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Surface Chemistry of Fluoropolymer Barrier Films: Relation of Solution Variables to Film Properties

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The quality of PFOMA barrier films, e.g., thickness, smoothness, surface texture, and resistance to lubricants, is shown to depend on the formulation variables of the PFOMA-solvent solutions from which they are cast. Thus, barrier film properties can be optimized by the choice of solvent composition and concentration. Scanning electron microscopy, optical microscopy, visual observation of drying films, and contact angle measurements all showed the relation of film properties to the solution variables. This was further established by calculating solubility parameters for the

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compositions studied, which showed that thermodynamically good solutions formed the best barrier films. Polymer phase partitioning probably occurred in a ternary solvent mixture resulting in unusually poor films. The relation of solution thermodynamics to the film properties was the basis for selection of an optimum solvent composition. From these techniques, an optimum concentration for casting was found to be one yielding a film thickness of about 0.5 μm.

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SURFACE CHEMISTRY OF FLUOROPOLYMER BARRIER FILMS: RELATION OF SOLUTION VARIABLES TO FILM PROPERTIES

INTRODUCTION

Bernett and Zisman's basic studies [1,2] of the surface properties of fluorinated materials demonstrated the very low surface energy of fluorinated acrylic ester polymers and their consequent nonwettability by most organic liquids. These polymers are soluble in volatile fluorinated solvents, and the resultant very thin films cast from their dilute solutions have an even lower surface energy than polyetrafluoroethylene (PTFE) reference surfaces. These characteristics led to the invention and subsequent use by the U.S. Navy of barrier films to confine lubricants or prevent their reaching critical sites [3,4]. One important application is miniature precision bearings for guidance systems; previous failures due to lubricant migration away from the raceways have been dramatically reduced by barrier films on the outer faces of the bearings [4,5]. Similarly, telephone relays are treated to keep oil from reaching and fouling the contact points [6]. Oil repellency is obtained with almost undetectably thin films [7], which do not interfere with normal operations.

In early studies, the polymer poly (1,1-dihydropentadecafluorooctyl methacrylate), or PFOMA, was found to have outstanding barrier film properties and to easily form coherent films [8]. It is now specified as the material of choice for barrier film use [9].

The long fluorinated side chains in PFOMA are responsible for the very low surface energy of its films and coatings. The measured critical surface energy γ_c of 10.6 mNm^{-1} ($mNm^{-1} \equiv$ dyn cm^{-1}) is lower than the γ_c of PTFE of (18 mNm^{-1}), and approaches the lower limit of 6 mNm^{-1} ascribed to a perfluoromethyl ($-CF_3$) surface [10,11]. This suggests that much of the surface is composed of the ($-CF_3$) end groups of the side chain and thus that the side chains must be alined in the outermost part of the films [12]. Similar fluoropolymers having regular side chain structures, with the ($-CF_3$) groups outermost, are effective oil-repellent fabric finishes [13]. A heat cure improves the finish durability and adhesion of fluoropolymer textile coatings [14]. Films of PFOMA for use as barrier films are likewise "cured" *in vacuo* to remove traces of solvent and improve durability [15].

In the decade that this polymer has been used as a barrier film, the commercially available formulations (dilute solutions in fluorinated solvents) have been offered in several combinations of polymer concentration and solvent type, including mixed solvents. The quality of cured barrier films of PFOMA have not been directly studied, but it appears to be affected by the polymer concentration, which governs the film thickness, and by the solvent type [16,17]. The present work reports the results of an experimental study of the effects of these variables on barrier film wettability, surface, and polymer

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properties, using contact angle and microscopy studies, and relates them to their optimization in barrier film oil repellency applications.

EXPERIMENTAL

Materials

Sample Substrates — In practice, barrier films are applied directly to bearing faces or other desired locations. In this study, glass or bearing steel flats were used as substrates. The glass slides were acid cleaned. The 52100 and 440C steel flats were polished with graded silicon carbide and then with 0.3-μm alumina to a mirror finish. Half of the 44°C samples were then chromate passivated [15]. The 52100 tool steel specimens were not passivated.

PFOMA Solutions — Commercial and experimental samples of PFOMA were obtained as solutions in three fluorinated solvents and their mixtures, i.e., hexafluoroxylene (HFX), 1,1,2-trifluoro-1,2,2-trichloroethane (Freon), and a perfluorinated cyclic ether, $C_8F_{16}O$ (PCE). Barrier film samples were prepared from solutions both as received and after dilution with one or more of the solvents, as listed in Table 1. Solvents were used as received except for HFX, which was distilled.

Table 1 — Composition and Film Properties of Barrier Film Solutions

Solution Number	Solution Composition		Cured Film Properties	
	Polymer Percent	Solvent*	Dry Film Type†	Appearance
I	2.0	HFX	A	Retracted, raised center
II	2.0	Freon	B	Wavy, raised edges
III	2.0	PCE	B	Smooth
IV	0.5	HFX	A	Retracted
V	0.5	HFX/Freon 75/25	A	Retracted
VI	0.5	PCE/Freon 75/25	B	Wavy surface
VII	0.5	PCE/Freon 90/10	C	Smooth
VIII	0.2	PCE/Freon 90/10	C	Smooth
IX	0.2	PCE/Freon/HFX 80/10/10	A	Retracted, raised center

*HFX: Hexafluoroxylene; Freon: 1,1,2-trifluoro-1,2,2-trichloroethane (Freon TF).
PCE: Perfluorocyclic ethers, $C_8F_{16}O$.
†Corresponds to Fig. 1.

Lubricants — The three oils, representative of lubricants used for miniature bearings, used for compatibility studies were military specification MIL-L-81846, a formulated polyol ester-diester instrument oil (γ = 25.5 mNM^{-1}) used in bearings at normal operating conditions; an unformulated chlorophenyl polysiloxane (γ = 21.0 mNM^{-1}) used for high-temperature bearing operation; and bis (2-ethylhexyl) sebacate, a diester base stock, unfoumulated, with γ = 31.1 mNM^{-1}. The sebacate was percolated through alumina before use; the other oils were used as received.

Contact Angle Test Liquids — Triply-distilled water (γ = 72.0), methylene iodide (γ = 50.8) and hexadecane (γ = 27.6) were the standard reference liquids used for contact angle measurement. Methylene iodide and hexadecane had been purified through various adsorbent columns before use.

Analyses

Solvent Analysis — Liquid-phase infrared spectra (4 cm^{-1} resolution) were obtained for the solvents and mixtures. The solvents were gas-chromatographed, using a 600' Apiezon M capillary column to obtain adequate retention times. A gas-chromatography-mass spectrometer was used to verify the solvent compositions. The PCE and Freon were more than 99% pure, and the HFX was 98% pure.

Polymer Analysis — Infrared spectra (4 cm^{-1} resolution) were obtained on PFOMA films cast on salt windows. Identical spectra were obtained from PFOMA from the several formulations supplied, and from the experimental mixtures.

Differential scanning calorimetry was performed with 10-mg samples obtained from the various solvents. A Perkin-Elmer DSC-2 was used at a sensitivity of 0.5 mcal/s full scale and ± 2°C from -77°C to +250°C. The DSC scans were identical for each sample before and after heating to 250°C, strongly suggesting that residual solvent was not present as a plasticizer.

Methods

Film Preparation — Barrier film samples were prepared by pipetting PFOMA solutions onto the glass or metal substrates, air-drying overnight, and curing at 50°C *in vacuo* for 3 to 4 h.

Appearance and Thickness Measurements — Film appearance was observed visually during and after the drying process, and the films were examined with an optical microscope at 40X to 100X before and after oil immersion studies. Scanning electron micrographs (SEM) were made before and after oil immersion on selected barrier film samples on both glass and metal substrates.

The PFOMA films were usually thin enough to exhibit interference color zones [9]; thicknessess of 0.05 to 1.5μm were estimated with an interference color gage calibrated in 0.025-μm steps.

Oil Resistance — The representative lubricants do not initially wet the barrier film or react with it. However, actual use could involve inadvertent gross exposure to lubricants, and the surfaces were evaluated after exposure to the lubricants, as in previous work [2,3]. Barrier film samples were immersed in the oils for 19 h or more at 100°C, then washed free of oil with detergent and water. The measurement of contact angles with the three test fluids has been shown to be a sensitive detector of surface changes. Advancing contact angles [18] with these liquids were measured before and after oil immersion. The data in Tables 2 and 3 were usually reproducible to ± 1 degree, for six or more determinations.

RESULTS

Film Drying Modes

Effects due to solvent type were observed while the films were air drying (Table 1). The general modes of film formation are also listed in Table 1 and shown as profiles in Fig. 1. Films from HFX and all mixtures containing it dried as in Fig. 1a, where the evaporating solution retracted from the film edges and formed a thick central portion. Films from PCE or Freon, and from PCE/Freon 75/25 dried as in Fig. 1b, with a flattening in the center causing thicker edges and occasionally a surface of many small, thinner zones (separated by slightly thicker boundaries). Films from PCE/Freon 90/10 dried as in Fig. 1c, with smooth, uniform surfaces and no retraction or edge effects.

Oil Repellency

Data in Table 2 show the effect of immersion in oils at 100°C on PFOMA surfaces on glass substrates. Advancing contact angles after oil exposure were slightly lower for all the films except those from solutions V and IX. These two solutions contained the combination of solvents HFX and PCE and produced films having markedly poor oil resistance and much lower contact angles.

Data in Table 3 are for films from solution VIII, on both bearing steels and glass. Oil immersion caused smaller contact angle changes in the films on the steels than those on glass. This suggests that data on the glass substrates can be used as a lower limit of film performance on bearing steels, and confirms previous work that noted higher oil resistance of barrier films on nonferrous metals than on glass [2].

Effects of Oil Immersion and Solvents on Surface Appearance

Films from the same solvent formulations on bearing steels and glass were initially similar. Their appearances after oil immersion are noted in Table 3. Films on glass and passivated 440C steel substrates became somewhat hazy and whitened, while those on unpassivated 440C and 52100 steels were essentially unchanged. Under the optical microscope the latter films appeared smooth and transparent. Films with hazy or whitened areas had small bubbles or pits, particularly in the thicker portions. Scanning electron microscopy revealed these surface changes after oil immersion even more clearly. Figure 2 shows a cured film from the PCE/Freon 90/10 solution (sample VIII)

Table 2 — Wettability of Barrier Films After Exposure to Lubricants*

Polymer Solution	Hexadecane Contact Angle (degrees)				CH_2I_2 Contact Angle (degrees)				H_2O Contact Angle (degrees)			
	Control	Instrument Oil†	Sebacate‡	Cl ϕ Silicone‖	Control	Instrument Oil	Sebacate	Cl ϕ Silicone	Control	Instrument Oil	Sebacate	Cl ϕ Silicone
I	75	70	71	65	98	92	96	79	116	108	113	114
II	74	70	69	66	98	95	95	90	112	107	107	109
III	74	67	67	66	98	93	94	94	116	108	108	108
IV	75	70	71	65	—	—	—	—	—	—	—	—
V	73	25	60	55	97	50	79	78	110	45	85	102
VI	74	70	69	65	98	90	97	93	113	109	108	110
VII	74	70	65	67	—	—	—	—	—	—	—	—
VIII¶	74	70	66	69	99	85	81	78	115	110	102	113
IX	74	15	10	66	—	—	—	—	—	—	—	—

*Films on glass substrates.
†A formulated ester instrument oil, MIL-L-81846.
‡Bis (2-ethylhexyl sebacate).
‖Chlorophenyl silicone fluid.
¶Solution produced very thin films on glass. The previously established experimental method of scrubbing the film to remove oil damaged from films on glass. This was not a problem in the metal substrates, as in Table 3.

Table 3 — Wettability of Barrier Films on Bearing Steels After Oil Immersion, Sample VIII (PCE/Freon, 90/10)

Substrate and Oil	Contact Angle (degrees)			Appearance
	$C_{16}H_{34}$	CH_2I_2	H_2O	
52100 Steel				
Control	74	99	116	Very Uniform
Instrument oil*	72	96	113	No changes after immersion
Sebacate	68	92	110	No changes after immersion
Cl ϕ Silicone	68	95	112	No changes after immersion
440C Steel, Unpassivated				
Control	74	99	119	Uniform
Instrument Oil	68	90	109	No changes after immersion
Sebacate	70	94	112	No changes after immersion
Cl ϕ Silicone	70	93	114	Edges whitened
Passivated 440C Steel				
Control	74	99	119	Uniform
Instrument Oil	70	90	108	Edges hazy; interference color lost
Sebacate	70	96	111	Hazy
Cl ϕ Silicone	70	93	114	Hazy, more so at edges
Glass				
Control	74	99	115	Uniform
Instrument Oil	70	85	110	Hazy and slightly crazed
Sebacate	66	81	102	No changes
Cl ϕ Silicone	69	78	113	Hazy and crazed

*Lubricants as in Table 2.

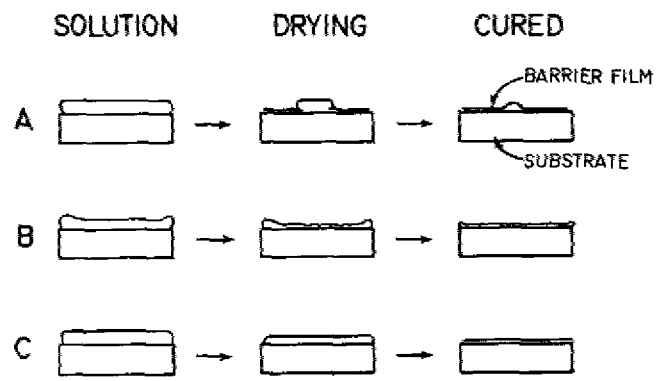
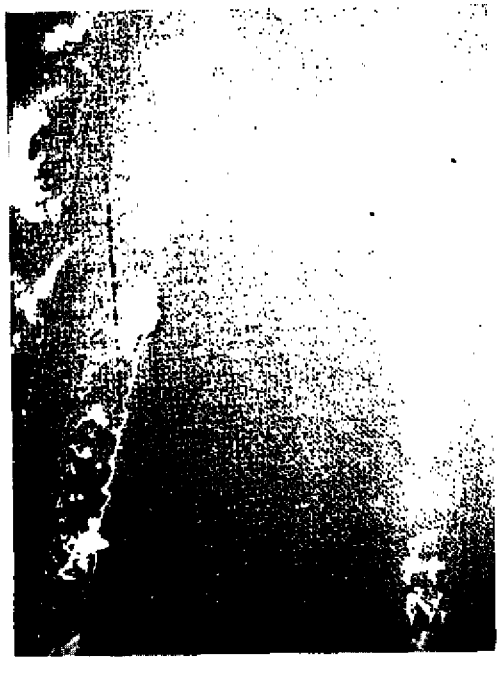
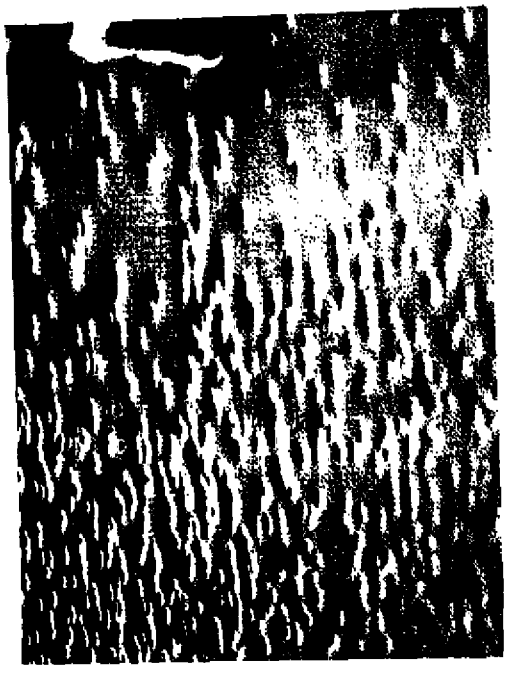


Fig. 1 — Barrier film profiles during drying

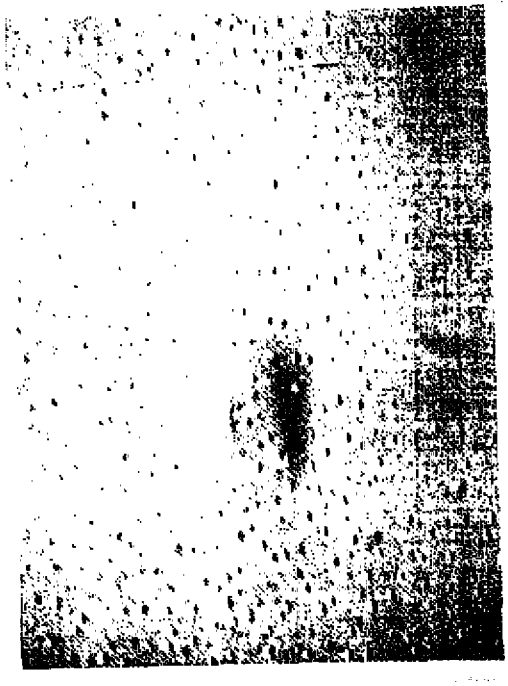


(a) Control, cast film from solution VIII, 1000X



(b) After immersion in instrument oil, 1000X

(c) After immersion in sebacate, 1000X



(d) After immersion in Cl ϕ silicone, 5000X

Fig. 2 — SEM of effect of oil immersion on barrier film surfaces

on a glass substrate, before and after immersion in the three test oils. The surface of the control film (Fig. 2a) was so smooth that a scratch is essentially the only feature seen. After immersion in the oils (Figs. 2b, c, d) the surface became pitted and rough. With uneven films (Figs. 1a, 1b) pitting occurred mostly in the thicker regions. Films cast from HFX/Freon 25/75 and HFX alone are shown in Fig. 3. The films from HFX and a mixture containing HFX are less smooth and adherent than the control film in Fig. 2a. Small patches and blisters appear where the film does not adhere firmly to the substrate; in Fig. 3b the film, where scratched, is seen to pull away from the substrate. This pulling back was also seen with some of these films in friction experiments [19]. A cast film from the PCE/Freon/HFX 80/10/10 solution (sample IX) is shown in Fig. 4 at several magnifications. The micrographs show distinct domains not seen in the other films, resulting in a very irregular surface. The oil resistance of these films was unusually poor (Table 2).

(a) Cast film from solution V (HFX/Freon), 500×

(b) Cast film from solution IV (HFX), 500×

Fig. 3 — SEM of barrier films

DISCUSSION

Barrier Film Thickness

The very thin films (0.05-0.15μm) on bearing steels are found to have the optimum overall oil repellency and durability. This thickness is the same as those of films of optimum textile oil repellency [14], and is also that of the best friction reduction by a metal-on-metal coating [20]. This suggests that the PFOMA barrier film behavior is that of a classical thin film on a substrate. When thin enough, the film—substrate interactions predominate, and optimum film values are achieved. When thicker, the inherent lack of toughness in the bulk polymer [21] becomes a factor in governing the properties of the film. Oil repellency is not a function of thickness in the range considered here. The thinner films (0.05-0.15μm) are less susceptible to removal by sliding metal, as in friction tests [19]. In actual use they are durable as well as more economical.

Effects of Solution Concentration

The choice of concentration of the polymer in solution was at first simply the means of controlling the average thickness of the resultant cast films. However, barrier films from the less concentrated solutions were found to be more uniform as well as thinner, probably because polymer concentration continually increases during evaporation of solvent from a cast film. When identical volumes of solutions having differing initial polymer concentrations evaporate, the concentrations at which polymer deposition must occur are reached at different drying times and at different heights of the pools of solution. With the initially more concentrated solution, viscosity and surface tension gradients generated by the evaporation process could have a greater effect on the drying surface of thicker pools of solution than on thinner ones from more dilute solutions. Surface tension gradients due to the solvent mixture and concentration changes near the interface can cause a Marangoni effect in a drying film, with local thinning in regions of the solution [22]. This effect is more pronounced in the thicker solution films, which offer less viscous resistance to surface fluctuations than thinner films [23]. Also, solvent trapped in or under a thicker film during casting will be a possible cause of unevenness even after the solvent is removed by a vacuum cure.

Retraction and edge effects are encountered in polymer films from solutions having polymer concentrations above 0.5%. In general-purpose applications involving thicker films and/or much higher concentrations, the effects seen here may not be of concern. For barrier films (or other very thin films), irregularities of a micrometer or so become significant. A PFOMA concentration of 0.2% by weight appears to be in the optimum range for maximizing the surface uniformity of barrier films.

Solvent-Polymer Interactions

The three fluorinated solvents and their mixtures produce films that differ in appearance and oil resistance. These differences could not be ascribed to solvent impurity or reactions in solution. The thermodynamic interactions involved in polymer solution processes, however, correlate fairly well with effects observed in solvent-PFOMA systems.

The solubility parameter δ, defined as (cohesive energy density)$^{1/2}$, was introduced by Hildebrand [24] as a convenient method of determining the heat of mixing of a solution. The heat of mixing is a function of ($\delta_{solvent} - \delta_{solute}$), and when $\delta_{solvent} \approx \delta_{solute}$, $\Delta H_{mix} \rightarrow 0$, so that solution is favored. The simple comparison of solubility parameters for solvent and solute can be used to predict solubilities. Solubility parameter values are tabulated for common polymers and solvents [25]. Solubility parameters calculated for PFOMA and the fluorinated solvents from group molar attraction constants by the method of Small [26] are given in Table 4. Parameters for mixed solvents, also in Table 4, were calculated from values proportional to the volume fraction of each component [27].

Table — 4 Solubility Parameters of Fluorinated PFOMA and Solvents

Solvent	δ (cal cm^{-3})$^{1/2}$	Hydrogen-Bonding Group*	Method	Solutions†
PFOMA	5.59	m	‡	—
	5.63	m	‖	—
HFX	7.76	p	‡	I, IV
Freon	7.3	p	¶	II
PCE	5.50	m	‡	III
HFX/Freon 75/25	7.60	p/p	**	V
PCE/Freon 75/25	5.95	m/p	**	VI
PCE/Freon 90/10	5.68	m/p	**	VII, VIII
PCE/Freon/HFX 80/10/10	5.90	m/p/p	**	IX

*m = moderately, p = poorly H-bonded.
†From Table 1.
‡Ref. 25.
¶ Calculated from group molar constants by method of Small [26].
**Calculated from $\delta = \Sigma_i \delta_i v_i$ [27].
‖Experimental value for a similar fluorobutyl polymer, Ref. 21.

The calculated δ value of 5.59 for PFOMA is most closely matched by the 5.68 δ value of the solvent mixture of solutions VII and VIII, PCE/Freon 90/10, which formed the most uniform barrier films with excellent oil resistance. Films not quite so uniform were obtained from PCE/Freon 75/25, whose δ value of 5.95 is also not far removed from that of PFOMA. The other solvents and mixtures had respectively poorer film properties; their δ values were farther from the 5.59 value.

The solubility parameter as described is not sensitive enough to account for the solution properties of all the mixtures studied. To describe the solvent — solute interaction more precisely, Hansen [28] and others [27] recently used a three-dimensional solubility parameter with

terms for hydrogen-bonding and polar interactions. The values are not available for the solvents studied here, but they do lead to a consideration of the relative polarities of the solvents and the polymer, in Table 4 which are designated as p = poorly, and m = moderately hydrogen-bonding. It is seen that bulk PFOMA is moderately hydrogen-bonding, as is PCE, the only one of the three pure solvents to be in that category. Our study demonstrates that films cast from solutions with large fractions of PCE are more uniform; several of the mixed solvents in which both solvent components were poorly hydrogen-bonded formed solutions that yielded films of lower quality. It thus appears that a match in the hydrogen-bonding nature of the solvent-solute pair, as well as in the δ values, contributes to better final films with improved properties.

Mixtures of solvents with widely different δ values may combine to produce a "good" or "poor" solvent. The ternary solvent mixture PCE/Freon/HFX, 80/10/10 produced very low-quality barrier films. This mixture is sufficiently disparate for a possible phase separation to occur during evaporation. If so, the polymer would tend to dissolve more in the better solvent at the expense of the poorer, yielding polymer-rich and polymer-poor phases. Such behavior is described by Flory [29] as relatively common in solutions using mixed solvents with different affinities for the polymer. The micrographs of Fig. 4, showing the cast film with domains, suggest that such a phase separation occurs. Films cast from the single solvents were not as uniform as those from the best mixtures. This was so even for PCE, whose calculated solubility parameter is as near to that of the polymer as the 90/10 PCE/Freon mixture.

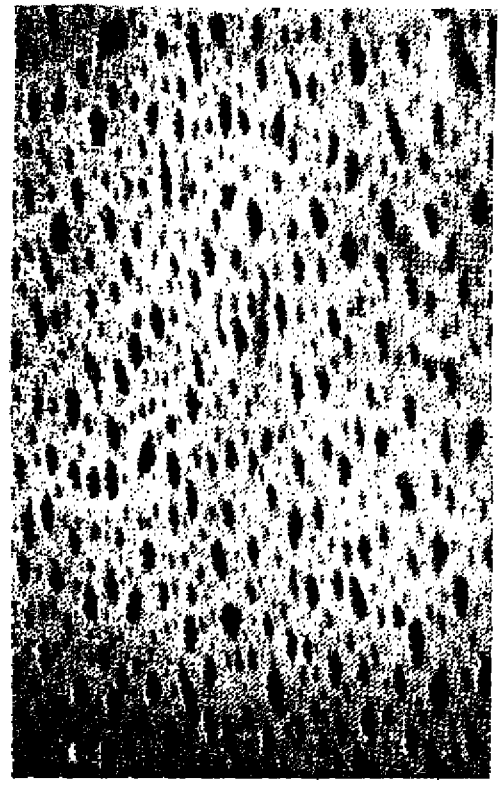
Because of the inexact nature of δ values, it is possible that one or more of the δ values used here may be shifted. While the solutions were being spread, qualitative observations indicated that solutions with PCE/Freon spread more uniformly than those with PCE alone. Since preferential evaporation from a mixed solvent undoubtedly occurs, the concentration gradients can combine with surface tension gradients to optimize effects. When the more volatile solvent is also the poorer solvent, its evaporation early in the drying process leaves the polymer in an increasingly better solvent system. The film may become flatter and smoother as it dries due to local surface tension gradients balancing out the concentration gradients; this appears to be the case for PCE/Freon mixtures.

Effects of Oil Exposure on PFOMA Films

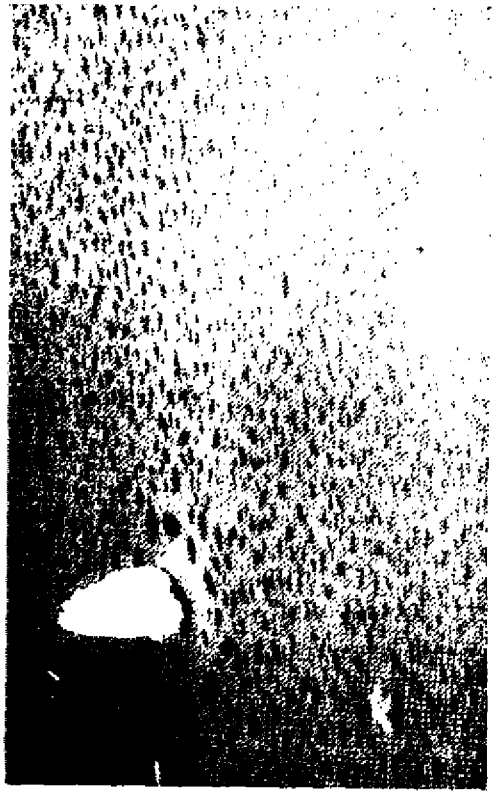
The SEM revealed that PFOMA films, after exposure to oil, had roughened somewhat. Contact angle measurements showed only a slight decrease with oil exposure. The possibilities of surface roughness, changes in surface polarity, or changes in the physical state of the PFOMA can be considered in discussing these data.

A general effect of increasing surface roughness is a decrease in contact angles initially lower than 90°, and an increase in angles higher than 90°. In our data, oil immersion caused only decreases in contact angles, even for angles initially above 90°, indicating that little or no roughening occurred. Since the measured angles were all not far from 90°, where hysteresis effects are the smallest and roughness causes little error [18], an estimate of the roughness, already shown to be small, was not made by this method.

The possibility of oil exposure increasing the surface polarity was examined by estimating the dispersion components of the PFOMA surface energy γ_{Sd}. Values were



(a) 2000X



(b) 5000X

(c) 20000X

Fig. 4 — SEM of barrier films solution IX — effect of ternary solvent.

obtained by the graphical method of Fowkes [30], and γ_{Ld} values from the literature [31]. For the control PFOMA films, γ_{Sd} was very close to γ_c, indicating no polar contribution. Oil immersion caused a slight increase in the calculated γ_{Sd} values, indicating a possible change in surface polarity.

Such physical alterations by the lubricant as swelling, crazing, and the like were not seen, but should be considered in any discussion of polymer — oil interactions. Apparently surface roughness is not a major factor, and a slight change in surface polarity of PFOMA may occur on oil exposure.

SUMMARY AND CONCLUSIONS

Properties of oil-repellent barrier films of PFOMA are shown to be related to solvent composition, concentration, the substrate, and conditions of film deposition.

The most effective barrier film formulation of those studied was a 0.2 wt% solution of PFOMA in a PCE/Freon 90/10 mixed solvent. This formulation consistently gave smooth, uniform, highly oil-repellent films.

Barrier films on polished metal substrates were more resistant to lubricants than those on glass substrates.

Choice of solvents in the casting solution appeared to be the most influential factor. Changes in surface tension gradients and solubilities during selective evaporation from mixed solvents are postulated to affect the surface properties of the dried films. Scanning electron microscopy showed differences in uniformity and also indicated surface changes induced by exposure of the films to lubricants at elevated temperatures.

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