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A New Approach to Surface Functionalization of Fluoropolymers

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There have been numerous surface chemistry studies directed at increasing the surface energy of fluoropolymers to improve wettability and promote adhesion.[1] Unlike most polymers, there are not direct chemical methods for the conversion of CF, CF_2, and CF_3 groups in perfluoroalkanes to any functionality. The most successful chemical reactions of fluoropolymers involve single electron reduction.[2] Plasma chemistry[3] and surface grafting[4,5] have also been used to modify fluoropolymer surfaces. None of the reported chemical methods introduce discrete functional groups, but rather a mixture of species. There are numerous reports from other research fields, however, of biopolymers spontaneously adsorbing to fluoropolymers.[6-9] There is one report of a homopolymer, poly(L-lysine), adsorbing to a fluoropolymer from aqueous solution.[10] These workers point out that it is the reduction of interfacial free energy (the displacement of high-energy water molecules from the fluoropolymer/water interface) that drives polymer or biopolymer adsorption ("hydrophobic interactions").

We report here the unique adsorption behavior of poly(vinyl alcohol) (PVOH) to poly(tetrafluoroethylene-*co*-hexafluoropropylene) (FEP) from aqueous solution. Our research group has been using the adsorption of functional polymers to the FEP/water interface as a method to incorporate discrete polar functionality ($-NH_2$, $-OH$, $-CO_2H$) to the fluoropolymer surface. Poly(allylamine hydrochloride), polyethylenimine, and poly(acrylic acid) have been adsorbed to FEP surfaces from aqueous solutions under different conditions.[11] The extent of surface functionalization is minimal using these polymers.[11] The adsorption behavior of PVOH is very different than that observed for other functional polymers.

There have been several reports of the adsorption of PVOH from aqueous solution onto silicon oxide particles,[12] metal oxide particles,[13] and a gold surface.[14] The adsorption of PVOH onto gold increases with increasing PVOH molecular weight, PVOH concentration, NaCl concentration, solution temperature, and the number of adsorption/drying steps, as analyzed using a quartz crystal microbalance. It was pointed out that PVOH aggregates by inter- and intramolecular hydrogen bonding and forms crystalline regions.[14] In the study reported here, the adsorption of PVOH to the FEP/water interface is demonstrated as a new approach to surface modification of fluoropolymers. The adsorption results in a dramatic improvement of wettability. The low solubility of PVOH and, most likely, the crystallization of PVOH at the FEP/water interface provide additional driving forces for adsorption.

A series of adsorption experiments of PVOH[15] to FEP[16] from aqueous solution[17] have been carried out. The effects of PVOH concentration, adsorption kinetics, ionic strength, and stepwise deposition on the adsorbed amount and wettability have been examined. All samples studied have been analyzed by water contact angle[18] and X-ray photoelectron spectroscopy (XPS).[19]

Initially experiments involved exposing FEP film samples to aqueous solutions of PVOH at different concentrations (0.005, 0.01, 0.05, 0.1, and 0.5 M) for 89 h.[20] These FEP−PVOH samples display indistinguishable water contact angles, $\theta_A/\theta_R = 65° \pm 3°/18° \pm 3°$, which are indistinguishable from those of solution-cast PVOH film, $\theta_A/\theta_R = 63°/17°$. Contact angles of virgin FEP are $\theta_A/\theta_R = 117°/93°$. This indicates that the thickness of the adsorbed PVOH reaches at least the sampling depth of contact angle, which is on the order of a few angstroms. O/F ratios obtained from XPS (at 15° takeoff angle) are 1.06, 1.14, 1.07, 1.01, and 4.21, respectively, for the different concentrations. This trend indicates that the adsorbed amount is independent of concentration except at the highest concentration studied and that high PVOH concentrations give relatively thick layers. We arbitrarily chose 0.01 M as the con-

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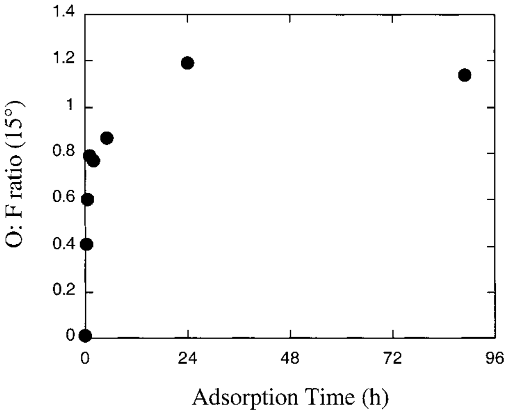

Figure 1. O/F ratios calculated from XPS atomic composition data at 15° takeoff angle as a function of adsorption time.

Table 1. XPS Atomic Composition Data (15° Takeoff Angle) and Advancing and Receding Water Contact Angles (deg) for FEP Derivatives

film samples	% C	% F	% O	% N	O/F	θ_A/θ_R
FEP	34.04	65.32	0.64			117/93
PVOH (cast film)						63/17
FEP−PLL	54.75	38.02	3.53	3.70	0.097[a]	104/16
FEP−PVOH (no salt)	54.04	21.02	24.94		1.19	63/17
FEP−PVOH (salt)	66.23	3.38	30.38		8.99	68/18
FEP−PVOH(1 layer)	51.29	27.45	21.26		0.79	73/20
FEP−PVOH(2 layers)	52.53	23.53	23.94		1.02	65/19
FEP−PVOH(3 layers)	57.36	19.39	23.25		1.28	64/19
FEP−PVOH(4 layers)	65.26	5.51	29.22		5.30	64/19

[a] N/F.

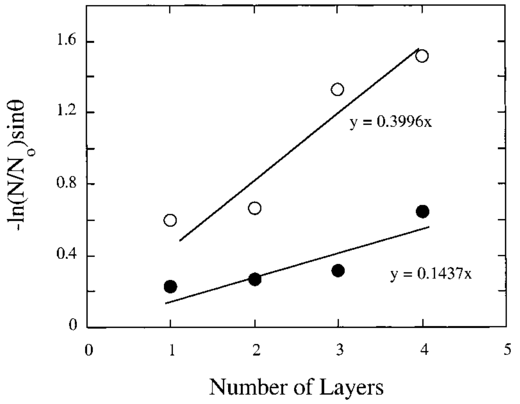

Figure 2. Plots of $-\ln(N/N_0)\sin\theta$ vs number of layers in the multilayer film. The closed (●) and open (○) symbols are data recorded at 15° and 75° takeoff angles, respectively.

centration for further adsorption studies.

Figure 1 shows the O/F ratios obtained from XPS at 15° takeoff angle as a function of adsorption time. O/F increases and reaches a plateau after 24 h adsorption time. Water contact angle data are consistent with this finding. XPS atomic composition (15° takeoff angle) and contact angle data of an FEP sample analyzed after adsorption in 0.01 M PVOH for 24 h are given in the fourth entry of Table 1. We also adsorbed poly(L-lysine) (PLL)[21] using conditions reported in the literature.[22] Atomic composition and contact angle data for FEP−PLL are given in Table 1. Comparing FEP−PLL and FEP−PVOH, the adsorbed amount and the improvement of wettability are much greater for PVOH than PLL. PVOH is a highly crystalline polymer—it is difficult to dissolve it in water. We suspect the low solubility of PVOH, and, likely more importantly, its strong tendency to crystallize at the FEP/water interface and the stabilization of the film by inter- and intramolecular hydrogen bonding give additional driving forces for adsorption.

To study the effect of solution ionic strength on adsorption, 2 M NaCl was added to the PVOH solution. Contact angles of FEP−PVOH (with salt) are not much different than solution-cast PVOH film, and this indicates that the adsorbed PVOH thickness has reached the sampling depth of contact angle. The O/F ratio of the sample obtained at 15° takeoff angle is 8.99, compared to 1.19 when no salt is added. Ions increase the surface tension of water, increasing the FEP/water interfacial free energy, and lower the solubility of PVOH. The thickness of the PVOH layer should be controllable by changing the ionic strength of the solution.

Stepwise assemblies of PVOH thin films on FEP that involved repetitive adsorption/drying[23] steps were carried out. Up to four layers of PVOH were assembled onto the FEP surface. XPS atomic composition (15° takeoff angle) and contact angle data of these multilayer assemblies (Table 1) indicate that the PVOH thickness increases as the number of layers increases. The average PVOH thickness can be calculated using eq 1,[24]

$$-\ln(N/N_0)\sin\theta = nz/\lambda \qquad (1)$$

where N is the fluorine content of FEP−(PVOH)$_n$, N_0 is the fluorine content for virgin FEP, n is the number of layers, z is the average layer thickness of the individual PVOH layers, λ is the mean free path of the F_{1s} electrons, and θ is the takeoff angle. The overall linearity of the data shown in Figure 2 indicates that the individual layer thicknesses are close to constant, the slopes of the lines correspond to z/λ, and a longer mean free path is indicated by the lower slope of the 15° takeoff angle data. Angular dependent mean free paths have been reported[24] and indicate an anisotropic structure of the assembly which allows the "channeling" of electrons at angles close to the plane of layer buildup at lower takeoff angle. The average PVOH layer thickness is calculated, using the 75° takeoff angle data, to be ~8.2 Å.[24] Thick layers of PVOH can be prepared on fluoropolymer surfaces using this stepwise process. The driving force for the multilayer assembly is presumably intermolecular hydrogen bonding between the adsorbed PVOH in the dry state and PVOH chains in aqueous solution.

The adsorbed PVOH thin film is sufficiently stable that it does not redissolve in aqueous solution under the testing condition (in Milli-Q water at room temperature for 14 days) based on both water contact angle and XPS atomic composition data.

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(15) PVOH ($M_w = 108$K), 99.7 mol % hydrolyzed, was obtained from Polysciences.

(16) FEP films (Berghof, 5 mil) were cleaned in 25 mL of concentrated H_2SO_4 solution containing 0.5 g of $KClO_3$ for 2 h, rinsed with Milli-Q water (5×) and THF (3×), and dried (0.1 mm, >24 h).

(17) Water was purified using a Millipore Milli-Q system that involves reverse osmosis followed by ion-exchange and filtration steps. PVOH was dissolved in Milli-Q water at ~100 °C for 1 h.

(18) Contact angle measurements are made with a Ramé-Hart telescopic goniometer and a Gilmont syringe with a 24-gauge flat-tipped needle. The probe fluid is Milli-Q water. Dynamic contact angles, advancing (θ_A) and receding (θ_R), were recorded while the probe fluid was added to and withdrawn from the drop, respectively. Contact angle assesses the composition of the outer few angstroms.

(19) X-ray photoelectron spectra (XPS) were recorded on a Perkin-Elmer Physical Electronics 5100 spectrometer with Mg Kα excitation (15 kV, 400 W). Spectra were recorded at both 15° and 75° takeoff angles (between the plane of the sample surface and the entrance lens of the detector optics), which give the composition of the outermost ~10 and ~40 Å, respectively. For all the samples analyzed in this study, more F from the substrate and less O from the adsorbed PVOH were observed at 75° takeoff angle. This indicates that the thickness of the adsorbed PVOH is <40 Å. The O/F ratio is used to represent the amount adsorbed.

(20) Clean FEP films were immersed in a PVOH aqueous solution at a prescribed concentration at room temperature for a certain period of time. Film samples were then rinsed with Milli-Q water (3×) and dried (room temperature, 0.1 mm, >24 h).

(21) Poly(L-lysine hydrobromide) ($M_w = 331\,000$) was obtained from Sigma.

(22) Clean FEP films were immersed in a 0.5 mM (based on repeat units) PLL aqueous solution (pH 11) at room temperature for 72 h. Film samples were then rinsed with Milli-Q water (3×) and dried (room temperature, 0.1 mm, >24 h).

(23) Clean FEP films samples were immersed in 0.01 M PVOH for 1 h, rinsed with Milli-Q water (3×), and dried for 1 h under reduced pressure before the next adsorption step.

(24) Chen, W.; McCarthy, T. J. *Macromolecules* **1997**, *30*, 78. For F_{1s} electrons, $\lambda = 21$ Å was calculated using refs 45−48 cited therein.

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