

On the Thickness and Spatial Distribution of a Fluoropolymer Film Deposited by Solution Dipping

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Synopsis

Poly-1H,1H-pentadecafluorooctyl methacrylate is a barrier compound used to prevent silicone oil from creeping to relay contacts. It is essentially a methyl methacrylate polymer with a fluorocarbon side chain substituted for one of the methyl hydrogens. It is applied by dipping the part into a solution, with Freon TF as the solvent and the fluorocarbon polymer as the solute. This work considers the spatial distribution of the resulting film of barrier compound when it is deposited in this manner. The specific variables considered are concentration and withdrawal velocity. The samples were withdrawn from the solution with velocity perpendicular to the surface, and we show that the macroscopic uniformity and thickness of the film is dependent on this velocity. There exists a critical velocity (dependent on concentration) above which the film is nonuniform and below which the film is macroscopically uniform. Below the critical velocity, the thickness varies with velocity with approximately a $v^{2/3}$ dependence. The critical velocity is about 13 mm/sec for a concentration of 0.2%. For macroscopically uniform films, a microscopic nonuniformity exists with a coverage of about $1/4$ for an average film thickness of 90 Å.

INTRODUCTION

The increased popularity and use of silicone oils in recent years have caused some problems in the field of electrical contacts. Because of low surface free energy, silicone oils are very prone to spreading. Insulating films of silicone oil degradation products are formed on operating relay contacts when certain voltage-current conditions are present.¹ One solution² to the creeping problem has been to use a thin film of a fluoropolymer as a barrier to the creeping oils. (The fluoropolymer has a lower surface free energy than the silicone oil.) The barrier compound presently being used for some relay contacts is poly-1H,1H-pentadecafluorooctyl methacrylate (PFOM) purchased from the 3M Company. The repeat unit of the polymer is shown in Figure 1. The molecular weight of the polymer is between 300,000 and 1,000,000 amu.

The material is received from the manufacturer as a 2% solution in Freon TF* solvent and is subsequently diluted further with the Freon TF solvent to the desired concentration. The samples to be coated are then dipped into and withdrawn from the solution. The solvent then evaporates leaving the film of PFOM. Previous work³ by one of the authors described the thermal degradation of PFOM and included a brief discussion on the deposition process. Some work⁴ has been done at the Naval Research Lab on the film distribution, but the films in that case were formed by pipetting a fixed quantity of the solution onto a horizontal surface and allowing the solvent to evaporate. Although the barrier film is the same one as we are studying, the results of their study are not applicable to our system.

* Du Pont trademark.

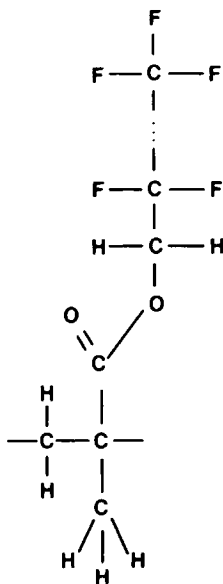


Fig. 1. Repeat unit for poly-1H,1H-pentadecafluorooctyl methacrylate (PFOM). This side chain is C_7F_{15} .

In the present work, the effect of several of the deposition parameters on the thickness and uniformity of the film is presented. Although this work was done on the fluoropolymer PFOM, the concepts are applicable to many other systems where a film is deposited by withdrawing a sample from a solution containing the film material. One other example is the application of a thin film of lubrication on a metal.

MACROSCOPIC VARIATIONS

General

Two kinds of substrates were used. First, coupons of a 60% Pd–40% Ag alloy (used for electrical contacts in relays), nominally 20 mm \times 6 mm \times $\frac{1}{2}$ mm, which had been given either a 600-grit finish or a mirror finish, were used. No differences were observed that depended on the finish. Secondly, silver-coated quartz crystals for a Sloan thin-film monitor were used. These are $\frac{1}{2}$ in. diameter and 0.015 in. thick. Because these samples are shaped differently from the Pd–Ag samples, comparisons and extrapolations between these two geometries should be made with care. Films were deposited by dipping in a solution with the desired concentration for 15 sec or more. Three different methods of withdrawal were used. The first method (used in the past by the authors) is to manually withdraw the sample rapidly and to wick away the drop which forms at the bottom of the coupon. It is estimated that the withdrawal velocity is about 500 mm/sec. A second method is to manually withdraw the sample very slowly at a rate which is estimated to be about 1 mm/sec. The slow withdrawal is continued in the vapor until the sample is about 2 cm above the solution. A third method is to withdraw the sample with a variable speed motor at a measured velocity.

Auger Electron Spectroscopy (AES) Measurements

The AES technique uses an incident electron beam which has been shown to be very destructive to C-F bonds.⁵ Correspondingly then, the spectrum obtained is that of the carbonaceous residue left after the destruction process. Although this somewhat limits the usefulness of this technique for analysis of the barrier compound film, some information can be obtained. Pd-Ag samples coated by the rapid manual withdrawal and samples coated by the slow manual withdrawal method were analyzed. The samples were withdrawn with the long dimension vertical. The slow-withdrawal samples appeared uniform visually, whereas the rapid-withdrawal samples showed a significant nonuniformity. Three stripes of excessively thick film were usually observed running in the direction parallel to the long dimension (or the direction of withdrawal). AES spectra were taken at various spots along a line across the sample (perpendicular to the long dimension) at about $1/8$ in. from the end. Information about the thickness of the residue can best be obtained from the Auger signal from the substrate, and this is shown in Figure 2. Figure 2(a) is a plot of the ratio of the silver signal to the signal for a clean Pd-Ag surface (obtained from a silver standard with appropriate scaling factors) for a rapidly withdrawn sample using a 0.2% solution. Figure 2(b) shows the same information for a slowly withdrawn sample from the same solution. The equation which describes the relative output signal in this situation is

$$I/I_0 = e^{-t/d}$$

where I/I_0 is the signal ratio described above, t is the thickness of the residue, and d is the escape depth of the Auger electrons through the residue; t is shown to the right of the plots in terms of d . Figure 2, then, is like an inverted thickness plot except that a zero value of the ratio means a thickness which is much greater than the escape depth. The signal (or absence of it) for the three stripes mentioned above is evident in Figure 2(a) as indicated by the arrows. Clearly, Figure 2(b) represents a much more uniform film than Figure 1(a). Similar data were obtained for a concentration of 0.02%, and the corresponding plots are shown in Figures 2(c) and 2(d). In this case the nonuniformity is also evident, but none of the regions have thicknesses grossly larger than the escape depth. Based on the work of Roberts et al.,⁶ the escape depth is estimated to be about 12 Å. It must be remembered, however, that the material which the electrons are escaping through is not the barrier coat itself, but the residue left after electron bombardment. Incidentally, the destruction due to the electron beam occurs in a few seconds, after which the signals are steady. It should be pointed out that we are making the explicit assumption that the spatial distribution of the residue is directly related to the spatial distribution of the barrier coat film before electron beam destruction.

Contact Angle Measurements

A method⁷ of measuring the surface free energy of a surface is to measure the angle that a drop of a specific liquid makes with the surface. Although this does not give direct information on the distribution of the barrier coat on the surface, it is a measure of the effectiveness of the film as a barrier. Hexadecane drops (1-2 μ l) were placed on films coated on Pd-Ag substrates and photographed from

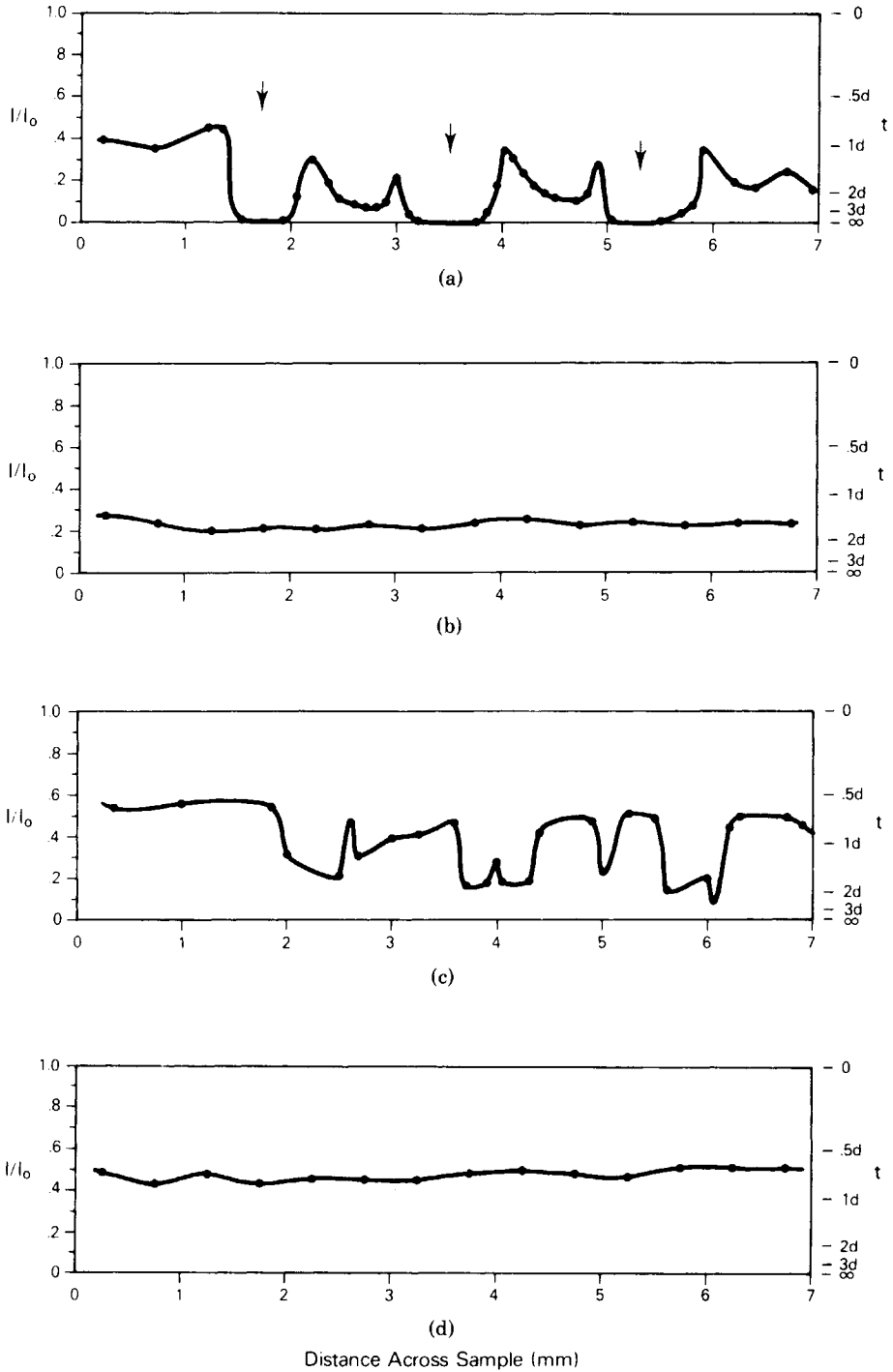


Fig. 2. Ratio of the Ag signal through the residue to the Ag signal of a clean R156 surface I/I_0 , as a function of position across the sample for (a) a sample which was rapidly withdrawn from a 0.2% solution, (b) a sample which was slowly withdrawn from a 0.2% solution, (c) a sample which was rapidly withdrawn from a 0.02% solution, and (d) a sample which was slowly withdrawn from a 0.02% solution.

the side. The angle of contact was then measured from the photograph. Samples were coated with various concentrations with slow manual withdrawal and with rapid manual withdrawal. Seven to nine drops were photographed for each condition. The results are shown in Figures 3(a) and 3(b), where the average and standard deviation is shown as a function of concentration. The $\cos \theta$ is plotted versus concentration. A value of $\cos \theta = 1$ represents a spreading condition, or total failure of the barrier coat film. In Figures 3(a) and 3(b) the average value of $\cos \theta$ versus concentration is very similar. The spread in the data for the lower concentrations is significantly different for the two withdrawal velocity conditions. For the rapid withdrawal samples and lower concentrations, there are regions that are significantly better as a barrier and regions which are significantly worse than for the corresponding slow withdrawal film. It should be noted, however, that this does not imply that films coated with the same concentration will have the same total amount of material on them with the velocity simply affecting the distribution. As will be shown later, the velocity affects the total amount of material deposited as well as the distribution.

Variable Withdrawal Velocity Visual Observations

A motor with controllable variable speeds was used to form films using different measurable withdrawal velocities. A string with a pair of clamping tweezers on the end was attached to the motor shaft. Running the motor at a fixed speed wound the string up on the shaft giving a fixed measurable withdrawal velocity. For the visual observations, Pd-Ag coupons were clamped in the tweezers and then immersed to just below the tweezers for 15 sec. The motor was then used to withdraw the sample at a given velocity. Up to a critical velocity the film appears uniform over the entire surface, visually. For 2% it is about 2 mm/sec, whereas for 0.2% it is about 13 mm/sec. Above the critical velocity there is a range of velocity where there is a uniform area in the center but within a few millimeters of the edge, the uniformity stops. This is shown in Table I where, for example, at a withdrawal velocity of 16.7 mm/sec for the 0.2% sample the film is uniform to within $\frac{1}{2}$ mm of the edge.

As the velocity increases, there is a second velocity above which there is no region which appears uniform in the center. This occurs at about 50 mm/sec for the 0.2% solution. These observations were made for the 2 and 0.2% solutions. The film is not visible for the 0.02% solution, but from the AES result shown previously, we would expect that samples deposited with this concentration would also exhibit similar behavior. It can be noted from Table I that although the same phenomena are occurring as a function of velocity, the critical values are different for the different concentrations. The geometry of the samples might also affect these values.

Quartz Crystal Monitor Measurements

A quartz crystal thin-film monitor is an instrument which measures weight gain per unit area using the fact that the natural vibration frequency of the quartz crystals changes when mass is added to the crystal. The technique is reasonably accurate to well within $0.05 \mu\text{g}/\text{cm}^2$ (or for a material of density, $1.0 \text{ g}/\text{cm}^3$, to 5 Å). Although normally used for metal films deposited under vacuum, it can be

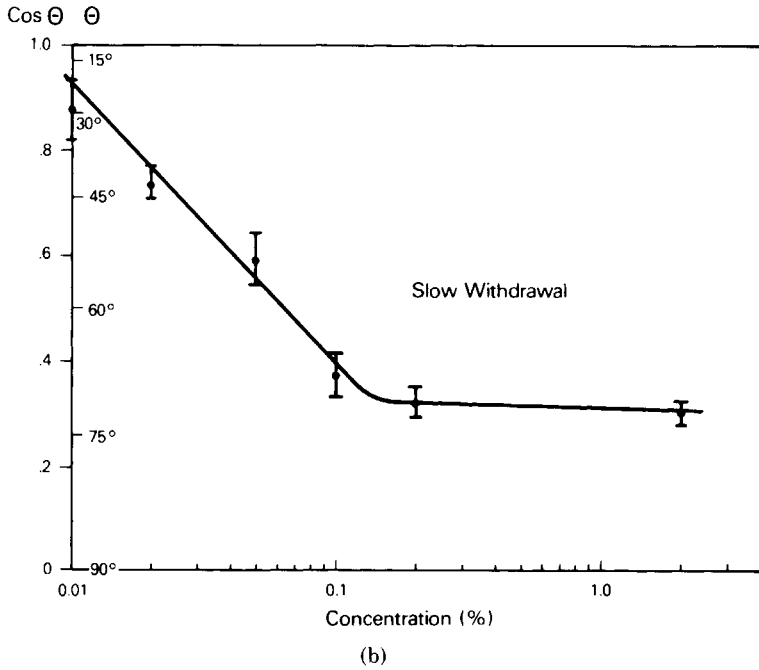
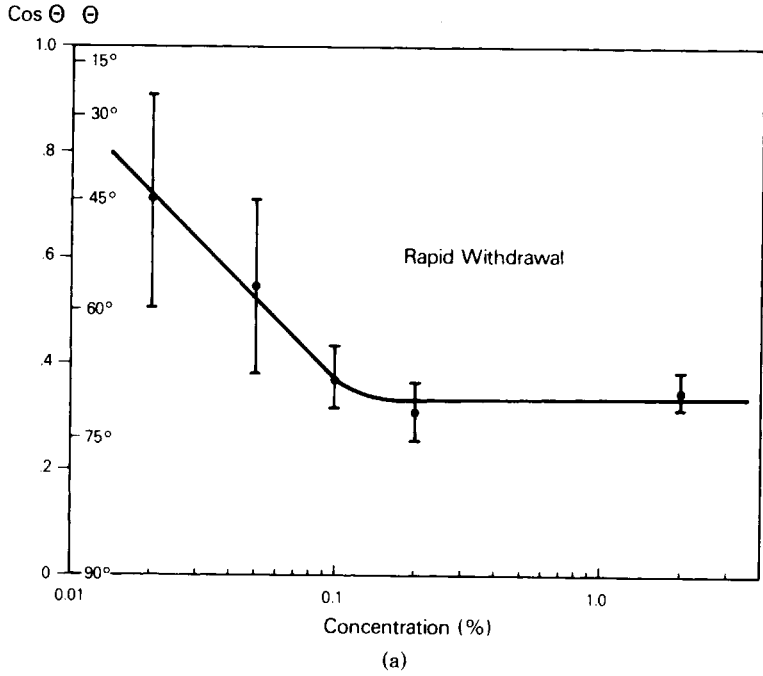


Fig. 3. Cos of the contact angle of a hexadecane drop vs. concentration of the solution: (a) sample withdrawn rapidly; (b) sample withdrawn slowly.

TABLE I
Variable Withdrawal Velocity Visual Observations

2% Concentration		0.2% Concentration	
Velocity, mm/sec	Uniformity	Velocity, mm/sec	Uniformity
1.9	entire surface	12.5	entire surface
5.6	to 1/2 mm of edge	16.7	to 1/2 mm of edge
16.7	to 1 mm	30	to 1 mm
33.3	to 2 mm	50	to 1 1/2 mm
>33.3	no uniform area	>50	no uniform area

used in other ways. In the present measurements, new quartz crystals coated with silver were used for each measurement. The crystal was rinsed in Freon TF, allowed to dry, and inserted into the monitor head. The instrument was zeroed and the crystal removed, coated, allowed to dry for several minutes, and reinserted into the head. The weight gain was then recorded.

The affect of both concentration and withdrawal velocity was measured. For the concentration part, the velocity was kept constant at 2.0 mm/sec. The concentration values used ranged from 2 (as received) to 0.02%. At least three measurements were made at each concentration value, and the results are shown in Figure 4. The dashed line, with a slope of unity, is a reasonable representation of the data. This implies that the amount of material deposited is directly proportional to the concentration, as would be expected.

For the velocity part, the concentration was kept at 0.2%. The crystals were coated using all three of the withdrawal techniques described previously. The

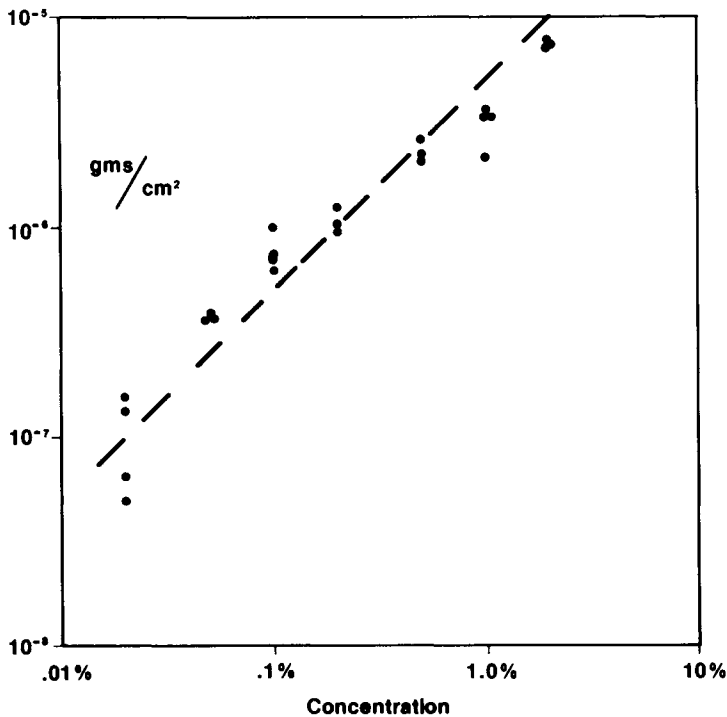


Fig. 4. Weight gain vs. concentration. Withdrawal velocity is 2 mm/sec. Dashed line has a slope of unity.

results are shown in Table II. The measured velocities are all below the critical velocity for uniform film as determined in the previous section, whereas the rapid manual withdrawal is well above the critical velocity. Clearly, a velocity effect is present with thicker film resulting from faster withdrawal.

Some theoretical work on this subject has been done by Levich.⁸ When a plate is withdrawn from a quiescent liquid at a constant velocity v , a thin film of liquid remains on the surface. In case of the solution of the barrier coat compound in Freon TF, the solvent evaporates and a thin layer of solute remains on the solid surface (plate). Considerable attention has been devoted to this problem by various investigators because of its importance in the migration of petroleum in earth strata and in accurate handling of chemical solutions, etc. Levich⁸ has studied this problem in detail and has shown that the thickness h of the film on the plate is a function of liquid viscosity μ , the velocity v , the surface tension σ , and the density ρ of the liquid. When the plate is withdrawn, a certain momentum is transferred from the plate to the liquid. This causes the entrainment of the liquid on the plate surface. The limiting thickness of the liquid layer entrained by the plate is given by

$$h = 0.93 \frac{(\mu v)^{2/3}}{\sigma^{1/6}(\rho g)^{1/2}}$$

It is seen that the thickness is but a weak function of the liquid density and surface tension. However, h is proportional to the $2/3$ power of velocity v and viscosity μ . For a given concentration, σ , ρ , and μ are constants and h is proportional to $v^{2/3}$. The weight gain, shown in Table II, should be proportional to h , the liquid layer thickness. Weight gain versus withdrawal velocity (from Table II) is shown in Figure 5 on a log-log plot. The $2/3$ slope line is shown as a dashed line and seems to fit the data reasonably well.

TABLE II
Weight Gain Values Versus the Withdrawal Velocity^a

Velocity, mm/sec	Weight gain, (g/cm ²) × 10 ⁸
Slow manual	77
	112
	84
	111
1.8	86
	87
	95
3.9	165
	184
	149
6.8	157
	154
	165
10.7	183
	269
	263
Rapid manual	566
	448
	485

^a 0.2% concentration. Critical velocity is ~13 mm/sec.

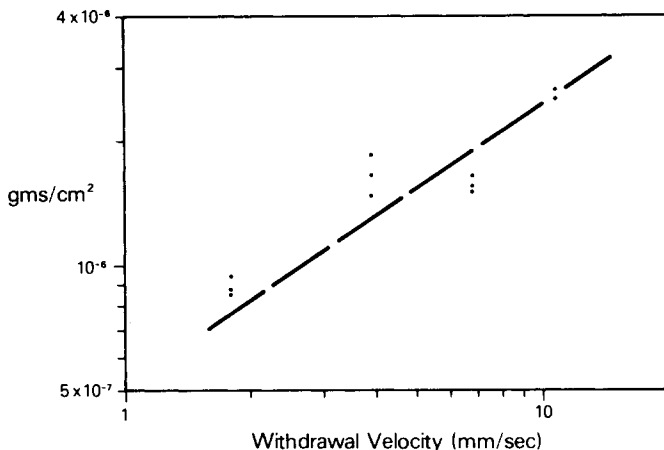


Fig. 5. Weight gain vs. withdrawal velocity. Dashed line has a slope of $2/3$ (see text). Concentration of the solution is 0.2%.

The results of the velocity dependence should be equally applicable to any system where a thin film is deposited by dipping in a solution. This dependence has been observed by the authors on the lubrication of electrical connectors.

Summary of the Macroscopic Observations

Two things are evident from the above observations. First, there is a critical withdrawal velocity below which macroscopically uniform films are deposited and above which rather nonuniform films are formed. The value of the critical velocity varies with concentration, being lower for higher concentrations. The value for a concentration for 0.2% is approximately 13 mm/sec. Secondly, the amount of material deposited is directly proportional to the solution concentration and is also a function of the withdrawal velocities with faster withdrawal giving thicker films.

MICROSCOPIC VARIATIONS

The above studies involved measurements which did not have a particularly good lateral resolution. The best resolution was that of the AES experiment where the beam size was of the order of $10 \mu\text{m}$ or $100,000 \text{ \AA}$. In this section we are concerned with spatial distribution on a smaller scale than this. Due to the thinness of the films, scanning spot techniques such as scanning electron microscopy cannot be used. We must obtain the information rather indirectly. The technique used is x-ray photoelectron spectroscopy (XPS). In XPS, the sample is bombarded with x-rays. The resultant photoelectrons are then measured. The sample damage is much less than with an incident electron beam (AES), and the technique has been used considerably for study of fluoropolymers.^{9,10}

Quartz crystal monitor silver-coated samples were used. The samples were coated in solutions of 2, 0.2, and 0.02% concentrations by dipping and withdrawing manually at about $1/2$ mm/sec. The film areal density (weight gain per unit area) was measured as described above under "Variable Withdrawal Velocity

Visual Observations." Using a 1.55 g/cm^3 density figure (given by the supplier), an average thickness can be calculated, and this is shown in angstroms in Table III for each sample. XPS measurements were then made on these samples using a Physical Electronics Industries instrument with a pass energy of 25 eV. Typical spectra are shown in Figure 6 for the 0.2% solution. The peaks used were the Ag $3d_{5/2}$ peak with binding energy of 368.2 eV and fwhm about 1.1 eV, the C 1s peak associated with the C-H bonds at 284.5 eV with fwhm of 2 eV, the C 1s peak associated with the C-F bonds at 291.8 eV with fwhm 1.7 eV, and the F 1s peak at 688.8 eV with fwhm of 2 eV. The fwhm and peak positions were reasonably constant for the different samples. The normalized peak heights for all of the concentrations are shown in Table III. The C-H carbon peaks are listed first, and the C-F carbon peaks are listed second. The escape depth of the carbon electrons and Ag electrons is considered to be about 22 \AA .⁶

The absence of any Ag peaks for the 2% sample shows that there are no areas that have thicknesses less than several escape depths. We get the most information from the XPS measurements of the 0.2% film. If the film were microscopically uniform with a thickness of 90 \AA , the Ag peak height should be

$$e^{-90/22} = 0.017$$

of the clean Ag value. Although the reference film has some carbonaceous residue (e.g., the carbon signal), the values of the Ag signals of the 0.2% sample and the reference signal are totally inconsistent with a uniform film. In addition, a uniform film 90 \AA thick would have nearly the same value for the F and C-F carbon signal as the 2.0% film.

The governing equation for the F signal for a uniform film is

$$I/I_{\infty} = 1 - e^{-t/d}$$

where I is the signal for the sample in question, I_{∞} is the signal for a sample which is much thicker than the escape depth, t is the thickness, and d is the escape depth for the F electrons (calculated to be 17 \AA using ref. 6 and the square root energy dependence).

If the signal for the 2% sample is taken as I_{∞} , then for uniform films, the signal for the 0.2% sample should be 0.98 of the 2% sample, and the signal for the 0.2% sample should be 0.47 of the 2% sample. From the data in Table III this is clearly not the case.

TABLE III
XPS Normalized Peak Heights in Counts/Scan^a

Concentration and average thickness	Ag (368.2 eV)	C	
		(284.5 eV)	F (688.8 eV)
Reference	264.4	17.3	
0.02%, 10.9 Å	201.3	11.2	26.75
		2.1	
0.2%, 90 Å	151.1	8.03	38.44
		4.66	
2.0%, 800 Å	0	6.98	152.75
		13.25	

^a C-H carbon peaks are listed first, and C-F carbon peak are listed second.

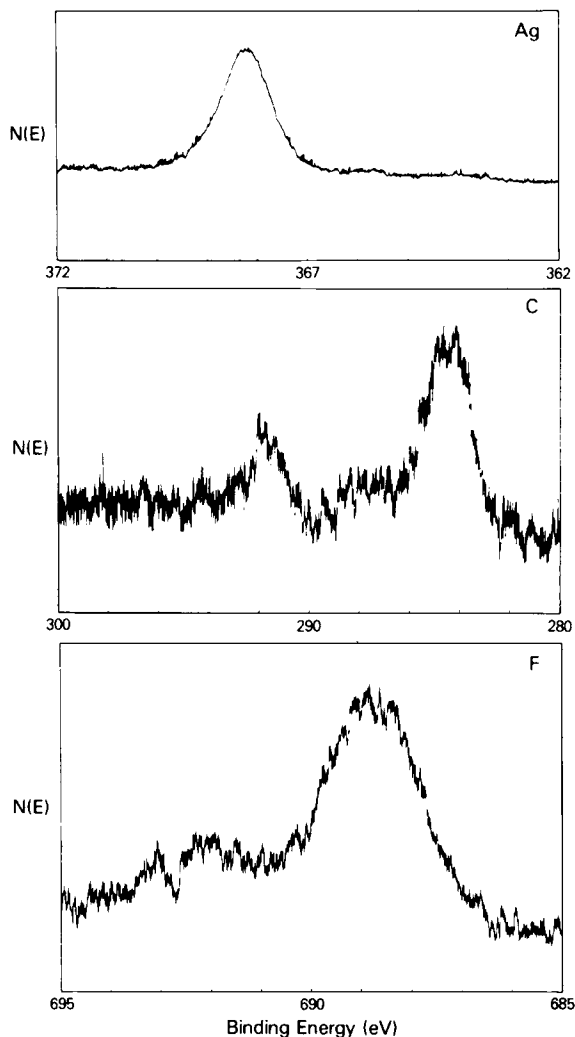


Fig. 6. Typical XPS spectra for a sample deposited from a 0.2% solution.

We have therefore established that although when coated by withdrawing slowly these films are macroscopically uniform, they are not microscopically uniform. The dimensions of nonuniformity are unknown but less than the AES spot size, or $10\ \mu\text{m}$.

Let us assume a model of patches of material considerably thicker than the escape depth separated by uncoated areas. The thickness values listed in Table III then are averages over the entire area. Since we are assuming thicknesses large compared to the escape depth, the ratio of the signal to the signal for the 2% sample, then, is just the fraction of the covered area. The values of the F signal for the 0.2% sample compared to the 2.0% sample suggest that about 25% of the surface is covered with barrier compound. Similarly, the data for the 0.02% sample suggest that about 18% of the surface is actually covered with barrier compound. As indicated earlier, the 2.0% sample has 100% coverage.

SUMMARY

We have studied the spatial distribution of PFOM barrier compound film both macroscopically and microscopically. We have shown that the macroscopic uniformity and thickness of the film are dependent on the withdrawal velocity. There exists a critical velocity (dependent on concentration) above which the film is nonuniform and below which the film is macroscopically uniform. Below the critical velocity the thickness varies with velocity with approximately a $v^{2/3}$ dependence. On rectangular Pd-Ag coupons, the critical velocity is about 13 mm/sec for a 0.2% concentration. We have shown that for macroscopically uniform films a microscopic nonuniformity exists with a coverage of about $1/4$ for the 0.2% solution samples.

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