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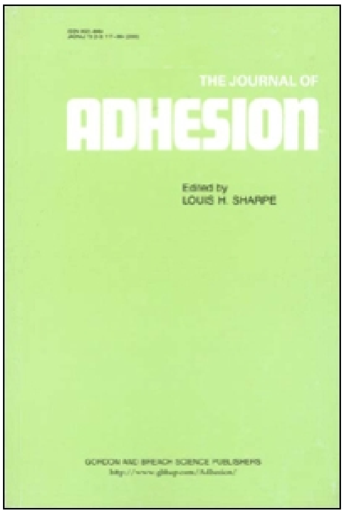

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Adhesion of Polyethylene to Metals: The Role of Surface Topography

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Previous work established the importance of the fibrous substrate topography in obtaining good adhesion of polyethylene to matt black oxide films formed on copper in alkaline solution. In this paper the effect of the very rough surface topography is shown to be general. Anodising treatments for copper and zinc and a high temperature oxidation for steel are described which give a very rough surface consisting (respectively) of fibrous, dendritic and blade-like growths. The peel strength of polyethylene to these substrates is high even under circumstances, for example when the polymer is stabilised with antioxidant, where adhesion to a chemically similar smooth surface is low. The high peel strength is associated with large amounts of energy being dissipated during peeling in plastic deformation of the polymer near the interface. It is suggested that this is caused by the development of high shear stress concentration at the fibre ends causing yielding in a large volume of polymer.

INTRODUCTION

In a previous paper[1] it was shown that the good adhesion of polyethylene to a matt black oxide formed on copper in alkaline chlorite solution or "Ebonol C" was a consequence of the fibrous nature of the substrate surface, and was independent of the oxidation of the polymer which usually occurs when polyethylene adheres strongly to metals. If this is the case, the phenomenon should be general, and polyethylene should adhere well to any high energy surface if a similar fibrous topography can be produced.

In this paper adhesion to a number of high energy substrates with fibrous or quasi-fibrous topographies is reported. Sykes[2] found that adhesion of polyethylene to copper which had been anodised was high, even when coatings were applied in nitrogen which, in the light of more recent work,[1] suggests that a fibrous topography may be involved. This system was examined as a starting point.

Adhesion to steel is impaired by inhibiting polyethylene oxidation. Therefore if a fibrous surface giving oxidation-independent adhesion can be prepared on steel, this will confirm the importance of surface topography.

Adhesion to zinc can be almost as low as that to copper so a similar treatment for zinc was sought.

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 density 0.916 g/cm^3 and m.f.i. 20. For some experiments, antioxidant (2,6-di-tert-butyl-p-cresol) and copper complexing agent (oxanilide) were incorporated into the polymer as previously described.[1]

Copper

Deoxidised sheet 1.2 mm thick (B.S. 1172) was chemically polished.[3] It was anodised at 90°C in 4 M sodium hydroxide solution using a copper cathode. A current density of 143 amp/m^2 was employed until, after 5 minutes, passivation occurred. The anodised copper was then rinsed with distilled water and acetone.

Steel

General purpose bright mild steel sheet 1.2 mm thick (B.S. 1149) was degreased, and etched in hydrochloric acid.[1] Some samples were heated for 4½ to 5 hours at 450°C in a furnace through which at a rate of 2 l/min flowed nitrogen which had been bubbled through water at 40°C.

Zinc

0.8 mm thick zinc sheet (B.S. 849) was degreased in trichloroethane and etched for 30 seconds in 10% sulphuric acid. For electroforming, zinc panels were made the cathode in a cell with zinc anode and 100 g/l potassium hydroxide containing 0.5 g/l zinc oxide as electrolyte. Electrodeposition was carried out for various times at room temperature using current densities of either 20 or 130 amp/m^2.

Polymer coating and peel testing

Panels of metal 10 × 15 cm were melt coated with polymer in air at 200°C and the adhesion was subsequently measured by a 180° peel test at a peel rate of 250 mm/min. These procedures have been described in detail.[3]

RESULTS AND DISCUSSION

Anodised copper

Hurd, Krieble and Pfeiffer[4] studied the anodising of copper in hot sodium hydroxide and found that at intermediate current densities (*ca.* 140 amp/m^{-2}) thick black oxide films were produced. It was to such films that Sykes[2] found good adhesion of polyethylene applied in nitrogen. Similar films were produced in this work. X-ray analysis of oxide scraped from the surface indicated it consisted of copper(II) oxide: no copper(I) oxide was detected. The peel strength of polyethylene applied to the surface was high irrespective of whether it was stabilised against oxidation (Table I). The scanning electron microscope revealed that the surface was uniformly covered with a fibrous oxide growth (Figure 1a).

TABLE I

Effect on adhesion of polyethylene to anodised copper of addition of antioxidant and complexing agent to the polymer

Substrate	Additives in polymer	Peel strength N mm^{-1}	No. of peels
Anodised copper	None	3.34±0.12	11
Anodised copper	100 ppm antioxidant	3.19±0.09	8
Anodised copper	2000 ppm antioxidant	3.50±0.18	4
Anodised copper	5000 ppm antioxidant	3.41±0.14	4
Anodised copper	2500 p.p.m. antioxidant +2500 p.p.m. oxanilide	3.29±0.04	7
Reduced anodised copper	None	2.59±0.37	8

(95% confidence limits are indicated)

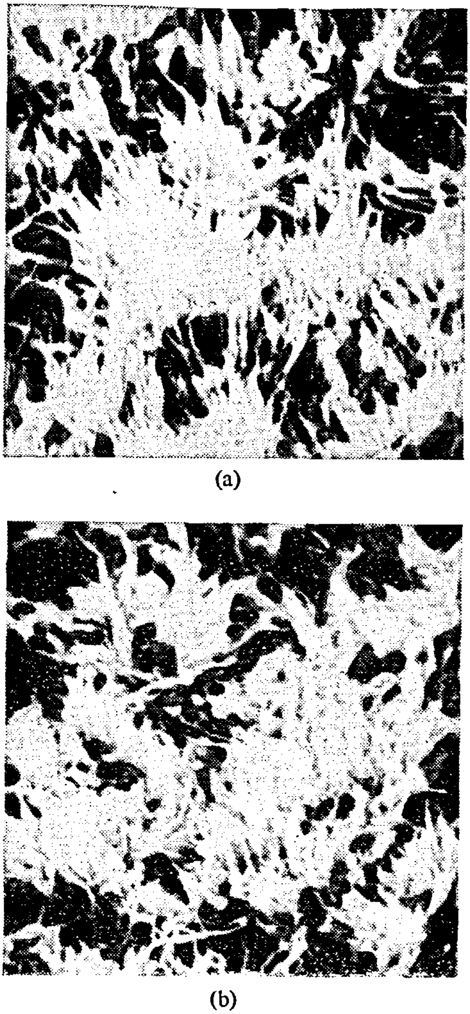


FIGURE 1 (a) Scanning electron micrograph of copper anodised at 90° in 4M sodium hydroxide at a current density of 140 amp/m^2.
(b) A similar anodised film subsequently electrolytically reduced to copper. (Base of micrographs represent 11 μm.)

Table I shows that when the anodised film was electrolytically reduced[1] to copper (and inevitably oxidised superficially in air to copper(I) oxide) the adhesion, although lower, was still good. The surface examined in the scanning electron microscope (Figure 1b) looked similar to the freshly anodised film, but it is likely that the additional processes of reduction, rinsing and so on have somewhat altered the topography leading to lower adhesion. A similar effect was found with the matt black oxide films formed chemically.[1]

Steel

In the literature there are several reports of the growth of very rough oxides on steel. Thus Gulbransen and Copson[5] were able to produce fine whiskers, blade like whiskers or larger semicircular platelets according to the oxidation conditions. The blade-like growths were formed when pure iron was oxidised at 450°C in an atmosphere of 10% water vapour and 90% argon. Electron diffraction indicated that the blades consisted of α iron(III) oxide. Under similar oxidation conditions Talbot and Bigot[6] found that the oxidation temperature affected the oxide formed. Below 400°C γ-Fe_2O_3, above 550°C α-Fe_2O_3, and at intermediate temperatures a mixture was produced. In both cases a magnetite layer was detected adjacent to the metal.

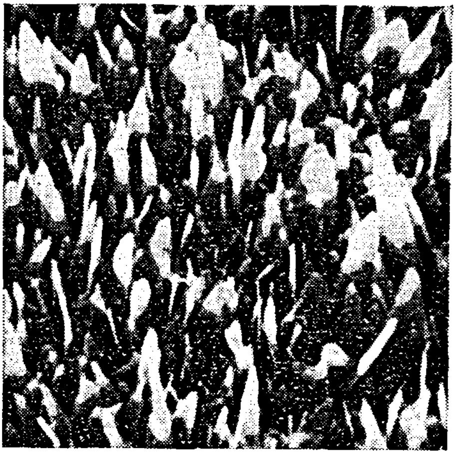


FIGURE 2 Scanning electron micrograph of a blade-like oxide coating prepared on steel by heating in a nitrogen/water atmosphere at 450°C. (Base of micrograph represents 5.5 μm).

This work provided a starting point for producing a fibrous oxide on steel as a substrate for polyethylene coating. Preliminary experiments showed that conditions for black-like growth of oxide were not critical. Uniform and reproducible oxidation occurred on etched mild steel heated for 4½ to 5 hours at 450°C in a stream of nitrogen which had been bubbled through water at 40°C. The oxidised surface was dark brown coloured and matt in texture.

The scanning electron microscope revealed an array of blades which had grown perpendicular to the metal surface (Figure 2).

Adhesion to the steel with blade-like oxide was good and independent of oxidation of the polymer (Table II). The peel strength in the region of 2.5 N mm^{-1} should be compared with values of 2.1 and 0.14 N mm^{-1} respectively for unstabilised polyethylene and polyethylene with 1000 p.p.m. antioxidant, applied to etched mild steel under similar conditions.

TABLE II

Effect of concentration of antioxidant in polyethylene on adhesion to steel treated to give a blade-like surface oxide

P.p.m. antioxidant in polyethylene	Peel strength N mm^{-1}	No. of peels
0	2.73±0.19	8
500	2.48±0.09	8
1000	2.12±0.23	4
2000	2.16±0.18	4
5000	2.53±0.20	4

(95% confidence limits are indicated)

Other work[7] on whisker growth suggests that it should be possible to grow oxide whiskers on nickel, chromium and stainless steel. Thus it is likely that pretreatments for these metals could be developed which would give good adhesion to polyethylene containing antioxidant.

The blade-like oxide on steel prepared at 450°C was matt in appearance. Using this as a possible indication of a fibrous surface, attention was given to well known steel colouring treatments. Simons[8] gives some thirteen treatments applied to steel by swabbing or dipping.

TABLE III

Three colouring solutions for steel[8] used as pretreatments for adhesive bonding

Solution A	Solution B	Solution C
2.8 g Ferric chloride	8.9 g Ferric chloride	4.5 g Mercuric chloride
1.5 g Ferrous sulphate	40.1 g Alcohol	4.5 g Ammonium chloride
8.5 g Nitric acid	50 g Water	91 g Water
3.2 g Alcohol		
84 g Water		

Three of these which were tried are shown in Table III. They gave matt black oxides of magnetite when the treated panels were immersed in boiling water for 10 minutes. This gave oxidation independent adhesion with polyethylene though inferior to the steel panels oxidised at 450°C. The oxides suffered from poor adherence to the metal in places. It is possible that other solutions mentioned by Simons[8] or modifications of the treatment will be more effective.

Zinc

Diggle, Despic and O'Bockris[9] have successfully electrodeposited dendrites of zinc onto a zinc wire cathode from potassium hydroxide solution. Arrowsmith[10] has used a similar technique to form nodules and pyramids on copper and nickel and has found that these improved adhesion of an epoxide resin.

In this work it was necessary to grow small denrites evenly all over a zinc panel. Zinc was made the cathode in a cell with a zinc anode and similar

TABLE IV

Adhesion of polyethylene to zinc electroformed at 20 amp/m^2 for various times

Electro-deposition time (minutes)	Peel strength N mm^{-1}	No. of peels
5	0.90±0.05	8
10	1.04±0.13	8
20	1.23±0.11	6
30	1.73±0.14	6

(95% confidence limits are indicated)

TABLE V

Effect of antioxidant in the polymer on the adhesion of polyethylene to zinc electroformed at 130 amp/m^2 for various times

Electrodeposition time (minutes)	P.p.m. antioxidant in polyethylene	Peel strength N mm^{-1}	No. of peels
5	0	1.13±0.19	4
5	2000	0.80±0.15	5
10	0	4.25±0.33	9
10	2000	4.83±0.94	6

(95% confidence limits are indicated)

electrolyte to that used by Diggle.[11] Two current densities, 20 and 130 amp/m^{-2}, were used. Adhesion to zinc treated at the lower current density increased with electrodeposition time to 1.73 N mm^{-1} for 30 minutes' treatment (Table IV). The higher current density gave good adhesion for shorter treatment times (Table V). The high level of adhesion was maintained when polymer containing antioxidant was used. Figure 3 shows the surface of the zinc treated for 10 minutes at 130 amp/m^{-2} and reveals a forest of zinc dendrites.

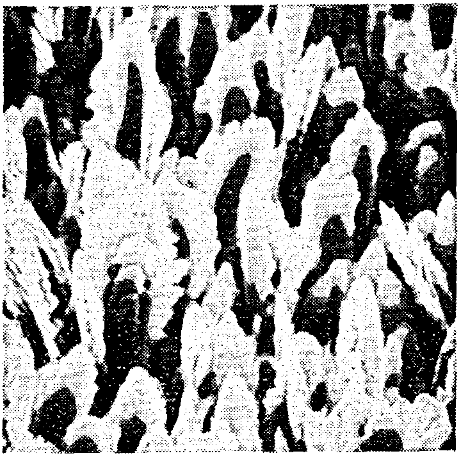


FIGURE 3 Scanning electron micrograph of zinc dendrites produced on zinc by electrodeposition in potassium hydroxide solution using a current density of 130 amp/m^2 for 10 minutes. (Base of micrograph represents 22 μm.)

The peel strengths in Tables IV and V should be compared with a value of 0.46±0.14 N mm^{-1} for chemically polished zinc and unstabilised polymer and of practically zero for polymer containing antioxidant.

A similar electroforming pretreatment might well give good bonds between stabilised polyethylene and other metals. Wranglen,[12] for instance, has shown that dendrites may be grown on lead, cadmium, silver and tin. Another pretreatment for zinc which might be successful is anodising in alkali which has been shown[12] to produce a porous oxide similar to those found effective on aluminium.[14] Anodising of magnesium is used as a base for paint,[15] and might also prove effective in this context.

Mechanism of adhesion

It seems that the adhesion of polyethylene to high energy substrates may fall into two extreme categories: (a) dependent on polymer oxidation and (b) for suitably fibrous and porous substrates independent of polymer oxidation. Many particular cases involve no doubt some combination of the two extremes.

This paper and the previous two in the series[1,3] have been concerned with systems falling into the second category. Some half dozen systems have been described in detail where adhesion to a smooth chemically similar surface was either very poor or dependent on the oxidation of the polymer, but adhesion to a rough fibrous surface was good and oxidation-independent.

TABLE VI

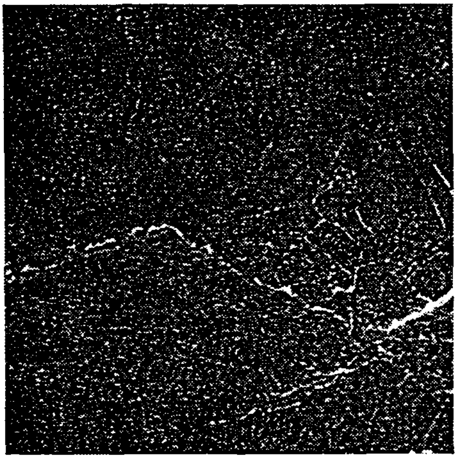
Effect on adhesion of polyethylene to copper of removal of low molecular weight material from the commercial polymer

Copper pretreatment	Polyethylene	Peel strength N mm^{-1}	No. of peels
Chemically polished	Commercial	0.14±0.02	21
	Purified	0.21±0.06	8
20 minutes chlorite-formed film[3]	Commercial	1.32±0.06	8
	Purified	1.62±0.14	8

(95% confidence limits are indicated)

The concept of the "weak boundary layer" has often been invoked to explain cases of poor adhesion. Bikerman[16] for example pointed out that thermodynamic incompatibility would mean that when polyethylene solidified from the melt, low molecular weight fractions and additives would tend to be rejected to the interface, forming such a layer. It could be argued that the low adhesion to, say, polished copper is because of this, but with a fibrous oxide film these deleterious fractions are occluded within the mass of fibres leaving stronger bulk materials to bear the stress. If this was the case, polyethylene purified from low molecular weight materials by precipitation from xylene would be expected to give markedly better adhesion to the polished surface substrate, but much the same level of adhesion to the fibrous surface. When this experiment was tried, however, there was only slight improvement to the polished surface and rather more to the fibrous one (Table VI). It seems more likely that these small changes in peel strength reflect changed mechanical properties of the polymer following the changed molecular weight distribution, rather than a boundary layer effect.

In seeking an explanation of the effect of such fibrous interfaces it needs to be borne in mind that peel strength is a measure of the energy per unit area dissipated in fracture. Thus the peel strength includes the surface energy required to create the fracture surfaces and the energy associated with viscoelastic and plastic deformation involved in the fracture. The surface energy term would be the work of adhesion for interfacial failure and the work of cohesion for cohesive failure. Under the conditions of test used both would be negligible compared with the measured peel strengths. Thus a peel strength of 1 N mm^{-1} is equivalent to 1 kJ m^{-2} but the work of cohesion of polyethylene based upon solid surface energy is only about 60 mJ m^{-2}.



(a)

(b)

FIGURE 4 Scanning electron micrograph of polyethylene remaining on: (a) chemically polished copper, (b) alkaline–chlorite oxidised copper substrates after peeling. (Base of micrograph represents (a) 40 μm, (b) 50 μm.)

Visual observation of the various substrate surfaces after peeling suggested that with low peel strengths little or no polymer remained, but for high peel strengths, there were significant quantities. Such observations have been reported by other workers.[17] The scanning electron microscope bore this out. Figure 4 shows both polished copper and chlorite oxidised copper surfaces after peeling. A straight forward, but somewhat insensitive, quantitative estimate for the polymer remaining on the substrate was made by scraping the polymer from defined areas of different substrates after peeling and obtaining the mass of polymer from the melting endotherm on a differential scanning calorimeter. These results show that the average thickness of polymer remaining on the substrate rises monotonically with peel strength (Figure 5). Similar results were obtained by Bair *et al.*[17]

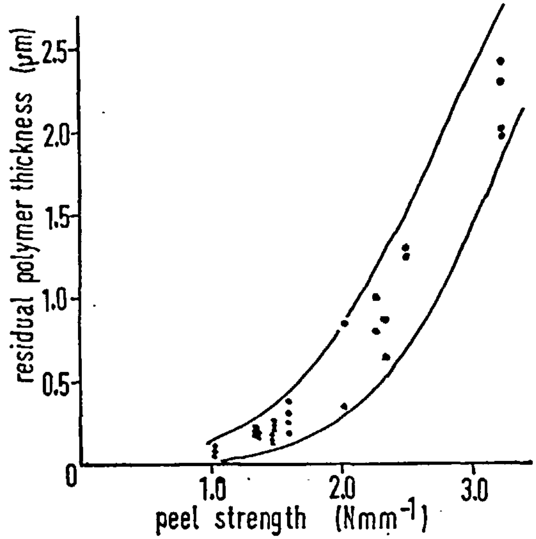


FIGURE 5 Adhesion of polyethylene to copper with various surface treatments. Thickness of polymer remaining on the substrate after peeling.

Electron micrographs, such as Figure 4b, show that the fracture region consists of large numbers of highly drawn filaments of polymer and Figure 5 implies that the mass of polymer involved in this severe deformation rises with peel strength. The higher peel strengths associated with the fibrous topography are the result of the extra work required for plastic deformation of larger volumes of polymer. Why should the fibrous surface cause so much more plastic deformation?

Bair *et al.*[17] in discussing their work on adhesion of polyethylene to Ebonol C formed films on copper attributed the additional plastic deformation to the presence of voids trapped between the fibres at the interface. By considering the stress concentrations produced by a circular hole in a linear elastic lamina they argued that the voids caused yielding in the polymer away from the interface in this way involving more polymer in plastic deformation. We do not think that this mechanism applies in the cases we have described. For the voids to be realistically idealised as hemispherical bubbles on a plane surface as Bair *et al.* have done, they must surely be at least comparable in size to the substrate surface roughness, i.e. the surface fibres. The scanning electron microscopy in this work has not detected such voids. The evidence is that there is good wetting between polymer and the fibrous substrates described here. However, in systems different from these, voids in the interfacial region have been found to improve adhesion.[18]

Wang and Vazirani[19] applied the theory of the strength of fibre reinforced composite materials to the adhesion of polyethylene *via* an epoxy resin layer to Ebonol C-formed films on copper. In some cases they obtained failure near the copper–epoxy interface, and their discussion in terms of the tensile strength of the fibres and the possibility of "pullout" would seem appropriate. In the present work, however, failure of the bond occurs within the polyethylene, and does not involve significant breaking or pulling out of fibres. Nevertheless fibre composite theory has some bearing on the problem.

Near the interface, the present system in some respects resembles a composite with discontinuous fibres in a resin matrix. When such a composite is stressed so that fibres and matrix are deformed elastically, stress is transferred from one to the other in the region of the fibre ends. This leads to the build up of high shear stresses at the fibre ends. Cox[20,21] has derived a relationship in terms of matrix shear modulus G_m and fibre tensile modulus E_f for the ratio of maximum shear stress $\tau_{\max}$ at the fibre ends to maximum tensile stress $\sigma_{f\,\max}$ carried by the fibre. For a fibre of length L the expression is

$$\tau_{\max}/\sigma_{f\,\max} = \left(\frac{G_m}{2E_f \ln R/r_f}\right)^{\frac{1}{2}} \coth\left[\left(\frac{2G_m}{R_f \ln R/r_f}\right)^{\frac{1}{2}} \frac{L}{4r_f}\right] \qquad (1)$$

where r_f is the fibre radius and R the interfibre spacing.

Substituting plausible values[21] into Eq. (1) indicates that the ratio $\tau_{\max}/\sigma_{F\,\max}$ would be about 0.04 for oxide fibres such as chlorite formed or Ebonol C formed films on copper. This suggests that before the fibre could be stressed to failure a shear stress greater than the polymer yield stress would be generated (Table VII). Failure then would be by fibre-matrix debonding or by plastic deformation of the polyethylene matrix. It is the latter which is observed here.

Two further considerations indicate the likelihood of polymer plastic deformation in this case. Stress concentration, which depends on the particular shape of the fibre end, will make the shear stresses even higher than Eq. (1) indicates.[22] Moreover, in a peel test the stress is applied at an angle to the fibre axis, and this makes shear failure of the interface or matrix favourable compared with tensile failure of the fibres, even with continuous fibres.[21]

Thus it is to be expected that the presence of fibres on the substrate would lead to high shear stresses around the fibre ends, giving failure by plastic deformation of the polymer initially around the fibre tips and then, as the stress concentration is relieved, further into the bulk of the polymer. In an artificial way the peeling process can be imagined as occurring in sequential stages. First the stress concentration builds up around the fibres nearest to the peel front, then yield in the polymer occurs moving away from the fibres into the bulk polymer relieving the stress concentrations. The plastic deformation is followed by fracture and the stress system builds up around fibres further from the peel front, so the process is repeated. In this way considerable work is done in plastic deformation of the polymer around the fibre ends and into the bulk.

TABLE VII

Fibre tensile stress σ_F and interfacial shear stress τ predicted by Eq. (1) for oxide (e.g. CuO) fibres in a low density polyethylene matrix

Material	Property	Value
Polymer	Shear modulus	30 MN/m^2
	Shear strength	†4.6 MN/m^2
Fibres	Tensile modulus	300000 MN/m^2
	Tensile strength	*2000 MN/m^2
	Length	2.5 μm
	Radius	0.05 μm
	Interfibre spacing	0.4 μm
Fibres in Polymer matrix	$\tau_{\max}/\sigma_{f\ \max}$	0.042
	Maximum fibre stress for $\tau_{\max}$=polymer shear strength	*110 MN/m^2
	Maximum interfacial shear stress for $\sigma_{f\ \max}$=fibre strength	†84 MN/m^2

* † These pairs of values should be compared.

By contrast, with a relatively smooth substrate, for example polished copper, and in the absence of chemical effects such as extensive polymer oxidation, the situation is analogous to a surface step in a stressed solid. Intense concentration of stress is produced close to the interface at the peel front. This would cause local yielding of the polymer near the interface and the high stress region to be translated along the interface in the peeling direction. Because of the absence of serious interfacial discontinuities, the high stress and failure region passes smoothly along the peel front and only involves a little polymer in plastic work giving a low peel strength. Similarly a low peel strength would be observed if, instead of cohesive failure, the polymer adhesive failure at the interface occurred.

SUMMARY AND CONCLUSIONS

It has been shown that the adhesion of polyethylene to high energy substrates with a fibrous or similar topography is good, even when the polymer is stabilised with antioxidant. Suitable treatments for copper, steel and zinc have been investigated and possible treatments for nickel, chromium, stainless steel, lead, cadmium tin and silver have been suggested.

The mechanism of adhesion to these substrates is associated with the deflection of the peeling path away from the interface into the bulk of the polymer where a much larger volume of polymer is plastically deformed during fracture. This large amount of plastic deformation accounts for the high peel strength.

The work opens the way to achieving strong bonding between stabilised polyolefins and high energy substrates.

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