Two-Step Surface Modification of Chemically Resistant Polymers: Blend Formation and Subsequent Chemistry[1]

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ABSTRACT: Supercritical fluid (SCF) carbon dioxide processing has been studied as a new route to polymer surface modification. Three fluoropolymer substrates were studied: poly(tetrafluoroethylene) (PTFE), poly(chlorotrifluoroethylene) (PCTFE) and poly(tetrafluoroethylene-*co*-hexafluoropropylene) (FEP) using a two-step modification procedure. In the first step, blends or semiinterpenetrating networks were prepared by carrying out a free radical polymerization of styrene (or styrene with divinylbenzene or triallyl cyanurate) within the SCF-swollen polymer substrate. The second step involved sulfonating the polystyrene using heterogeneous (solution−solid) sulfonation conditions. Composition of the surfaces was determined by X-ray photoelectron spectroscopy, and wettability was assessed using water contact angle measurements. Depressed advancing and receding contact angles indicate increased wettability of all of the fluoropolymer samples.

Introduction

We recently reported the synthesis of polymer composite materials including polymer blends and metal−polymer nanocomposites using supercritical carbon dioxide (SCF CO_2) as the solvent/processing agent. Polymer blends[2,3] were prepared by the SCF CO_2-assisted infusion of a vinyl monomer into polymer substrates followed by free radical polymerization within the substrate. Metal−polymer nanocomposites[4] were prepared by infusing polymer substrates with organometallic compounds which were subsequently reduced to form metal clusters. These syntheses can be regarded as polymer modification reactions and the most striking result of this research is that reaction-rate-limited chemistry can be carried out within SCF CO_2-swollen semicrystalline polymers at temperatures well below T_m. The shape of the substrate sample is maintained with low levels of nascent polymer, and the basic geometry of highly infused substrates is conserved. The polymer blends that result from the polymerization reactions in semicrystalline substrates have structures that are much different from those of blends prepared using conventional methods. The nascent polymer forms in the amorphous regions of the substrate and precipitates. Large scale phase separation is frustrated by the crystalline phase that is not affected by the modification.

We have had a long-term interest in polymer surface modification and have modified polymer surfaces using techniques including chemical modification,[5,6] polymer adsorption,[7] thermal reconstruction,[8] and layer-by-layer deposition of polyelectrolytes.[9,10] We report here application of the SCF technology described in the earlier reports[2−4] to polymer surface modification. A polymer blend is prepared by polymerization of a monomer within the polymer substrate we wish to surface modify (Figure 1). The nascent polymer then functions as a "reactive handle" which is chemically modified to impart the desired surface chemistry or property. The work described here uses semicrystalline fluoropolymers as substrates, and polystyrene/fluoropolymer blends are prepared by polymerizing styrene within the SCF CO_2-swollen fluoropolymer matrixes. The polystyrene near the surface is subsequently modified by an unexceptional sulfonation reaction.

This approach is more versatile and general than is demonstrated by the results reported here, and we emphasize five advantages of this technique: One, any polymer that is insoluble in SCF CO_2, but is swollen by CO_2 (essentially all polymers), can be used as a substrate. Two, any monomer that is soluble in SCF CO_2 (essentially all monomers) and can be free radically polymerized can be used to prepare the nascent phase of the blend. A monomer can be chosen to form a polymer that will, by itself with no subsequent chemistry, effect the desired surface modification. Three, the polymerization reaction can be carried out either homogeneously (by equilibrating the monomer and initiator throughout the amorphous phase of the substrate prior to initiation) or surface-selectively (by controlling the relative infusion and polymerization rates[3]), and gradient structures that are between these two extremes can be prepared. Four, the bulk composition of the blend can be controlled by external variables (pressure, monomer concentration, reaction time).[2] If the bulk properties of the substrate are desired (which is normally the case for surface modifications) they can be maintained. We have recently demonstrated,[11] however, that some blends prepared by this method exhibit mechanical properties that are improved over those of the substrate. Five, this approach can be easily extended to prepare semiinterpenetrating networks (semi-IPNs) by incorporating cross-linking agents (we demonstrate this below) or IPNs if the substrate is a cross-linked polymer.

We chose three fluoropolymers, poly(tetrafluoroethylene) (PTFE), poly(tetrafluoroethylene-*co*-hexafluoropropylene) (FEP), and poly(chlorotrifluoroethylene) (PCTFE), as substrates to demonstrate this modification strategy because they are, in many respects, the most challenging substrates to surface modify. Significant effort has been extended to modify fluoropolymer surfaces and a reasonably comprehensive review has been published.[12] A range of techniques is available, but in

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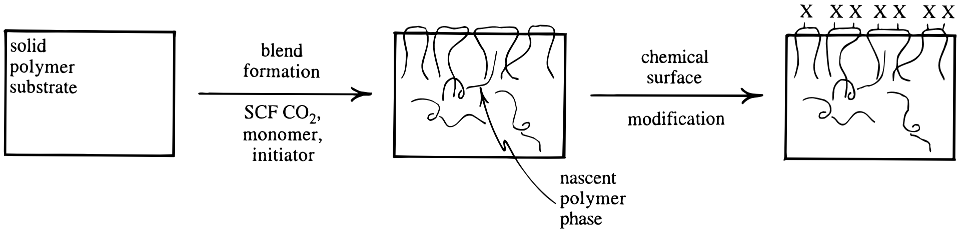

Figure 1. Two-step polymer surface modification.

general they can be described as harsh and not rendering controllable surface chemistries or properties. This choice was also convenient for us because we have determined the phase behavior of SCF CO_2 in PCTFE[3] and FEP[13] and have prepared blends using these polymers as substrates; for this reason most of the experiments described here are with PTFE, which we have not previously studied in any detail. Styrene was chosen as the monomer for several reasons: we have polymerized styrene in a number of substrates (including FEP and PCTFE) using SCF CO_2, its phase behavior in SCF CO_2 has been determined,[14] it is easily cross-linked, and polystyrene can be further chemically modified using a range of chemical reactions. In this paper we describe the preparation of polystyrene blends and semi-IPNs with PTFE, FEP, and PCTFE as well as the surface sulfonation of the nascent polymer "reactive handle".

Experimental Section

General Data. PTFE and PCTFE were obtained from Patriot Plastics in the form of 0.015 and 0.065 in. thick sheets, respectively. FEP was obtained from Du Pont (FEP 4100) in the form of pellets and was compression molded at 250 °C to form 0.052 in. thick sheets. All samples were cleaned by ultrasonication in hexane and then methanol. Carbon dioxide (Coleman grade) was obtained from Merriam Graves and used as received. Styrene and divinylbenzene (both obtained from Aldrich) were distilled from calcium hydride under reduced pressure. *tert*-Butyl perbenzoate, triallyl cyanurate, sulfuric acid, chlorosulfonic acid, and dichloromethane were obtained from Aldrich and used as received. The blend syntheses were performed in 316 stainless steel vessels using high pressure techniques that have previously been described.[2,3] The blends were characterized using X-ray photoelectron spectroscopy (Perkin-Elmer-Physical Electronics 5100 ESCA), attenuated total reflectance infrared spectroscopy (ATR−IR) (Bruker IR 38 Spectrometer with a resolution of 2 cm^{-1} and a 45° KRS-5 internal reflectance element) and contact angle analysis (Ramé−Hart telescopic goniometer). Dynamic advancing (θ_A) and receding (θ_R) angles were determined, respectively, while adding and withdrawing the probe fluid (deionized water) using a Gilmont syringe with a flat-tipped 24 gauge needle. Scanning electron microscopy was performed on JEOL 35 CF SEM and JEOL 6320F SEM instruments and transmission electron microscopy was performed on a JEOL 100 CX 100 kV TEM instrument on samples that were microtomed at −150 °C (PTFE−PS blends) and subsequently stained with ruthenium tetraoxide.

Determination of SC CO_2 Solubility in PTFE. PTFE film samples weighing approximately 0.3 g were sealed individually in reaction vessels which were subsequently purged with CO_2. The vessels were allowed to equilibrate in a temperature bath at 80 °C and were filled with SCF CO_2 at 80 °C and 240 atm. The films were soaked in SCF CO_2 for a prescribed period of time over a 24 h range. At the end of the soaking period, the vessels were vented and the films were transferred to an electronic balance. The desorption of CO_2 as a function of time was recorded, starting approximately 25 s after the vessels were vented.[15,16]

Synthesis of Blends. PTFE film samples (~0.3 g) were sealed individually in high-pressure reaction vessels. To each vessel were added 2 mL of styrene (distilled from calcium hydride) and 10 μL of *tert*-butyl perbenzoate (0.34 mol % initiator) via syringe. The vessels were flushed with CO_2, placed in a circulating temperature bath at 80 °C for ~5 min, and filled with SCF CO_2 at 80 °C, which was added to the vessel in stages until the desired pressure was reached. The reaction was allowed to proceed in three stages: (1) an initial soaking period (at 80 °C and at the desired pressure) during which the monomer and initiator diffuse into the solid polymer, (2) a reaction period at 120 or 100 °C, and (3) a postreaction period under nitrogen (120 °C, 1300 psi of N_2) to complete the polymerization process. The soaking and postreaction periods were held constant at 4 h and the reaction time period was varied from 1 to 10 h (for reactions at 120 °C) to determine its effect on the polystyrene mass uptake. The mass uptake of polystyrene in the blends was determined gravimetrically. Parameters such as the styrene concentration, soaking pressure, initiator concentration, and the duration of the reaction time were varied to observe their effect on the final polystyrene mass uptake in the blends. Several experiments were performed using a reaction time of 48 h at 100 °C and no postreaction period. Blends of PCTFE and polystyrene were synthesized according to the same procedure described for PTFE using a reaction temperature of 120 °C. FEP−PS blends were synthesized using a soaking period of 5 h at 80 °C and 240 atm, a reaction period of 4 h at 120 °C, and a postreaction period of 4 h under nitrogen (120 °C, 1300 psi of N_2).

Synthesis of Semi-IPNs. Semi-IPNs were prepared using procedures analogous to those for the blends and adding divinylbenzene (DVB) (10% v/v based on styrene) or triallyl cyanurate[17] (TAC) (10% w/w based on styrene) to the monomer/initiator solution.

Sulfonation of Blends. Sulfonation was carried out by submerging composite samples in a solution of sulfuric acid (70 vol %) and chlorosulfonic acid. The blends were rinsed in dichloromethane, hydrolyzed in deionized water for 48 h, and air-dried.[17,18]

Results and Discussion

Phase Behavior and Absorption Kinetics. The solubility of CO_2 in PTFE at 80 °C, 240 atm was determined using a method similar to that described by Berens.[15,16] PTFE samples were exposed to CO_2 in pressure vessels under these conditions for various periods of time (1−24 h), the vessels were depressurized, and the isolated sample mass was measured as a function of time. Figure 2 shows a representative desorption curve (for a PTFE sample exposed to CO_2 for 3 h). The observed dependence of mass on the square root of time is nonlinear, which implies that the diffusion is non-Fickian in nature—this is not the case for either FEP or PCTFE (or several other substrates that we have studied) which show linear desorption behavior.[3,13] We suspect that the initial rapid desorption is due to CO_2 that is trapped in the samples rather than dissolved and that the PTFE samples have some degree of porosity due to the processing conditions. Desorption curves for samples exposed to CO_2 under

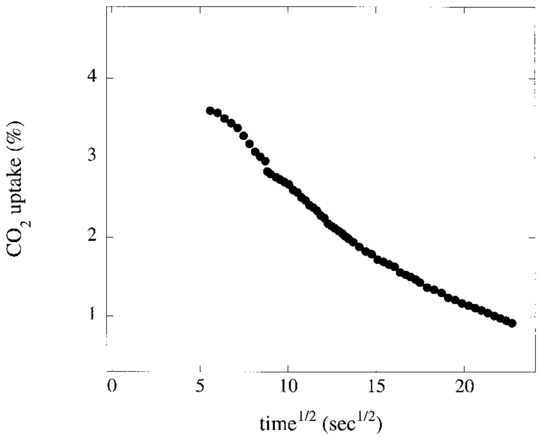

Figure 2. Representative CO_2 desorption data used to calculate SCF solubility in PTFE (80 °C, 240 atm, 3 h).

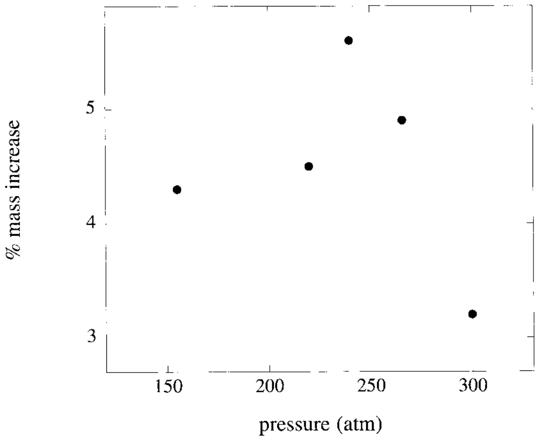

Figure 3. Polystyrene uptake as a function of soak/reaction pressure (80 °C, 4 h reaction, ~47 wt % styrene).

these conditions for times greater than 3 h were indistinguishable from the one shown in Figure 2, indicating that saturation is reached within this time period. Samples exposed to SCF CO_2 for 1 or 2 h were not yet saturated. The nonlinearity of the data makes it difficult to accurately determine the equilibrium CO_2 solubility, and we expect that extrapolating the curved data to zero time would bias the estimate high (due to trapped CO_2). Linear extrapolation of the later mass loss data (that is due primarily to diffusion) to zero desorption time gives an estimate of ~3.5 wt %.

We have previously determined[3,13] that the equilibrium solubilities of CO_2 in PCTFE and FEP under identical conditions are ~5.3% and ~4.5%, respectively and that these conditions are reached for the sample geometries used here in ~4 h for PCTFE and ~30 min for FEP.

PCTFE and FEP Blends and Semi-IPN Syntheses. PCTFE−polystyrene and FEP−polystyrene blends were prepared using conditions under which the polystyrene content can be conveniently controlled with reaction time.[3,13] PCTFE−polystyrene blends that contained ~35 wt % polystyrene and FEP−polystyrene blends that contained ~10 wt % polystyrene were prepared using the conditions detailed in the Experimental Section using reaction times of 4 h at 120 °C. Semi-IPN versions of these samples were also prepared by adding ~10% (v/v) divinylbenzene or ~10% (w/w) triallyl cyanurate to the monomer/initiator solution. The addition of cross-linking agents did not greatly affect the mass uptake that occurred as the result of polymerization. The semi-IPNs also contained ~35 and ~10 wt % nascent polymer for PCTFE and FEP, respectively. We have reported[3] structural information about PCTFE−polystyrene blends and will report[13] the characterization of FEP−polystyrene blends. Both of these samples contain polystyrene throughout their thickness in the amorphous regions of the fluoropolymers as evidenced by transmission electron microscopy of microtomed samples. Differential scanning calorimetry indicates that the crystalline regions of the substrates are unaffected by the polymerization.

PTFE−Polystyrene Blend and Semi-IPN Syntheses and Bulk Characterization. The reaction conditions used for the synthesis of PTFE-polystyrene blends and semi-IPNs were chosen to satisfy several criteria. A soaking time period of 4 h was chosen since the absorption kinetics indicates that equilibrium is reached within ~3 h. The soaking (80 °C) and reaction temperatures (120 or 100 °C), were chosen due to the thermal behavior of the initiator. *tert*-Butyl perbenzoate decomposes very slowly at 80 °C (the half-life is hundreds of hours) and has half-lives of ~1.8 and ~18 h[19] at 120 and 100 °C, respectively. All reactions were run under conditions where styrene and CO_2 exist as a single phase. The effects of the variables of styrene concentration, soak and reaction pressure, reaction time, and reaction temperature were assessed individually, and each is discussed briefly.

With the temperature (80 °C for the soak period; 120 °C for the reaction period), reaction time (4 h), pressure (240 atm at 80 °C), and initiator concentration constant, three experiments were conducted with the styrene concentration set at 18.5, 47, and 80 wt %. The dependence of the polystyrene mass uptake was essentially linear with respect to styrene concentration; the three increasing concentrations rendered blends containing 2.8, 5.4, and 8.6 wt % polystyrene. Increasing the styrene concentration increases the rate at which styrene diffuses (repartitions) into the PTFE during the polymerization reaction.

The soaking period pressure was varied from 155 to 300 atm (the reaction pressures and SCF densities vary as well), keeping the styrene molar concentration (47 wt % at 240 atm) and other variables constant at the same values for the experiments that measured the effect of styrene concentration. Figure 3 shows a plot of mass uptake vs soaking period pressure. A maximum in polystyrene uptake is observed at ~240 atm. At lower pressures, we expect that the CO_2 solution does not swell the PTFE as well and/or that the kinetics of infusion are slower. At higher pressures, the fluid phase is a better solvent and styrene partitions more preferentially in the fluid phase. At values of pressure in between, these competing effects balance and a maximum in the polystyrene mass uptake is observed.

The reaction time period was varied from 1 to 10 h keeping the other variables constant at the values just discussed (47 wt % styrene, 240 atm soak pressure). Figure 4 shows a plot of mass uptake vs reaction time, indicating that the polystyrene content increased from 2.8 to 5.3 wt % when the reaction time period was increased from 1 to 4 h but did not change significantly when further increased. The half-life of the initiator (*tert*-butyl perbenzoate) at 120 °C is ~1.8 h; therefore, approximately 20% of the initiator should remain at the end of a 4 h reaction time period. We infer that the initiator does not repartition into the CO_2-swollen PTFE

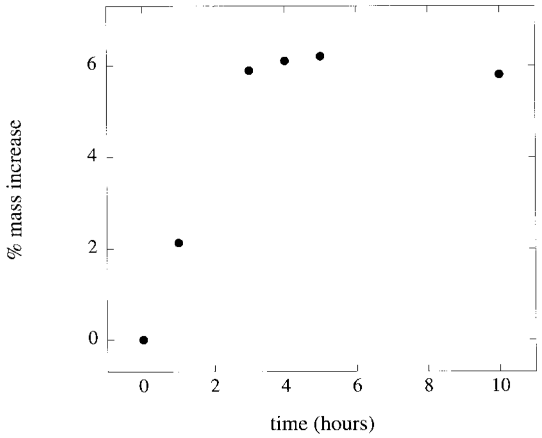

Figure 4. Polystyrene uptake as a function of reaction time (80 °C, 240 atm, ~47 wt % styrene).

as fast as styrene does (as indicated by the styrene concentration experiments) and that further polymerization takes place preferentially in the fluid phase.

PTFE−PS composites were also prepared using a reaction temperature of 100 °C (at which temperature the half-life of the initiator is approximately 18 h) and the results are consistent with the inference made above. A sample reacted for 48 h (approximately the same concentration of initiator should be present after this time as in the reaction at 120 °C for 4 h) had a mass uptake of 12 wt %. The styrene polymerization proceeds in a more controlled manner at the lower temperature, and with its longer half-life, the initiator has time to repartition into the solid phase. As the objective of this work was surface modification, we did not further pursue control of the PTFE−polystyrene blend composition. We anticipate, by analogy with other substrates, that at 100 °C or lower temperatures, reaction time can be used to control blend composition over a wide range. Semi-IPNs were prepared by adding ~10% (v/v) divinylbenzene or ~10% (w/w) triallyl cyanurate to the monomer/initiator solution and using conditions that gave blends of ~5 wt % polystyrene. The semi-IPNs prepared with divinylbenzene and triallyl cyanurate contained ~3 and ~7 wt % (cross-linked) polystyrene, respectively.

The morphology of the PTFE−polystyrene blends was investigated by transmission electron microscopy of a cryomicrotomed (−150 °C) cross section of a sample containing 9.5 wt % polystyrene that was stained with ruthenium tetraoxide. The blend is qualitatively similar to other blends of this type[3,11,13] with a continuous discrete phase of polystyrene throughout the entire cross section of the sample.

Surface Characterization of Blends and Semi-IPNs. The PCTFE− and FEP−polystyrene blends and semi-IPNs described above and certain samples of PTFE−polystyrene blends and semi-IPNs were selected for surface analysis and sulfonation (described below). The surfaces were characterized by SEM, ATR IR, XPS, and water contact angle analysis. Table 1 summarizes the samples studied along with XPS and water contact angle data; values for the individual polymers are given as well for comparison. The XPS data (fluorine:carbon atomic ratios) were determined using a 75° takeoff angle (between the plane of the surface and the entrance lens of the detector optics) and represent the outermost ~40 Å of the samples.[20] Spectra were also recorded using a 15° takeoff angle (that indicates the composition of the outermost ~10 Å) and the data show little or no takeoff angle dependence, indicating that the outer 40 Å of the samples is compositionally homogeneous. We note that oxygen (generally 2−5 at. %) is also present and in higher concentration in the 15° takeoff angle data. We have not determined the source of this oxygen or whether polystyrene prepared in SCF CO_2 contains more surface oxygen than that prepared in conventional solvents. Polystyrene photooxidizes quite easily,[21,22] and (in our hands) it is difficult to prepare oxygen-free (as assessed by XPS) samples. We note also that the oxygen content is not great enough to affect the contact angle data. The values in the column (Table 1) labeled %PS were determined from the 75° takeoff angle F:C ratios and represent the mole percent polystyrene repeat units (C_8H_8 with the remainder being C_2F_4 or C_2F_3Cl) present in the outermost 40 Å. The volume percent of polystyrene is higher than the values given due to the density differences between polystyrene (~1 g/cm^3) and the fluoropolymers (~2 g/cm^3).

Table 1. Contact Angle and XPS (Atomic Composition) Data for Composite Surfaces

sample	θ_A, deg	θ_R, deg	F:C	%PS
PTFE−PS	91	63	1.13	16
PTFE−PS^{dvb}	92	86	1.10	17
PTFE−PS^{tac}	83	75	0.31	58
PTFE−PS^{100}	93	81	0.03	94
PCTFE−PS	92	73	0.11	81
PCTFE−PS^{dvb}	96	87	0.09	80
PCTFE−PS^{tac}	90	82	0.01	97
FEP−PS	108	92	1.57	6
FEP−PS^{tac}	92	82	1.20	14
FEP	105	92	2.00	0
PCTFE	97	61	1.50	0
PTFE	105	83	2.00	0
polystyrene	90	73	0.00	100

Table 1 has four PTFE−PS composite entries: The PTFE−PS blend was prepared using a 4 h reaction time at 120 °C and has a bulk polystyrene content of ~5 wt %. PTFE−PS^{dvb} and PTFE−PS^{tac} are semi-IPNs that were prepared identically except that divinylbenzene and triallyl cyanurate were added to the monomer/initiator solutions; they have similar (cross-linked) polystyrene bulk compositions (~3 and ~7 wt %, respectively). PTFE−PS^{100} was prepared with a 48 h reaction time at 100 °C and contains ~11 wt % polystyrene. The surface polystyrene content varies significantly between these samples, and we have no defensible explanation for the differences but note that the values are reproducible to ±5%. The water contact angle values of each of the four surfaces have changed from those of the PTFE substrate, becoming more polystyrene-like. The low advancing contact angle for PTFE−PS^{tac} is likely due to the presence of the more polar cyanurate functionality at the surface (nitrogen is observed by XPS). The low receding contact angle for PTFE−PS (and the resulting high contact angle hysteresis) is due to sample roughness/topography and/or chemical heterogeneity. SEM indicates that the PTFE−PS surface contains phase separated, circular polystyrene domains that are ~0.05 to ~0.7 μm in diameter (Figure 5a). This (or any other) topographical feature was not observed in any of the other blends or semi-IPN samples studied. Similar structures have been reported in sulfonated FEP-*g*-PS membranes.[23] This polystyrene present on the surface dissolves upon extraction with THF and the circular features are replaced with pits in the PTFE substrate (Figure 5b).

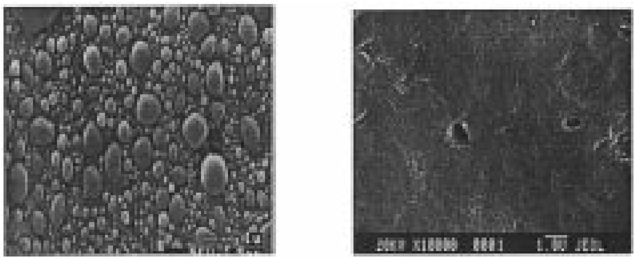

Figure 5. SEM micrographs: (a) PTFE−PS; and (b) PTFE−PS refluxed in THF for 30 min.

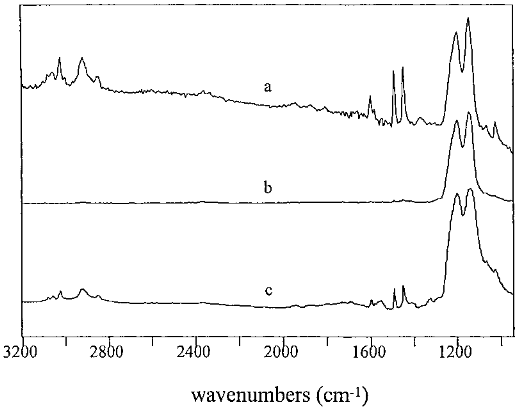

Figure 6. ATR−IR spectra: (a) PTFE−PS; (b) PTFE−PS refluxed in THF for 30 min, (c) PTFE−PS^{tac} (semi-IPN) refluxed in THF for 30 min.

The PTFE−PS composites were also characterized by ATR IR spectroscopy. Strong absorbances assigned to polystyrene are present in all spectra indicating that polystyrene is present in significant concentration throughout the outer few microns. The bands in the spectrum of the PTFE−PS blend weaken in intensity (almost disappear) after the blend is submerged in refluxing THF for 30 min (Figure 6a,b). This indicates that the polystyrene is not grafted to the PTFE substrate. We note that gravimetric analysis indicates that a significant amount of polystyrene remains in the bulk (at depths below which ATR IR samples). In contrast, the infrared bands due to polystyrene do not change appreciably in semi-IPNs that have been refluxed in THF for 30 min (Figure 6c). GPC analysis of extracted polystyrene indicates high molecular weight polymer (M_n = 46K; M_w = 268K) and this is evidence that the polymer was formed in the substrate phase and not in the fluid phase.[24]

The data in Table 1 for FEP and PCTFE composites also indicate the presence of polystyrene in the outermost 40 Å of samples. The PCTFE−PS, PCTFE−PS^{dvb}, and PCTFE−PS^{tac} samples have high surface concentrations of polystyrene (80−97% and bulk compositions of ~35%), while the FEP−PS and FEP−PS^{tac} samples have quite low surface polystyrene content (6 and 14% and bulk compositions of ~10%). Portions of the linear polystyrene extracted from samples of PCTFE−PS and FEP−PS made similarly (not these samples) also are of high molecular weight (M_w > 200K). We note that the contact angle data for FEP−PS show no evidence of the presence of polystyrene (and the XPS data show little), and we point out that we did not attempt to control the surface polystyrene content in any of these composite samples. The fact that significant amounts of polystyrene can be extracted from samples indicates that solutions can access subsurface polystyrene and suggests that polystyrene that is not (initially) in the outermost 40 Å may be available for reaction.

Table 2. XPS (Atomic Composition) and Contact Angle Data for Sulfonated Composite Surfaces

sample	% C	% F	% O	% S	%N	θ_A, deg	θ_R, deg
PTFE−PS−SO_3^-	45.6	46.4	6.3	1.7		73	68
PTFE−PS^{dvb}-SO_3^-	45.4	45.1	7.2	1.7		68−90	45−70
PTFE−PS^{tac}-SO_3^-	46.2	47.9	4.4	1.0	0.4	55−75	40−62
PTFE−PS^{100}-SO_3^-	63.8	20.2	12.8	3.2		47	35
PCTFE−PS−SO_3^-	81.1	1.2	15.9	1.1		49−70	30−53
PCTFE−PS^{dvb}-SO_3^-	68.2	2.0	23.5	5.8		10	5
PCTFE−PS^{tac}-SO_3^-	68.3	2.4	22.9	3.5	2.4	6	0
FEP−PS−SO_3^-	55.3	33.8	8.4	2.3		34	25
FEP−PS^{tac}-SO_3^-	53.2	41.0	4.0	1.1	0.53	34	24

Sulfonation of Blends and Semi-IPNs. The conditions used for the sulfonating the (polystyrene present in the) composite samples were optimized by modifying a reported procedure[17,18] to maximize the sulfur content of the samples (assessed by XPS) and minimize the water contact angles, while not degrading (and roughening) the samples. The temperature and the chlorosulfonic acid:sulfuric acid ratio were varied, and room temperature and 30 vol % chlorosulfonic acid in sulfuric acid were chosen, respectively. Sulfonations carried out at lower concentrations were less efficient, and composite samples sulfonated using higher chlorosulfonic acid concentration exhibited nonuniform sulfonated surfaces. We emphasize that this modification is not a simple heterogeneous solution−solid reaction but is much more complex. In the optimization of conditions, we have balanced the extent of the sulfonation reaction against the degradation that occurs under these conditions. The sample is first exposed to the acid mixture, then to dichloromethane, and finally to water. We have not examined the extent to which these solutions degrade polymer chains (retro-Friedel−Crafts chemistry leading to dearylation, carbocation rearrangements and fragmentation reactions are plausible side reactions in acid), nor have we examined the extent to which the solutions swell and/or dissolve the sulfonated product (dichloromethane dissolves polystyrene and water dissolves polystyrene sulfonate).

Atomic concentration data obtained from XPS measurements (75° takeoff angle) and water contact angle data for the sulfonated composite samples are given in Table 2. The incorporation of sulfur and the decreases in contact angles indicate that sulfonation occurs in all cases. The XPS data indicate (and can be used to calculate) both the composition of the surface (relative concentrations of fluoropolymer and polystyrene repeat units) and the yield of the sulfonation reaction (percentage of polystyrene units that contain sulfonate groups). The oxygen:sulfur ratio should in principle be 3:1, but in most cases it is ~4:1. This is consistent with other samples of poly(styrene sulfonate) that we have studied,[10] and this may be due to adsorbed water or to adventitious oxidation. The first three entries in the table are for composites of PTFE prepared at 120 °C, and the F:C ratio for each of these sulfonated samples is ~1.0 indicating that the outermost ~40 Å of the samples contain ~20 mol % polystyrene and 80 mol % PTFE. The ratio of the sulfur atomic concentration to the carbon concentration that is due to polystyrene indicates that the sulfonation yield is not high: ~36% for PTFE−PS^{tac}−SO_3^- and ~60% for PTFE−PS−SO_3^- and PTFE−PS^{dvb}−SO_3^-. These calculations indicate that the total concentration of sulfonate groups on the surface is not high. The contact angles also reflect a low level of sulfonation: although depressed from those of their precursors, none of the data indicate very hydrophilic surfaces. The data presented in Table 2 as ranges of contact angle values are for samples in which the variability was greater than ±5°. The wide ranges of values observed for PTFE$-$PS$^{dvb}-SO_3^-$ and PTFE$-$PS$^{tac}-SO_3^-$ indicate that the surfaces are functionalized in a "patchy" manner. The sample prepared at 100 °C (PTFE$-$PS$^{100}-SO_3^-$) is uniformly hydrophilic and much more densely sulfonated. The C:F ratio is 3.16 and indicates that the surface region is composed of 57% polystyrene repeat units. The sulfur atomic concentration indicates that 48% of the polystyrene repeat units have been sulfonated. We point out that the fluorine content in PTFE$-$PS$^{100}-SO_3^-$ is significantly higher than in its precursor, PTFE$-$PS^{100}, indicating dissolution of polystyrene or sulfonated polystyrene during the sulfonation procedure or significant reconstruction of the composite surface.

The blends prepared using PCTFE as the substrate yielded patchy surfaces that were hydrophilic in some regions and not very hydrophilic in others. This is similar to what was observed for the PTFE composites prepared at 120 °C, but for a different reason. The surface contains very little fluorine, indicating that it is essentially pure polystyrene and not a mosaic-like structure of fluoropolymer and polystyrene, but only ~10% of the styrene repeat units are sulfonated. There is no reason to expect that the sulfonation reaction is any less efficient in this case; thus, we suspect that significant dissolution of sulfonated polystyrene in the aqueous workup occurs, resulting in a lightly sulfonated surface. The semi-IPNs, PCTFE$-$PS^{dvb} and PCTFE$-$PS^{tac} are much better substrates for the sulfonation reaction, and the sulfonated products are extremely wettable, exhibiting water contact angles of less than 10°. These surfaces also contain very little fluoropolymer, but the polystyrene is cross-linked and does not dissolve (without prior degradation reactions) in water after sulfonation. From the sulfur atomic concentrations in PCTFE$-$PS$^{dvb}-SO_3^-$ and PCTFE$-$PS$^{tac}-SO_3^-$, yields of 69% and 42% for the sulfonation reactions are calculated.

Both FEP$-$PS and FEP$-$PS^{tac} behave well as substrates for sulfonation, becoming quite hydrophilic: $\theta_A/\theta_R = 34°/25°$ for FEP$-$PS$-SO_3^-$ and $\theta_A/\theta_R = 34°/24°$ for FEP$-$PS$^{tac}-SO_3^-$. Significant concentrations of fluorine exist in both these surfaces, and this indicates that an extensive modification of this type (at least for some substrates) is not required to significantly change surface properties. The surface of FEP$-$PS$-SO_3^-$ contains 36 mol % polystyrene repeat units (and 64 mol % FEP units) and the sulfonation proceeded in 48% yield. FEP$-$PS^{tac}-SO_3^- contains 29 mol % polystyrene, and 27% of the styrene repeat units are sulfonated.

Table 2 also contains nitrogen atomic composition data for sulfonated composites containing triallyl cyanurate. PTFE$-$PS$^{tac}-SO_3^-$ contains 0.41% N, FEP$-$PS$^{tac}-SO_3^-$ contains 0.53% N and PCTFE$-$PS$^{tac}-SO_3^-$ contains 2.4% N. The theoretical value (based on monomer ratios) is approximately 1%. The discrepancies could be due to several factors: differences in partitioning of triallyl cyanurate and styrene between SC CO_2 and the substrates, the relative rates of polymerization, and surface reconstruction of the products.

The concentration of sulfonate ions in these samples was also assessed by radioisotope labeling[25] with $^{45}Ca^{2+}$. In all cases the concentrations measured ($10^{-8} - 10^{-9}$ mol of $-SO_3^-/cm^2$) were far in excess of that expected for a densely sulfonated surface layer, indicating that the sulfonation proceeds relatively deeply in the samples.

Summary

Polymer blends and semi-IPNs can be prepared by polymerizing styrene (with or without a cross-linking agent) within SCF$-CO_2$-swollen fluoropolymer substrates. We demonstrated in other research[3,13] that polystyrene is present throughout the bulk of blends prepared using PCTFE and FEP as substrates and here, that polystyrene is present throughout blends with PTFE and also that polystyrene is present at the surfaces of blends and semi-IPNs of each of the three substrates. The polystyrene can serve as a "reactive handle" that can be used to introduce sulfonate groups to the fluoropolymer substrate. The "surface yields" of both the polystyrene incorporation and sulfonation reactions were calculated from XPS data. It was demonstrated by water contact angle analysis that wettable surfaces of all three fluoropolymer substrates can be prepared using this two-step modification procedure. We have not assessed the extent to which incorporation of polystyrene within the fluoropolymer substrates induces changes in bulk mechanical properties as surface modification was the focus of this work. In another study,[11] it was shown that strength and modulus of polyethylene substrates are enhanced upon incorporation of polystyrene.

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