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 properties¹. 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 Broughton² 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. Katoh³ 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. Cre€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.

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The purpose of this paper is to describe experimental observations on the surface treatment of UHMWPE to improve bonding and conductivity properties. In previous work⁶, 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 previously⁷, 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 ($M_w > 10^6$) manufactured by Hoechst. A lower molecular weight polyethylene PE0006-60 ($M_w = 1.3 \times 10^5$, $M_n = 2 \times 10^4$) 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.
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 aluminum and Araldite adhesive is \( \sim 30 \text{ MPa} \).

**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 \( \text{h} \). 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 \( 50 \text{ mm min}^{-1} \). 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 aluminum and polyethylenes under different curing conditions. No sand blast treatment was applied to the aluminum surface. It can be seen that under certain conditions, a lap shear strength of \( 7 \text{ MPa} \) can be achieved with aluminum/PE006-60 and \( 7-10 \text{ MPa} \) with pretreated HG415. Poor bonding corresponds to a measured lap shear strength of \( <0.2\text{ MPa} \) and from the table it can be seen that poor bonding

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 \( \sim 5 \mu\text{m} \). 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 aluminum 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 \( \sim 30\text{ min} \). In both cases, the metal surface was dried in the ambient conditions for at least 1 \( \text{h} \) before bonding.

**Table 1** Lap shear bond strength (MPa) obtained under different curing conditions

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Pressure (MPa)</th>
<th>PE006-60</th>
<th>HG415</th>
<th>Pretreated HG415</th>
</tr>
</thead>
<tbody>
<tr>
<td>180</td>
<td>0.25</td>
<td>Poor</td>
<td>Poor</td>
<td>Poor (1), (4)</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>7.0</td>
<td>Poor (1), (4)</td>
<td>Poor (1), (4)</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>( \sim 7.0 )</td>
<td>Poor (2)</td>
<td>Poor (2)</td>
</tr>
<tr>
<td>150</td>
<td>0.25</td>
<td>Poor</td>
<td>Poor (1), (4)</td>
<td>( \sim 7.0 )</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>( \sim 1.0 )</td>
<td>Poor (1), (4)</td>
<td>( \sim 10.0 )</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>( \sim 1.0 )</td>
<td>Poor (1), (2)</td>
<td>( \sim 10.0 )</td>
</tr>
<tr>
<td>120</td>
<td>0.25</td>
<td>Poor (3), (5)</td>
<td>Poor (3), (5)</td>
<td>Poor (3), (5)</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>Poor (5)</td>
<td>Poor (5)</td>
<td>Poor (5)</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>Poor (5)</td>
<td>Poor (5)</td>
<td>( \sim 1.0 )</td>
</tr>
</tbody>
</table>

\(^4\)In all cases, curing was held for 1 \( \text{h} \)

\(^5\)A 'poor' bond strength refers to a lap shear strength of \( <0.2\text{ MPa} \). For explanation of the numbers in parentheses, see Discussion and Conclusions

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; \( W/W_p \), 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, 16kHz cm\(^{-1} \). Time: (---) 1543 s; (---) 1264 s; (--·) 829 s; (--) 301 s; (--) 173 s.

Figure 3 Lap shear test specimen for determination of bondability of treated UHMWPE.
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 and subsequently degreased with acetone.

We can see 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 $10^{14}$ Ω, 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
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.

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 7mm x 3mm (width x depth): (a) volumetric flow rate, 0.76 cm³ min⁻¹; (b) volumetric flow rate, 11.4 cm³ min⁻¹. Temperature, 180°C. Bright field observation.
cause an increase in bond strength. Indeed, extended temperatures tested, it was not possible to obtain a bond strength of >0.2 MPa for UHMWPE. These data suggest that once initial bonding of the polymer and Araldite. The enhancement in bond strength 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 Tm (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 Tm, 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 \( \gamma_{sp} \) is the free surface energy of the solid/polymer interface, \( \gamma_{sa} \) the solid/air interface and \( \gamma_{pa} \) 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\(^1\)\(^2\) 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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