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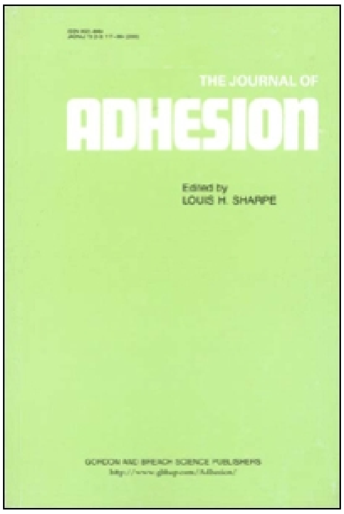

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The Influences of Environment and Glass Finishes on the Fracture Energy of Glass-Epoxy Joints

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ABSTRACT

A new test method for the measurement of adhesion is described and demonstrated. This method measures the debonding fracture energy between epoxy resin and glass. The effect of moisture on such a joint is shown as are the influences of different glass finishes. Analysis of these data show that the decrease of fracture energy of a joint that results from moisture penetration is directly proportional to the quantity of water present at the joint interface.

INTRODUCTION

THE MEASUREMENT of adhesion is a far more complex problem than we like to believe. A common adhesion test comprises of bonding of two coupons of given dimensions, the tensile separation of these coupons, and then a brief simplistic calculation to give the shear of the bond on failure.

This cannot be a true shear strength. When the bond fails, a crack propagates; either through the adhesive or through the adherend, unless we cause the crack to propagate along the adhesive-adherend interface in such a way as to give the impression of the bond failing at the interface.

In effect, we have propagated a crack through a brittle medium where the resistance to the propagation of such a crack would be a more significant measure of adhesion. Such a measurement could be made by the determination of the fracture energy of the bond.

The purpose of this paper is to show a simple method of obtaining such values of fracture or debonding energy. They are related to the adhesive, the exposure to the environment, as well as to the glass finish and are used to show the mechanics by which the environment affects the bond.

THE MEASUREMENT OF DEBONDING ENERGY

A series of glass bristles about 0.008 cm. diameter were cast in epoxy resin. The bristles were parallel and about 1 cm. apart. The resin was of composition: 100 parts Epon 826, 90 parts Nadic methyl anhydride and 1 part BDMA. It was cured at 120°C for 24 hours.

The cast plate was then cut into sections which could be subjected to the propagation of a tensile opening mode crack patterned after the specimens in references 1 and 2.

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A rectangular section (5 cm. by 25 cm.) of a casting with an embedded glass filament parallel to the shorter side was loaded in double torsion and examined under crossed polarized light indicating the shear field in the resin around the glass bristle under tension as shown in Fig. 1. The illustration shows a concentration of strain around the fiber at a point distant from the crack. This point is where the fiber has debonded from the resin[2]. During debonding the strain field observed in Fig. 1 moved along the fiber with essentially no relative movement of the fringes indicating a small strain energy release from the resin during debonding. Such a similarity of strain pattern suggests a condition when fracture energy methods could be applied in a one dimensional situation. The portion of the fiber between this point and the crack is debonded and beyond this point it is bonded. The length of this debonded portion depends on the tension in the fiber, the debonding energy in shear between the fiber and the resin and other factors.[2]

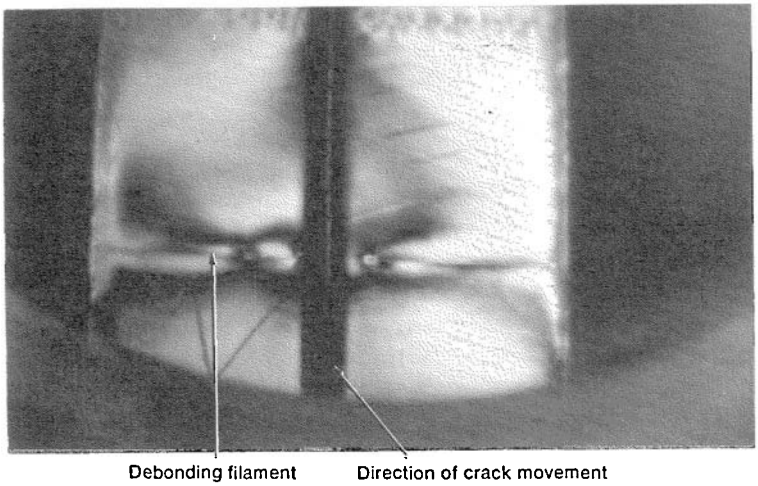

Figure 1. Crack front in polarized light showing the debonding of a filament.

The portion of the fiber that has debonded still has an interaction with the resin. When resin shrinks on the fiber during the curing process[3] there will still be a continuing normal pressure on the fiber despite the fact that it has debonded and thus moved relative to the matrix[2]. The normal pressure will remain essentially constant[4] and will not change as a result of the fiber debonding. This normal pressure in combination with the friction between the fiber and the resin will result in a shear τ on the surface of the fiber and this will be substantially constant along the debonded length of the fiber.

The above is the condition of the fiber embedded in resin and, as the debonded length depends on the debonding energy in shear, it might be possible to use the above experiment to determine this energy. In practice, it is not so easy: the specimens are relatively complicated and the interaction of several fibers makes computation awkward. Instead of this type of specimen

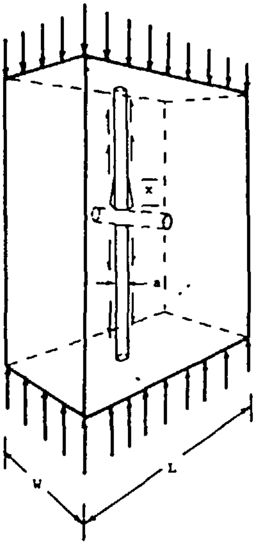

Figure 2. Sketch of technique used to determine the debonding fracture energy between the resin and the fiber.

we will modify it by studying the effects of compressing a prism of resin in which is embedded a bristle of glass. If the ends of the bristle are only loaded by shear transmitted from the resin then we will obtain expressions similar to the ones in the tensile case[2] to enable us to determine the debonding energy in shear.

Consider a bristle of diameter a, cross sectional area A, modulus E_f, embedded in a resin block and severed by a central hole as in Fig. 2. If the bristle has previously debonded a distance x from its ends, then the strain energy released by debonding an additional distance dx would be the difference between the strain energy in the fiber before and after debonding, as the strain energy released by the resin would be relatively small. This difference would be

$$(\sigma_{f_b}{}^2 - \sigma_{f_a}{}^2)\,\frac{Adx}{2E_f}$$

where σ_{f_b} and σ_{f_a} are the stresses in the bristle before and after debonding respectively. This energy is equal to the debonding fracture energy of the fracture area or $G_{II}\,\pi adx$; thus,

$$G_{II}\,\pi adx = (\sigma_{f_b}{}^2 - \sigma_{f_a}{}^2)\,\frac{Adx}{2E_f} \tag{1}$$

Substituting $\pi a^2/4$ for A, equation (1) simplifies to

$$G_{II} = (\sigma_{f_b}{}^2 - \sigma_{f_a}{}^2)\,\frac{a}{8E_f} \tag{2}$$

To relate σ_{f_b} to readily measurable quantities, we need only assume that the strain in the resin before debonding, ε_r, is equal to the strain in the fiber, ε_f. This gives us

$$\sigma_{f_b} = \varepsilon_r E_f \tag{3}$$

The stress in the bristle after debonding is due to friction between the bristle and its matrix sheath in the absence of end loads on the fibers; therefore, if the frictional shear, τ, is constant along the length we get

$$\sigma_{f_a} = \frac{\tau \pi a x}{\frac{\pi a^2}{4}} \tag{4}$$

Substituting for σ_{f_b} and σ_{f_a} in equation (2) we get

$$G_{II} = \left[(\varepsilon_r E_f)^2 - \left(4\tau \frac{x}{a}{}^2\right) \right] \frac{a}{8E_f} \tag{5}$$

So for initial debonding, where x = 0, we get

$$G_{II} = \frac{\varepsilon_r^2 E_f a}{8} \tag{6}$$

We have then a simple expression for the value of the energy required to debond glass from its matrix. The utilization of this relationship to give a test method is as follows: Bristles of glass are cast in a resin matrix. The casting is then cut into rectangular parallelpipeds 1 x 1 x 3 cm with the bristle running down its center. A hole is then drilled through the center to cut the bristle and expose the ends. This piece can then be compressed until the debonding is visible and the compressive load measured. Fig. 2 shows such a sample.

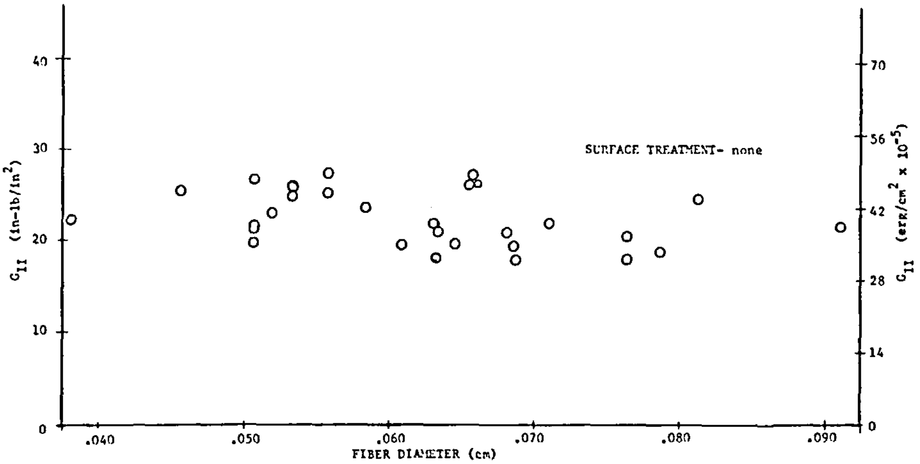

Figure 3. A plot of debonding fracture energy versus fiber diameter showing the debonding fracture energy to be independent of fiber diameter.

EXPERIMENTAL

In order to prove the validity and reproducibility of the techniques described above, it was first necessary to make and test the samples with different diameter fibers. We would expect the debonding energy to be the same regardless of the fiber diameters. This was done and the results are shown in Fig. 3. The values of fracture energy are substantially independent of the diameter as would be expected. This is a good indication of the validity of the assumptions and of the usefulness of the method in determining the values of G_{II}. It should be pointed out that the crack does in fact develop from a precrack that is induced by the drilled hole. The precrack length is of the order of the hole diameter. The load required to initiate crack movement determines the debonding fracture energy, G_{II}. It was not possible to use specimens of great length as buckling of the specimens occurred.

The utility of this technique is broad indeed but the first question that we approached was to determine the effects of finish on glass; particularly how these effects would be altered by the exposure to different environments. The finishes were applied by dipping cleaned glass fibers into a 1% solution of finishing agent and water. An examination of these results might suggest the exact mechanism of interaction with environment.

A series of specimens were made of fire polished Pyrex glass bristles embedded in the above epoxy resin. They were exposed to atmospheres of different humidity and temperature for increasing periods of time. During the increasing periods of time specimens were randomly selected from the environment, subjected to a compressive load and the crack movement load was noted. These specimens remained exposed to laboratory air for a period

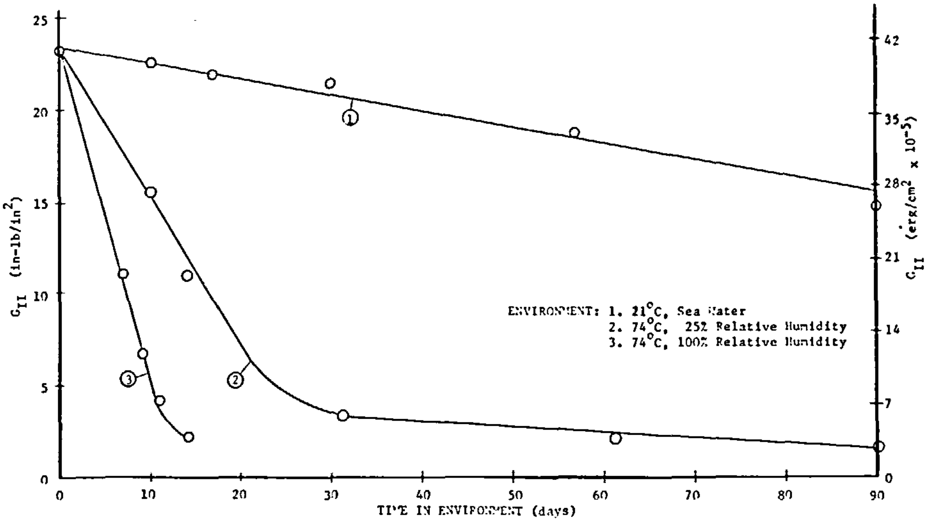

Figure 4. Plots showing the effect of time in various environments on the debonding fracture energy between glass and resin.

up to 50 days to determine the extent of any rehealing effect. No appreciable rehealing was observed. The results are shown in Fig. 4. It is quite apparent that the moisture has a dramatic effect on the debonding energy. It decreases in an essentially linear fashion to a uniformally low level. The rate of decrease depends on the concentration of moisture in the atmosphere and on the temperature of the environment.

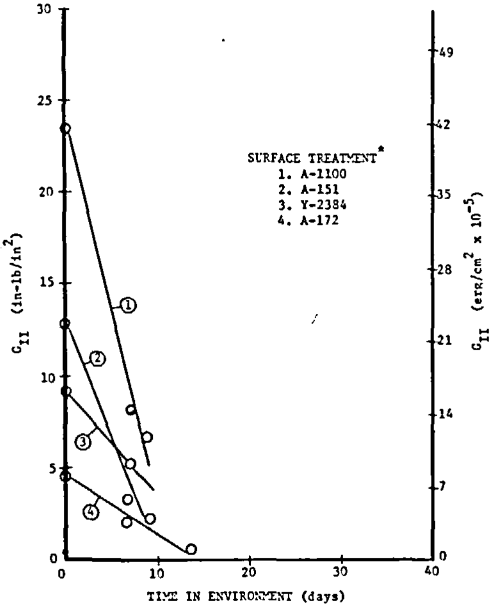

Figure 5. Plots showing the effects of time in a high temperature and humidity environment (74°C, 100% relative humidity) on the debonding fracture energy between surface treated glass and resin.

Repeating the tests using different finishing agents on the glass, we obtained the results in Fig. 5. Again we observe that the effect of the finish, so far as its influence on the debonding energy between the glass and the matrix, is reduced to a low level indeed after a period of exposure. The implications of both these experiments are interesting:

1. We can expect vastly different effects of the finish before and after exposure to a moist environment.
2. It appears that the debonding energy is the same after prolonged exposure to a moist environment regardless of the finish used.

DISCUSSION

Above are the facts in regard to the debonding energy in shear after exposure to a moist environment. The reasons for these changes require comment. It is apparent that water affects the debonding energy. The first question was whether the water affected it by diffusion into the resin-glass interface through the resin or always along the surface of the glass.

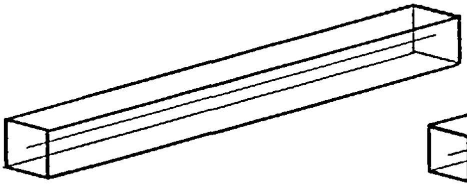

Figure 6a. A sketch of a resin strip containing a central glass bristle.

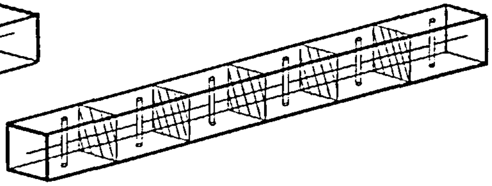

Figure 6b. A sketch of a resin strip which has been cut into six compression specimens.

To explore this problem, the resin with glass bristles cast into it was cut into long strips as in Fig. 6a. These strips were then exposed to the environment. After exposure they were cut into portions and drilled to give the fracture energy measuring specimens Fig. 6b. These are similar to the one in Fig. 2. These specimens were then tested to show how the fracture energy in shear between the glass and the resin might vary along the length of the glass bristle. This might reveal the effects of the water seeping in at the end along the exposed glass-resin interface. The results are shown in Fig. 7.

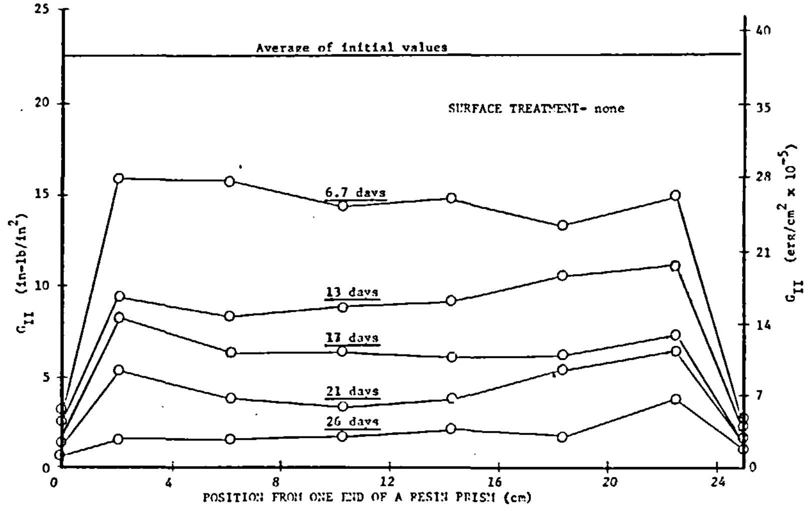

Figure 7. A plot showing the debonding fracture energy for positions along fibers cast in square resin prisms which were exposed to a 74°C, 100% relative humidity environment. Each line represents the duration of exposure before testing.

Examination of Fig. 7 shows what has happened after different periods of exposure and how the position along the length of the bristle controlled the G_{II} value. The end was surely affected as might be expected, but it was only the end portion that was affected and the water did not appear to penetrate along the interface beyond a certain distance about 0.75 cm. The fall off in the G_{II} was, however, proceeding over the central portion of the glass. The reason for this hesitancy on the part of the water to enter the interface might well be that the radial pressure of the epoxy on the glass is high—perhaps 2000 psi[3]—and this might inhibit the penetration of the water.

Plotting the values of G_{II} of the portion of the strips distant from the affected ends against time of exposure we get the curve shown in Fig. 8. We wish now to relate the amount of water at the interface with the decrease of G_{II}: assume that any water that diffuses to the surface of the glass is trapped there. This is a reasonable assumption as the water on a glass surface will increase up to several molecular layers and be hard indeed to remove[5]. With this assumption we can determine that the amount of water on the surface of the glass will be that which would diffuse to the center of a homogeneous square prism of resin, Fig. 6a. This thickness of the water layer on the glass will be directly proportional to the amount of water that has penetrated to the central region. A theoretical analysis of the diffusion of water radially into a square section is shown in Appendix I.

Let us also assume that the decrease of the fracture energy in shear is proportional to the thickness of the water layer. The validity of this assumption can be checked as follows: The values of G_{II} are plotted in Fig. 8. Also shown in Fig. 8 is a curve of the family described in the diffusion equation (j) to give an optimum fit with the G_{II} curve. This diffusion curve is changed in slope by different values of the diffusion coefficient, D. The value of D that makes the curves fit as shown is 7.1 x 10^{-8} cm^2/sec.

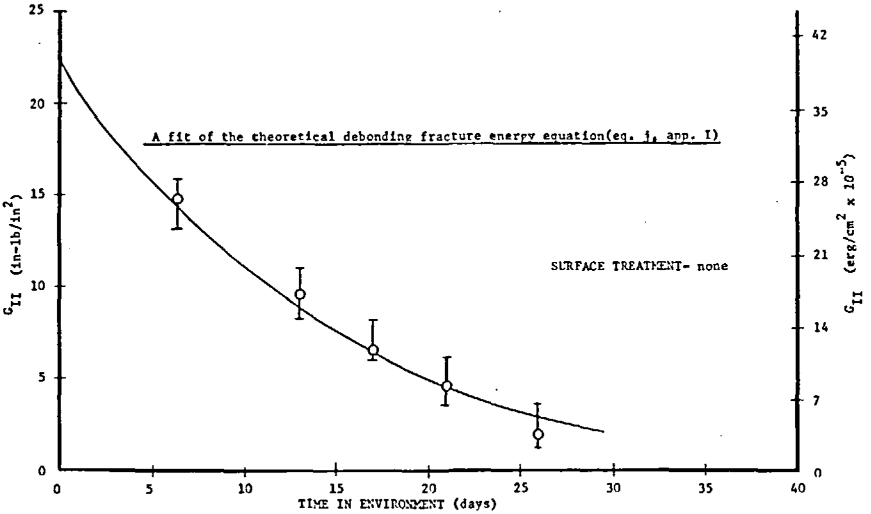

Figure 8. A plot showing the bond deterioration rate for glass bristles contained within long resin prisms which were exposed to a 74°C, 100% relative humidity environment.

The diffusion coefficient of water into epoxy resin can be determined independently by exposing resin specimens to a high relative humidity environment for periods of time and then weighing the resin. The diffusion coefficient for water is found to be 7.7 x 10^{-8} cm^2/sec by substitution in equation (d). This is close indeed to the value found by fitting a diffusion curve to the G_{II} curve.

The coincidence of these values of diffusion coefficients obtained by different techniques demonstrates the validity of our assumptions.

The amount of water dissolved in a resin before polymerization does not appear to be sufficient to affect the debonding energy; hence, it is not important to dry resins for use in the preparation of reinforced plastics if the only purpose is to ensure the continuing presence of a bond. The bond will deteriorate progressively and irreversibly on exposure to air with water in it. This fact suggests that there is not much we can do about maintaining a bond indefinitely as water is sure to diffuse to the surface of the adherend when the adherend is exposed to atmospheric conditions.

The diffusion rate through the resin is much slower than that along the interface between the glass and the resin. This great difference overshadows the measurement of the deterioration of the bond in reinforced plastics. Ends reach the surface at many points even with the most carefully manufactured laminates and it is through these ends that moisture penetrates. Without the strong radial pressure engendered by the sheath of resin[3], the water will diffuse readily into the laminate.

CONCLUSIONS

The conclusions that we can obtain in regard to the effects of finishes and environment on the fracture energy of epoxy-glass joints as a result of the careful study of the changes are significant:

1. The decrease of the fracture energy of the bond is proportional to the apparent thickness of the water film that is on the glass until a low value of energy is reached.
2. Water can penetrate along the bond interface from an exposed edge of the glass unless it is inhibited by normal pressure of the resin on the glass.
3. Water can diffuse to the interface through the resin.
4. The effect of any water that might be dissolved in the resin after curing is insignificant in regard to the decrease of fracture energy.
5. The effects of finishes are to alter the initial values of the fracture energy.
6. Regardless of finish, the fracture energy decreases essentially linearly with time to the same low value.
7. The time required to reach the low value depends only on the environment and is substantially independent of the finish.

These conclusions yield an important insight into the behavior of glass-resin joints. More importantly, a novel method of studying the fracture energy of bonds is demonstrated that may yield a sound method of measuring and interpreting phenomena of adhesion.

ACKNOWLEDGEMENTS

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APPENDIX I

The basic equations of mass diffusion through solids are according to Fick's Laws:

$$J_X = -D\frac{\partial C}{\partial X},$$

$$J_Y = -D\frac{\partial C}{\partial Y} \qquad \text{(a)}$$

and

$$\frac{dC}{dt} = D\left(\frac{\partial^2 C}{\partial X^2} + \frac{\partial^2 C}{\partial Y^2}\right) \qquad \text{(b)}$$

where C is the concentration of solute in the solvent,
D is the coefficient,
J_X and J_Y are the mass flux in the X and Y directions respectively,
t is time.

The solution for the analogous case of two dimensional transient heat flow is stated in reference 6.

The concentration at any point across a section of an infinitely long square prism of edge 2L with a constant surface concentration, C_0, is

$$C = C_0\left[1 - \frac{16}{\pi^2} \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)} e^{-D(2n+1)^2\pi^2 t/4L^2} \cos (2n+1)\, \pi X/2L \bullet \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)} e^{-D(2n+1)^2\pi^2 t/4L^2} \cos (2n+)\, \pi Y/2L\right] \qquad \text{(c)}$$

The average concentration, C_a, over a section of the prism is obtained by integrating equation (c) over the area $4L^2$, or

$$C_a = C_o\left[1 - \frac{64}{\pi^4}\left(\sum_{n=0}^{\infty} \frac{e^{-D(2n+1)^2\pi^2 t/4L^2}}{(2n+1)^2}\right)^2\right] \qquad \text{(d)}$$

Whereas the concentration of water, C, at some point in the resin is difficult to measure, the average concentration, C_a, is relatively easy to determine experimentally. This was done by the periodic weighing of long resin prisms.

For the purpose of this analysis, the fiber is assumed to act in a passive manner; that is, whatever water accumulated on the fiber would be the same as the quantity of water that would be contained by a central cylindrical volume equivalent to that of the bristle at the center of a long square resin prism containing no fiber. In this case the centerline concentration is

$$C_c = C_o\left[1 - \frac{16}{\pi^2}\left(\sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)} e^{-D(2n+1)^2\pi^2 t/4L^2}\right)^2\right]: \qquad \text{(e)}$$

Let us assume that the initial value of debonding energy is $(G_{II})_0$, and that the decrease in G_{II} due to the presence of water is proportional to the apparent thickness, T, of the water film on the bristle. Then

$$G_{II} = (G_{II})_o - k_1 T \qquad \text{(f)}$$

where k_1, etc. are constants. Considering the volume of water that would be on the surface of the bristle of diameter, a, to be that of an annular cylinder of wall thickness, T, we get

$$\pi a T = C_c\, \pi\, a^2/4 \qquad \text{(g)}$$

or

$$T = k_2 C_c a$$

Substituting for T in equation (f), the expression for debonding fracture energy becomes

$$G_{II} = (G_{II})_o - k_3 C_c \tag{h}$$

if we use bristles of constant diameter.

So

$$G_{II} = (G_{II})_o - k_3 C_o \left[1 - \frac{16}{\pi^2} \left(\sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)} e^{-D\,(2n+1)^2 \pi^2 t / 4L^2} \right)^2 \right] \tag{i}$$

from equation (e).

But from the experimental results G_{II} tends towards zero with increasing exposure to environment; consequently $(G_{II})_0 = k_3 C_0$ or

$$G_{II} = k_4 \left(\sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)} e^{-D\,(2n+1)^2 \pi^2 t / 4L^2} \right)^2 : \tag{j}$$