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GLASS FIBRE/EPOXY RESIN INTERFACE LIFE-TIME PREDICTION.(U)

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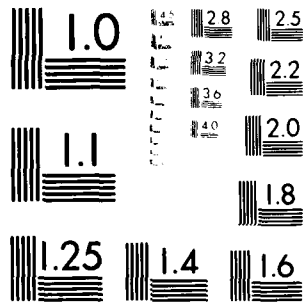
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and might therefore offer a non destructive evaluation technique for monitoring at least one of the causes of mechanical degradation. This possibility has been appraised and experimentally verified.

Two models have been developed and applied to interfacial fracture at pressure pockets attributable to osmosis. Direct photoelastic measurements indicative of load transfer in short fibre composites have been used to test the rates of debonding predicted by the two models.

The net stress across the boundary of the first Wigner cell in a fibre reinforced composite must be zero from which it is inferred that, moving around a fibre, the radial principal stress changes sign several times. The origin of the stress can be differential thermal contraction between fibre and matrix materials during cooling from the resin cure temperature, or inhomogeneous swelling associated with water uptake, or externally applied loads. The number of reversals of sign is determined by the fibre lay-up geometry. In the light of this, interfacial failure is expected to initiate at sites located on the loci of maximum residual radial tension. Also, subsequent propagation of individual pressure pockets is expected to be favoured along these loci rather than around the fibre circumference. The fact that such preferred initiation and propagation are not observed is taken to mean that residual stress is more uniformly distributed than expected. The nature of residual stress generated during resin curing and during water uptake/expulsion has consequently been further investigated.

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The solution of the differential equation is given by

(1)  $y = C_1 e^{2x} + C_2 e^{-2x}$

$$y'' - 4y = 0$$

$$\text{Characteristic equation: } r^2 - 4 = 0 \implies r = \pm 2$$

$$\text{General solution: } y = C_1 e^{2x} + C_2 e^{-2x}$$

(2)  $y'' + 4y = 0$

$$y'' + 4y = 0$$

$$\text{Characteristic equation: } r^2 + 4 = 0 \implies r = \pm 2i$$

$$\text{General solution: } y = C_1 \cos(2x) + C_2 \sin(2x)$$

$$\text{Particular solution: } y = \frac{1}{4} \cos(2x)$$

The general solution of the differential equation is given by

$y = C_1 \cos(2x) + C_2 \sin(2x) + \frac{1}{4} \cos(2x)$





Polarising microscopy of very low fibre volume fraction specimens, Figure 4, reveals the occurrence of interfacial pressure pockets during the first 200 hours. During this time, the resin is also undergoing swelling in order to accommodate the diffused water, Figure 5. Before saturation, at around 200 hours, the concentration of diffused water and hence the swelling is (approximately) distributed and this, in turn, introduces compression near the external surface and tension deeper inside the composite. This stress field is superimposed on to that already generated by the differential thermal contraction between matrix and fibre materials during cooling from the resin cure temperature. The cumulative effect of these changing stresses is evidently discontinuous during the initial stages of water uptake.

Each pressure pocket is filled with aqueous solution and the critical angle over the area of contact between it and the fibre is larger than that for contact between resin and fibre. However, the expected propagation of a larger solid angle of light is not realised until continuous air pressure pockets and absence of elastic deformation is established along the whole length of the waveguide, i.e. not until a very much later stage of water uptake (200 hours in Figure 5).

1.2.2. DISCUSSION OF EXPERIMENTAL RESULTS

1.2.2.1. Optical Effects

On when the light is incident on the surface subjected to an osmotic pressure, diffraction occurs. A typical example of a completely isotropic solution of a rigid polymer in water is that of the solution of the solid walls of the normal fibre polymer in water. In equilibrium with the dissolved polymer, when water is added to the solution (i.e. water) will enter the matrix of the polymer, increasing the volume and hence the pressure of the walls of the normal fibre polymer. This increase, owing to the pressure exerted by the osmotic pressure, is the pressure we have termed osmotic pressure.

In this regard, it is reasonable to infer that pockets of water (or other solvent) which are introduced into the composite environment and the liquid and water solution located at the interface would correspond to the frequency components required to split the TET component further, and the solid walls of the normal fibre polymer would be expected to act as a diffraction grating. The osmotic pressure, for the concentration of a normal fibre polymer, is the osmotic pressure we have termed osmotic pressure. This is the osmotic pressure we have termed osmotic pressure and is shown in Figure 5.

### 3.2 Model 1

When formed, each interfacial pocket closely resembles a penny-shaped crack that has grown in a solid tensioned between fixed grips. The overall change in energy is from  $U_0$ , corresponding to the state of strain energy prior to fracture, to  $U_1 - U_G$ , where the Griffith energy  $U_G$  given by the Zener approximation is

$$U_G = \frac{1}{2} \frac{\sigma_1^2}{E} \pi a b^2 = \frac{\sigma_1^2}{2E} \pi a b^2$$

$\sigma_1 = \sigma_1$  is the tensile stress applied externally and perpendicular to the crack,  $E$  is Young's modulus,  $a$  and  $b$  respectively are the half thickness and radius of the crack. Referring to figure 8, if the interfacial cavity could be closed by application of traction on its wall, the stress  $\sigma_c$  acting across the walls could rise from 0 to  $\sigma_1$  and, correspondingly, its volume would decrease from  $V_1$  to 0.

The Griffith energy gained by this process would be

$$U_{G1} = \frac{1}{2} \frac{\sigma_1^2}{E} \pi a b^2 = \frac{\sigma_1^2}{2E} \pi a b^2$$

Hence

$$\sigma_1 = \sqrt{\frac{2E U_{G1}}{\pi a b^2}}$$

By making  $\sigma_1$  a function of the interfacial crack length with respect to external stress, the stress  $\sigma_1$  is now, instead, a function of an internal pressure, and an internal pressure  $p = \sigma_1$  gives the same  $\sigma_1$ , see figure 9.

$$\sigma_1 = \sqrt{\frac{2E U_{G1}}{\pi a b^2}}$$

and the elastic potential energy is

$$U_{el} = \frac{1}{2} \frac{\sigma_1^2}{E} \pi a b^2 = \frac{\sigma_1^2}{2E} \pi a b^2$$

Therefore  $\sigma_1 = \sqrt{\frac{2E U_{G1}}{\pi a b^2}}$

and  $U_{el} = \frac{1}{2} \frac{\sigma_1^2}{E} \pi a b^2$

A solute exerts an osmotic pressure equal to the pressure that would be exerted by a gas having the same number of molecules in a volume equal to that occupied by the solution. Consider a change in volume of the interfacial cavity from  $V_0$  to  $V_1$  resulting from dissolution of  $n$  moles of solute.

$$pV = nRT$$

$$\text{The strain energy release} = \int p dV$$

$$= \int \frac{nRT}{V} dV$$

$$= nRT \log_e \frac{(V_0 + V_1)}{V_0}$$

$$= nRT \log_e \frac{p_1}{p_0}$$

$p_0$  and  $p_1$  are the values of the osmotic pressure corresponding to volumes  $V_0$  and  $V_1$  respectively.

The overall energy  $E = E_{\text{gas}} + E_{\text{elastic}}$

$$= nRT \log_e \frac{(V_0 + V_1)}{V_0} + \frac{3}{8\pi} \frac{F V_1^2}{ab^3}$$

This function is sketched in Figure 10.

The value of  $V_1$  corresponding to minimum energy release may be found by differentiation

$$\frac{dE}{dV_1} = nRT \frac{1}{V_0 + V_1} + \frac{3}{4\pi} \frac{F V_1}{ab^3}$$

$$= 0 \text{ when } V_1^2 + V_1 V_0 = \frac{4\pi}{3} ab^3 nRT = 0$$

$$\text{i.e. when } V_1 = \frac{-V_0}{2} + \sqrt{\frac{V_0^2}{4} + \frac{4\pi ab^3 nRT}{3}}$$

We must take the positive root, hence

$$V_1 = -\frac{V_0}{2} + \sqrt{\frac{4ab^2 nRT}{3E} \left( 1 + \frac{3EV_0^2}{16\pi ab^2 nRT} \right)}$$

$$\sim -\frac{V_0}{2} + \sqrt{\frac{4ab^2 nRT}{3E}} \quad \text{for large values of } b$$

### 3.3 Model 2

Alternatively, interfacial failure due to cracks inflated by osmotic pressure could be modelled as follows. Suppose a constant pressure reservoir supplies the "gas"

$$\begin{aligned} \text{Energy, } E &= -p_1 V_1 + \frac{1}{2} p_1 V_1 = -\frac{1}{2} p_1 V_1 \\ &= -E_{\text{elastic}} = -\frac{2\pi}{3} \frac{p_1^2}{E} ab^2 \end{aligned}$$

but  $E_{\text{surface}} \sim 2\gamma \pi ab$ , where  $\gamma$  is the specific surface energy

$$\text{so } E_{\text{total}} = 2\gamma \pi ab - \frac{2\pi}{3} \frac{p_1^2}{E} ab^2$$

$$\begin{aligned} \frac{\partial E_{\text{total}}}{\partial b} &= 2\gamma \pi a - \frac{4\pi}{3} \frac{p_1^2}{E} ab \\ &= 2\pi a \left( \gamma - \frac{2}{3} \frac{p_1^2}{E} b \right) \end{aligned}$$

which is negative if

$$b > \frac{3E\gamma}{2p_1^2} \quad \text{i.e. if } p > \sqrt{\frac{3E\gamma}{2b}}$$

$$\frac{\partial E_{\text{total}}}{\partial a} = 2\gamma \pi b - \frac{2\pi}{3} \frac{p_1^2}{E} b^2 = 2\pi b \left( \gamma - \frac{p_1^2}{3E} b \right)$$

and is negative if  $b > \frac{3E\gamma}{p^2}$

$\frac{\partial E}{\partial b}$  total is evidently more negative than  $\frac{\partial E}{\partial a}$  total, so the expression

for  $p_{crit}$  is taken from the former.

Taking as trial values  $E = 3\text{GPa}$ ,  $\gamma = 1\text{J/m}^2$  and  $b = 10\mu\text{m}$ ,

$$p_{crit} = \sqrt{\frac{3.3 \times 10^9 \cdot 1}{2 \cdot 10^{-5}}} = 10\text{MPa}$$

### 3.4 Observations

It is important to note the distinctive behaviour of pressure filled interfacial cracks under the two extreme types of inflation outlined in models 1 and 2. Model 2 corresponds to the uniform tensile stress type of loading that was treated by Griffith, and gives rise to an unstable critical crack size such that a smaller crack will not grow while a larger one will grow without limit. This critical crack size corresponds to a maximum in the sum of mechanical and surface energies. Model 1 implies loading at the mouth of the interfacial crack (as by the driving in of a wedge) and results in a stable crack size corresponding to a minimum in the sum of mechanical and gas energies.

Thus, model 2 predicts instantaneous interfacial failure if a constant osmotic pressure equal to a critical pressure can be maintained, whereas model 1 predicts interfacial failure at a rate determined by the requirement that each pressure pocket maintains its volume at a minimum energy level.

In Figure 11, the overall rate of interfacial failure is taken as the rate of loss of load transfer index in short fibre composites. The load transfer index is the optical retardation measured through diameters close to the centre of an individual short fibre minus the optical retardation measured through diameters near the ends of the same fibre. It is evident that interfacial failure proceeds at a rapidly decelerating rate such as would be expected if model 2 dominates at the time of initiation but gives way to model 1 during propagation.

According to model 1, interfacial pressure pockets maintain their volumes at values determined by the square root of the number of moles of dissolved solute. It has been observed that solutes can be leached from the fibre in some cases<sup>(4)</sup>, leaving an 'etched' fibre surface, and in such cases the availability of the solute is presumably governed by the rate of diffusion of the solute to the surface of the fibre. The simplest diffusion model predicts dependence on the square root of time, and the combination of these two processes leads to a dependence of the volume of the interfacial pressure-filled cavities on the fourth root of time. The broken line in Figure 11 corresponds to a  $(\text{time})^{1/4}$  law.

#### 4. ON THE ASSUMPTION THAT EPOXY RESINS ARE FREE FROM SHEAR STRESS DURING CURE

##### 4.1 Hypothesis

The accelerated cure reactions that take place during the elevated temperature curing of epoxy resins promote cross-linking and thereby give rise to shrinkage. There are no superimposed dimensional changes attributable to such processes as chain scissioning, as could be the case in polyesters that contain diffused water, or to the release of volatiles, as might be the consequence of condensation reactions in polyamides for example. The shrinkage is assumed to be homogeneous because any tendency to create shear stress is thought to be relieved by viscoelastic flow. This assumption is based on the premise that before it gels, the fluid resin behaves in a Newtonian fashion and is unable to support shear stress.

##### 4.2 Experimental

19mm diameter soda-lime glass cover slips of two different thicknesses were bonded to 1mm thick soda-lime glass microscope slides. The cover slip thicknesses were 140 $\mu$ m and 230 $\mu$ m respectively and, the epoxy adhesive was Redux 312/5. The cover slips and microscope slides were thoroughly cleaned by ion bombardment before manufacturing the joints. Each specimen was mounted in a specimen chamber so that the free surface of the cover slip was in close proximity to an optical flat. This assembly was then mounted on an optical bench. In order that a uniform temperature distribution was maintained across the specimen, it was mounted on a thick disc of copper. This in turn was held in good thermal contact with the aluminium specimen chamber. Figure 12 is a schematic diagram of the optical components. The space between cover slip and optical flat is made small enough to allow optical interference between light incident upon and reflected from the free surface of the cover slip. Any changes in shape of the interference cavity, due to deformation of the cover slip caused by non-uniform changes in dimensions of the epoxy layer, cause the pattern of interference fringes to change.

Figure 13 shows a sequence of interference photographs recorded during the warm up period of a specimen manufactured with a 140 $\mu$ m thick cover slip. The time taken for the specimen to reach the cure temperature was 30 minutes and a substantial amount of the shape change occurred during this heating-up period. Initially, the cover slip is slightly deformed convex upwards but this soon gives way to a much larger concave deformation, the subsequent development of which is further examined in Figure 14 by creating Moiré patterns between successive photographs of the interference pattern and the pattern photographed when the specimen had completed its half hour cure. The Moiré fringes are the circumferential fringes, each

of which is the locus of points that have suffered identical displacement normal to the joint. The normal displacement of adjacent loci differ by half a wavelength.

#### 4.3 Results and Discussion

Figure 15 shows the normal displacement at different points across a diameter of the same specimen after 5 minutes at the cure temperature, where  $t_0 = 30$  minutes is the total time at the cure temperature. The sign of the displacement field was established by applying an identical positive pressure to the cover slip. The curve fits the parabola

$$w = .071 (x - .0095)^2$$

where  $w$  is the normal displacement and  $x$  is the distance measured from the edge of the specimen

To a first approximation, the deformation of the cover slip can be regarded as identical to that of a circular membrane, rigidly supported at its edge and subjected to a pressure drop ( $p$ ) across its surfaces. For such a membrane, Love<sup>(5)</sup> has shown that the fourth differential of the normal displacement is a measure of  $p$ . The cover slip is thin. If thin enough for Love's analysis to be applied, then

$$\nabla^4 w = 0 \text{ when } p = 0$$

Since the data presented in Figure 15 is described by a parabola, the fourth differential  $\nabla^4 w / \Delta x^4$  and hence the normal stress  $\sigma_{zz}$  are evidently zero.

Hence it is concluded that the deformation presented in Figure 15 is caused by radial stresses transmitted from the resin to the cover slip and not the stresses created normal to the joint. To check that curing really does cause the parallel sided disc of resin to transform into a concave lens shape, a specimen was manufactured using cover slips for both adherends. As expected, curing caused this sandwich to deform into a double concave lens as might have been produced by the application of edge tractions.

The analogy to the buckling of a thin circular plate simply supported around its edge and subjected to a uniformly distributed edge force applied in the plane of the plate, has been used to estimate the radial stress in the specimen shown in Figure 13.

The relations between the strains, displacements and stresses as given by Stoker (6) are

$$\epsilon_{xx} = \frac{\partial u}{\partial x} + \frac{1}{2} \left( \frac{\partial w}{\partial x} \right)^2 = \sigma_{xx} + \nu \sigma_{yy}$$

$$\epsilon_{xy} = \frac{1}{2} \left( \frac{\partial u}{\partial y} + \frac{\partial v}{\partial x} + \frac{\partial^2 w}{\partial x \partial y} \right) = \tau_{xy}$$

$$\epsilon_{yy} = \frac{\partial v}{\partial y} + \frac{1}{2} \left( \frac{\partial w}{\partial y} \right)^2 = \sigma_{yy} + \nu \sigma_{xx}$$

where the  $u, v, w$  components of the displacement of a point on the middle surface of the plate are denoted by  $u, v, w$  respectively.

The middle surface stresses divided by the modulus of elasticity  $E$  are denoted by  $\sigma_{xx}, \sigma_{yy}, \tau_{xy}$  and the middle surface strains by  $\epsilon_{xx}, \epsilon_{yy}, \epsilon_{xy}$ .

Since we assume radial symmetry, we may put  $\sigma_{xx} = \sigma_{yy}$  and making the approximation that  $\partial w/\partial x$  is sufficiently small relative to  $1/2(\partial w/\partial x)^2$  such that it may be neglected gives

$$\frac{1}{2} \left( \frac{\partial w}{\partial x} \right)^2 = \sigma_{xx} (\nu - 1)$$

where  $\nu$  = Poisson's ratio.

Figure 15 shows the distribution of stress  $\sigma_{xx} = \tau_{xy}$  obtained using the above equation for the deformation shown in Figure 14.

The above estimate is based on a deformation which is wholly elastic. An alternative estimate, using a simple viscoelastic model, is as follows. The raw adhesive film has a larger thermal expansion coefficient than glass. During heating to the cure temperature, the resin is free to expand in the thickness direction but radially it has to work against viscosity and its velocity relative to the glass is zero or close to zero at contact, becoming progressively larger at deeper layers. As a consequence, the cover slip is deformed convex upwards. Approaching the cure temperature, the shrinkage associated with the accelerated cure reaction dominates and the cover slip deformation is reversed to the concave shape sketched in Figure 15. An order of magnitude estimate of the in-plane shear stresses is obtained as follows. The adhesive layer is 150 $\mu$ m thick and 19mm in diameter, so the ratio of unrestricted in-plane shrinkage to thickness shrinkage is

$$= 150 \times 10^{-6} / 9.5 \times 10^{-3} = 1.58 \times 10^{-2}$$

During the isothermal annealing of the glass surface is of the order  $1.5 \times 10^{-7}$  to  $1 \times 10^{-6}$ . Most of this annealing occurs during the first few minutes of annealing. During that time the average annealing rate is  $(\frac{1}{t}) \approx 10^{-7}$  to  $10^{-2}$  to  $1 \times 10^{-3}$  sec $^{-1}$  to  $1.5 \times 10^{-4}$  sec $^{-1}$ , which is still a small, and before it becomes a lot, the viscosity ( $\eta$ ) of the glass is probably in the range 10<sup>10</sup> Pa.

During the anneal  $\eta = \eta_0$

$$= 1.5 \times 10^{-7} \text{ Pa}$$

The time dependence of the annealing rate is somewhat different than for the usually annealed and that for the usually isothermal annealing. During it is concluded that, even at the same temperature, a thin layer of glass surface having a thickness equal to the spacing between fibers in a composite does indeed support an annealing rate of order  $10^{-7}$  to  $10^{-2}$  sec $^{-1}$ .

Figure 17 shows a sequence of Moiré patterns during a 1000 cycle of a specimen annealed with a 1000 cycle anneal. A partial deformation is established equal to that obtained for the specimen in Figure 13 but of smaller magnitude.

Figure 18 shows a sequence of Moiré patterns for the specimen from Figure 13 on cooling from the annealing temperature. In addition to a small increase in the annealing rate during cooling (which the fiber probably behaves as an isothermal annealing with contraction in the fiber, especially that in the glass core) the Moiré pattern tends to a partially complete deformation, as shown by small steps and indentations on the deformation surface. These may be associated with local inhomogeneities in the annealing rate.

1. THE EFFECTS OF THE DIMENSIONAL CHANGES IN POLYMER FILMS UNDER GOING UPON THE POLYMERIZATION OF WATER

1.1. Introduction

It is well known that the dimensional changes of water in epoxy resins and the corresponding changes in mechanical properties are of great importance for the design of epoxy resin systems. In the case of epoxy resin systems, the dimensional changes are of great importance for the design of epoxy resin systems. The dimensional changes of water in epoxy resins are of great importance for the design of epoxy resin systems. The dimensional changes of water in epoxy resins are of great importance for the design of epoxy resin systems.

1.2. Methods

1.2.1. Materials

1.2.2. Apparatus

The specimens of epoxy resin were prepared by the method described in the literature. The specimens were prepared by the method described in the literature. The specimens were prepared by the method described in the literature. The specimens were prepared by the method described in the literature.

The specimens of epoxy resin were prepared by the method described in the literature. The specimens were prepared by the method described in the literature. The specimens were prepared by the method described in the literature. The specimens were prepared by the method described in the literature.



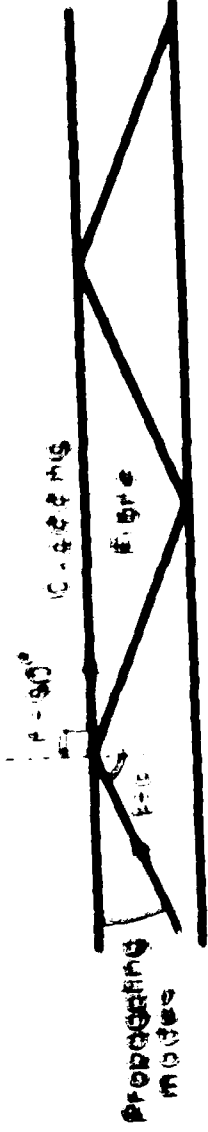
REFERENCES

1. S. A. Mikhlin and E. I. Zhurav, *Doklady Akad. Nauk SSSR*, 21, 107 (1957).
2. E. I. Zhurav, *Dokl. Akad. Nauk SSSR*, 146, 107 (1962); 151, 107 (1963).
3. E. I. Zhurav, *Dokl. Akad. Nauk SSSR*, 151, 107 (1963).
4. E. I. Zhurav and E. S. Gerasimov, *Dokl. Akad. Nauk SSSR*, 151, 107 (1963).
5. *Journal of the American Chemical Society*, 80, 107 (1958).
6. *Journal of the American Chemical Society*, 80, 107 (1958).
7. *Journal of the American Chemical Society*, 80, 107 (1958).
8. *Journal of the American Chemical Society*, 80, 107 (1958).
9. *Journal of the American Chemical Society*, 80, 107 (1958).
10. *Journal of the American Chemical Society*, 80, 107 (1958).

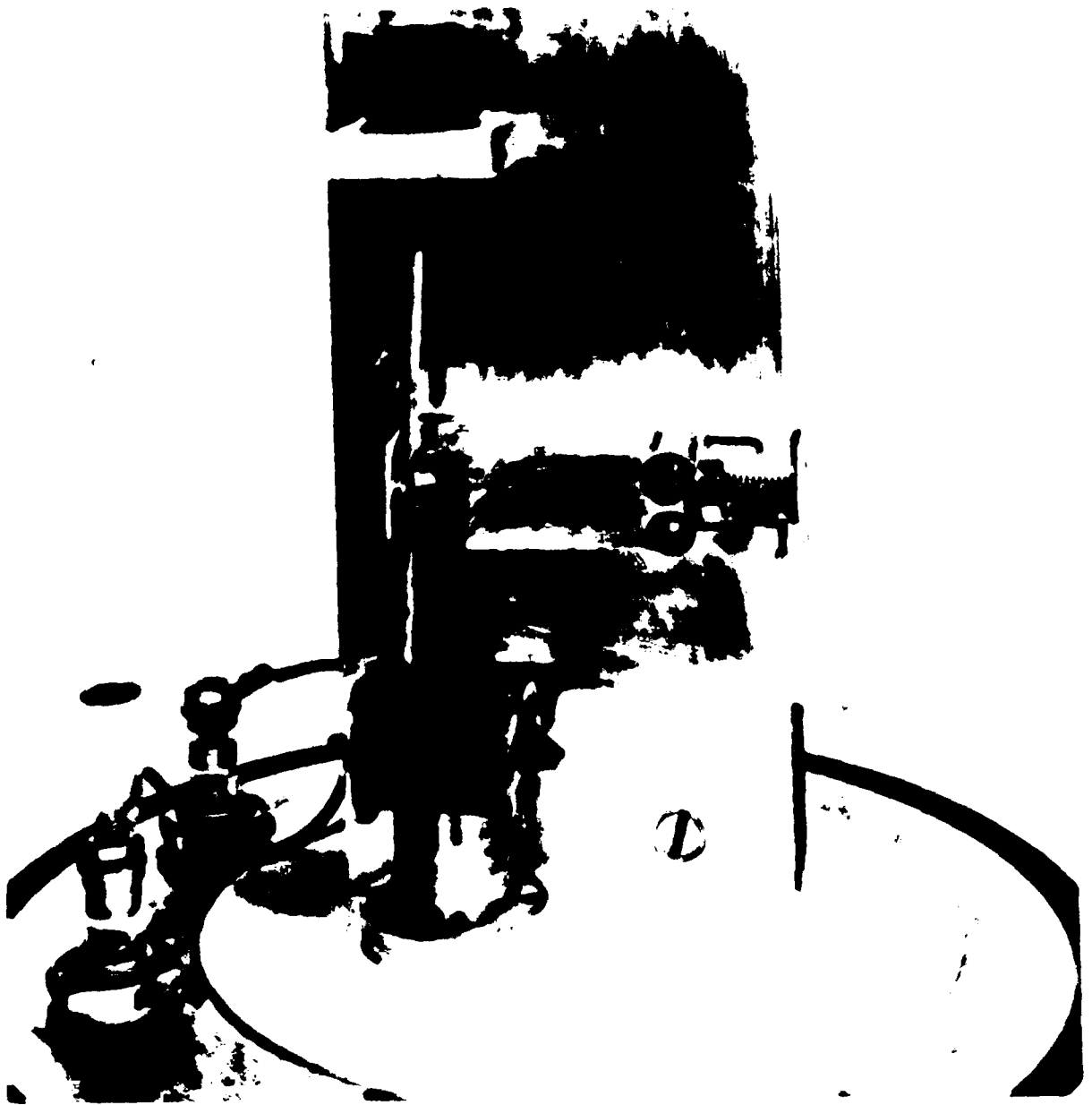
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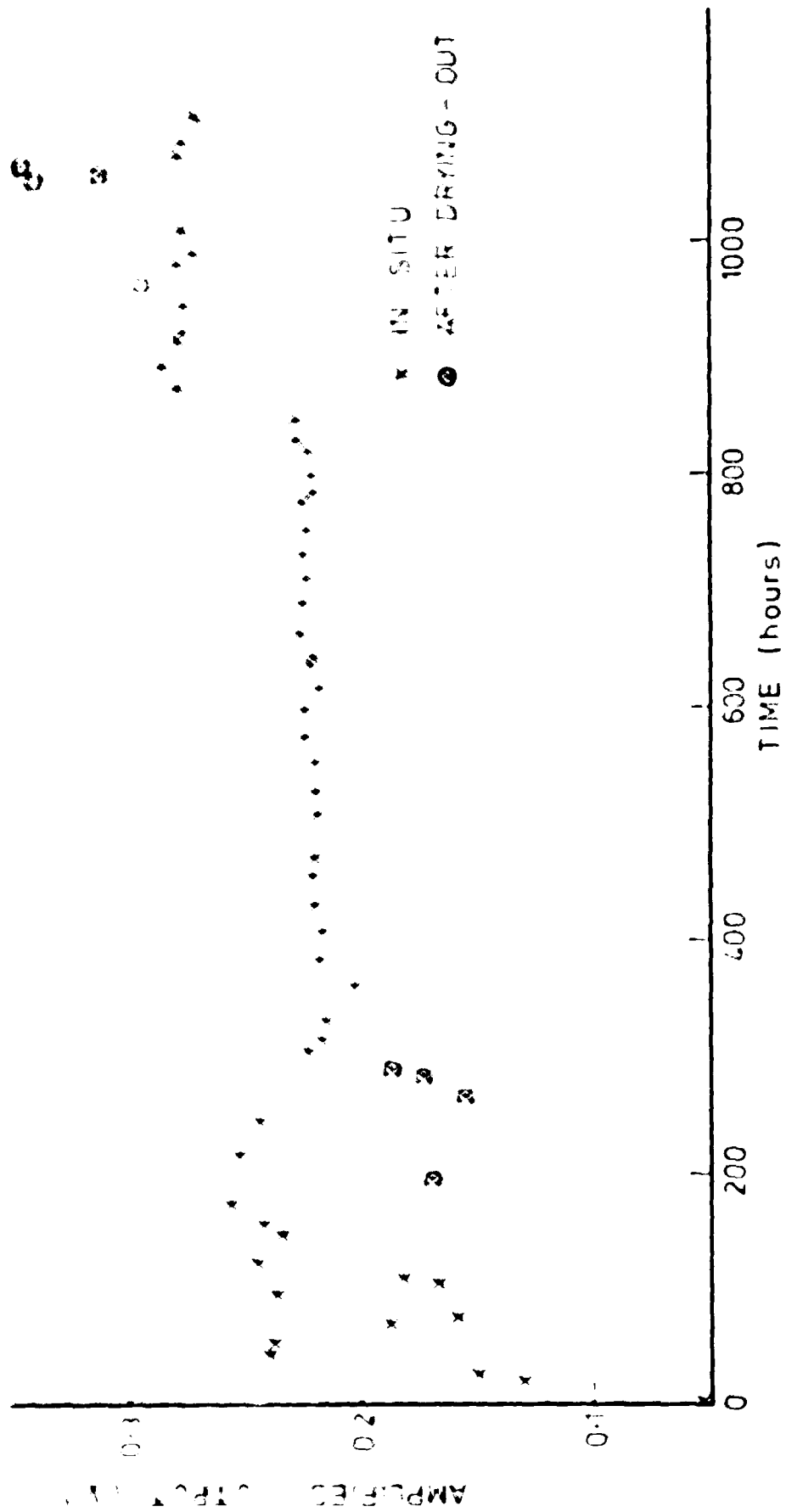
1. *Journal of the American Chemical Society*, 80, 107 (1958).
2. *Journal of the American Chemical Society*, 80, 107 (1958).
3. *Journal of the American Chemical Society*, 80, 107 (1958).
4. *Journal of the American Chemical Society*, 80, 107 (1958).
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6. *Journal of the American Chemical Society*, 80, 107 (1958).
7. *Journal of the American Chemical Society*, 80, 107 (1958).
8. *Journal of the American Chemical Society*, 80, 107 (1958).
9. *Journal of the American Chemical Society*, 80, 107 (1958).
10. *Journal of the American Chemical Society*, 80, 107 (1958).





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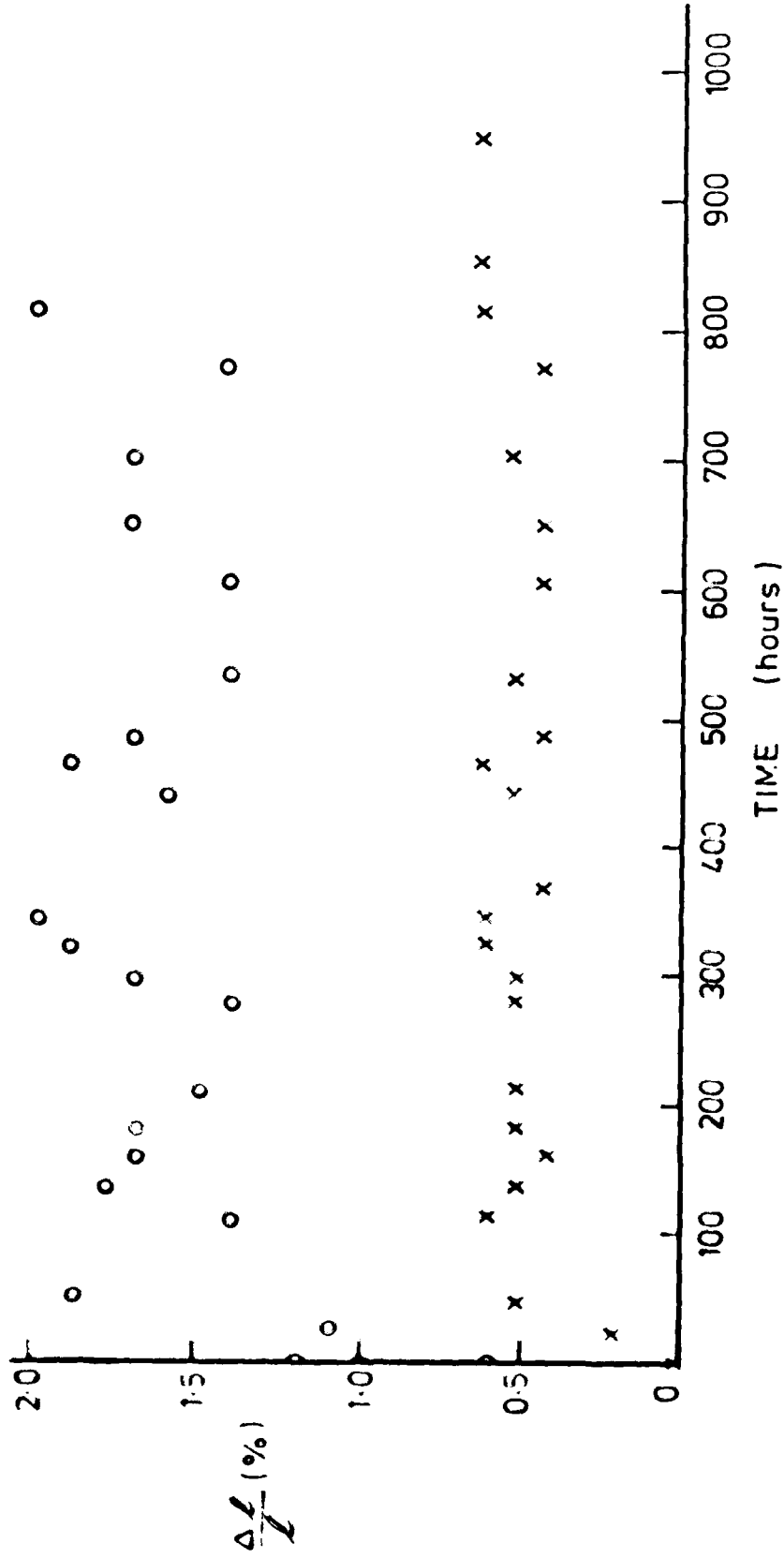




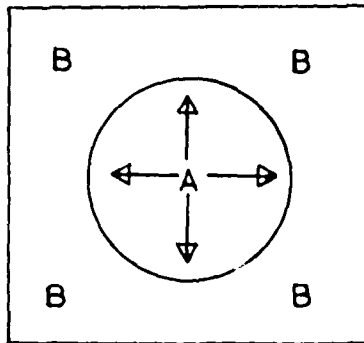
3. Optical waveguide test on GPP. Top of 10μ diameter Encliss fibres in aqueous solution. Bottom, same fibre immersed in distilled water at



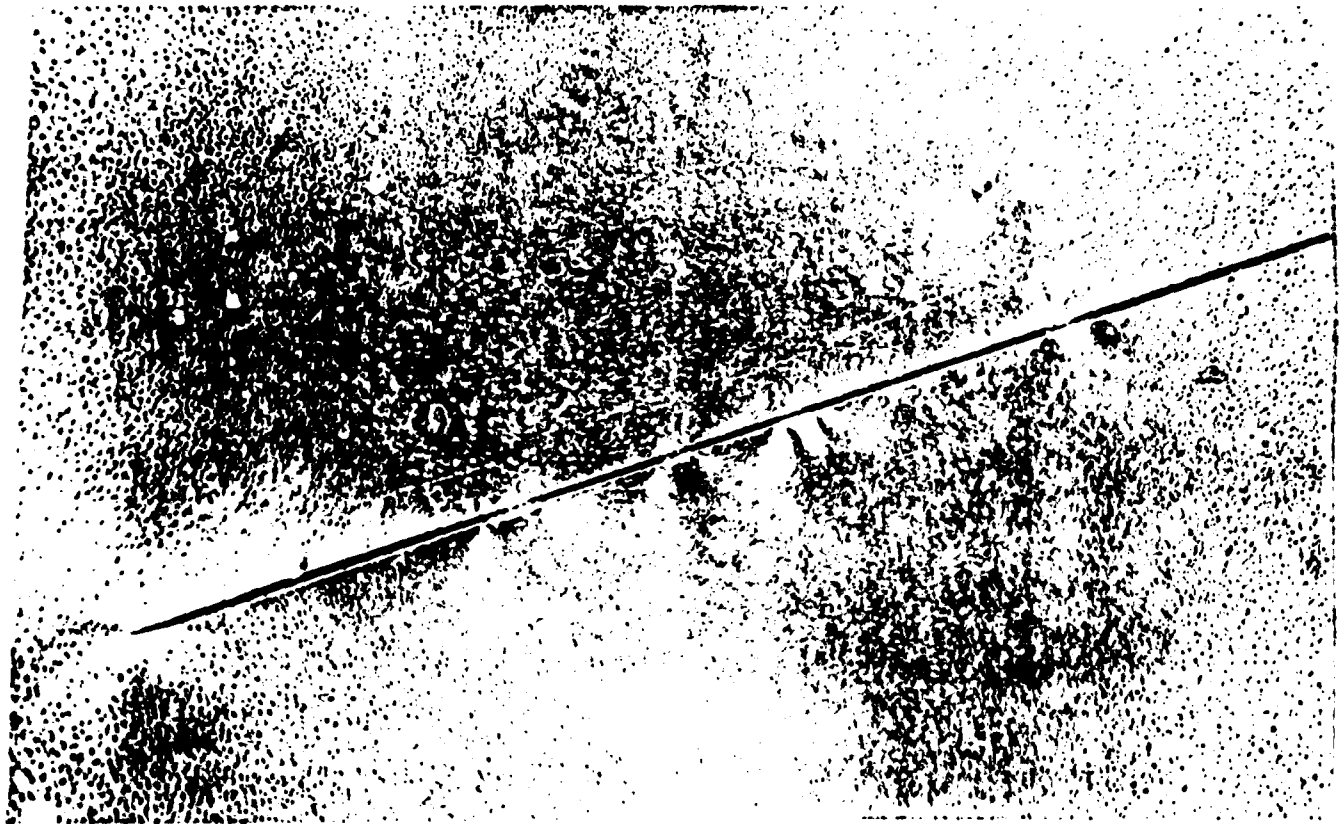
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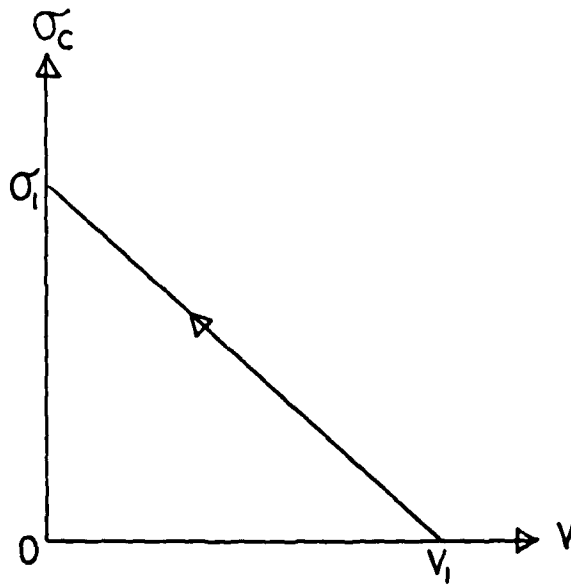
5. Change in linear dimensions during swelling associated with water uptake at 100°C by two epoxy resin slabs



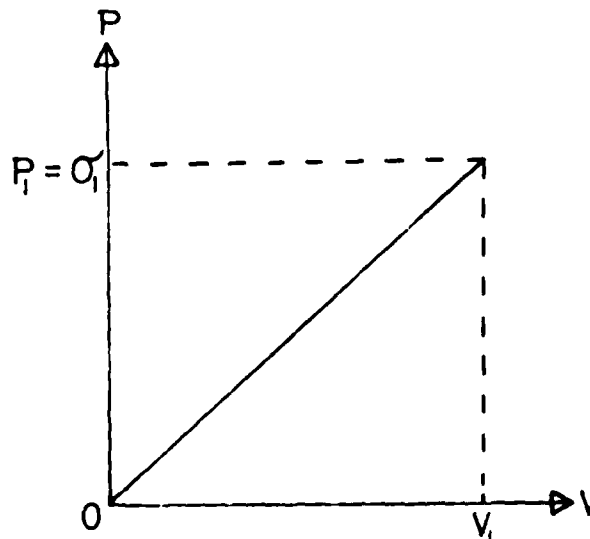
6. After van't Hoff (1888)<sup>(3)</sup>



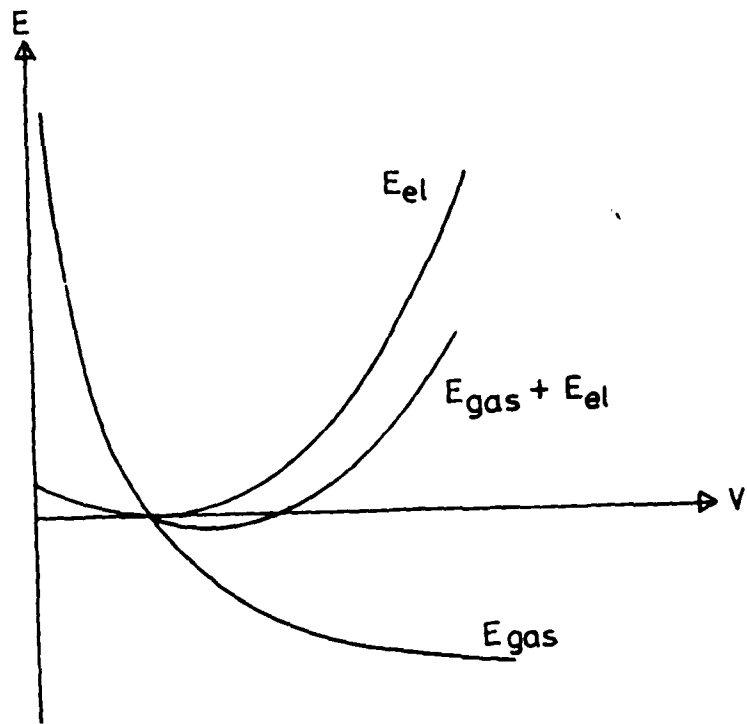
7. Photoelastic contrast caused by pressure pockets on the surface of a graphite fibre in an epoxy matrix composite after 600 hrs immersion in distilled water at 80C



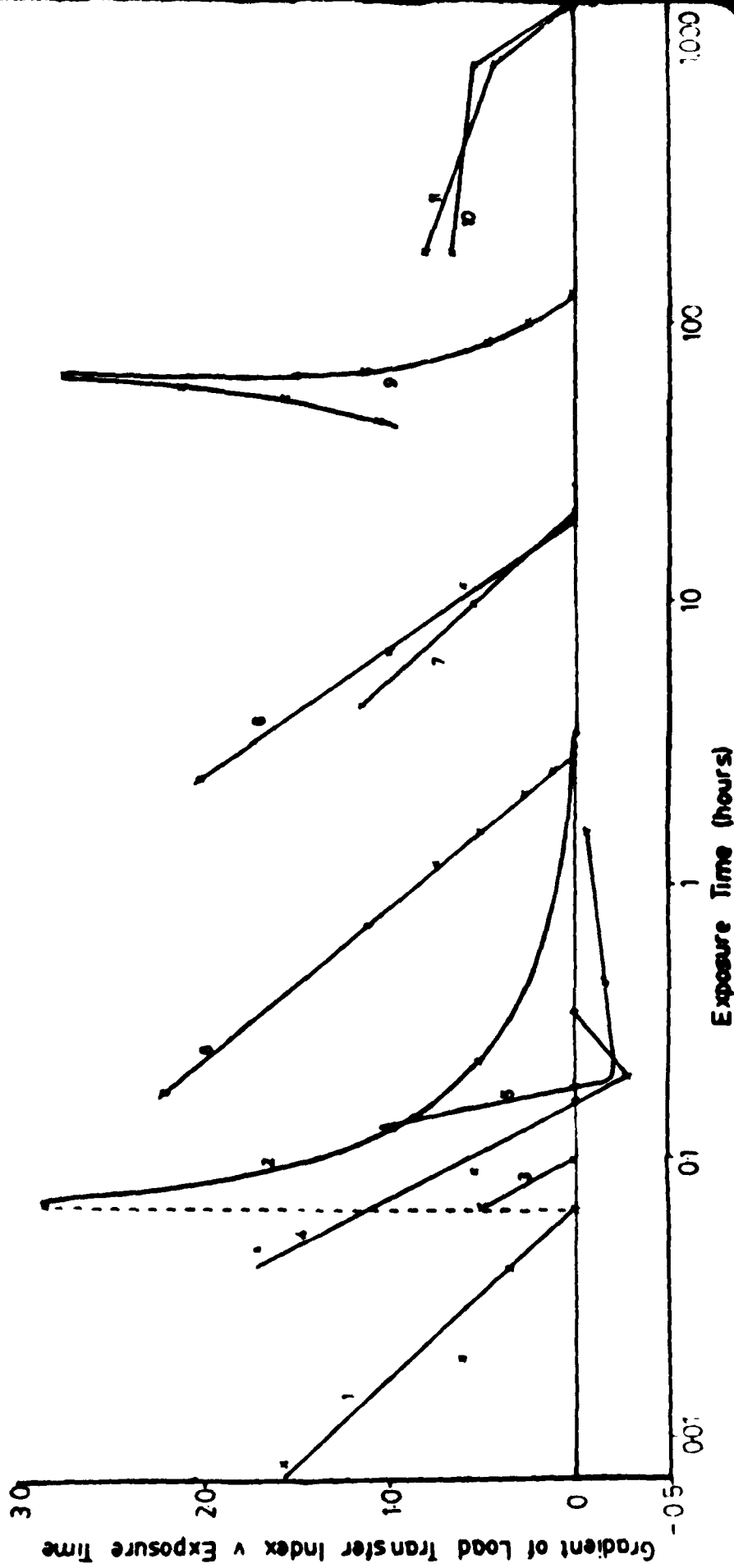
8. Applied stress as a function of volume of a Griffith's crack



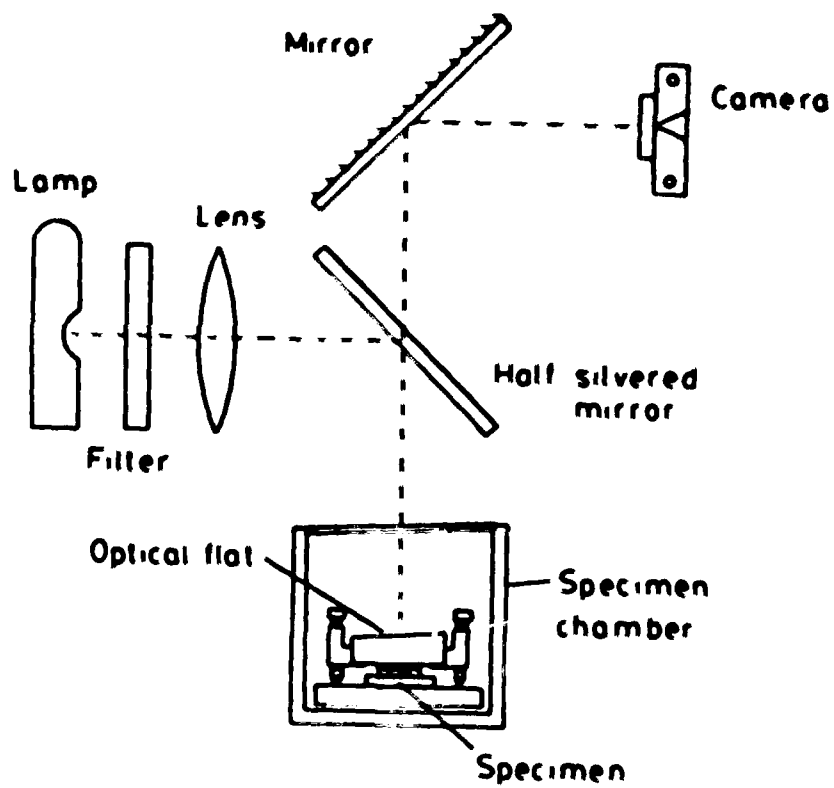
9. Crack volume versus internal pressure for an inflated crack



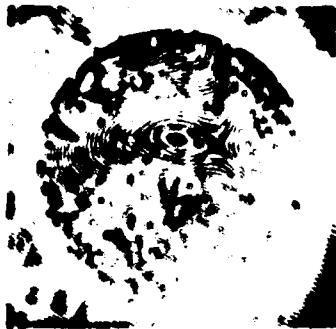
10. Energy versus volume of an inflated crack



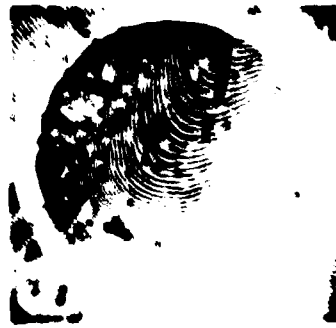
11. Rate of loss of lead transfer index during water uptake by various resin matrix composites.  
 (1) E-glass/polyester 100C  
 (2) Second immersion of specimen 1 after drying 100C  
 (3) E-glass (no coupling agent) polyester 100C  
 (4) E-glass (no coupling agent) polyester 100C  
 (5) E-glass/polyester 100C  
 (6) E-glass/polyester 200  
 (7) E-glass/polyester 200  
 (8) E-glass/epoxy 100C  
 (9) E-glass/polyester 100C  
 (10) S-glass/epoxy 80C  
 (11) S-glass/epoxy 100C



12. Schematic representation of the optical bench used for optical interference studies of dimensional stability of resins



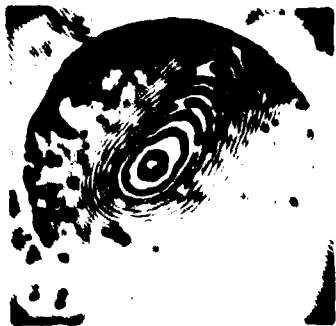
280



281



282



283

13. Part of a sequence of interference patterns photographed during the 10 minute warmup period for a glass slide (cryst. film) / 150 $\mu$ m thick cover slip sandwich.

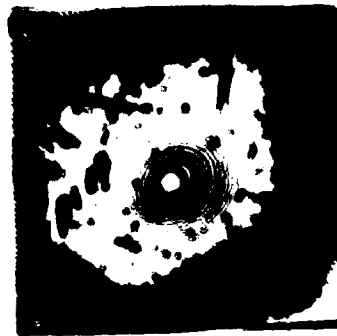
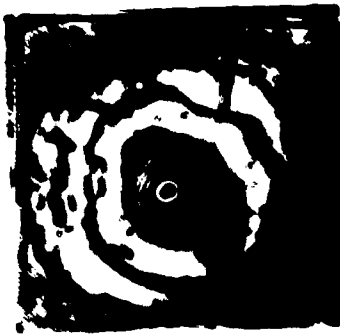
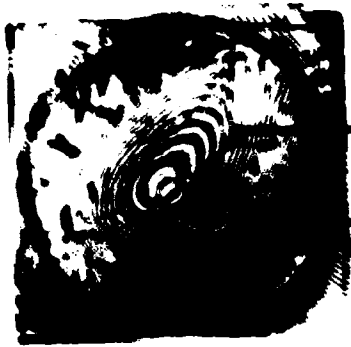


Fig. 1. Micrographs of the cross-sections of the superconducting of the first order  
pattern. The micrographs show the structure of the superconductor  
after cooling the superconductor (1) and (2). The superconductor was 1.5 m  
EPR.

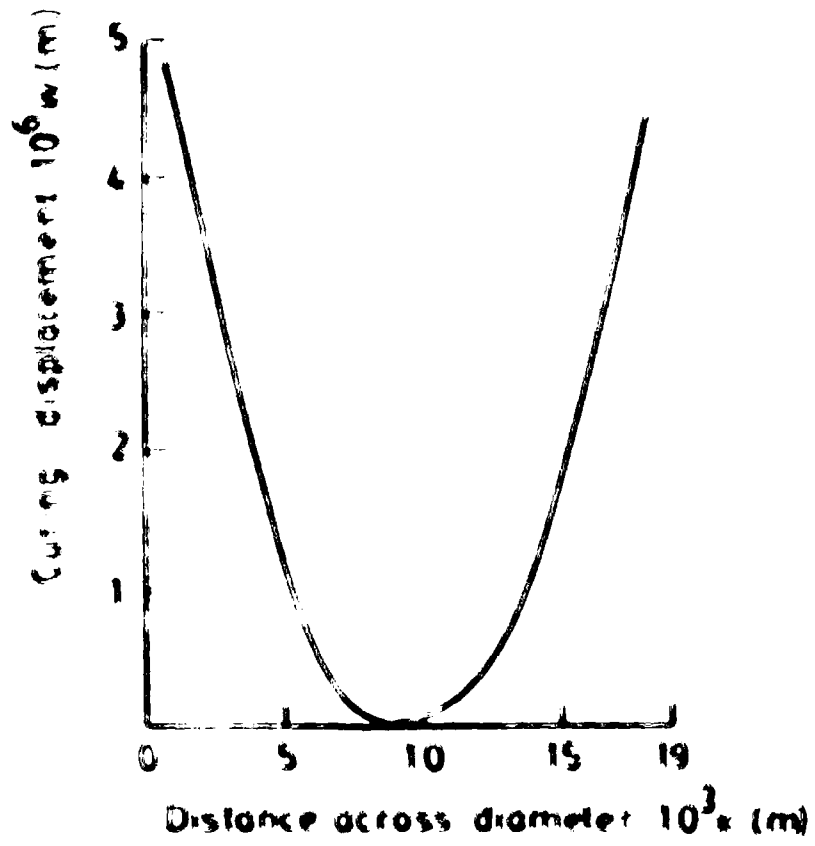
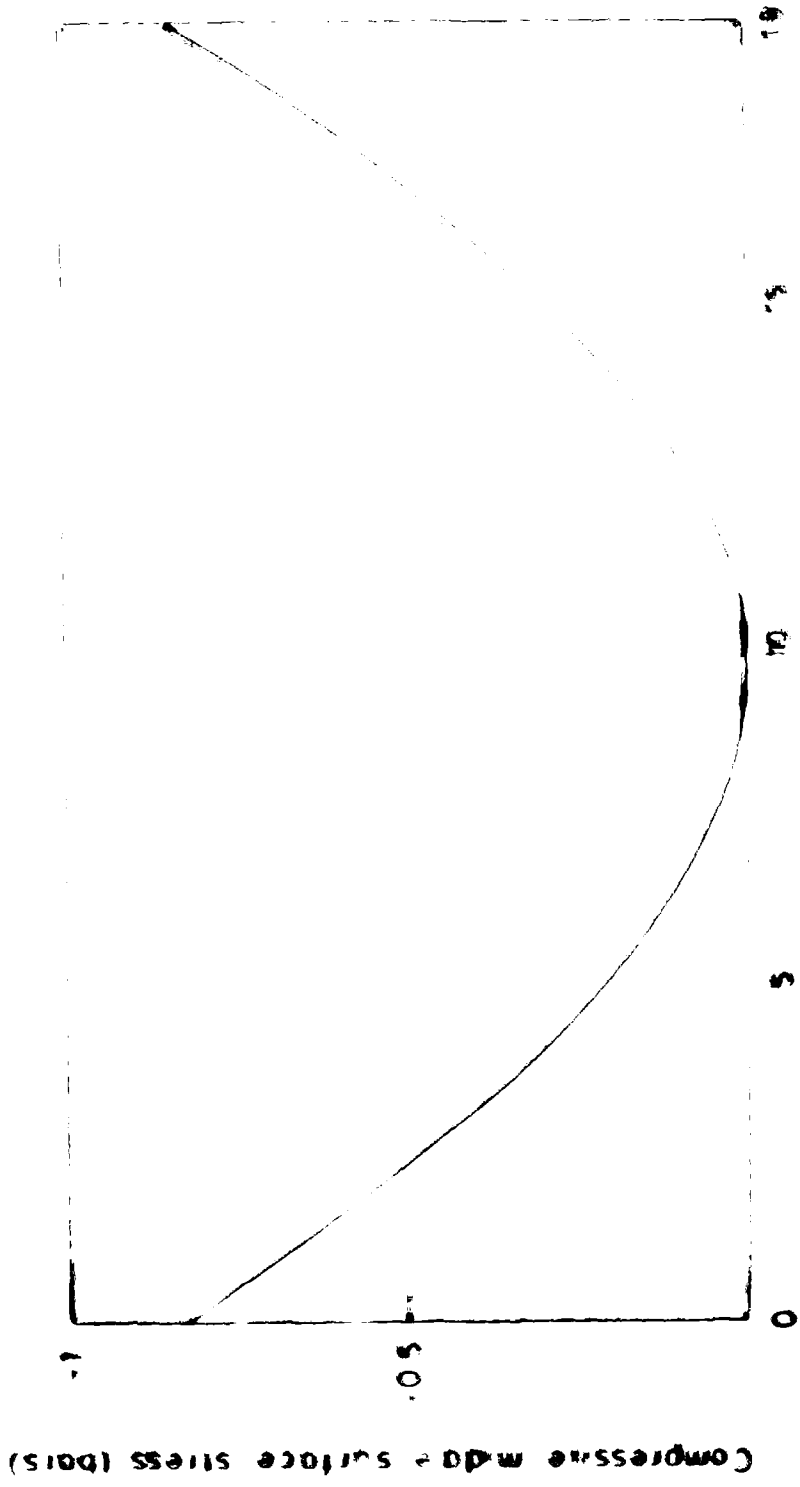


FIG. 10. Normalized displacement curves and parameter of the curve  $\alpha(1)$  after 5 minutes at the river bank at  $x=10$  and  $18$  m.

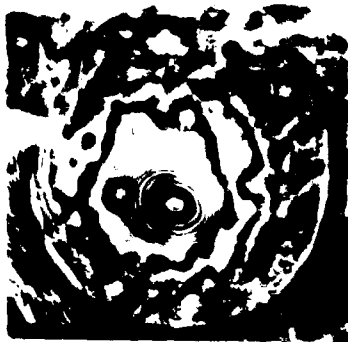


Distance across diameter (inches)

14. Substituting the value of the constant  $k$  in the equation  $\sigma = kx^2$  and solving for  $\sigma$  at the surface of the cylinder ( $x = r$ ) gives the maximum compressive stress at the surface.



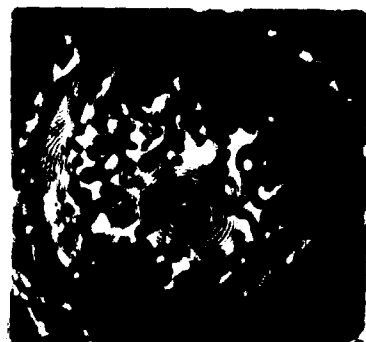
Fig. 1. Micrographs of the cross-sections of the shells of the mollusk *Hydrobia ulvae* (L.) showing the structure of the shell wall. The shells were stained with methylene blue. The magnification is 100x.



100x



200x



300x

Fig. 2. Micrographs of the cross-sections of the shells of the mollusk *Hydrobia ulvae* (L.) showing the structure of the shell wall. The shells were stained with methylene blue. The magnification is 100x.

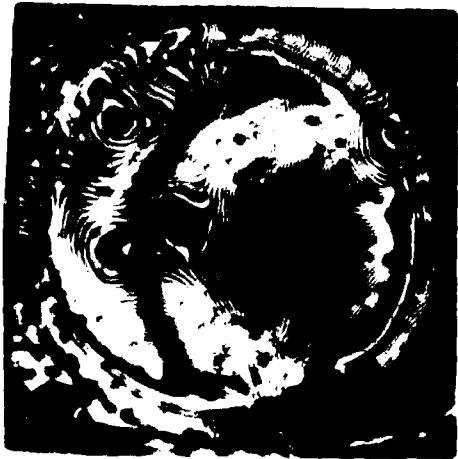


Figure 1



Figure 2

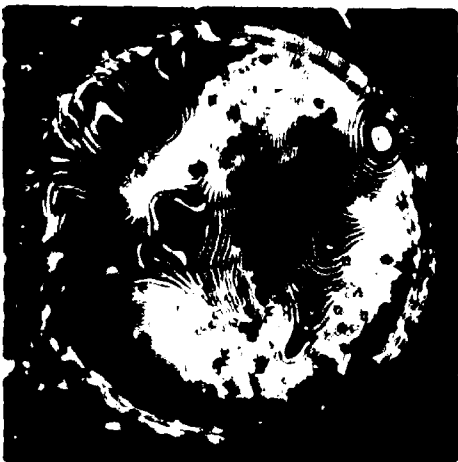


Figure 3

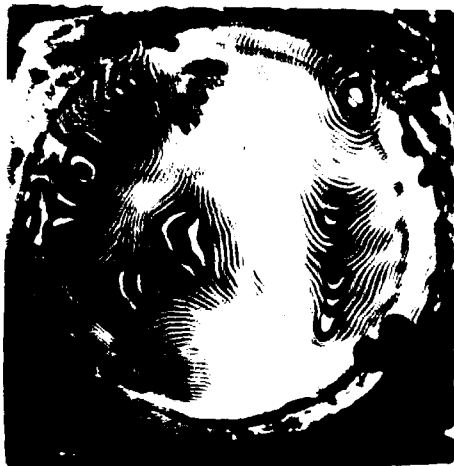


Figure 4



Figure 5

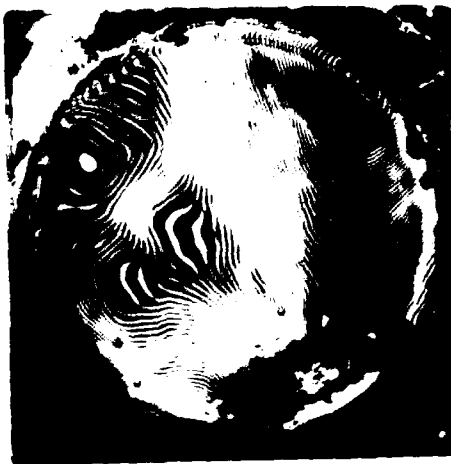
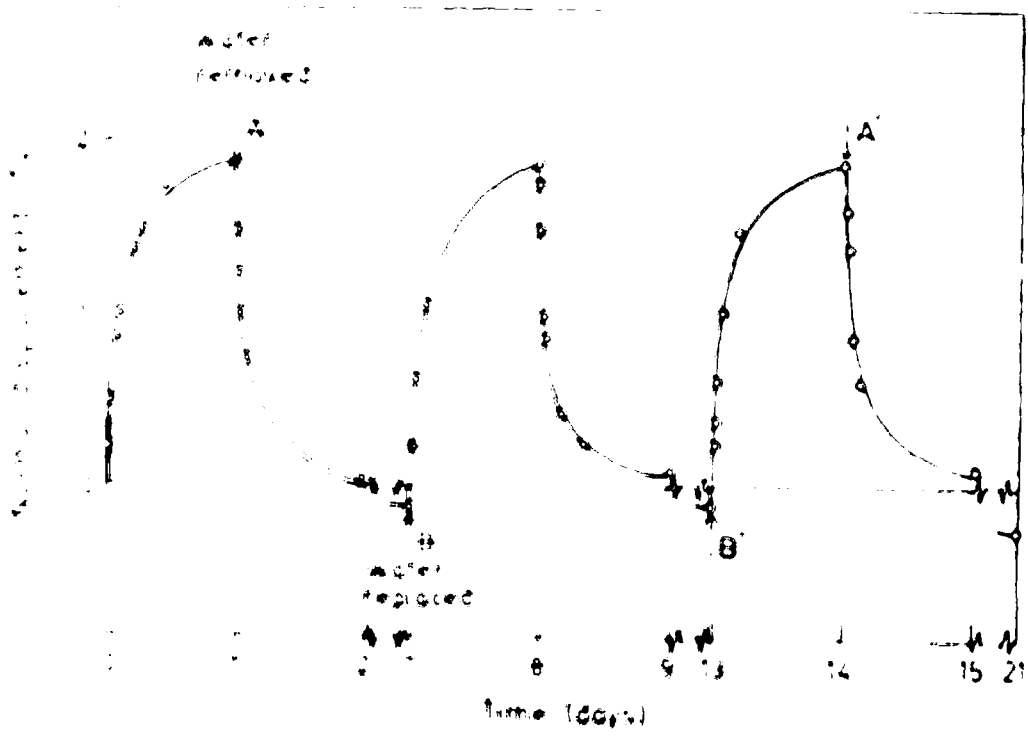


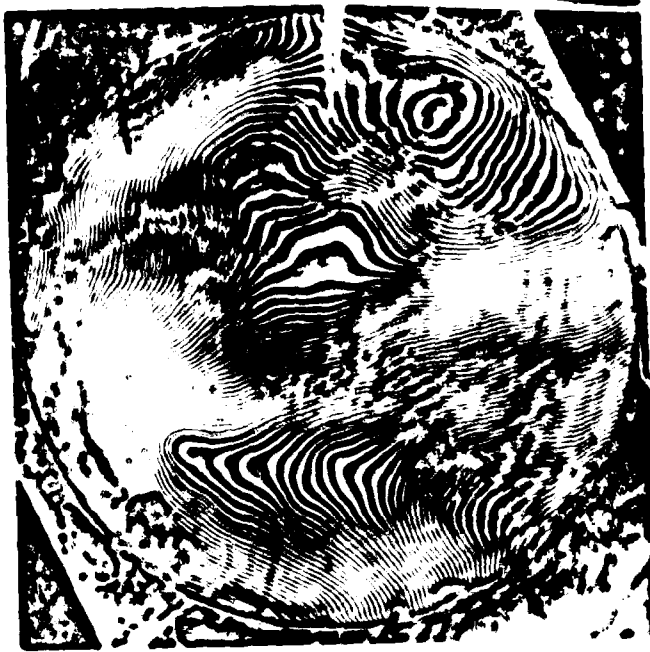
Figure 6

Figure 1 shows a circular object with a textured surface, possibly a metal component. The object is centered and surrounded by a dark, irregular border. The texture is composed of fine, concentric lines, suggesting a circular or cylindrical shape. The lighting is high-contrast, with bright highlights and deep shadows, emphasizing the surface irregularities.



The graph shows the variation of signal intensity over time. The signal starts at 0, rises to a peak of 10 at day 2, falls to a trough of 0 at day 8, rises to a peak of 10 at day 14, and falls to a trough of 0 at day 21. A horizontal dashed line is drawn at approximately y=4.5. Points A and B are marked on the curve. A legend indicates 'water removed' with a circle and 'water replaced' with a triangle.

(A)



(B)



21. (A) Micrograph formed between points indicated as A and A' in Figure 2. (B) Micrograph formed between photographs taken at points indicated as C and C' in Figure 2.



1:0



1:40 Mrs



1:200 Mrs

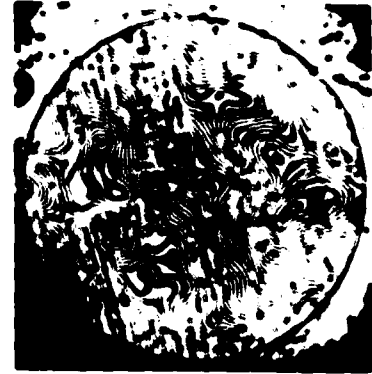
(A)



1:200 Mrs



1:266 Mrs



1:720 Mrs

(B)

22. Sequence of interference patterns for a series of vater specimens.  
(1) Immersed in distilled water at 42°C and (2) exposed to dry air at 42°C. The arrow indicates the onset of feinting.



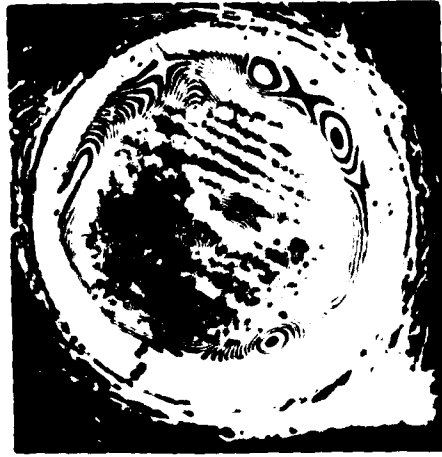
6 hrs



192 hrs



2 hrs



76 hrs

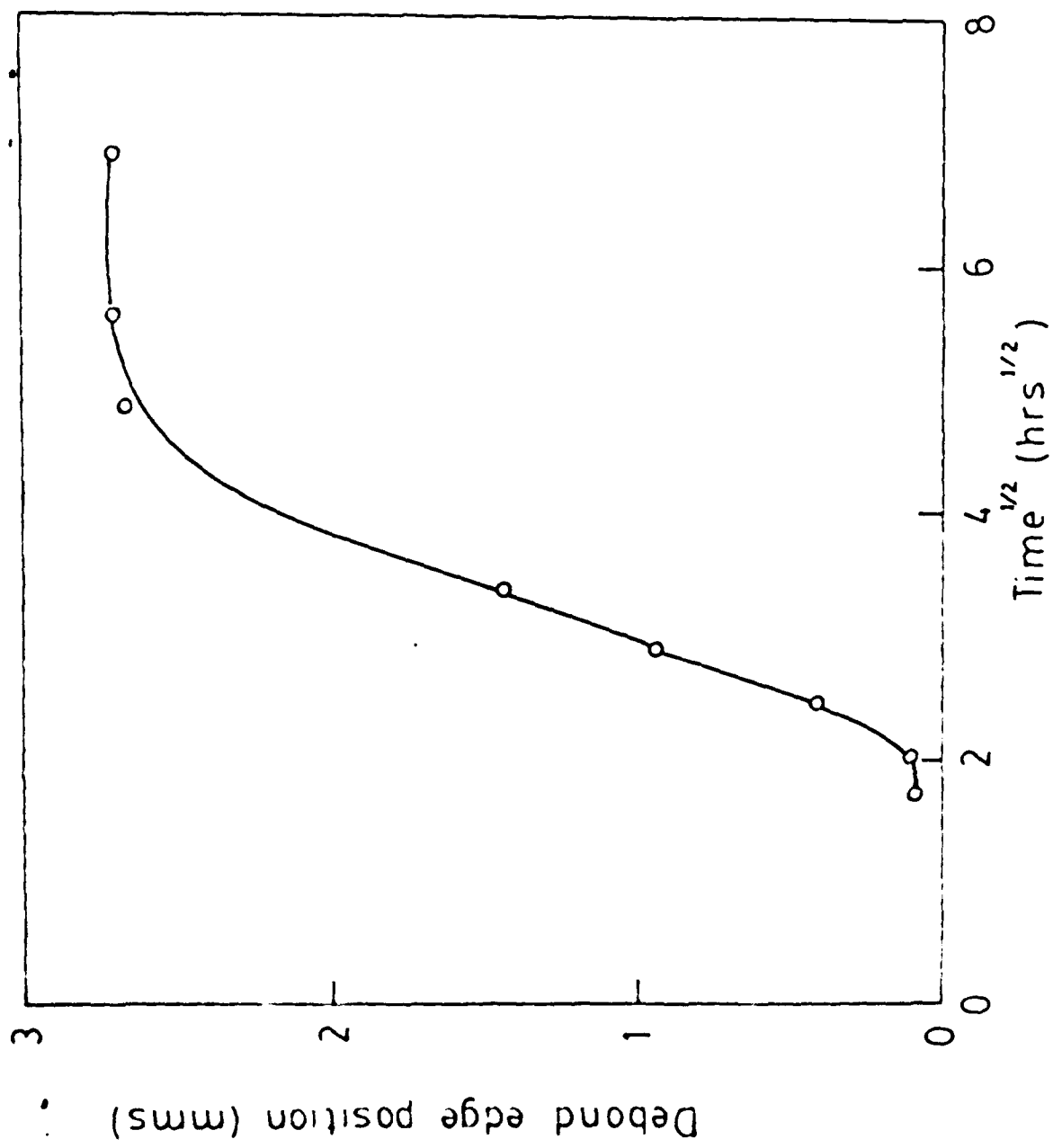


1/2 hr

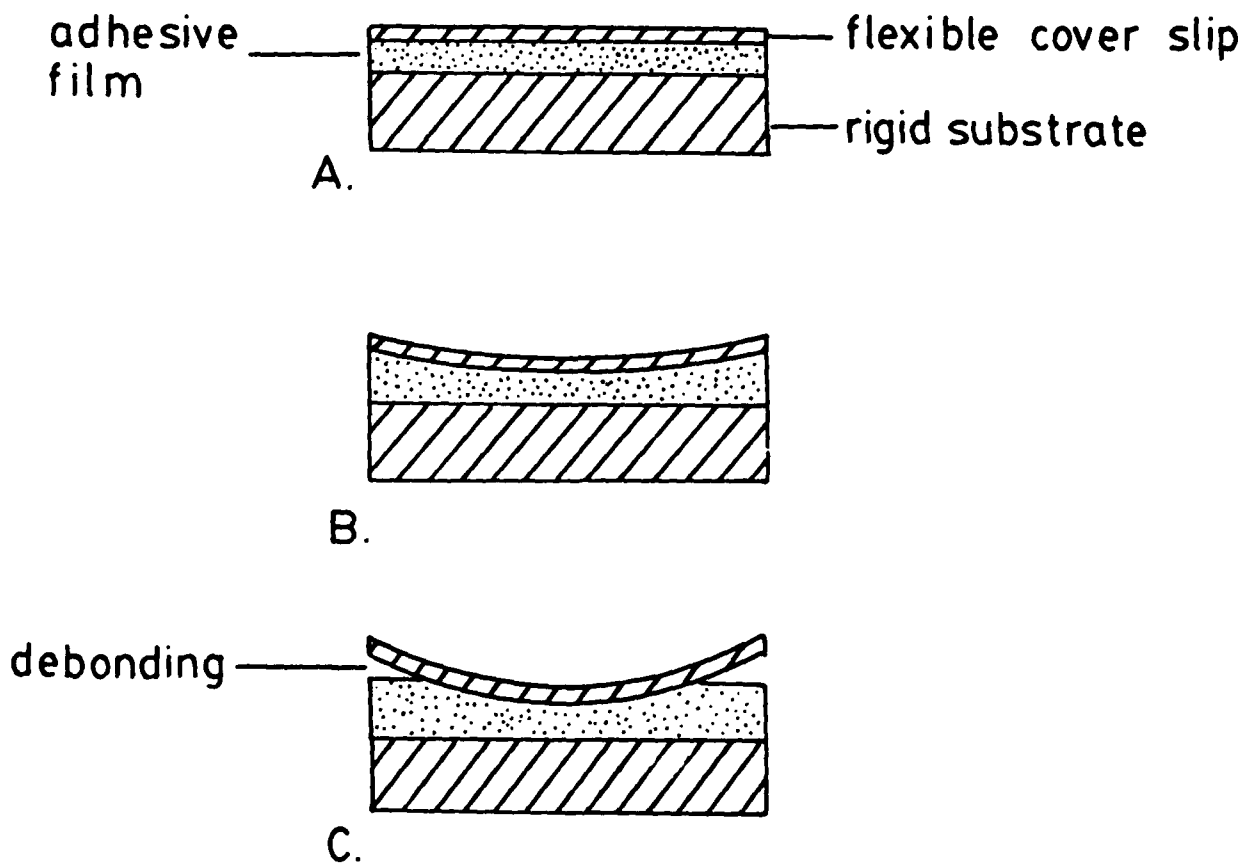


23 hrs

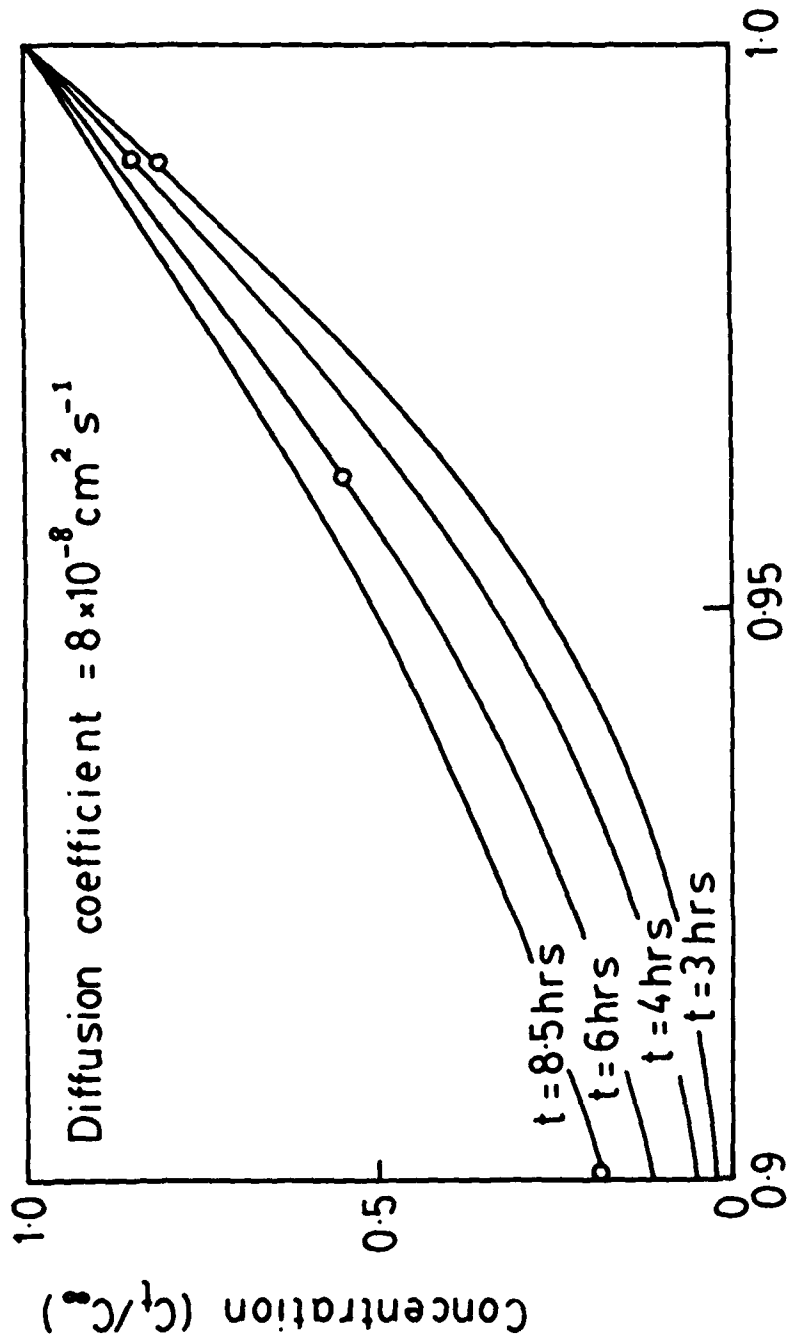
23. Sequence of interference photographs for a FV 1000 specimen inverted



24. Graph of the position of the debonding edge at the cover slip/adhesive interface plotted as a function of time<sup>1/2</sup> for the specimen shown in Figure 21



25. Schematic diagram to illustrate the changing geometry of the cover slip during swelling of the adhesive in a joint exposed to an aqueous environment. Debonding follows saturation of swelling at the rim of the joint



26. Graph of the predicted water concentration ( $C_t/C_\infty$ ) as a function of fractional distance from the centre of the specimen. O, points representing critical concentrations for positions corresponding to the debonding edge shown in Figure 25. After Kinloch.

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