# Polymerization in Supercritical Fluid-Swollen Polymers: A New Route to Polymer Blends

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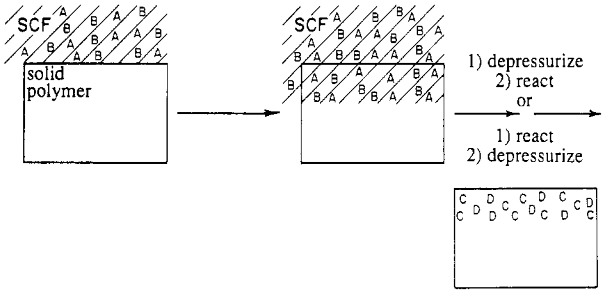
*Received April 6, 1994*
*Revised Manuscript Received June 17, 1994*

We have begun a research program directed at the modification of solid organic polymers by carrying out chemical reactions within supercritical fluid (SCF)-swollen solid polymer substrates. The general objective of this program is summarized in eq 1; reagents (A and B in eq 1) are infused into a solid polymer as a SCF solution where



(1)

they are induced to react and form products (C and D in eq 1). The reaction can be run either in the presence of the SCF solution or subsequent to removal of the solution by depressurization. Issues that we are addressing or will address include the kinetics of the infusion, the control of modification depth, and the gradient structure, morphology, and thermal stability of the products. SCFs offer several distinct advantages as reaction media that we will make use of: (1) they increase (significantly) diffusion rates of penetrants in solid polymers (see below); (2) the solvent strength can be adjusted over wide ranges by manipulating temperature and pressure; therefore the degree of swelling and the partitioning of reagents between the swollen polymer matrix and the SCF solution are controllable; (3) common SCF solvents are gases at atmospheric pressure; thus, the solvent will rapidly dissipate upon release of pressure, trapping penetrants in the polymer substrate. This report describes the infusion of $CO_2$ solutions of styrene into a variety of semicrystalline and glassy polymer substrates and thermally-initiated radical polymerizations within the swollen substrates to generate polystyrene–substrate polymer blends.

The properties of SCF solvents are well-known, and comprehensive reviews on the subject are available.[1] The interaction of supercritical $CO_2$ with solid polymers has been studied in some detail.[2-8] While $CO_2$ is a poor solvent for most polymers,[9] it swells most polymers including those that are generally considered solvent-resistant.[10] Diffusion rates in SCF-plasticized polymers are dramatically increased over nonswollen samples. For example, the work of Berens[2,3] demonstrates that the diffusivity of $CO_2$ increases by over 2 orders of magnitude when glassy polymers, e.g., poly(methyl methylacrylate), are plasticized with $CO_2$. Berens[11] and Sand[12] have demonstrated that polymer substrates can be impregnated by swelling the polymer with a solution of an organic penetrant in $CO_2$ followed by rapid venting of the SCF solution. Berens studied glassy polymers and concluded that plasticizing the substrates with $CO_2$ accelerates the kinetics of penetrant absorption and that the amount of penetrant which can be incorporated is limited by the solubility of the penetrant in the polymer matrix. Berens's patent[11] gives an example that is the report most closely related to the process we described here; poly(ethylene glycol) diacrylate and 4,4′-dichlorobenzophenone (a photoinitiator) were infused into polycarbonate as a $CO_2$ solution. Following depressurization and removal from the autoclave, UV photolysis initiated a reaction that consumed ~25% of the acrylate residues. Sand[12] disclosed the $CO_2$-assisted impregnation of fragrances and pharmaceuticals in thermoplastic polymers such as polyethylene and polypropylene.

**Table 1. Mass Uptake Results**

| substrate | mass uptake (%) protocol 1 | protocol 2 | protocol 3 |
|---|---|---|---|
| poly(chlorotrifluoroethylene) (PCTFE) | 4.8 | 13.4 | 75.7 |
| poly(4-methyl-1-pentene) (PMP) | 23.7 | 75.1 | *a* |
| poly(ethylene) (HDPE) | 6.9 | 11.8 | 118.0 |
| nylon 66 | 0.5 | 3.2 | 26.7 |
| poly(oxymethylene) | 2.8 | 6.7 | 34.3 |
| Bisphenol A polycarbonate | 30.2 | 50.9 | *a* |

[a] An experiment using this set of conditions was not run for this substrate.

Three experimental protocols were used in the work reported here to prepare infused polystyrene blends with six polymer substrates (detailed in Table 1). The substrates were cut to dimensions of ~1 × ~4 cm from commercially available sheets ranging in thickness from 63 to 125 mil (~1500–3000 μm), rinsed with isopropyl alcohol, dried, and weighed prior to reaction. No attempt was made to remove additives that may have been present in the commercial products. Samples were placed (individually) in high-pressure stainless steel reactors that consisted of ~1.2 cm (i.d.) × ~10 cm sections of $^1/_2$-in. schedule 160 seamless pipe with a plug at one end and a high-pressure needle valve at the other. The reactors were purged with $CO_2$, weighed, and immersed in a circulating temperature-controlled bath. Initiator was dissolved in styrene, and the solution was introduced to the reactor via a syringe. $CO_2$ was introduced via a high-pressure manifold[13] to the desired pressure, and the reactor contents were mixed using a vortex mixer. The reactor was equilibrated in the temperature bath and repressurized to the desired pressure (which drops due to dissolution of the monomer and initiator). The mass of $CO_2$ transferred was then determined gravimetrically.

Each of the experimental protocols involves a "soaking" period of 4 h at a temperature in which the half-life of the initiator is hundreds of hours[14] and a polymerization period at a temperature in which the initiator half-life is ~2 h.[14] In protocol 1, azobis(isobutyronitrile) (AIBN) is the initiator and the soaking period is at 40 °C and 103 atm of $CO_2$. The reactor is drained and then pressurized with $N_2$ (100 atm) and heated at 80 °C for 4 h. In protocol 2, *tert*-butyl perbenzoate is the initiator, the soaking period is at 80 °C at 241 atm of $CO_2$, and the polymerization period (subsequent to draining) is 4 h at 120 °C and 100 atm of $N_2$. Protocol 3 uses *tert*-butyl perbenzoate and entails a soaking period (4 h, 80 °C, 150 atm of $CO_2$), a polymerization period (8 h, 120 °C) prior to draining, and a second postdraining polymerization period (12 h, 120 °C, 100 atm of $N_2$). In each experiment the concentration of styrene in carbon dioxide was 37 ± 2 wt %; this mixture is a single phase under all the conditions of these experiments.[15] The initiator concentration used was ~0.3 mol %.

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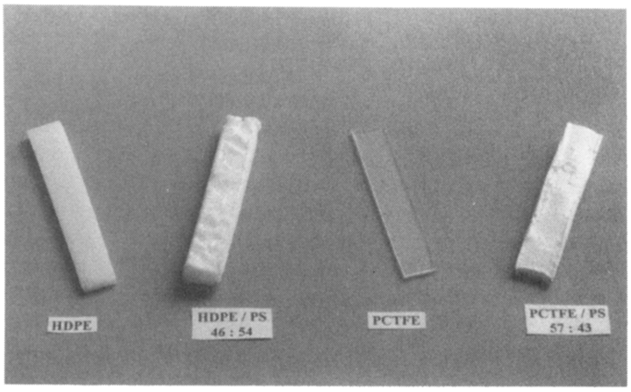

**Figure 1.** HDPE and PCTFE before and after modification using protocol 3. The ratios given are weight percents of the blend components.

Table 1 gives the mass uptake results as a percentage of the initial substrate masses. Mass was determined after drying the sample under vacuum to constant mass. It is apparent from the data that significant amounts of polystyrene can be incorporated into all of these samples using this method and that the mole fraction of polystyrene incorporated in the blend can be controlled. The presence of polystyrene in the substrates was confirmed by DSC: glass transitions at 100–108 °C were observed for modified poly(chlorotrifluoroethylene) (PCTFE), poly(ethylene) (HDPE), poly(4-methyl-1-pentene) (PMP), and nylon samples. With the exception of the samples prepared from PCTFE and HDPE using protocol 3 and from PMP using protocol 2, the film samples retained their initial shape, undergoing small dimensional enlargement. The exceptional samples exhibited foamlike structures which, although expanded, were the basic geometry of the original substrates. This indicates that the temperatures at which the modifications were carried out are below the depressed (by $CO_2$/styrene) melting transitions for these semicrystalline polymers. Figure 1 shows a photograph of PCTFE and HDPE samples before and after modification using protocol 3. The expansion occurs during depressurization and is the result of a high concentration of absorbed $CO_2$ in the affected samples.

We have not demonstrated that all the products formed are indeed blends and not graft copolymers (or a combination of the two). There are reasonable (and likely) mechanisms for chain transfer to the substrate polymers, but we have demonstrated for two substrates that graft polymerization does not contribute significantly. All of the polystyrene from a PMP blend was extracted using toluene, and >70% of the polystyrene from a PCTFE blend was extracted using THF. Infrared analysis of the extracts indicated that pure polystyrene and no soluble graft copolymers were extracted.

The modification conditions reported here were chosen to render blends containing polystyrene throughout the entire thickness of the substrate. We have proven this rigorously only in the case of PCTFE (this will be discussed in a future publication that will report a detailed study of PCTFE–polystyrene blends prepared by this method): TEM and energy-dispersive X-ray analysis indicate the presence of both polystyrene and PCTFE throughout the entire sample. The expanded products prepared from HDPE and PMP suggest complete penetration for these samples as well. Control samples (without styrene) did not expand, and unexpanded cores would have been observed if HDPE and PMP did not contain polystyrene throughout.

Berens has emphasized[3,11] that SCF-assisted infusion of penetrants affects only the kinetics of absorption and that the amount of penetrant which can be incorporated in a polymer is limited to the solubility of the penetrant. Figure 2 shows plots of mass uptake versus time for four sets of experiments. When PCTFE is exposed to ethylbenzene (a model for styrene) in $CO_2$ (40 wt % ethylbenzene) at 80 °C and 240 atm, the absorbed amount levels at <5% (we assume this to be the solubility of ethylbenzene—and styrene—in PCTFE). The mass uptake when PCTFE is exposed to neat ethylbenzene at 80 °C is slower. These results are in line with the statements of Berens; however, when PCTFE is exposed to the soaking conditions of protocol 2, the mass uptake is significantly above that expected for equilibrium styrene solubility. This indicates that styrene polymerizes during the soaking period and precipitates within the PCTFE matrix. Polystyrene is neither soluble in $CO_2$ nor miscible with PCTFE; it becomes a discrete phase trapped in the PCTFE matrix. The polymerization drives a continuous absorption of styrene into the modified substrate. The nascent polystyrene phase is also swollen by $CO_2$/styrene. $CO_2$ is quite soluble in polystyrene,[6] and this solubility is the major cause of the expansion that occurs in some polystyrene-rich (highly modified) samples. Also shown in Figure 2 is a plot of the mass uptake of PCTFE during the soaking conditions of protocol 2, except that the inhibitor, 4-*tert*-butylcatechol (~10 ppm), was not removed from the styrene. An induction period, during which time the inhibitor is exhausted, is observed followed by an accelerated gain in mass.

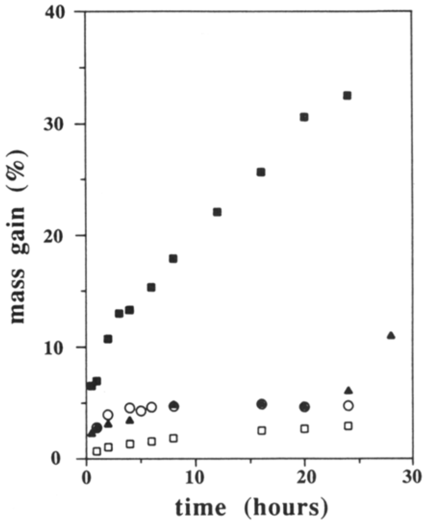

**Figure 2.** Plots of mass increase of PCTFE substrate vs time for neat ethylbenzene (□), ethylbenzene/$CO_2$ (○), inhibited styrene/$CO_2$ (▲), and styrene/$CO_2$ (■).

In summary, we have demonstrated that polymer blends can be prepared by polymerization within a SCF-swollen polymer substrate. We emphasize that the blend composition is *not* limited by the solubility of the monomer in the matrix polymer. We have shown that both dense structures and expanded foamlike materials can be prepared, and we suspect that a range of morphologies are accessible through experimental parameter control. Extensions of this process to prepare IPNs and semi-IPNs by polymerization in a cross-linked matrix and/or use of multifunctional comonomers should prove straightforward.

**Acknowledgment.** We thank the Office of Naval Research (Grant N00014-92-J-1040) and the Army Natick Research Center (Grant DAAK-93-K-0006) for financial support.

## References and Notes

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(10) There are not compilations of $CO_2$ solubility in chemically-resistant polymers at high pressures; however, considerable data are available regarding $CO_2$ permeability (the product of solubility and diffusion rate) in these materials.[16] We will discuss in a future paper the solubility of $CO_2$ in PCTFE.

(11) Berens, A. R.; Huvard, G. S.; Korsmeyer, R. W. U.S. Patent 4,820,752, 1986.

(12) Sand, M. L. U.S. Patent 4,598,006, 1986.

(13) The manifold was fabricated by fitting a stainless steel high-pressure threaded nipple (Autoclave Engineers) with a two-O-ring piston. One end of the manifold was connected to a syringe-type pressure generator (High Pressure Equipment) using water as the working fluid. The other end was connected to an in-line pressure transducer (Omega) and a series of high-pressure needle valves. The entire manifold was maintained at the desired temperature using a PID controller (Omega) and a silicone-coated resistance heating tape.

(14) The half-lives were estimated from values reported in benzene solution.[17] The decomposition rate for AIBN in $CO_2$ has been reported,[18] however the use of these values would not be appropriate because of the high concentration of styrene in the $CO_2$ solutions used in the work reported here.

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