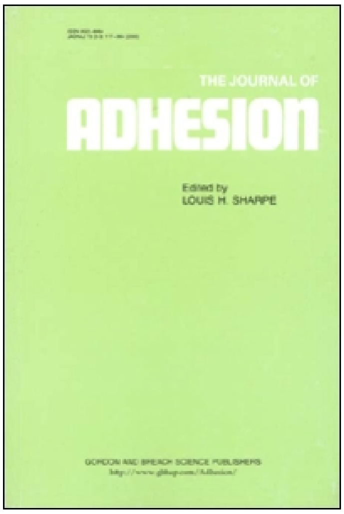

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

# Peel Strength and Failure Mechanisms in Oxidized Copper-Polyethylene Lap Joints Bonded with Flexible Epoxy

Tsuey T. Wang[a]; H. N. Vazirani[a]
[a] Bell Telephone Laboratories, Incorporated, Murray Hill, New Jersey, U.S.A.

**To cite this Article** Wang, Tsuey T. and Vazirani, H. N.(1972) 'Peel Strength and Failure Mechanisms in Oxidized Copper-Polyethylene Lap Joints Bonded with Flexible Epoxy', The Journal of Adhesion, 4: 4, 353 — 364
**To link to this Article: DOI:** 10.1080/00218467208075013
**URL:** http://dx.doi.org/10.1080/00218467208075013

*J. Adhesion*, 1972, Vol. 4, pp. 353-364

Printed in Northern Ireland

# Peel Strength and Failure Mechanisms in Oxidized Copper-Polyethylene Lap Joints Bonded with Flexible Epoxy

TSUEY T. WANG and H. N. VAZIRANI

*Bell Telephone Laboratories, Incorporated,*
*Murray Hill, New Jersey* 07974, *U.SA.*

(*Received February* 7, 1972)

A study was made of the failure mechanisms in peeling of a composite consisting of copper-copper oxide-flexible epoxy-polyethylene. The morphology of the copper oxide (needle shaped) had a profound effect on the peel strength. The surfaces of the oxidized copper and the peeled specimens were examined with a scanning electron microscope and the results were used as a basis for analyzing the load transfer mechanisms at the interfacial regions. It is pointed out that the higher tensile strength of the oxide needles and the increased adhesion at the polymer-oxide interface are both important for the improvement in the peel strength. The failure process in polyethylene was shown to be equivalent to a continuous sequence of the reversed indentation problem of Prandtl. Using Prandtl's model it was possible to explain the regular ridge patterns observed at the surfaces of the peeled samples and relate the failure mode to the peel strength.

## INTRODUCTION

In bonding a polymer to metals, it is generally known that the peel strength can be improved substantially if the metal surface is properly prepared and oxidized[1,2]. This is especially the case when the metal to be bonded is copper. The strengthening effect of the metal oxide has been attributed to a better contact between the polymer and the surface[3]. For oxidized copper-polyethylene lap joints, Bair *et al.*[4] have shown that as a result of the improved contact at the oxide-polyethylene interface, a larger amount of polyethylene is constrained to yield near the interface during the failure process. A higher peel force is therefore needed to initiate a large scale plastic flow or failure in polyethylene.

The work of Bair *et al.*[4] is applicable to adhesive joints which fail exclusively in the ductile polymer. If the polymer in contact with the oxide is relatively strong, failure may also occur in the oxide itself. The strengthening effect of the oxide is then governed by the strength of the oxide as well as by the contact at the oxide-polymer interface.

The relation between the peel strength and the mode of failure has been studied extensively on the basis of elasticity theory[5-8]. The results of these analyses are naturally intended for applications where the medium involved in the failure process remains elastic or nearly elastic up to failure. If the medium is ductile, it is likely to yield and flow before separation occurs in the joint. In such an instance, it would be more fruitful to study the peel strength on the basis of plasticity theory.

In this paper we shall examine the strengthening roles of the oxide as well as the ductile failure in the polymer and its effect on the peel strength. The peel test is carried out on lap joints prepared by bonding polyethylene to the Ebonol C† treated copper surface with a flexible epoxy.

## EXPERIMENTAL

The copper strips, each 1″ × 6″ in size, were cut from a 1/16″ thick sheet of half hard copper alloy 110 (99.4% Cu.). The copper surfaces were carefully degreased and acid treated, then oxidized in an 18% aqueous solution of Ebonol C at 205° ± 5°F for various times. For quick identification, the lap joints prepared from these copper strips will be referred to as x-min. joints or x-min. samples where x is the oxidation time of the copper strip.

The polyethylene strips, also each 1″ × 6″ in size, were cut from a 0.052″ thick sheet. The sheet was compression molded from a medium density (0.924), high molecular weight polyethylene (melt index 0.2, Union Carbide) at 350°F, and air cooled outside the press. The polyethylene strips were surface treated in chromic acid solution (100 ml of 30% $Na_2Cr_2O_7$ aqueous solution made up to one liter with conc. $H_2SO_4$) for one minute at 160°F, then rinsed with distilled water and air dried.

The treated copper and polyethylene strips were bonded with a flexible epoxy resin system based on Epon 828 (Shell Chemical Co.) and curing agent 62[9] based on POPTA (polyoxypropylene triamine, M.W. 403, Jefferson Chemicals, Houston, Texas) and POPDA 1000 (polyoxypropylene diamine, M.W. 1000, Jefferson Chemicals). Caution was taken not to entrap air bubbles in the adhesive layer during bonding. The lap joints were cured for one day at room temperature and two days at 140°F under one psi pressure. The adhesive layer had a thickness of about 0.001″ (±0.0001″).

The peel strength was determined on a table model Instron at a crosshead speed of 0.2 in./min. The peel angle was 90°.

The mechanical properties of polyethylene and epoxy cured with agent 62

---

† A proprietary material from Enthone, Inc., New Haven, Connecticut.

TABLE I

Mechanical Properties of Polyethylene and Epoxy

| Material | Young's Modulus (psi) | Yield Stress (psi) | Strain at Yield Limit (%) | Strain at Failure (%) |
|---|---|---|---|---|
| Polyethylene | $2.3 \times 10^4$ | $1200 \sim 1800$ | 25 | > 1000 |
| Epoxy | $10.5 \times 10^4$ | $3140 \sim 3400$ | 5 | 36.3 |

were tested in simple tension at the respective strain rates of 2 in./in.-min. and 0.2 in./in.-min. Both samples were microtensile type specimens having a cross section of 0.05″ × 0.25″ for polyethylene and 0.09″ × 0.187″ for epoxy. The gage length was one inch and the neck region at each end of the sample was about 1/16″ along the gage length. The results are summarized in Table I.

The surfaces of the oxidized copper and the peeled samples were examined with a scanning electron microscope.

## RESULTS

Figures 1 and 2 show the distributions of the needle or fiber shaped oxide at the copper surface after different oxidation times. The approximate density of

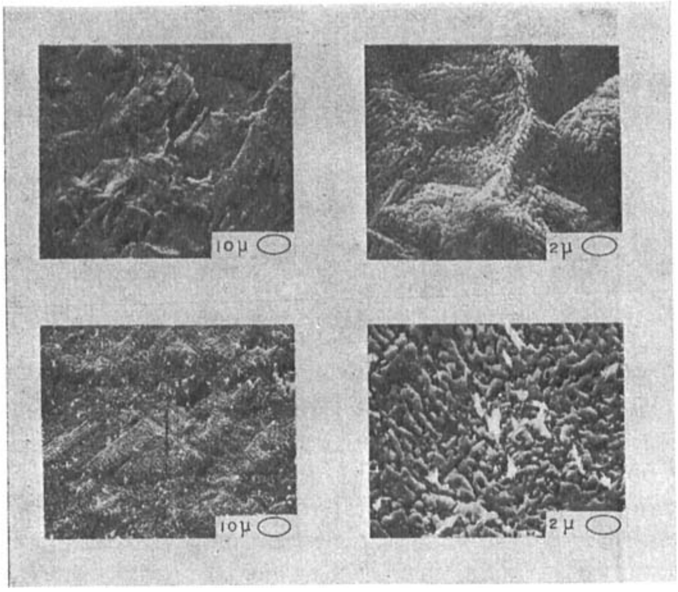

FIGURE 1 Scanning electron micrographs of copper surfaces oxidized for 0 minute (top) and 1 minute (bottom).

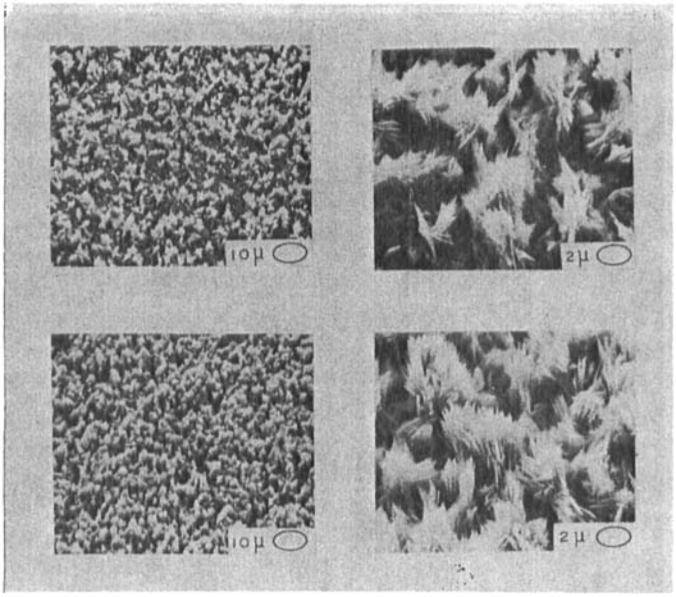

FIGURE 2 Scanning electron micrographs of copper surfaces oxidized for 2 minutes (top) and 8 minutes (bottom).

the oxide needles at the copper surface is plotted against the oxidation time in Figure 3.

The peel strength of the lap joints with varying oxidation times is shown in Figure 4. At shorter oxidation times the peel strength increases progressively with time but it levels off quickly at about 2 minutes. Close examination of the peeled samples revealed that failure occurred near the copper-epoxy interface at lower peel strength. But the locus of failure shifted to the epoxy-polyethylene interface region at higher peel strength. In the 2 min.—sample a mixed mode of failure along the peel path was observed and the peel strength of the same sample fluctuated more widely than other samples failed by either mode.

Figure 5 displays the micrographs of the typical surfaces of the peeled samples. The two pictures at the top and those in the middle were obtained separately from a 0 min. (untreated) sample and a one min.-sample. Only a small amount of epoxy could be found on the copper surfaces even at a larger magnification as shown in Figure 6(a) and (b). The two micrographs at the bottom of Figure 5 correspond to the peeled surfaces of an 8 min.-sample. Failure in the sample appeared to have resulted from yielding and tearing in the polyethylene strip. Micrographs of the same peeled surfaces with a smaller magnification are shown in Figure 6(c) and (d). The torn polyethylene forms

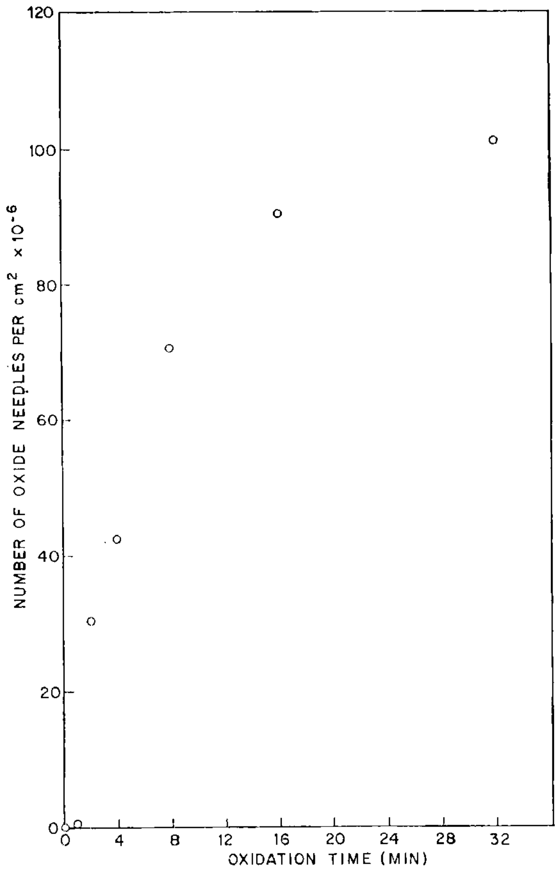

FIGURE 3 Density of oxide needles at the copper surface vs. oxidation time.

surprisingly regular patterns with the wavy ridges running parallel to one another. The wavy ridges run approximately at right angle to the peeling direction. The distance between the two nearest ridges is nearly constant throughout the peeled surfaces and measures about 0.01″.

## DISCUSSION

### 1 Failure in copper-epoxy interfacial region

The test has shown that the peel strength increases with the oxidation time as long as failure occurs near the copper-epoxy interface. The improvement in the peel strength is apparently due to the reinforcement of the interfacial region by the copper oxide. It is seen from the micrographs in Figures 1, 2

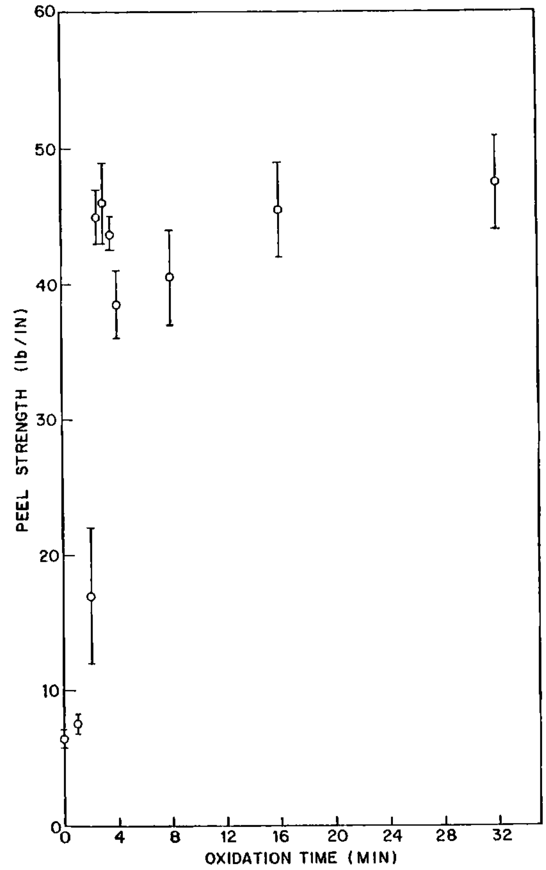

FIGURE 4 Peel strength of lap joints vs. oxidation time of copper strips.

and 5 that the oxide needles either fractured at their roots and detached with the epoxy layer or pulled out of the epoxy matrix and remained at the copper surface. The strengthening roles of these microfibrils in the interfacial region are probably similar to those of whiskers and fibers in the fibrous composites[10].

If we denote the tensile stress at the root section of an oxide fiber by $\sigma$ and the average shear stress acting along its longitudinal surface by $\tau$, then the force transmission within the oxide fiber having an average diameter $d$, and a length $l$ can be written as

$$\tau \pi d l \eta_w = \frac{\sigma \pi d^2}{4} \qquad (1)$$

or

$$\tau = \frac{d}{4 l \eta_w} \sigma \qquad (2)$$

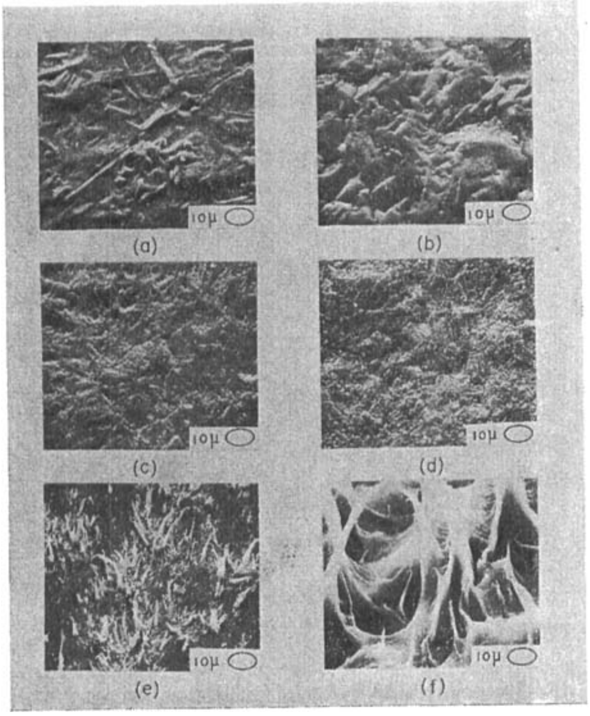

FIGURE 5 Scanning electron micrographs of the surfaces of peeled samples. (a) copper surface, 0 min.—sample. (b) polyethylene surface, 0 min.—sample. (c) copper surface, 1 min.—sample. (d) polyethylene surface, 1 min.—sample. (e) copper surface, 8 min.—sample. (f) polyethylene surface, 8 min.—sample.

Here $\eta_w$ $(\leq 1)$ denotes the average efficiency of contact between the epoxy and the oxide.

When $\sigma$ reaches the tensile strength $\sigma_w$, the oxide fiber would break away at its root. The corresponding shear stress is given by

$$\tau_0 = \frac{d}{4l\eta_w}\sigma_w \tag{3}$$

Thus, if the shear strength $\tau_w$ at the oxide-epoxy interface is greater than $\tau_0$, fracture would occur at the root of the oxide fiber. On the other hand, the oxide fiber would pull out of the epoxy matrix if $\tau_0 > \tau_w$.

If we further denote the density of those oxide fibers which would break away at their roots by $\rho_1$ and the density of those which would pull out of the epoxy matrix by $\rho_2$, then the maximum peel force, $T_w$, that the oxide can

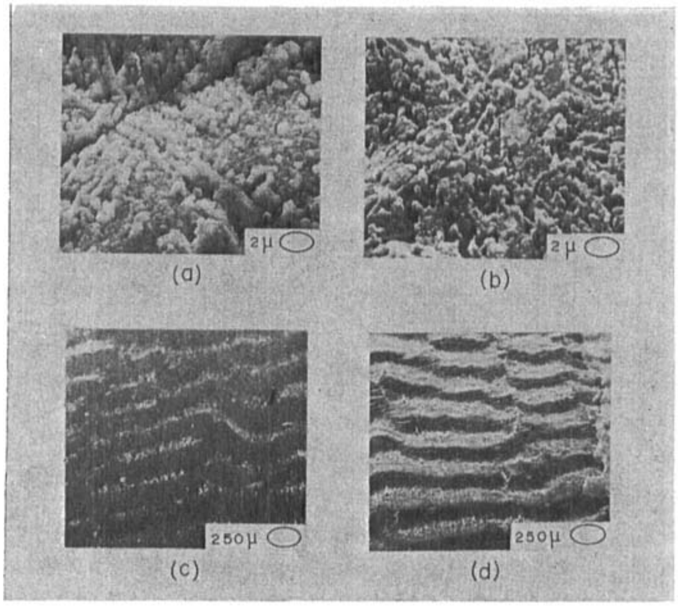

FIGURE 6 Scanning electron micrographs of the surfaces of peeled samples. (a) copper surface, 1 min.—sample, (b) polyethylene surface, 1 min.—sample, (c) copper surface, 8 min.—sample. (d) polyethylene surface, 8 min.—sample.

transmit per unit area of the copper surface is given by

$$T_w = \frac{\sigma_w \pi d^2 \rho_1}{4} + \tau_w \pi d l \eta_w \rho_2 \tag{4}$$

where

$$\frac{\pi d^2}{4}(\rho_1 + \rho_2) \leq 1 .$$

Over the rest of the copper surface not occupied by the oxide needles, the peel force is borne by the interfacial bond between copper and epoxy. The maximum force, $T_c$, that this bonded area can carry per unit area of the copper surface is

$$T_c = \left[1 - \frac{\pi d^2}{4}(\rho_1 + \rho_2)\right]\sigma_c \eta_c \tag{5}$$

where $\sigma_c$ is the bond strength per unit bonded area between epoxy and the needle free copper surface, and $\eta_c$ $(\leq 1)$ is the efficiency of contact at the copper-epoxy interface.

The total bond strength, $T$, per unit area of the copper surface is then given by

$$T = T_w + T_c$$

or

$$T = \eta_c\sigma_c + \rho_1 \frac{\pi d^2}{4}(\sigma_w - \eta_c\sigma_c) + \rho_2 \frac{\pi d^2}{4}\left(4\frac{l}{d}\eta_w\tau_w - \eta_c\sigma_c\right) \tag{6}$$

Thus the bond strength $T$ could be improved effectively if the two terms $(\sigma_w - \eta_c\sigma_c)$ and $[4(l/d)\eta_w\tau_w - \eta_c\sigma_c]$ are both positive. In other words, higher strength of the oxide fibers $(\sigma_w > \eta_c\sigma_c)$ and better shear strength $[4(l/d)\eta_w\tau_w > \eta_c\sigma_c]$ at the oxide-epoxy interface are essential to improvement in the peel strength.

The shear strength at the oxide-epoxy interface is proportional to the interfacial area $\pi\, dl$ of the oxide fiber. We have noted from close examination of the oxidized copper surface that the oxide fibers grew longer while their diameters remained about the same with increase in oxidation time. In addition, the total bond strength, $T$, in Eq. (6) is seen to increase linearly with the population of the oxide fibers as long as the two terms just mentioned are positive. It is therefore not surprising that, at shorter oxidation times, the peel strength should increase with the oxidation time in the same manner as the population growth of oxide fibers (cf. Figure 3).

At longer oxidation times (>2 min.) the bond strength $T$ at the copper-epoxy interface region apparently increased beyond the bond strength at the epoxy-polyethylene interface region. The peel strength is then no longer governed by the bond strength $T$.

## 2 Failure in epoxy-polyethylene interfacial region

Two interesting features were observed in this failure mode, namely, (a) failure occurred exclusively in polyethylene and (b) the two new surfaces of the peeled sample showed regular patterns of polyethylene ridges running parallel to one another. The ridge patterns appear to have resulted from localized yielding and tearing of polyethylene near the interface.

The yielding process of polyethylene in peeling may be viewed as a series of reversed indentation problems of Prandtl in plasticity theory[11]. Prandtl considered a flat rigid die being pressed against a semi-infinite substrate of rigid plastic material† and investigated the stress field in the substrate when the substrate begins to yield under the die pressure. If we regard the portion of epoxy adhered to the yielded polyethylene as a flat die being pulled away from the polyethylene substrate, then the cohesive failure in polyethylene would be

---

† A material that is rigid when stressed below the yield point is called a rigid plastic material.

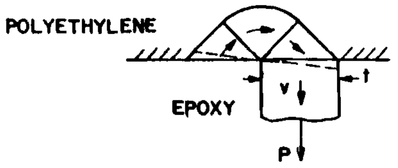

FIGURE 7 Velocity field of the reversed indentation problem of Prandtl. V: velocity of the punch.

reasonably equivalent to the reversed indentation problem of Prandtl (Figures 7 and 8). A series of parallel ridges similar to those observed in the peeled samples would then form at the surface when, by a repeated sequence, the yielded polyethylene is torn away and a new plastic zone created ahead of the point of peeling.

It is perhaps worth pointing out that the similarity between the two problems is based upon the consideration that there is a plastic zone in polyethylene immediately ahead of the point of peeling. Such a plastic zone can be expected to develop in the ductile polymer from the action of a large tearing stress near the point of peeling[7,8]. In a recent peel study of lap joints with a ductile adhesive, Kaelble[12] has reported the existence of a highly deformed but nearly constant stress region in the adhesive directly behind the peeled edge. The plateau in the stress distribution profile strongly suggests that the adhesive in this region is already stressed beyond its yield point.

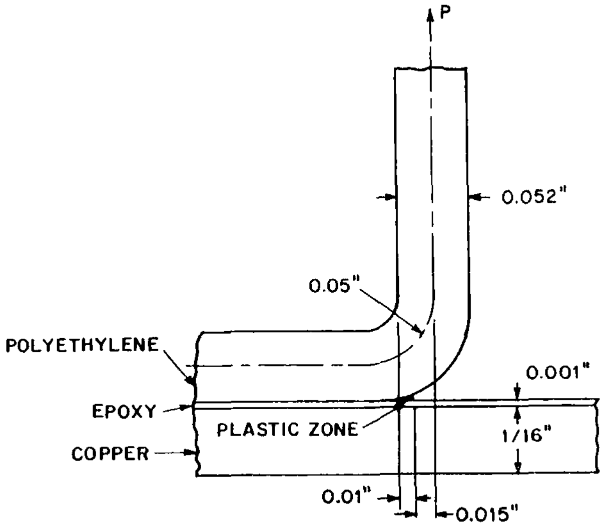

FIGURE 8 Profile of the lap joint at the steady state of peeling, with failure occurring in the epoxy-polyethylene interface region.

According to Prandtl[11], the tensile stress $p$ acting at the die (epoxy) surface when polyethylene begins to yield is given by

$$p = (2 + \pi)\frac{\sigma_y}{\sqrt{3}} \tag{7}$$

where $\sigma_y$ is the yield stress of polyethylene in simple tension. This solution is rigorous in that the stress field and the flow pattern (velocity field) satisfy the equilibrium and boundary conditions[13].

To relate the tearing stress $p$ at the epoxy surface to the peel strength, we note that because of the relatively large peel force, the low rate of peeling and the high flexibility of the polyethylene strip, the bending radius of the polyethylene strip near the point of peeling should be very small. Indeed the bending radius was found to be only about 0.05″ in our peel test. Furthermore, the point of peeling was seen to be located very close to the acting line of the peel force (about 0.025″, see Figure 8). On the basis of these findings it is reasonable to ignore the bending effect and assume the tearing stress to be in direct balance with the peel force $P$. Consequently we have for the peel force,

$$P = pt = \frac{t\sigma_y}{\sqrt{3}}(2 + \pi) \tag{8}$$

where $t$ is the size of the plastic zone. According to the reversed indentation model, $t$ is equal to the distance between the two nearest ridges at the peeled surfaces, which is about 0.01″. The nominal yield stress of polyethylene is about 1200–1800 psi (Table I) so that from Eq. (8),

$$P = 36 \sim 53 \text{ lb/in.} \tag{9}$$

These values are in good agreement with the test data obtained in our experiment (cf. Figure 4).

In Eq. (8) the peel strength is seen to increase with the size of the plastic zone. This is consistent with the observation of Bair *et al.*[4] that the peel strength of copper-polyethylene lap joints increases with the volume of polyethylene involved in the plastic deformation. To obtain the peel strength in Eq. (9) we have used the value of $t$ measured from the surfaces of peeled samples. From an analytical point of view it is preferable to determine the size of the plastic region from the elastic-plastic analysis, for this will enable us to predict the peel strength of a lap joint directly from Eq. (8). The subject is, however, very complicated and will not be pursued in this study. Nevertheless it may be noted in passing that the size of the plastic zone is likely to depend on such factors as the angle and rate of peeling, the properties and thickness of polyethylene and epoxy layers, and the bonding defects at the interface.

In applying the Prandtl's solution to the peel strength analysis, the tearing stress at the epoxy surface was assumed to be constant even at the advanced phases of plastic deformation. This is reasonable in view of the *nominal* stress-strain behaviour of polyethylene which shows little work hardening even at large *nominal* plastic strains. We have also ignored in the anaylsis the elastic deformation in the plastic zone prior to yielding. This is permissible because the thickness of the plastic zone is extremely small so that distortion of the plastic region due to the elastic deformation is negligibly small.

## References

1. R. G. Baker and A. T. Spencer, *Ind. Eng. Chem.* **52**, 1015 (1960).
2. H. N. Vazirani, *J. Adhesion* **1**, 208 (1969).
3. D. Taylor and J. E. Rutzler, 135th Meeting, ACS, Division of Organic Coatings and Plastics Chemistry, **19**, No. 1, 219, Boston, Mass., April 1959.
4. H. E. Bair, S. Matsuoka, R. G. Vadimsky and T. T. Wang, *J. Adhesion* **3**, 89 (1971).
5. G. J. Spies, *Aircraft Eng.* **25**, No. 289, 64 (1953).
6. J. J. Bikerman, *J. Appl. Phys.* **28**, 1484 (1957).
7. D. H. Kaelble, *Trans. Soc. Rheol.* **4**, 45 (1960).
8. Y. Inoue and Y. Kobatake, *Appl. Sci. Res.* **A8**, 321 (1959).
9. H. N. Vazirani, paper in preparation.
10. A. Kelly, *Strong Solids* (Oxford University Press, 1966). Chapter V.
11. W. Johnson, R. Sowerby and J. B. Haddow, *Plane-Strain Slip-Line Fields: Theory and Bibliography* (American Elsevier Publishing Co. Inc., New York, 1970). P. 64.
12. D. H. Kaelble, *Trans. Soc. Rheol.* **9**, 135 (1965).
13. J. F. W. Bishop, *J. Mech. Phys. Solids* **2**, 43 (1953).