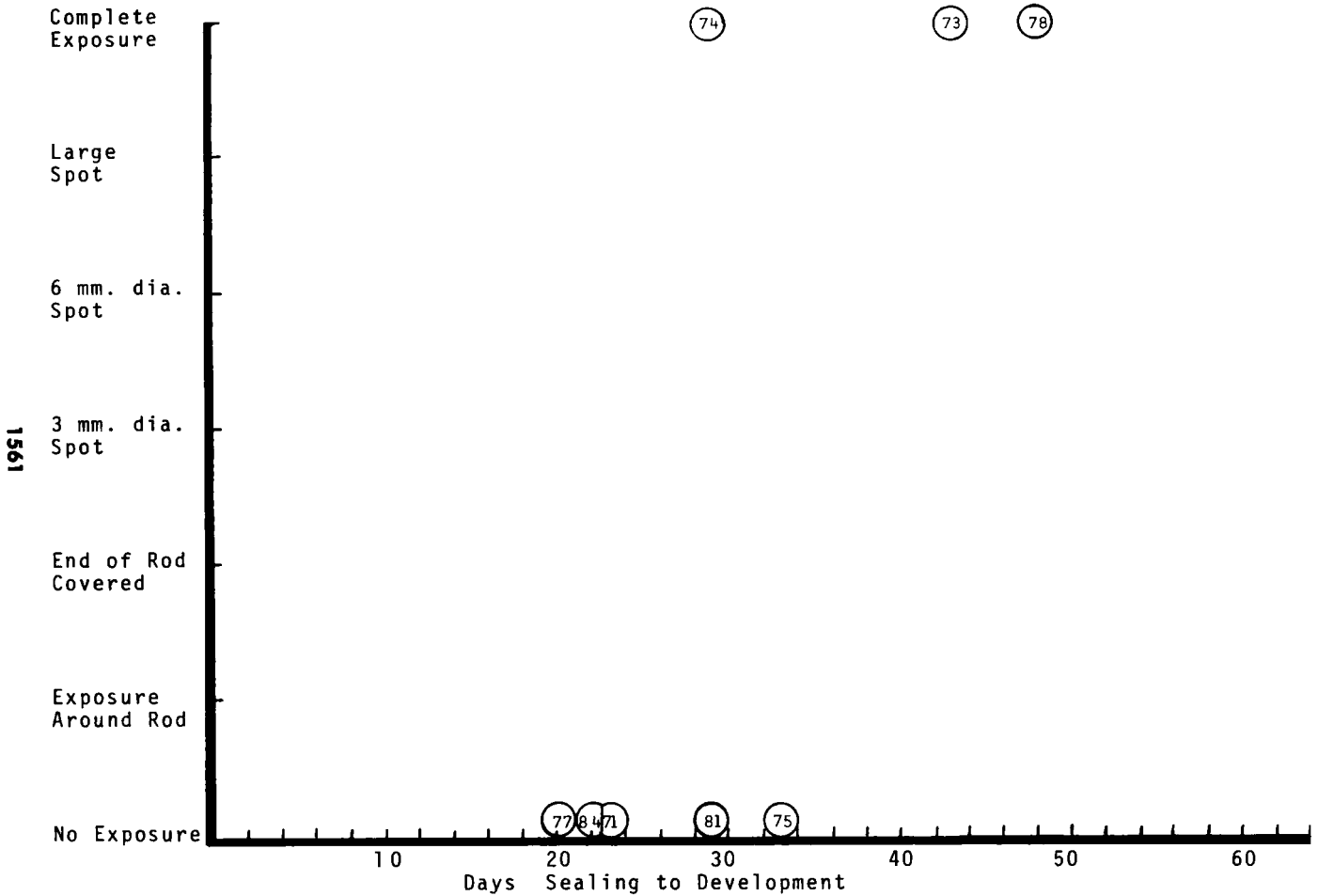

FIG. 15. Diffusion losses of cells made with air-exposed rods without silane treatment.

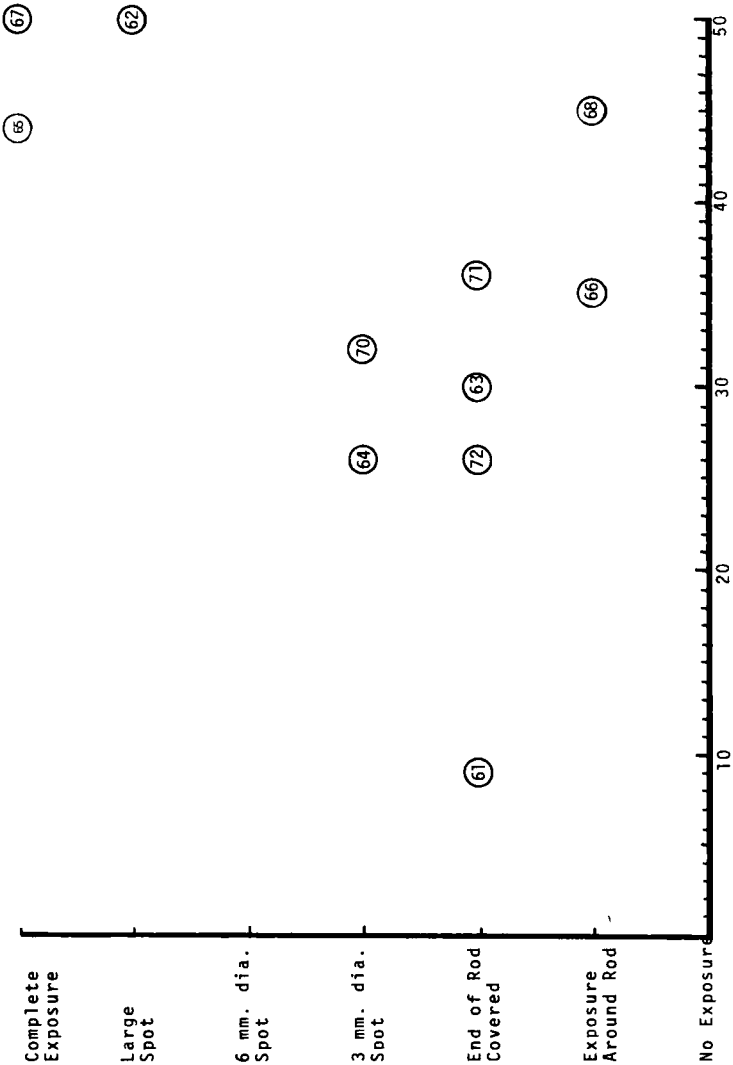

FIG. 16. Diffusion losses of cells made with anhydrous rods treated with ¼% A-1100, in hexane.

points are cylindrical and are mounted in bearings which permit free rotation (see Fig. 19). The force applied to the cell was measured by observing with strain gauges the deflection of a ring through which the load was applied (see Fig. 20). The output of the strain gauges was amplified by a circuit containing a Philbrick P65A operational amplifier module, which was in turn recorded with a Consolidated Electrodynamics Model S-124 recording oscillograph. With this oscillograph, traces are recorded on a sensitized paper strip with a light beam and moving-mirror galvanometer. The ordinary pen-and-ink chart recorder was found to be unsuitable, owing to its relatively slower pen response.

RESULTS OF MODULUS OF RUPTURE TESTS

The MOR test is unfortunately subject to a rather large amount of experimental scatter, which makes it necessary to obtain a considerable number of datum points to obtain meaningful results.

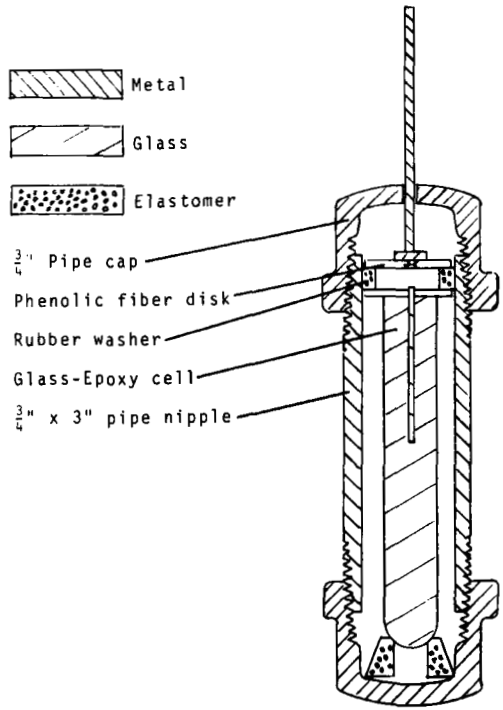

FIG. 17. Cross section of a cell holder designed to apply stress to a cell.

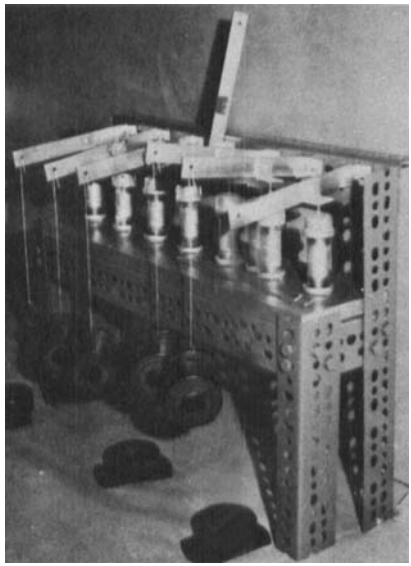

FIG. 18. Test rack for cell holder illustrated in Fig. 2.

Data were collected on approximately 300 rods (under somewhat different conditions used previous to the development of the standardized procedures listed above), which were tested for MOR as soon as possible (within 1 min) after drawing from the melt. Rods of the same, or nearly the same, diameter were grouped into collections of 10 ± 3 rods and the average MOR of each group was plotted vs. average rod diameter. The best curve was visually fitted to these points (see Fig. 21). While a completely homogeneous material should have a MOR independent of its diameter, it is interesting to note that a curve of the type $\text{MOR} = Kd^{-1}$, where d is rod diameter, approximates the data much better.

This is exactly what would be expected of a model in which the flaws which cause fracture initiation are proportional in distribution to the area of the rod. On the other hand, if the flaws which cause fracture initiation are distributed in proportion to the *volume* of the rod, a curve of the type $\text{MOR} = Kd^{-2}$ should be observed. Fibers in which the population of flaws is proportional to the mass of the sample would indicate a volume dependence (3,4); however, it should be realized that a flaw in a fiber would be so close to the surface that a surface-dependent relationship might appear to be a pseudo-volume-dependent relationship. Data on rods drawn in

anhydrous nitrogen and tested under the standard conditions listed above are less extensive, but indicate a somewhat decreased diameter dependence and generally increased values of MOR.

INFLUENCE OF STIRRING—UNCOVERED CRUCIBLE

The influence of stirring of the glass on MOR was investigated, as it was thought that possibly nonhomogeneity due to a lack of mixing of the glass in the crucible might be a factor (5). It was thought that a stirring of the melt would result in higher MOR values. The MOR's of 51 rods drawn from stirred melts in uncovered crucibles were tabulated and statistical adjustments were made to compensate for the diameter effect. A group of values for 183 rods drawn from unstirred melts was similarly treated. These data were obtained from melts heated in uncovered crucibles in an anhydrous atmosphere and were measured with another MOR cell (see Fig. 22). All the rods in this series appeared to be perfect to the unaided

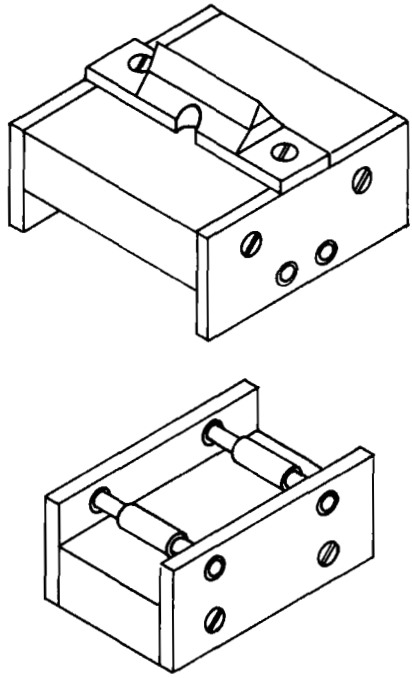

FIG. 19. New modulus of rupture cell.

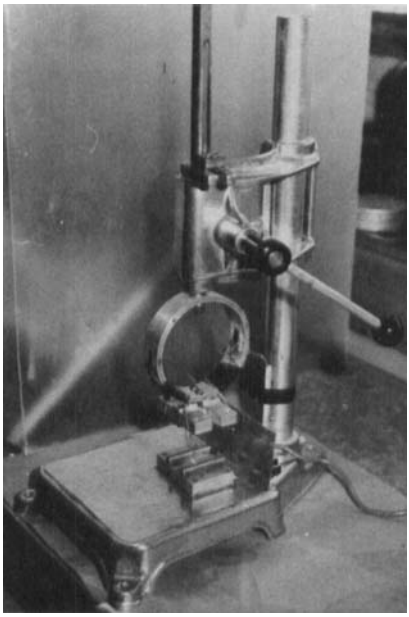

FIG. 20. MOR test appararus; test cell mounted in a drill press frame.

eye. The average MOR of the rods from unstirred melts was 1.34×10^5 psi, while the corresponding value for stirred glass was 9.8×10^4 psi. From this we may conclude that stirring of the melt definitely decreases MOR. This would suggest that one of the causes of weakness of glass rods is present in the melt and is retained when the rod is drawn. When the diameter was plotted against MOR separately for stirred and unstirred glass, two distinctly separated curves were obtained.

MODULUS OF RUPTURE AS A FUNCTION OF DRAWING TEMPERATURE

Modulus of rupture as a function of drawing temperatures was studied with data from 94 rods prepared as above, and is illustrated in Fig. 23. Data are adjusted to a constant rod diameter of 0.052 in. as per the relationship above. A small negative trend of MOR vs. draw temperature is indicated for stirred glass samples and a small positive trend for unstirred glass. Owing to the inherent scatter of the data, it is our opinion that MOR does not depend on draw temperature.

MODULUS OF RUPTURE AS A FUNCTION OF COOKOUT TIME—UNCOVERED CRUCIBLE

Modulus of rupture as a function of cookout time was studied with rods drawn from both stirred and unstirred melts. Data are adjusted for the diameter of rods, and the drawing temperature was 2375–2550°F (see Fig. 24). The data do not clearly indicate a relationship between MOR and stirred glass, but there is a clear-cut relationship indicated with unstirred glass. Over the range examined, the MOR increases linearly with the logarithm of cookout time. This result is in agreement with our observation that glass contains large numbers of bubbles and other inhomogeneities which require

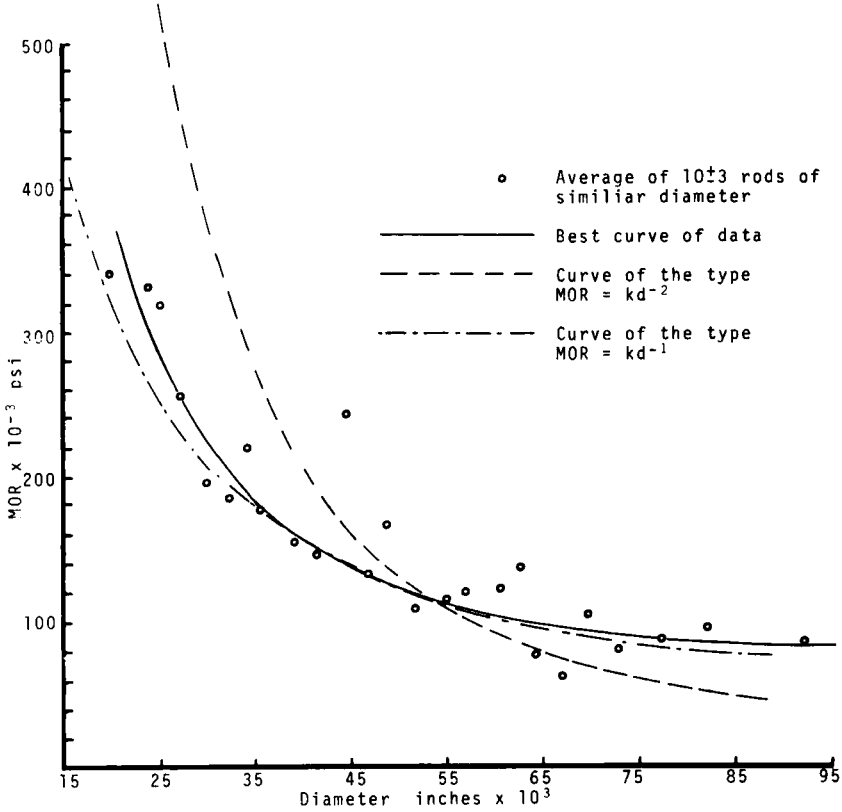

FIG. 21. MOR of freshly drawn E-glass as a function of diameter. Glass was drawn from an uncovered crucible and tested with the old MOR test device.

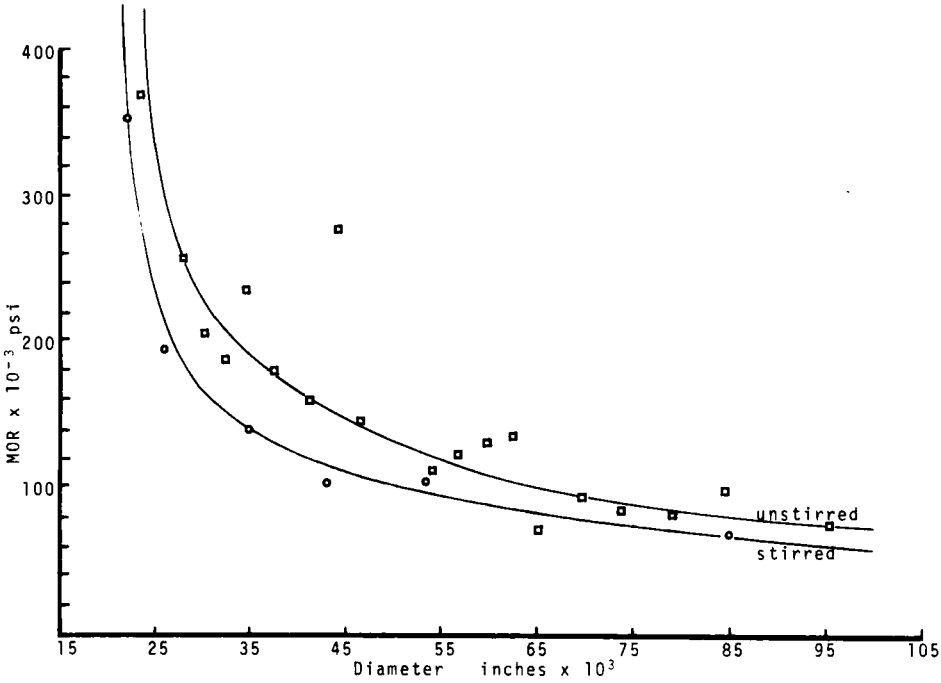

FIG. 22. Effect of stirring of the melt upon MOR of freshly drawn E-glass.

a number of hours to dissolve or reach the surface, where they may be skimmed off.

MODULUS OF RUPTURE AS A FUNCTION OF COOKOUT TEMPERATURE

We do not have sufficient numerical data to clarify this relationship; however, empirically it appears that the quality of the glass is considerably improved when it is cooked out at a higher temperature.

MODULUS OF RUPTURE OF E-GLASS DRAWN IN AIR

Seventy-two rods were drawn by hand in the open air and tested at an age of approximately 1 min with the apparatus previously described. The average of the 72 rods is $2.57 \pm 0.17 \times 10^5$ psi (90% confidence). This compares well with the values reported below for rods drawn in anhydrous nitrogen. The conclusion may be

drawn that there is no difference in the MOR of freshly drawn rods in an anhydrous nitrogen or normal atmosphere.

MODULUS OF RUPTURE OF E-GLASS DRAWN IN ANHYDROUS NITROGEN

Measurements of the MOR of 37 rods drawn in an atmosphere of nitrogen containing approximately 5 ppm of water vapor were obtained. The average value obtained was $2.44 \pm 0.24 \times 10^5$ psi.

The application of a combination of these tools should permit a relatively complete analysis of the stress concentrations within a body with moderate structural complexity.

ROASTING STUDIES

Anhydrous glass surfaces can be prepared by roasting the glass at 650°C. However, the anhydrous surface thus prepared is not necessarily identical to the surface of a freshly drawn rod, as there is evidence that hydration and subsequent dehydration of a glass surface alters the surface permanently. Preliminary experiments have indicated that the freshly dehydrated surface is extremely sensitive to moisture uptake from the air as soon as the surface is cooled, making necessary the meticulous protection of the surface after roasting until testing can be performed.

A test procedure that is particularly suitable for detection of water on a surface is to substitute tritiated water (THO) for ordinary water. Low energy β^- emitters can be detected with a high degree

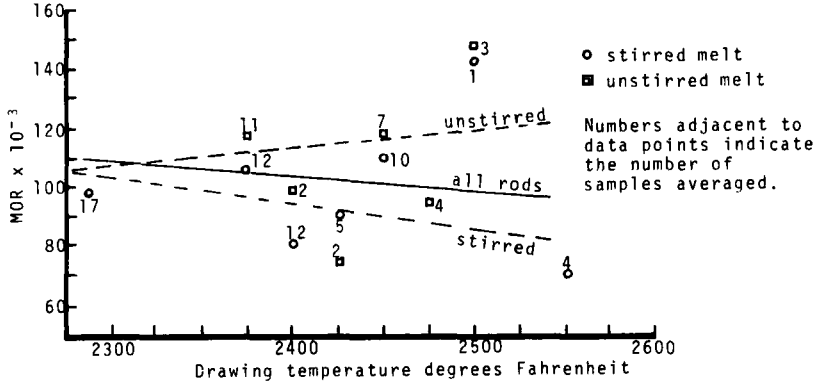

FIG. 23. Modulus of rupture as a function of drawing temperature.

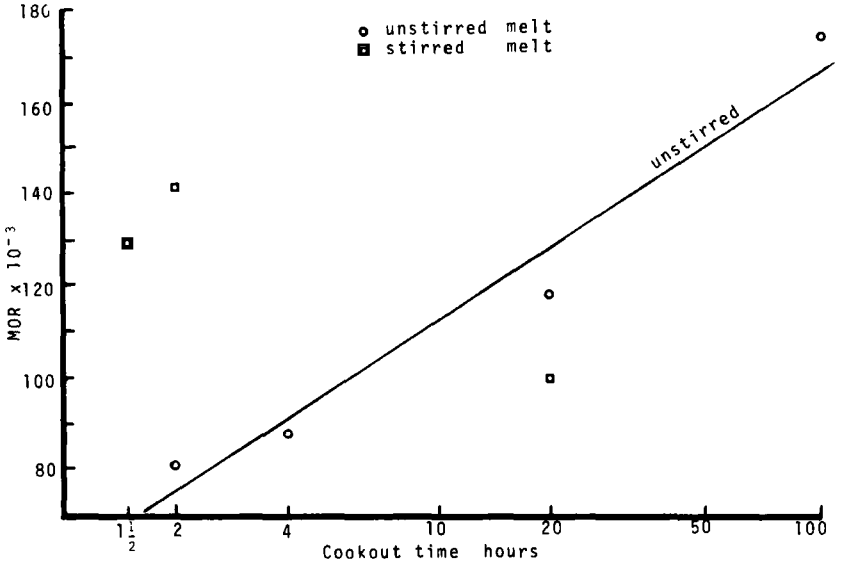

FIG. 24. Modulus of rupture as a function of cookout time.

of sensitivity by immersing the sample in scintillation solution and counting the resulting visual manifestations of radioactive decay in a scintillation counter (*6*). Tritium is a low-energy β^- emitter and must be in close proximity to the scintillation solution to be detectable. This technique is sufficiently sensitive to measure an amount of tritiated water corresponding to a quantity less than one molecule thick. It is several orders of magnitude more sensitive than detection with a photographic emulsion.

To meaningfully compare data from different samples of glass, it is necessary to refer them to a common base line. To this purpose, we have selected the most elementary glass surface of which we can conceive—that of a rod freshly drawn in an anhydrous atmosphere. It should be possible to trace the effect of the history of a glass surface by subjecting the rod in turn to a variety of influences, such as roasting, sintering, soaking in water, drying in atmosphere, etc.

E-glass rods were drawn in an anhydrous atmosphere, allowed to cool for approximately 1 min, then dropped into tritiated water and allowed to soak for 10 min. The rods were allowed to dry in the atmosphere for 2 hr, then counted by the scintillation technique (*7*).

Averaging the counts of sampling of approximately 30 rods per experiment reduced experimental scatter. Although results are not wholly reproducible from experiment to experiment, the results indicated that a quantity of water corresponding to a layer less than half a molecule thick is retained on the surface after this treatment. Aging of the freshly drawn glass for 24 hr in an anhydrous or normal atmosphere prior to exposing it to THO appears to increase the uptake of water slightly, but it is not certain that this observed increase is beyond experimental error.

CONCLUSIONS

1. Losses of water through a model composite may occur by at least two mechanisms. Water can pass through discrete microscopic channels in the body of the epoxide itself. It may, under certain circumstances, diffuse along the glass-epoxide interface. Water does not diffuse uniformly through the body of the epoxide.
2. Interfacial diffusion can occur in glass–epoxide composites in which the glass is pretreated with A-1100 in hexane solution. Interfacial diffusion does not occur in similar composites not treated with A-1100. Exposure of the glass to water or air prior to being made into a composite appears not to cause interfacial diffusion.
3. The amount of water retained by freshly drawn E-glass dipped in water and dried corresponds to a layer less than one molecule thick.
4. Measured MOR increases with a decrease of rod diameter over the range of diameters tested approximately according to the relationship $\mathrm{MOR} = Kd^{-1}$, suggesting that MOR is more area-dependent than volume-dependent.
5. MOR is not a function of the drawing temperature of the melt. However, MOR does increase with cookout time, and decreases when the melt is stirred.
6. Tentative results indicate freshly drawn E-glass drawn in air has the same MOR as if drawn in anhydrous nitrogen.
7. The MOR of E-glass drawn in anhydrous nitrogen appears to increase slightly up to an age of 5 min, then declines.
8. Occasionally some extremely high values of MOR are obtained on freshly drawn E-glass. The highest we have obtained is 1.86×10^6 psi.

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Zusammenfassung

Eine Untersuchung der Vorgänge, die sich an der Grenzfläche zwischen Glas und Kunstharz abspielen, wurde durchgeführt. Die Rolle des Wassers an der Grenzfläche wurde untersucht indem E-Gasstäbe verwendet wurden, die in einer wasserfreien Atmosphäre aus der Schmelze gezogen wurden und die als Standardmaterial benutzt wurden für einen Vergleich mit E-Glasstäben, die gealtert wurden, die mit A-1100 Silan behandelt wurden, mit Wasser und Hitze.

Modellsubstanzen aus Glas-Epoxid Gemischen wurden hergestellt und gravimetrisch und radiographisch in Bezug auf die Diffusion von Wasser durch dieselben untersucht. Der Einfluss der oben angeführten Variablen wurden auch durch Bruchmodulmessungen und Scintillationszählung nach Behandlung mit tritiumhaltigen Wasser untersucht.

Résumé

Une étude fondamentale des phénomènes prennant place à l'interface des composites verre-résine. On a examiné le role joué par l'eau à l'interface en utilisant des tiges de verre-E, etirées d'une fusion dans une atmosphère anhydre, comme materiel de base à comparer avec des tiges en verre-E subissant un vieillissement, traitées avec le silane A-1100, avec de l'eau, et grillées.

On a construit des modèles des composites verre-epoxyde et on les a examiné gravimétriquement et par radiographie pour la diffusion de l'eau. L'influence des variables mentionnés plus haut est aussi examinée par des modules des tests de rupture, et à l'aide des compteurs de scintillation, après un traitement avec de l'eau tritiée.

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