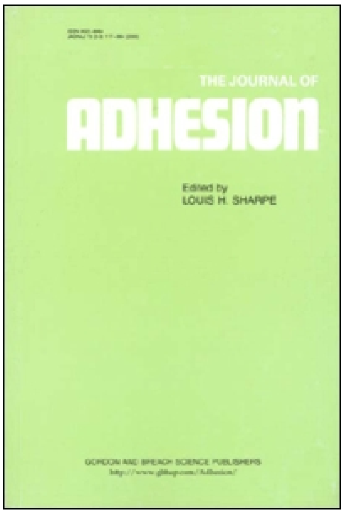

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Effect on Wettability of FEP Teflon Surface Morphology

by

KATSUYUKI HARA AND HAROLD SCHONHORN

Bell Telephone Laboratories, Incorporated
Murray Hill, New Jersey 07974

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ABSTRACT

Wettability of FEP Teflon® (a perfluorinated ethylene-propylene copolymer) is vastly improved by heterogeneous nucleation and crystallization in contact with gold, a high surface free energy substrate. The critical surface tension of wetting (γ_c) increases from 18.8 dynes/cm to 40.4 dynes/cm. We compute that this rise in γ_c results from a 20 percent increase in the surface density of gold-nucleated FEP Teflon®. The increase in critical surface tension from 18.8 dynes/cm to 20.6 dynes/cm, for as received FEP Teflon which had been crosslinked by helium in a glow discharge (CASING technique), suggests an increase of the surface density with crosslinking. The critical surface tension of the gold-nucleated FEP Teflon® is sharply decreased from 40.4 dynes/cm to 22.0 dynes/cm by short exposure to the CASING treatment in helium. The results of ATR infrared spectroscopy show that in the surface region of the polymer there are no chemical changes such as the presence of unsaturated groups or the introduction of polar groups by oxidation. We conclude from this study that wettability of the polymer surface is affected by the surface morphology.

INTRODUCTION

THE CRITICAL surface tension of wetting, γ_c, of a polymer is an important parameter in describing the wetting characteristics of the solid when in contact with a variety of liquids.[1] Recently, it has been demonstrated that polymers crystallized in contact with high surface free energy substrates have critical surface tensions of wetting in excess of those previously reported in the literature?[2,3] These results[2,3] suggest that the morphology of the polymer surface has a profound affect on the wettability of the polymer. The purpose of this paper is to demonstrate that for FEP Teflon there exists a relation between wettability and the morphology of the surface region.

EXPERIMENTAL

1. Heterogeneous Nucleation and Crystallization on Gold Surface

Evaporated gold films [3000 Å on standard glass microscope slides (1x3 in.)] were used as nucleating surfaces. Sandwiches were formed consisting of a glass microscope slide (1x3 in.) with an evaporated gold film—FEP Teflon® (DuPont Teflon® FEP fluorocarbon, 10 mil film)—evaporated gold film on a glass microscope slide (1x3 in.). Three sandwiches were placed side by side in a press at 600°F for varying lengths of time under 330 psi, cooled down to room temperature and then unloaded. To obtain a constant FEP Teflon® thickness of 3 mils, a spacer was used which consisted of two glass microscope slides and a 3 mil polytetrafluoroethylene film. To separate the polymer from the gold, the gold sandwiches were placed in a saturated aqueous sodium cyanide solution at room temperature overnight. This effectively removed the gold from the surface of the FEP Teflon® without damage to the surface region of polymer.[4,5] To remove any traces of carbonates which might have formed at the surface of the FEP Teflon® film during exposure to the aqueous sodium cyanide solution, the polymer films were rinsed with hydrochloric acid (ca. 19%). After washing (for 5 min. in running water) the polymer films were dried in air and their wettabilities determined.

2. Crosslinking by Activated Species of Inert Gases[6,7]

FEP Teflon® films were exposed to helium in a glow discharge for varying lengths of time. Two polymer films were used in this study. One was untreated FEP Teflon® (10 mils, as received) and the other was a gold-nucleated FEP Teflon® film (3 mil), prepared at 600°F and 330 psi for 30 minutes. Gas pressure and the power of bombardment were 1 mm Hg and 100 watts, respectively. The FEP Teflon® films were rinsed in acetone prior to exposure to activated inert gas species to remove obvious dust and surface contamination.

3. Contact Angle Measurements

For contact angle measurements, FEP Teflon® film specimens were mounted on microscope cover glass (0.8x0.8 in.) employing double-backed adhesive tape. The contact angles of a variety of liquids on the FEP Teflon® were measured directly at room temperature by employing a telescopic device equipped with an ocular protractor[8] (Gaertner Scientific Corp.). Table 1 lists the liquids used for the wetting experiments along with their surface properties. Polar liquids were used only on the gold-nucleated polymer.

Table I. Surface Tension of Liquid at 20°C

Liquid	γ_{LV}, *dynes/cm*	*Liquid*	γ_{LV}, *dynes/cm*
Glycerol	63.4	Hexadecane	27.6
Formamide	58.2	Tetradecane	26.7
Methylene iodide	50.8	Dodecane	25.4
α-Bromonaphthalene	44.6	Decane	23.9
		Octane	21.8

RESULTS AND DISCUSSION

The data in Fig. 1 illustrate the variation of the critical surface tension of wetting of the FEP Teflon® film with increasing molding time. As illustrated in Fig. 1, the γ_c increases from 18.8 dynes/cm to 40.4 dynes/cm when the polymer is nucleated and crystallized in contact with gold. A similar behavior has been observed in both polyethylene[3] and polytetrafluoroethylene.[9] Schonhorn and Ryan[5] have shown that when polyethylene was nucleated and crystallized on a high energy surface such as chemically etched aluminum or gold, a transcrystalline region[10] resulted in the surface règion of the polymer. The wetting behavior of this surface was quite different than previously reported. The γ_c was approximately 70 dynes/cm.[5]

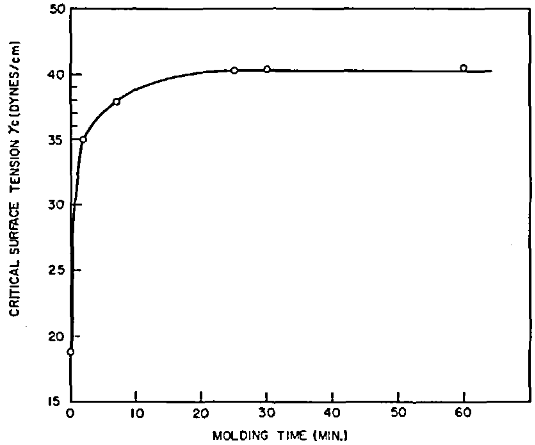

Figure 1. Critical surface tension of wetting of FEP Teflon as a function of the molding time in contact with evaporated gold. Molding temperature and pressure were 600°F and 330 psi, respectively.

The correlation between the molding time and the critical surface tension of wetting, as shown in Fig. 1, may be related to the high viscosity of polymer melt.[8] In the initial stages of molding, there was insufficient contact generated between the gold and the polymer melt. This lack of extensive solid-liquid interfacial contact resulted in a relatively amorphous polymer interfacial region. Longer dwell times of the polymer melt maximized the area of contact and the influence of the gold in generating a more dense interfacial region.

An estimate of the density of the surface layer may be obtained by the following simplified analysis. Based on a considerable amount of wettability and surface tension data for non-polar polymers, it has been suggested that[11]

$$\gamma_{LV} = \gamma_c = \gamma^d_{SV} \qquad (1)$$

This is true for non-polar polymers and non-polar liquids where only dispersion forces are operative. Obviously, when $\gamma^d_{LV} \neq \gamma_{LV}$, Eq. (1) is no longer valid. Since the surface tension can be related to the density by means of the parachor,[12,13] a value for the amorphous density of the polymer may be conveniently calculated. Here,

$$\gamma_{LV} = \left(\frac{P}{M}\rho_s\right)^4 \tag{2}$$

where M is the molecular weight, P is the parachor and ρ_s is the density of the polymer. Combining Eq. (1) and (2) yields

$$\gamma_c = \left(\frac{P}{M}\rho_s\right)^4 \tag{3}$$

Variation of γ_c with the change of density in the same polymer system is given in Eq. (4).

$$\frac{\gamma_{c2}}{\gamma_{c1}} = \left(\frac{\rho_{s2}}{\rho_{s1}}\right)^4 \tag{4}$$

where γ_{C1} and ρ_{S1} refer to the critical surface tension and the density of original or amorphous polymer surface, γ_{C2} and ρ_{S2} are the critical surface tension and the density of gold-nucleated or crosslinked (CASING treated) polymer surface region, respectively.

An application of Eq. (4) to gold-nucleated FEP Teflon® film shows that the density of the surface region of FEP Teflon® film increased from 1.85 gm/cm^3 for the amorphous surface to 2.24 gm/cm^3 for the gold-nucleated or crystalline surface. Although there are no data for $(\rho_s)_a$ and $(\rho_s)_c$ in the literature, these values are quite reasonable.[14] Recently, Van Krevelen and Hoftyzer[14] have indicated that $\rho_C \cong (1 + 0.15\,\alpha)\,\rho_a$, where α is the degree of crystallinity. When $\alpha = 1$, $\rho_C = 1.15\,\rho_a$, in excellent agreement with our results.

The wettability of FEP Teflon® films which have been treated by the CASING technique for varying lengths of time are shown in Fig. 2. The γ_c is plotted as a function of bombardment time in excited helium. It has been suggested[6] that crosslinking is the predominant reaction taking place in the polymer surface region during the CASING treatment, while both scisson and crosslinking have been reported to result from electron bombardment.[7] Examination of the surface region by ATR infrared spectroscopy reveals that no unsaturation or polar groups are introduced by exposing gold-nucleated or as-received polymer film to the CASING technique. It appears then, that the increased wettability of the CASING treated FEP Teflon® surfaces results from a crosslinking in the surface of the polymer which increases the surface density, although no solvent for FEP Teflon® was available to estimate such a gel fraction.

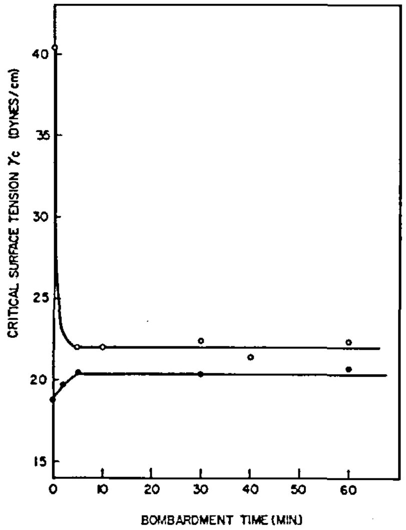

Figure 2. Critical surface tension of wetting of FEP Teflon films (both as received and gold-nucleated) 1 mm Hg and 100 watts.
CASING treated in helium for varying length of time at
○ - gold-nucleated film
● - as received film

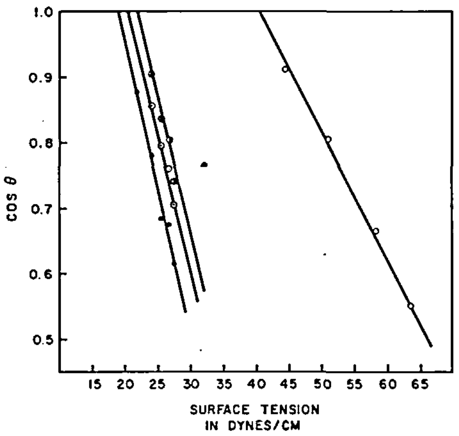

Figure 3. Zisman plot for several different FEP Teflon films.
● - original (as received)
⊙ - CASING in helium for 30 min.
◑ - gold nucleated film CASING treated in helium for 30 min.
○ - gold nucleated film

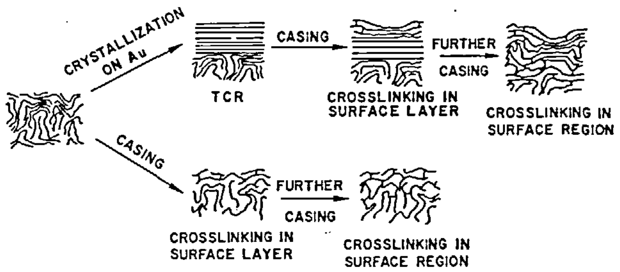

Figure 4. Schematic diagram depicting the effect of a variety of surface treatments on the surface morphology of FEP Teflon®.

Using the γ_c value of 20.6 dynes/cm, and Eq. (4), an increase of 1.05 times in the density of the as-received polymer surface region is obtained by the CASING technique. The data in Fig. 2 also show the variation of the wettability of FEP Teflon® films which have been gold-nucleated then exposed to the CASING technique for varying lengths of time. The critical surface tension of wetting sharply decreases on short exposure to the CASING treatment. This suggests that the crystallinity at the polymer surface was easily disrupted by the CASING treatment.

The γ_c of the gold-nucleated FEP Teflon® film exposed to the CASING treatment attained a constant value of 22.0 dynes/cm after about 5 min treatment in activated helium. The difference in wettability between the two treated samples (20.6 dynes/cm and 22.0 dynes/cm), apparently depends on the original crystallinity in the polymer surface.

In Fig. 3 the wettabilities are shown for four typical FEP Teflon® films with different morphologies.

Various surface structures are suggested and their changes in morphology by gold-nucleation and CASING are shown in Fig. 4. These illustrations are based on the experimental results in this report.

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