Surface Enrichment of Poly(trifluorovinyl ether)s in Polystyrene Blends

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ABSTRACT: Surface modification can be achieved with polymer blends when one component of the system is more surface active than the others. Numerous factors affect the interfacial properties, including the type and concentration of polymers, the solvent, and the interface. Blends of polystyrene (PS) and poly(trifluorovinyl ether) (PTFVE)—having a fluorocarbon backbone and an oligoether pendant group—were cast as films from chloroform or toluene. The air−polymer interface was investigated and found to be enriched with PTFVE at very low bulk concentrations (<1 wt %) as determined by XPS and contact angle analysis. Both surface fluorine and oxygen increased with bulk PTFVE content. Interestingly, PTFVE-enriched surfaces were increasingly hydrophilic with PTFVE content, indicating that oligoether groups were dominant at the outermost layer. This observation was confirmed by angle-resolved XPS and ToF SIMS. AFM of PTFVE cast on mica indicated the presence of large aggregates on the order of 200 nm in diameter. We hypothesize that PTFVE in PS/PTFVE blends form similar structures at the interface, with aggregates having PTFVE cores and oligoether coronas, thereby accounting for oligoether pendant groups, and not fluorocarbon backbone, at the air−polymer interface. The nature of the solvent influenced the surface properties of the blends; films cast from toluene, which is a better solvent for PS than chloroform, required greater PTFVE content in the bulk for surface activity than those cast from chloroform. Furthermore, the type of PTFVE used affected surface activity and the resulting surface hydrophilicity.

Introduction

Surface modification via surface enrichment of one component of a multicomponent system, such as a blend, has been of interest for numerous years.[1−5] The driving force for surface modification in such a system is largely thermodynamic, where the component with the lowest critical surface tension rises to the air−polymer interface, thereby lowering the interfacial free energy. The miscibility and mobility of the components influence the kinetic driving force toward the interface.[6−8] Consequently, fluorochemicals and fluoropolymers have often been studied as surface-modifying molecules for applications such as coatings and lubricants.[9] Polymeric blends are advantageous because the polymeric additive is anchored to the matrix via entanglements or dispersive forces, thereby making the surface more stable than that achieved with a small molecule additive. For example, fluorine-enriched surfaces have been prepared with (1) blends of a poly(urethane) and fluorocarbon-terminated poly(urethane),[10] (2) poly(acrylate)s having fluorocarbon pendant groups,[11,12] and (3) hydrocarbon polymer−fluoropolymer blends.[13] The latter, blends of hydrocarbon and fluorocarbon polymers, are advantageous, providing a relatively simple way of controlling surface properties while maintaining the bulk properties of the hydrocarbon polymer.[14]

We have synthesized a series of new trifluorovinyl ether polymers (PTFVEs) that are soluble in most organic solvents, thermally stable to ∼320 °C, and thus processable as additives in blends.[15,16] As shown in Figure 1, unlike other fluorocarbon vinyl ether polymers which are either mostly fluorinated[17] or have a hydrocarbon backbone and a fluorocarbon pendant group,[18] our PTFVEs have a fluorocarbon backbone and a hydrocarbon oligoether group: poly{1-[2-(2-ethoxyethoxy)ethoxy]-1,2,2-trifluoroethylene} [poly(Et-TFVE)] and poly{1-[2-(2-ethoxyethoxy)ethoxy]-1,2,2-trifluoroethylene-*co*-1-[2-(2-hydroxyethoxy)ethoxy]-1,2,2-trifluoroethylene} [poly(Et-TFVE-*co*-TFVE-OH)]. The oligoether pendant group enhances solubility in organic solvents and may provide improved miscibility with polymers capable of hydrogen-bonding interactions. These PTFVEs are viscous liquids at room temperature, having T_g's of −60 °C for poly(Et-TFVE) and −19 °C for poly(Et-TFVE-*co*-TFVE-OH) (50/50 mol/mol). Consequently, they are highly mobile at room temperature, thereby increasing their propensity for surface activity in polymer blends.

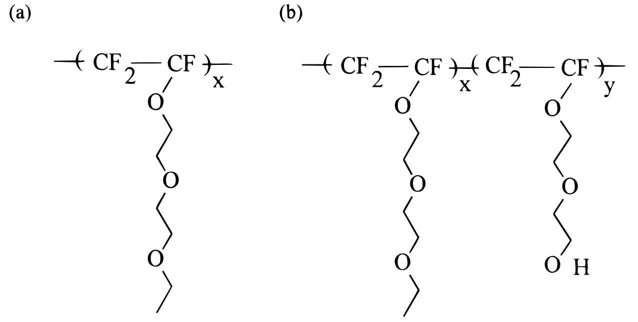

Figure 1. Structure of (a) poly(Et-TFVE) and (b) poly(Et-TFVE-*co*-TFVE-OH) (1/1 mol/mol).

We prepared blends of our PTFVEs (shown in Figure 1) and polystyrene (PS) and hypothesized that our PTFVEs would enrich the air−polymer interface of solvent-cast films. We expected that the fluorocarbon backbone would drive the PTFVE to the interface, thereby lowering the interfacial free energy. Furthermore, we hypothesized that the pendant oligoether groups would be oriented at the polymer−water interface, due to both the greater hydrophilicity and mobility of the pendant group ends relative to the fluorocarbon backbone. We expect that such oligoether-enriched

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surfaces may ultimately be useful in biomedical applications, where oligoether-modified,[19] poly(ethylene glycol)-modified,[20] and PEG-blended[21] surfaces have been shown to reduce protein adsorption. We chose the two PTFVEs shown in Figure 1 because poly(Et-TFVE) has an oligoether group similar to PEG and poly(Et-TFVE-*co*-TFVE-OH) has a terminal hydroxyl group which would likely increase the hydrophilicity of the surface. (The homopolymer of TFVE-OH is not readily soluble in chloroform and thus unsuitable for use in solvent-cast blends.) We chose PS because it is soluble in common organic solvents, and it consists of only carbon and hydrogen, thereby simplifying surface analysis by X-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectrometry (ToF SIMS), and dynamic water contact angle. To gain a better perspective on the surface structure of poly(Et-TFVE), dilute solutions of poly(Et-TFVE) were cast from ethanol onto mica and examined by atomic force microscopy (AFM).

Experimental Section

All reagents were purchased from Aldrich unless otherwise specified. Poly(Et-TFVE) and poly(Et-TFVE-*co*-TFVE-OH) were synthesized as previously described by aqueous emulsion polymerization using a redox initiator, potassium persulfate, and ferrous sulfate with sodium bisulfite.[15,16] PS (128 000 g/mol) was purified by repeated dissolution in $CHCl_3$ and precipitation in ethanol and then dried ($P < 0.1$ mmHg, 50 °C). Water was deionized and distilled from Millipore Milli-RO 10 Plus and Milli-Q UF Plus (Bedford, MA) systems and used at 18 MΩ resistance.

PS/PTFVE Blends. PS and one of poly(Et-TFVE) or poly(Et-TFVE-*co*-TFVE-OH) were dissolved in either $CHCl_3$ or toluene at a total concentration of 5% w/v with a total mass of 0.20 g. Relative to PS, the content of PTFVE varied from 0.05 to 5 wt %. Films of the blend were prepared by casting solutions into aluminum pans, allowing the solvent to evaporate overnight at room temperature (RT), and then drying under vacuum for 6−8 h at RT. The surface at the air−polymer interface was characterized.

Surface Characterization. Dynamic water contact angle data were collected on 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 an average of at least five measurements at different areas on the film surface. Surface elemental composition was determined by XPS (Leybold LHMax 200) using a Mg Kα X-ray source at 15 kV and 20 mA emission current and an aperture size of 13 × 7 μm; data were collected at takeoff angles between 5° and 90°. Static ToF SIMS data were collected from film surfaces using a Physical Electronics PHI 7200 spectrometer. Primary Cs^+ cations were excited with 8 keV at an angle of 60° with a 1.7 pA current and a pulse length of 18.75 ns. The secondary ions were accelerated to ±3 keV by applying a bias to the sample. For each sample, both positive and negative secondary ion mass spectra were collected using a total primary ion dose of 1×10^{11} ions/cm^2, which is well below the damage threshold value of 1×10^{13} ions/cm^2 for static SIMS. AFM images (Nanoscope III, Digital Instruments) were obtained at ambient conditions of dilute solutions of poly(Et-TFVE) in ethanol (0.02 mg/mL) cast on fresh mica surfaces and allowed to evaporate overnight.

Results

Blends of PS and PTFVE were prepared by codissolution in either chloroform or toluene and then cast as films. We were interested in modifying the air−polymer interface and thus focused our attention there. Films cast from chloroform were analyzed by XPS, dynamic contact angle, and ToF SIMS to gain a thorough understanding of surface properties.

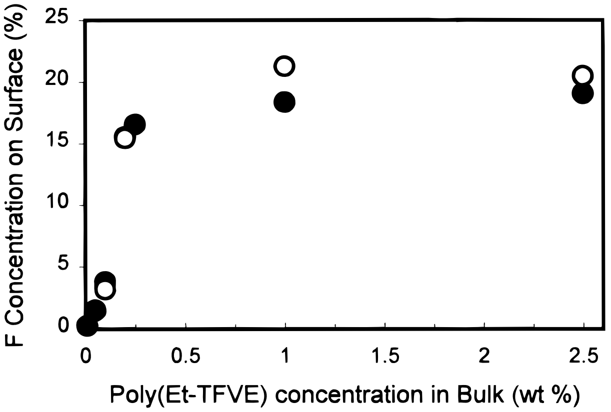


Figure 2. Surface fluorine atomic concentration increased with poly(Et-TFVE) bulk content at both XPS takeoff angles of (●) 15°and (○) 90°.

XPS. PS/PTFVE chloroform-cast films were translucent, with opacity increasing with PTFVE content, indicating that PS and PTFVE are immiscible. The air−polymer interface of the films was characterized by XPS to determine whether the surfaces were enriched with PTFVE relative to the bulk. The XPS-determined surface atomic fluorine concentration, which is representative of poly(Et-TFVE), was compared with the bulk concentration of poly(Et-TFVE) used in the blend. As shown in Figure 2, the surface fluorine atomic concentration increases rapidly with poly(Et-TFVE) bulk content in the blend and reaches a plateau at 1% poly(Et-TFVE) in PS (w/w). Poly(Et-TFVE) appears to have saturated the surface composition of the blend at the 1 wt % bulk poly(Et-TFVE) given that (1) the 1 wt % blend has a *surface* concentration of fluorine between 19 and 22 at. % (15° and 90° takeoff angles, respectively), (2) pure poly(Et-TFVE) has 21.4 at. % fluorine, and (3) the 1 wt % blend has a *bulk* concentration of fluorine of 0.214 at. %. Thus, by XPS, the blend air−polymer interface is composed of between 89% and 100% poly(Et-TFVE), according to the 15° and 90° takeoff angle data, respectively. The fluoropolymer is surface active due to both the low interfacial surface tension associated with the fluorocarbon backbone and its high mobility as reflected by its low T_g (−60 °C). Interestingly, the fluorine concentration is slightly higher at the XPS takeoff angle of 90° than that of 15°, indicating the fluorine concentration is higher at greater depths from the surface. Thus, while the fluorocarbon backbone is one of the likely driving forces to the surface, it itself is not likely at the surface.

To gain greater insight into the surface composition of the PS/1 wt % poly(Et-TFVE) film blend, the oxygen to fluorine atomic concentration ratio was compared at a series of takeoff angles, with higher takeoff angles representing a greater depth of penetration. As shown in Figure 3, the O/F atomic ratio decreases with increasing takeoff angles or depths of penetration, to a takeoff angle of ∼55° where the O/F ratio reaches a plateau value of 1. Given that the calculated O/F ratio for pure poly(Et-TFVE) is 1 and the XPS-determined O/F ratio is 1.4 at lower takeoff angles (or depths of penetration), the outermost blend surface has a higher oxygen content than the bulk and thus appears to be enriched with oligoether groups.

While we had anticipated that the poly(Et-TFVE) would be surface active in a PS blend, it was surprising that the outermost surface was enriched with oligoether

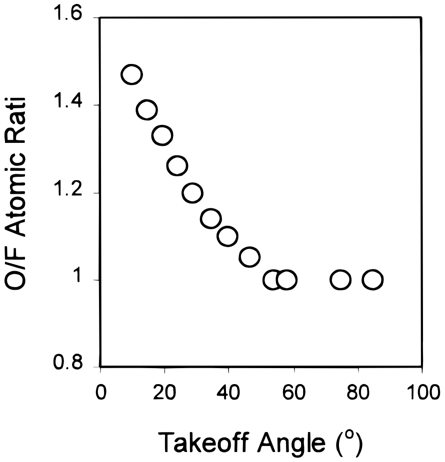


Figure 3. XPS O/F atomic concentration ratio decreased with increasing takeoff angle.

groups and not fluorocarbon groups under the dry evacuated atmosphere of the XPS. For example, perfluorodecanoyl-modified PEO films had fluorine-enriched surfaces due to the lower critical surface energy provided by the fluorocarbon tail and its greater mobility relative to the PEO backbone.[22] In our system, the pendant oligoether groups may dominate the surface structure due to their increased mobility relative to the fluorocarbon backbone. To confirm our observations by XPS, we conducted ToF SIMS and contact angle analyses.

ToF SIMS. The air–polymer interface of PS/PTFVE blends was further characterized by ToF SIMS to gain better insight into the outermost surface composition. The positive ToF SIMS spectra for PS, PS/0.25% poly(Et-TFVE), and PS/2.5% poly(Et-TFVE) are shown in Figure 4, a, b, and c, respectively. The dominant mass fragment peaks were observed between 0 and 200 $m/z+$. The dominant peak for PS at 91 amu is attributed to $C_7H_7^+$, the tripylium ion formed by cleavage of the phenyl group (cf. Figure 4a), and is used to represent the presence of PS in blend film surfaces.[23,24] For blends containing 0.25% poly(Et-TFVE), a small peak at 91 amu is observed, reflecting the presence of PS at the surface; however, the dominant peaks at 29, 45, and 73 are attributed to $C_2H_5^+$, $C_2H_5O^+$, and $C_2H_5OC_2H_4^+$, respectively, reflecting the dominance of the oligoether of poly(Et-TFVE) at the air–polymer interface (cf. Figure 4b). The strongest peak at 45 amu, $C_2H_5O^+$, is also observed for pure poly(ethylene glycol).[24] For blends containing 2.5 wt % poly(Et-TFVE), only oligoether peaks were present, indicating that the surface was saturated with poly(Et-TFVE) (cf. Figure 4c). These data confirm those obtained by XPS.

When negative ion spectra were collected of both 0.25% and 2.5% poly(Et-TFVE) blend surfaces, oxygen, hydroxyl, and fluorine negative ions were detected, indicating the presence of both oligoether pendant groups and fluorocarbon backbone groups at the surface. A small peak at 97 amu, assigned to HSO_4^-, was also observed in the negative ion spectrum, suggesting the presence of initiator fragments at the polymer chain termini.

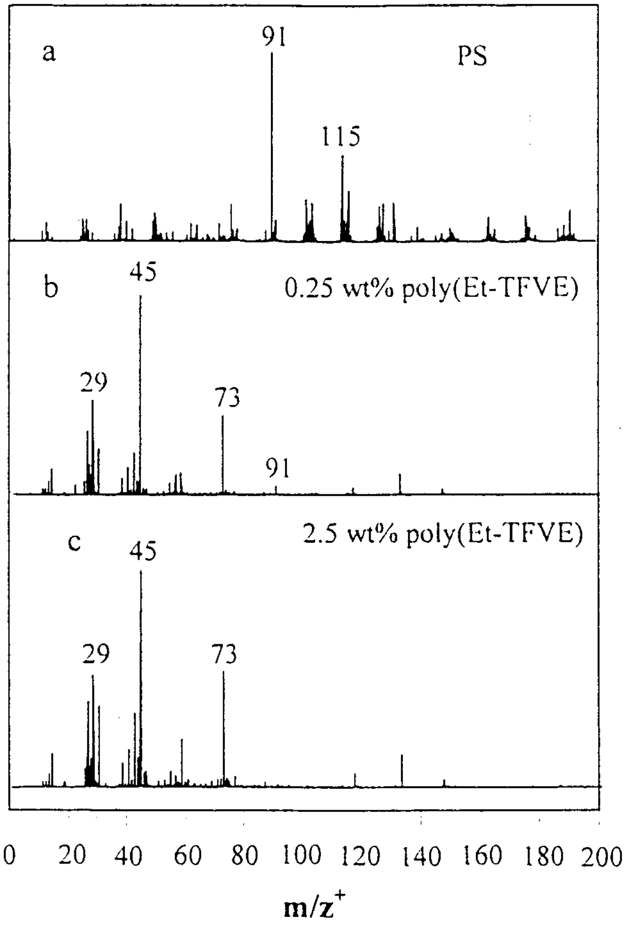


Figure 4. ToF-SIMS spectra of (a) PS, (b) PS/PTFVE blend having 0.25 wt % poly(Et-TFVE) in the bulk, and (c) PS/PTFVE blend having 2.5 wt % poly(Et-TFVE) in the bulk.

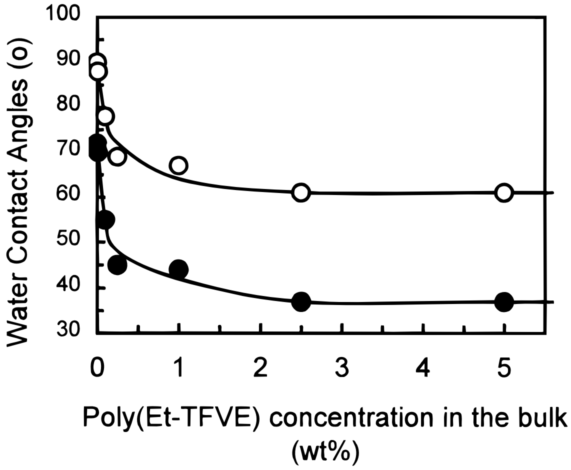


Figure 5. Dynamic (○) advancing and (●) receding water contact angles of PS/poly(Et-TFVE) blend film surfaces cast from *chloroform* decrease with increasing poly(Et-TFVE) bulk content.

Contact Angle. To gain further insight into the properties of the blend surface, it was characterized by dynamic water contact angle. As shown in Figure 5, both advancing and receding water contact angles decreased with increasing bulk poly(Et-TFVE) in the PS blend, reflecting increased surface hydrophilicity. Pure PS has advancing and receding contact angles of 89°/72°, while PS/1% poly(Et-TFVE) blends have contact angles of 72°/45°. The contact angles reached plateau values of 61°/37° at 2.5% bulk poly(Et-TFVE) concentration in PS, indicating that the surface was saturated with poly(Et-TFVE). All contact angles had standard deviations of 1°–2°.

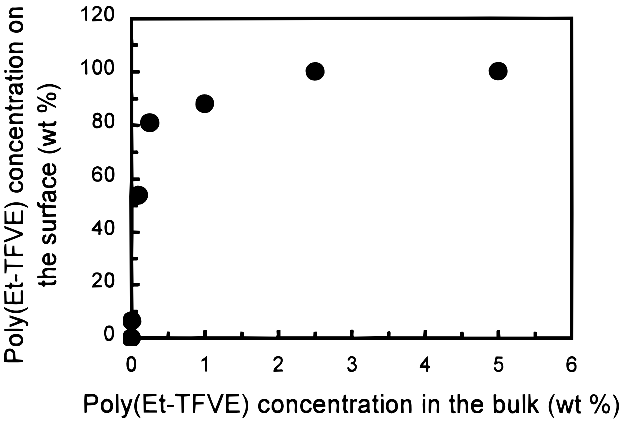


Figure 6. Surface composition of PS/poly(Et-TFVE) blends were estimated by the Cassie equation: poly(Et-TFVE) saturated the surface as poly(Et-TFVE) content in the bulk increased.

The contact angle data were used to estimate surface polymer composition relative to bulk composition, according to $f_{\mathrm{TFVE}} + f_{\mathrm{PS}} = 1$ and the Cassie equation[25] which is shown in eq 1:

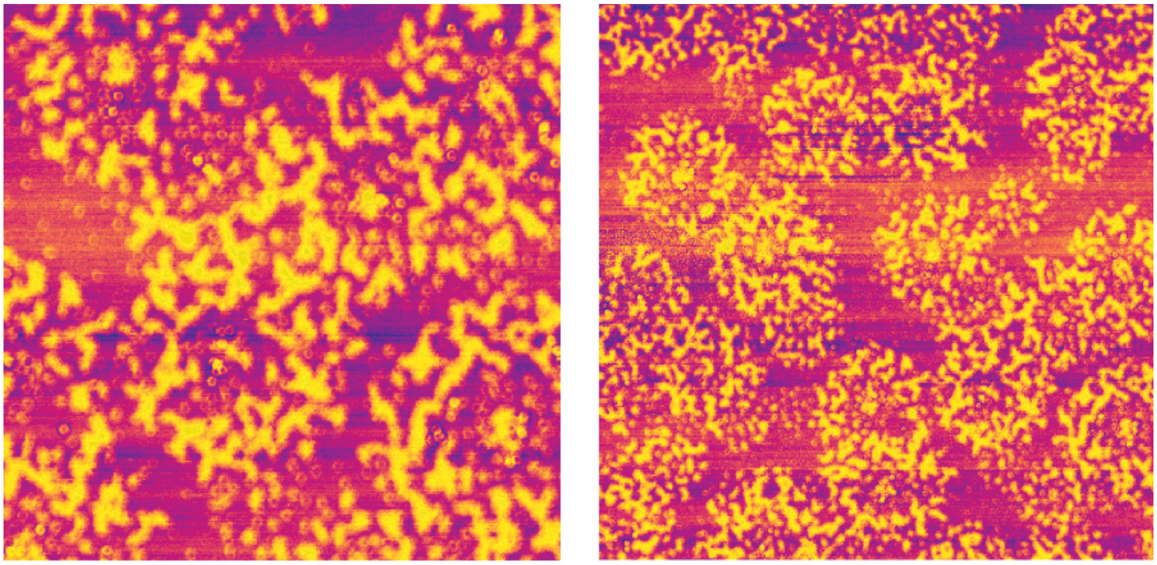
$$\cos\theta = f_{\mathrm{TFVE}}\cos\theta_{\mathrm{TFVE}} + f_{\mathrm{PS}}\cos\theta_{\mathrm{PS}} \qquad (1)$$

where f_{TFVE} and f_{PS} are the surface weight fractions of poly(Et-TFVE) and PS in the blend, respectively, θ is the receding water contact angle measured of the blend, and θ_{TFVE} (=37°) and θ_{PS} (=72°) are the receding contact angles of pure poly(Et-TFVE) and pure PS, respectively. (The advancing contact angle data were inappropriate to use because that of PS is almost 90° and cos 90° is 0.) The surface compositions of PS/PTFVE blends were estimated from contact angle data in terms of poly(Et-TFVE) content and plotted against bulk poly(Et-TFVE) composition, as shown in Figure 6. At 0.25% bulk poly(Et-TFVE), the surface is 81% poly(Et-TFVE) and reaches 100% poly(Et-TFVE) at 2.5% bulk composition. At 1% poly(Et-TFVE) bulk composition, the Cassie equation estimates surface composition at 85% poly(Et-TFVE), which is in close agreement with that calculated by XPS (89−100%) for the same composition.

AFM Imaging. The XPS, ToF SIMS, and contact angle data all indicated that PTFVE was surface active in PS blends and that the air−polymer interface was enriched with oligoether pendant groups. To gain a greater understanding of the conformation of poly(Et-TFVE) at the surface, we attempted to image it by AFM. Since images of blend surfaces were unclear, AFM images were captured of dilute solutions of poly(Et-TFVE) cast on mica. Spherical particles with diameters of 200−250 nm were observed, as shown in Figure 7a. Each particle likely consists of several hundred polymeric chains, thereby accounting for the large diameter observed. Several spherical particles seemed to aggregate together, having chainlike or clusterlike morphologies, as shown in Figure 7b.

Solvent Effects. To determine the effect of solvent on the polymer−air interface, we repeated our experiments by casting films of PS/PTFVE dissolved in toluene. Toluene is a better solvent for PS, it is less polar than $CHCl_3$, and it has a lower vapor pressure, thus affecting film formation and surface properties. Dynamic water contact angle data were used as a measure of surface enrichment, the results of which are summarized in Figure 8 for blends of PS and poly(Et-TFVE).

Little to no change in advancing water contact angles was observed for films composed of PS with up to 0.75 wt % bulk poly(Et-TFVE); the receding contact angle decreased from 72° to 58° for the same composition. These results indicate that already a small concentration of poly(Et-TFVE) is present at the surface since receding contact angles are more sensitive to low concentrations of hydrophilic groups on chemically heterogeneous surfaces. For compositions containing >1 wt % poly(Et-TFVE) in PS, both advancing and receding contact angles decreased significantly, reflecting the increased hydrophilic nature of the surface. While films cast from chloroform showed significant changes in both advancing and receding contact angles at 0.25 wt % poly(Et-TFVE), those cast from toluene showed significant changes only after 1 wt % poly(Et-TFVE), thereby



a (full scale: 5 μm) b (full scale: 10 μm)

Figure 7. AFM images of poly(Et-TFVE) aggregates on mica surface at (a) high magnification (field width = 5 μm) and (b) low magnification (field width = 10 μm).

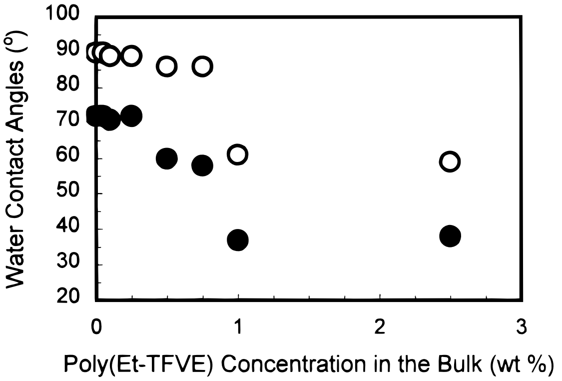


Figure 8. Dynamic (○) advancing and (●) receding water contact angles of PS/poly(Et-TFVE) blend film surfaces cast from *toluene* decrease with increasing poly(Et-TFVE) bulk content.

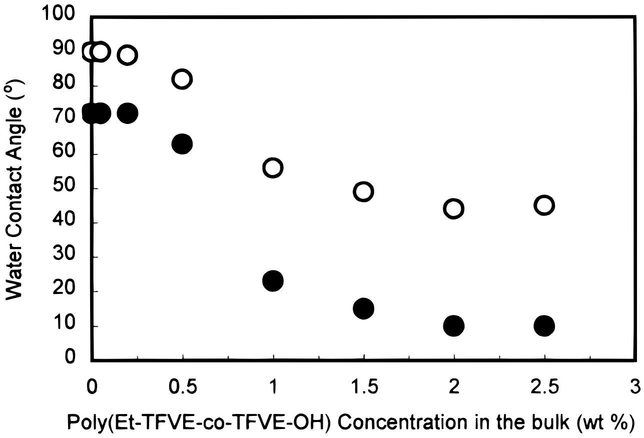


Figure 9. Dynamic (○) advancing and (●) receding water contact angles of PS/poly(Et-TFVE-*co*-TFVE-OH) blend film surfaces decrease with increasing poly(Et-TFVE-*co*-TFVE-OH) bulk content.

reflecting primarily the influence of polymer−solvent interactions on interfacial properties.

Poly(Et-TFVE-*co*-TFVE-OH) Blends. We were interested in studying PS/poly(Et-TFVE-*co*-TFVE-OH) blends because we anticipated that the TFVE-OH component would provide a more hydrophilic surface at the air−polymer interface than that of the Et-TFVE. Blends of PS and poly(Et-TFVE-*co*-TFVE-OH) having 50 mol % TFVE-OH were prepared and cast as films from chloroform as described for PS/poly(Et-TFVE). As shown in Figure 9, both advancing and receding water contact angles decreased with increasing poly(Et-TFVE-*co*-TFVE-OH) bulk content, reaching plateau values at 2% bulk composition. Thus, the contact angles decreased from 89°/72° for pure PS to 45°/10° for blends with surfaces apparently saturated with poly(Et-TFVE-*co*-TFVE-OH).

While the contact angle data demonstrated that surface saturated blends of PS/poly(Et-TFVE-*co*-TFVE-OH) blends were more hydrophilic than those of PS/poly(Et-TFVE) blends (61°/37°), some differences in blend behavior were observed. Specifically, the contact angles changed *in*significantly for poly(Et-TFVE-*co*-TFVE-OH) blends yet significantly for poly(Et-TFVE) blends having up to 0.25 wt % bulk PTFVE. PTFVE behavior can be rationalized by the differences in bulk properties of poly(Et-TFVE-*co*-TFVE-OH) and poly(Et-TFVE), where, for example, poly(Et-TFVE-*co*-TFVE-OH) has a higher T_g of −19 °C than that of poly(Et-TFVE) (−60 °C). The higher T_g is reflective of greater inter- and intramolecular hydrogen-bonding interactions resulting in less mobility of poly(Et-TFVE-*co*-TFVE-OH) chains.

Discussion

Poly(Et-TFVE) comprises a hydrophobic and oleophobic fluorinated backbone and hydrophilic pendant oligoether groups. Considering that PEG, having a solubility parameter of 24 MPa$^{0.5}$, is immiscible with PTFE, having a solubility parameter of 12.7 MPa$^{0.5}$, the fluorinated backbone and oligoether pendant groups of poly(Et-TFVE) are likely segregated in solution or in bulk, thereby resulting in a complex morphology. Given that poly(Et-TFVE) is soluble in many polar organic solvents, such as ethanol, acetone, and chloroform, poly(Et-TFVE) may form an aggregate structure, having an inner poly(Et-TFVE) domain and an outer oligoether corona which interacts with the solvent. The proposed aggregate structure enhances the solubility of the PTFVEs in polar organic solvents, where the fluorocarbon backbone is masked from the polar solvent with which the oligoether groups interact.

AFM images of poly(Et-TFVE) cast from ethanol onto mica indicate the presence of large spherical aggregates. We propose that these aggregates consist of several hundred polymer chains and that they have a poly(Et-TFVE) core and an oligoether corona. It is likely that mica interacts more favorably with the oligoether pendant group than with the fluorocarbon backbone due to the hydrophilic nature of both mica and the oligoether. Minimizing the mica−fluorocarbon interaction is likely thermodynamically more favorable.

The XPS, ToF SIMS, and contact angle data demonstrate that our PTFVEs are surface active in PS blends, and the oligoether groups of the pendant chains enrich the surface relative to the fluorocarbon backbone. We were unable to visualize the surface structure of our blends by AFM because we were unable to distinguish PS from poly(Et-TFVE) at the surface; however, we are investigating this in greater detail in ongoing studies. Notwithstanding, since (1) poly(Et-TFVE) seems to form aggregates in both ethanol and in the bulk, (2) PS is more miscible with PEO than PTFE, and (3) blend surfaces of PS/poly(Et-TFVE) were hydrophilic relative to PS alone, we propose that poly(Et-TFVE) forms an aggregate structure in PS, having a poly(Et-TFVE) core and an oligoether corona. This minimizes the thermodynamically unfavorable interactions between PS and the fluorinated backbone and also rationalizes the increased hydrophilicity with poly(Et-TFVE) content. A model is proposed in Figure 10 to account for both the formation of the spherical aggregates observed by AFM and the surface enrichment of oligoether groups in PS/PTFVE blends. As shown, aggregates with a poly(Et-TFVE) bulk core surrounded by an oligoether corona agglomerate to saturate the surface, enriching the air−polymer interface with oligoether pendant groups. Without the AFM data, we may have proposed an alternate rationale for oligoether groups at the interface: oligoether pendant groups have more mobility than the fluorocarbon backbone, thus presenting themselves at the interface. A similar rationale, i.e., greater mobility of chain ends relative to backbone, was used to explain the predominance of PEG at the air−polymer interface of films prepared from blends of PMMA and PMMA−PEG copolymers.[21]

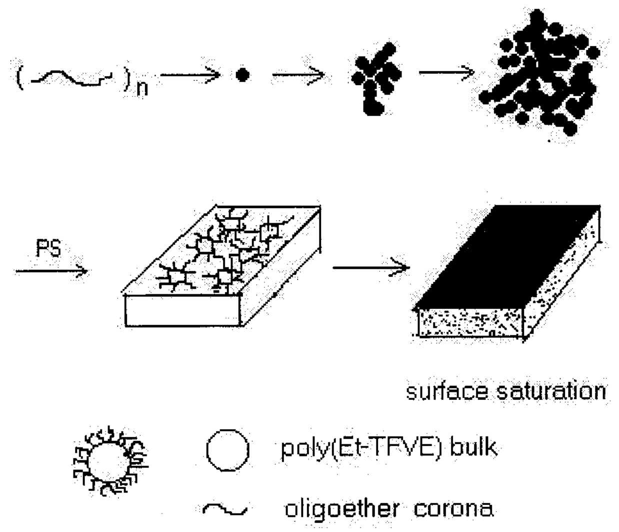


Figure 10. Proposed formation of PTFVE aggregates in solution and the implication of this structure on surface properties of solvent-cast blend films.

The nature of the solvent used to cast films had a profound effect on surface properties.[26,27] When toluene, a favorable solvent for PS, was used to cast a PS/PTFVE blend film, the surface was considerably more hydrophobic than one cast from chloroform for poly(Et-TFVE) contents <1 wt % in the bulk. Similar studies by Thomas and O'Malley demonstrated the importance of the casting solvent.[27] They found that the air−polymer interface of a diblock PS−PEO copolymer film was influenced by the casting solvent: films cast from ethylbenzene, a favorable solvent for PS, had a higher content of PS than those cast from less favorable solvents for PS, such as chloroform and nitromethane. Our results are consistent with these. Since toluene is a better solvent for PS than chloroform, PS dominates the air−polymer interface at low poly(Et-TFVE) bulk content, thereby accounting for the hydrophobic surface observed by dynamic water contact angles. With higher poly(Et-TFVE) content, however, other factors such as surface activity of the fluorocarbon backbone and mobility of the poly(Et-TFVE) dominate, resulting in a poly(Et-TFVE) saturated air−polymer interface.

The nature of the blended PTFVE with PS also affected surface properties. Using poly(Et-TFVE-*co*-TFVE-OH), we measured lower advancing and receding water contact angles for saturated surfaces than those using poly(Et-TFVE). At 0.25 wt % PTFVE, the contact angles measured on blends with poly(Et-TFVE) changed more significantly than those with poly(Et-TFVE-*co*-TFVE-OH). The hydroxyl group present in TFVE-OH accounts for both the increased hydrophilicity of the saturated surface and slower change in hydrophilicity with bulk PTFVE content due to intra- and intermolecular hydrogen-bonding interactions.

Conclusions

Blends of PS/PTFVE are surface-enriched with PTFVE at low bulk concentrations, indicating that PTFVE affects interfacial properties and may be useful as additives for industrial applications. Furthermore, PS/PTFVE film surfaces are hydrophilic and not hydrophobic as one normally expects when a fluorocarbon additive is added to a blend. Having an oligoether-enriched surface may be useful for applications requiring protein repellency, such as blood-contacting materials. In ongoing studies, we are investigating the protein adsorption of blend surfaces relative to homopolymers to determine the suitability of these PTFVEs for biomedical applications.

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