

Adhesion of Evaporated Metallic Films onto Polyethylene and Poly(tetrafluoroethylene): Importance of Surface Crosslinking

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Synopsis

Ni, Fe, Ti, Al, Au, and Cu were each evaporated and deposited onto both sides of polyethylene and poly(tetrafluoroethylene) (PTFE) films. Adhesive joint strengths of the different metal-polymer-metal composites were compared and subsequent surface modifications due to metalization were investigated. Studies show no change in wettability of polyethylene or PTFE after a metal layer was deposited onto their surfaces and subsequently removed. There was also no evidence of oxidation or unsaturation of the surface. Gel fractions of polyethylene show a definite correlation between joint strength and crosslink density at the surfaces of the different metal-polymer composites. Metals forming the strongest joints with polyethylene yield the greatest amount of crosslinking. Conversely, metals forming the weakest joints result in the least amount of crosslinking.

INTRODUCTION

Many workers have studied the adhesion of metals to polymers. From their work stem various theories of adhesion, which include chemical,^{1,2} mechanical interlocking,³⁻⁵ electrostatic,⁶⁻⁹ and "weak boundary" layer mechanisms.^{10,11} Strong adhesive joints between metals and polymers can be formed by treating the polymer films prior to metal deposition, by melting the polymer onto the metal, or by surface treatment of both and use of conventional adhesives. Surface treatment of polymers by exposure to radiation,¹² electrical discharge,^{13,14} gas discharge,^{15,16} or chemicals¹⁷ enhances the joint strength by altering the surface properties of the polymer, both with respect to possible changes in wettability and mechanical properties. In addition, there has been speculation that an increase in joint strength may also result from decreasing the surface roughness of the polymer film.^{4,5} Although an increase in crosslink density is found in some surface-treated polymers,¹⁸⁻²⁰ its contribution to the adhesive joint strength has been neglected.²¹ Rather, the increase in joint strength has been considered a consequence of electret formation which alters the properties of the surface of the polymer.²¹

In this investigation we have studied the possible surface modification of untreated polyethylene and poly(tetrafluoroethylene) (PTFE) after a metal layer has been deposited by evaporation on both sides of each film. In order to compare relative adhesive joint strengths and the effects on surface properties of the polymers brought about by deposition of different metals, iron, nickel, titanium, aluminum, gold, and copper, were evaporated onto the surfaces of the films. Various properties of the metalized polymer were then studied. Any changes in properties such as surface crosslinking of the polymer, polymer wettability,

adhesive joint strength of the composite, unsaturation, or oxidation at the polymer interface could then be attributed solely to the deposition of these particular metals onto the untreated polymer and not be considered a consequence of polymer pretreatment.

EXPERIMENTAL

du Pont Alathon 5496 polyethylene was compression molded in an electrically heated press (Pasadena Hydraulics Inc.) at 117°C into 250- μm -thick films. To facilitate removal of the polymer, the polyethylene was molded between poly-(tetrafluoroethylene) sheets. (Subsequent wetting studies of the polyethylene surface indicated no transfer of PTFE onto the molded polyethylene.) Commercially obtained 125- μm -thick high-purity PTFE du Pont film DF-100 was used as received for testing PTFE-metal joints. Evaporation of the various metals onto both sides of the polymer films was performed in a Veeco 770 high-vacuum thin film evaporator. Enough wire was placed on the tungsten heating filament to allow for the deposition in each case of a 1000- Å -thick layer of metal onto the polymer substrate. Metal deposition was carried out at 5.0×10^{-6} torr.

Specimens for lap shear determinations were prepared by making composites of Al-epoxy-metal-polymer-metal-epoxy-Al.¹¹ The polymer samples were cut into 2.54×3.8 cm pieces. The composites were bonded at 60°C overnight. Joint strength was determined using an Instron (Instron Engineering Corp., Canton, Mass.) at a rate of 0.125 cm/min.

Determination of crosslinking by gel fraction was performed on polyethylene substrates whose metal layers had been removed previously. Fe, Ni, Al, and Cu were removed by immersing the metalized polymer in 75% warm HCl, washing with deionized water, and air drying. Au was removed by amalgamating the metal with Hg, whereas Ti was dissolved in 75% warm HF. The clean polymer was then washed with deionized water and air dried. Polyethylene films which were not metalized were used as controls and were also tested for crosslinking. The unmetalized polymers were subjected to the same pretreatment as the coated polymers. The bare polymer films were then placed into platinum cones and extracted with refluxing xylene until a constant weight was attained. The resulting residue films were air dried at least 2 hr and then weighed.

RESULTS

Joint strength data for the polymer-metal composites are compared in Figures 1 and 2. The range of strengths for each metal of the metal-polyethylene composite may be attributed to experimental differences in molding procedure or to changes in ambient room conditions. Despite this fact, it can clearly be seen that for both polymers, Fe, Ni, and Ti yield the strongest adhesive joints, Al yields intermediate ones, and Au and Cu form the weakest joints. The joint strength for the Ti-PTFE composite is larger than the joint strengths for corresponding Fe- or Ni-PTFE composites. The reverse is true, however, when working with polyethylene films. It appears that the strength of the titanium-polyethylene joint is less than the strength of either the Fe- or Ni-polyethylene joint.

A 55-ampere current was used in evaporating Fe, Ni, and Ti onto polyethylene and PTFE films. The current used for evaporating Al was 45 amperes, whereas

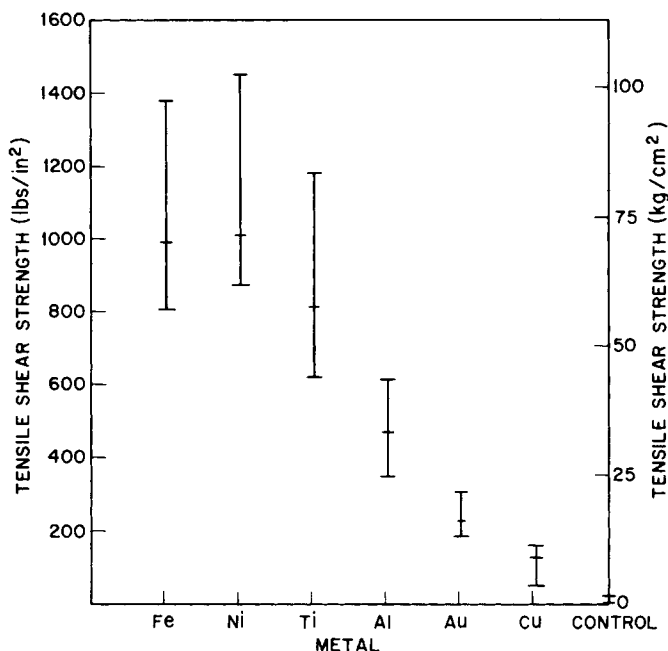


Fig. 1. Tensile shear strengths for composites of Al-epoxy-metal-polyethylene-metal-epoxy-Al.

for Au and Cu it was 35 amperes. In order to determine whether there was any correlation between joint strength and evaporation temperature or current, Al, Au, and Cu were evaporated and deposited onto the polymer films at various currents ranging from 35 to 60 amperes. Joint strength data for the polymer-metal composites of these three metals was consistent for each metal, regardless of the temperature of evaporation. It can clearly be seen, therefore, that the joint strengths for the various metals do not reflect evaporation temperature or current, but are rather inherent properties of the polymer-metal interfaces themselves.

Surface crosslinking is difficult to demonstrate in PTFE because of its insolubility. Polyethylene, however, can be extracted in refluxing xylene. Crosslinked polyethylene is insoluble in xylene and therefore remains as a residue of crosslinked "skin." Results from gel fraction determinations are shown in Table I. The data clearly show that the greatest crosslink density in polyethylene is obtained as a result of evaporating Fe or Ni. The gel fraction decreases in order from Ti, Al, Au, to Cu. It can clearly be seen that this order of decrease corresponds to the order of decrease in joint strength of the metal-polyethylene composite.

To determine unsaturation in both polymers, all the deposited metals were removed and the films were then immersed in Br_2/CCl_4 solution overnight. No bromine incorporation was detected by x-ray fluorescence in either polymer for any metal.

ATR was used to investigate the possible presence of unsaturation, oxidation, crystallinity, and other surface changes. Only the Fe-deposited polyethylene film was studied since this sample yields the largest joint strength and crosslinked residue. A 50-Å-thick layer of Fe was deposited on the polyethylene film and the sample was examined from the metal side by ATR. Although the intensity

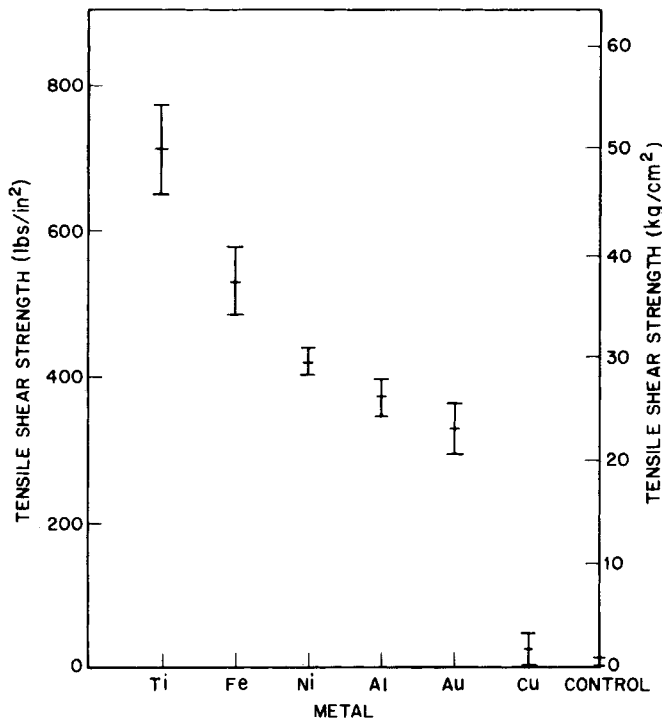


Fig. 2. Tensile shear strengths for composites of Al-epoxy-metal-PTFE-metal-epoxy-Al.

of the spectrum was somewhat reduced, the spectrum that was revealed showed no evidence of oxidation, unsaturation, or other chemical changes in the surface region of the polymer.

Wettability measurements of polyethylene and PTFE are given in Table II. The table lists the contact angles of various liquids on polyethylene and PTFE after the evaporated metals have been removed. The data clearly indicate that

TABLE I
Thickness of Crosslinked Layer on Polyethylene Resulting from the Evaporation of Various Metals

Metal	Thickness of crosslinked layer, Å ^a
Fe	707
Ni	449
Ti	118
Al	116
Au	58
Cu	48
Control	0

^a Effective film thickness calculated in the following manner:

$$\left[\frac{1}{\text{weight of specimen residue}} \times \text{density} \times \text{area of metalized polyethylene} \right] - \left[\frac{1}{\text{weight of control residue}} \times \text{density} \times \text{area of unmetalized polyethylene} \right]$$

In all cases, the metal was removed prior to measuring gel fraction.

TABLE II
Wettabilities of Polyethylene and Teflon at 23°C

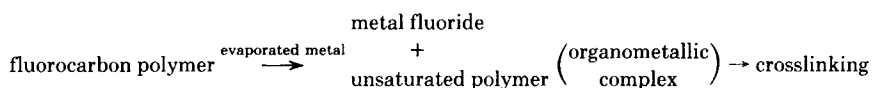
Liquid	Metalized polyethylene (θ , degrees)				Unmetalized polyethylene (θ , degrees)				Metalized PTFE (θ , degrees)				Unmetalized PTFE (θ , degrees)
	Ni	Fe	Ti	Al	Au	Cu	Ni	Fe	Ti	Al	Au	Cu	
Glycerol	80	79	79	80	79	79	100	98	97	99	100	100	100
1-Bromonaphthalene	35	35	35	35	35	35	71	71	72	71	70	72	72
Methylene chloride _r	50	54	52	50	52	52	45	45	44	46	45	45	45
Formamide	80	79	79	80	79	79	90	92	90	91	92	92	92

there is no significant change in wettability of polyethylene or PTFE due to the deposition of these metals by evaporation. This indicates that if there is any change in the surface constitution of the substrate, it is not sufficient to cause any significant change in wettability.

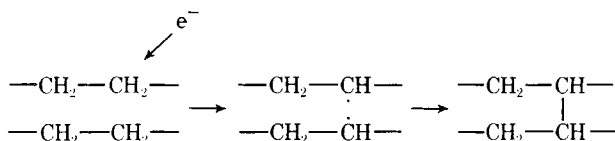
DISCUSSION

It is interesting to note that the order of adhesive joint strength follows that of increased crosslink density in polyethylene. Since the polymer film was not pretreated nor showed any significant oxidation, it appears that crosslinking is significantly involved in the formation of strong adhesive joints.

Previously, it has been shown by ESCA analysis that when certain metals are evaporated onto the surface of FEP Teflon, fluorine is abstracted.²² As the FEP polymer is bombarded with metal atoms, a metal fluoride or organometallic complex may be formed which catalyzes the reaction of resultant unsaturated sites. These unsaturated sites immediately crosslink. A schematic is as follows:



Keeping this process in mind, one may suggest that as evaporated metal atoms impinge upon the surface of the polyethylene, radicals are again formed. These radicals may then abstract hydrogen atoms from neighboring chains and eventually lead to crosslinking:



Differences in adhesive bond strength between each metal-polymer composite appear to result from differences in crosslink density and depths of crosslinking. Crosslinking appears to strengthen the boundary layer of the polymer film, with a subsequent increase in its cohesive strength. This could reduce the influence of a "weak boundary" layer of the kind referred to by so many workers.^{10,11} The higher the surface crosslink density and depth of crosslinking, the stronger joint the film forms.

Many factors such as electrostatic and chemical attraction, as well as mechanical interlocking, may affect adhesion of metal-polymer composites. Our results clearly show, however, that crosslinking is indeed significant in the formation of a strong joint.

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