Surface treatment of ultra high molecular weight polyethylene to enhance adhesion and conductivity properties*

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We have found that swelling the surface of ultra high molecular weight polyethylene (UHMWPE) with an organic solvent and then subsequently cooling with the solvent present can significantly modify surface properties. In particular, metal/polymer adhesion can be enhanced and, if graphite is added to the solvent, surface conductivity can be enhanced. The enhanced adhesion properties may relate to an increased ductility of the preswollen polymer at elevated temperatures. The modified conductivity can be attributed to graphite particles trapped at the surface of the material. In order to qualitatively explain some of our results, rheological and optical observations on UHMWPE melts are also presented.

(Keywords: polyethylene; molecular weight; conductivity)

INTRODUCTION

The bonding of polyolefins and ultra high molecular weight polyethylene (UHMWPE) has proved to be a difficult problem and a number of techniques have been developed to promote their bondability and other associated properties[1]. These include treatment with a chromic acid mixture, flame treatment, introduction of functional groups, photo-grafting treatment and treatment with solvents. It was suggested that a solvent pretreatment appears to be both economical and effective and hence most development has been concentrated on this method. Osborne and Broughton[2] developed a solvent treatment technique to promote the bondability of polyolefin materials with vulcanizable elastomers. A sheet of isotactic polypropylene was immersed in xylene at 130°C for 15 s and then dried for 2 h in air. The treated sheet was placed in a slab mould with a natural rubber. The assembly was vulcanized under positive pressure at 141°C for 45 min. A high bond strength was claimed. Katoh[3] developed a low temperature solvent treatment technique followed by exposing the treated surface to u.v. radiation to promote the dyeing and bonding ability of the polyolefin surfaces. In particular, improvement on bonding to vulcanizable elastomers has been achieved. Cree[4] developed a method of improving the bondability of high modulus, high strength polyethylene fibres using the solvent treatment technique. The material was exposed to solvent xylene at 110°C for 1 min and then incorporated into an epoxy resin to form a composite material. Bastenbeck, *et al.*[5] discovered that by first swelling the polycarbonate surface, followed by etching the treated surface, a satisfactory metal coating onto the surface could be achieved.

The purpose of this paper is to describe experimental observations on the surface treatment of UHMWPE to improve bonding and conductivity properties. In previous work[6], we have shown that UHMWPE can absorb solvent locally at the surface without any appreciable dissolution occurring. The kinetics of solvent uptake is shown in *Figure 1* for UHMWPE in decalin at a temperature of 125°C. At this temperature the weight uptake is linear with time and very large solvent loadings can be achieved if required. The solvent penetrates as a sharp front as observed from SEM and n.m.r. imaging experiments. *Figure 2* shows the n.m.r. image of the time dependence for the developing decalin concentration profile, where both solvent uptake and swelling can be followed. Scanning electron micrographs that have been shown previously[7], also indicate a sharp concentration profile. In addition, Gao *et al.*[6] have shown that the swollen material has a significantly enhanced elevated temperature ductility when compared to the normal bulk deformation behaviour of UHMWPE. In this paper, local surface swelling and ductility to improve bonding and conductivity are explored.

EXPERIMENTAL

Materials

The polymer used was UHMWPE HG415 ($\bar{M}_w$, $\bar{M}_n > 10^6$) manufactured by Hoechst. A lower molecular weight polyethylene PE0006-60 ($\bar{M}_w = 1.3 \times 10^5$, $\bar{M}_n = 2 \times 10^4$) from BP Chemicals was also used for comparison. For the bonding test, the polymer was pretreated using decalin as solvent. This simply entailed immersing the polymer sample in a bath of decalin that was preheated to the required swelling temperature (125°C) and holding the sample in the bath for the required time. On removal, the sample was allowed to dry for a period of at least 24 h in ambient conditions.

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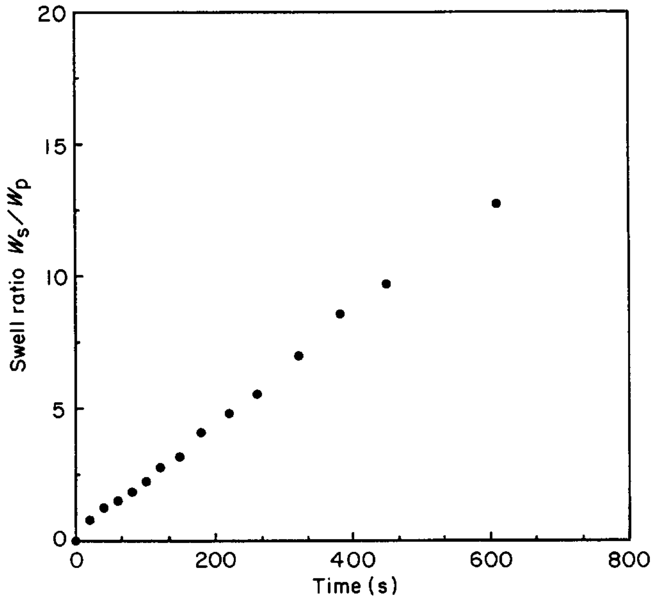

Figure 1 Solvent weight uptake *versus* period of immersion time for HG415 in decalin: swelling temperature, 125°C; sample thickness, 0.585 mm; initial disc diameter, 25 mm; W_s/W_p, weight of solvent/weight of initial sample (from Gao *et al.*[6])

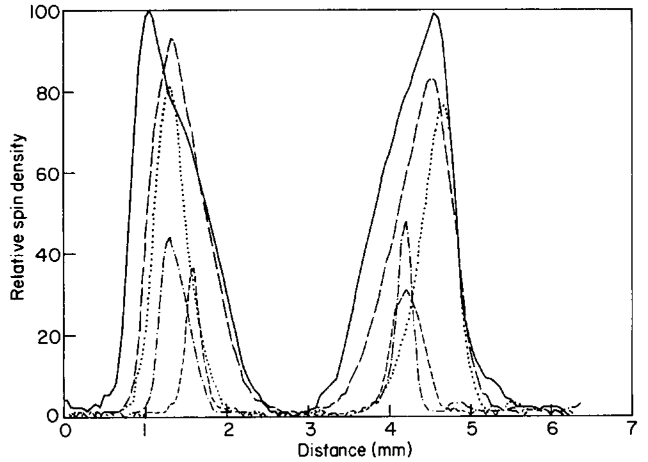

Figure 2 Solvent concentration profiles measured using spin echo n.m.r. imaging: swelling temperature, 120°C; initial sample thickness, 2.1 mm; field gradient, 16 kHz cm^{-1}. Time: (——) 1543 s; (– –) 1264 s; (···) 829 s; (–·) 301 s; (-·-) 173 s

Samples with dimensions of 40 mm x 40 mm x 2 mm were used. In the case of the surface impregnation test, the polymer was pretreated using a decalin/graphite suspension. A 30% w/w concentration of graphite was added and the swelling procedure was as described before. The mean particle size of the graphite used was ~5 μm. The experimental method for surface swelling is described in more detail elsewhere[6–8]. Swelling experiments using PE006-60 could not be successfully carried out because simultaneous dissolution occurred with the swelling causing severe distortion and loss of material.

Bonding experiments were carried out using aluminium strips. Two types of pretreatment were applied to the metal surface before bonding: (1) sand blasting, in which case the metal surface was first blasted using sand and then degreased in acetone; (2) the metal was simply immersed in acetone for ~30 min. In both cases, the metal surface was dried in the ambient conditions for at least 1 h before bonding.

In order to enhance bonding properties between the above two interfaces in some cases, adhesive was also applied. In this study, Araldite adhesive was used as a basis for comparison. The maximum lap shear strength between aluminium and Araldite adhesive is ~30 MPa.

Bonding test

The lap shear test was used to quantify the bonding properties between polymer and metal. The joint geometry for the lap shear test is illustrated in *Figure 3*. When used, the Araldite adhesive was applied onto the polymer and metal surface as a very thin layer and left to partially cure at room temperature before bonding. The two surfaces were then brought together under a positive specified pressure at an elevated temperature for a period of 1 h. Subsequent cooling to ambient temperature was carried out at the curing pressure. Mechanical testing was carried out on a JJ tensile testing machine at a fixed cross-head speed of 50 mm min^{-1}. The lap shear strength was simply determined by the ratio of the force at failure and the cross-sectional area of the joint.

Table 1 shows a summary of the lap shear strength obtained from joints between aluminium and polyethylenes under different curing conditions. No sand blast treatment was applied to the aluminium surface. It can be seen that under certain conditions, a lap shear strength of 7 MPa can be achieved with aluminium/PE006-60 and 7–10 MPa with pretreated HG415. Poor bonding corresponds to a measured lap shear strength of <0.2 MPa and from the table it can be seen that poor bonding

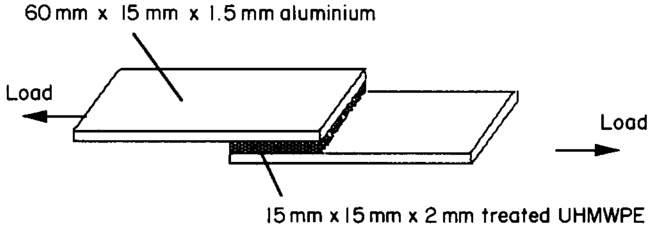

Figure 3 Lap shear test specimen for determination of bondability of treated UHMWPE

Table 1 Lap shear bond strength (MPa) obtained under different curing conditions[a]

		Materials		
Temperature (°C)	Pressure (MPa)	PE006-60	HG415	Pretreated HG415
180	0.25	Poor	Poor (1), (4)[b]	Poor (1), (4)
	10	7.0	Poor (1), (4)	Poor (1), (4)
	50	~7.0	Poor (2)	Poor (2)
150	0.25	Poor	Poor (1), (4)	~7.0
	10.0	~1.0	Poor (1), (4)	~10.0
	50.0	~1.0	Poor (1), (2)	~10.0
120	0.25	Poor (3), (5)	Poor (3), (5)	Poor (3), (5)
	10.0	Poor (5)	Poor (5)	Poor (5)
	50.0	Poor (5)	Poor (5)	~1.0

[a] In all cases, curing was held for 1 h

[b] A 'poor' bond strength refers to a lap shear strength of <0.2 MPa. For explanation of the numbers in parentheses, see Discussion and Conclusions

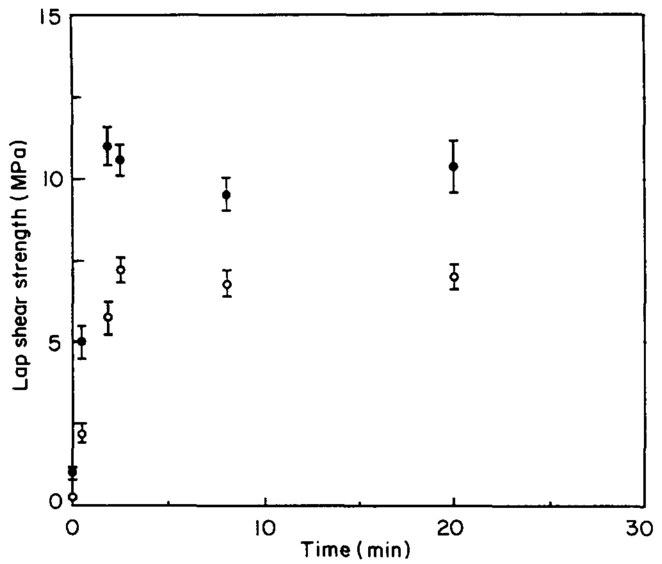

Figure 4 Maximum lap shear strength *versus* initial solvent treatment time: (○) adhesion of aluminium/polyethylene/aluminium; (●) adhesion of aluminium/Araldite/polyethylene/Araldite/aluminium. Curing conditions: temperature, 150°C; pressure, 0.25 MPa; time, 1 h. The aluminium surface has been pretreated with sand blasting and subsequently degreased with acetone

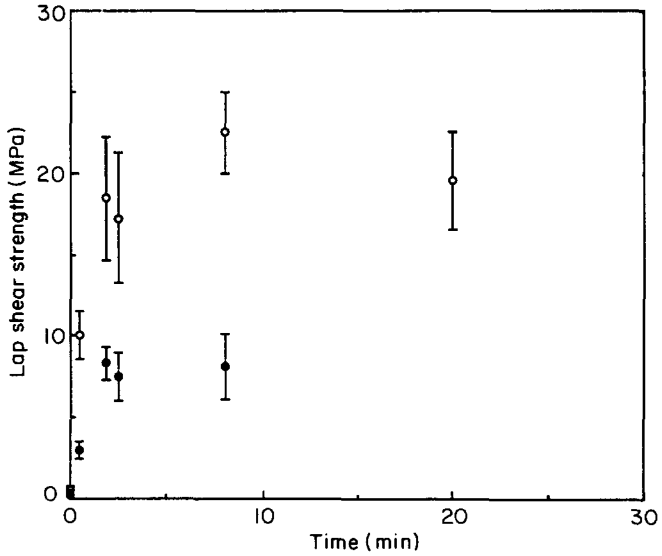

Figure 5 Maximum lap shear strength for two-state curing *versus* initial solvent treatment time: (○) adhesion of aluminium/Araldite/polyethylene/Araldite/aluminium; (●) adhesion of aluminium/polyethylene/aluminium. Curing conditions for stage I: temperature, 120°C; pressure, 0.25 MPa; time, 1 h; for stage II: temperature, 160°C; pressure, 0.25 MPa; time, 20 min

occurred for untreated UHMWPE under all conditions tested.

We now concentrate on the regime where good bonding for treated UHMWPE was obtained in the region of 150°C. *Figure 4* shows the maximum lap shear strength *versus* solvent treatment time. Two sets of data are shown in the graph: the open symbols represent the lap shear strength *versus* swelling time for the adhesion of aluminium and HG415 surface without any adhesive; and the filled symbols for the adhesion with the addition of Araldite adhesive. Error bars represent the standard deviation of five tests at each condition. The bonding took place under a pressure of 0.25 MPa at a temperature of 150°C. The curing time was 1 h. The metal surface was pretreated with sand blasting in both cases. It can be seen from *Figure 4* that the lap shear strength increased rapidly initially with swelling and then levelled off after ~1 min of treatment. The maximum lap shear strength without Araldite was 7 MPa and 10 MPa with adhesive.

Figure 5 shows the lap shear strength *versus* swelling time for 'two-stage curing'. At stage I, the joint was brought together under a pressure of 0.25 MPa at a temperature of 120°C and cured for 1 h. At stage II, the joint was further heated to 160°C with the pressure remaining at 0.25 MPa and kept under constant conditions for another 20 min. The effect of the addition of Araldite adhesive was also studied. The filled symbols represent data without adhesive and the open symbols represent data with adhesive. As can be seen from *Figure 5*, a maximum lap shear strength of 10 MPa was achieved in the former case and 20 MPa in the latter case. (Note, the metal surface in these tests was not sand blasted and the maximum lap shear strength for aluminium/Araldite/aluminium is 30 MPa.)

Figures 6a–c show the scanning electron micrographs of bonding surfaces. *Figure 6a* shows the pure aluminium surface without sand blast treatment. It shows that the metal has a relatively rough surface structure. *Figure 6b* shows a cross-section of the bonded surface between preswollen HG415 and aluminium. *Figure 6c* shows the ruptured aluminium surface from the two-stage curing process without Araldite. The residue of polymer left on the metal surface showed that the rupture has occurred in the bulk of the polymer.

Surface impregnation

Table 2 shows the resistance on the surface of the material measured between resistance probes placed 2.5 cm apart *versus* polymer pretreatment time. The discs used were 5 mm thick and had 40 mm diameters. The treatment temperature was 120°C. The excess amount of graphite accumulated on the surface of the specimen was removed by immersing the dried treated specimen in pure decalin at room temperature. The samples were again left to dry at 80°C for at least 2 h. It can be seen from *Table 2* that the pure polymer has a resistance well above $10^{14}\,\Omega$, whereas, after a short treatment time with the graphite/decalin suspension, the resistance is reduced to ~800 Ω. *Figure 7* shows the scanning electron micrograph of the surface. The graphite has become impregnated into the surface and there is sufficient polymer present to ensure that the graphite particles are bonded to the surface.

Melt structure and rheology

In an attempt to explain some of the results on the regimes where poor and good bonding occurs as described by *Table 1*, some observations made on the flow characteristics of UHMWPE are included. The structure of polyethylene melt was studied by extruding polyethylene melt at 180°C through a slit die connected

Table 2 Surface resistance *versus* pretreatment time

Treatment time (min)	Resistance (Ω)
0	$>10^{14}$
0.5	800
5	650
10	700

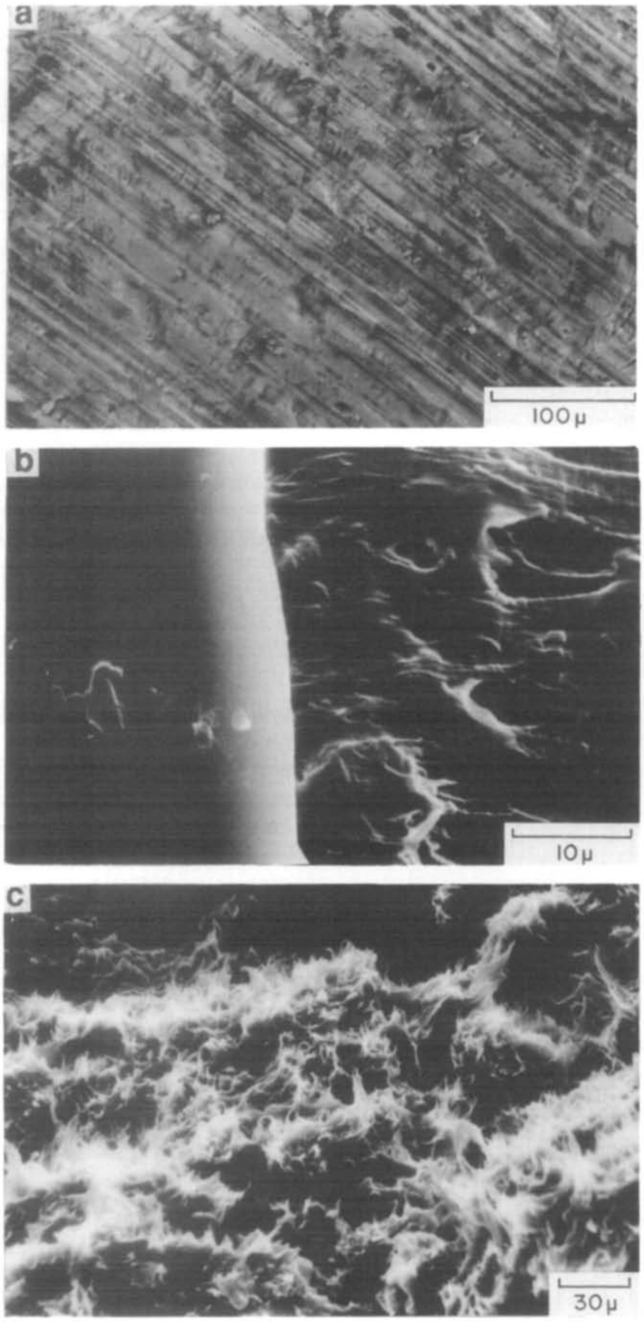

Figure 6 Scanning electron micrographs of bonding surfaces: (a) pure aluminium surface; (b) cross-section of the aluminium/pretreated HG415 bonding surface; (c) ruptured aluminium surface from aluminium/pretreated HG415 bond

to a Davenport extrusion rheometer. A detailed description of the optical set-up and experimental procedure is given elsewhere[9]. In the experiments described here, the optical depth of melt viewed was 3 mm and the width of channel was 7 mm. The most striking feature observed for molten UHMWPE was that there is intrinsic light scattering visible in the quiescent melt. Lower molecular weight polyethylenes such as PE006-60 are optically transparent, but as seen in *Figure 8a* UHMWPE shows a persistent and strong scattering. The material retains a memory of its initial powder form and the scattering associated with the individual grains of UHMWPE powder remains even during flow. At certain flow rates we observe further effects, some of which can be seen in *Figure 8b*. When flow occurs it became clear that there is

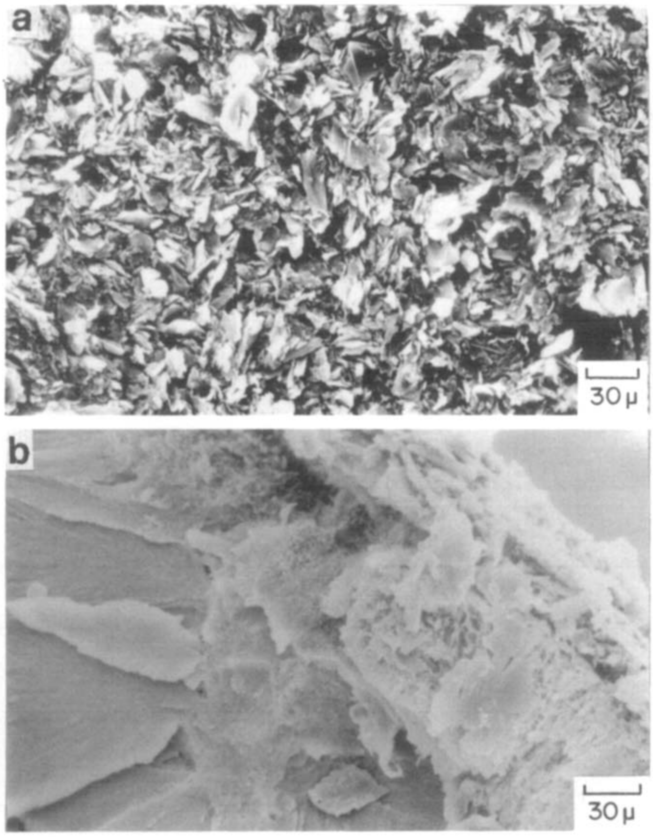

Figure 7 Scanning electron micrographs of the impregnated HG415 surfaces using a graphite/decalin suspension: (a) main surface; (b) cross-section

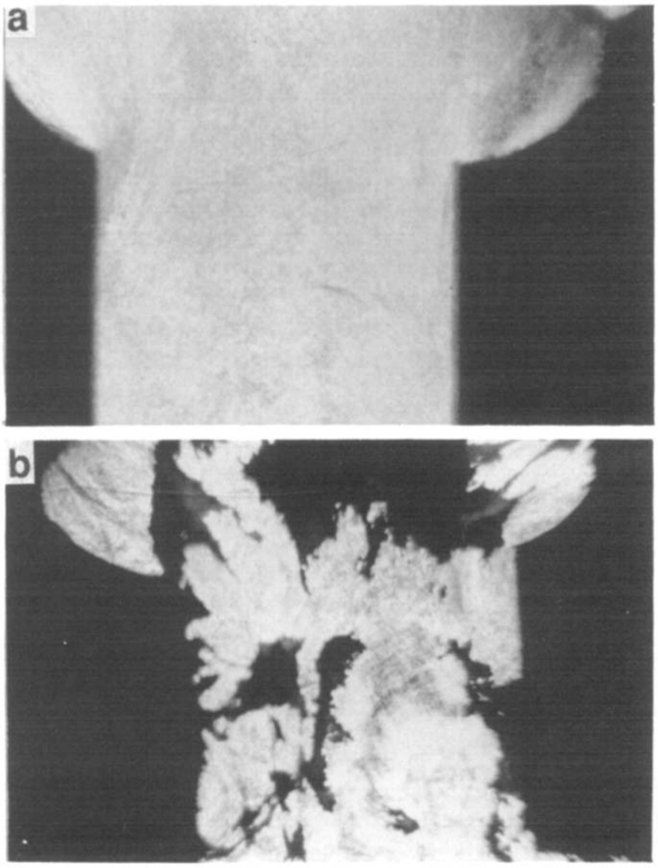

Figure 8 Photographs showing the melt structure of HG415 melt extrusion through a slit die with the dimension of 7 mm × 3 mm (width × depth): (a) volumetric flow rate, 0.76 cm^3 min^{-1}; (b) volumetric flow rate, 11.4 cm^3 min^{-1}. Temperature, 180°C. Bright field observation

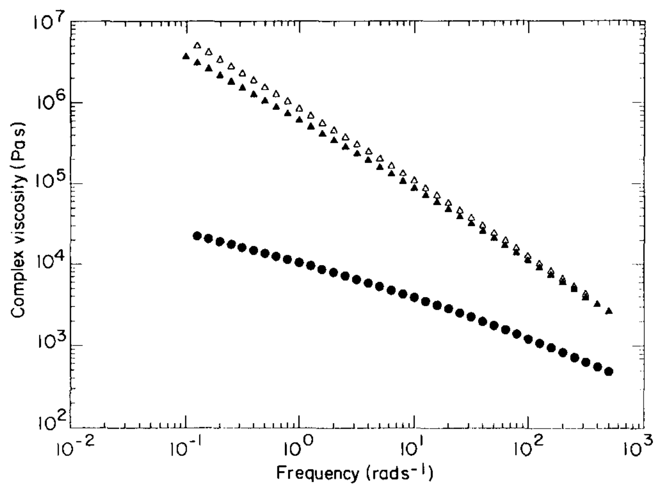

Figure 9 Plot of complex viscosity as a function of angular frequency for (●) PE006-60, (△) HG415 and (▲) pretreated HG415 (swollen in decalin for 500 s at 125°C followed by drying at room temperature): Rheometrics RDS II; temperature, 180°C; strain, 5%

Table 3 Summary of melt structure and rheological results

Material Melt structure	PE006-60 Structure free	HG415 Structured	Gel crystallized UHMWPE Structured
Wall slip $T = 180°C$	No slip	Slip, voidage and fracture	Slip, voidage and fracture
Rheology $T = 180°C$ $\omega = 0.1$ rad s^{-1}	$\eta^* = 2 \times 10^{4a}$	$\eta = {}^*5 \times 10^6$	$\eta^* = 4 \times 10^6$

[a] η^*, complex viscosity (in Pa s)

considerable slip at the wall. Again for PE006-60 no sign of slippage has been observed by us. In addition, surface voidage can become apparent and this is shown in *Figure 8b* by the large black regions that appear adjacent to the glass window polymer interface. In some instances this can also be associated with visible fracture of the polymer within the bulk of the material.

In addition to these optical observations, plots of the complex viscosity of the materials under test are shown. Data were obtained from a rheometrics RDS-II at 180°C over a frequency range of 0.1–500 rad s^{-1}. Strains of 5% were used for each material. *Figure 9* shows that the complex melt viscosity of UHMWPE is considerably greater than that of PE006-60 and it also shows that a preswollen HG415 material returns essentially to its original melt form when reheated above its melting range in a way described previously by Bastannansen *et al.*[10]. The collective findings reported here are summarized in *Table 3*.

DISCUSSION AND CONCLUSIONS

It has been shown that at 150°C, reasonable surface bonding can be achieved between a pretreated UHMWPE and aluminium surface. Without pretreatment, and at all temperatures tested, it was not possible to obtain a bond strength of >0.2 MPa for UHMWPE. *Figures 4* and *5* show that with pretreatment, surface swelling can rapidly cause an increase in bond strength. Indeed, extended swelling times offer no further advantage to bond strength. The addition of Araldite adhesive further assists bond strength as does the two-stage cure process.

Swelling creates a locally porous surface with a low entanglement density[7,11]. This leads to a surface that has good ductility above 80°C and below the melting region ($T_m \sim 145°C$) as demonstrated by the high drawability and subsequently high modulus of fully swollen samples[6,7]. Above T_m, the very high zero shear viscosity inhibits material fluidity.

It is assumed that enhanced surface ductility achieved by preswelling assists bonding between metal and polymer. It is difficult to envisage that the surface treatment has caused chemical modifications to the polymer and therefore the enhanced bonding seems to be related to the physical bonding of the polymer and metal surfaces.

A persistent structural feature of the swollen interface is shown in *Figure 6b* where striations parallel to the metal surface can be seen within the polymer. This feature is not observed if there is no swelling treatment. The striations indicate plastic ductility near the interface and it is this that appears to assist bonding. If adhesion of the treated polymer is carried out well above T_m (say, ~170°C) the lap shear strength would be similar to that of the untreated polymer, i.e. ~0.2 MPa. The implication here is that above T_m, the polymer 'returns' to its usual fully entangled state in the same way as reported by Bastannansen *et al.*[10] for gel fibres.

The two-stage curing data show a further improvement in bond strength. These data suggest that once initial low temperature ductility has taken place, further elevated temperature annealing can help both the bonding of the polymer and Araldite. The enhancement here is perhaps due to the re-entanglement at the swelled polymer surface, which will in turn result in an increase in the polymer strength.

There appear to be a number of possible reasons why poor bonding is observed under a range of conditions indicated in *Table 1*, and the optical observations offer some possible explanations.

A necessary condition to form a good polymer/solid interface is that the two surfaces 'wet' each other and form intimate molecular contact. A number of factors that could lead to poor wetting are listed below:

1. Surface voidage. The flow experiments of UHMWPE melts show that under certain circumstances regions of voidage can occur between the polymer/glass interface of the test cell. This effect was not seen for lower molecular weight polyethylene melts. Surface voidage will inevitably reduce interface contact area and may also cause local surface stress concentrations. Both effects would reduce potential bond strength.
2. Surface and bulk fracture. UHMWPE melts do not always flow as a continuum and fracture planes were seen both at the surface and within the bulk. These planes will weaken bonding.
3. Low contact pressure. If the contact pressure between the interfaces is too low, intimate contact will not be possible.
4. Slip at wall. For UHMWPE melts, slip at the wall is observed, and this is clearly a manifestation of poor bonding between the two interfaces.

Given that the necessary wetting has been generated, a further condition for good bonding between the interfaces is necessary (no. 5) and this requires that $\gamma_{sp} < \gamma_{sa} + \gamma_{pa}$, where γ_{sp} is the free surface energy of the solid/polymer interface, γ_{sa} the solid/air interface and γ_{pa} the polymer/air interface.

In *Table 1* the mechanisms that may be responsible for poor bonding in some of the regions studied are indicated by the above numbers. For example, for pretreated UHMWPE at 180°C and 0.2 MPa pressure we believe that surface voidage (1) and wall slip (4) are reasons why poor bonding was seen at these conditions. The results that seem most difficult to explain are associated with PE006-60. It is not clear why PE006-60 at 180°C and 0.2 MPa pressure should give poor bonding when 10 MPa pressure gives 7.0 MPa. At 0.2 MPa and 180°C the material can readily flow, which means that poor contact pressure (3) is an unlikely reason for weak bonding.

Concerning conductivity enhancement, the surface swelling technique offers other advantages in terms of its ability to modify surface structure when graphite was suspended in the swelling solvent. It was found that these particles could penetrate into the surface of the material as shown in *Figure 7*. In the case of graphite, this leads to a modest improvement in the surface conductivity of the material. It was found that the conductivity appeared to be relatively insensitive to swelling time, swell temperature and particle concentration. From the micrographs shown in *Figure 7*, it is estimated that a graphite particle concentration of ~25% was achieved at the surface and if this could be raised to the percolation limit for the particles, it might be expected that the conductivity could be further increased.

It has been shown that UHMWPE has melt structure and also that surface voidage, slip and fracture may contribute to poor melt adhesion. If surface preswelling is carried out, reasonable bonding can be achieved at a temperature close to the melting range of the material but if the temperature is reduced further to 120°C, below the melting range, poor bonding results. The science behind interface bonding is not well understood. De Gennes[12] has made recent attempts to explain polymer/polymer interface bonding but the polymer/metal interface remains unexplained. Our results suggest that material ductility appears to play a role in the essential wetting of the two interfaces although many other factors must also influence the problem.

At present, we are unable to develop a useful mathematical model to describe the bonding results reported here and clearly further experiments need to be carried out. However, there does appear to be clear evidence that polymer surface ductility is an important aspect, at least for UHMWPE.

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REFERENCES

1 Kinlock, A. J. 'Adhesion and Adhesives', Chapman and Hall Ltd, London, 1987
2 Osborne, A. P. and Broughton, R. M. *UK Pat. 3699459*, 1960
3 Katoh, K. *Eur. Pat. Appl. 883020000*, 1988
4 Cree, S. H. *Eur. Pat. Appl. 881168889*, 1989
5 Bastenbeck, E. W., Haydu, J. and Bellemare Jr, R. A. *Eur. Pat. Appl. 883087538*, 1989
6 Gao, P., Mackley, M. R. and Nicholson, T. M. *Polymer* 1990, **31**, 237
7 Mackley, M. R. and Solbai, S. B. *Polymer* 1987, **28**, 1115
8 Gao, P. *PhD Thesis* University of Cambridge, 1990
9 Mackley, M. R. and Moore, I. P. T. *J. Non-Newt. Fluid Mech.* 1986, **21**, 337
10 Bastannansen, C. W. M., Froehling, P., Pijpers, A. J. and Lemstra, P. J. in 'Integration of Fundamental Polymer Science and Technology' (Eds P. J. Lemstra and L. A. Kleintjens), Elsevier, London, 1985, pp. 508–526
11 Smith, P. J. and Lemstra, P. J. *J. Mater. Sci.* 1980, **15**, 505
12 De Gennes, P. G. *CR Acad. Sci. Paris* 1990, **310**, 1169