

## Surface Treatment of Polymers. II. Effectiveness of Fluorination as a Surface Treatment for Polyethylene

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### Synopsis

An effective surface treatment for adhesive bonding of polyethylene has been developed. It involves exposing the polymer to an environment of elemental fluorine or fluorine diluted in argon. By this treatment, extensive fluorination of the surface region is effected. The fluorinated surface permits formation of strong adhesive joints by conventional adhesive bonding techniques even though the wettability of the new surface is similar to polytetrafluoroethylene. We believe that treatment of the polymer with elemental fluorine effectively eliminates the weak boundary layer associated with polyethylene by either crosslinking or by increasing the molecular weight in the surface region.

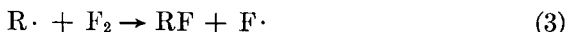
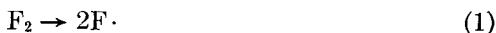
### Introduction

Failure to prepare a strong adhesive joint has most often been attributed, until recently, to the weak interfacial forces exerted between adherend and adhesive. It was believed that strong adhesive joints could only be prepared by oxidizing the surfaces of polymers of low surface energy to increase polarity and enhance wettability. The notion of polarity was so widely accepted that existence of a mechanically weak surface region was overlooked generally. However, after crosslinking the surface region of low surface energy polymers by exposure to a variety of excited and metastable species of rare gases,<sup>1,2</sup> strong joints can be prepared with conventional adhesives. Such exposure considerably increases the mechanical strength of the surface region in polyethylene, polytetrafluoroethylene, and many other polymers of low surface energy which exhibit a weak boundary layer. Furthermore, since polar groups are not introduced, polymers may be prepared for adhesive bonding without their wettabilities being changed.

In this communication, we report the strengthening of the surface region of polyethylene by exposing the polymer to fluorine gas at atmospheric pressure and ambient temperatures. In this process, the surface region of polyethylene is converted to a polymer resembling polytetrafluoroethylene.<sup>3</sup> However, unlike untreated polytetrafluoroethylene (PTFE), this polymer surface is highly amenable to conventional adhesive bonding even though its wettability is similar to conventional PTFE.

### Reaction Mechanisms

Miller and Dittman<sup>4</sup> and Bigelow<sup>5</sup> have pointed out that fluorination reactions involving elemental fluorine and *n*-hydrocarbons have all the characteristics associated with free-radical reactions.



The approximate heat of reaction of reactions (2) and (3) are  $-34.0$  and  $-68.0$  kcal./mole, respectively. The ease of fluorination of polyethylene is in agreement with the above mechanism. Details of the kinetics will not be discussed here. Tedder<sup>6</sup> has reviewed briefly and informatively the theoretical aspects of fluorination as applied to organic compounds. Fredricks and Tedder<sup>7</sup> have suggested that a substituent fluorine deactivates hydrogen atoms adjacent to it so that progressive fluorination becomes increasingly difficult. Fluorination of compounds ranging from methane to lubricating oils has been investigated.<sup>7</sup> These reactions, like other free radical reactions, invariably have been accompanied by both fragmentation and polymerization. When polyethylene is treated with fluorine, it is assumed that more polymerization (i.e., crosslinking) occurs than fragmentation, for a mechanically strong surface region is obtained which resembles that produced during exposure of polytetrafluoroethylene to activated species of inert gases.

### Experimental

Details of the preparation of the tensile shear specimens and their testing are given elsewhere.<sup>8</sup> Polyethylene film (approximately  $\sim 10$  mils) (Marlex 5003, from Phillips Petroleum Co., Bartlesville, Oklahoma) was exposed to fluorine gas and mixtures of fluorine in argon at ambient temperatures and one atmosphere pressure in a nickel vessel. The shortest convenient time for exposure was 10 min., although dilution of the fluorine with argon may be comparable to shorter exposure to fluorine. Wettability studies were performed on the polymer sheet that was exposed to fluorine gas. The experimental details are described elsewhere.<sup>9</sup> The polytetrafluoroethylene-like skins were isolated by extracting the exposed polymer film in a perforated platinum crucible in a Soxhlet extractor with refluxing xylene. After a suitable interval had elapsed and the specimen had been extracted to constant weight, microanalysis was performed on the residue.

The melting characteristics of the residue were followed by using a Perkin-Elmer differential scanning calorimeter (DSC 1B). In addition, attenuated total internal reflection techniques were employed on the fluorinated surface and the residue to observe any obvious changes in the chemical constitution.

### Results

After exposure to fluorine gas and mixtures of fluorine in argon for a period of 1 hr., tensile shear specimens were prepared and tested. The data in Figure 1 illustrate the effectiveness of the fluorine treatment in eliminating the weak boundary layer that normally exists on the surface of melt-crystallized polyethylene film. Joint strengths are comparable to those produced by the CASING technique.<sup>1,2</sup> The results in Figure 2 indicate that an interval much shorter than 10 min. is probably sufficient to strengthen the weak boundary layer normally present in the polyethylene surface. All joints were prepared below the melting temperature of polyethylene to avoid any reorganization in the surface region. An alternate way of plotting the data described in Figure 1 is shown in Figure 3. The apparent decrease for the 50% fluorine treatment is probably an experimental error. It is apparent that increasing the temperature of cure of the epoxy adhesive results in a stronger joint. This is due to the increased

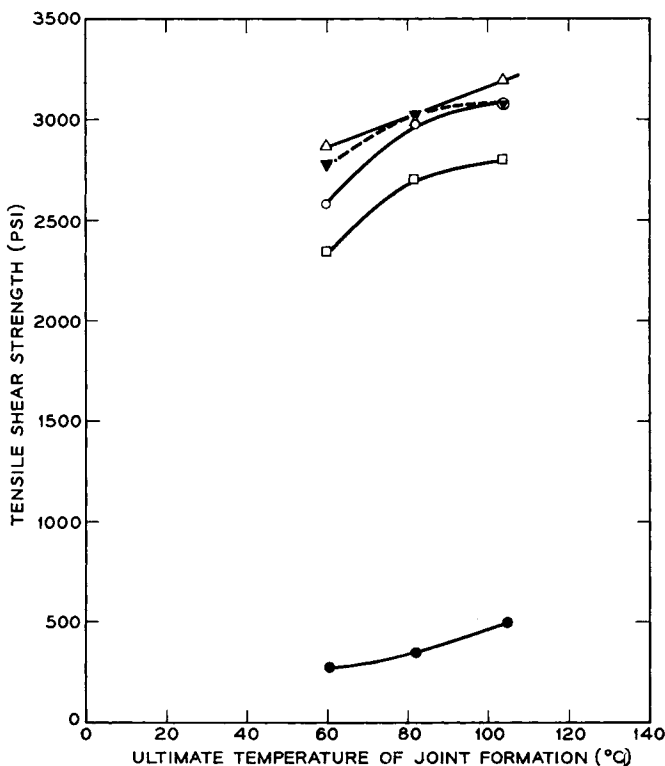


Fig. 1. Tensile shear strength of the composite aluminum-epoxy adhesive-fluorine treated polyethylene-epoxy adhesive-aluminum plotted as a function of the temperature of the joint formation. Polyethylene was exposed for 1 hr. at ambient temperatures and 1 atm. pressure to mixtures of fluorine in argon: (○) 100% fluorine; (Δ) 82 (vol.-% fluorine in argon; (□) 50 vol.-% fluorine in argon; (▼) 1 vol.-% fluorine in argon; (●) 100% argon.

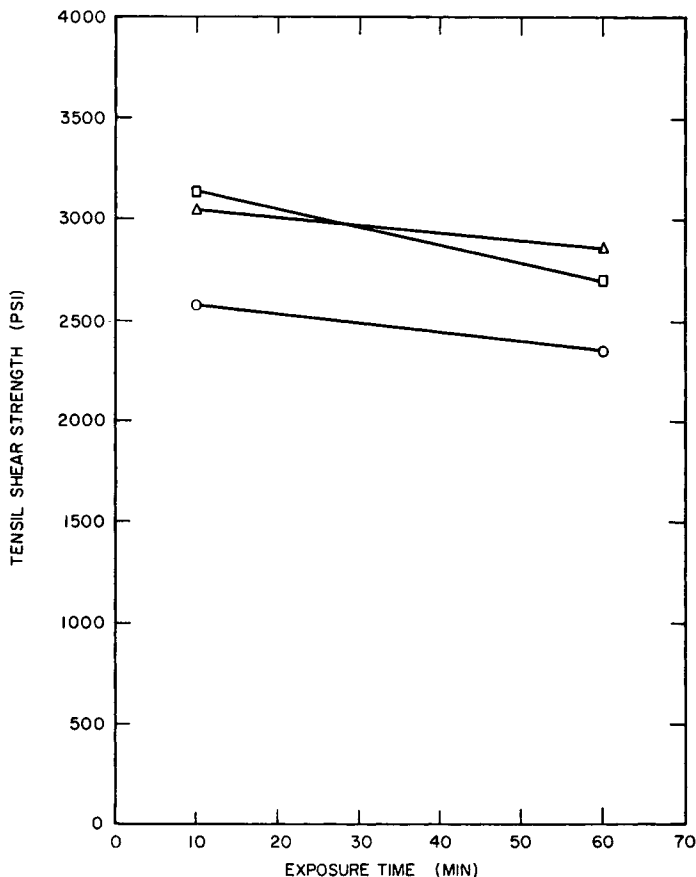


Fig. 2. Tensile shear strength of the composite aluminum-epoxy adhesive-treated polyethylene-epoxy adhesive-aluminum plotted as a function of exposure time to a 1:1 by volume mixture of fluorine in argon: (O) 60°C. cure temperature; ( $\Delta$ ) 82°C. cure temperature; ( $\square$ ) 104°C. cure temperature.

mechanical strength of the epoxy adhesive when cured at higher temperatures.

The effective depth of penetration of fluorine is shown in Figure 4. The treated films were extracted; the residues remaining after extraction appeared similar to those obtained in the CASING technique.<sup>1,2</sup> There was no measurable swelling during extraction and the geometric nature of the film was preserved as it was during extraction of films prepared by bombardment with activated rare gases. Effective thickness was based on the geometric area and the density of the skins. Density was determined by noting the floating or sinking of the skin in a variety of fluorocarbon oils and other dense liquids. The apparent density was slightly greater than 2.0 g./cm.<sup>3</sup>. This is indicative of extensive fluorination and is in agreement with the results of Rudge.<sup>3</sup> Microanalysis of the skin reveals a

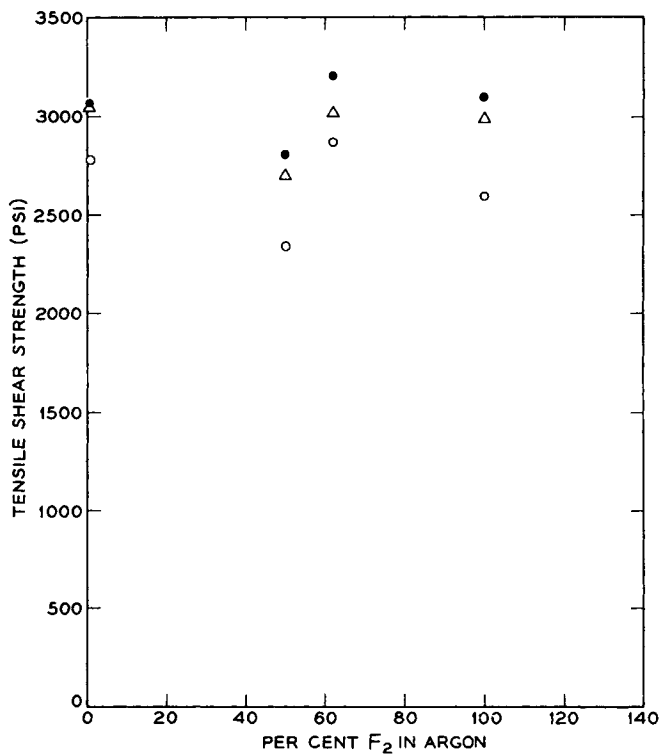


Fig. 3. Tensile shear strength of the composite aluminum-epoxy adhesive-fluorinated polyethylene-epoxy adhesive-aluminum plotted as a function of volume per cent of fluorine in argon. Polyethylene was exposed to these mixtures for a period of 1 hr.: (O) 60°C. cure temperature; (Δ) 82°C. cure temperature; (●) 104°C. cure temperature.

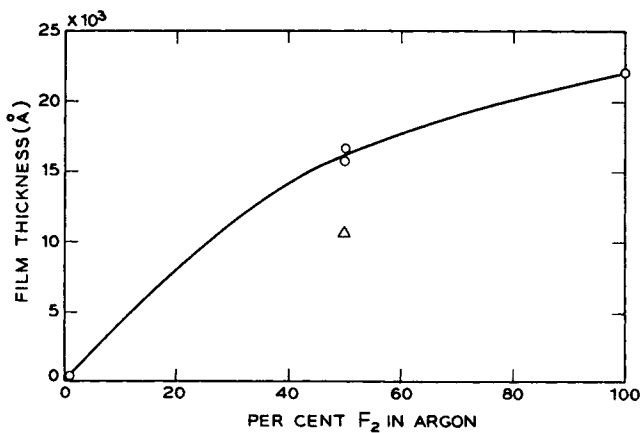


Fig. 4. Estimated thickness of crosslinked region as determined from the gel fraction after Soxhlet extraction plotted as a function of the volume per cent of fluorine in argon: (O) 1 hr. exposure; (Δ) 10 min. exposure.

composition  $C_2F_3H$ , which is to be expected for thick films. Since reaction occurs first at the surface, we might expect a gradient in composition as reaction proceeds deeper into the bulk of the polymer. Calorimetric studies of the skin revealed no endotherm in the vicinity of the melting temperature of polyethylene, but there was some indication of an endotherm at about  $300^\circ C$ . This is in agreement with the proposed fluorocarbon structure. Attenuated total internal reflection spectra of treated polyethylene surfaces were indistinguishable from spectra of PTFE specimens. Whether we are dealing with a crosslinked fluorocarbon or a high molecular weight species cannot be ascertained from our data, since there are apparently no appropriate solvents for these types of fluorocarbons.

### Discussion

Previously, methods to prepare the surface of polyethylene for adhesive bonding were believed to be based on increasing intermolecular forces and wettability between the adhesive and adherend.<sup>10,11</sup> These methods provided polar groups on the surface of polyethylene resulting in low contact angles with the adhesive. In this investigation we have substantially lowered the critical surface tension of wetting,  $\gamma_c$ , of polyethylene by extensive fluorination. The  $\gamma_c$  of 20 dyne/cm. for the new surface is representative of the perfluorinated species.<sup>12</sup> Here we have lowered the  $\gamma_c$  but have increased joint strength by almost an order of magnitude, as evidenced from Figure 1. Joint strengths comparable to those obtained with the CASING technique<sup>1,2</sup> are obtained with fluorination of the polyethylene surface region. We believe that it is necessary to eliminate weakness in the surface region in order to prepare a strong adhesive joint to a polymer. Once this has been accomplished, then it is important to consider wettability aspects.

Note that we are not proposing that wettability is unimportant. Quite the contrary. We propose that it is less important than was commonly believed. For example, a low or zero contact angle of the adhesive on the adherend does not always assure formation of a strong joint. Nylon (Allied Chem. Co., Capran 77A and 77C), normally wets readily but, does not generally form strong adhesive joints unless its surface has been treated.<sup>13</sup> Therefore, it is necessary to consider the rheological properties of the surface region of the adherend. After the weak boundary layer has been strengthened or eliminated, wettability then becomes important. This has been shown quite effectively during the preparation of strong adhesive joints with chlorotrifluoroethylene-based polymers.<sup>14</sup> Decreasing the surface tension of the adhesive had a marked effect on wettability and resultant adhesive joint strength. Apparently, the chlorotrifluoroethylene-based polymers, as a result of their method of preparation, do not have an inherent weak boundary layer. This may be a function of the molecular weight and/or crystallization behavior of the polymer. Similarly, poly(vinylidene fluoride) has a  $\gamma_c$  of about 28 dynes/cm. but it does not have an inherently weak boundary layer as normally prepared and,

consequently, does not require a surface treatment prior to adhesive bonding.<sup>2</sup>

The CASING technique dramatically illustrates the importance of increasing the mechanical strength of weak boundary layers (in polymers where this phenomenon is observed) in order to prepare strong adhesive joints. By use of this technique, strong joints may be formed without measurable change in wettability. We have now shown that fluorination of the polyethylene surface also results in the formation of strong adhesive joints, even though wettability is decreased. Therefore, we believe that techniques for the surface treatment of polyethylene all must have in common the ability to alter mechanical properties of the polymer in the surface region.

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