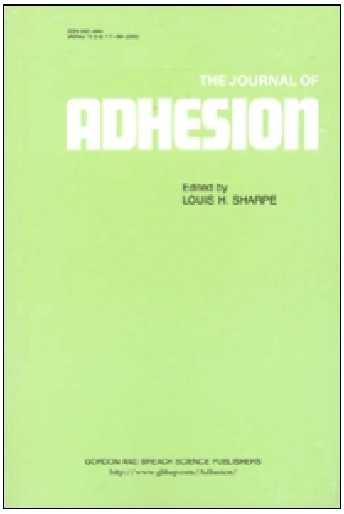

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The Contribution of Osmosis to Dimensional Instability of Adhesive Joints

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The Contribution of Osmosis to Dimensional Instability of Adhesive Joints

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Direct evidence, in the form of photoelastic images around partially dissolved water soluble inclusions, and indirect evidence, in the form of the control effected by reducing the difference between the chemical potential of water in the solution around inclusions and that of water in the aqueous environment to which adhesive joints are exposed, is presented for concluding that a substantial part of the swelling is attributable to osmosis. Suggestions are offered for possible origins of water soluble material, and attention is drawn to the fact that the equilibrium shape of an osmotic pressure filled pocket is indistinguishable from that of an internal crack.

INTRODUCTION

The application of a moiré technique to interference patterns generated between an optical flat and a thin adherend, during water uptake by model adhesive joints, has previously been used to detect and measure the swelling behaviour of proprietary adhesives[1,2]. Also previously reported[3] are the mitigating effects on the rate of swelling and on the absolute magnitude of swelling at saturation, of inorganic salts in the aqueous environment to which joints are exposed. This latter observation appears to be indirect evidence for suspecting that osmotic pressure generation contributes to the swelling, and was attributed[3] to the possible presence of water soluble inclusions introduced as a consequence of the surface treatment applied to adherends.

MATERIALS

In order to confirm or rule out the adherend as origin of water soluble inclusions which, when dissolved by diffused water, might generate sufficient osmotic pressure to influence the overall swelling, three different batches of model adhesive joints, conforming to the geometry reported in references 1 and 2, were fabricated. The first two employed a 150 μm thick soda-lime glass cover slip as flexible adherend and, respectively, soda-lime glass and aluminium pre-primed† by Westland Helicopters Ltd as rigid adherend. (All glass components were first thoroughly cleaned by degreasing using a commercial detergent, washing in distilled water, drying and then subjecting to ion-bombardment). The third batch of joints employed freshly cleaved 150 μm and 500 μm slabs of mica as flexible and rigid adherends respectively.

Two proprietary epoxy resin adhesive films were used to manufacture the joints. For reasons which will become evident, most of the joints were manufactured with Cyanamid FM 1000, a nylon modified epoxy film adhesive curing at 170°C. The remainder were manufactured with Redux 312/5, a carrier supported nitrile rubber modified epoxy curing at 120°C.

All interference patterns were photographed during 60°C immersion of the joint in either distilled water, or saturated KCl solution, or saturated NaCl solution.

RESULTS

Circumferential moiré fringes, obtained by superimposition onto the initial undeformed interference pattern of the interference patterns rephotographed during an immersion test, faithfully records the normal displacement[1]. Successive moiré fringes represent contours with $n\lambda/2$ normal displacement, where n is the fringe number, and may be used to determine the changing geometry of the cover slip. The innermost moiré fringe, representing the boundary between undisplaced cover slip and cover slip which has been displaced by $\lambda/2$ normal to the joint, migrates inwards as water uptake proceeds and can be used as a marker with which to determine the kinetics of swelling.

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† The primer was a hot curing phenolic primer, identified as BR 1009/49.

Experiments with different adherends

Figure 1 shows plots of the position of the first moiré fringe for various combinations of substrate and immersion medium. Figure 2 shows plots of the swelling profile, across half a diameter, for adhesive joints made from cover slip/FM 1000/glass and cover slip/FM 1000/aluminium, each immersed in distilled water and saturated NaCl solution respectively. It is evident that, within the limits of experimental uncertainty, both the swelling rate and magnitude of swelling at saturated water uptake are independent of the nature of the adherends, and are primarily functions of the immersion medium. Swelling is faster for joints immersed in distilled water than for identical joints immersed in salt solution. Also, the swelling at saturation is smaller for immersion in saturated salt solution than it is for immersion in distilled water. This behaviour is similar to that observed for cover slip/FM 1000/titanium joints[3].

It is evident from these findings that, for a given adhesive, the distribution and magnitude of the swelling that accompanies water uptake is independent of the choice of adherends. The swelling characteristics must therefore be attributed to the adhesive itself. It is also evident, from a comparison of the swelling behaviour for water uptake when immersed in distilled water and salt solutions, that the adhesive behaves as a semi-permeable membrane. It is clear therefore, that the search for osmotic pressure filled pockets should be directed away from the adhesive/adherend interface and towards the adhesive itself.

Direct observation of pressure filled cracks

Figure 3(a) shows a cover slip/FM 1000/glass joint after immersion for 48 hrs in distilled water at 60°C. The regions of dark contrast are small undissolved inclusions contained within the adhesive. Under crossed polars the resin adjacent to each inclusion shows a characteristic pattern of stress birefringence, Figure 3(b). The pattern of the birefringence is consistent with there being a pressure associated with each inclusion. Accompanying any sizable concentration of inclusions is a marked local deformation of the cover slip. Figure 3(c), the interference pattern obtained from one such region, demonstrates this fact; the circular pattern of fringes indicates a small "hillock". Careful inspection of Figure 3(c) reveals that in the centre of the image there are discontinuities in the interference fringes where the local pressure must have been of sufficient magnitude (the tensile strength of glass is of

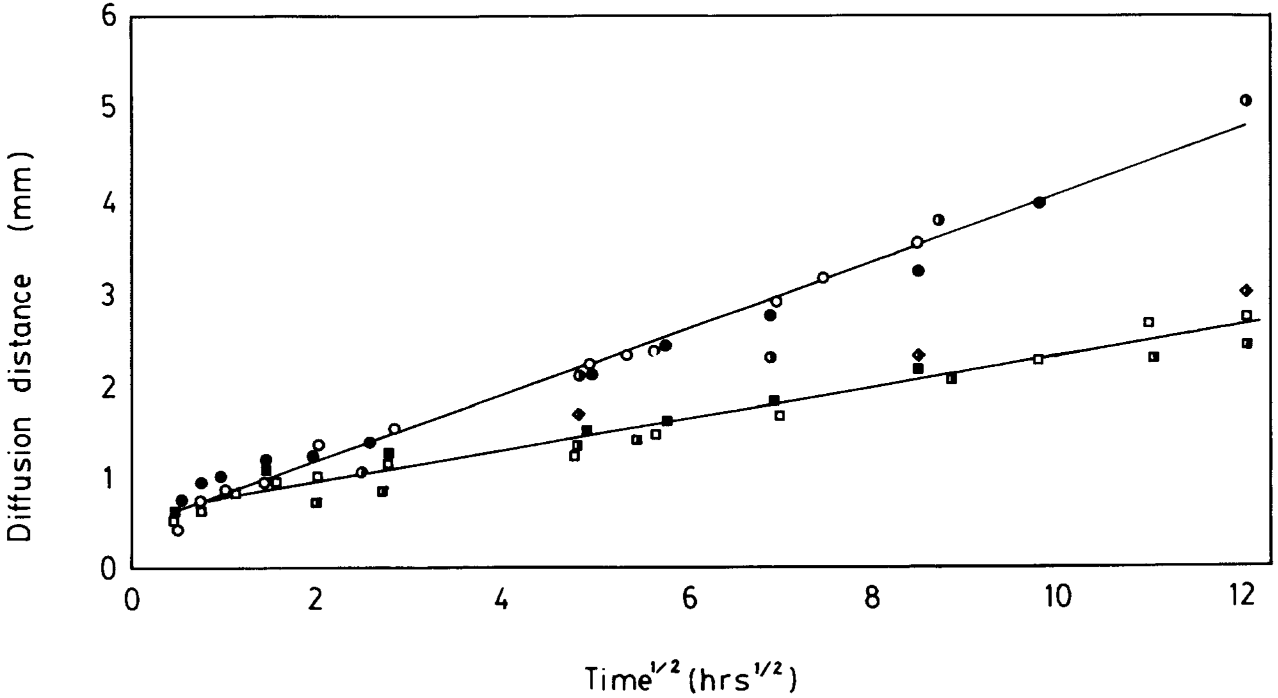


FIGURE 1 Migration rate of the 1st moiré fringe plotted against Time$^{1/2}$ for various combinations of adherends and immersion media. All at 60°C.

○ cover slip/FM 1000/glass; distilled water
◑ mica/FM 1000/mica; distilled water
● cover slip/FM 1000/aluminium; distilled water
□ cover slip/FM 1000/glass; saturated NaCl solution
◨ mica/FM 1000/mica; saturated NaCl solution
■ cover slip/FM 1000/aluminium; saturated NaCl solution
◆ mica/FM 1000/mica; saturated KCl solution

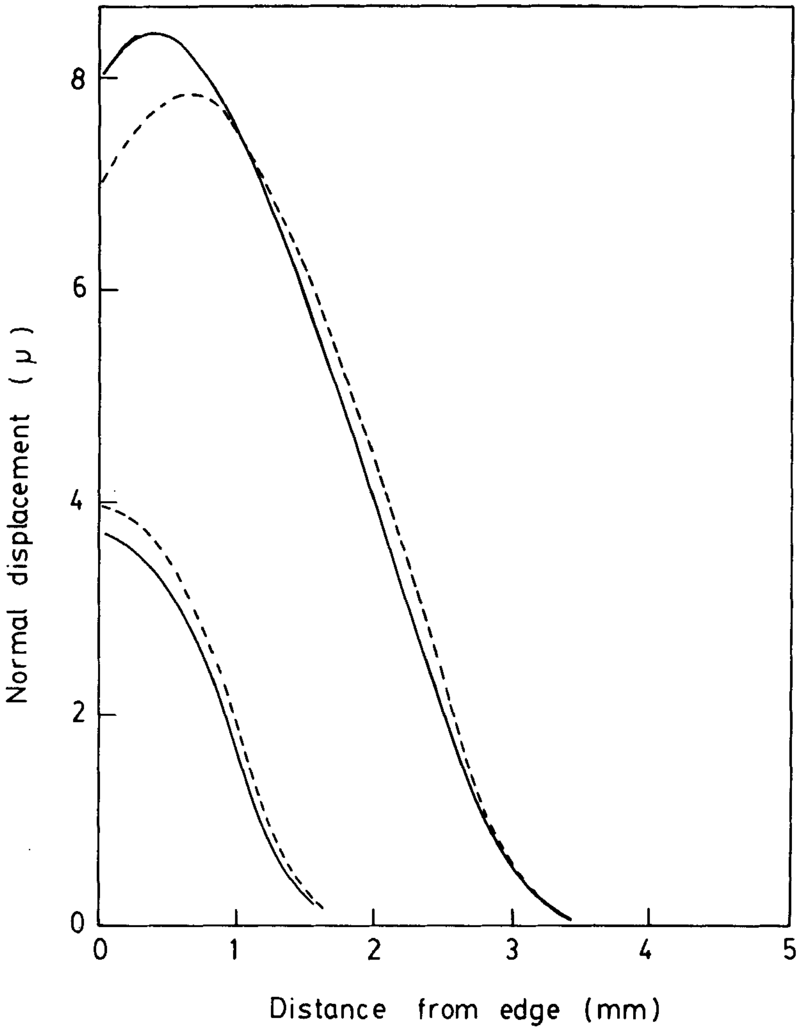


FIGURE 2 Radial distribution of displacement of the cover slip normal to FM 1000 joints after 48 hours immersion at 60°C.

Upper curves ——— cover slip/FM 1000/glass;distilled water

----- cover slip/FM 1000/aluminium, distilled water

Lower curves ——— cover slip/FM 1000/glass; saturated NaCl solution

----- cover slip/FM 1000/aluminium; saturated NaCl solution

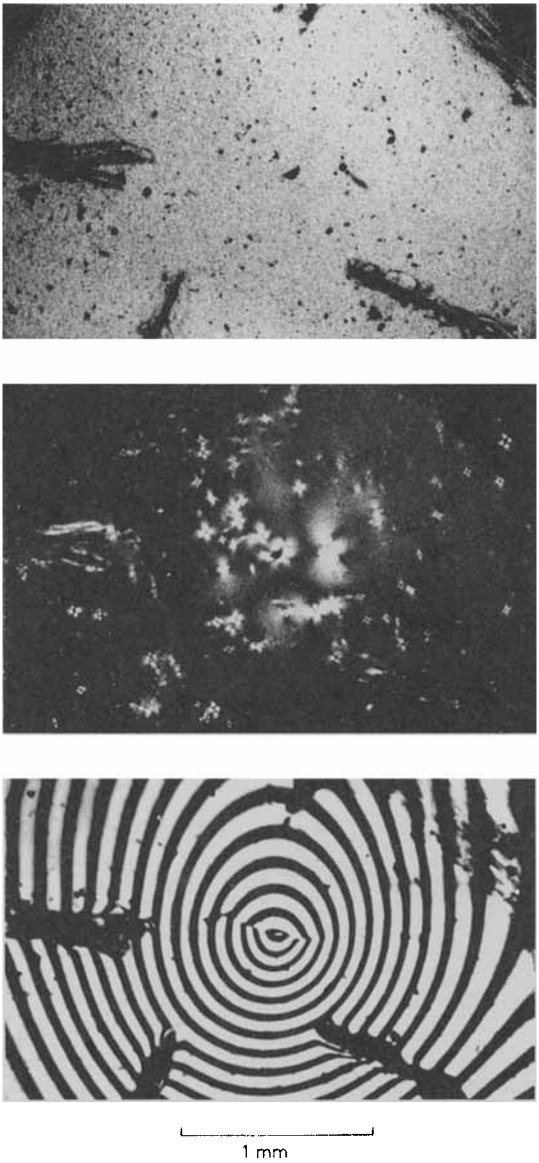


FIGURE 3a Photomicrograph of a region of a cover slip/FM 1000/glass joint after immersion in distilled water for 40 hours at 60°C
b. Same as (a) with crossed polars
c. Interference pattern revealing the normal displacement for the region shown in (a)

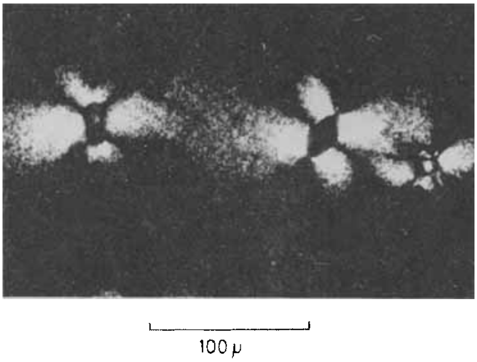


FIGURE 4 Photoelastic image of pressure pockets located within the adhesive after 48 hours immersion in distilled water at 60 C.

the order of 2k bars) to burst the cover slip. Photoelastic evidence of pressure pockets was observed throughout this particular joint. Figure 4 shows an enlarged crossed polars image from a region which contains two inclusions.

Examination of an identical joint, after immersion in a saturated salt solution for 360 hrs at 60 C, revealed a much lower incidence of pressure filled pockets. This is expected if osmosis attributable dissolution of water soluble material at the inclusions is responsible for the photo-elastic contrast; the pressure generated by osmosis is determined by the difference between the chemical potential of water in the solution at a particle and that in the aqueous environment outside the joint, and this difference is smaller for saline environments than it is for pure water environments.

In order to check that the pressure pockets were not peculiar to this batch of adhesive (batch No. 4169), a second batch was acquired (batch No. 4307). Examination of a representative joint from this batch showed a similar, though slightly reduced, distribution of pressure pockets.

Experiments with a different adhesive

Figure 5 shows a plot of the swelling profile across a half diameter for a cover slip/Redux 312-5/glass joint. Immersion in saturated NaCl solution has a mitigating effect upon the swelling, as was the case for FM 1000 joints, but no pressure filled pockets were observed.

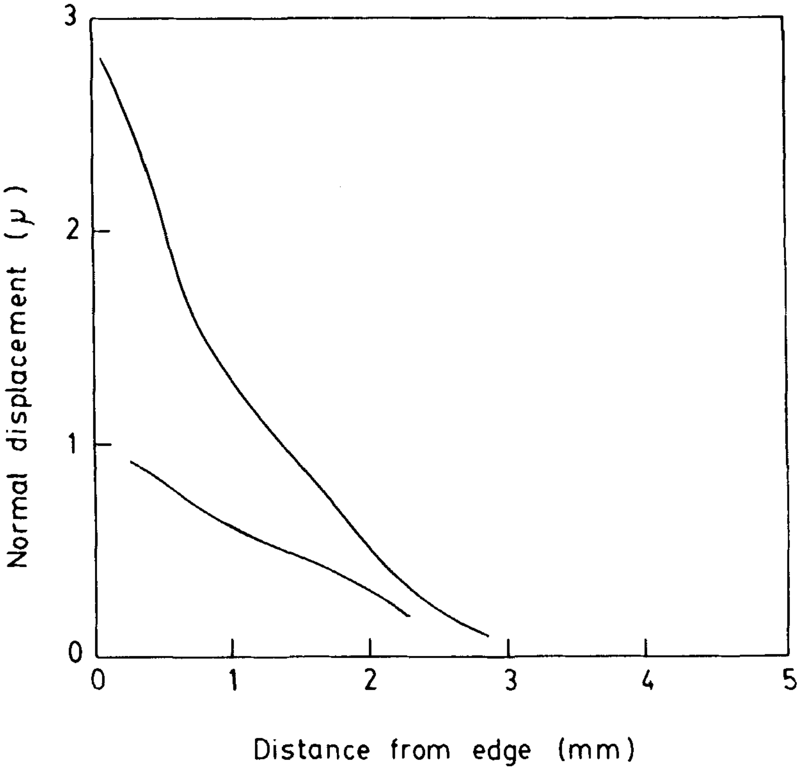


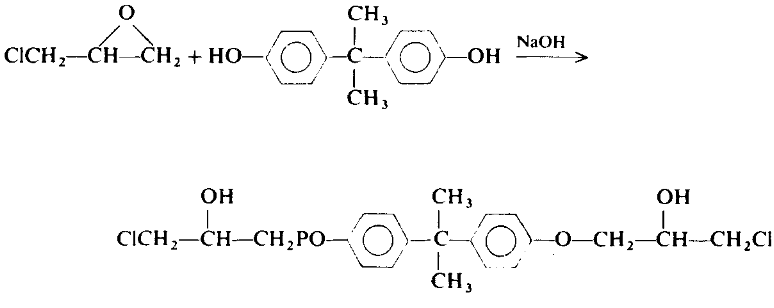
FIGURE 5 Radial distribution of displacement of the cover slip normal to a Redux 312/5 joint after 120 hours immersion at 60°C. Upper curve; cover slip/Redux 312-5/glass; distilled water. Lower curve; cover slip/Redux 312-5/glass; saturated NaCl solution

ORIGINS OF WATER SOLUBLE INCLUSIONS

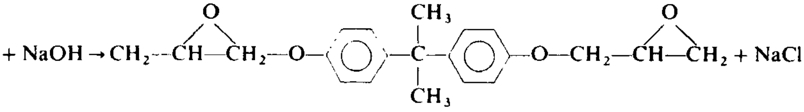
There are three possible explanations for the presence of water soluble inclusions in proprietary adhesives.

Indigenous salt

Water solubles in the form of inorganic salts are formed during the manufacture of some epoxy formulations. For example, one proprietary epoxy is obtained by reacting an excess amount of epichlorohydrin with bisphenol A in the presence of a caustic such as sodium hydroxide. The caustic catalyses an initial reaction to form the chlorohydrin inter-



SCHEME 1 Synthesis of chlorohydrin intermediate



SCHEME 2 Origin of sodium chloride as a by-product during manufacture of DGEBA

mediate, Scheme 1. The caustic then acts as a dehydrohalogenating agent to form the epoxide rings (DGEBA-diglycidyl ether of bisphenol A) and neutralise hydrogen chloride resulting from the reaction in Scheme 2. It would be expecting a lot of the subsequent washing process to remove completely all traces of the NaCl.

In epoxy systems, unreacted hardener can also dissolve in water; dicyandiamide, for example, is water soluble to the extent of 33gm per litre at 20°C rising to 800gm per litre at 80°C.

A third potential source of water soluble inclusions during resin manufacture is any chemical drying process to which raw materials might be subjected.

Contamination by airborne solutes during storage

Published[4] concentrations of pollutants in the air at sampling stations throughout the world include data for a variety of organic and inorganic water solubles. To take just one example, the concentration of salt in normal air is in the range 0.005–0.05 milligrams per cubic metre. The particle size of airborne salt is typically a few tens of micrometres, *i.e.*, at least the size of the inclusions which caused the pressure filled pockets shown in Figure 3. It is therefore evident that casual storage of materials in the open air is tantamount to doping the products with solutes known to lead to osmosis.

Near the ocean, the possibility of airborne sea spray enhances the risk of water soluble material landing on materials stored outside. The composition of sea water[5] includes sodium chloride, magnesium chloride, sodium sulphate, magnesium sulphate, calcium chloride, potassium chloride, sodium bicarbonate, sodium bromide and potassium bromide as water soluble constituents.

Solute pick-up from body fluids

The composition of sweat[6] in normal healthy humans includes sodium 22, potassium 9 and chlorine 18 milli-equivalents per litre. For persons suffering from cystic fibrosis of the pancreas, the numbers are increased to 103, 15 and 97 respectively. The near certainty of passing salts from the hands to adhesive formulations is strong recommendation for wearing gloves whenever handling the raw materials.

GENERAL DISCUSSION

The osmotic pressures for hot saturated water solutions of inorganic salts are typically a few hundred bars[7]. It is evident, therefore, that osmosis is a very real source of substantial localised internal stress in adhesive joints. Even more worrisome is the fact the equilibrium shape of a pressure filled pocket in any elastic solid is penny-shaped[8,9], *i.e.*, is pseudo-crack shaped. Once formed, a penny shaped crack will magnify the stress experienced during even a modest impact.

Finally, it should be noted that there are other mechanisms whereby interaction between impurity inclusions and permeated water could create pressure pockets. Hydration of salts and evolution of gas are two which spring to mind.

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