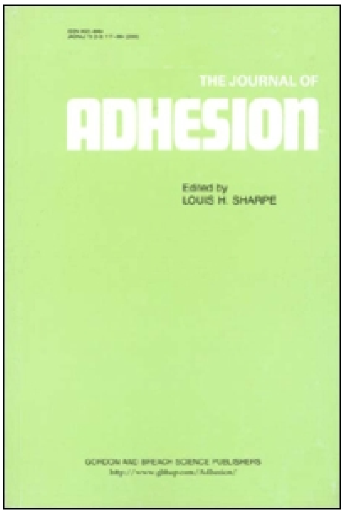


The Journal of Adhesion

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

The Effect of Bubbles at the Interface on the Adhesion of Polyethylene to Metals

T. Adam; J. R. G. Evans; D. E. Packham

To cite this Article Adam, T. , Evans, J. R. G. and Packham, D. E.(1980) 'The Effect of Bubbles at the Interface on the Adhesion of Polyethylene to Metals', The Journal of Adhesion, 10: 4, 279 — 291
To link to this Article: DOI: 10.1080/0021846808544634
URL: http://dx.doi.org/10.1080/0021846808544634

J. Adhesion, 1980, Vol. 10, pp. 279-291
0021-8464/80/1004-0279 $04.50/0

Printed in Great Britain

The Effect of Bubbles at the Interface on the Adhesion of Polyethylene to Metals

T. ADAM, J. R. G. EVANS and D. E. PACKHAM†

*School of Engineering and School of Materials Science,
University of Bath, Bath BA2 7AY, U.K.*

(*Received August 20, 1979; in final form November 15, 1979*)

By use of a blowing agent bubbles of a few hundred microns diameter were introduced at the interface of copper and steel substrates coated with low density polyethylene. The presence of the bubbles leads to an improvement in peel strength. An explanation is put forward in terms of a suggested stress perturbation produced by the bubbles which leaves the interface itself relatively lowly stressed and leads to the expenditure of work in plastic deformation of the polymer away from the interface. Support for the explanation was obtained by photoelastic study of a model system and by scanning electron microscopy of the peeled surfaces.

INTRODUCTION

Air bubbles and other voids at the interface of a joint between adhesive and substrate can arise in several ways. The nature of the two phases may mean that complete wetting is thermodynamically impossible, especially with a rough substrate.[1] Even where thermodynamic principles suggest that wetting will occur, the adhesive may set leaving voids before equilibrium can be established. Air entrapment by the adhesive while still fluid can also lead to interfacial bubbles.

The presence of such bubbles and similar voids in an adhesive layer near the interface is generally considered to be a source of weakness in a joint.[1,2,3] They would reduce the real area of contact between adhesive and substrate

---

† To whom communications should be addressed.

and would produce stress concentrations which in a brittle adhesive lead to failure at a lower nominal stress.

Occasionally in work previously reported[4] on the adhesion of polyethylene to metals, bubbles have inadvertently become trapped in the polymer near the interface. Sometimes such specimens were found to have higher peel strengths than expected. This lead to the present work which investigates the effect of bubbles near the interface in polyethylene–metal bonds. The bubbles were deliberately introduced by incorporating a blowing agent into a layer of polymer close to the substrate.

EXPERIMENTAL DETAILS

Polyethylene

Low density polyethylene, Alkathene 190400 from I.C.I. Ltd. was used. The manufacturer stated it to be additive-free and to have a density of 0.916 g/cm^3 and a melt flow index of 20. For some experiments antioxidant (2,6-di-*tert*-butyl-*p*-cresol) was incorporated into the polymer as previously described.[4]

Blowing agent

A blowing agent, EPB from Fisons Ltd., was mixed with the polyethylene powder to give either 0.5 or 1.0% by weight of blowing agent. EPB is based on azodicarbonamide and decomposes to give off nitrogen at around 200°C.

Copper

Deoxidised sheet 1.2 mm thick (B.S. 1172) was cut into panels 10 × 15 cm and rinsed in dilute hydrochloric acid followed by water and acetone.

After degreasing (in trichloroethane) the panels were *chemically polished* by immersion for 10 minutes at room temperature in a solution of orthophosphoric acid (60 ml, S.G. 1.75), nitric acid (10 ml, S.G. 1.42), acetic anhydride (30 ml) and water (8 ml). They were then washed with distilled water and acetone.

Some panels were further treated by immersion for 30 minutes in an aqueous solution at 90°C of sodium chlorite (3 g/l), trisodium phosphate (10 g/l) and sodium hydroxide (5 g/l). This produced matt black films of surface oxide which will be referred to as *chlorite-formed films*.

Steel

10 × 15 cm panels of general purpose bright mild steel sheet 1.2 mm thick (B.S. 1149) were prepared for bonding by degreasing in trichloroethane

followed by etching for 30 seconds at room temperature in 6 M hydrochloric acid and rinsing in water and acetone.

Coatings with polyethylene

To produce *coatings with bubbles* at the interface, the metal panels were heated at 150°C for 10 minutes in a nitrogen-filled oven. They were removed and the polymer containing blowing agent was sprinkled on one side. The excess material was immediately tipped off leaving a thin partially molten layer on the panel. A second layer of polymer without blowing agent was then sprinkled on top and left for 2 minutes for a thicker layer to fuse. The excess polymer was again tipped off, and the panel returned to the oven (now containing air). The thermostat was turned up to 200°C and the panel left in the oven for the 25 minutes required to attain this temperature. During this coating time the polymer fused to give an even coating about 1 mm thick and the blowing agent decomposed to produce nitrogen bubbles at the interface. The panel was then removed and allowed to cool in air.

Coatings without bubbles for comparative experiments were produced by the same procedure except, of course, no polymer with blowing agent was used.

Peel tests

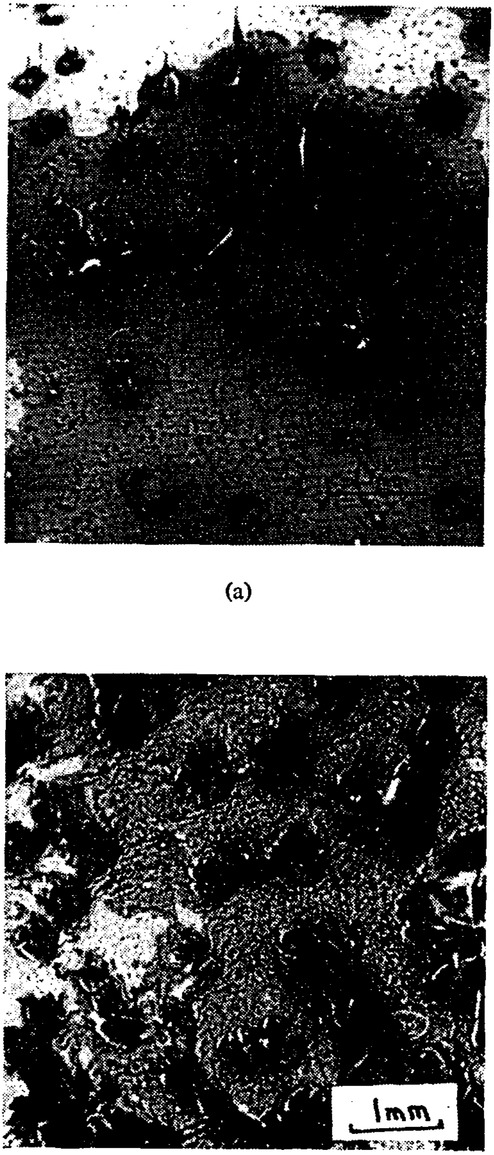
2 cm wide strips of polymer were peeled on an Instron testing machine at a peel rate of 250 mm/min and peel angle of 180°.

Photoelastic measurements

For modelling the effect of bubbles on the stress pattern transparent polyurethane elastomer sheets 1.5 mm thick were used (Elastomer DP9450 from Baxenden Chemical Company Ltd., Accrington, Lancashire). These were examined when stressed in circularly polarised light from a sodium lamp.

RESULTS

Adhesion of polyethylene to chemically polished copper is very low. The peel strength of 0.14 N/mm shown in Table I indicates that the polymer strip is easily pulled off by hand. The failure mode is such that little or no polymer remains on the substrate.[5] It is therefore surprising that the incorporation of bubbles at the interface should produce an improvement in peel strength to 0.80 or 1.80 N/mm, depending on the concentration of blowing agent (Table I).



(a)

(b)

See caption opposite.

FIGURE 1 Adhesion of polyethylene to various substrates. Scanning electron micrographs of peeled specimens showing remains of interfacial bubbles.

a) Distribution of bubbles on copper with chlorite-formed film.

b) The polymer strip peeled from a substrate such as (a).

c) Plastically deformed polymer around the site of a bubble on chemically polished copper.

TABLE I

Effect of addition of blowing agent (EPB) and antioxidant (AO) to polyethylene on adhesion to various substrates

Substrate	Additives	Peel strength N mm^{-1}	No. of peels
Chemically polished copper	Nil	0.14±0.02	21
	0.5% w/w EPB	0.80±0.15	9
	1.0% w/w EPB	1.80±0.24	8
Etched mild steel	1000 p.p.m. AO	0.12±0.05	4
	1000 p.p.m. AO +0.5% w/w EPB	0.92±0.13	13
Chlorite-formed film on copper	Nil	1.48±0.08	4
	0.5% w/w EPB	5.76±1.44	4
	1.0% w/w EPB	Sample tore	

95% confidence limits are indicated.

Similarly, polyethylene stabilised with antioxidant adheres poorly to mild steel. When a layer of polymer with blowing agent is introduced near the interface improved adhesion again results (Table I).

By contrast with chemically polished copper, the copper with a chlorite formed film bonds well to polyethylene.[6,7] Here too the presence of blowing agent gives higher adhesion. With 1% of blowing agent the adhesion was so high that the polymer strip could not be peeled (Table I).

The effect of the blowing agent on the failure mode can be seen by examining the members in the scanning electron microscope after peeling. Figure 1(a) shows the remains of bubbles on a copper substrate with chlorite-formed film. Figure 1(b) shows the polymer strip peeled from such a substrate. It is clear from both of these pictures that the polymer around the edges of the bubbles is extensively drawn as the bond fails. Figure 1(c) shows at higher magnification the drawn polyethylene around the site of a bubble on a polished copper substrate.

DISCUSSION

Peel strength is a measure of the work dissipated per unit area during debonding. If some feature of a bond causes large amounts of work to be used in (say) plastic deformation of the polymer, this will increase the peel strength. Thus it has been suggested[5] that the good adhesion of polyethylene to substrates with a fibrous topography (such as chlorite-formed films on copper) is due to the stress field around the fibre tips leading to extensive plastic deformation of the polymer. In the results reported here there is evidence of extensive plastic deformation of the polymer around the edges of the bubbles at the interface.

It is therefore necessary to consider the effect of an interfacial bubble on the stress field. This question has already been discussed by Bair *et al.*[8] For a similar, but significantly different, system, Bair and his colleagues sought to explain the good adhesion of polyethylene to copper with a fibrous surface oxide like the chlorite-formed films mentioned above. They suggested that poor wetting of the substrate by the polymer would leave voids which could be idealised as hemi-spherical bubbles on a smooth substrate (Figure 2). For reasons stated elsewhere[5] the present authors do not favour this model as an explanation of adhesion to fibrous substrates. Bair's ideas however worth developing for their relevance to the results in this paper.

Also whilst it is appreciated that other theories of failure exist[9] such as maximum shear stress and either total or shear strain energy, we will pursue Bair's use of the stress component parallel to the applied load.

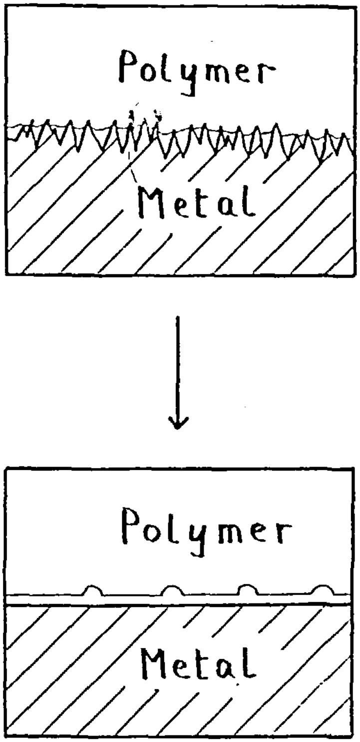


FIGURE 2 The model of Bair *et al.*,[8] for poor interfacial contact between polyethylene and copper with a fibrous surface oxide.

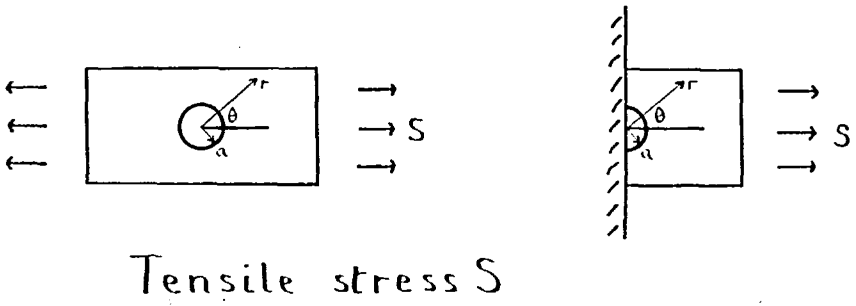


FIGURE 3 Symbols for describing stress distribution around (a) a circular hole in an elastic lamina (b) a semicircular hole in an elastic lamina bonded to a rigid substrate.

Bair took from Timoshenko and Goodier[10] the equations for the stress around a circular hole in a linearly elastic lamina. It was assumed that the same equations would apply to a semicircular void at the interface between a rigid substrate and a polymer (Figure 3), if the dilational stress arising from the rigid interface could be neglected.

The equations concerned in terms of the symbols defined in Figure 3 are[10]

$$\sigma_r = \frac{s}{2}\left(1-\frac{a^2}{r^2}\right)+\frac{s}{2}\left(1+\frac{3a^4}{r^4}-\frac{4a^2}{r^2}\right)\cos 2\theta \qquad (1)$$

$$\sigma_\theta = \frac{s}{2}\left(1+\frac{a^2}{r^2}\right)-\frac{s}{2}\left(1+\frac{3a^4}{r^4}\right)\cos 2\theta \qquad (2)$$

$$\tau_{r\theta} = -\frac{s}{2}\left(1-\frac{3a^4}{r^4}+\frac{2a^2}{r^2}\right)\sin 2\theta \qquad (3)$$

Bair *et al.*[8] then considered the stress σ_x in the direction of the applied stress at the apparently arbitrary value of $\theta = \pi/4$.

$$\sigma_x = \sigma_r \cos^2\theta+\sigma_\theta \sin^2\theta-2\tau_{r\theta}\sin\theta\cos\theta \qquad (4)$$

At $\theta = \pi/4$ this becomes

$$\sigma_x(\theta = \pi/4) = s+\frac{s}{2}\left(\frac{2a^2}{r^2}-\frac{3a^4}{r^4}\right) \qquad (5)$$

where the first term is the stress in the absence of the void and the second term the perturbation of stress due to the void. Equation (5) is wrongly described as giving a monotonic increase in σ_x with r.

Bair *et al.* imply (their Figure 10) that where the $\theta = \pi/4$ lines from two neighbouring bubbles intercept, σ_x will be doubled as in Eq. (6).

$$\sigma_x(2\text{ voids}) = 2s+s\left(\frac{2a^2}{r^2}-\frac{3a^4}{r^4}\right) \qquad (6)$$

They then speculate that failure will initiate at this point of intersection, and will involve deformation of material from the point of intersection to the interface.

Two considerations weaken the strength of their argument. In the first place when two bubbles are considered it is only the perturbation term in Eq. (5) which is doubled, so Eq. (6) should be

$$\sigma_x(2\text{ voids}) = s+s\left(\frac{2a^2}{r^2}-\frac{3a^4}{r^4}\right) \qquad (7)$$

This predicts a much smaller concentration of stress. The second point is that there are much higher concentrations of stress associated with the void at values of θ greater than $\pi/4$.

By substituting Equs (1), (2) and (3) into (4), the general equation for σ_x is obtained

$$\sigma_x = s+s\left[\frac{3}{2}\frac{a^4}{r^4}\cos 4\theta-\frac{a^2}{2r^2}(3\cos 2\theta-2+4\cos^2 2\theta)\right] \tag{8}$$

This may be written in the form:

$$\sigma_x = s+\Delta s \tag{9}$$

where Δs is the perturbation on the stress at infinity. The fractional perturbation $\Delta s/s$ is plotted for various values of θ between 0 and $\pi/2$ in Figure 4. The value of σ_x at $\theta = \pi/4$ (Eq. 5) passes through a maximum at $r = a\sqrt{3}$. The locus of such mathematical maxima is shown on the figure. The greatest stress concentrations occur for relatively high values of θ and low values of r: for a hemispherical bubble, around the base. It can be seen that the perturbation of stress Δs increases most significantly in the region bounded approximately by the 60° and 90° vectors and the radii of a and $1.5a$. Incidentally, from the levelling off of the 60° curve below $r = 1.5a$, the σ_x stress in this

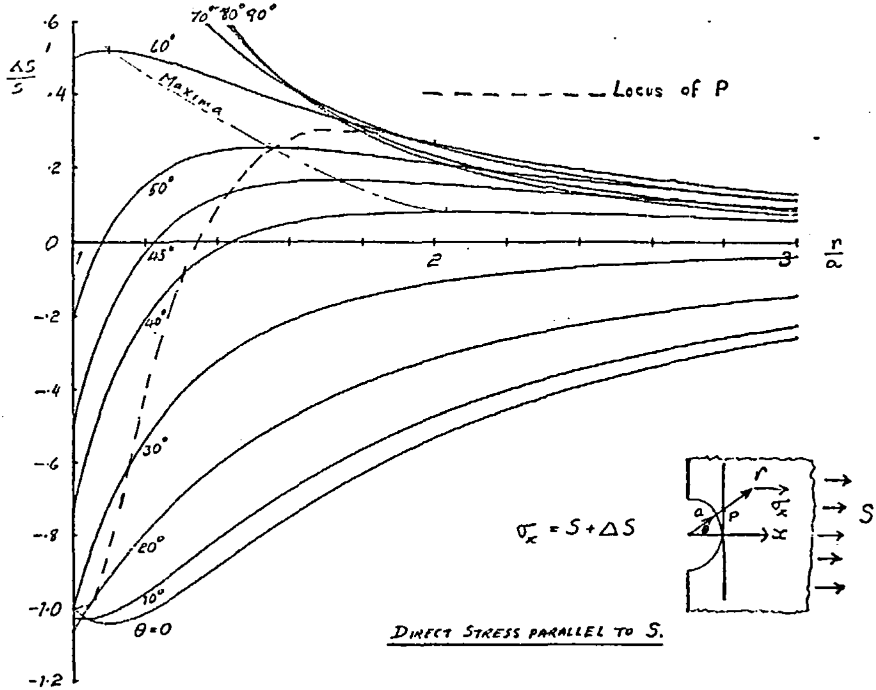


FIGURE 4 Stress distribution around a semicircular hole in an elastic lamina bonded to a rigid substrate. The fractional perturbation of the direct stress parallel to S is plotted against normalised distance from the centre of the hole. P is the locus of points of distance a from the interface.

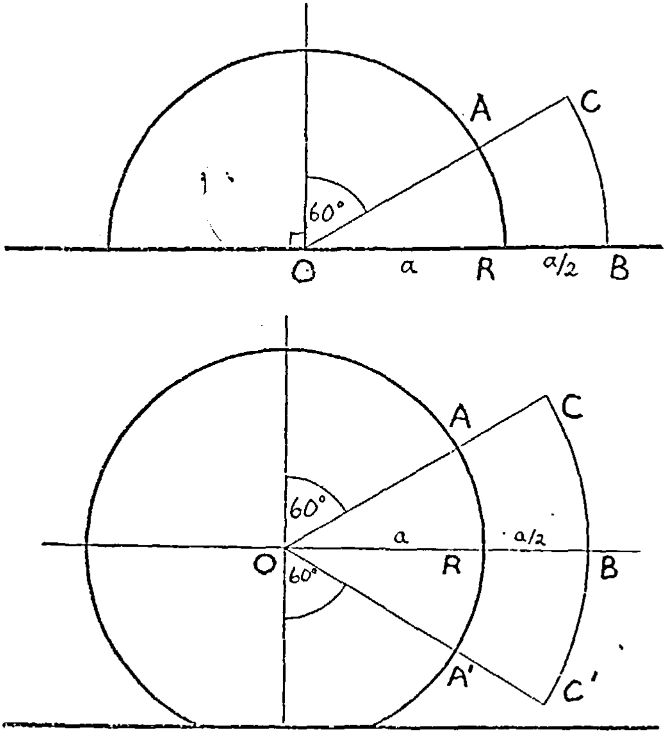


FIGURE 5 The highly stressed region around interfacial bubbles (a) ARBC for a hemispherical bubble, (b) ARA′C′BC for a larger bubble.

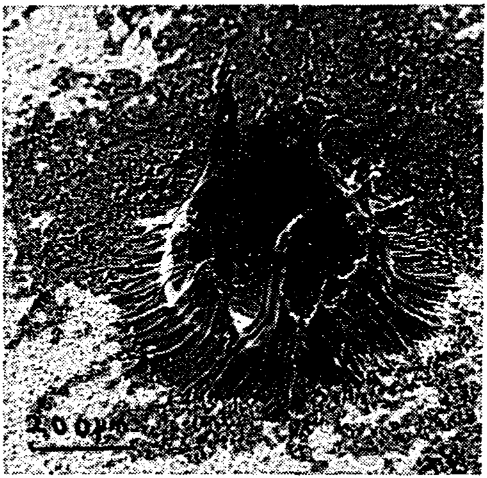


FIGURE 6 Scanning electron micrograph showing the shape of the remains of a bubble after peeling polyethylene from a steel substrate.

"high stress" region exceeds s by at least 50%. This region is approximately area ARBC in Figure 5(a).

The bubble considered by Bair is a hemispherical idealisation of the supposed voids between the polymer and a fibrous substrate. The interfacial bubbles in this work are different. They actually exist as parts of spheres near the interface. Examination of the peeled surfaces in the scanning electron microscope shows that the bubbles are generally more than hemispheres, being major segments of spheres cut by the interface (Figure 6).

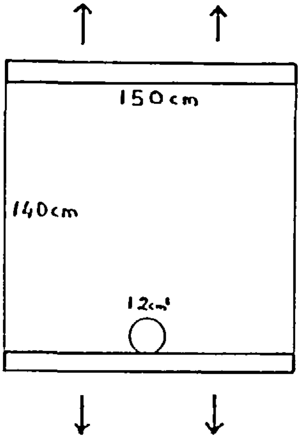


FIGURE 7 Arrangement of polyurethan rubber sheet for photoelastic analysis.

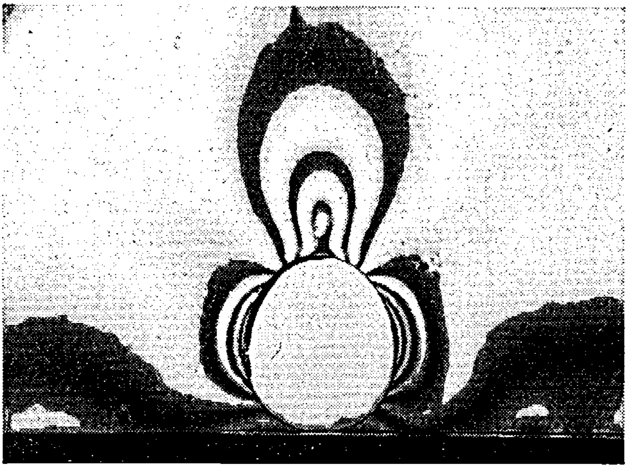


FIGURE 8 Stress pattern obtained by illuminating a stressed polyurethan rubber sheet (Figure 7) with circularly polarised monochromatic light.

This is to be expected from what is known about the contact angle of molten polyethylene on high energy surfaces.[11-13]

The stress situation given by Eq. (8) and Figure 4 is still relevant, with the same limitations about linear elasticity and dilational stresses. Symmetry considerations require and Eq. (8) predicts that the perturbation of stress from $\theta = 0$ to $\theta = \pi/2$ will be mirrored between $\theta = \pi/2$ and $\theta = \pi$. Thus the fractional perturbation in Figure 4 for any θ will be the same for $180° - \theta$. This means that the highly stressed region ARBC for a hemispherical bubble in Figure 5(a) will be extended to ARA′C′BC as shown in Figure 5(b) for a more extensive bubble. Moreover near the interface the polymer will be lightly stressed.

Confirmation was sought that the equations used give at least a qualitative indication of the stress pattern in a polymer with a bubble near a rigid interface. A rectangle of transparent polyurethane rubber sheet with a circular hole punched in it was clamped top and bottom (Figure 7) and the stress pattern observed in circularly polarised sodium light. Figure 8 shows a typical pattern obtained. The stress is concentrated, as expected, at the ends of the diameter of the circle at right angles to the applied stress, although there is a slight shift in the location of the most highly stressed region away from the interface.

The electron micrographs (Figure 1) of the fracture surfaces also support this. The region of high plastic deformation is in a similar position around the periphery of the bubbles.

It seems then that the mode of action of the interfacial bubbles in increasing peel strength is that they produce stress concentrations which cause extensive plastic deformation of the polymer around their edge.

CONCLUSIONS

Using polymer containing blowing agent it is possible to produce polyethylene coatings on metal which have small bubbles close to the interface. The peel strength of such coatings is found to be significantly higher than similar, bubble-free coatings.

Standard mathematical treatments of the effect of circular holes on the stress distribution in plates can be used to get some idea of the effect of the bubbles on the stresses in the system during debonding. These suggest that the interface itself is relatively lightly stressed and that stress is concentrated in a volume of polymer located about one bubble's radius from the substrate. Photoelastic studies give support to this kind of stress distribution. Examination of the fracture surfaces in the scanning electron microscope shows quantities of plastically deformed polyethylene around the sites of the bubbles as expected from the stress concentrations envisaged.

The improved peel strength of the coatings with bubbles is attributed to the influence of the bubbles on the stress distribution. The bubbles form "nuclei" of regions of extra plastic deformation of the polymer. The work involved in this deformation contributes to the augmentation of peel strength.

Acknowledgements

The receipt of a grant from the Science Research Council including post-doctoral support (for J.R.G.E.) is gratefully acknowledged.

References

1. N. A. de Bruyne, *Aero Research Technical Notes Bull.* No. 168 (Aero Research Ltd., Cambridge, 1958).
2. W. A. Zisman in *Contact Angle, Wettability and Adhesion*, Ed. R. F. Gould (American Chemical Society, Washington 1964), p. 44.
3. C. W. Jennings in *Recent Advances in Adhesion*, Ed. L. H. Lee (Gordon and Breach, London 1973), p. 469.
4. J. R. G. Evans and D. E. Packham, *J. Adhesion* **10** (1), 39 (1979).
5. J. R. G. Evans and D. E. Packham, *J. Adhesion* **10** (3), 177 (1979).
6. J. M. Sykes, Ph.D. Thesis, Cambridge 1967.
7. J. R. G. Evans and D. E. Packham, *J. Adhesion* **9** (4), 267 (1978).
8. H. E. Bair, S. Matuoka, R. G. Vadimisky and T. T. Wang, *J. Adhesion* **3** (2), 89 (1971).
9. F. B. Seely and J. O. Smith, *Advanced Mechanics of Materials*, 2nd edn., p. 76 (John Wiley & Sons, New York 1952).
10. S. P. Timoshenko and J. N. Goodier, *Theory of Elasticity*, 3rd edn., p. 91 (McGraw-Hill, New York, 1970).
11. H. Schonhorn, H. L. Frisch and T. W. Kwei, *J. Appl. Phys.* **37**, 4967 (1966).
12. B. W. Cherry and C. M. Holmes, *J. Coll. Interf. Sci.* **29**, 174 (1969).
13. J. M. Sykes and T. P. Hoar, *J. Polym. Sci.* **A2**, **9**, 887 (1971).