

High-Pressure Supercritical CO₂ Assisted Melt Spinning

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This abstract briefly describes a combination of two processes (conventional and alternative): melt spinning and supercritical fluid technology. Supercritical fluids (such as carbon dioxide, CO₂) can be used to produce materials with interesting and controllable properties, including biologically active protein micro-particles and biocompatible polymers micro-spheres, for drug delivery applications, ceramic precursor powders and high-modulus, heat resistant polymers fibers. Supercritical CO₂ (SC-CO₂) has a great potential to treat a novel polymers that are used for biomedical applications. Carbon dioxide has been shown to be more environmental friendly solvent (non-toxic) in comparison to many of the conventional organic solvents used in many industrial processes. An experimental high-pressure view cell was designed and constructed to study the equilibrium swelling, swelling kinetics and diffusion of SC-CO₂ into a solid polymer matrix. Experiments were performed using a novel copolymer [styrene-iso-butylene-styrene (SIBS)] in our high-pressure view cell equipment. The main objective was to observe whether or not SIBS polymer swells on exposure to or when treated with SC-CO₂ under elevated pressures (17 Pa – 38 Pa) and at mild temperatures (338 K and 358 K).

Preliminary results showed the novel copolymer swelling at the experimental conditions operated. Data showed an initial trend that the diffusion of CO₂ at high operating pressures had a significantly effect on the melt viscosity of the polymer. The operating temperature was also shown to have a direct effect on the melt viscosity of the polymer. Furthermore, increased system pressure was observed to enhance the extent of the swelling phenomenon while a maximum was noted with increasing temperature, at operating pressure of ~ 28 Pa.

The ultimate goal was to develop an alternative process using SIBS copolymer that can combine supercritical fluid technology and melt spinning. A modified high pressure single screw extruder was used to run the melt spinning experiments at high pressure. An injection port for CO₂ has been installed into the extruder barrel, located at ~ 70% of the distance from the dispenser (feed) to the extruder exit. The addition of supercritical CO₂ to the polymer during processing accomplished several goals: allowed lower the melt viscosity during processing and the polymer was processed at temperatures below the polymer's degradation temperature. Also, this process eliminated any toxicity issued by using carbon dioxide (non-toxic solvent or additive) and eliminated long term toxicity post processing due to leaching of the processing aids out of the polymer as CO₂ sublimates to a gas at ambient pressure and was removed from the polymer. The biggest challenge hindering the widespread use of CO₂ as a plasticizer involves the lack of understanding of its effect on polymer swelling and the concomitant reduction in material viscosity.

Keywords: melt, spinning, supercritical, diffusion, viscosity, polymer

INTRODUCTION

There is a need to explore and demonstrate that the use of supercritical CO₂ or other supercritical fluids (with or without co-solvents) can be used as a processing aid (a plasticizing agent) for many polymers [1]. Melt (thermal) spinning of a styrene-iso-butylene-styrene (SIBS) copolymer with between 17 to 30 mole% of styrene so as to produce fibers in the 10 μm level requires the melt viscosity to be in the range of 30 – 60 MPa.sec. Under normal thermal processing conditions, SIBS cannot be extruded at extruder barrel temperatures greater than about 491 K (475 °F) without degradation occurring. Degradation is observed as a darkening of the extruder. At that temperature, even at high shear rates, the melt-viscosity is about 150 MPa.sec. which is too high for small diameter fiber melt-spinning. Fluids near the critical point can be used to form materials with interesting and controllable properties, including biological active protein micro-particles and biocompatible polymer micro-spheres, for drug delivery applications, ceramic precursor powders and high-modulus, heat resistant polymer fibers. Carbon dioxide has been shown to be more environmental friendly solvent in comparison to many of the conventional organic solvents. Therefore, the addition of supercritical CO₂ to the melt in the desired concentrations can reduce the melt viscosity significantly, allowing thermal processing at lower melt viscosities at temperatures that do not exceed the degradation temperatures of the polymer. In addition, once extruded, the CO₂ sublimates into a gas and is totally eliminated from the extruder, rendering the final extruder to be 100 % SIBS with no additives that might subsequently leach out.

Polymers have been and still are widely used for the preparation of devices for medical applications. Many medical devices are used for long-term implantation in the human body [2]. Major requirements for the selection of a material for an implantable medical device are that the surgical implant material, one fabricated and sterilized, be: 1) bio-stable, 2) blood compatible, 3) non-carcinogenic, 4) non-cytotoxic, 5) has no ethanol sterilization residuals, 6) has flexural endurance, 7) low heavy metals content, 8) low implant toxicity and 9) be tissue compatible. Many polymers are able to meet the above requirements as a pre-processed material, and some even in the post processed condition. However, the thermal processing some of these polymers, especially ones that have and high melt viscosity at the processing temperatures, into final medical devices, require the addition of components such as plasticizers, waxes, other resins and anti-oxidants to the polymer, to facilitate flow during its processing (lower the melt viscosity) and protect the polymer from degrading during processing. This additive technique is common for devices that will not be exposed to the human environment for very long. Typical resin and plasticizer additives are polypropylene and di-octyl phthalate respectively. Typical waxes would be paraffin wax. A typical anti-oxidant would be a phosphate blended with a phenolic stabilizer. Another direct and most effective method cited to achieve this lower melt viscosity/no degradation problem goal is to exclude oxygen while processing at temperature. This process helps in the case of many polymers, but does not completely solve the problem of degradation of some polymers. Polymers have been used in the past with supercritical fluids [2, 3], but the goal in the past has been to focus strictly on improving the process ability of the polymer.

On the other hand, some thermal processing methods require that the melt-viscosity of the polymer be low, for example in the order of 30 – 60 MPa.sec. (300 – 600 cP) for fiber melt spinning and injection molding. The achievement of this level of melt-viscosity at the normal thermal processing temperatures, is a difficult problem to resolve, and has prevent some materials being used for melt or thermal spinning.

EXPERIMENTAL PROCEDURES AND APPARATUS

The experimental procedure was developed and optimized by exposing samples of SIBS polymer to supercritical CO₂ in a high pressure view cell ($\sim 3.2 \times 10^{-6} \text{ m}^3$) under controlled conditions so as to determine whether there were changes in polymer mass, melt-viscosity and other thermal properties. Figure 1 shows the experimental high-pressure apparatus (view cell, manual CO₂ pump, CO₂ cylinder (bone dry grade, 99.8% purity), heating/cooling bath and temperature controller) to perform the swelling trials. The standard procedure was as follow:

- 1) Weight the small foam polymer samples to be treated with supercritical CO₂.
- 2) Load cut polymer samples (rectangular shape) into the view cell (Figure 2) and sealed to ensure no leaking. Total polymer weight load into the view cell is $\sim 0.007 \text{ kg}$.
- 3) Open CO₂ cylinder main valve and fill the high pressure system with liquid CO₂.
- 4) Purge the inlet lines and view cell (displace air bubbles) by releasing small amount of gas CO₂ from the pressurized system.
- 5) Turn ON the heating bath and set the operating temperature by using the bath temperature controller (white color in Figure 1).
- 6) Increase the pressure system by using a high-pressure manual CO₂ pump (blue color in Figure 1) with cooling mantle to the desired pressure selected.
- 7) Close the inlet CO₂ needle valve to the view cell and hold the experimental conditions (pressure and temperature) at equilibrium for $\sim 86400 \text{ s}$.
- 8) Collect pressure change of CO₂ as a function of time until it reached the desired pressure.
- 9) After the swelling time is reached (minimum 86400 s), slowly release the CO₂ pressure from the pressurized system.
- 10) Unload the treated polymer samples from the view cell and weight to compare with the initial weights (Figure 3).

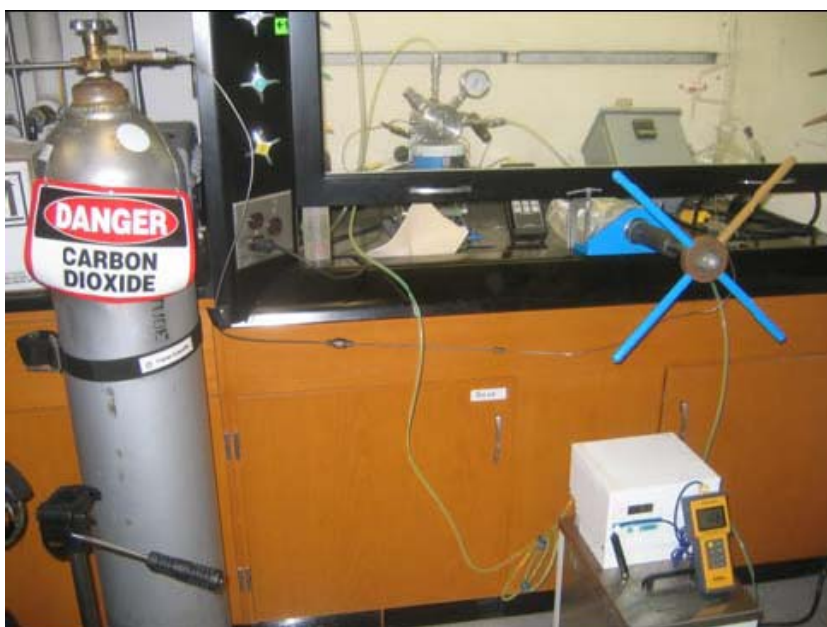


Figure 1: High-pressure system used to perform the swelling experiment in this study.

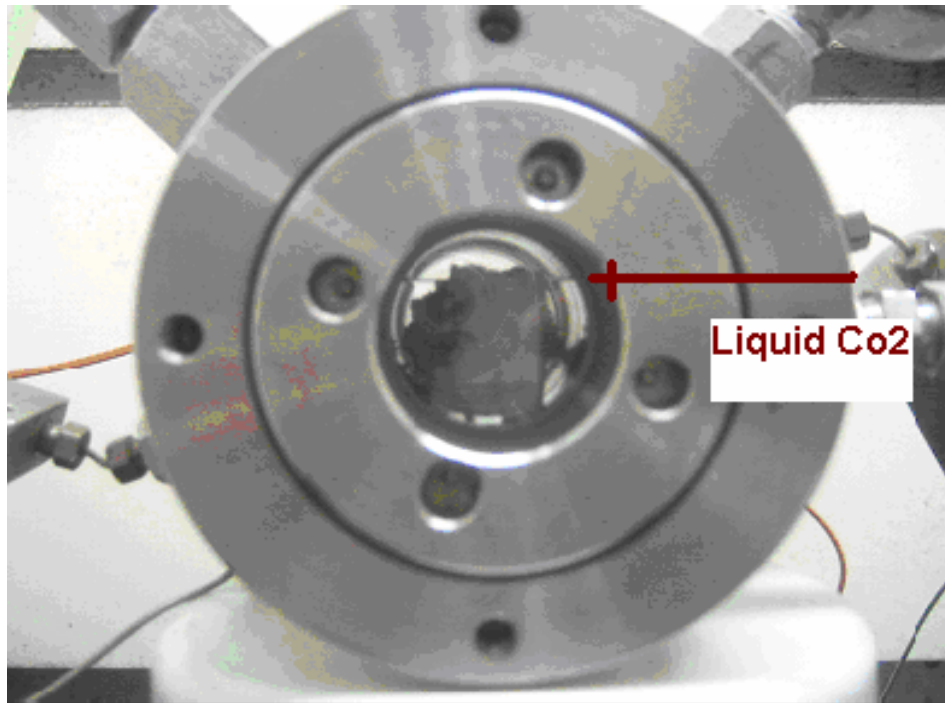


Figure 2: Homemade high-pressure view cell [4] used to observe the swelling behavior of the SIBS polymer in supercritical CO_2 .



Figure 3: Unloaded SIBS polymer samples (L-Front; Center and R-Back) exposed with SC- CO_2 at $P = 28 \text{ Pa}$ and $T = 318 \text{ K}$ for an equilibrium time of 86400 s.

RESULTS AND DISCUSSION

The swelling experiments of the novel copolymer (SIBS) in this study are summarized in Tables 1 and 2. Also, Figures 4 and 5 showed melt-viscosity measurements of the 17 mole% styrene SIBS as a function of temperature and time by comparing the different operating conditions of pretreatment of SC-CO₂ under 28 Pa and 38 Pa. In most of swelling experiments, it was visually that the polymer samples were gained weight. One interesting result was that the degree of swelling was different among the three (3) polymer pieces according to their location in the view cell. It was observed that the center piece of polymer was most large in size compared with the polymer piece that was located in the back part of the cell and it hardly change in size. The swelling studies were confirmed by conducting melt-viscosity measurements with the CO₂ treated polymer samples.

Table 1 and Figure 6 show a significant effect of operating temperature on the melt-viscosity of CO₂ pretreatment pressure at 28 Pa. Initial (control) melt-viscosity measurement for 17 mole% SIBS is 930 Pa.s as shown in Tables 1 and 2. The reduction in melt-viscosity at 338 K was lower than at 318 K however at 358 K was not a significant reduction compared with 338 K. Similar trends were observed when the operating pressure was increased from 28 Pa to 38 Pa at different temperatures as shown in Table 2 and Figure 7. Also, it was observed that there was not as significant decreases on the met-viscosity when the swelling temperature was 358 K compared with 338 K.

Tables 1 and 2 showed that additional reductions in melt-viscosity were observed by increasing the operating pressure from 28 Pa to 38 Pa at different temperatures. By increasing system pressure was observed to enhance the extent of the swelling effect while a maximum value (~440 Pa.s) was measured by increasing temperature, at the operating pressure of ~ 28 Pa. Finally, none of the supercritical CO₂ pretreatments swelling experiments were able to decrease the level of melt-viscosity of the 17 mole% styrene SIBS polymer into the optimum target value of < 100 Pa.s.

Table 1: Comparison of melt-viscosity measurements of CO₂ pretreated SIBS polymer at 28 Pa

Polymer	Pressure (Pa)	Temperature (K)	Melt viscosity (Pa.s)
17 mole% SIBS	Control and CO ₂ pretreated SIBS at 473 K		930
17 mole% SIBS	28 (4000 psi)	318 (45 °C)	580
17 mole% SIBS	28 (4000 psi)	338 (65 °C)	440
17 mole% SIBS	28 (4000 psi)	358 (85 °C)	460

Table 2: Comparison of melt-viscosity measurements of CO₂ pretreated SIBS polymer at 38 Pa

Polymer	Pressure (Pa)	Temperature (K)	Melt viscosity (Pa.s)
17 mole% SIBS	Control and CO ₂ pretreated SIBS at 273 K		930
17 mole% SIBS	38 (5500 psi)	338 (65 °C)	430
17 mole% SIBS	38 (5500 psi)	358 (85 °C)	400

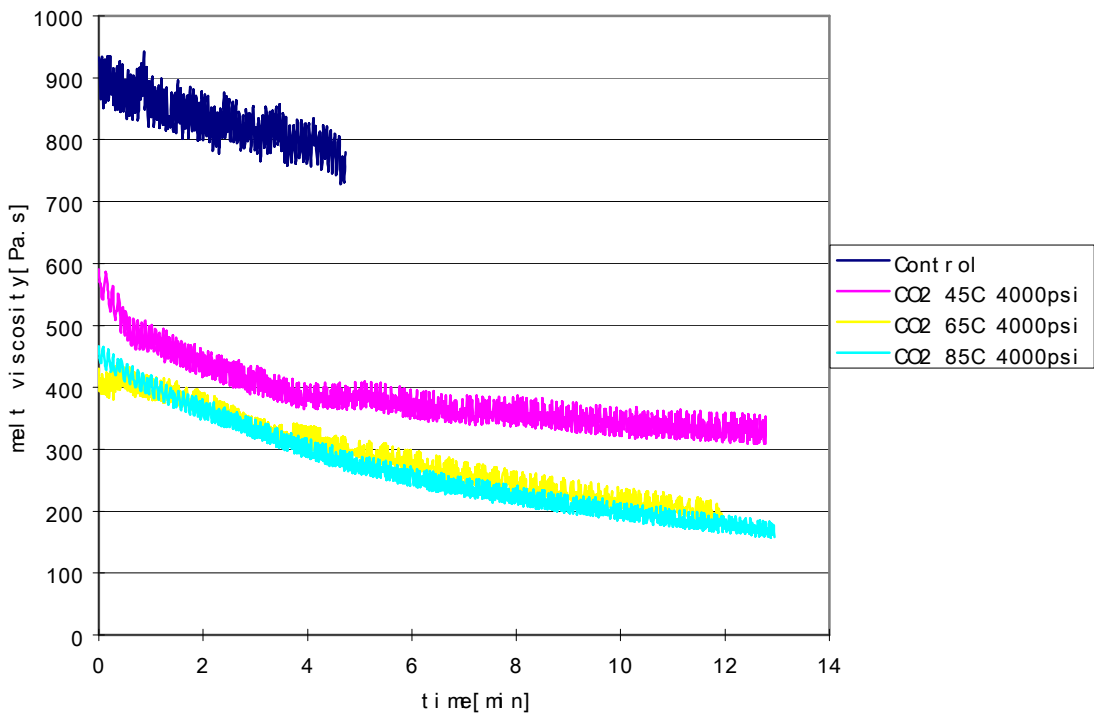


Figure 4: Melt-viscosity of SC-CO₂ pretreated SIBS under 28 Pa at different temperatures.

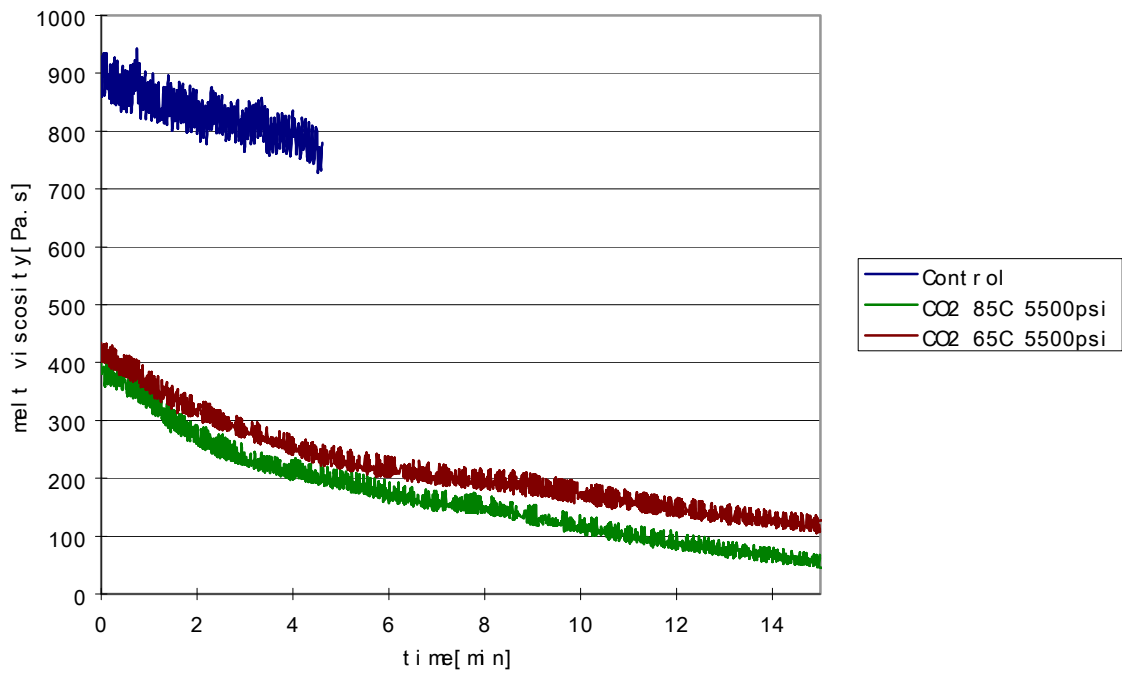


Figure 5: Melt-viscosity of SC-CO₂ pretreated SIBS under 38 Pa at different temperatures.

CONCLUSIONS AND REMARKS

This paper summarizes preliminary results obtained during the swelling experiments under supercritical CO₂. Laboratory apparatus was designed, constructed and tested with a novel styrene polymer at P = 28 Pa and T = 318 K for 86400 s. The control (polymer sample no exposure with CO₂) experiment showed that the melt-viscosity of 17 mole% styrene has an initial value of ~930 Pa.s. at 473 K. Range of key process variables has been identified and methods implemented for their quantifications.

Swelling experiments showed an initial trend that the diffusion of CO₂ at high operating pressures had a significantly effect on the melt-viscosity of the styrene polymer. Future work will be performed on process analysis, increased yield, and optimization of processing operating conditions to produce a better reproducibility of the reactions.

Preliminary results from this on-going research demonstrate that supercritical CO₂ assisted in the reduction of the melt-viscosity of the styrene polymer (SIBS) by several orders of magnitude. Supercritical CO₂ swells into the polymer matrix and it can extract low molecular weight solvent from the polymer-rich phase. Carbon dioxide is an excellent solvent for use as a processing aid (plasticizer) and then easily removed from a polymer through evaporation to obtain the original physical properties of the unplasticized polymer matrix. Carbon dioxide is inexpensive, non-toxic, non-flammable, environmentally friendly, and chemical inert under many operating conditions.

The investigation presented in this paper has focused on the study of the use of supercritical CO₂ induced plasticization of polymeric materials with specific emphasis on styrene-isobutylene-styrene (SIBS) copolymer. Our preliminary results showed that the diffusion of CO₂ at high operating pressures had a significantly effect on the melt viscosity of this novel polymer.

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