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Surface Modification of Poly(tetrafluoroethylene-*co*-hexafluoropropylene) Film by Adsorption of Poly(L-lysine) from Aqueous Solution

The low surface energies of organic polymers are the origin of interface problems in materials applications where wetting, spreading, or adhesion is needed. The traditional methods for overcoming these problems increase the surface energy by introducing polar functional groups to the polymer surface.[1] Graft polymerization of polar monomers from reactive sites generated on the surface, reactive gas discharge treatment (corona, plasma), and chemical reaction (usually oxidation) are the usual methods. The chemical resistance of fluoropolymers makes them difficult to modify by these standard methods, and alternative approaches, using reducing agents, have been developed.[2]

We report in this manuscript the application of a well-known process as a new approach to surface modification of low surface energy polymers: the adsorption of a polymer (which will increase the surface energy of the film substrate) from solution to the interface between the solvent and the low surface energy polymer. Adsorption of poly(L-lysine) (PLL) to poly(tetrafluoroethylene-*co*-hexafluoropropylene) (FEP) from aqueous solution is described. The process of reducing interfacial free energy between a polar liquid and a nonpolar solid surface by polymer adsorption is hardly new; it is well-recognized in such processes as protein adsorption from blood to biomedical devices,[3] polymer stabilization of colloids,[4] and protein fouling of membranes.[5] Usually referred to as "hydrophobic interaction", it has been suggested[6] that the forces driving these adsorptions are better described as "interfacial forces". The process has not, however, been exploited as a surface modification technique. The adsorption and subsequent polymerization of amphiphilic monomers to the polyethylene/water interface have been described as a surface modification technique.[7]

We are carrying out a series of adsorption experiments of PLL[8] to FEP[9] from buffered aqueous solutions at different pH and alcohol/water mixtures. We are examining the effects of solvent, concentration, PLL molecular weight, FEP surface functionality, and adsorption kinetics on the structure, properties, and reactivity of the modified surface (FEP-PLL). This paper comments on the importance of the adsorption variables and demonstrates the effectiveness of the technique for surface modification in terms of wettability, adhesion, and chemical reactivity.[10] FEP was chosen as a film substrate because we can conveniently introduce carboxylic acids to its surface[11] to affect adsorption. The identity of the polymer film substrate is likely of little importance to the results reported here; only its hydrophobicity is important.

Figure 1 shows XPS spectra[12] of virgin FEP and an FEP-PLL sample prepared by adsorption of PLL (M_w = 400K) to FEP from pH 11 solution.[13] The FEP spectra indicate the expected F$_{1s}$ and high binding energy C$_{1s}$ photoelectron lines. The FEP-PLL spectra show, in addition to the FEP features, O$_{1s}$ (536 eV), N$_{1s}$ (403 eV), and low binding energy C$_{1s}$ peaks, indicating the presence of poly(L-lysine). These spectra represent the composition of the outer $\sim$10 Å[14] of the film sample and suggest a very thin PLL film ($\sim$6 Å) or partial coverage; XPS cannot distinguish between these possibilities. Scanning electron micrographs of FEP and FEP-PLL are indistinguishable.[15] Figure 2 plots the amount of adsorbed PLL, expressed as the ratio of nitrogen to fluorine present in the XPS sampling region, vs adsorption time. The darkened point (■) represents the data in Figure 1, and these kinetics suggest complete coverage and argue for a thin layer as opposed to a thicker patchy layer. We emphasize that the adsorbed film that is analyzed by XPS (dry) may be very different in structure than the adsorbed hydrated film present at the solution-film interface. A continuous adsorbed film may segregate to a patchy surface on drying. Other data in Figure 2 indicate that PLL film thickness is molecular weight dependent and that PLL (4K) does not adsorb.

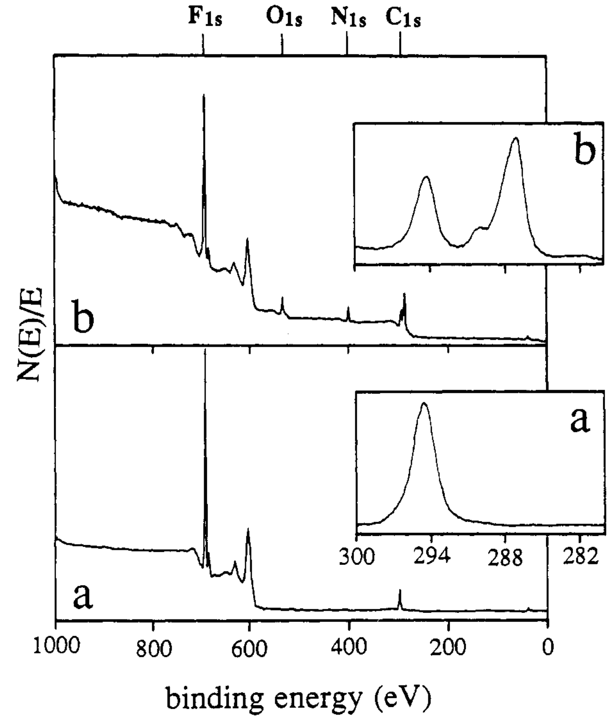

Figure 1. XPS survey and C$_{1s}$ region spectra of FEP (a) and FEP-PLL (b).

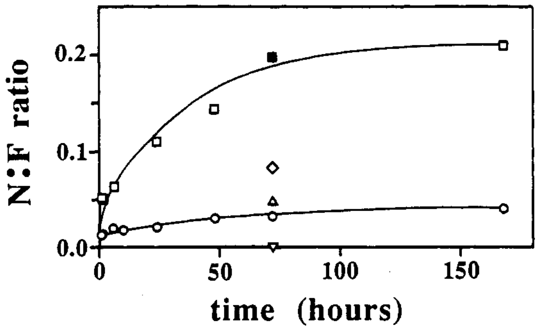

Figure 2. Adsorbance of PLL to FEP as a function of time. N/F is the ratio of the atomic compositions of nitrogen and fluorine in the outer $\sim$10 Å of FEP-PLL samples. PLL molecular weights: □, 400K; ◇, 100K; △, 50 K; ○, 20 K; ▽, 4K.

The thermodynamics of polymer adsorption potentially involves enthalpic and entropic changes in the surface, dissolved polymer, and solvent. We view the important factors in the adsorption of PLL to FEP to be as follows: (1) the release of water molecules from the interface (both decreasing interfacial free energy entropically and enthalpically increasing hydrogen bonding), (2) the change in PLL solvation, and (3) the entropic changes in PLL upon adsorption. PLL in solution at pH 11 exists as a neutral, hydrogen-bonded α-helix.[16] Unfolding of the α-helix concomitant with adsorption may compensate for entropy lost upon adsorption.

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The results of several experiments suggest that both a decrease in interfacial free energy (FEP–H_2O) and the relaxation of a constrained solution structure (PLL α-helix) are necessary to drive adsorption. PLL in pH 7 solution (0.1 g/L) does not adsorb to FEP after 7 days of contact. At pH 7, PLL exists as a charged random coil. It is already "unfolded" and cannot further unfold by adsorbing. The highly charged chain may not be capable of lowering interfacial free energy and may lose solvation enthalpy upon adsorption. PLL (4K) does not adsorb to FEP from pH 11 solution. This low molecular weight chain does not form an α-helix at pH 11;[17] thus, this entropic driving force is unavailable. An alternative explanation that no control experiment will discount is a molecular weight dependent adsorption. PLL does not adsorb to FEP from methanol/water (96:4, v/v) or isopropyl alcohol/water (82: 18, v/v), solvents in which the polymer exists as a charged α-helix.[18,19] The FEP–solution interfacial free energy is substantially lower in these cases than between water and FEP: methanol/water and isopropyl alcohol/water exhibit contact angles[20] of 75°/70° and 48°/40° (θ_A/θ_R), respectively, on FEP whereas water exhibits contact angles of 115°/100°.

We have, briefly thus far, examined the surface properties (wettability, adhesion, chemical reactivity) of FEP–PLL. The surface is significantly more wettable than FEP, exhibiting water contact angles as low as 80°/16° (θ_A/θ_R). The pronounced contact angle hysteresis is expected because of (and can be rationalized on the basis of) hydration of the PLL layer during analysis. Surface roughness and surface chemical heterogeneity may also give rise to hysteresis and cannot be ruled out as partial causes. A noncontinuous PLL layer (patchy on some scale) would be both rougher than FEP and chemically heterogeneous. The relative adhesive joint strength of FEP and FEP–PLL with two 3M contact adhesive tapes was determined.[21] The thin PLL layer improves adhesion significantly. Peel forces of ~6 and ~18 g/cm, respectively, were measured for delaminating 3M 850 and 3M 750 tapes from FEP. In identical experiments with FEP–PLL, peel forces were increased to ~57 and ~50 g/cm. The availability for reactivity of the ϵ-NH_2 groups in FEP–PLL was assessed by reaction with 3,5-dinitrobenzoyl chloride.[22] XPS analysis of the N_{1s} region showed a -*N*O_2 (412 eV) to -*N*HC(O)- (405 eV) peak ratio of 0.67, indicating ~67% of the ϵ-NH_2 groups react to form amides.

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References and Notes

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(8) PLL samples with molecular weights of ~4K, ~20K, ~50K, ~100K, and ~400K were obtained as the hydrobromides from Sigma.

(9) FEP (5-mil, Du Pont) film samples (3 × 2 cm) were cleaned by extraction with dichloromethane for 1 h and dried (0.05 mm, >24 h).

(10) A complete report is forthcoming.

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(12) XPS spectra were recorded on a Perkin-Elmer Physical Electronics 5100 at pass energies of 89.45 eV for survey and 35.75 eV for C_{1s} region spectra with Mg Kα excitation (400 W). Spectra reported were acquired at a 15° takeoff angle (between the film sample plane and the entrance to the detector optics); the pressure was maintained below 3 × 10^{-8} mm during data acquisition, and the samples were exposed to irradiation for less than 12 min. Atomic sensitivity factors used to determine atomic ratios were as follows: F_{1s}, 1.00; N_{1s}, 0.34. Reported binding energies are not corrected for sample charging. X-ray satellites were subtracted from the C_{1s} spectra using the instrument's provided software.

(13) A nitrogen-sparged PLL solution (20 mL, 0.1 g/L) was introduced via cannula to a nitrogen-purged Schlenk tube containing an FEP film sample. The solution in the tube was agitated with a Precision shaker in a water bath at 25 °C for 72 h. After this time the solution was removed, and the film sample was washed with water (20 mL), pH 11 buffer (2 × 20 mL), and then water (2 × 20 mL) and dried (0.05 mm, >24 h).

(14) These values are calculated using 14 Å as the mean free path of C_{1s} electrons ejected by Mg Kα irradiation. This value was measured in poly(*p*-xylylene): Clark, D. T.; Thomas, H. R. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 2843.

(15) Scanning electron microscopy was performed on gold-coated samples with a JEOL 100CX SEM.

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(20) Dynamic advancing (θ_A) and receding (θ_R) contact angles were measured with a Ramé-Hart telescopic goniometer equipped with a Gilmont syringe and a 25-gauge flat-tipped needle using doubly distilled water.

(21) Peel tests (180°) were performed on an Instron with a peel rate of 1 cm/min. The polymer (FEP or FEP–PLL) film was held stationary in the upper clamp and the tape was peeled from the film by the moving lower clamp assembly.

(22) The reaction was carried out under nitrogen in THF/pyridine (20:1, v/v); the product film sample was washed with THF (3 × 20 mL) and methanol (6 × 20 mL), extracted (Soxhlet) with THF (36 h), and dried (0.05 mm, >48 h).

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