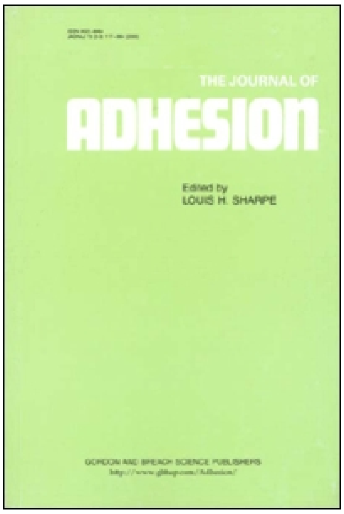

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Bonding of Polyethylene to Gold

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NOTE
Bonding of Polyethylene to Gold

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I. INTRODUCTION

X-ray photoelectron spectroscopy (XPS) has had a profound impact on the surface chemical analysis of polymers, particularly in the identification of chemical species resulting from surface treatments that render so-called "unbondable" or non-polar polymers such as polyethylene suitable for adhesive bonding.[1] This has occurred because XPS is a sensitive probe for examining the chemical nature of organic and inorganic surfaces. Recently, several investigators have adopted the XPS techniques as a primary method for attempting to answer some questions which are basic to adhesion science.[2] These are, i) Is it necessary to oxidize polymer surfaces prior to adhesive bonding or to generate such polar surfaces in situ in order to obtain a strong adhesive joint?, and ii) Does one have to invoke covalent bonding at the polymer-metal interface to explain a strong adhesive joint?

That both of these phenomena do exist is not disputed. What we shall demonstrate in this report, however, is that strong adhesive joints can be made with the polyethylene-gold couple without oxidation of the polymer at the interface and without generating organometallic (covalent) bonds across the interface. Dispersion forces are more than sufficient to support the large shear stresses that we report. Our earlier efforts[3] using wettability, infrared spectroscopy, microscopy and dynamic mechanical properties, have shown that i) the manner in which a polymer surface is formed and ii) the associated mechanical properties of the surface region are of prime importance in the fabrication of a strong adhesive joint. Clearly, in trying to answer the important questions posed earlier, it is imperative that we choose surfaces which are intrinsically free of oxygen.

We have chosen to fabricate our specimens for adhesive bonding in a vacuum chamber at ~10^{-4}Pa (~10^{-6} torr) to avoid the possibility of spurious oxidation. The ubiquitous nature of oxygen dictated this approach. To avoid difficulties in separating the bonded composite for examination, we have elected to view the interface through a thin layer of gold which was transferred to the polyethylene during the bonding operation. A schematic of our composite is shown in Figure 1.

II. EXPERIMENTAL

1. Materials

a. Polyethylene

The polyethylene used in this study was a high purity, high molecular weight material characterized by extremely low levels of contamination. The polymer had a melt index of 0.20, density $\rho = 0.923$ g/cm^3 and an antioxidant concentration of 0.06 pbw. The melting point was 115°C as determined by DSC. The antioxidant was 1,3,5, trimethyl-2,4,6 tri(3,5 ditertbutyl-4-hydroxy benzyl benzene), obtained from

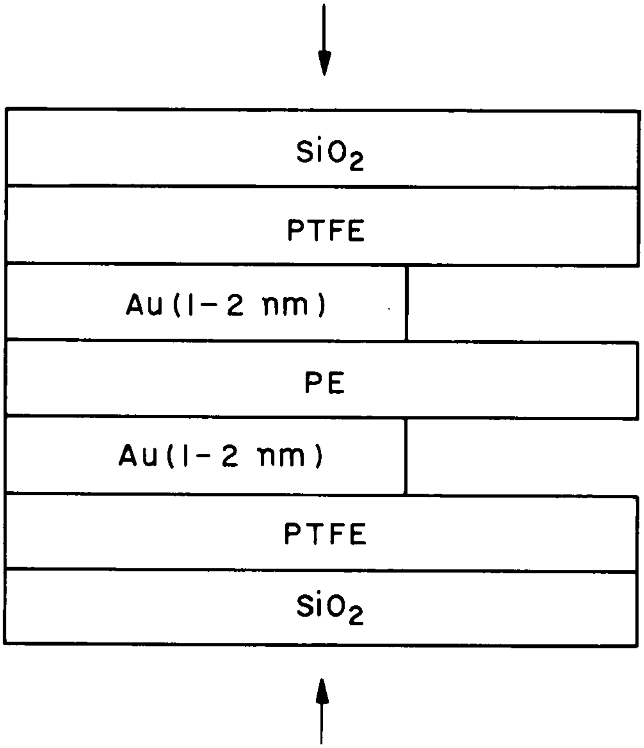

FIGURE 1 Schematic of the composite used to fabricate polyethylene-gold specimens for both XPS and adhesive joint strength measurements.

Ethyl Corp. as Ethyl 330. The polymer did not contain any reprocessed or scrap compound.

The polyethylene was supplied as an extruded tube ~5 cm in diameter. We removed any effects due to orientation of the film by suspending the tube on two quartz rods and relaxing the polymer in a forced air oven at a temperature of 125°C for 5 minutes. Since the tubing was uniaxially orientated, there was considerable relaxation in the axial direction. The polyethylene was solidified by lowering the oven temperature. The polymer was easily removed from the glass rods while exercising care not to abrade the inner portion of the tubing since this was the surface that would ultimately come in contact with the gold. These specimens were extracted for a period of 10 minutes with refluxing HPLC grade methylene chloride (D-143 Fisher Scientific Co.). This process was repeated a minimum of two times. The polyethylene was air dried to remove most of the solvent, then placed into a vacuum station (Edwards, Model 306) and pumped down to 10^{-4}Pa and kept at this pressure for 1 hour to remove all traces of residual solvent. The purpose of this procedure was to remove antioxidant and other spurious contaminants to prevent their migration to the interface during the bonding operation.

Examination of the polyethylene by transmission FTIR infrared spectroscopy revealed a complete absence of any oxidized species (Figure 2). In addition, XPS analysis showed essentially no oxygen-containing species (Figure 2 and 3B), in the

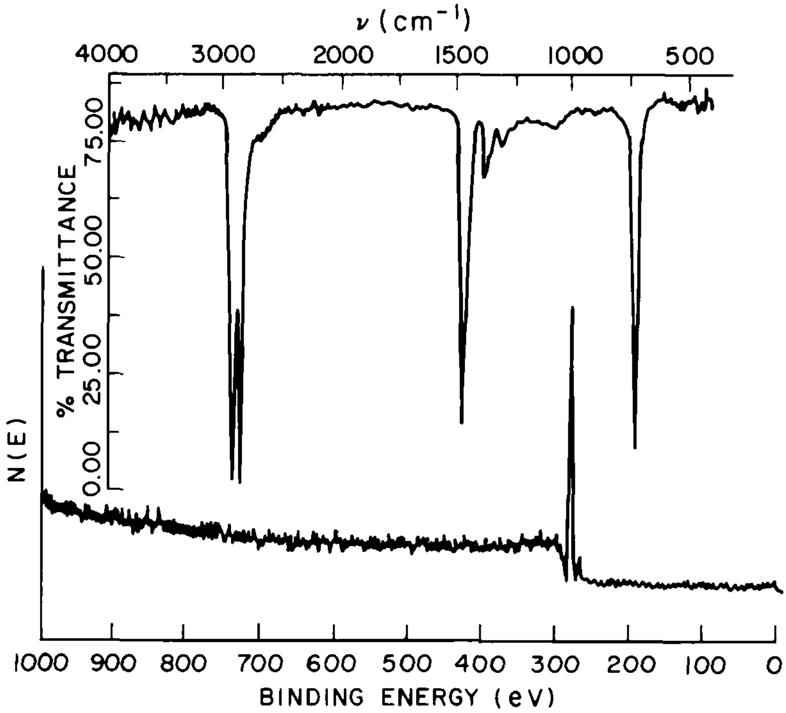

FIGURE 2 Transmission FTIR and XPS spectra of the polyethylene used in the adhesive bonding experiments. The polyethylene is essentially free of oxygenated species in both the surface region and the bulk.

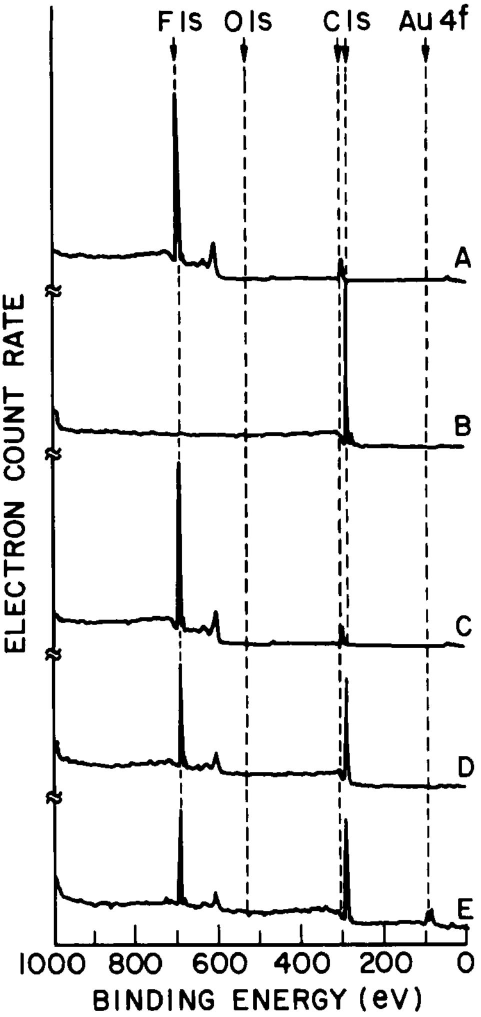

FIGURE 3 XPS spectra for the various interfaces illustrated in Figure 1.
A. PTFE spectrum.
B. Polyethylene spectrum.
C. Spectrum of polytetrafluoroethylene in contact with molten polyethylene which was subsequently solidified. The composite was manually separated. No polyethylene is transferred to the PTFE.
D. The spectrum of the polyethylene that has been in contact with the fluoropolymer during the melt bonding procedure. Clearly, fluoropolymer is transferred to the polyethylene.
E. The spectrum of the polyethylene-gold interface viewed through the gold that was transferred to the polyethylene.

O_{1s} region (electron binding energy ~530eV) of the spectrum. These results are further borne out by wettability measurements ($\gamma_c = 35$ mN/m). Clearly, essentially no oxidized species are present on the surface or in the surface region of the polyethylene prior to being melted in contact with gold. This polymer was judged suitable for investigating the joining of polyethylene to gold.

b. Gold

The gold used in this study was Alfa (m6N) pure (99.9999%) in the form of 0.8–6 mm shot. An XPS analysis of the gold prior to and after evaporation showed no evidence of metallic or oxide contaminants.

c. Polytetrafluoroethylene

The polytetrafluoroethylene (PTFE) film, 127 μm (5 mil) thick, used in this was supplied by Dielectrix. The polymer was extracted in a fashion identical to the polyethylene. An XPS spectrum of this material is shown in Figure 3A. No O_{1s} signal was observed.

2. Fabrication of Composite (Figure 1)

To avoid contamination from the tungsten heating element during evaporation of the gold, the tungsten was heated in excess of 300°C for 10 minutes at 10^{-4}Pa. This should have removed any possible organic contaminants prior to the evaporation of gold. The gold shot was placed in the tungsten boat and heated to above the melting point of gold at 10^{-4}Pa without evaporation, but to form a continuous coating of gold on the tungsten heating element. This approach was found suitable for the evaporation of thin films (<5 nm).

To examine the polyethylene-gold interface, we resorted to the composite structure shown in Figure 1. Since deposited gold films of 1–2 nm are far from continuous (see Fig. 4), it is imperative that when the molten polyethylene comes into contact with a substrate that neither the substrate is oxidized by the polyolefin nor the polyolefin by the substrate. Otherwise, oxygenated species may transfer to the polyethylene. The use of PTFE, rather than of silica, precluded oxidation of polyethylene by the substrate. Further, if the polyethylene does nucleate and crystallize in contact with a substrate, the substrate material should transfer to the polyethylene. As we shall see, PTFE-gold eminently fills the role.

The thickness of the evaporated gold film was monitored by using a quartz oscillator that had been calibrated with an Inficon thickness analyzer. It is estimated from SEM analysis that for gold films of 1–2 nm on PTFE, only about 30% of the PTFE surface is covered with gold (Figure 4). In effect, when we deposit a film of nominally 1–2 nm, we actually have islands of gold with thicknesses of ~3 nm, still thin enough to explore the polyethylene-gold interface in situ.

The composite, clamped together by clips, was placed 2 cm from the heating element. The temperatures attained during the melting and wetting of polyethylene to gold were monitored and calibrated using thermocouples. After a suitable time at a bonding temperature of 125°C, the current to the heating element was turned off and the composite cooled down in the vacuum station at a pressure of 10^{-4}Pa. Approximately 2 hours was required for this operation. The specimen was then removed for analysis or the fabrication of adhesive joints.

3. Adhesive Joint Strength

Specimens for lap shear strength determinations were prepared by making composites of aluminum-epoxy-gold-polyethylene-gold-epoxy-aluminum. The gold was

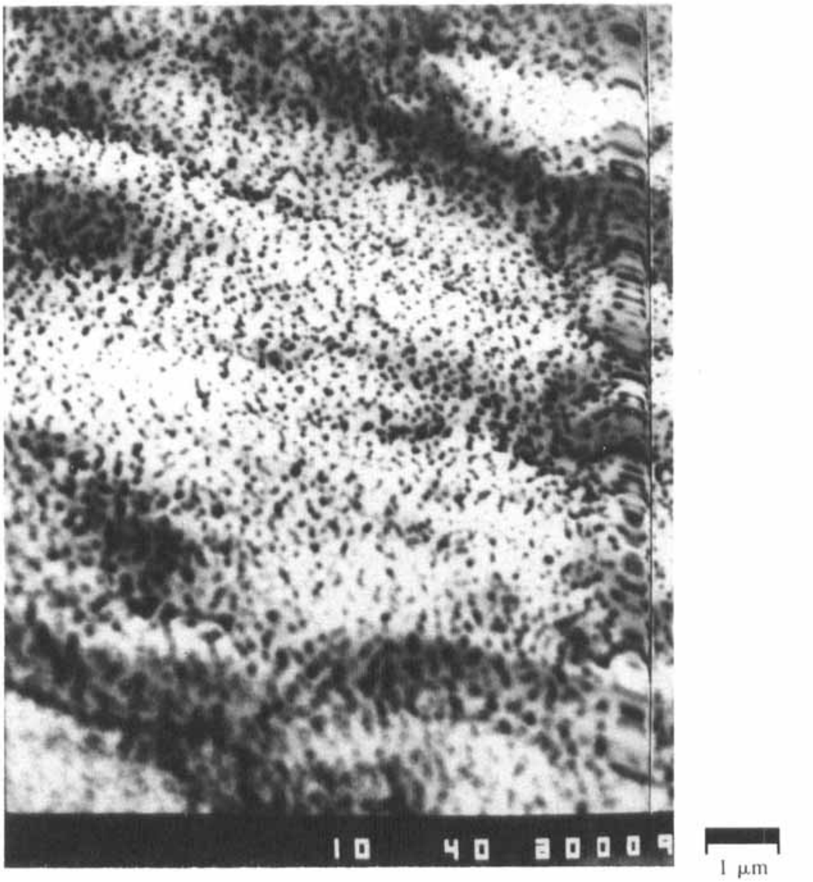

FIGURE 4 A scanning electron micrograph (20,000X) of the gold-PTFE composite prior to the melting of polyethylene. The evaporated gold film actually exists in discrete islands which would coalesce if the film were thicker.

transferred to the polyethylene during the melt bonding operation in vacuum. The control samples consisted of polyethylene film that was relaxed in a forced air oven at 125°C and then extracted with methylene chloride. The polyethylene specimens were cut into 2.5×3.8 cm pieces and joined to the aluminum with an Epon 828 (Shell)-Jeffamine T403 (Texaco) (100:30 by volume) epoxy adhesive at 60°C overnight in a forced air oven. Joint strengths were determined using an Instron (Instron Engineering Corp., Canton, Mass.) at a rate of 0.125 cm/min.

4. XPS Analysis

XPS spectra were obtained using a Kratos ES300 spectrometer system with MgK radiation (1253.6 eV) as the excitation source in conjunction with a Kratos DS300 data system. The pressure in the spectrometer during measurement was $\sim 10^{-5}$Pa, and the temperature ~35°C. The XPS data for the components of the composite are shown in Table I.

TABLE I
XPS data for composite

Sample	O/C (atomic %)
Polytetrafluorethylene (PTFE)	0.36
Polyethylene (PE) (Control)	.19
PTFE-PE	.33
PE-PTFE	.18
PE-Gold	.21

III. RESULTS AND DISCUSSION

Specific care has been exercised in choosing a well-characterized polymer which was essentially oxygen free on its surface and a substrate that was oxide free and showed no tendency to bond convalently to the nonpolar polyolefin. Clearly, in an experiment designed to ascertain the effect of oxygen on the bondability of a polyolefin, it was mandatory that an oxide-free substrate be chosen. In addition, it was important to view the metal-polymer interface in a nondestructive manner. It is possible that any destructive means required to remove the metal from the polymer after bonding may modify the polymer surface by virtue of exposing active sites, or by presenting a higher surface free energy to the environment.

The main thrust of the arguments associated with the composite shown in Figure 1 is whether, upon viewing the polyethylene-gold interface in a nondestructive manner using XPS, any oxidation of the polymer is observed. Further, if no oxidation of the polyethylene occurred, could strong adhesive joints be made to those metallized surfaces. Using XPS, we are limited to probing the surface region of the solid specimen down to a depth from which photoelectrons from the polyolefin-metal interface can still escape without suffering an inelastic scattering event. Noting that this so-called escape depth is related to the mean free path for inelastic scattering, which is a function of photoelectron kinetic energy and material, one recognizes that XPS will allow probing the surface region of the samples down to the depth of ~3 nm. Figure 4 clearly shows the disposition of the evaporated gold on the PTFE surface. Since these evaporated films were not pinhole free, there existed the possibility that the surface of polyethylene may become contaminated with oxygenated species from the substrate during the melt bonding process. To preclude this, we evaporated 1–2 nm of gold on a PTFE film to be used as a substrate, rather than silica, for the melting of polyethylene. The XPS spectrum of the PTFE is shown in Figure 3B. Clearly, no O_{1s} photoelectron signal is detected indicating that <0.10 atom % oxygen is present. After melt bonding the polyethylene for various periods of time, the composite in Figure 1 was manually separated. The gold which has been evaporated on to the PTFE was transferred completely to the polyethylene (Figure 3).

The purpose of the overlap in Figure 1 was to ascertain whether polyethylene was oxidized in contact with PTFE (exposed between the islands of gold; see Fig. 4) under the bonding conditions. It is possible that the polymer could have oxidized in contact with a low surface free energy solid such as PTFE. Figure 3C reveals that this is not the case.

The electron spectrum of the PTFE-gold interface prior to melting polyethylene is virtually identical to Figure 3A; no O_{1s} photoelectron signal was observed. Figure 3C is the electron spectrum of the PTFE surface that had been in contact with the polyethylene melt. Clearly, no polyethylene transferred to the PTFE. However, upon observing the polyethylene that was in contact with the PTFE as a melt, then solidified, it is apparent that a fluorocarbon layer (actually fluorine, according to the XPS results) was transferred (Figure 3D). This indicates that failure occurs in the PTFE and not in the polyethylene. Precisely the same behavior was observed when the gold transferred to the polyethylene; some PTFE was also transferred. It is not clear whether this is due to the PTFE being wet through the holes in the gold film or whether PTFE is adhered to gold and transferred in that manner. Figure 3C is the spectrum of the polyethylene-gold-PTFE interface. Again, no oxidation was observed to have occurred in this specimen.

In Figure 5 are the joint strength data for the polyethylene-Au-PTFE films joined to aluminum *via* the epoxy adhesive described earlier to form a lap shear specimen. Clearly, a significant increase in joint strength occurred when the above polymer films were used in preparing adhesive joints. The zero time point in Figure 5 represents the joint strength for polyethylene film which was free of oxygenated species but did not undergo the melt bonding process. The increase in joint strength was observed in the virtual absence of any oxidation at the polyethylene-gold interface.

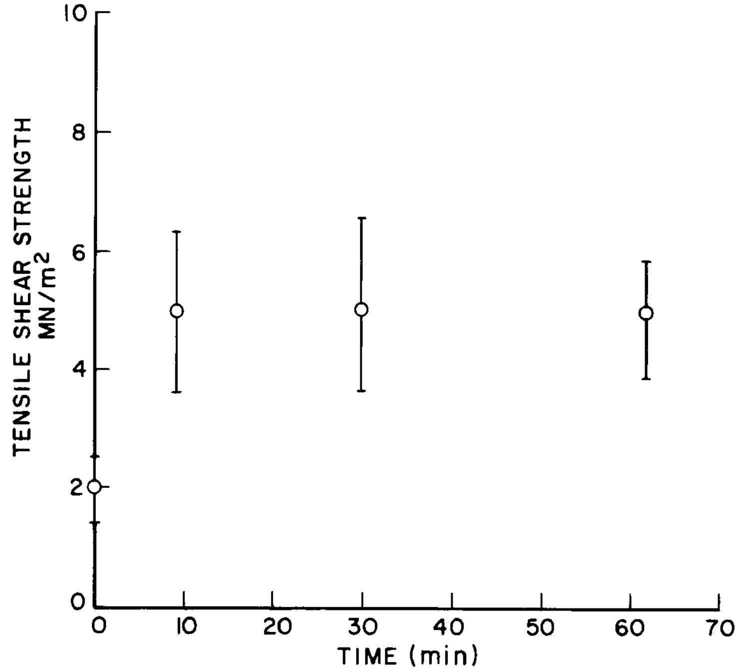

FIGURE 5 The tensile shear strengths for the composite, aluminum-epoxy-gold-polyethylene-gold-epoxy-aluminum as a function of the bonding time in the vacuum station at 10^{-4}Pa. The adhesive joints were prepared by curing the adhesive at 60°C for 16 hrs.

The joint strength data in Figure 5 are for polyethylene samples which show virtually no oxidation in the XPS spectrum.

IV. CONCLUSION

Specimens of polyethylene-gold composites, prepared at low temperatures (~125°C) in a vacuum of 10^{-4}Pa, formed strong adhesive joints with a conventional epoxy adhesive without any oxidation of the polyolefin surface. In view of the results of the present study, where oxidation is precluded while strong bonding is obtained, the strength of the metal-to-polymer bond has no simple correlation with the extent of oxidation at the interface.

References

1. D. T. Clark, A. Dilkes and D. Shuttleworth, in *Polymer Surfaces,* D. T. Clark and W. J. Feast, Eds. (John Wiley and Sons, N.Y. 1978), p. 185.
2. D. Briggs, D. M. Brewis and M. B. Konieczko, *J. Mat. Sci.*, **12,** 429 (1977).
3. H. Schonhorn, in *Polymer Surfaces,* D. T. Clark and W. J. Feast, Eds. (John Wiley and Sons, N.Y., 1978), p. 213.