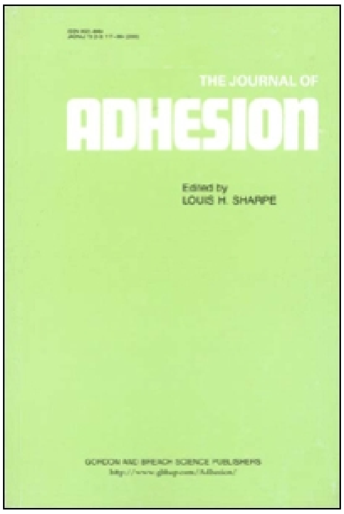

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J. P. Sargent[a]; K. H. G. Ashbee[a]
[a] H H Wills Physics Laboratory, University of Bristol, Bristol, England

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Aviation Fuel Uptake by Epoxy Adhesives

J. P. SARGENT and K. H. G. ASHBEE

H H Wills Physics Laboratory, University of Bristol, Bristol BS8 1TL, England

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The changes in thickness of model butt joints during uptake of hot kerosene have been observed and measured using an optical interference technique. Three proprietary adhesive formulations were studied, all of which exhibit shrinkage adjacent to the joint edge and one of which is characterised by the occurrence of localised swellings throughout the main body of the adhesive layer. The localised swellings are associated with clusters of internal pressure pockets identified by their associated photoelasticity. The origin of this internal pressure generation is believed to be osmosis. The temperature dependence of the swelling indicates an activation energy of 88 $kJmol^{-1}$ for the rate controlling mechanism.

INTRODUCTION

The cut of hydrocarbons generally considered to constitute kerosene is from C_8 to C_{16}. Thus, the molecular weights of the species diffusing through resins during aviation fuel uptake are as a large as, say, 200. Such a molecule is large compared with the water molecule. The latter easily diffuses through fully cured epoxy based materials. However, the paraffin molecules are more or less linear and no doubt are able to migrate through holes of about the same physical size as those which accommodate the diffusion of water. When considering the kinetics of diffusion through resins it is evident that, to let a water molecule through, the connected succession of holes representing the diffusion path do not have to be open all the time; in the case of C_nH_{2n} it might be thought that they do. However, de Gennes[1] postulates that, by first accumulating and then circulating a kinked portion of a stored length, a long chain molecule should be able to facilitate its migration. De Gennes calls this migration mechanism "reptation".

METHOD

A moiré interferometric technique[2] has been used to measure the geometry of swelling normal to model adhesive joints during kerosene uptake. The joints consist of a thin, and therefore flexible, microscope cover slip bonded to a thick substrate of glass or other material. The technique relies on the creation of Fizeau interference fringes formed within the cavity between the free surface of the microscope cover slip and an optical flat. The pattern of interference fringes is determined by the surface topography of the cover slip and hence of the underlying adhesive. Moiré fringes, created by superimposition of the changing interference pattern during adhesive swelling upon the initial interference pattern, are used to map *changes* in the surface topography.

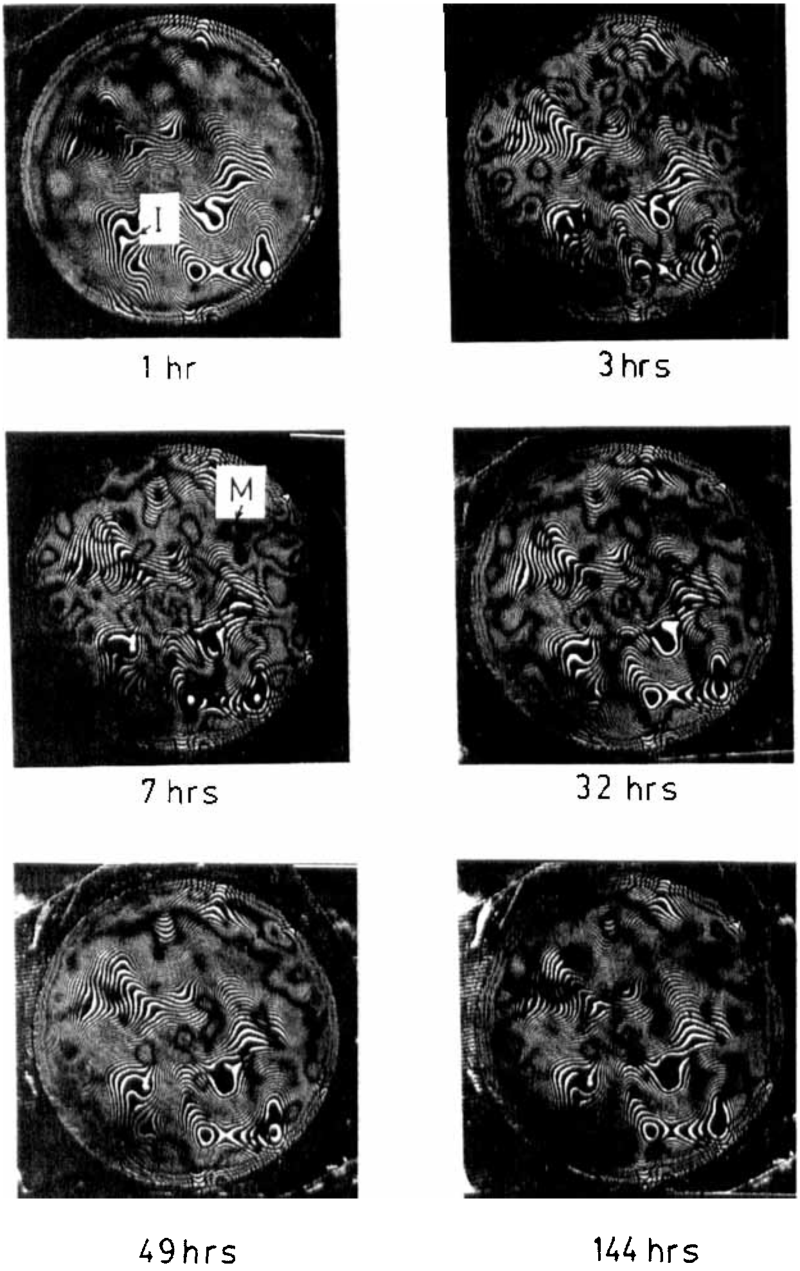
MATERIALS

Three proprietary epoxy adhesive formulations were selected for this investigation. One of these, FM1000, a nylon modified epoxy film adhesive manufactured by American Cyanamid, is known to generate pockets of internal pressure and swelling during hot water uptake.[3] The other two, FM 73M manufactured by American Cyanamid and Redux 312/5 manufactured by Ciba-Geigy plc, exhibit swelling during hot water uptake.[3] All of the joints studied here were joints between glass cover slips and glass plates.

RESULTS

Dimensional changes

Figure 1 is a sequence of moiré images obtained for an FM1000 joint when immersed in kerosene at 100°C. The moiré fringes are the broad



1 hr 3 hrs 7 hrs 32 hrs 49 hrs 144 hrs

FIGURE 1 Interference fringes (I) and moiré fringes (M) for an FM 1000 adhesive joint after various times of immersion in kerosene at 100°C. The cover slip diameter is 18 mm.

dark lines labelled M and the interference fringes are the narrower dark lines labelled I. The changes in the moiré fringe patterns indicate an initial gradual growth of regions of localised swelling. At this stage, the displacement field is one of "hills" and "dales" with a circumferential region of negative displacement (contraction) of magnitude ~0.3% adjacent to the rim of the joint. At longer times of immersion > ~ 2 days, the moiré patterns demonstrate that the magnitude of localised swelling gradually declines. There is no evidence of any superimposed homogeneous resin swelling.

Similar observations of circumferential shrinkage, no overall swelling but extensive localised swelling, were recorded for an identical joint immersed in kerosene at 60°C. This swelling pattern was also recorded for a joint prepared from a second batch of FM1000 film adhesive immersed in kerosene at 100°C.

The activation energy for diffusion of kerosene in FM1000 may be estimated from the times required to produce a given distribution of resin swelling. At 60°C this time differs from that at 100°C by a factor of about 30. If diffusion of kerosene in epoxy adhesives follows an Arrhenius law then this gives an activation energy of 88 kJ mol^{-1}. This is similar in magnitude to the value of 168 kJ mol^{-1} reported by Sarti[4] for the diffusion of n-alkanes in polystyrene, and also to the value of 57 kJ mol^{-1} reported by the present authors[5] for the diffusion of water molecules in an epoxy adhesive.

Joints prepared from Redux 312/5 (Figure 2) and FM73M (Figure 3) only undergo small shrinkage at the joint edge when immersed in kerosene at 60°C; no localised swelling distribution patterns were observed. The shrinkage observed at the periphery is common to all three proprietary adhesives studied here. It corresponds to generation of tensile stress normal to the joint and is probably the origin of cracks in joints in contact with aviation fuel. The shrinkage is attributed to the leaching out of low molecular weight material.

Evidence for generation of pockets of internal pressure

The local curvatures on the individual moiré fringes in Figure 1 indicate the appearance of a large number of localised pockets of adhesive swelling. The occurrence of internal pockets of pressure, beneath each hill, would account for this observation. Accordingly a search was made for photoelastic contrast indicative of pressure-filled pockets within the

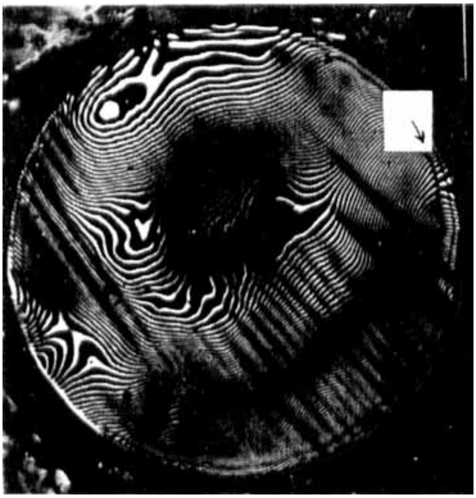


FIGURE 2 Circumferential moiré fringes (indicated by an arrow) for a Redux 312/5 adhesive joint after 120 hours immersion in kerosene at 60°C.

FIGURE 3 Same as Figure 2 but for an FM73M adhesive joint after 144 hours immersion.

kerosene-immersed FM1000 joints. Figure 4 shows a small region within one such adhesive joint viewed (a) in transmitted light and (b) between crossed polars. The bright regions in (b) are areas of stress birefringence, the nature of which is consistent with that expected for pockets of

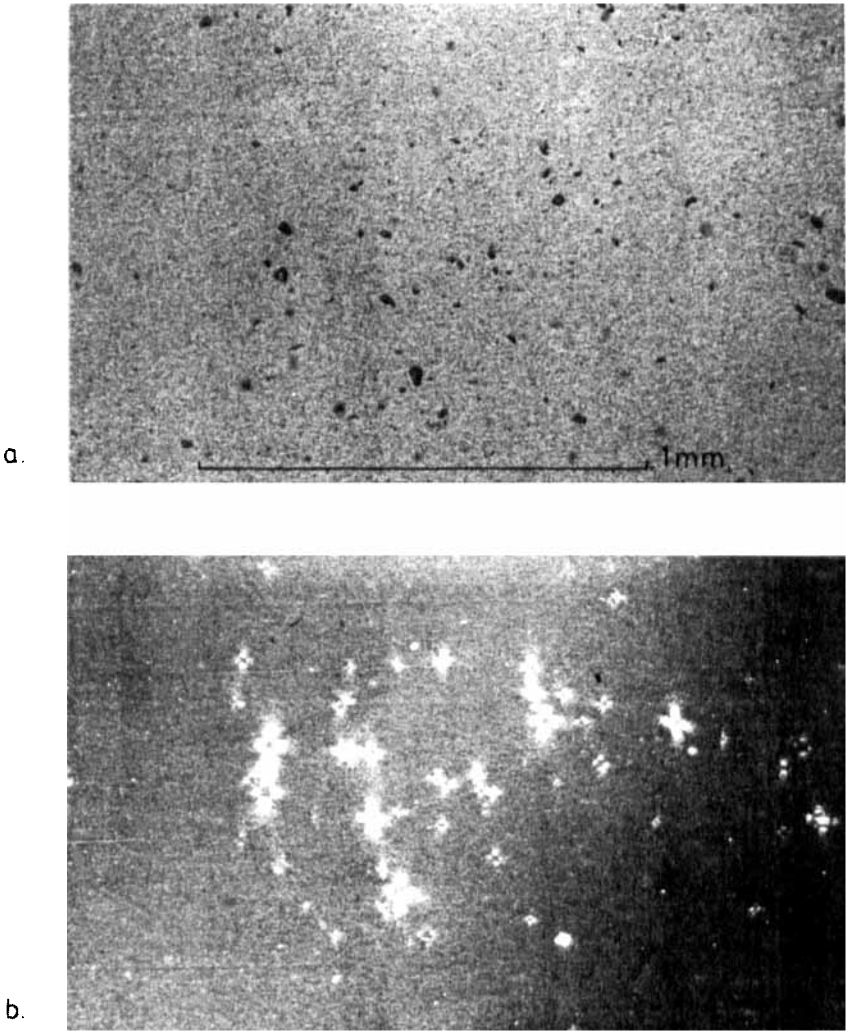


FIGURE 4 FM1000 adhesive joint viewed in a polarising microscope (a) with polars uncrossed and (b) with polars crossed.

internal pressure. Figure 5 is a mosaic constructed from micrographs of the adhesive joint photographed between crossed-polars and upon which data from the moiré fringe pattern obtained after 3 hours immersion have been superimposed (only the hills and dales are shown,

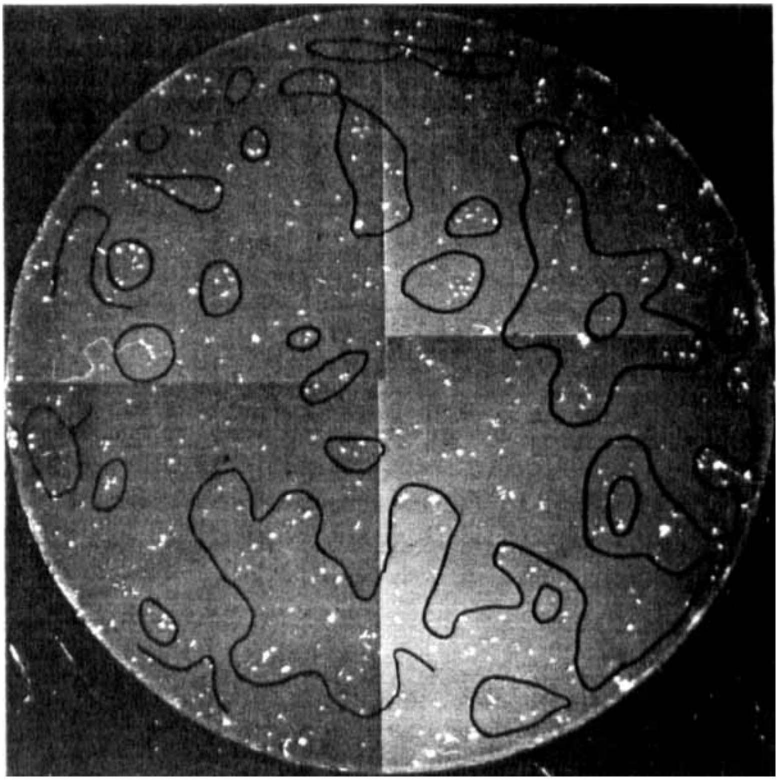


FIGURE 5 Mosaic of crossed polars micrographs upon which is superimposed the moiré fringe pattern for the specimen from Figure 1 after 3 hours immersion in kerosene.

the circumferential shrinkage rings having been omitted for clarity). Careful examination of this photograph reveals that many of the hills can be directly associated with clusters of pressure-filled pockets. Note that most of the flares of photoelasticity seen in Figure 4(b) can be identified with individual impurity inclusions in Figure 4(a).

Osmotic pressures of organic solutions

A likely mechanism for the generation of internal pressure by diffused kerosene is osmosis. Very few direct measurements of osmotic pressures, even for aqueous solutions, are reported in the literature and this is attributed[6] to the unavailability of semi-permeable membranes suitable for laboratory experiments. The most commonly used indirect method is to calculate osmotic pressures from measurements of the lowering of vapour pressures.

Osmotic pressure data and vapour pressure data (from which osmotic pressures can be easily calculated) for solutions of several organic solvents are collected in Landolt-Bornstein.[7] Most of these data are for dilute solutions of organic solutes such as sugar in acetic acid, starch in acetic acid, glucose in acetic acid, tetraphenylethylene in benzene, etc. If osmotic pressure due to dissolution of impurity inclusions by diffused kerosene is responsible for localised swelling then the observation of undissolved impurity (solute) in Figure 4(a) presumably means that the pockets of solution are saturated. The only data listed in Landolt-Bornstein for concentrated solutions of organic solvents are for solutions of inorganic solutes, namely calcium chloride in ethanol, aluminium chloride in phosgene, boron trifluoride in methanol, cadmium bromide in ethanol and sodium iodide in acetone. Data for three of these are reproduced in Figure 6, from which it is evident that

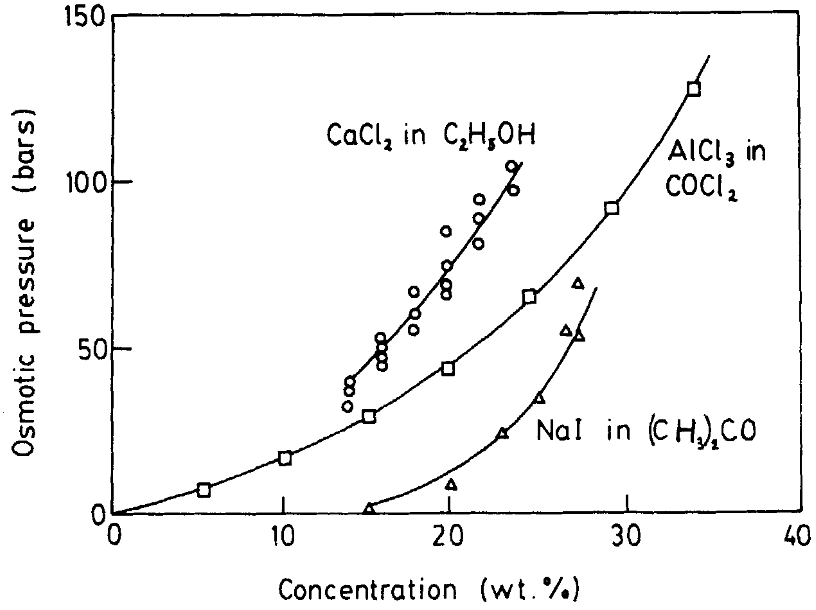


FIGURE 6 Osmotic pressures for solutions of calcium chloride in alcohol at temperatures of 20°C, 30°C, 40°C, 50°C and 60°C, of sodium iodide in acetone between 10°C and 30°C, and for aluminium chloride in phosgene at temperatures of 0°C and 25°C. Data calculated from published[7] values of vapour pressure.

osmotic pressures of the order of 100 bars are common for solutions of inorganic solutes in organic solvents. At 60°C and 100°C, epoxy based materials subjected to stresses of 100 bars are expected to exhibit measurable viscoelastic flow.

We have not established that the postulated solutes are organic or inorganic in nature. If they are organic, for example unreacted amine curing agent or undistributed plasticiser, an order of magnitude estimate for the osmotic pressure may be obtained as follows.

For ionic solutes dissolved in water the osmotic pressure is a non-linear function of solute concentration; for non-ionic solutes the relationship is linear. An osmotic pressure of one atmosphere is generated when one mole, say 100 gm if the solute is plasticiser, is dissolved in 22.4 litres of solvent. The strength of warm epoxy saturated with kerosene is probably of the order of 100 bars (10 MNm^{-2}). If we assume that a linear relationship holds for solutes dissolved in kerosene, then measurable displacements due to osmotic pressures of 100 bars attributable to dissolution of plasticiser are expected if the plasticiser concentration can locally exceed ~68 wt%. When used in epoxy formulations the overall concentration of plasticiser in epoxy formulations is typically ~5 wt%.

CONCLUSIONS

1. Epoxy adhesives undergo dimensional changes during uptake of aviation fuel. For each of three proprietary adhesives investigated, the dimensional changes include measurable shrinkage adjacent to the joint edge.
2. For one of the adhesives investigated (FM 1000), the dimensional changes also include inhomogeneous swelling throughout the joint and each region of swelling is associated with the occurrence of pockets of internal pressure.
3. The temperature dependence of the above adhesive swelling indicates an activation energy of 88 $kJmol^{-1}$.
4. Osmosis is a likely mechanism for the generation of internal pressure pockets. Although no osmotic pressure data exists for kerosene solutions, there are published data for solutions of other organic solvents. A survey of these data reveals that osmotic pressures in excess of 100 bars are common. At the test temperatures (60°C and

100°C) appreciable viscoelastic flow can be expected in localised stress fields as large as this.

Acknowledgments

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