

Polymer Processing with Supercritical Fluids

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Received March 16, 2000;

Revised manuscript received April 19, 2000

Abstract—Supercritical fluids have a unique and valuable potential for the enhanced processing of many materials. This review describes research in the applications of supercritical fluids to polymer processing. The ability of supercritical carbon dioxide to swell and plasticize polymers is crucial to the impregnation, extraction, and modification of polymeric materials. This plasticization also reduces viscosity and facilitates the processing of polymers due to lower shear stresses. Spectroscopy plays an important role in probing these interactions at a molecular level and to follow *in situ* the processes of CO₂-induced plasticization and the crystallization of polymers. Opportunities exist for improving the processing of many polymeric-based materials ranging from textile to food and biomaterials. The implications of interactions between supercritical carbon dioxide and polymers for drying, dyeing, foaming and extrusion are also discussed with an outlook for further opportunities in this and related areas of polymer processing.

I. INTRODUCTION

Supercritical fluids (SCFs) have unique properties that may enhance many types of chemical process operations. An additional advantage of using SCFs stems from the fact that they may replace many environmentally harmful solvents currently used in industry. In particular, SCFs represent an attractive alternative to organic solvents for use as additives in polymer processing. For example, supercritical carbon dioxide (scCO₂), which is by far the most widely used SCF, is relatively cheap, nontoxic, and nonflammable and has zero ozone-depletion potential. Moreover, the fact that CO₂ is a gas under ambient conditions makes its removal from the polymeric product very easy, avoiding, for example, the costly processes of drying or solvent removal, which is very important in the processing of polymer-based materials.

But what are the properties of an SCF? A supercritical fluid is defined as a substance above its critical pressure and temperature. However, there is still no apparent distinction between a high-pressure gas and an SCF because, under all circumstances, such a fluid will occupy the full volume of its container, demonstrating the typical behavior of a gas. Nevertheless, such a fluid is usually not called a high-pressure gas but a supercritical fluid. The reason is that one cannot liquefy such a fluid under any pressure once it is heated above its critical temperature (it should be noted, however, that it can still be solidified at extremely high pressures!). No phase separation occurs for any substance at pressures or temperatures above its critical values,

thus, one should never see a meniscus once the substance has become supercritical (Fig. 1). In other words, the critical point represents the highest temperature and pressure at which gas and liquid can coexist in equilibria. However, it is very important to note that this definition is for a pure substance.

Once a small amount of another soluble substance is introduced into the SCF, its critical parameters could change depending on the concentration of the additive. In addition, the critical parameters of the fluid might

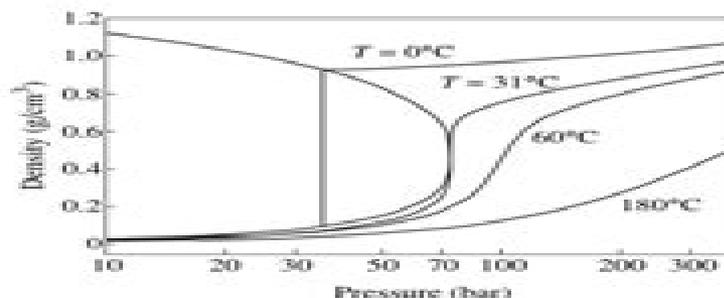


Fig. 1. Liquid–vapor phase diagram of carbon dioxide showing 4 isotherms: 0°C (below the critical temperature), 31°C (critical temperature), 60°C and 180°C (above the critical temperature). Note that at a temperature above 31°C and a pressure of 73 bar only one phase is present.

¹ This work was submitted by the author in English.

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