

## A Study of the Adhesion of Polyethylene to Porous Alumina Films Using the Scanning Electron Microscope

B. W. MALPASS,\* D. E. PACKHAM,† and K. BRIGHT,\* *Van Leer (U.K.) Limited, Passfield Research Laboratories, Liphook, Hampshire, United Kingdom*

### Synopsis

An adhesive bond was formed by sintering low-density polyethylene onto aluminum with a porous anodic film. The topography of the polymer surface in contact with the anodized aluminum was studied in a scanning electron microscope, having removed the aluminum and alumina by dissolution in aqueous sodium hydroxide. The surface of the polymer appeared very rough with large projections of various forms, all of which were many times larger than the pores revealed in the anodic films by transmission electron microscopy. These projections are shown to consist, most probably, of "stacks" or "tufts" of much smaller polyethylene fibers, each of which had entered a pore in the anodic film. Thus, the scanning electron-microscopic investigation confirms the keying mechanism for the adhesion of polyethylene to porous anodic films on aluminum proposed in an earlier paper.

### INTRODUCTION

The previous paper<sup>1</sup> presented evidence to show that the mechanism of adhesion of polyethylene sintered onto porous films formed on aluminum by anodic oxidation in sulfuric or phosphoric acid involved penetration of the polymer into pores in the film. The evidence given was of an indirect nature, as it showed the effect on adhesion of varying the structure of the anodic film. Direct evidence of pore penetration was sought by examining with the scanning electron microscope the surface of the sintered polymer from which the substrate had been removed by dissolution. Interpretation of the micrographs obtained required study of the structure of the anodic films concerned in the transmission electron microscope.

### EXPERIMENTAL

Details of the polymer and substrates used, together with the methods used for anodizing, bonding, and testing were given in an earlier paper.<sup>1</sup>

\* Present address: Formica International Ltd., 84-86, Regent Street, London W.1, England.

† Present address: School of Materials Science, The University, Bath, United Kingdom.

### Scanning Electron Microscopy

Aluminum with polyethylene sintered onto it was immersed in 50% w/v sodium hydroxide solution for ca. four days. The freed polyethylene was carefully rinsed in deionized water, allowed to dry in air, and stuck to a microscope specimen stub.

Polyethylene was freed from steel substrates in a similar manner, except that immersion in ca. 5*M* hydrochloric acid for about 1/2 hr was sufficient to free the polymer.

The specimens on the stubs were coated with a thickness of ca. 100 Å gold-palladium alloy (60:40) in an apparatus evacuated to about  $2 \times 10^{-4}$  mm Hg. Samples were examined in a Stereoscan scanning electron microscope (Cambridge Instrument Co. Ltd.).

In some cases, the top surfaces of the anodic films were examined by sticking the anodized aluminum directly onto a specimen stub and coating it as described above.

### Transmission Electron Microscopy

The technique used for studying the structure of the anodic film has been described by O'Sullivan and Wood.<sup>2</sup>

A strip of ca. 5 mm by 20 mm was cut from the anodized sample and was bent into a tight U. This caused the base metal to stretch and the oxide film to fracture (see Fig. 1). The sample was shadowed with a carbon-platinum mixture at an angle approximately that indicated by arrow B in Figure 1, and carbon was then deposited from a direction indicated by arrow A. The shadowed replicas were freed from the specimen by treatment with hydrofluoric acid solution in aqueous ethanol.

Replicas, mounted on a copper specimen grid, were examined in a Siemens Elmiskop 1 electron microscope operated at 60 kV or 80 kV.

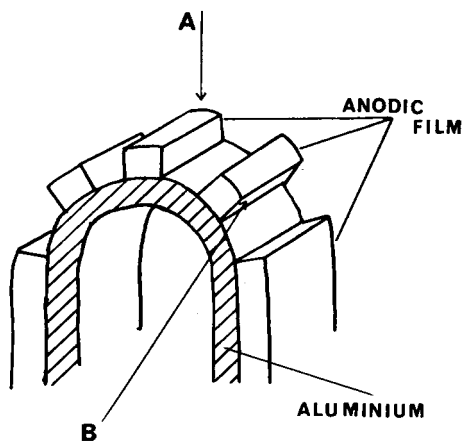


Fig. 1. Preparation of sections through anodic film for electron microscopy.

### Epoxy Resin Replicas

Araldite CY 219 and hardener HY 219 [from CIBA (A.R.L.) Ltd.] were mixed in proportions 2:1 by weight. The viscosity of this uncured resin was stated by the manufacturers to be 7 to 12 poises.

The resin was run from a tap funnel onto the surface of the anodic film to be replicated which was situated under vacuum in a desiccator. After 20 to 30 min, the air was admitted to the desiccator and the sample with the resin was carefully removed and stored at room temperature for seven days for the resin to cure.

The substrate was removed from the resin and the resin prepared for examination in the scanning electron microscope as described above for polyethylene surfaces.

### DISCUSSION AND RESULTS

Before considering the topography of the polyethylene surface revealed in the scanning electron microscope, it is convenient to discuss the structure of the anodic films from which the polymer was freed.

#### Structure of Porous Anodic Films

Aluminum anodized at constant voltage in phosphoric and sulfuric acids was used in this work.<sup>1</sup> These films would be expected to have cylindrical pores running normally from the top surface almost to the base metal.<sup>1</sup> One estimate of their diameters is 330 Å and 120 Å, respectively.<sup>3</sup>

The anodic films used were examined by transmission electron microscopy using a single-stage carbon replica technique<sup>2</sup> as described above. In one operation, both the top surface of and a section through the anodic coating could be replicated. In fact, both regions can appear on one micrograph as it flattens out when the replica is freed from the substrate, so that the parts corresponding to the two regions become coplanar or nearly so.

Figure 2 shows the two regions in a phosphoric acid-formed film. The pore openings show clearly and have irregular cross section. In certain places, it seems that two or more have merged. The cross section shows the pores, and in some cases the circular section base of the cell next to the barrier layer can be seen. Individual pores and cells show considerable deviation from their idealized cylindrical form. The formation of short-side branches is common; some pores appear to cease to function before reaching the surface, some show quite a lot of twisting along their length.

The pores in the sulfuric acid-formed films were expected to be much smaller and proved more difficult to observe. The openings could only be observed on the top surface when a chemical polishing stage was used before anodizing to remove spurious features from the metal surface. The section showed a much more regular cell structure than the phosphoric acid-formed films. The fracture surface usually passed between cells

rather than across pores, but with one specimen a taper section effect was produced enabling the pores to be clearly seen (Fig. 3).

For accurate values of pore dimensions to be obtained, measurements would have had to be made on a large number of micrographs showing the

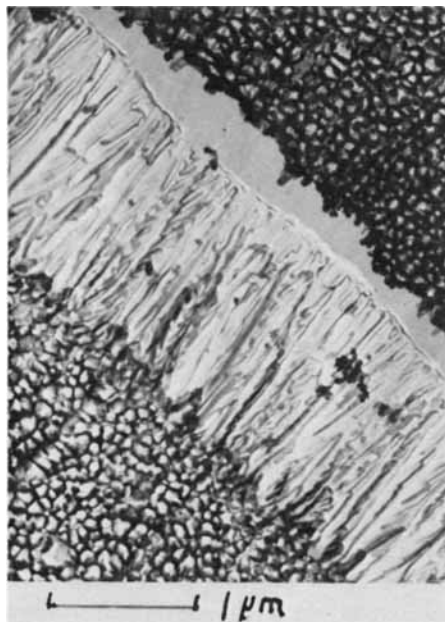


Fig. 2. Electron micrograph of top surface and section through an anodic film formed at 24 V in phosphoric acid for 60 min. Barrier layer and some of the pore bases are shown (original magnification 20,000 $\times$ ).

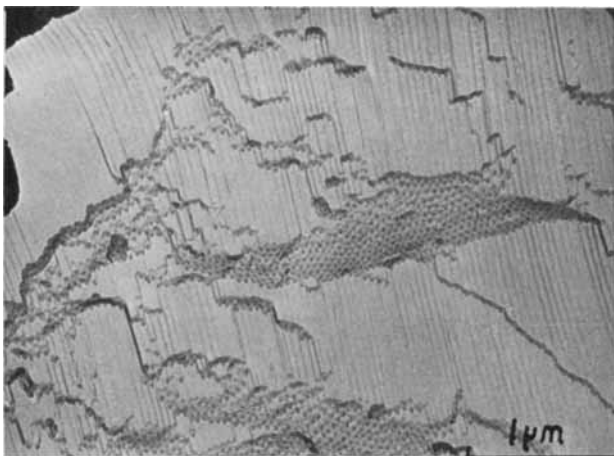


Fig. 3. Electron micrograph of a section through an anodic film formed at 20 V in sulfuric acid for 60 min. Pores can be seen where cells have fractured obliquely (original magnification 20,000 $\times$ ).

pore structure clearly.<sup>4</sup> This was not the purpose of the present work. However, measurements from the micrographs taken confirmed that the pore diameters were of the order of magnitude expected. These were for films formed in phosphoric acid, ca. 450 Å; in sulfuric acid, 200 Å.

### Topography of Polyethylene Surface

Results, previously presented,<sup>1</sup> showed that conditions favoring oxidation of the polymer are usually necessary to obtain good adhesion between polyethylene and a high-energy substrate. An exception to this was shown to be adhesion to porous anodic films on aluminum where it was suggested that some form of mechanical keying contributes to the bond. Thus, the surfaces of polyethylene which had been bonded to steel (where adhesion is oxidation dependent) and to anodized aluminum were examined in the scanning electron microscope. Preliminary examination shows that the surfaces removed from steel had only slight roughness even at high magnification, whereas those from anodized aluminum were very rough with large projections in various forms (Figs. 4, 5, and 6).<sup>5</sup>

Before considering the micrographs in more detail, it is necessary to be sure that what they show is in fact a polyethylene replica of the anodic film, and not the effect of either incomplete removal of aluminum or aluminum oxide from the polymer or of action of the etchant used on the polymer itself.

Examples of anodic films formed in both the anodizing electrolytes used were given short etches in sodium hydroxide solution, and the etched sur-

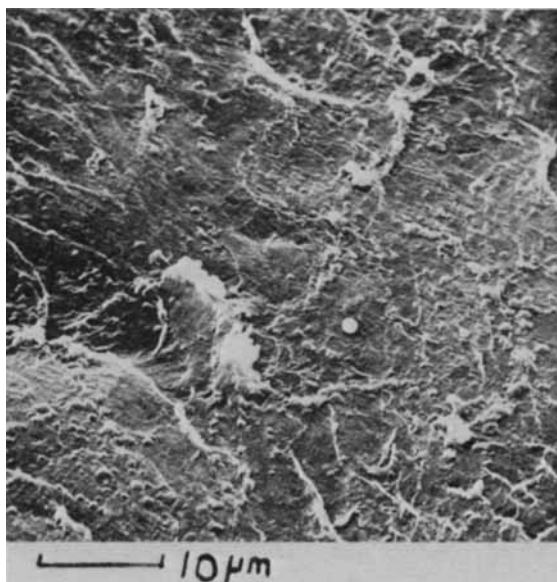


Fig. 4. Scanning electron micrograph of the polyethylene surface which had adhered to steel (original magnification 2,400 $\times$ ).



(a)



(b)

Fig. 5. Scanning electron micrograph of the polyethylene surface which had adhered to aluminum anodized in sulfuric acid at 20 V for 60 min (original magnification (a) 55 $\times$ , (b) 2,200 $\times$ ).

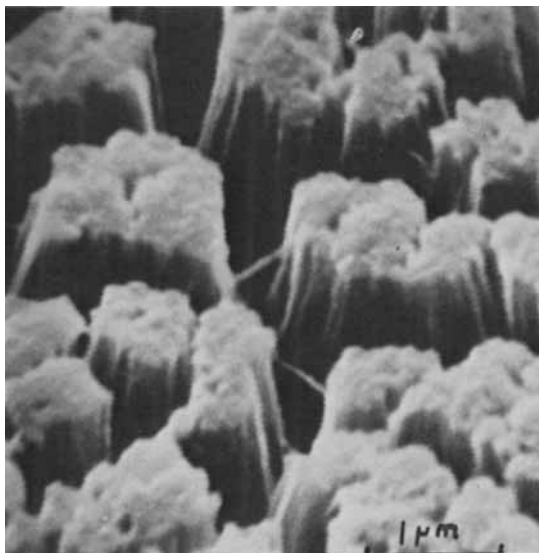


Fig. 6. Scanning electron micrograph of the polyethylene surface which had adhered to aluminum anodized in phosphoric acid at 20 V for 60 min (original magnification 26,000 $\times$ ).

faces were examined in the scanning electron microscope. The micrographs obtained in no way resembled those shown in Figures 4, 5, and 6. In some later work, one or two samples of polymer bonded to the substrate were removed from the sodium hydroxide prematurely, and these showed signs of the structure shown partly submerged beneath another more featureless layer.

Similarly, compression-molded discs of the polymer were prepared, and some were left in the sodium hydroxide etchant for about four days. The alkali had little or no effect on the surface features of the polymer as viewed in the scanning electron microscope.

Having established that the technique yields micrographs of the polyethylene surface, difficulties of interpretation remain. The projections shown in Figures 5 and 6 are several orders of magnitude greater than the expected pore size of the corresponding anodic films. Thus, the projections in the polymer from the 20-V 60-min sulfuric acid-formed films are ca. 50  $\mu\text{m}$  in diameter, and those from the 20-V, 60-min. phosphoric acid-formed films are ca. 1  $\mu\text{m}$ . The corresponding pore diameters according to Keller, Hunter, and Robinson<sup>3</sup> are 120  $\text{\AA}$  and 330  $\text{\AA}$ .

#### Interpretation of Scanning Electron Micrographs

During the sintering process forming the bond with the polymer, the anodized specimens were held at 200°C for 30 min.<sup>1</sup> It was considered whether this might have brought about a drastic change in the structure

of the film producing much larger pores. Certainly, anodic films are known to loose water under similar conditions.<sup>6</sup>

Such a drastic change appeared improbable as pores of the size envisaged ( $50\ \mu\text{m}$  or  $1\ \mu\text{m}$ ) would be visible in scanning electron micrographs of the anodic film, but none were seen. Similarly, transmission electron-microscopic examination of one phosphoric acid-anodized specimen which had been subjected to the heat treatment showed no significant differences from those which had not been treated.

That the features seen in the polyethylene were not associated with the heating was clearly established by preparing replicas of unheated anodic films using a cold-setting epoxy resin in the place of the polyethylene. A resin with low viscosity in the uncured state was chosen to facilitate penetration of the pores by the resin. The micrographs obtained from the cured resin (e.g., Figs. 7 and 8) were very similar to those obtained from corresponding films with polyethylene.

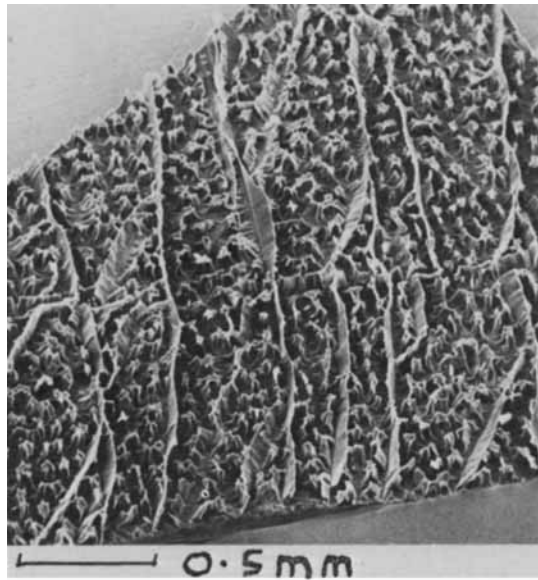
Having established that the anodic alumina films had a pore structure of the order of magnitude expected and that this was not significantly changed by the heating treatment, other explanations of the projections of the polyethylene in Figures 5 and 6 were sought. Three further possibilities were considered: (a) that the polymer only spread on the substrate where the projections occurred, (b) that the pores in the anodic film were not uniformly distributed but occurred in clusters, or (c) that the projections observed consisted of tufts or stacks or polyethylene fibers each of diameter about  $120\ \text{\AA}$  or  $330\ \text{\AA}$ .

The first possibility seems unlikely on theoretical grounds. Polyethylene, with low surface energy, should spread readily on a high-energy solid such as alumina. The epoxy resin used, despite having a different surface tension and viscosity from the polyethylene, seems to have spread in a very similar way (Figs. 5 and 6, cf. Figs. 7 and 8). Moreover, most projections observed in the micrographs appear to be much broader at the base, which does not suggest that the area between them was not wetted.

There is evidence that under certain circumstances, pores in anodic films can occur in clusters, as suggested in the second possibility above. This usually occurs for very short anodizing times and is associated with the "pseudo sub-grain structure" of the aluminum<sup>7,8</sup> The transmission electron microscopic work described above was initially undertaken to investigate this point. No evidence of pore clusters was found.

Thus, the evidence supports the last suggestion made above, that the projections of polyethylene in the scanning electron micrographs consist of "stacks" or "tufts" of the polyethylene fibers which had penetrated a pore in the anodic film. The fibers might come together under the influence of static charge or of surface tension forces when the polymer, freed from the anodic film, was withdrawn from the alkali solution. The different configurations could be a consequence of different fiber diameter or, more probably, of different length.





(a)



(b)

Fig. 7. Scanning electron micrograph of the surface of a cold-setting epoxy resin which had adhered to aluminum anodized in sulfuric acid at 20 V for 60 min (original magnification (a) 50 $\times$ , (b) 1,000 $\times$ ).

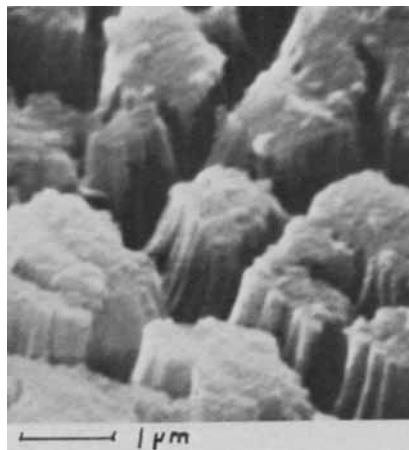


Fig. 8. Scanning electron micrograph of the surface of a cold-setting epoxy resin which had adhered to aluminum anodized in phosphoric acid at 20 V for 60 min (original magnification 24,000 $\times$ ).

In some high-magnification scanning electron micrographs (e.g., Figs. 5b and 6), the polyethylene appears to have a fibrous structure supporting this interpretation.

## CONCLUSIONS

Work previously reported<sup>1</sup> produced indirect evidence that when polyethylene is sintered onto porous anodic films on aluminum, penetration by the polymer of the pores of the film occurs and this contributes to the adhesion. This paper describes a technique for examining the topography of the polymer at the interface with the substrate which confirms that the polymer penetrates a significant proportion of the length of the pores of the anodic film.

This work was carried out from the Passfield Research Laboratories of Van Leer (U.K.) Limited. The permission of the Research Director to publish it is gratefully acknowledged. The transmission electron microscopy was done with the help of Mr. L. Phillips at the City University, London.

## References

1. D. E. Packham, K. Bright, and B. W. Malpass, *J. Appl. Polym. Sci.*, **18**, 3237 (1974).
2. J. P. O'Sullivan and G. C. Wood, *Trans. Inst. Metal Finishing*, **47**, 142 (1969).
3. F. Keller, M. S. Hunter, and D. L. Robinson, *J. Electrochem. Soc.*, **100**, 411 (1953).
4. J. P. O'Sullivan and G. C. Wood, *Proc. Roy. Soc.*, **A317**, 511 (1970).
5. K. Bright, B. W. Malpass, and D. E. Packham, *Nature*, **223**, 1360 (1969).
6. G. A. Dorsey, *J. Electrochem. Soc.*, **115**, 1057 (1968).
7. N. C. Welsh, *J. Inst. Metals*, **85**, 129 (1956).
8. M. G. Hollo, *Proc. 1st Int. Congr. Metallic Corrosion*, Butterworths, London, 1962, p. 45.

Received August 23, 1973

Revised May 3, 1974