Synthesis, Characterization, and Expansion of Poly(tetrafluoroethylene-*co*-hexafluoropropylene)/Polystyrene Blends Processed in Supercritical Carbon Dioxide

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ABSTRACT: Poly(tetrafluoroethylene-*co*-hexafluoropropylene) (FEP)/polystyrene blends were prepared by the heterogeneous free-radical polymerization of styrene in supercritical (SC) CO_2-swollen FEP substrates. Volume incorporations of up to 50% polystyrene were achieved, and the composition and phase morphology of the blends were controlled by varying the styrene monomer concentration and reaction time. The crystallinity and glass transition temperature of the FEP substrate are unaffected by the addition of the polystyrene component, indicating that polymerization occurs exclusively in the amorphous phase and that the polymers are immiscible. The molecular weight of the polystyrene formed within the FEP substrate is significantly higher than that which forms in the SC CO_2 phase outside of the substrate. Attempts were made to prepare composite foams by saturation of the blends with SC CO_2 and subsequent rapid depressurization. At lower temperatures (conditions under which polystyrene foams) the crystalline domains of FEP prevent expansion. At higher temperatures, in addition to expansion, large-scale phase segregation of the blends occurs.

Introduction

We have recently reported a method for producing polymer composite materials that involves the supercritical fluid (SCF)-assisted infusion of reagents into and subsequent reaction within organic polymer substrates.[1−6] An example of this that we have focused on is the infusion of vinyl monomer and free-radical initiator as a supercritical (SC) CO_2 solution into a range of semicrystalline and amorphous polymers and subsequent thermally induced polymerization. Styrene can be polymerized within semicrystalline polymer substrates to create polymer blends with kinetically trapped morphologies.[3,4] The SC solution swells the amorphous phase in which a reaction rate-limited polymerization occurs. The nascent polystyrene is neither soluble in the SC solution nor miscible with the amorphous substrate; thus it precipitates, forming a discrete phase within the amorphous network. The polymerization drives reequilibration of styrene from the fluid phase into the amorphous phase of the substrate, equilibration of styrene into the nascent polystyrene phase, and further polymerization. Blends with polystyrene content in great excess over the equilibrium concentration of styrene in the substrate can be prepared. The crystalline phase of the substrate frustrates any large-scale phase segregation, and co-continuous blends result. Using a technique introduced by Beckman,[7,8] we have also recently studied the supercritical (SC) CO_2 foaming of polystyrene, demonstrating control over the cell structure and foam density.[9]

The properties of SCFs are well-known, and reviews are available.[10] Advantages of using SCFs as solvents and foaming agents include their adjustable solvent strength,[11−13] ability to plasticize many polymers,[14−18] and their ability to enhance diffusion rates.[12,13] Since CO_2 is a gas at ambient conditions, the solvent rapidly dissipates upon release of pressure. A pressure quench from SCF conditions at constant temperature ensures that no vapor/liquid boundary is encountered which could damage the cellular structure of a foam. Additionally, CO_2 presents an environmental advantage over conventional organic or chlorofluorocarbon foaming agents or solvents.

We have recently combined the foaming and blend synthesis procedures used in our laboratory to create composite microcellular foams using SC CO_2 both as the solvent for chemical modification reactions and as the foaming agent. Composite foams can be created either directly during the synthesis procedure or by foaming the dense composite in a subsequent processing step. It is observed that composite foams can be produced when synthesis temperatures exceed the crystalline melting point of the polymer substrate (which may or may not be depressed by the CO_2/styrene solutions).[19]

This has been observed for two substrate materials: high-density polyethylene (HDPE) and poly(4-methyl-1-pentene) (PMP). HDPE/polystyrene composite foams of various compositions are produced when the reaction temperature (140 °C) is greater than the crystalline melting point of HDPE (137 °C). Closed-cell foams that completely fill the reaction vessel are produced. Foaming is observed (in a view cell) to occur during the depressurization step following the reaction period. Expanded foam composites are also observed with PMP/polystyrene. In this case the foams are created at temperatures approximately 100 °C below the melting point of PMP. The melting point of the PMP is depressed in the presence of the monomer/CO_2 solution. We are currently studying the formation and structure of these composite foams in more detail.

We report here the investigation of poly(tetrafluoroethylene-*co*-hexafluoropropylene) (FEP) as a substrate for blends and composite foams. This substrate was chosen for several reasons: it is not easily modified by conventional means and blends may function as useful modified materials, fluoropolymers have been shown to be compatible with CO_2, and the elemental contrast

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between FEP and polystyrene should aid in analysis. Mertdogan et al. have shown that FEP copolymers can be dissolved in CO_2, although at pressures in excess of 14 000 psi.[20] The conditions we use for foaming and preparing blends, however, are well below (<8000 psi) the conditions required for dissolving FEP. Our objectives were to (1) determine the phase behavior of CO_2 and styrene in FEP, (2) prepare blends and determine conditions that can be used to control composition, (3) characterize the blends in terms of their morphology, thermal stability, and the molecular weight of the nascent polystyrene phase, and (4) assess their suitability as foam precursors.

Fluoropolymer foams are attractive due to their outstanding physical, chemical, and electrical properties, making them suitable for use in corrosive and high-temperature environments. Commercially, melt extrudable fluoropolymers are expanded using blowing agents such as CO_2, Freons, and nitrogen in combination with nucleating agents such as talc, silicon dioxide, zinc stearate, aluminum oxide, or clay.[21] FEP is foamed commercially by continuous melt extrusion using difluorochloromethane as a blowing agent. Void fractions are controlled by extruder pressures, which, in turn, control the amount of gas dissolved in the polymer. The primary end use for closed-cell FEP foams is as a low dielectric constant insulator for electronic, plenum, and aerospace applications.

Experimental Section

Materials. Styrene was purchased from Aldrich and refluxed over and distilled from calcium hydride. Ethylbenzene and *tert*-butyl perbenzoate were obtained from Aldrich and used as received. Carbon dioxide (Coleman Grade, 99.99%) was purchased from Merriam Graves and passed through columns containing alumina and a copper catalyst (Engelhard Q-5) to remove water and oxygen.

The FEP, donated by DuPont, was reported to contain tetrafluoroethylene and hexafluoropropylene comonomer units in the ratio of 87/13. Crystallinity was measured by DSC to be in the range 24−28%, using a value for heat of fusion of 22.2 cal/g.[22] A melting transition of 241 °C was measured by DSC, and a T_g of 85 °C was measured by DMTA. The density was measured and found to be 2.1 g/cm^3.

General Procedures. Densities were calculated by measuring the volume of water displaced by a sample and dividing this value into its mass. Differential scanning calorimetry (DSC) measurements were conducted on a DuPont 2000 differential scanning calorimeter under flowing, dry nitrogen at a heating rate of 10 °C/min. Dynamic mechanical thermal analysis (DMTA) was performed on a Polymer Laboratories Mark I dynamic mechanical thermal analyzer at a frequency of 1 Hz and a heating rate of 2 °C/min. Molecular weight determinations were made by gel permeation chromatography (GPC) on a Polymer Laboratories gel permeation chromatograph with a UV detector and THF as the mobile phase. Scanning electron microscopy (SEM) was performed on a JEOL 35 CF scanning electron microscope. Backscattered electron images were obtained on a JEOL 6320F field emission scanning electron microscope (FESEM). Samples for FESEM were prepared by cryomicrotoming the sample with a glass knife at −120 °C to create a smooth, featureless surface. The sample was then stained with ruthenium tetraoxide, which reacts with the polystyrene phase in the blend.

Blend Synthesis. Reactions were run in 316 stainless steel reaction vessels fabricated from hexagonal pipe which was threaded to accept $^1/_4$ in. NPT fittings. One end of the vessel was plugged and the other attached to a $^1/_8$ in. high-pressure valve (High Pressure Equipment). The reaction vessels were filled with CO_2 from a high-pressure manifold described elsewhere.[1] A preweighed FEP substrate is placed in the reaction vessel along with the styrene monomer and initiator, and the vessel is purged with CO_2. The vessel is then weighed, preheated to the fill temperature, and filled with SC CO_2. It is then allowed to soak at a temperature at which the half-life of the initiator is on the order of hundreds of hours, to allow the reactants and CO_2 to diffuse into the substrate. After this soak period, the temperature is raised to initiate the polymerization. After the reaction period, the CO_2 and any excess monomer in the fluid are vented from the vessel. This is followed by a postreaction period under nitrogen to allow any residual monomer to polymerize or diffuse from the substrate.

In all experiments the soak conditions were kept unchanged at 80 °C, 3530 psi, and 5 h. The postreaction conditions were also kept constant at 100 °C and 6 h. The initiator used was *tert*-butyl perbenzoate at a concentration of 0.3 mol % relative to styrene. Reaction temperatures of both 100 and 120 °C were examined, but due to the low equilibrium solubility of the monomer in the FEP substrate, the 100 °C temperature was found to yield higher polystyrene uptakes. This can be attributed to a slower reaction rate (at the lower temperature) which allows the repartitioning of the reactants into the substrate during the reaction period. In all the experiments described here, a 100 °C reaction temperature was used. The half-life of the initiator in benzene at 100 °C is reported to be 18 h.[23]

Foaming Procedure. Foaming experiments were performed in the same vessels described above. The samples to be foamed were soaked in SC CO_2 until saturated and then rapidly depressurized to atmospheric pressure. The external temperature of the vessel was maintained constant during the depressurization step. After decompression, the vessel was removed from the temperature bath and allowed to cool, and the specimen was removed.

Results and Discussion

Absorption/Desorption Kinetics. To determine the equilibrium solubility, diffusivity, and equilibration kinetics for CO_2 in FEP at a given set of processing conditions (80 °C, 3530 psi), the absorption/desorption kinetics were measured according to the method described by Berens.[12,13] A preweighed $^1/_{16}$ in. thick compression molded FEP sample was placed in the reaction vessel, which was then purged with CO_2, filled to the desired sorption pressure and temperature, and left to soak for a prescribed period of time. After rapid venting of the vessel, the sample was removed and immediately transferred to a balance interfaced with a computer to record mass loss as a function of time. From these measurements, percent mass uptake was calculated, and the results were plotted versus the square root of desorption time. This procedure yielded linear plots indicative of Fickian diffusion kinetics, an example of which is shown in Figure 1. Linear extrapolation to zero desorption time gives the uptake of CO_2 at the end of the sorption period. A series of sorption times were studied in order to determine when equilibrium is reached. We found that the equilibrium mass uptake of 4.4% CO_2 was attained in less than 30 min under these conditions. The FEP samples remained clear and unfoamed during the absorption experiments.

In addition to the uptake of CO_2 by the substrate, we also determined the equilibrium uptake of styrene by FEP. To determine this value, ethylbenzene, a nonpolymerizing model for styrene, was used. To measure the amount absorbed by the substrate in CO_2, 30 wt % of ethylbenzene (based on CO_2) was added to the vessel along with CO_2 at 80 °C and 3530 psi. Samples were soaked for various lengths of time and then vented. The CO_2 was allowed to desorb from the sample prior to

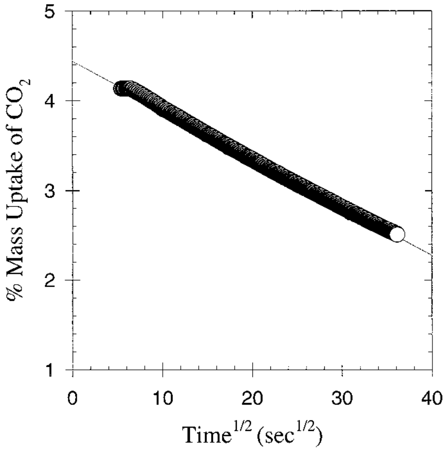

Figure 1. Representative (2 h absorption) desorption profile of CO_2 from FEP. An equilibrium mass uptake of 4.4% is attained in less than 30 min for a $^1/_{16}$ in. thick sample.

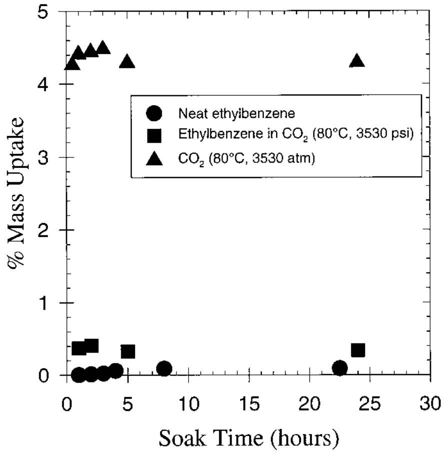

Figure 2. Absorption of CO_2 and ethylbenzene (a nonpolymerizing model for styrene) into FEP at conditions of 80 °C and 3530 psi.

recording mass loss over a period of several days. These values were then extrapolated back to zero desorption time to determine the amount of ethylbenzene absorbed by FEP at the end of the sorption period. Again, absorption was very rapid, with an equilibrium uptake of 0.4% attained in less than an hour. For comparison, the uptake of ethylbenzene was measured under neat conditions by soaking the samples in ethylbenzene at 80 °C. Under these conditions, less than 0.1% uptake was attained after 8 h (Figure 2).

FEP/Polystyrene Blend Synthesis. To control the resulting blend composition, two synthetic variables were examined: the concentration of styrene monomer in CO_2 and the length of the reaction period. To study the effect of styrene concentration on the blend composition, the reaction time was fixed at 16 h. Beyond a monomer concentration of 30 wt % styrene in CO_2, the fraction of polystyrene in the FEP substrate reaches a plateau value of approximately 19 wt % as shown in Figure 3. We therefore chose to use a concentration of 30 wt % styrene in all subsequent experiments.

We note that all of these blends were recovered as dense materials (they were not foamed). To make composite foams using the reaction procedure, we decided to create blends with a higher concentration of polystyrene, which foams readily at 100 °C.

With the styrene concentration now held fixed at 30 wt %, the length of the reaction period was varied, holding all other conditions constant. Again, the amount of polystyrene incorporated into the blend levels off at a value of approximately 35 wt % (Figure 4). With the density of FEP being more than twice that of polystyrene, greater than half the volume of these blends consists of polystyrene. It is also interesting to note that these blends did not foam, even with such large amounts of polystyrene in the blend. We have shown previously[9] that polystyrene alone foams readily under these conditions.

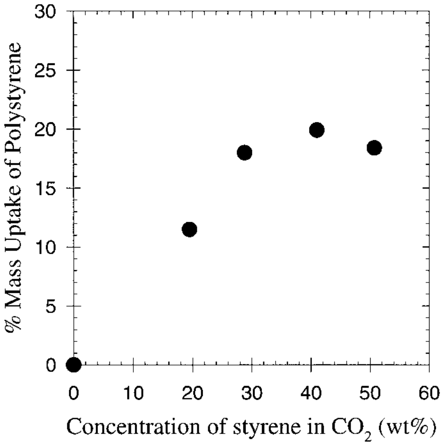

Figure 3. Effect of styrene concentration in CO_2 on the composition of the resulting blends. Reaction time was held constant at 16 h at 100 °C.

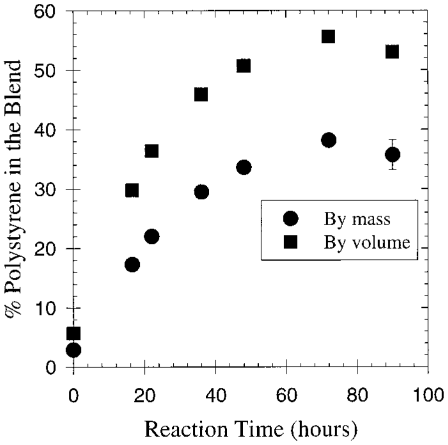

Figure 4. Effect of reaction time on the composition of the resulting blends. Monomer concentration was held constant at 30 wt % in CO_2.

Blend Characterization. Thermal properties of the blends were measured using DSC and DMTA. There were two questions to be answered by these techniques: does the incorporation of the polystyrene affect the crystallinity of the FEP substrate, and are the individual T_g's preserved for the two components of the blend? A DSC scan for a FEP/polystyrene blend containing 18 wt % polystyrene is shown in Figure 5. No T_g for the FEP is observed by DSC, either alone or in the blend sample. In the blend, a distinct polystyrene T_g is observed at 100 °C, its normal value. In addition, the melting point of the FEP remains essentially unchanged from the unmodified sample. The percent crystallinity of the blend is lower than that in the unmodified FEP, but when the incorporation of the amorphous polystyrene component is accounted for, the percent crystallinity of the FEP component also remains unchanged. These facts indicate that the polystyrene

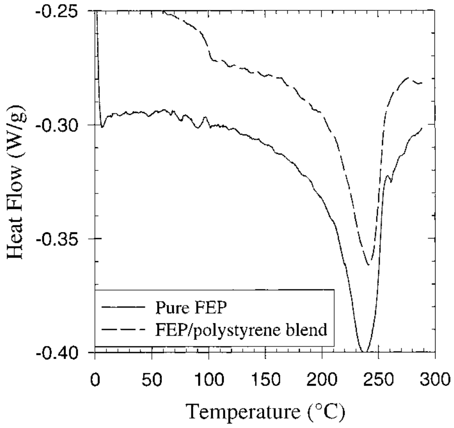

Figure 5. DSC scan at 10 °C/min for a pure FEP sample and an FEP/polystyrene blend sample containing 18 wt % polystyrene.

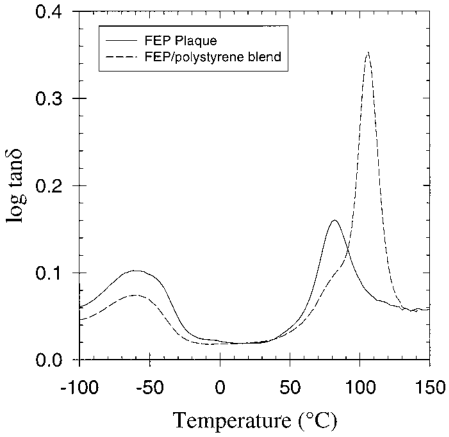

Figure 6. DMTA scans at 2 °C/min for a pure FEP sample and an FEP/polystyrene blend sample containing 11 wt % polystyrene.

is formed only within the amorphous regions of the FEP, leaving the crystalline portions unaffected. Additional studies have shown this to be the case for HDPE/polystyrene[4] and poly(chlorotrifluoroethylene)/polystyrene[3] blends prepared by this method as well.

To determine the T_g for the unmodified FEP as well as the blend samples, DMTA scans were conducted at a heating rate of 2 °C/min using a single cantilever beam sample. The tan δ plots are shown in Figure 6. The FEP shows two transitions, a T_g at 85 °C and a lower temperature transition near −50 °C. In the blends, these two transitions remain unchanged, and a polystyrene T_g appears at slightly higher than 100 °C.

To determine the molecular weight of the polystyrene synthesized within the FEP substrate, blend samples were extracted in refluxing THF overnight and the resulting THF/polystyrene solutions analyzed by GPC. Results are shown in Table 1. As was the case for another system,[4] the molecular weight of the polystyrene formed within the blends is significantly higher than that which polymerizes in the CO_2 phase outside of the substrate. The molecular weight also appears to increase with the addition of a postreaction period and increases with the length of the reaction period. The postreaction also lowers the polydispersity. It should also be noted that some polymerization does occur during the soak period, although uptakes are quite low. From these data, we conclude that high molecular weight polystyrene is formed within the FEP substrates. We have not, however, removed all of the polystyrene during the extraction due to the extreme solvent resistance of the FEP substrate. We cannot, therefore, be assured that these numbers are representative of the entire amount of polystyrene within the blend samples.

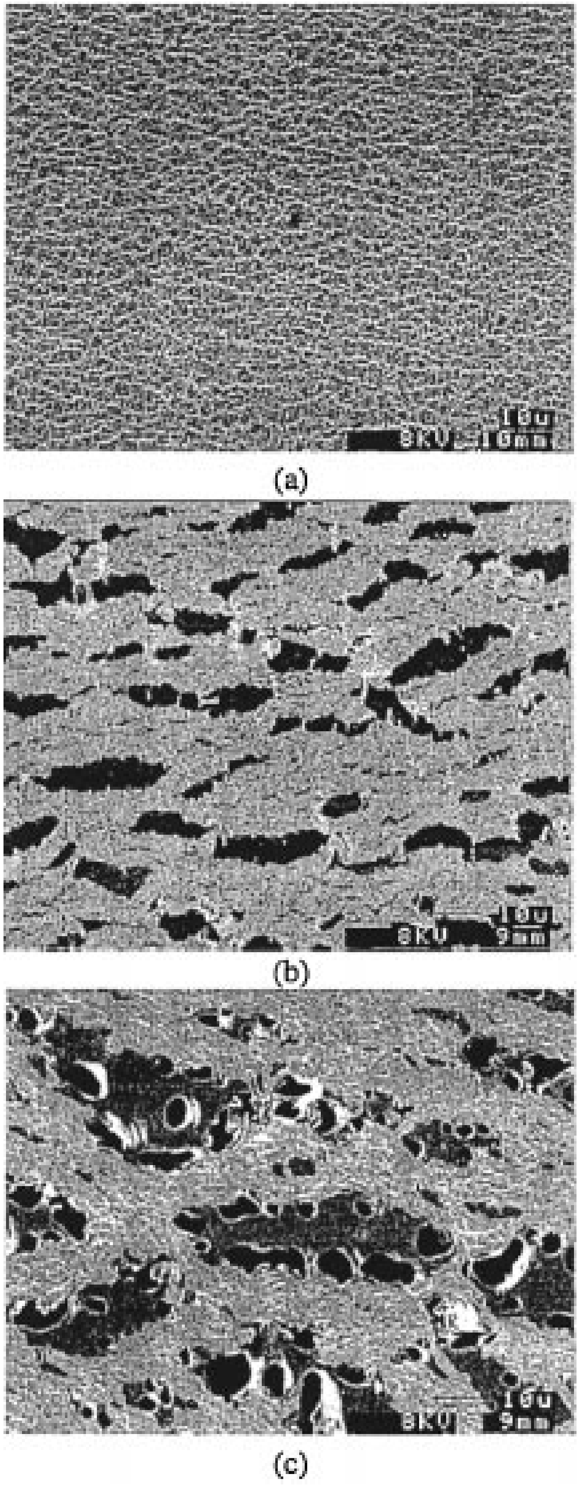
(a)
(b)
(c)

Figure 7. Backscattered electron images of ruthenium tetraoxide stained FEP/polystyrene blends: (a) blend containing 29 vol % polystyrene prepared with a 16 h reaction period; (b) blend containing 50 vol % polystyrene prepared with a 90 h reaction period; (c) the same 50 vol % sample as in (b), but which was subsequently annealed in CO_2 at 200 °C and 6800 psi.

To determine the phase morphology of the FEP/polystyrene blends that were prepared, three samples

Table 1. Molecular Weight Data for Polystyrene Prepared in Blend Syntheses

	5 h soak	5 h soak, 16 h reaction	5 h soak, 16 h reaction, 6 h postreaction	5 h soak, 90 h reaction	5 h soak, 90 h reaction, 6 h postreaction
inside the sample	$M_n = 59\ 000$ $M_w = 347\ 000$ PDI = 5.8	$M_n = 96\ 000$ $M_w = 390\ 000$ PDI = 4.1	$M_n = 196\ 000$ $M_w = 485\ 000$ PDI = 2.5	$M_n = 165\ 000$ $M_w = 545\ 000$ PDI = 3.3	$M_n = 214\ 000$ $M_w = 546\ 000$ PDI = 2.6
outside the sample	$M_n = 16\ 000$ $M_w = 64\ 000$ PDI = 4.1	$M_n = 16\ 000$ $M_w = 60\ 000$ PDI = 3.8		$M_n = 41\ 000$ $M_w = 236\ 000$ PDI = 5.8	

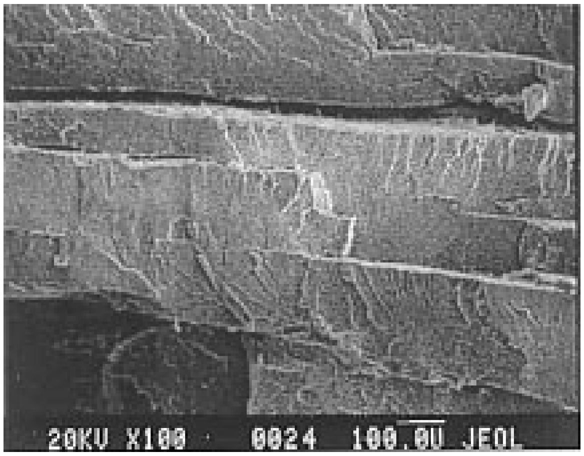

Figure 8. SEM micrograph of a FEP/polystyrene blend containing 50 vol % polystyrene

were viewed in the backscattered electron imaging (BEI) mode using a FESEM. The samples were first cryomicrotomed to create a smooth, featureless surface and then stained with ruthenium tetraoxide which reacts with the polystyrene, causing the polystyrene-rich phases to appear bright in the images. The samples were then carbon-coated and viewed using the FESEM. In secondary electron imaging (SEI) mode, which predominantly reveals topographical features, the surfaces appear smooth with only a faint compositional contrast coming from the backscattered electrons which are also collected by the SEI detector. In the BEI mode, however, the two phases are distinct. The micrographs in Figure 7 show these BEI images for three different samples. Parts a and b are blends prepared with 16 and 90 h reaction times containing 29 and 50 vol % polystyrene, respectively. Both phases appear much larger for sample b. In addition to there being twice as much polystyrene in the blends, the longer reaction time allowed for additional phase separation. The image in part c came from the 50 vol % sample which was subsequently annealed in CO_2 at 200 °C and 6800 psi. This blend has undergone further phase separation in addition to voiding which is discussed further in the section below.

Foaming of the Blends. The carbon dioxide-induced foaming of polystyrene has been studied in detail in previous work.[9] Under the conditions used to prepare these blends, polystyrene itself would have foamed readily. As made, however, these FEP/polystyrene blends are dense, nonfoamed materials, presumably held together by the crystallinity of the FEP substrate. Pure FEP is not foamable below its normal melting point because the SC CO_2 does not penetrate the crystalline regions of the polymer and depress the melting point. With the addition of a highly foamable polystyrene component, we had hoped that the blends might be capable of foaming at temperatures below the melting point of the FEP.

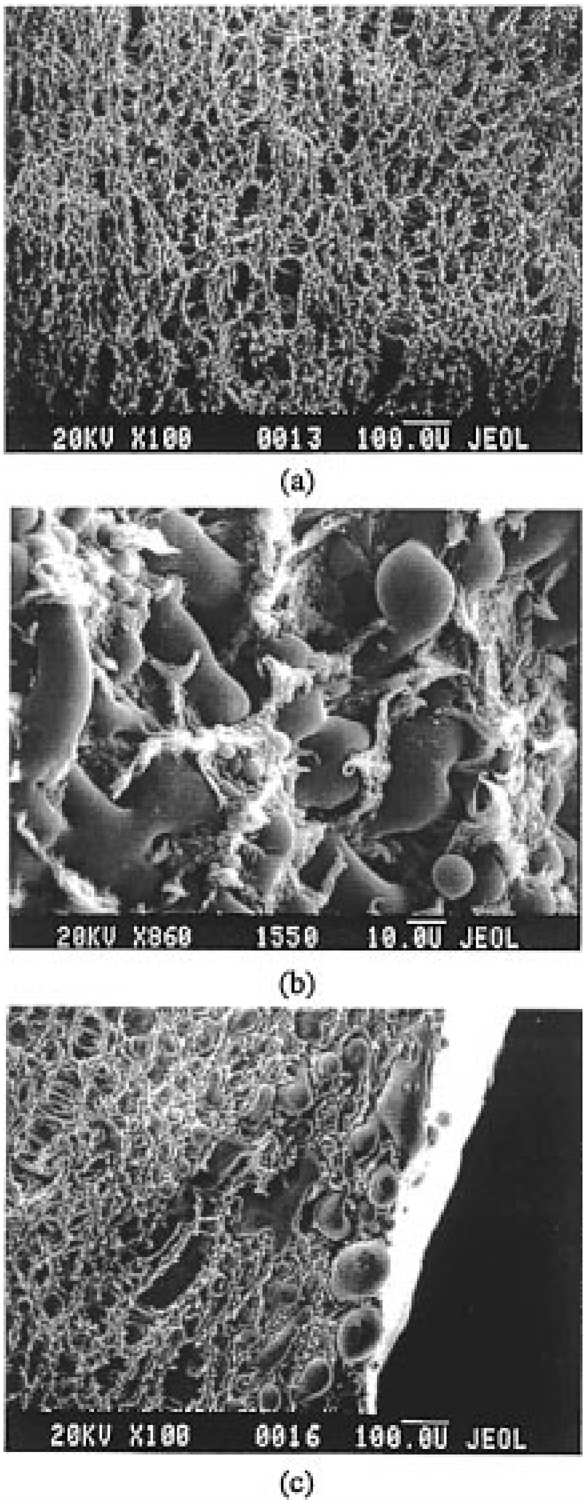

Figure 9. SEM micrographs of an FEP/polystyrene blend containing 50 vol % of polystyrene after a 6 h soak in CO_2 at 140 °C and 6100 psi followed by rapid depressurization: (a) middle of the sample, (b) higher magnification, and (c) edge of the sample.

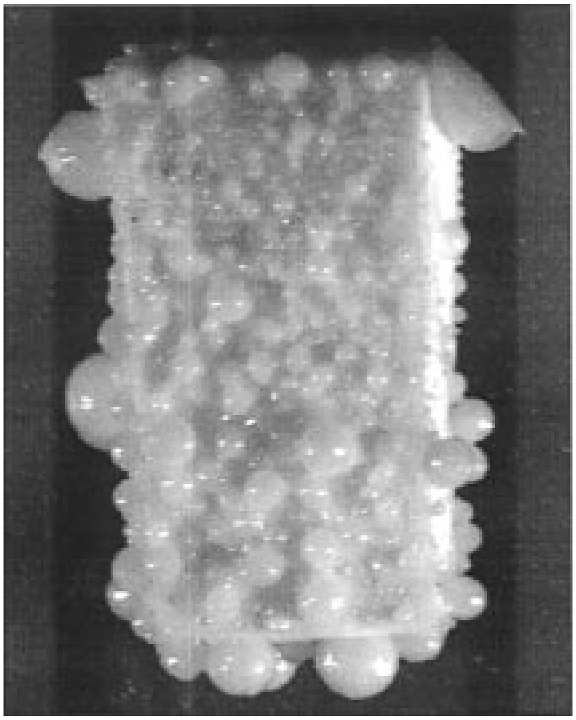

Figure 10. Photograph of an FEP/polystyrene blend sample originally containing 50 vol % polystyrene following a soak in CO_2 at 200 °C and 6800 psi.

All attempts at foaming FEP/PS blends were conducted on samples having approximately 50 vol % of each polymer, as these contained the highest polystyrene content, making them most likely to foam. An SEM micrograph of the initial blend is shown in Figure 8. Even at higher magnifications, there is no evidence of a cellular structure. The density of this blend was measured to be 1.4 g/cm^3.

The first postreaction foaming experiments were conducted at conditions of 140 °C and 6100 psi of CO_2, with rapid depressurization after a soak period of 6 h. The resulting material retained its planar geometry but had a density which was reduced to 0.93 g/cm^3. Upon examining the sample by SEM (Figure 9), however, it appears as though the FEP and polystyrene phases debonded from one another instead of forming a cellular structure within either or both of the individual phases. Figure 9c reveals that the polystyrene phase migrates toward the edges of the sample under these conditions.

At 200 °C and 6800 psi, the polystyrene is even more mobile, allowing approximately 25 wt % to migrate completely out of the sample and coat the outside surface as “beads” of polystyrene. Figure 10 (a photograph of the sample following the soak in CO_2) shows graphically that the blend undergoes large-scale phase separation in preference to forming a composite foam. Little or no expansion is observed under these conditions.

Several control foaming experiments were carried out above the melting point of the FEP substrate (at a temperature of 250 °C). These materials are grossly phase-separated, cannot be considered composite foams, and were not studied in any detail. One sample exhibited a density of 0.55 g/cm^3 and an irregular cellular structure (Figure 11).

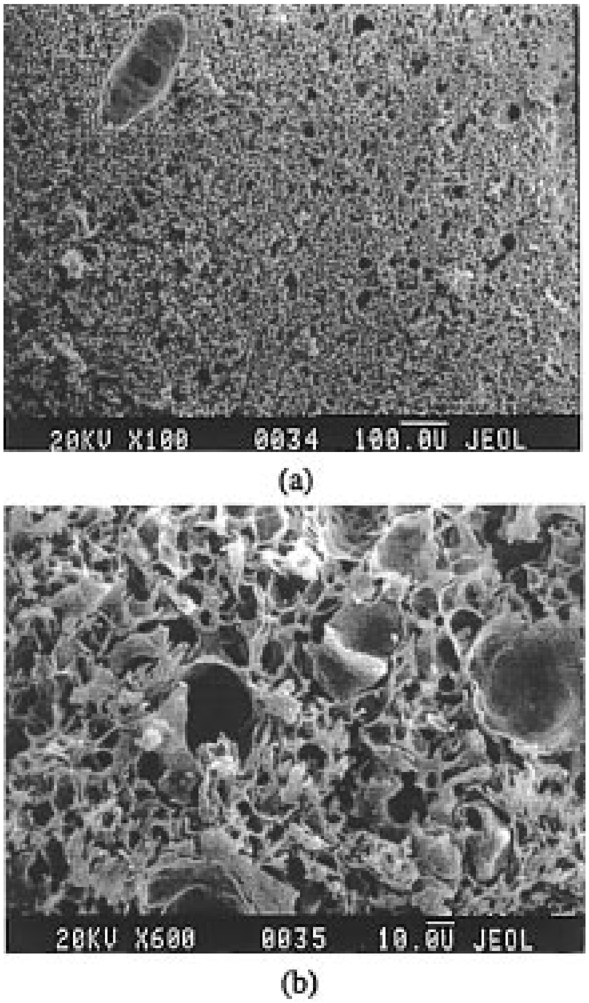

Figure 11. SEM micrographs of an FEP/polystyrene blend containing 50 vol % polystyrene after a soak in CO_2 at 250 °C, followed by rapid depressurization: (a) middle of the sample and (b) higher magnification.

Summary and Conclusions

An equilibrium mass uptake of 4.4% CO_2 in FEP is attained in less than 30 min at 80 °C and 3530 psi. Less than 0.5% ethylbenzene (a nonpolymerizing model for styrene) is absorbed by FEP under the same conditions. FEP/polystyrene blends, with volume incorporations up to 50% polystyrene, have been prepared by free-radical polymerization of styrene in SC CO_2-swollen FEP. Polystyrene incorporation and phase morphology can be readily controlled by styrene concentration and reaction time. The crystallinity and glass transition of the FEP are unaffected by the addition of the polystyrene component, indicating that the polymerization occurs exclusively in the amorphous domain of FEP and that the two polymers are immiscible. The molecular weight of the polystyrene formed within the FEP substrate is significantly higher than that which forms in the SC CO_2 phase outside of the substrate. At conditions under which expansion in polystyrene occurs, these blends are not foamed to low-density materials even with large amounts of incorporated polystyrene. The crystalline domains remain unaffected by either the polystyrene component or the CO_2 and presumably prevent expansion. During high-temperature soaks in CO_2, the polystyrene phase becomes highly mobile due to a high degree of plasticization by CO_2, which leads to large-scale phase segregation and even migration of the polystyrene out of the blends.

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