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# Enhancing the processability of plastics using carbon dioxide and water

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*The synergy obtained by combining supercritical carbon dioxide and superheated water enables polyethersulfone to be processed at significantly lower temperatures than in conventional processes.*

Polyethersulfone (PES) is notable for its use in a variety of high-performance applications (e.g., in the automotive, aerospace, biomedical, and water-purification industries). This wide application space is largely due to the polymer's high heat resistance, flame retardance, high mechanical strength, and antifouling properties.

Unfortunately, these properties also pose a challenge in terms of PES processing, since they make necessary the use of excessive temperatures and toxic solvents. Such conditions increase the production costs associated with PES and can degrade the material's properties. Moreover, the residual toxic and flammable solvents in PES products are hazardous.

To circumvent the use of high processing temperatures for PES, we have investigated the use of a melt-extrusion process that can be carried out at temperatures as low as 90°C below those used in conventional methods.[1] In our first approach, we coextruded the PES with small fractions of a surfactant (calcium stearate) to reduce its melt viscosity. The incorporated surfactant also significantly increased the material's flame retardance. However, surfactant additives are not desirable in some applications (e.g., ultrafiltration and fuel cells). To overcome these issues, we have more recently proposed the use of supercritical carbon dioxide ($scCO_2$)—which is environmentally safe and can reduce the processing temperature of many thermoplastics[2]—as a promising alternative. However, when used alone, $scCO_2$ typically produces closed-cell foams, which are not suitable for water-purification processes. Therefore, to further improve the polymer processability and to readily achieve closed- and open-cell foams, we have explored the use of $scCO_2$ and superheated water.

Known to be soluble in many polymers, $scCO_2$ effectively plasticizes the polymer and reduces its melt viscosity.[2] When first introduced, $scCO_2$ elevates the pressure and temperature of the polymer, causing it to swell. A valve is then opened to allow the $CO_2$ to exit the pressure vessel, thus causing the polymer to foam, in accordance with classical nucleation theory.[2] In contrast, superheated water ($shH_2O$, i.e., water above 100°C and at elevated pressures) exhibits a less polar character. Thus, $shH_2O$ achieves favorable interaction with the less polar PES. Consequently, $scCO_2/shH_2O$ comedia could enhance the

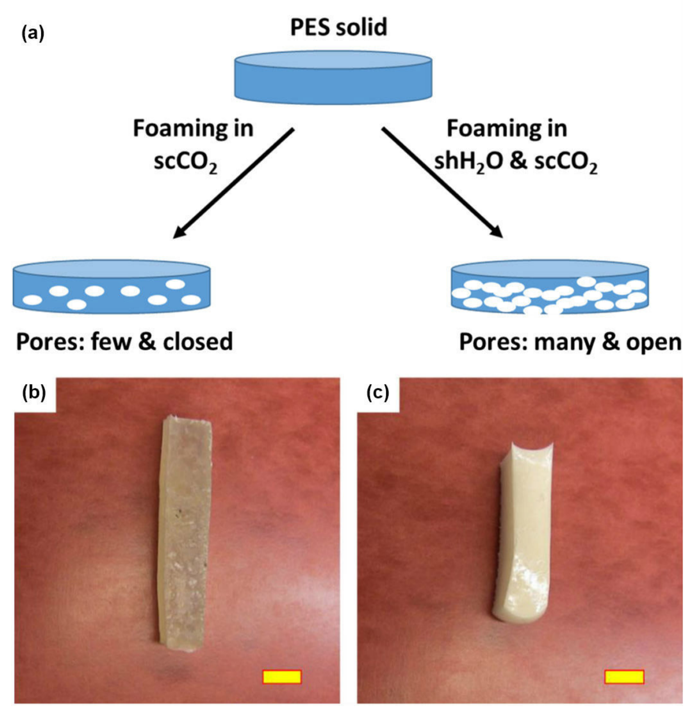


***Figure 1.*** *(a) Illustration showing the results obtained in polyethersulfone (PES) foamed with supercritical carbon dioxide ($scCO_2$), and with comedia of $scCO_2$/superheated water ($shH_2O$). Photographs show PES in the form of (b) a solid block (after treatment with $scCO_2$) and (c) foam (after treatment with $scCO_2/shH_2O$ comedia).*

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polymer's processability by inducing a greater plasticization (compared with $scCO_2$ alone) of the high-glass-transition-temperature polymer.

To explore the processability of PES using this approach, we foamed solid samples with $scCO_2$ alone, and with $scCO_2/shH_2O$ comedia.[3] In all experiments, we used a constant $CO_2$ saturation pressure (276 bar) and varied the temperature (from around 145 to 250°C). We found that $scCO_2$ alone could not produce a PES foam at 165°C—see Figure 1(a)—but that treatment with the $scCO_2/shH_2O$ comedia produced a uniform PES foam—see Figure 1(b)—with 52% porosity.[3] This result provides a clear indication of the superior plasticization effect of the $scCO_2/shH_2O$ combination.

Further effects on the material properties that arise due to the $scCO_2/shH_2O$ comedia are shown in Figure 2. Our results for the temperature-dependent porosities of the PES foams, after treatment with the various media, show that successful foaming was achieved using the $scCO_2/shH_2O$ comedia at 85°C below the 225°C glass transition temperature ($T_g$) of PES. Interestingly, at higher temperatures (>180°C)—i.e., under which $scCO_2$ is able to produce PES foams—the porosities achieved in samples processed using $scCO_2/shH_2O$ were significantly higher (by ~25%). We also found that, for temperatures below the $T_g$ of PES, a combination of argon and $shH_2O$ produced foams with lower porosities than the $scCO_2/shH_2O$ comedia. Thus, there is likely a favorable interaction between $scCO_2$ and $shH_2O$ that enhances the processability of PES.

Finally, to investigate the morphological differences of the PES foams, we analyzed scanning electron micrographs of their cross-sections (see Figure 3). The images show that $scCO_2$ alone produced closed cells and a low cell density. In contrast, and in addition to the

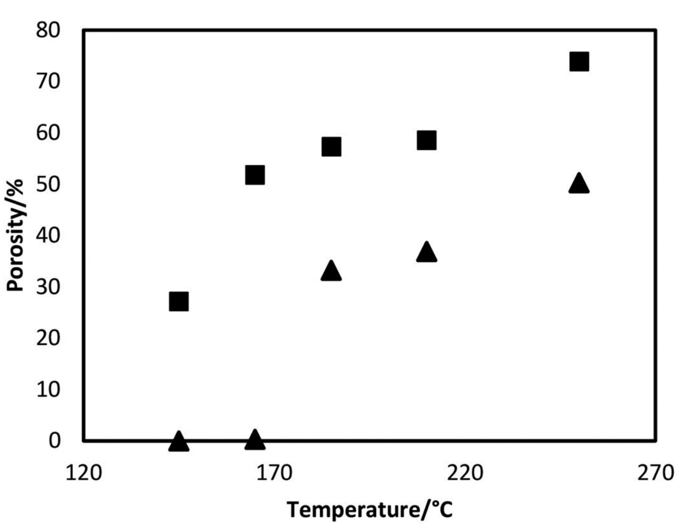


*Figure 2.* *Porosity vs. foaming temperature in PES processed with $scCO_2$ (triangles) and $scCO_2/shH_2O$ (squares).*

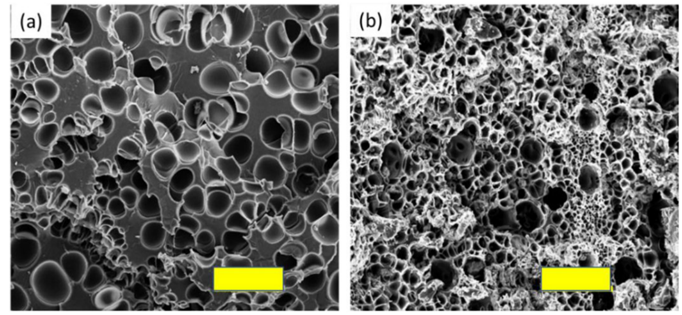


*Figure 3.* *Scanning electron micrographs of cross sections of PES foamed with (a) $scCO_2$ and (b) $scCO_2/shH_2O$. Scales are 50µm.*

enhanced processability, $scCO_2/shH_2O$ produced an open-cell morphology. To investigate the continuity of the open pores obtained using $scCO_2/shH_2O$, we tested the water permeability of a 1mm-thick disc-shaped membrane cut out of the foamed PES sample with a cylindrical geometry. We recorded water fluxes of over $600L/m^2hbar$ for the membranes. Such water fluxes, comparable to those of commercial polymeric membranes, indicate that $scCO_2/shH_2O$ is promising for producing filtration and purification membranes.

In summary, we have found that the use of $scCO_2/shH_2O$ comedia offers a cost-effective and green approach to enhancing the processability of PES via plasticization. Our approach enables processing to be carried out at significantly lower temperatures compared with conventional methods, thus limiting the release of hazardous byproducts. Using the $scCO_2/shH_2O$ comedia, we achieved remarkable PES foaming at temperatures as low as 85°C below its $T_g$.[3] Furthermore, the benign constituents of the comedia—as well as the open-cell morphology that it allows—are promising for biomedical and purification applications. In the next stage of our work, we will focus on applying the $scCO_2/shH_2O$ comedia to other thermoplastics. We will also investigate the use of $scCO_2$ with other solutions.

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Alan J. Lesser is a professor of polymer science and engineering, and an expert in polymers and composite processing using $scCO_2$. He has produced several peer-reviewed articles, patents, and conference proceedings. He is the editor-in-chief of a number of journals (*Polymer Engineering & Science, Polymer Composites,* and *Journal of Vinyl and Additive Technology*) and is a member of the advisory board of the *Journal of Applied Polymer Science*. He has chaired and co-chaired Society of Plastics Engineers events, including ANTEC, on several occasions.

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