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Insight into the Surface Properties of Fluorocarbon–Vinyl Acetate Copolymer Films and Blends

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ABSTRACT: Fluorocopolymers of vinyl acetate (VAc) and one of tetrafluoroethylene (TFE), chlorotrifluoroethylene (CTFE), or vinylidene fluoride (VDF), or fluorocopolymer blends with PVAc, were cast from solution on Teflon-coated glass slides and analyzed for surface composition at both the air–polymer and Teflon–polymer surfaces. Since the fluorocopolymers, synthesized in supercritical CO_2, had a random distribution of monomers, we were interested in determining whether surface enrichment of the fluorocarbon repeat units was possible relative to the bulk composition. Film surfaces were characterized by X-ray photoelectron spectroscopy (XPS) and dynamic advancing and receding water contact angles, which demonstrated that fluorocopolymer films were more hydrophobic than PVAc homopolymer film surfaces. By XPS, films of P(TFE-*co*-VAc) had both air and Teflon surfaces enriched with TFE relative to its bulk composition. Films of P(CTFE-*co*-VAc) had CTFE-enriched air surfaces for CTFE bulk concentrations >26 mol % and CTFE-enriched Teflon surfaces for all P(CTFE-*co*-VAc) compositions. Films of P(VDF-*co*-VAc) had VDF-depleted air surfaces for all P(VDF-*co*-VAc) bulk compositions yet VDF-enriched Teflon surfaces. Relative to the fluorocopolymers, greater surface activity of the fluorocarbon repeat units was evident for fluorocopolymer blends with PVAc at both air–polymer and Teflon–polymer surfaces for both P(TFE-*co*-VAc) and P(CTFE-*co*-VAc). Similar results were obtained for P(VDF-*co*-VAc) at the Teflon surface. Together these results demonstrate that even random fluorocopolymers can create surfaces enriched with fluorocarbon relative to the bulk composition. The important driving forces for surface activity include surface tension, polarity differences, and chemistry of the "counter" surface. Ultimately, these fluorocopolymers may be useful additives for coatings or paint applications.

Introduction

Fluoropolymers are advantageous for numerous applications because they exhibit thermal stability, chemical resistance, low surface free energy, and hydrophobic and oleophobic character. These properties make fluoropolymers particularly well-suited to coatings and paint applications;[1–5] however, the limited solubility of highly fluorinated polymers, such as poly(tetrafluoroethylene) (PTFE) and poly(chlorotrifluoroethylene) (PCTFE), makes formulations difficult to obtain.[6] To take advantage of the exceptional properties presented by fluoropolymers in a useable resin system, fluoromonomers have been copolymerized with a variety of hydrocarbon monomers. The resulting copolymers are more easily formulated due to their solubility in organic solvents, compatibility with pigments, cross-linking reactivity, and improved adhesion, hardness, and flexibility of coated films.[1,4,5] For example, copolymers of TFE or CTFE with either vinyl ether or acrylic acid are widely used in coatings applications.[7] Furthermore, fluorocarbon polymers are advantageous for coatings applications because they are surface-active and minimize interfacial free energy, as we and others have observed for numerous polymers and polymer blends.[8–14]

We previously reported the supercritical CO_2 synthesis and bulk characterization of a series of linear fluorocarbon–vinyl acetate (VAc) random copolymers: P(TFE-*co*-VAc), P(CTFE-*co*-VAc), and poly(vinylidene fluoride-*co*-vinyl acetate), P(VDF-*co*-VAc).[15,16] We demonstrated that a diversity of compositions and molar

masses are possible by polymerization in CO_2 that are not observed by emulsion, likely due to the greater fluorocarbon solubility in CO_2. Herein, we explore the surface properties of these fluorocopolymer films and their blends with PVAc.

All copolymers and blends were cast from solution on Teflon sheets and analyzed at both air and Teflon surfaces. While the fluorocopolymers have a random distribution of repeat units, the fluorocarbon in the backbone (and not the pendant chain), and T_g's greater than room temperature,[16] we wanted to test whether surface enrichment of fluorocarbon segments was possible and thus studied the surface properties of these films. Surface composition has been shown to differ from bulk composition due, in part, to surface orientation of certain repeat units and the greater mobility of these units at the surface.[17] In general, high molecular weight polymers are nonequilibrium structures and exhibit a range of relaxations and transitions in response to time, temperature, and environment. The spontaneous migration of segments to the polymer surface has been shown to depend on bulk concentration,[8] polymer molar mass,[18] polarity differences, incompatibility of the components[19] and the nature of the surface-migrating species.[20] While molar mass may influence surface activity for low molar mass molecules, the effect diminishes significantly when the molar mass is greater than ~3000 g/mol.[21] All of the polymers studied herein have molar masses in excess of 100 000 g/mol.[16] We were also interested in testing whether the fluorocopolymer/PVAc blends exhibited similar surface properties to fluorocopolymer films as this would make them attractive for additives in coatings formulations. Given that PVAc has

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a surface tension of 36.5 dyn/cm and PTFE has one of 23.9 dyn/cm,[21] we expected the fluorocopolymers to be driven to the surface in the blend systems, thereby lowering the interfacial free energy. We studied both air−polymer and Teflon−polymer surfaces to determine the effect of the "counter" surface on fluorocarbon migration; we expected greater fluorocarbon migration to the Teflon vs air surface due to the higher interfacial free energy.

Experimental Section

Reagents. All chemicals were purchased from Aldrich Chemical Co. (Ontario, Canada) and used as received unless otherwise specified. P(TFE-*co*-VAc), P(CTFE-*co*-VAc), P(VDF-*co*-VAc), and PVAc were synthesized as previously described[16] without a surfactant and by radical copolymerization in supercritical fluid CO_2 using diethyl peroxydicarbonate initiation.[22] Water was deionized and distilled from Milli-RO 10 Plus and Milli-Q UF Plus (Bedford, MA) systems and used at 18 MΩ resistance.

Film Preparation. Fluorocarbon−VAc copolymers and blend films were prepared by dissolving 10% w/v polymer in acetone and then pouring this solution onto Teflon-coated glass sheets. Films were dried at room temperature and pressure prior to drying them under vacuum for several hours (also at room temperature). Since TFE and CTFE copolymers with fluorocarbon concentrations greater than 40 mol % were insoluble in acetone, only those copolymers with <40 mol % of fluorocarbon were analyzed by XPS and dynamic water contact angle. All of these copolymer films were transparent and easily manipulated.

Surface Characterization. Advancing and receding water contact angles were measured on air−film surfaces using a Ramé-Hart NRL telescopic goniometer equipped with a Gilmont syringe and a 22 gauge flat-tipped needle. The data presented are the average and standard deviation of at least seven measurements made at different areas on the film surface. All contact angles had standard deviations of 1°−2°.

Surface elemental composition was determined by X-ray photoelectron spectroscopy (XPS, Leybold LHMax 200) using an Al Kα X-ray source at 15 kV and 25 mA emission current; data were collected at a takeoff angle of 90° between the sample and detector. Samples were exposed to X-radiation for less than 5 min using pass energies of 192 and 42 eV for survey and C_{1s} spectra, respectively. X-ray damage of film surfaces was negligible under these conditions.

Results and Discussion

Surface Analysis of Fluorocarbon-*co*-VAc Films. Fluorocarbon−VAc copolymer films were cast from acetone onto Teflon-coated glass slides, and both air−polymer and polymer−Teflon surfaces were analyzed by XPS. Air−polymer surfaces were also analyzed by dynamic advancing and receding water contact angles. All fluorocarbon−VAc copolymer films were transparent. As shown in Figure 1, both advancing and receding water contact angles were greater for all fluorocarbon−VAc copolymer films than for PVAc homopolymer films, indicating the greater hydrophobicity of the former. For example, advancing and receding water contact angles for PVAc homopolymer are 69° and 33°, respectively, while those for P(TFE-*co*-VAc), with 7 mol % TFE, are 86° and 45°, respectively.

Interestingly, within the P(TFE-*co*-VAc) series, from 7 to 35 mol % TFE, the advancing contact angle increased but was relatively constant at 86°−90° while the receding contact angle increased progressively with increased TFE concentration in the bulk from 45° to 66°. Given that the receding contact angle is more suscep-
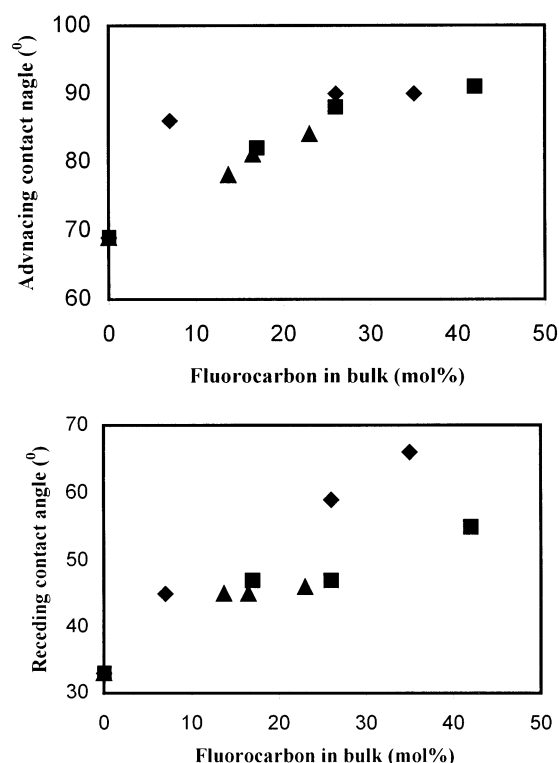
Figure 1. Dynamic water contact angle data for P(fluorocarbon-*co*-VAc) and PVAc films at the air−polymer surface: (◆) P(TFE-*co*-VAc), (■) P(CTFE-*co*-VAc), (▲) P(VDF-*co*-VAc) (*n* = 7, average reported; standard deviation is 1−2° for each average).

tible to small changes in surface hydrophilic species, the changes observed likely reflect the presence (or absence) of VAc at the surface. The advancing and receding contact angles for the P(CTFE-*co*-VAc) series, from 17 to 42 mol % CTFE, demonstrated a small increase in advancing and receding contact angles of 82°−91° and 47°−55°, respectively. Similarly, the advancing contact angles for the P(VDF-*co*-VAc) series, from 13.7 to 23 mol % VDF, increased slightly from 78° to 84°, yet the receding contact angles were relatively constant at 45°−46°.

To gain greater insight into these contact angle data, we compared them to those predicted by eq 1[23]

$$(1 + \cos \theta)^2 = f_1(1 + \cos \theta_1)^2 + f_2(1 + \cos \theta_2)^2 \quad (1)$$

where θ_1 and θ_2 are the contact angles of homopolymers 1 (fluoropolymers) and 2 (vinyl acetate) and f_1 and f_2 are the bulk molar fractions of 1 and 2 in the copolymer. We used the following published contact angles for (1) PTFE, $\theta_A/\theta_R = 116°/92°$;[21] (2) PCTFE, $\theta_A/\theta_R = 104°/80°$;[17] (3) PVDF, $\theta_A/\theta_R = 89°/67°$;[24] and (4) PVAc, $\theta_A/\theta_R = 69°/33°$ which we measured. The advancing and receding water contact angles for P(TFE-*co*-VAc) 26:74 were predicted to be 80°/49° vs those measured at 90°/59°. Similarly, P(CTFE-*co*-VAc) 42:58 had predicted contact angles of 82°/54° vs those measured at 91°/55°, and P(VDF-*co*-VAc) 23:77 had predicted contact angles of 74°/42° vs those measured at 84°/46°. Thus, the contact angle data measured were consistently higher than that predicted according to eq 1, indicating a true enrichment of fluorocarbon segments at the interface.

To better understand the hydrophobic nature of the fluorocarbon−VAc copolymer films, both air−polymer and Teflon−polymer surfaces were analyzed for elemen-
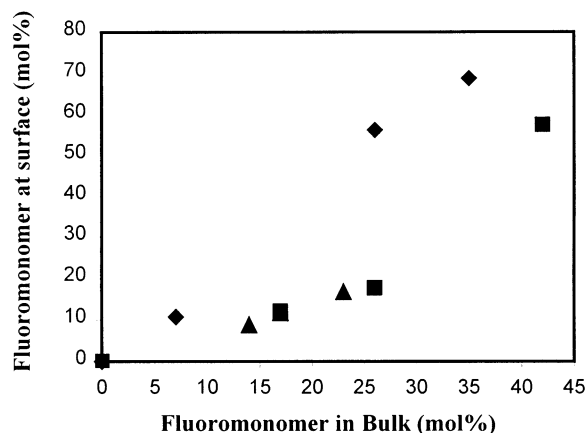
Figure 2. XPS analysis of fluorocarbon−VAc copolymers at air−polymer interface: (◆) P(TFE-*co*-VAc), (■) P(CTFE-*co*-VAc), (▲) P(VDF-*co*-VAc).

Table 1. Surface Tension and Polarity Data[21]

| polymer	surface tension (dyn/cm)	polarity (X^p)
PVAc	36.5	0.329
PTFE	23.9	0.089
PCTFE	30.9	0.282
PVDF	33.2	0.376

tal composition by XPS within the top 100 Å. XPS-determined surface compositions were compared to elemental analysis-determined bulk compositions;[16] while each technique is well-accepted, we do not account for differences between these methods in comparing compositions. As shown in Figure 2, the air surface concentration of fluorine of P(TFE-*co*-VAc) films increased with TFE concentration in the bulk. Interestingly, there was an enrichment of fluorocarbon repeats at the surface—greater than that predicted by the bulk concentration—which was unexpected given the random composition of this copolymer. In an attempt to better understand these results, we re-examined the bulk structure of these P(TFE-*co*-VAc) samples and found that there is a high percentage of VAc triads, as was shown by ^{1}H NMR,[16] which may indicate the presence of fluorine-rich segments. While the NMR data reflect the average bulk composition, the fluorocopolymers may be polydisperse in terms of fluorine content, with those fluorocarbon-rich segments segregating to the surface. The large polarity difference between PTFE and PVAc (cf. Table 1) and the low surface energy of PTFE starts to explain the surface enrichment of TFE relative to bulk concentration. Furthermore, the greater mobility of the fluorocopolymer chain at the surface vs the bulk may explain the differences in surface vs bulk concentrations;[17] for example, either individual chains may adopt conformations to lower surface energy or individual diads/triads/tetrads may rotate to minimize surface energy.[25,26]

In contrast to P(TFE-*co*-VAc) films, the surface fluorine concentration of P(VDF-*co*-VAc) films was lower than that predicted by the bulk fluorine concentration, indicating surface depletion of VDF. P(CTFE-*co*-VAc) films demonstrated fluorocarbon surface enrichment behavior between that of P(TFE-*co*-VAc) and P(VDF-*co*-VAc) films. For P(CTFE-*co*-VAc) films there was less fluorocarbon at the surface than predicted by the bulk at low fluorocarbon concentrations yet greater enrichment at higher concentrations. The decreased surface activity of the fluorocarbon units at low bulk concentrations, for both P(CTFE-*co*-VAc) and P(VDF-*co*-VAc),

suggests that either the fluorocarbon repeat units are unable to migrate to the surface due to perhaps bulk entanglement or there is simply insufficient fluorocarbon content for surface activity. For the former, bulk entanglement is supported by similar polarity values and thus greater interactions, at least for PVDF and PVAc. For the latter, it suggests a minimum-energy barrier for surface activity associated with composition which may be true for P(VDF-*co*-VAc) and P(CTFE-*co*-VAc) but is belied by the P(TFE-*co*-VAc) films where the surface was enriched with TFE for all compositions. For example, for bulk TFE concentrations of 7−35 mol %, the surface TFE concentration is 10.7−68.8 mol %, respectively. For P(CTFE-*co*-VAc) films, the fluorocarbon enriched the surface relative to the bulk at higher CTFE bulk compositions, as was observed when the CTFE bulk content was ∼40 mol %. For P(VDF-*co*-VAc) films, no enrichment of VDF at the surface relative to the bulk was observed for VDF bulk concentration of 14−23 mol %.

At least two factors may explain the differences observed in water contact angles and fluorine enrichment for the different fluorocopolymer films at the air−polymer surface: surface tension and polarity. As shown in Table 1, the surface tensions of the homo-fluoropolymers are all lower than that of PVAc. Given that lowering the surface free energy is an important driving force for fluorocarbon surface enrichment, we anticipated that the fluorocarbon would enrich the surface and thus decrease wetting relative to PVAc homopolymer. However, the difference in surface tensions varies between PVAc and each fluoropolymer, and this difference is reflected in the wettability of each surface and the extent of fluorocarbon enrichment. For example, the difference in surface tension between PTFE and PVAc is much greater than that between PVDF and PVAc, thereby accounting, at least partially, for the greater change in contact angles observed. The surface tension effect likely explains the differences in fluorocarbon surface coverage observed by XPS as well. The differences in polarity also impact migration and surface enrichment. For example, of the three halocarbons, PTFE is the least polar, and the difference in polarity between PTFE and PVAc is the greatest. This suggests that TFE repeats will be driven away from VAc repeats in the bulk and toward the air−polymer surface. In contrast, PVDF and PVAc have similar polarity, suggesting greater miscibility of VDF and VAc repeats (relative to TFE-VAc) and thus decreased driving force of VDF repeats to the air−film surface. Last, there are likely some weak intermolecular acid−base type interactions between PVAc and either PCTFE or PVDF that result in less PCTFE/PVDF at the air−polymer interface relative to PTFE because PVAc is considered slightly basic whereas PCTFE and PVDF are considered slightly acidic.[27]

To gain a greater appreciation for the elements contributing to the driving force for surface enrichment, we examined the "other side" of the films, that is, the Teflon−polymer film surface. While we had already gained insight into the importance of bulk concentration, surface tension, and polarity differences as contributors to fluorocarbon surface enrichment, we wanted to test how a nonpolar, hydrophobic surface, such as Teflon, would impact surface properties relative to those observed at air. We expected that the fluorocarbon repeat units would enrich the Teflon interface more
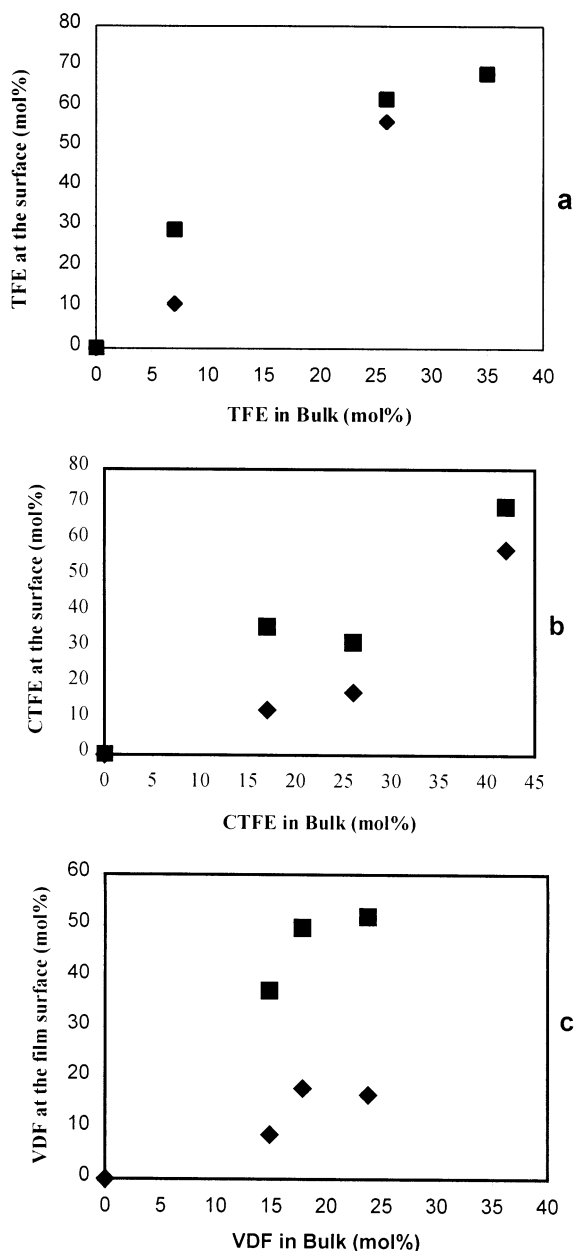
Figure 3. XPS analysis of P(fluorocarbon-*co*-VAc) films at air−polymer (◆) and Teflon−polymer (■) surfaces for (a) P(TFE-*co*-VAc), (b) P(CTFE-*co*-VAc), and (c) P(VDF-*co*-VAc).

than that with air due to the greater interfacial free energy at Teflon relative to air. As shown in Figure 3 for the XPS data, all fluorocarbon−VAc copolymer films demonstrate an enrichment of fluorine at the Teflon surface relative to both bulk and air−polymer surface compositions. It is important to note that PVAc control films had an air−surface composition of $C_{70}O_{30}$ and a Teflon−surface composition of $C_{70}O_{30}F_{0.7}$, indicating that most, if not all, of the fluorocarbon observed at the Teflon interface derives from the fluorocopolymers and not from the Teflon surface. The greatest surface enrichment of fluorine was observed for P(TFE-*co*-VAc). For example, for 26 mol % fluorocarbon bulk composition, P(TFE-*co*-VAc) had 62 mol % TFE at the Teflon interface while P(CTFE-*co*-VAc) had 32 mol % CTFE at the same surface. Interestingly, P(VDF-*co*-VAc) films had significantly more VDF at the Teflon surface than both bulk and air surface compositions. For P(VDF-*co*-VAc) having 23 mol % VDF in the bulk, there was 52

mol % VDF at the Teflon surface whereas only 17 mol % at the air interface. For P(VDF-*co*-VAc), the Teflon surface was enriched with VDF (and depleted with VAc), perhaps because of greater interactions between VDF and Teflon and decreased interactions between VAc and Teflon. These results demonstrate the importance of the counter surface as a driving force for the fluorocarbon to the surface. Thus, the Teflon interface is an important driving force for our fluorocopolymers and others.[28]

Surface Analyses of P(Fluorocarbon-*co*-VAc)/ PVAc Blends Films. Since the fluorocarbon−VAc copolymers may be useful as additives in coatings formulations, we prepared several compositions of P(fluorocarbon-*co*-VAc)/PVAc blends by co-dissolving a small fraction (less than 15%) of fluorocarbon−VAc copolymer and PVAc homopolymer in acetone prior to casting films. Films were characterized as before by dynamic advancing and receding water contact angles and XPS. As shown in Table 2, three blends were prepared where the composition of the fluorocarbon in the blend was maintained between 2.5 and 3.5 mol %. The contact angles were similar for copolymers and blends. The greatest similarity was observed between a P(TFE-*co*-VAc) film having 26 mol % bulk TFE and a P(TFE-*co*-VAc)/PVAc blend film having 2.6 mol % bulk TFE. Thus, while the TFE content was reduced by 10-fold, the advancing and receding contact angles were unaffected.

The advancing and receding contact angles decreased for P(CTFE-*co*-VAc)/PVAc blend films having 2.5 mol % vs P(CTFE-*co*-VAc) copolymer films having 42 mol % bulk CTFE, from 91°/55° for the latter to 83°/47° for the former. By comparison to copolymer films, water contact angles (shown in Figure 1), P(CTFE-*co*-VAc)/ PVAc blends having 2.5 mol % CTFE in the bulk demonstrated similar contact angles to P(CTFE-*co*-VAc) copolymer films of 26 mol % CTFE. Thus, the advancing and receding contact angles were again unaffected by an order of magnitude decrease in CTFE content for blends vs copolymer films. The advancing and receding water contact angles decreased for P(VDF-*co*-VAc)/PVAc blend films having 3.45 mol % VDF vs P(VDF-*co*-VAc) films having 23 mol % bulk VDF, from 84°/46° for the latter to 78°/42° for the former. Thus, unlike P(TFE-*co*-VAc)/PVAc and P(CTFE-*co*-VAc)/PVAc blends, P(VDF-*co*-VAc)/PVAc blends did not maintain the same hydrophobicity after a 10-fold decrease in halocarbon bulk concentration. The strong polar interactions between VDF and VAc may limit the surface activity of VDF. Interestingly, the predicted contact angles calculated according to eq 1 were 70°/35° for all blends, demonstrating that all blends had contact angles greater than predicted and thus a surface enrichment of fluorocarbon segments.

As shown in Table 3, XPS analysis of blend films reflected the contact angle data. For example, both P(TFE-*co*-VAc)/PVAc blends and P(TFE-*co*-VAc) had significantly greater fluorocarbon at the air−polymer surface than was present in the bulk. For P(TFE-*co*-VAc), there was twice as much fluorocarbon on the surface vs the bulk whereas for the P(TFE-*co*-VAc)/PVAc blend, there was ~16 times as much. While the contact angles were similar for P(TFE-*co*-VAc) and its blend with PVAc, the surface fluorocarbon concentrations differed. For P(CTFE-*co*-VAc) and its blend with PVAc, the surface fluorocarbon concentrations were greater than that of the bulk, with the greatest increase being that of the blend where there was ~7 times more

Table 2. Comparison of Dynamic Water Contact Angles between Films of P(fluorocarbon-*co*-VAc) and Their Blends with PVAc at the Air Surface

copolymer composition (mol %)	blend composition (w/w %)	fluorocarbon bulk concentration (mol %)	advancing contact angle (deg)	receding contact angle (deg)
P(TFE-*co*-VAc) 26:74		26	90 ± 1	59 ± 1
	P(TFE-*co*-VAc)/PVAc 10/90	2.6	90 ± 1	62 ± 1
P(CTFE-*co*-VAc) 42:58		42	91 ± 1	55 ± 2
	P(CTFE-*co*-VAc)/PVAc 6/94	2.55	83 ± 1	47 ± 1
P(VDF-*co*-VAc) 23:77		23	84 ± 1	46 ± 1
	P(VDF-*co*-VAc)/PVAc 15/85	3.45	78 ± 1	42 ± 1

Table 3. Surface Elemental Composition of P(fluorocarbon-*co*-VAc) Films and Their Blends with PVAc As Determined by XPS Analysis (90° Takeoff Angle) at the Air−Polymer Surface

copolymer and blend compositions	fluorocarbon at air−polymer surface (mol %)	F_{1s} (%)	O_{1s} (%)	C_{1s} (%)	Cl_{2p} (%)
P(TFE-*co*-VAc) (26 mol % TFE)	56.22	32.71	12.73	53.72	
P(TFE-*co*-VAc)/PVAc 10% (2.6 mol % TFE)	43.05	28.56	18.89	52.48	
P(CTFE-*co*-VAc) (42 mol % CTFE)	57.46	25.72	12.69	53.29	8.20
P(CTFE-*co*-VAc)/PVAc 6% (2.55 mol % CTFE)	17.05	6.42	20.82	70.50	2.10
P(VDF-*co*-VAc) (23 mol % VDF)	16.61	5.1	25.59	68.73	
P(VDF-*co*-VAc)/PVAc 15% (3.45 mol % VDF)	3.82	1.17	29.43	69.37	

Table 4. Surface Activity of P(fluorocarbon-*co*-VAc)/PVAc Blends Films: XPS Data Comparison of Composition at the Teflon−Polymer and Air−Polymer Surfaces

blend composition (w/w %)	film surface	fluorocarbon at polymer surface (mol %)	F_{1s} (%)	O_{1s} (%)	C_{1s} (%)	Cl_{2p} (%)
PVAc (control)	air			29.87	69.81	
PVAc (control)	Teflon		0.68	29.87	69.81	
P(TFE-*co*-VAc)/PVAc 10% (2.6 mol % TFE)	air	43.05	28.56	18.89	52.48	
	Teflon	62.76	42.25	12.53	45.22	
P(CTFE-*co*-VAc)/PVAc 6% (2.55 mol % CTFE)	air	17.05	6.42	20.82	70.50	2.10
	Teflon	55.96	27.22	14.28	54.82	3.68
P(VDF-*co*-VAc)/PVAc 15% (3.45 mol % VDF)	air	3.82	1.17	29.43	69.37	
	Teflon	44.38	17.73	22.22	60.06	

fluorocarbon on the surface (17 mol %) vs the bulk (2.55 mol %). Unlike the other copolymer samples, the surface fluorocarbon enrichment vs the bulk was not apparent for P(VDF-*co*-VAc) and its blends. This may be explained, as above, by the greater miscibility[29] and polar interaction between VDF and VAc repeat units coupled with the decreased surface tension of VDF relative to those of TFE and CTFE (cf. Table 1).

To test whether the interfacial surface could affect surface activity in the blends, as was demonstrated with fluorocopolymers, we investigated the surface composition of fluorocarbon−VAc copolymer blend films at the polymer−Teflon surface by XPS. As shown in Table 4, the film surface properties are affected by the Teflon surface, as was observed for the fluorocopolymer films. There was an enrichment of the fluorocarbon at the Teflon surface vs that at air for all blend films, with the most dramatic results observed for P(VDF-*co*-VAc)/ PVAc blends. Whereas there was no enrichment of VDF at the air−polymer blend surface, there was a significant 13-fold enrichment at the Teflon−polymer blend surface of 3.45 mol % in the bulk to 44.4 mol % at the surface. Thus, Teflon appears to overwhelm the polar interactions that we hypothesized as limiting the migration of VDF to the air surface. Two potential driving forces likely have a synergistic effect: (1) the unfavorable hydrophilic−hydrophobic interactions between VAc and Teflon and (2) the favorable hydrophobic−hydrophobic interactions between VDF and Teflon. Similarly,

a greater fluorocarbon concentration was observed at the Teflon surface for P(TFE-*co*-VAc)/PVAc blends relative to the bulk and the air−polymer surface. Relative to the bulk concentration, there was 24 times more TFE at the Teflon surface and 16 times more at the air surface for the blend films. For P(CTFE-*co*-VAc)/PVAc blend films, there was 22 times as much CTFE at the Teflon surface and 6 times as much at the air surface, relative to bulk CTFE concentration, confirming the importance of the "counter" surface as a driving force for surface property determination. Interestingly, for P(CTFE-*co*-VAc)/PVAc blend films, the XPS ratio of chlorine to fluorine is 1:3 at the air surface (as expected), but 1:7 at the Teflon surface. This unexpected ratio may indicate that fluorocarbon groups from Teflon are the cause for the increased surface fluorine concentration; however, controls of PVAc cast on Teflon show insignificant fluorine on PVAc surfaces, suggesting this explanation to be unlikely. Alternatively, there may be some orientation of −CF$_2$− groups at the Teflon surface.

Conclusions

We have defined the critical parameters that drive polymer segments of even random copolymers to the surface: surface tension, polarity, interfacial free energy at the counter surface. While we had expected fluorocopolymers to be more hydrophobic than PVAc, we did not expect to have surface enrichment of fluorocarbon segments at the surface, which reflects the greater

mobility of chain segments at the surface relative to the bulk. Overall, P(TFE-*co*-VAc) was most surface active, followed by P(CTFE-*co*-VAc) and P(VDF-*co*-VAc), likely due to differences in polarity and surface tension among the fluorocarbons and relative to VAc. Teflon was a greater driving force than air for fluorocarbon enrichment. The blends demonstrated enriched fluorocarbon content relative to fluorocopolymers at the surface, which may make the fluorocopolymers useful as additives in coatings or paint formulations.

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