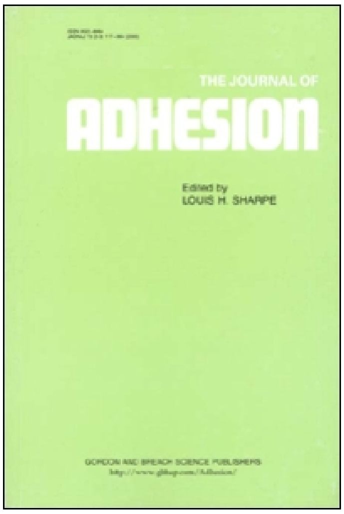

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Adhesion of Polytetrafluoroethylene

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Adhesion of Polytetrafluoroethylene

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ABSTRACT

Nucleation and crystallization of polytetrafluoroethylene in contact with gold produces a surface region of high mechanical strength in the polymer as evidenced from the strong adhesive joints prepared with a conventional epoxy adhesive. In addition, the wettability of the gold-nucleated polytetrafluoroethylene, after dissolution of the gold, is vastly improved. The critical surface tension of wetting increases from 18.5 dynes/cm to 40 dynes/cm, indicating an increase in the surface density of the gold-nucleated polymer. We conclude from this study, that the occurrence of the normal weak boundary layer on polytetrafluoroethylene is a consequence of the morphology of the surface region and is therefore influenced by the method of preparation.

INTRODUCTION

POLYTETRAFLUOROETHYLENE (PTFE) has long been regarded as a thermoplastic polymer which must be surface treated prior to coating or joining with conventional adhesives [1]. However, Korelev, Bek and Grishin [2] have shown that strong adhesive joints can be formed between PTFE and stainless steel under certain experimental conditions. Korelev et al [2] concluded that the molten PTFE could wet the high surface energy metal oxide. They further demonstrated that molten metals could not be used to form strong joints with PTFE below the melting point of the polymer. The wetting aspects of the joint formation were considered by Korelev et al, to be of prime importance. Although the wettability considerations are not to be minimized, a detailed account of the rheological properties of the surface and bulk regions of the polymer are essential in understanding the requirements for forming strong adhesive joints [3]. Surface treatments, in general, modify not only the constitution of the surface but also the mechanical strength of the surface region. Although, Korelev et al [2] chose to use a molten metal to demonstrate the nonbonding characteristics of untreated PTFE, an adhesive which could have wet the PTFE would have produced the same results.

In this paper we shall consider the influence of gold as a substrate in the nucleation and crystallization of PTFE. We shall show that the substrate governs the morphology generated in the surface region of the PTFE which in turn dictates the mechanical strength of the surface layer. Wettability results show that dense surface layers are formed in the interfacial region. This dense region is more wettable than the normally occurring amorphous surface layer.

EXPERIMENTAL

Film Preparation

Two pieces of 1″ x 3″ x 1/16″ glass microscope slides (which had ~2000 Å of gold evaporated on one side) were sandwiched together with a film of 3/4″ x 2-1/2″ x .010″ PTFE (G-80, Allied Chem. Co.) to form a composite consisting of glass-gold-PTFE-gold-glass. The composite was placed in a Carver Press and molded at 400°C and 250 psi for 30 minutes. Composites were cooled rapidly by placing them on a bench top. Slower cooling rates (1°C/min) produced similar results.

The composites were immersed in a saturated aqueous NaCN solution at ambient temperatures overnight to dissolve the gold. Mechanically removing the PTFE from the composite disrupts the surface region, thereby leaving an exposed weak boundary layer. The PTFE was then rinsed in distilled H_2O and given a final rinse in 50-50 v/v HCl to remove any surface contaminants (e.g., carbonates, etc.). The PTFE was again washed in distilled water and air dried. The final thickness of the films was approximately 2 mils. The films appeared quite transparent (glasslike). An alternate technique for separating the PTFE film from the gold, which is equally as effective, involves amalgamating the gold with mercury. This precludes the formation of residues (e.g., carbonates, etc.) on the PTFE.

Adhesive Joint Preparation:

The preparation of the adhesive joints and the physical testing of the joints are described elsewhere [4].

Contact Angles:

Contact angles for a variety of liquids on the PTFE surface were measured as described previously [5].

RESULTS

The adhesive joint strength data in Figure 1 illustrate the effectiveness of a variety of surface treatments for PTFE. Untreated polymer film (as

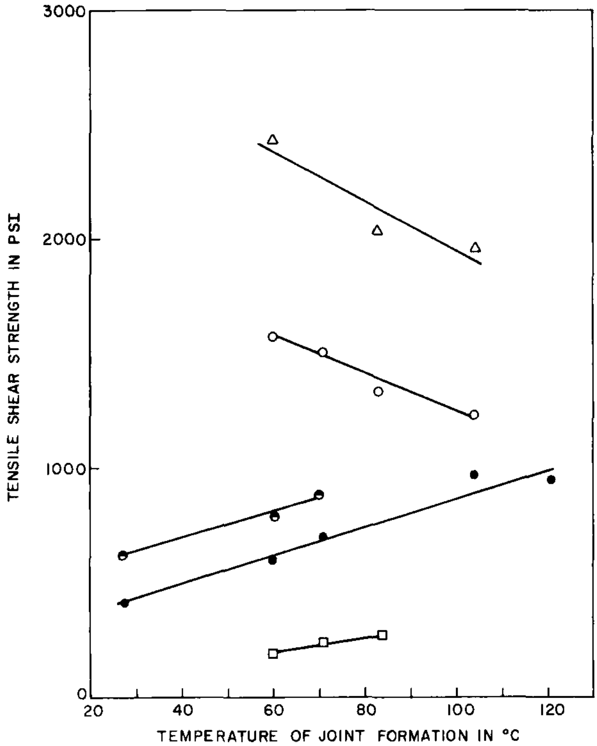

Figure 1. The tensile shear strength of the composite aluminum-epoxy adhesive-PTFE film-epoxy adhesive-aluminum plotted as a function of the ultimate temperature of joint formation.

□—Skived; no treatment.
●—Van de Graaff irradiation of PTFE in air; 11 Mrads.
○—CASING-treated for 1 hour in helium at 100 Watts power.
○—PTFE film nucleated and crystallized in contact with gold.
△—Tetra—Etch treated PTFE film.

received), which had been skived from a billet, resulted in extremely low adhesive joint strength. Van de Graaff irradiation in air, while somewhat effective in modifying the mechanical strength of the surface, degraded the bulk properties so that the films became waxy and mechanically weak. The CASING (glow discharge) technique [6], while superior to Van de Graaff irradiation, was not as effective as the proprietary Tetra-Etch technique [7]. In contrast to the Tetra-Etch treatment, there was no discoloration of the PTFE in the glow discharge [6], but the mechanical strength of the surface region was considerably higher than in the case of skived film. Nucleation and crystallization of the PTFE in contact with gold produced a surface region of rather high mechanical strength, resulting in high adhesive joint strengths.

The contact angles for a variety of liquids on PTFE, which was nucleated and crystallized in contact with gold are shown in Table 1, compared with the results of Zisman [8].

DISCUSSION

Recently, Schonhorn and Ryan [3, 9] have investigated the weak boundary layer from a morphological point of view. It was concluded in these investigations that the weak boundary layer normally present in the surface region of many melt-crystallized polymers results from the manner in which both their surface and bulk regions are generated. This is borne out again in the present work which tends to corroborate the efforts of Korelev et al [2]. A strong boundary layer is generated in the PTFE when the polymer, after achieving intimate contact with the substrate, is crystallized against gold. The normally present weak boundary layer that occurs on PTFE results from the manner in which the surface is generated. Generally, PTFE film is skived from a billet to produce a film of definite thickness. We have found that mechanically sectioning a polymer film, whether or not the film is cooled to liquid nitrogen temperatures prior to sectioning, disrupts the mechanically strong interphase and a weak boundary layer is formed. Here we see that the difficulty in joining the PTFE with conventional adhesives is primarily a function of how the interfacial region was generated. Gold has been shown to be the best nucleating phase for a variety of polymers and presumably this is the case for PTFE [10].

Whereas CASING-treated films were difficult to wet, nucleation and crystallization of the polymers in contact with high energy surfaces resulted in marked improvements in their wettability, provided the nucleating surface was removed chemically. The contact angle data for the gold-generated PTFE films are presented in Figure 2 in a Zisman type plot. Here is seen a striking change from the earlier data of Zisman [8]. The critical surface tension of wetting is about 40 dynes/cm for the treated surface, more than twice the value of the untreated polymer. Not only do we observe a change

Table 1. Wettability of Polytetrafluoroethylene at 20°C

Liquid	γ_{LV} dynes cm^{-1}	Gold-Nucleated θ deg.	Skived* θ deg.
glycerol	63.4	59	100
formamide	58.2	42	92
α Bromonaphthalene	44.6	34	73
hexadecane	27.6	spreads	46

*Data of ref 8

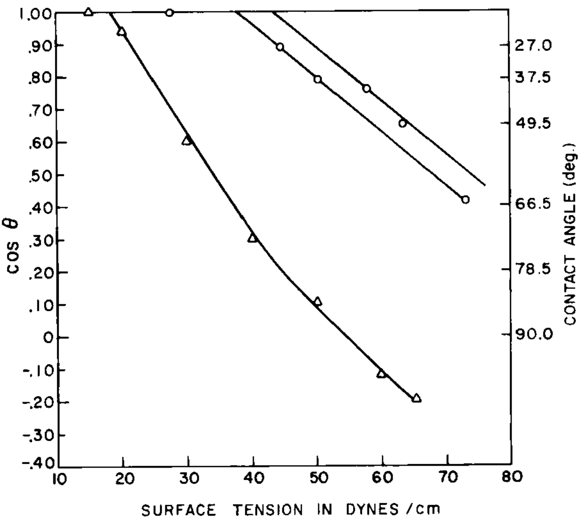

Figure 2. Zisman plot of contact angle data in Table 1.
△—data ref. 8.
○—gold nucleated PTFE.

in the mechanical strength, but also a marked change in wettability. This change in wettability is thought to arise from an increase in the surface density of the PTFE. The polymer surface is no longer representative, with respect to density, of an amorphous or supercooled liquid state.

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