

The Wettability of Fluoropolymer Surfaces: Influence of Surface Dipoles

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The wettabilities of fluorinated polymers were evaluated using a series of contacting probe liquids ranging in nature from nonpolar aprotic to polar aprotic to polar protic. Fully fluorinated polymers were wet less than partially fluorinated polymers, highlighting the weak dispersive interactions of fluorocarbons. For partially fluorinated polymers, the interactions between the distributed dipoles along the polymer backbone and the dipoles of the contacting liquids were evaluated using both polar and nonpolar probe liquids. The results demonstrate that the surface dipoles of the fluoropolymers generated by substituting fluorine atoms with hydrogen or chlorine atoms can strongly interact with polar contacting liquids. The wettabilities of the partially fluorinated polymers were enhanced by increasing the density of dipoles across the surfaces and by introducing differentially distributed dipoles.

Introduction

Since the discovery of poly(tetrafluoroethylene) (PTFE, Figure 1) by Plunkett in 1938,¹ fluorocarbon-based polymers have been used in various applications that require, for example, chemical inertness, thermal and mechanical resistance, and low adhesion.² Fluorocarbon resins are widely used across the chemical, semiconductor, and biotechnology industries to seal and isolate materials, especially under harsh conditions.^{3,4} The unique and remarkable inertness to harsh conditions reflects the useful interfacial properties and strong integrity of the chemical structure. The strong C–F bonds and weak polarity of fluoropolymers eventually lead to low solubility, low friction, high thermal stability, low permeability, and strong chemical resistance.^{2,5–7} When selected fluorine atoms in a fluorocarbon resin are replaced by hydrogen or chlorine atoms, a distinct change in the polarity and mechanical properties of the polymers occurs as a result of the different electronegativities of fluorine and the replacement atom.^{8,9} Although the substitution typically leads to enhanced mechanical strength, there is a concomitant loss of thermal and/or chemical inertness.

In contrast to fully fluorinated polymers, partially fluorinated resins have increased polarity because the substituted elements (hydrogen or chlorine) possess electronegativities that are less than that of fluorine (see the structures in Figure 1). Furthermore, the length of the C–X bonds (X = H or Cl) along the polymer backbone differs from that of C–F bonds. The electronegative

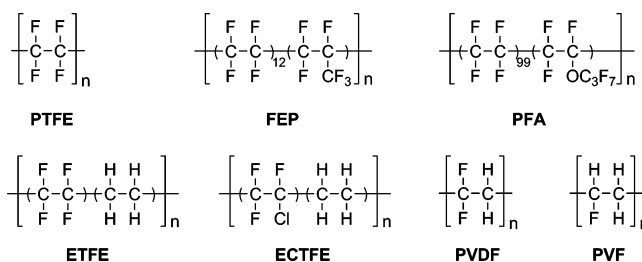


Figure 1. Structures of the fluoropolymers studied in this report: poly(tetrafluoroethylene) (PTFE), fluoroethylene–propylene copolymer (FEP), polyperfluoroalkoxyethylene (PFA), ethylene–tetrafluoroethylene copolymer (ETFE), ethylene–chlorotrifluoroethylene copolymer (ECTFE), poly(vinylidene fluoride) (PVDF), and poly(vinyl fluoride) (PVF).

and electropositive centers are balanced but distanced within the chain, leading to differential separation of charges to permit electrostatic interactions between adjacent chains (Figure 2).¹⁰ The existence of polarity in the partially fluorinated polymers strongly influences the interfacial properties, which leads to an enhanced wettability toward contacting liquids as a function of the degree of polarity.

In this report, we evaluate the interfacial wettabilities of several commercially important fully fluorinated polymers (Figure 1), including PTFE, fluoroethylene–propylene copolymer (FEP), and polyperfluoroalkoxyethylene (PFA) and partially fluorinated polymers including ethylene–tetrafluoroethylene copolymer (ETFE), ethylene–chlorotrifluoroethylene copolymer (ECTFE), poly(vinylidene fluoride) (PVDF), and poly(vinyl fluoride) (PVF). To distinguish the various contributions to the interfacial wettabilities, we employed a combination of three different types of contacting liquids: nonpolar aprotic (heptane, octane, decane, tridecane, hexadecane, decalin, squalene), polar aprotic (nitrobenzene, dimethyl sulfoxide (DMSO), dimethylformamide (DMF), acetonitrile, α -bromonaphthalene, methylene iodide, bromoform, pyridine, 1,4-dioxane), and polar protic (water, formamide, glycerol, ethylene glycol). Through these efforts, we wished to develop a greater understanding of the relationships between the structure and the interfacial properties of fluo-

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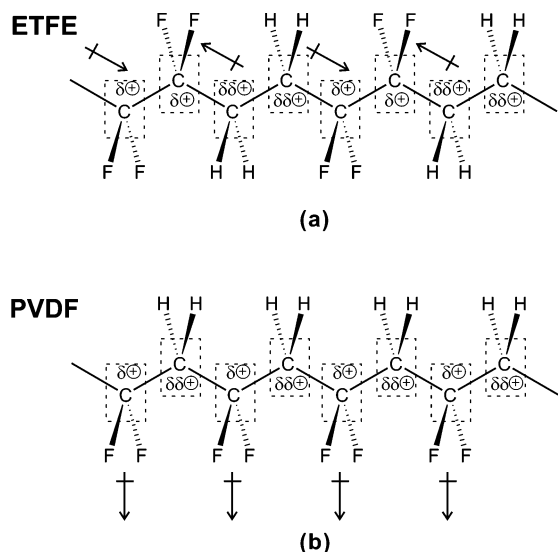


Figure 2. The distribution of dipoles within the polymer backbones: (a) ETFE, (b) PVDF.

ropolymer surfaces. Importantly, the observed trends in wettability are evaluated here for the first time in the context of surface dipoles (where applicable).

Experimental Section

Materials. The contacting liquids were of the highest purity available and were used as purchased from commercial suppliers. Fluoropolymer samples (5 mil thickness unless indicated otherwise) were obtained from the following companies: (i) DuPont: Teflon FEP, PFA, Tefzel ETFE, and Tedlar PVF; (ii) Ausimont: Halar ECTFE, Solef PVDF; and (iii) TEX-A-LON: PTFE. The PVF film (1.5 mil thickness with both sides adherable) was available only as TTR15BG5. The chemical repeat units for all of the fluoropolymers are shown in Figure 1. The polymers can be broadly classified into two major categories: fully fluorinated (PTFE, FEP, and PFA) and partially fluorinated (ETFE, ECTFE, PVDF, and PVF).

Contact Angles. Contacting liquids were dispensed and withdrawn on the fluoropolymer surfaces at the slowest possible rate ($\sim 1 \mu\text{L/s}$) using a Matrix Technologies micro-Electrapette 25. Contact angles of various liquids were measured at room temperature and ambient relative humidity using a Ramé-Hart model 100 contact angle goniometer while the pipet tip was kept in contact with the drop. The reported contact angles are the average values of at least three independent droplets (i.e., six measurements) per sample.

X-ray Photoelectron Spectroscopy (XPS). The surface composition of fluoropolymers was characterized using a PHI 5700 X-ray photoelectron spectrometer equipped with a monochromic Al K α X-ray source ($h\nu = 1486.7 \text{ eV}$) incident at 90° relative to the axis of a hemispherical energy analyzer. The spectrometer was operated at high resolution with a pass energy of 23.5 eV, a photoelectron takeoff angle of 45° from the surface, and an analyzer spot diameter of 1.1 mm. The spectra were collected at room temperature and a base pressure of 2×10^{-9} Torr for C $_{1s}$, F $_{1s}$, O $_{1s}$, and Cl $_{2p}$. The XPS spectra were referenced by adjusting the F $_{1s}$ binding energy to 688.65 eV to eliminate charging effects. Prior to analysis by XPS, the samples were pretreated by sonication in ethanol for 10 min.

Atomic Force Microscope (AFM) Measurements. The surface configuration of the pristine samples was measured using a PSIA XE-150 AFM in noncontact mode at a scan rate of 1 Hz. The probing tip scanned an area of $10 \times 10 \mu\text{m}$ squares at different locations of the sample, followed by postacquisition processing to give three-dimensional topographic images and vertical roughness of the sample surface. Surface roughness was determined from the AFM images using the software to calculate the root-mean-square roughness from the standard definition.

Table 1. Elemental Percentage Composition and Root-Mean-Square Surface Roughness of Fluoropolymers Measured by XPS and AFM, Respectively

polymers	C	O	F	F/C	R_{rms}^a
PTFE	33.85	5.00	61.86	1.83	58.6
FEP	34.38	0.10	65.33	1.90	10.5
PFA	34.01	0.46	65.54	1.93	17.0
ETFE	44.35	0.19	55.46	1.25	11.1
ECTFE	52.19	0.32	37.74 (9.75) ^b	0.91 ^c	29.1
PVDF	52.45	1.04	46.50	0.89	25.9
PVF	69.81	4.56	25.63	0.37	41.7

^a R_{rms} is the root-mean-square surface roughness measured by AFM on scanned areas of $10 \times 10 \mu\text{m}^2$. ^b The number in brackets for ECTFE indicates the % composition of chlorine. ^c In the ratio of F/C, the numerator includes both the F and Cl compositions.

Results and Discussion

Surface Composition of the Fluoropolymers. Before evaluating the interfacial wettabilities of fluoropolymers, we first examined the surface composition of the polymers by XPS because the presence of contaminants on the surface can appreciably influence the wettabilities. The XPS spectra of the fully fluorinated polymers exhibited a major C $_{1s}$ peak at 292 eV and a minor one at ca. 283 eV (data not shown), suggesting the presence of hydrocarbon contamination.¹¹ In contrast, the XPS spectra of the partially fluorinated polymers exhibited two major peaks at 292 and 287 eV (data not shown), corresponding to CF $_2$ and CH $_2$ groups, respectively,^{11,12} and a very minor peak at ca. 283 eV, again attributed to contamination. To verify that the peak at ca. 283 eV arises from contaminants rather than inherent polymer composition, we exposed samples of PTFE to ultrasonic cleaning in solution and separately to cleaning with ambient air plasma. While the ultrasonic cleaning left the samples unchanged when analyzed by XPS, treatment with air plasma caused the intensity of the peak at ca. 283 eV to decrease substantially ($\geq 80\%$ loss), without giving rise to any additional oxidized species. Furthermore, the O $_{1s}$ peak observed for the PTFE samples also decreased substantially ($\geq 80\%$ loss) upon plasma treatment. Taken together, these observations support the model of surface contamination.

The amount of contamination in the surface layers can be semiquantitatively estimated from the fluorine-to-carbon ratio and the content of oxygen (assuming that the oxygen arises from the contaminants; note that the observation of oxygen in the XPS spectra of the partially fluorinated polymers might also arise from partial oxidation of the C–H bonds along the backbone).¹² Given, for example, that the F/C ratio for PTFE should be 2.00 and that PTFE should contain no oxygen, the data presented in Table 1 for PTFE suggest a nontrivial amount of hydrocarbon and oxygenated contamination.¹¹ We note that all of the other fluoropolymer samples showed substantially lesser contamination (see Table 1); nevertheless, the possible influence of initial trace contaminants on the wettability of fluoropolymers must be considered (vide infra).

The relevance of the preceding analysis depends in part on the sampling depth probed by XPS. The inelastic mean free path (IMFP) for the C $_{1s}$ photoelectrons produced by a monochromic Al K α X-ray source ($h\nu = 1486.7 \text{ eV}$) is estimated to be ~ 3.3

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nm.^{13,14} This distance, however, is only the average distance traveled by an electron with a given energy through the organic material, and the signal drops off exponentially with depth. To account for the drop off, the information depth (sampling depth) is usually taken as 3 times the IMFP times the cosine of the takeoff angle (45° in our case).^{13,14} This calculation gives the depth from which 95% of the photoemissions originate. Therefore, the sampling depth for the C_{1s} photoelectrons is estimated to be 7.0 nm in our measurements. We note, however, that the vast majority of the photoelectrons still come from a depth that is much shallower than this value.

Surface Dipoles and Acidities of the Fluoropolymers. The wettability of a surface can be strongly influenced by the distribution of acidic groups and/or surface dipoles across the interface.¹⁵ In contrast to fully fluorinated polymers, partially fluorinated polymers possess enhanced acidity and enhanced surface dipoles due to the differing electronegativities of carbon, fluorine, and hydrogen (or chlorine). In particular, the strong inductive effect of the fluorine atoms polarizes the electronic distribution along the polymer backbone of all of the partially fluorinated polymers. Figure 2 illustrates, for example, an ideal trans-planar (or extended zigzag) conformation for ETFE and PVDF, showing the distribution of electronic charges along the polymer backbone.^{16,17} Since fluorine atoms are strongly electron withdrawing, the attached carbons exist in a highly electron-deficient state. This deficiency in electron density is compensated, in part, by a shift of the electrons away from adjacent carbons and their attached hydrogens, thereby increasing the acidity of the hydrogens.⁸ This effect scales with the proximity of the fluorines: since the electron-withdrawing effect of fluorine decreases with increasing distance along the chain, the acidity of nearby hydrogens decreases as the fluorines become more remote.^{9,18} In particular, the hydrogen of the CHF group in PVF is the most acidic of all of the fluoropolymers in Figure 1, since the fluorine is attached geminally. Therefore, the acidity of the polymers is expected to increase in the following order: PTFE ~ FEP ~ PFA ≪ ECTFE < ETFE ≪ PVDF ≪ PVF.

ETFE consists of two alternating units of $-\text{CH}_2\text{CH}_2-$ and $-\text{CF}_2\text{CF}_2-$, which should give rise to net surface dipoles that lie along the polymer backbone (Figure 2a). On the other hand, PVDF consists of two alternating units of CH_2 and CF_2 , leading to stronger dipoles that essentially bisect the tetrahedral C–F bonds when compared to ETFE (Figure 2b).¹⁹ In the case of ECTFE, more than two types of dipoles exist due to anisotropic polarization of the C–C bonds depending on whether the CH_2 unit is adjacent to a CF_2 unit or a CFCl unit. This effect gives rise to a relatively high density of dipoles per unit area, and thus argues for stronger dipole effects for ECTFE when compared to ETFE. The naked C–F dipole in PVF, however, should give rise to the strongest dipole effects of all for this polymer. Given these considerations, the surface dipole effects for the polymers are expected to increase in the following order: PTFE ~ FEP < PFA ≪ ETFE < ECTFE ≪ PVDF ≪ PVF. These analyses provide a basis for evaluating the contributions of surface dipoles and acidity to the interfacial interactions (e.g., wettability) of fluoropolymers, in addition to the commonly recognized contribution of dispersive interactions.

Wettabilities of the Fluoropolymer Surfaces. Advancing contact angles were measured using several liquids in contact with the surfaces of fluoropolymers. To provide a comprehensive evaluation of the interfacial energies of the fluoropolymers, we chose liquids ranging from nonpolar aprotic to polar aprotic to polar protic. Among these liquids, polar aprotic contacting liquids can be further divided into two distinct categories depending on their Lewis acid–base character. Fowkes considered two types of acid–base interactions (by their favorable miscibilities with squalene) in polar aprotic liquids.²⁰ The bifunctional liquids include the strongly self-associated liquids (e.g., DMF, acetonitrile, nitrobenzene, and DMSO), where the term “bifunctional” reflects the presence of both Lewis acidic and basic sites within the molecules. The monofunctional liquids include less strongly self-associated polar aprotic liquids (e.g., pyridine, 1,4-dioxane, bromoform, methylene iodide), which consist of molecules having only basic or acidic sites. Given their relatively weak dipoles and small dielectric constants, the monofunctional liquids are routinely described as nonpolar (or “virtually nonpolar”).

Figure 3a shows that the contact angles of the nonpolar aprotic liquids on the polymer surfaces decreased in the following order: FEP > PFA > PTFE > ETFE > PVDF > ECTFE > PVF. The wettability of FEP is lower than those of PFA and PTFE; by analogy to hydrocarbon surfaces, this behavior can be rationalized on the basis of dispersive interactions in which interfacial methylene groups are more wettable than interfacial methyl groups.^{21–23} The surfaces that consist predominantly of CF_2 groups can provide an increased number of attractive dispersive contacts per unit area when compared to those composed of CF_3 groups, leading to enhanced wettability of the former surfaces.²² By the same reason, the wettability of PFA is expected to be lower than that of PTFE; however, Figure 3a shows that the contact angles of nonpolar aprotic liquids on the PFA surface were close to those on the PTFE surface. This observation can be rationalized on the basis of the low ratio of OC_3F_7 to CF_2 group (1:199) in PFA and also the apparently enhanced contamination in PTFE (Table 1).

The wettabilities of nonpolar surfaces by nonpolar aprotic liquids arise solely from dispersive interactions, which can vary with a number of factors such as packing density, intercalation, and surface morphology. As shown in Figure 3a, the nonpolar liquids almost wet the surfaces of the partially fluorinated polymers. For measurable contacting angles of decalin and squalene, the wettability of ECTFE was observed to be greater than that of PVDF, even though the latter possesses stronger surface dipoles. This observation suggests that other factors, including packing density and surface morphology, cannot be excluded for the enhanced wettability of ECTFE toward these nonpolar liquids. In practice, ECTFE is less densely packed due to the presence of the large chlorine atoms (e.g., the specific gravities of PVDF and ECTFE are 1.78 and 1.68, respectively).²⁴ It is also known that the large chlorine atoms disturb the crystalline structure of ECTFE, inducing a slightly kinked chain conformation.¹⁶ These structural considerations might lead to enhanced solvent intercalation (and thus the observed enhancement in

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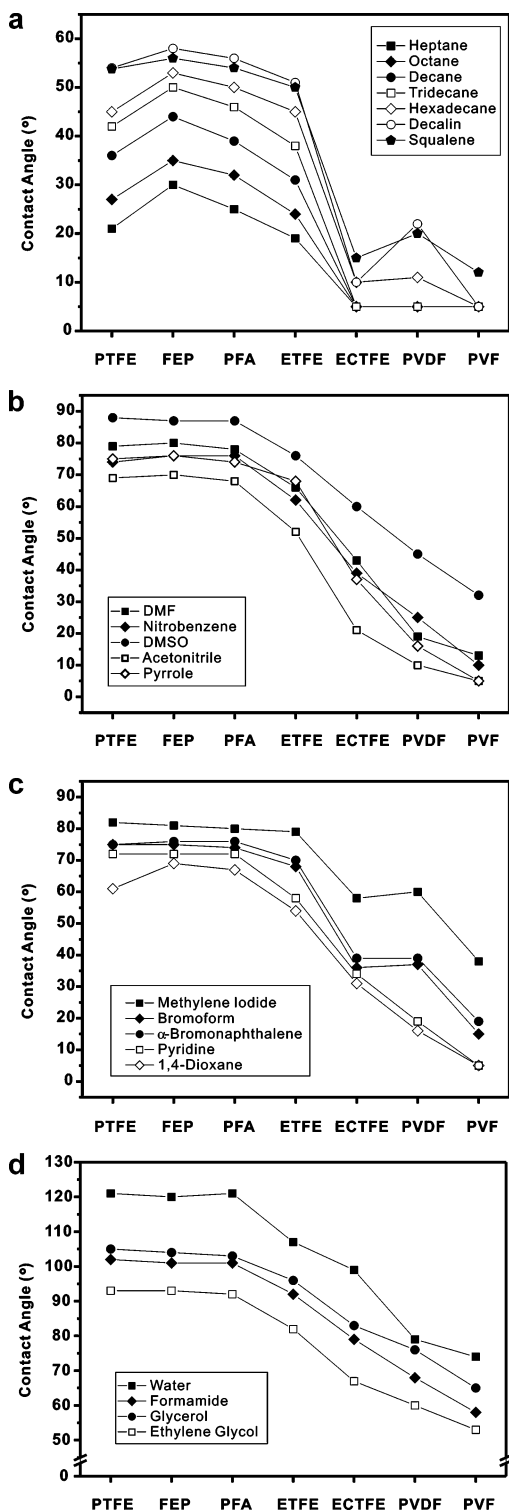


Figure 3. Advancing contact angles of various liquids on the surfaces of fluoropolymers. (a) Nonpolar aprotic liquids: heptane (filled squares), octane (filled diamonds), decane (filled circles), tridecane (open squares), hexadecane (open diamonds), decalin (open circles), squalene (filled pentagons). (b) Polar aprotic (bifunctional) liquids: DMF (filled squares), nitrobenzene (filled diamonds), DMSO (filled circles), acetonitrile (open squares), pyrrole (open diamonds). (c) Polar aprotic (monofunctional) liquids: methylene iodide (filled squares), bromoform (filled diamonds), α -bromonaphthalene (filled circles), pyridine (open squares), and 1,4-dioxane (open diamonds). (d) Polar protic liquids: water (filled squares), formamide (filled diamonds), glycerol (filled circles), and ethylene glycol (open squares).

wettability) for ECTFE. We note, however, that the hysteresis data in Table 2, when compared collectively for all of the surfaces

and probe liquids, fail to support the assertion of enhanced solvent intercalation on ECTFE.

We then examined the advancing contact angles of polar aprotic (bifunctional) liquids on the fluorinated polymers. Figure 3b shows that these contact angles decreased in the following order: PTFE, FEP, PFA > ETFE > ECTFE > PVDF > PVF. The wettability for a given polar liquid was observed to decrease with increasing fluorination in polymers, which is in accordance with previous observations by Zisman and co-workers.²⁵ Given that there were no distinct differences in the contact angle values for the fully fluorinated polymers, we conclude that these substrates exhibit roughly identical dispersive interactions. However, for the partially fluorinated polymers, there were distinct differences in wettability that are attributable to polar interactions (e.g., dipole–dipole, dipole–induced dipole, and acid–base interactions). In particular, PVDF and PVF, which possess strong dipoles and high acidities, exhibited the greatest wettabilities among the fluorinated polymers.

Figure 3c shows that the contact angles of the monofunctional polar aprotic liquids on the polymer surfaces exhibited a similar trend when compared to the bifunctional polar aprotic liquids: PTFE, FEP, PFA > ETFE > ECTFE \geq PVDF > PVF. Only 1,4-dioxane exhibited a variation in contact angle for fully fluorinated polymers: FEP > PFA > PTFE. Here, the lower contact angles for PFA and particularly PTFE might arise from the oxygen-containing ($-\text{OC}_3\text{F}_7$) groups and the aforementioned contaminants, respectively. For methylene iodide, bromoform, and α -bromonaphthalene, the contact angles of ECTFE were similar to those of PVDF within the error range of $\pm 2^\circ$. All of the other polar aprotic liquids gave distinctly lower contact angles for PVDF when compared to ECTFE, reflecting the complexity of polar interactions across these interfaces. In the next section, we will examine the contribution of polar interactions in greater detail using the concept of interfacial energies.

Figure 3d shows that the wettability trends for the polar protic liquids were consistent with those of the bifunctional polar aprotic liquids. The measured contact angles for the fully fluorinated polymers were indistinguishable within the error range of $\pm 2^\circ$. The contact angles for the partially fluorinated polymers, however, were distinctly different due to variations in polar interactions. In particular, PVDF and PVF possess strong surface dipoles and acidic hydrogen atoms; consequently, their surfaces can interact with contacting liquids via dipole–dipole, dipole–induced dipole, and acid–base (including hydrogen-bonding) interactions, leading to the greatest wettability among the investigated partially fluorinated polymers. In contrast, ECTFE with a high density of weak surface dipoles is less wettable than PVDF and PVF but more wettable than ETFE, which possesses a lower density of weak surface dipoles than does ECTFE.

Estimation of Interfacial Energies from Contact Angle Data. To provide a clearer understanding of the trends in wettability observed for the fluoropolymer surfaces, we chose to evaluate the energetic contributions of dispersive interactions and nondispersive interactions separately. In this analysis, three different types of interactions between contacting liquids and fluoropolymers will be considered: (1) dispersive interactions, (2) dipolar interactions, and (3) acid–base interactions (including hydrogen bonding).

Fowkes originally proposed that the surface tension of a polar interface consists of dispersive, inductive, dipole–dipole, and hydrogen bonding interactions.²⁶ Later, Dann suggested that the polar work of adhesion arises from nondispersive forces, such

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Table 2. Contact Angles and Hysteresis Data for Probe Liquids on Fluoropolymer Surfaces^{a,b}

liquid	PTFE			FEP			PFA			ETFE			ECTFE			PVDF		
	adv	rec	Δ	adv	rec	Δ	adv	rec	Δ	adv	rec	Δ	adv	rec	Δ	adv	rec	Δ
WA	122	94	28	119	98	21	121	90	31	108	84	24	99	78	21	80	52	28
FA	103	74	29	101	83	18	100	79	21	94	71	23	79	65	14	67	23	44
GL	105	79	26	104	82	22	103	80	23	96	75	21	83	69	15	76	35	41
EG	93	64	29	93	77	17	92	75	17	82	63	19	67	53	14	60	28	32
PR	75	52	23	76	63	13	74	54	20	68	44	24	37	21	15	16	^c	<16
NB	74	52	22	76	63	13	76	66	10	62	41	21	39	17	22	45	20	15
DMF	79	48	31	80	67	13	78	62	16	66	44	22	43	30	13	19	13	6
α -Br	75	54	21	76	64	12	76	61	15	70	47	23	39	27	12	39	20	19
MI	85	68	17	84	74	10	84	68	16	81	63	18	58	43	15	60	31	29
BF	74	54	20	75	58	17	74	57	17	68	51	17	36	19	17	37	13	24
PY	72	54	18	72	63	9	72	60	12	58	41	17	34	17	17	19	10	9
DIO	61	46	15	69	56	13	67	53	14	53	37	18	31	18	13	18	10	8
HD	45	21	24	53	39	14	50	33	17	45	26	19	10	^c	<10	11	^c	<11
DC	54	28	26	58	44	14	56	42	14	50	35	15	15	^c	<15	20	10	10
SQ	54	28	26	56	42	14	54	40	14	50	35	15	15	^c	<15	20	10	10

^a adv = advancing contact angles, rec = receding contact angles, $\Delta = \theta_{adv} - \theta_{rec}$. ^b WA = water, FA = formamide, GL = glycerol, EG = ethylene glycol, PR = pyrrole, NB = nitrobenzene, DMF = dimethylformamide, α -Br = α -bromonaphthalene, MI = methylene iodide, BF = bromoform, PY = pyridine, DIO = 1,4-dioxane, HD = hexadecane, DC = *cis*-decalin, SQ = squalene. ^c Immeasurable contact angles less than 10°.

as electrostatic, acid–base, and hydrogen-bonding interactions.^{27,28} In recent work,^{14,29} Colorado and Lee have proposed that the total work of adhesion for a solid–liquid interface (W_{SL} ; eq 1) can most simply be expressed as the sum of its dispersive component (W_{SL}^d ; eq 2) and polar component (W_{SL}^p ; eq 3):

$$W_{SL} = \gamma_{LV}(1 + \cos \theta_a) \quad (1)$$

$$W_{SL}^d = 2\sqrt{\gamma_{SV}^d \gamma_{LV}^d} \quad (2)$$

$$W_{SL}^p = \gamma_{LV}(1 + \cos \theta_a) - 2\sqrt{\gamma_{SV}^d \gamma_{LV}^d} \quad (3)$$

To determine W_{SL}^d , the dispersive component of the free energy of the solid–vapor interface (γ_{SV}^d) must first be calculated using the Good–Girifalco–Fowkes (GGF) approximation (eq 4),^{30–32} which relates the total work of adhesion, $\gamma_{LV}(1 + \cos \theta_a)$, to the dispersive components of the surface free energy of the solid (γ_{SV}^d) and the surface tension of the liquid (γ_{LV}^d):

$$\gamma_{LV}(1 + \cos \theta_a) = 2\sqrt{\gamma_{SV}^d \gamma_{LV}^d} \quad (4)$$

The GGF approximation can be used to estimate the solid surface tension by assuming that the solid–liquid interface is entirely and ideally dispersive for the contacting liquids. Therefore, assuming that $\gamma_{LV}^d = \gamma_{LV}$ for a series of nonpolar aprotic liquids (e.g., heptane, octane, decane, tridecane, hexadecane, decalin, squalene), one can obtain γ_{SV}^d as an average value for a given surface. Similarly, average values of γ_{LV}^d can be estimated for nonpolar and/or protic liquids by measuring their contact angles on ideal purely dispersive thin films (e.g., those derived from the adsorption of hexadecanethiol on gold)^{15,29} and plugging the appropriate values into eq 4. Once values of γ_{SV}^d and γ_{LV}^d are known for a given surface and contacting liquid, respectively, values of W_{SL}^d can be calculated from eq 2, and values of W_{SL}^p can be calculated from eq 3.

(27) The work of adhesion is defined as the work done on the system when a unit area of solid–liquid interface is destroyed to form unit areas of liquid–vapor and solid–vapor interfaces. The work of adhesion at a solid–liquid interface is dependent on the free energies of the liquid–vapor, solid–vapor, and solid–liquid interfaces ($W_{SL} = \gamma_{LV} + \gamma_{SV} - \gamma_{SL}$).

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Table 3. Dispersive Solid Surface Tensions (γ_{SV}^d , mJ m⁻²) from Various Methods

polymers	GGF avg.	Zisman plot	GGF plot	literature
PTFE	19.2 ^a	17.9 ^b	19.6 ^b	18–19 ^{c,d}
FEP	17.6 ^a	16.6 ^b	17.7 ^b	16–18 ^{c,d}
PFA	18.5 ^a	17.5 ^b	18.6 ^b	18 ^e
ETFE	20.0 ^a	18.8 ^b	<i>f</i>	25.5 ^g
ECTFE	28.2 ^h	<i>i</i>	<i>f</i>	31 ^j
PVDF	27.5 ^h	26.5 ^k	<i>f</i>	25 ^{d,l} , 30 ^l
PVF	40.6 ^m , 35.2 ⁿ	<i>i</i>	<i>f</i>	40 ^{c,o}

^a Average for all nonpolar contacting liquids examined (i.e., heptane, octane, decane, tridecane, hexadecane, squalene, and decalin). ^b Obtained using the nonpolar contacting liquids listed in footnote a. ^c Reference 33. ^d Reference 38. ^e Reference 35. ^f Linear plot could not be obtained on the polar surface of partially fluorinated polymers. ^g Reference 36. ^h Obtained using squalene only. ⁱ The surfaces of ECTFE and PVF were wet by all nonpolar aprotic liquids except squalene. ^j Reference 39. ^k Obtained using hexadecane, decalin, and squalene; all other liquids wet the PVDF surface. ^l Reference 37. ^m Obtained assuming CH₂L₂ is a virtually nonpolar liquid (i.e., $\gamma_{LV}^d = 50.8$ mJ m⁻²).²⁰ ⁿ Obtained considering the nonideal interaction of methylene iodide by using γ_{LV}^d calculated through the interactions of methylene iodide with three fully fluorinated surfaces as described in the text (i.e., $\gamma_{LV}^d = 44.0$ mJ m⁻²). ^o Reference 34.

We estimated the solid surface tension of the fluoropolymers using the GGF approximation averaged over all contacting liquids examined and compared these values with those obtained from a Zisman plot, a GGF plot, and those reported in the literature (see Table 3).^{33–39} The data in Table 3 indicate that the Zisman plot underestimates the dispersive component of the fluorinated surfaces. In contrast, the solid surface tensions estimated by plotting $\cos \theta_a$ vs $\gamma_{LV}^{-1/2}$, known as a the GGF plot, gave numbers comparable to those calculated using the GGF approximation; however, the GGF plot method could not be applied to most of the partially fluorinated polymers because of nonlinearities arising perhaps from nonideal interactions between fluorocarbons and hydrocarbons.²⁹

Dispersive Interactions. We calculated the dispersive component of the work of adhesion (W_{SL}^d) using eq 2. As noted

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Table 4. Values of γ_{LV}^d Cited from the Literature and Estimated Values of γ_{LV}^d from Measurements of θ_a and γ_{SV}^d for Fully Fluorinated Surfaces Using the GGF Equation (mJ m^{-2})

contacting liquids	γ_{LV}	literature values, γ_{LV}^d or γ_{LV}^{LW}			experimental values, γ_{LV}^d			
		Fowkes ^a	van Oss ^b	T.R. Lee ^c	PTFE	FEP	PFA	avg.
water	72.40	21.1	21.8	16.5 ^b	15.1	18.6	16.7	16.8
formamide	58.00	28.0	39.0	^d	26.3	30.5	29.8	28.9
glycerol	64.00	^d	34.0	^e	29.2	33.4	33.3	32.0
ethylene glycol	48.00	^d	29.0	^d	26.9	29.3	29.0	28.4
DMF	36.80	30.2	^d	25.0 ^e	25.0	26.5	26.7	26.0
nitrobenzene	43.80	38.7	41.0	30.8 ^e	40.6	42.0	40.1	40.9
DMSO	44.00	29.0	36.0	26.3 ^e	26.9	29.7	29.0	28.6
acetonitrile	27.00	19.4	^d	16.9 ^e	17.5	18.6	18.6	18.2
α -bromonaphthalene	44.40	^d	44.4	^d	40.6	43.1	41.2	41.6
methylene iodide	50.80	50.8	50.8	^d	44.8	44.6	42.6	44.0
bromoform	41.50	^d	^d	^d	35.5	38.7	37.9	37.4
pyridine	38.00	38.0	^d	^d	32.2	35.1	33.5	33.6
1,4-dioxane	33.50	33.5	^d	^d	32.2	29.4	29.4	30.3

^a Reference 20. ^b Reference 40. ^c Reference 29. ^d For certain contacting liquids, values of γ_{LV}^d and γ_{LV}^{LW} were not available from the indicated source. ^e In reference 29, values of γ_{LV}^d were calculated from a series of terminally perfluorinated SAMs on gold ($\gamma_{SV}^d = 13.8 \text{ mJ m}^{-2}$) using *cis*-perfluorodecalin as the purely dispersive liquid.

above, the calculation of W_{SL}^d requires the dispersive component of the surface energy of fluorinated surfaces (γ_{SV}^d , Table 3) and the dispersive surface tension of the contacting liquids (γ_{LV}^d). A past study demonstrated the calculation of γ_{LV}^d for polar contacting liquids through the interaction of the liquids with squalene.²⁰ The γ_{LV}^d values determined by this method, however, might lead to errors in the calculations for fluorinated interfaces because the dispersive forces of polar contacting liquids possibly interact in a nonideal manner with the dispersive forces of the fluorinated surfaces.²⁹ We therefore calculated γ_{LV}^d for the contacting liquids through their interactions with fully fluorinated surfaces rather than squalene.^{15,20}

Using the GGF average γ_{SV}^d values of the fully fluorinated polymers listed in Table 3 and well-known literature values of γ_{LV} ,²⁰ we calculated γ_{LV}^d for the polar contacting liquids for three nonpolar fluoropolymers from eq 4. The results are given in Table 4 along with published values from the literature.^{20,29,40} While the average values of γ_{LV}^d obtained here are largely consistent with those reported in the literature, the value of γ_{LV}^d obtained for water on PTFE (15.1 mJ m^{-2}) is markedly lower than the commonly reported value (ca. $21\text{--}22 \text{ mJ m}^{-2}$); it is also lower than the value reported recently by Lee and co-workers in studies of fluorinated self-assembled monolayers (SAMs) on gold (16.5 mJ m^{-2}),²⁹ which is itself lower than the commonly reported value. The origin of the latter discrepancy lies in the use of hydrocarbon interfaces^{20,40} rather than fluorocarbon interfaces²⁹ to derive the energies of interaction. Simply put, the dispersive component of any common probe liquid is typically stronger when contacting a hydrocarbon interface than when contacting a fluorocarbon interface. We and others refer to this phenomenon as “nonideal” behavior.²⁹ An unfortunate consequence of nonideal wettability is that values of γ_{LV}^d actually vary with the nature of the substrate (i.e., hydrocarbon vs fluorocarbon).

Nevertheless, the value of γ_{LV}^d obtained for water on PTFE appears to be anomalously low, perhaps because of excess contamination or surface heterogeneity for this polymer (supported by the XPS data and surface roughness data in Table 1 as well as the contact angle hysteresis data in Table 2). We note also that the presence of OC_3F_7 groups on the surface of PFA suggests that the interactions involving this polymer might not be entirely dispersive in nature. In contrast, FEP contains no heteroatoms other than fluorine, is the least contaminated, and

has the smoothest surface among the fully fluorinated polymers. Therefore, FEP appears to be the truest purely dispersive surface examined here. As such, the remainder of our analysis and discussion is based on this assumption.

Using the values of γ_{LV}^d calculated above for the contacting liquids and γ_{SV}^d for FEP in Table 3, we calculated the dispersive work of adhesion (W_{SL}^d) according to eq 2 and plotted the values of W_{SL}^d for the respective fluorinated surfaces. Figure 4 shows that W_{SL}^d increases in the following order with roughly the same magnitude, regardless of the nature of the contacting liquid: FEP < PFA < PTFE < ETFE < PVDF < ECTFE. We note that values of W_{SL}^d (and of W_{SL}^p below) for PVF were not reliably obtained due to the enhanced wettability (reflected by contact angles of less than 10° for many of the probe liquids) observed on this surface. Among the fully fluorinated polymers, values of W_{SL}^d were lower for FEP than for PTFE and PFA. As noted above, this behavior can be rationalized on the basis of dispersive interactions in which interfacial methylene groups are more wettable than interfacial methyl groups (as a result of enhanced van der Waals contact per unit area).²² Similarly, since hydrogen is smaller than fluorine, it is reasonable that partially fluorinated ETFE (more densely packed) gives higher values of W_{SL}^d than the fully fluorinated polymers. By analogy, one might propose that ECTFE would exhibit a lower W_{SL}^d than ETFE, given the diminished molecular packing of ECTFE. This proposal, however, is contrary to our observations. While it is possible that the enhanced W_{SL}^d for ECTFE arises from intercalation of the contacting probe liquids (vide supra) or because Cl is more polarizable than F, we can offer no similar rationalization(s) for the enhanced W_{SL}^d for PVDF. Perhaps, however, the molecular packing density of PVDF is somehow greater than that of ETFE.

Non-Dispersive Interactions. The wettability studies described above found, for example, that ECTFE was more wettable than PVDF toward nonpolar liquids (see decalin and squalene in Figure 3a), while PVDF was more wettable than ECTFE toward most other polar liquids (see Figures 3b–3d). The contrasting behavior highlighted here suggests the existence of complex nondispersive interactions at fluoropolymer interfaces. As noted above, ECTFE possesses multiple surface dipoles as well as chemical heterogeneity, while PVDF possesses strong surface dipoles and high surface acidity. To rationalize the relative contributions of nondispersive phenomena in fluorinated polymer surfaces as a

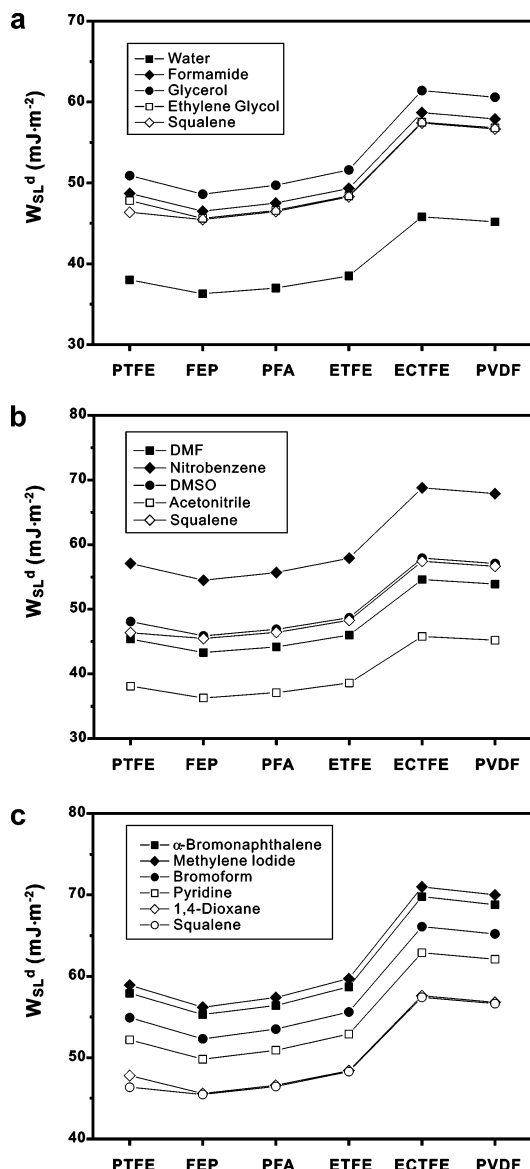


Figure 4. Dispersive works of adhesion of various liquids on the surface of fluoropolymers. (a) Polar protic liquids: water (filled squares), formamide (filled diamonds), glycerol (filled circles), ethylene glycol (open squares), squalene (open diamonds). (b) Bifunctional liquids: DMF (filled squares), nitrobenzene (filled diamonds), DMSO (filled circles), acetonitrile (open squares), squalene (open diamonds). (c) Monofunctional liquids: α-bromonaphthalene (filled squares), methylene iodide (filled diamonds), bromoform (filled circles), pyridine (open squares), 1,4-dioxane (open diamonds), squalene (open circles). Average values of γ_{SV}^d for FEP were used (obtained from θ_a and γ_{LV}^d for nonpolar aprotic liquids according to the GGF equation). Squalene was included as a standard for all types of liquids. Note the absence of data for PVF for which no purely dispersive standard is available. Also, most of the polar aprotic liquids wet the surface of PVF.

whole, we now consider dipole interactions (Keesom and Debye forces) and acid–base interactions (including hydrogen bonding) separately.

1. Dipole Contributions. We estimated the contribution of the nondispersive interactions to the works of adhesion by calculating W_{SL}^p according to eq 3 on the fluoropolymer surfaces. Figure 5 shows that the polar works of adhesion for the fully fluorinated polymers are zero within the error range of $\pm 2 \text{ mJ m}^{-2}$ (except for PTFE, which is contaminated/heterogeneous; vide supra), suggesting that the total work of adhesion for these materials arises exclusively from the dispersive interactions that comprise

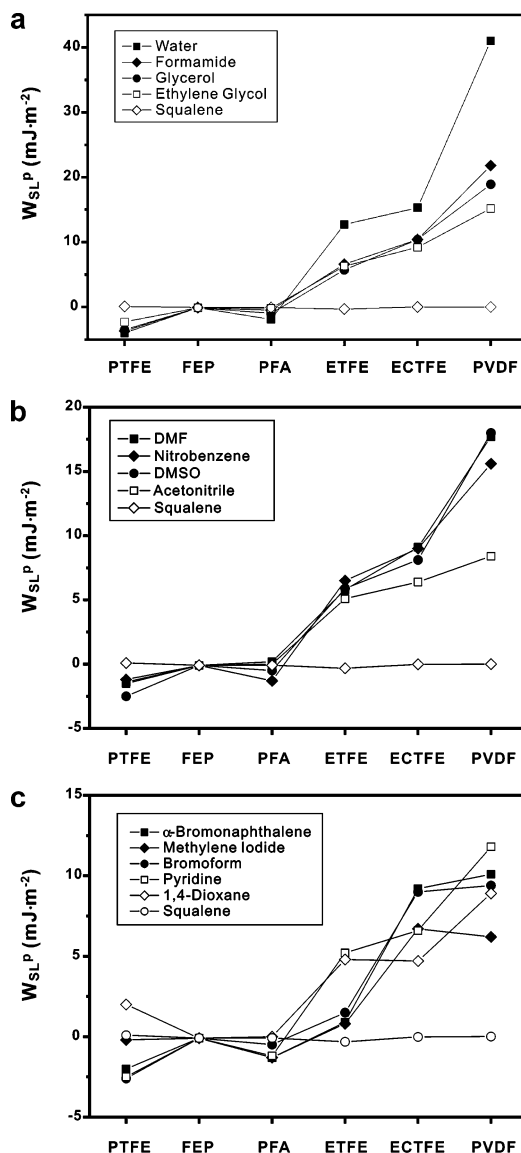


Figure 5. Polar works of adhesion of various liquids on the surface of fluoropolymers. (a) Polar protic liquids: water (filled squares), formamide (filled diamonds), glycerol (filled circles), ethylene glycol (open squares), squalene (open diamonds). (b) Bifunctional liquids: DMF (filled squares), nitrobenzene (filled diamonds), DMSO (filled circles), acetonitrile (open squares), squalene (open diamonds). (c) Monofunctional liquids: α-bromonaphthalene (filled squares), methylene iodide (filled diamonds), bromoform (filled circles), pyridine (open squares), 1,4-dioxane (open diamonds), squalene (open circles). Average values of γ_{SV}^d for FEP were used (obtained from θ_a and γ_{LV}^d for nonpolar aprotic liquids according to the GGF equation). Squalene was included as a standard for all types of liquids. Note the absence of data for PVF for which no purely dispersive standard is available. Also, most of the polar aprotic liquids wet the surface of PVF.

W_{SL}^d . In contrast, the nonzero values of W_{SL}^p for the partially fluorinated polymer surfaces suggest the existence of interactions other than those that are truly dispersive. As described above, we estimate that the strength of the surface dipoles of the fluorinated polymers increases in the following order: PTFE \sim FEP $<$ PFA \ll ETFE $<$ ECTFE \ll PVDF \ll PVF. Given that these surface dipoles can interact with the contacting liquids to enhance W_{SL}^p , we would predict, in the absence of other conflicting nonpolar interactions, that values of W_{SL}^p would correlate with the strength of the surface dipoles in the fluoropolymers. To this end, Figure 5 shows that the values of

W_{SL}^p for the fluoropolymers increase in the following order: PTFE, FEP, PFA < ETFE < ECTFE < PVDF, which is in good agreement with the predicted trend in surface dipole strengths (recall that PVF is missing from the latter series because we were unable to calculate reliable values of W_{SL}^d and W_{SL}^p for this substrate; vide supra). It is important to note that this correlation holds on all three partially fluorinated surfaces for all of the polar contacting liquids, save for methylene iodide (virtually nonpolar) on PVDF. We therefore conclude that the contribution of polar interactions to the total works of adhesion is strongly dependent on the surface dipoles of the polymers.

2. Acid–Base Contributions. For the polymers and probe liquids considered here, no formal proton transfer occurs when the liquids are placed in intimate contact with the polymers. Consequently, it is inappropriate to consider the interfacial acid–base interactions from a Brønsted (proton donor/acceptor) perspective. Given, however, the presence of lone pairs in both the polymers and the polar liquids, it is reasonable to consider these interactions from a more general Lewis (lone-pair donor/acceptor) perspective. Specifically, these interactions might best be described as hydrogen bonds, as illustrated by the following two examples, where X = heteroatom O or N: $(\text{polymer})\text{C}-\text{H}\cdots\text{X}_{(\text{liquid})}$ for certain polar liquids and $(\text{polymer})\text{C}-\text{F}\cdots\text{H}-\text{X}_{(\text{liquid})}$ for polar protic liquids. While a distinction between the hydrogen bonds illustrated here and the dipole interactions discussed in the preceding section might seem arbitrary, the data in Figure 5 argue that polar forces beyond those attributable to dipoles must be operative here. In particular, the values of W_{SL}^p for the partially fluorinated substrates are uniformly higher when using polar protic liquids (Figure 5a) than when using polar aprotic liquids (Figure 5b), and there are no obvious correlations with the dipole strength or the dielectric constant of the contacting liquids.

2a. Hydrogen Bonding.³⁸ Regarding the polymeric substrates, the presence of acidic moieties is limited to the partially fluorinated polymers, and the acidity order is expected to increase in the following order: PTFE \sim FEP \sim PFA \ll ECTFE < ETFE \ll PVDF (vide supra). As such, monofunctional basic contacting liquids such as pyridine and dioxane can be expected to exhibit polar works of adhesion that increase in the same order. Figure 5c confirms this trend, save for a minor deviation for pyridine on ETFE. In contrast, the monofunctional acidic bromoform and the virtually apolar methylene iodide and α -bromonaphthalene exhibit a different trend on the partially fluorinated polymers, where the polar works of adhesion on ECTFE are comparable to those on PVDF.

Figure 5b shows that the polar works of adhesion for the bifunctional liquids follow the same trend as the monofunctional basic liquids pyridine and dioxane. The magnitude of W_{SL}^p is, however, slightly higher for the bifunctional liquids, plausibly reflecting the greater basicity of the latter. Figure 5a shows that the same trend also holds for the polar protic liquids, but with an even further enhancement in the magnitude of W_{SL}^p . Notably, this enhancement is particularly evident for water, which possesses a relatively small dipole moment ($\mu = 1.84$).⁴¹ Further evidence of the enhancement is perhaps illustrated by a direct comparison of dimethylformamide with formamide on PVDF, where $W_{SL}^p = 18$ and 23 mJ m^{-2} , respectively. While the dipole strengths of both liquids are similar ($\mu = 3.86$ and 3.37 , respectively),⁴¹ and both liquids can undergo hydrogen bonding of the type $(\text{polymer})\text{C}-\text{H}\cdots\text{X}_{(\text{liquid})}$, formamide can additionally undergo hydrogen

bonding of the type $(\text{polymer})\text{C}-\text{F}\cdots\text{H}-\text{N}_{(\text{liquid})}$, and thus give rise to an enhanced W_{SL}^p relative to that for dimethylformamide. This line of reasoning suffers, however, from the necessary deduction that hydrogen bonding of the type $(\text{polymer})\text{C}-\text{F}\cdots\text{H}-\text{X}_{(\text{liquid})}$ occurs only for the partially fluorinated polymers, given that values of W_{SL}^p are ~ 0 for the fully fluorinated polymers.

Considering as a whole the nondispersive interactions that give rise to W_{SL}^p , we can reasonably argue that dipole interactions appear to be the dominant attractive forces acting across the interface of the partially fluorinated polymers.^{15,29} Furthermore, these interactions appear to be complemented by hydrogen bonding of the type $(\text{polymer})\text{C}-\text{H}\cdots\text{X}_{(\text{liquid})}$. Although additional enhancement of W_{SL}^p is observed when using polar protic contacting liquids, the exact origin of this enhancement is obscure.

2b. VCG Method. In an effort to clarify the phenomena highlighted above, we employed the van Oss, Chaudhury, and Good (VCG) method to evaluate the magnitude of the acid–base contributions to the polar works of adhesion.⁴² In the late 1980s, van Oss, Chaudhury, and Good proposed a revision of Fowkes's surface tension²⁶ by grouping the various contributions into only two components: Lifshitz–van der Waals (LW) forces and acid–base (AB) interactions.⁴² In this approach, the acid–base component of the free energy of interaction across a solid–liquid interface (ΔF_{SL}^{AB}) is given by the relation shown in eq 5:

$$\Delta F_{SL}^{AB} = -\gamma_{LV}(1 + \cos \theta_a) + 2\sqrt{\gamma_S^{LW}\gamma_L^{LW}} = -2\sqrt{\gamma_S^+\gamma_L^-} - 2\sqrt{\gamma_S^-\gamma_L^+} \quad (5)$$

where γ^{LW} is the Lifshitz–van der Waals component, γ^+ is the electron-acceptor (acidic) surface tension, and γ^- is the electron-donor (basic) surface tension. Note that ΔF_{SL}^{AB} is numerically equivalent but has the opposite sign of the polar work of adhesion (W_{SL}^p) defined by eq 3. Empirically, the VCG method has been shown to suffer from an overestimation of the Lewis basicity, even for surfaces that are characteristically acidic.^{30,33} Additionally, there is no simple way to compare the characteristic parameters γ^+ and γ^- with other independent measurements of solid surface acidity and basicity.^{32,41} Despite these limitations, the VCG method can often lend insight by helping to define the specific nature (i.e., electron donor vs acceptor) of the interfacial acid–base interactions.

To employ the VCG method, it is convenient to use a virtually nonpolar liquid and two polar liquids having known values of γ_L^+ and γ_L^- .^{42,43} For each of the polymer substrates examined here, we first determined the values of γ_S^{LW} using the contact angles of the methylene iodide (or α -bromonaphthalene) as the virtually nonpolar liquid (i.e., assuming that both γ_L^+ and $\gamma_L^- = 0$). We then estimated the values of γ_S^+ and γ_S^- using the contact angles of both water and glycerol. We also calculated the surface tension components of the fluorinated polymers using the actual (nonzero) values of γ_L^+ and γ_L^- for methylene iodide and α -bromonaphthalene.^{42–48} As shown in Table 5, the use of nonzero γ_L^+ and/or γ_L^- values for methylene iodide and α -bromonaphthalene gave values of γ_S^{AB} that were slightly diminished

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Table 5. Lifshitz–van der Waals Components and Acid–Base Parameters of Fluoropolymers from the Contact Angles and Surface Tension Data for the Indicated Set of Test Liquids^a

polymer	γ_S^{LW}	γ_S^{AB}	γ_S^+	γ_S^-	γ_S^{tot}
Methylene Iodide–Water–Glycerol ^b					
PTFE	15.37(15.72)	0.14(0.12)	0.04(0.03)	0.13(0.13)	15.51(15.84)
FEP	14.96(15.24)	0.18(0.17)	0.09(0.08)	0.09(0.09)	15.14(15.41)
PFA	14.96(15.48)	0.47(0.42)	0.19(0.15)	0.29(0.30)	15.43(15.90)
ETFE	17.48(16.51)	0.54(0.71)	0.08(0.13)	0.91(0.96)	18.02(17.22)
ECTFE	29.73(28.90)	0.47(0.56)	0.14(0.19)	0.39(0.41)	30.20(29.46)
PVDF	28.58(24.39)	1.76(3.75)	0.07(0.30)	11.1(11.7)	30.34(28.14)
PVF	40.61(36.20)	2.02(3.58)	0.12(0.36)	8.46(8.90)	42.63(39.78)
α -Bromonaphthalene–Water–Glycerol ^c					
PTFE	17.59(17.80)	0.00(0.00)	0.00(0.00)	0.17(0.17)	17.59(17.80)
FEP	17.12(17.23)	0.08(0.07)	0.01(0.01)	0.12(0.12)	17.20(17.30)
PFA	17.12(17.27)	0.29(0.28)	0.06(0.05)	0.35(0.36)	17.41(17.55)
ETFE	20.00(19.45)	0.13(0.21)	0.10(0.01)	0.80(0.82)	20.02(19.66)
ECTFE	34.01(33.52)	0.01(0.15)	0.01(0.02)	0.30(0.31)	34.13(33.67)
PVDF	32.70(30.41)	0.04(0.92)	0.00(0.02)	10.6(10.88)	32.74(31.33)
PVF	46.46(44.06)	0.15(0.88)	0.00(0.02)	7.93(8.14)	46.61(44.94)

^a All surface tension units are in mJ m^{-2} . The surface tension components were calculated from the advancing contact angles based on the reference values for water: $\gamma_L^+ = \gamma_L^- = 25.5$.⁴⁵ Values less than 0.01 were considered as 0.00. ^b Values in parentheses calculated using the nonzero value of $\gamma_L^+ = 0.72$ for methylene iodide.⁴⁷ ^c Values in parentheses calculated using the assumed values of $\gamma_L^+ = 0.39$ and $\gamma_L^- = 0.48$ for α -bromonaphthalene.⁴⁸

for the fully fluorinated polymers but slightly elevated for the partially fluorinated polymers. In other words, neglect of the liquid acidity/basicity leads to an underestimation of γ_S^{AB} for the partially fluorinated surfaces.

Regardless of whether nonzero values of γ_L^+ and γ_L^- values were used for the virtually nonpolar liquids, the data in Table 5 indicate that PVDF and PVF are characterized by a preponderantly strong γ_S^- monopole among the fluoropolymers examined.³⁴ Given that γ_S^- monopolar polymer surfaces can interact strongly with γ_L^\pm bifunctional liquids and γ_L^+ monofunctional liquids, this result is consistent with our observation of the enhanced wettability of these two polymer surfaces toward all of the bifunctional probe liquids (Figure 3b) and polar protic liquids (Figure 3d) employed. Surprisingly, however, the wettability trend for PVDF in Figure 3c holds for the γ_L^- monofunctional bases (pyridine and 1,4-dioxane) but not the γ_L^+ monofunctional acid (bromoform) and the virtually nonpolar liquids (methylene iodide and α -bromonaphthalene). As an acid–base interaction, we anticipated that the γ_S^- monopolar nature of PVDF would have interacted more strongly with the γ_L^+ monofunctional acids than the γ_L^- monofunctional bases. Perhaps this discrepancy reflects the important but largely ignored⁴⁹ role of dipole–dipole interactions in dictating the wettability of polar interfaces.^{15,29,50}

To explore this issue further, we plotted the polar works of adhesion (W_{SL}^p) determined on ETFE, ECTFE, and PVDF versus the dipole moments of the contacting liquids (see Figure 6).⁵¹ Examination of the plot reveals that the polar works of adhesion on ETFE increase with increasing dipole moment of the probe liquids, save for an invariance or slight decrease at $\mu \geq 3.75$, which corresponds to the range of dipole moments for bifunctional contacting liquids. While PVDF exhibits a similar (albeit more erratic) trend, the polar works of adhesion on ECTFE are relatively independent of the dipole moments of the probe liquids. Given

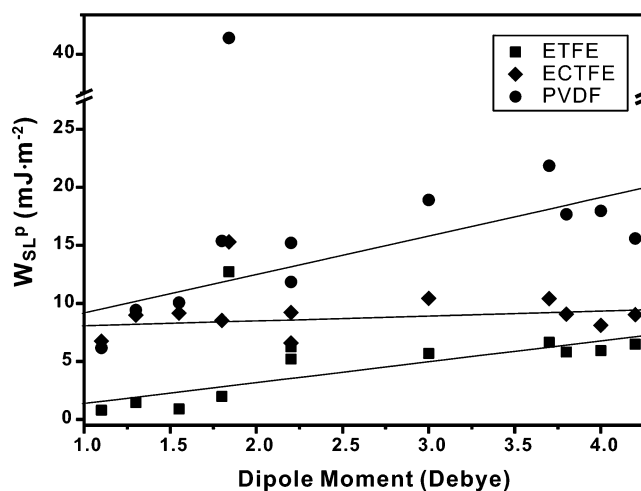


Figure 6. Plot of the polar works of adhesion (W_{SL}^p) determined versus the dipole moments of the contacting liquids on the partially fluorinated surfaces: ETFE (filled squares), ECTFE (filled diamonds), PVDF (filled circles). The data for water ($\mu = 1.84$) were excluded in the linear regression because of their significant deviation from linearity.

that ECTFE is more polar than ETFE but the least acidic among these partially fluorinated polymers, this latter observation might be interpreted to indicate that acid–base interactions also contribute to the polar works of adhesion.

In Figure 6, we note that water ($\mu = 1.84$) exhibits a marked deviation from the noted trend for all three surfaces; the magnitude of the deviation increases in the following order: ECTFE < ETFE < PVDF, which correlates with our estimated order of acidity for the polymers. These results are consistent with a model in which the deviation of polar works of adhesion for water arises from acid–base (i.e., hydrogen-bonding) interactions. Moreover, Figure 6 shows that the polar works of adhesion for bifunctional liquids such as DMF, DMSO, and nitrobenzene ($\mu \geq 3.75$) are generally smaller than those for polar protic liquids such as glycerol and formamide ($\mu = 3.0$ and 3.7 , respectively). Given that the latter liquids possess slightly smaller dipoles but are capable of hydrogen bonding while the former liquids possess slightly larger dipoles but are incapable of hydrogen bonding, these observations can also be interpreted to indicate that acid–

(49) For example, see ref 36 and Fowkes, F. M. In *Physicochemical Aspects of Polymer Surfaces*; Mittal, K. L., Ed.; Plenum: New York, 1983; Vol. 2, p 583.

(50) Graupe, M.; Takenaga, M.; Koini, T.; Colorado, R., Jr.; Lee, T. R. *J. Am. Chem. Soc.* **1999**, *121*, 3222.

(51) In Figure 6, the data for 1,4-dioxane ($\mu = 0$) were excluded because of their marked deviation from the noted trend; it appears that this liquid experiences unusually strong Debye forces (i.e., dipole-induced dipole forces) when contacting polar surfaces.

base/hydrogen-bonding interactions contribute (along with purely dipolar interactions) to the polar works of adhesion.

Conclusions

The interfacial wettabilities of various fluoropolymers were evaluated using a series of nonpolar, polar aprotic, and polar protic contacting liquids. The trends in advancing contact angles of the fluoropolymers were observed to decrease as follows: (1) for nonpolar aprotic liquids, FEP > PFA > PTFE > ETFE > PVDF > ECTFE > PVF; (2) for polar aprotic liquids, PTFE ~ FEP ~ PFA > ETFE > ECTFE ≥ PVDF > PVF; and (3) for polar protic liquids, PTFE ~ FEP ~ PFA > ETFE > ECTFE > PVDF > PVF. The fully fluorinated polymers exhibited nearly ideal dispersive interactions across the interface with the contacting liquids, while the partially fluorinated polymers exhibited nonideal dispersive interactions in addition to dipolar and acid–base (hydrogen bonding) interactions across the interface. As a general rule, the dispersive interaction energies

were greater in magnitude than the dipolar interaction energies, which were themselves greater in magnitude than the acid–base interaction energies. The relative magnitudes of the dipolar energies were readily predicted on the basis of the chemical structure of the polymer backbones. Moreover, the wettabilities of a wide range of contacting liquids were observed to correlate with the predicted relative dipole strengths. The results presented here highlight the important role that surface dipoles play in the wettability of solid interfaces.

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