

Polymer Processing with Supercritical Fluids

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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 equilibrium. 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

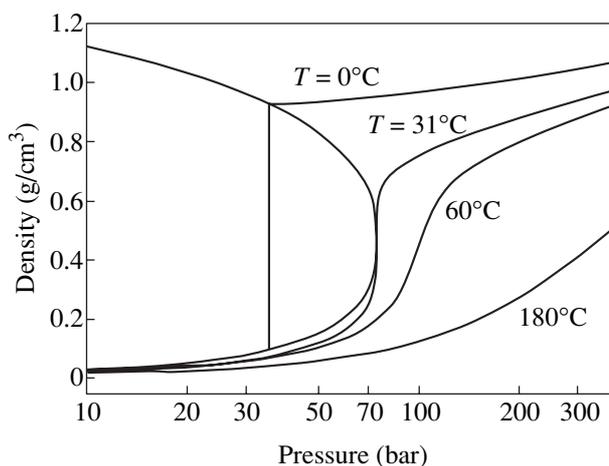


Fig. 1. Liquid–vapor phase diagram of carbon dioxide showing 4 isotherms: 0°C (below the critical temperature), 31°C (critical temperature), 60°C and 180°C (above the critical temperature). Note that at a temperature above 31°C and a pressure of 73 bar only one phase is present.

¹ This work was submitted by the author in English.

also change when it is confined within a very small space. Nevertheless, the critical temperature can rise just a few degrees due to the confined space, thus still preventing phase separation when one operates at temperatures several degrees above the critical value for a specific substance. Single-phase solvents play an important role in many processes where phase separation would be undesirable because of the appearance of meniscus and of capillary forces that could play a negative role in some of the processes of mass transport (e.g., drying) within porous materials. CO₂ has a critical temperature of $T_c = 304.15$ K, and the critical pressure $P_c = 7.38$ MPa; the critical parameters of other substances can be found in the book by Reid *et al.* [1].

Although the SCF remains as a single phase, its density can be easily "tuned" from gas to liquid values merely by changing the pressure of the fluid. This remarkable "tunability" of the solvent power of an SCF without changing its molecular structure makes an SCF a unique solvent for adjusting many facets of process operations via "density tuning." SCFs exhibit a number of interesting phenomena, especially in close proximity to the critical point due to their extremely high compressibility, thus making the study of fundamental properties of SCFs an exciting field of research. This review, however, is not intended to be a comprehensive analysis of the current state of the science and engineering of SCFs; rather it provides a concise overview of the applications of SCFs to polymers and related areas. For recent reviews on the topics describing the research of fundamental properties of SCFs, the reader is directed to recent reviews [2–4].

The study of SCFs began in the 19th century, but it was only in the 20th century when the advantages of SCFs for chemical processes began to be realized. Jessop and Leitner [4] have recently provided a concise historical essay on the early applications of SCFs and mentioned, quite rightly, the names of C. Cagniard de LaTour, M. Faraday, D.I. Mendeleev, T. Andrews, van der Waals, and others who made important contributions to establish the research on supercritical fluids. It should be added that Soviet scientists also made a significant contribution to the development of supercritical science. Thus, Krichevski predicted the existence of large negative molar volumes in infinite dilute solutions near the critical point [5, 6], which was confirmed later experimentally [7, 8]. Unfortunately, these groundbreaking studies were largely ignored at the time by Western scientists. In contrast, a paper by Tsekhan-skaya *et al.* [9] on the solubility of naphthalene in scCO₂ became a reference point for many further studies on solubilities in supercritical fluids.

Pioneering SCF work of relevance to polymer processing was performed by V.N. Ipatiev at the beginning of the 20th century; he discovered that when ethylene is heated above its critical temperature in a high-pressure autoclave, it can oligomerize noncatalytically into higher molecular mass alkanes. Three decades later,

ICI developed this process further, leading to the manufacture of polyethylene from supercritical ethylene using oxygen as the initiator. A notable development of this process was then made by DuPont, when the "tunable" density of the supercritical ethylene was utilized for polyethylene fractionation via selective precipitation [10, 11]. Over the past decade, it has been shown that CO₂ is an attractive alternative to traditional organic solvents used in polymer synthesis. DuPont has recently announced a major investment into the use of supercritical CO₂ for producing fluorinated polymers.

This review is intended to stimulate further research into applications of supercritical fluids to polymer science and engineering. In this context, one should distinguish the use of supercritical fluid and high-pressure gases in polymer processing from other promising methods of modifying polymers and polymer composites with the use of high pressures alone [12]. The role of supercritical fluids in polymer synthesis has been the subject of several recent reviews. Therefore, polymer processing rather than synthesis will be the focus here. Furthermore, the topics of polymer solubility in supercritical solvents and the phase behavior of polymer-supercritical fluid solutions will not be discussed in this article, as these topics have been discussed and reviewed in a series of recent papers [13–20].

The references listed in this review article are by no means exhaustive, as there have been several hundred articles published during the past few years covering subjects relevant to supercritical fluids and polymers. Therefore, Table 1 (below) serves as a guide to previously published reviews on related topics involving applications of SCFs in polymer science and engineering.

II. PLASTICIZATION OF POLYMERS WITH SUPERCRITICAL FLUIDS

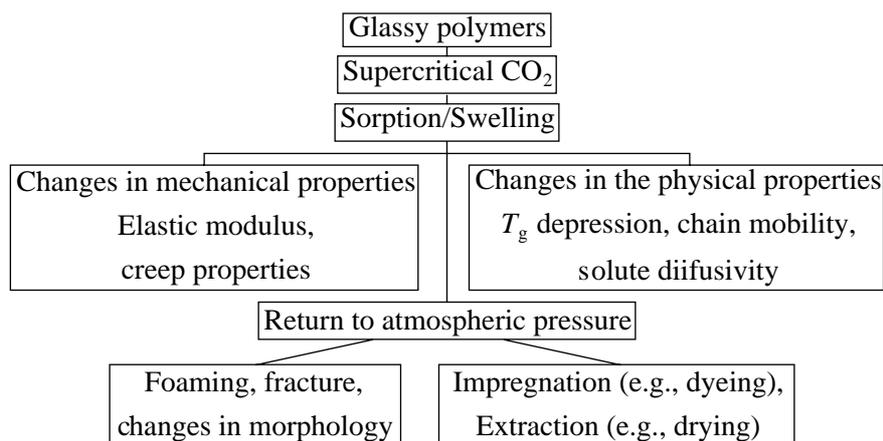
The motivation for using SCFs in polymer processing stems not just from the environmental impetus for their use as the benign solvents. As explained above, SCFs have a number of unique properties that could be utilized for polymer synthesis in these media. In addition, it is the molecular structure of some specific fluids, primarily supercritical CO₂, that plays a major beneficial role in polymer processing. The sorption of scCO₂ into polymers results in their swelling and changes the mechanical and physical properties of the polymers. The most important effect is the reduction of the glass transition temperature (T_g) of glassy polymers subjected to scCO₂, often simply called plasticization. The plasticization of polymers induced by scCO₂ has an impact on many polymer-processing operations, which will be discussed in this review. These include viscosity reduction for polymer extrusion and blending, enhancement of the diffusion of additives through polymer matrices for impregnation and extraction, enhancement of monomer diffusion for polymer synthesis,

Table 1. Recent books and review articles in supercritical fluids processing

Year	Titles of recent books and reviews in the field of SCF processing	Reference
1986/1994	Supercritical Fluid Extraction: Principles and Practice	[21, 22]
1987	Process Polymers with Supercritical Fluids	[23]
1991	Biocatalysis in Supercritical CO ₂	[24]
1991	Supercritical Water—a Medium for Chemistry	[25]
1993	Supercritical Fluid Engineering Science: Fundamentals and Applications	[26]
1995	Theoretical Foundations of the Use of Supercritical Fluids in Extraction, Separation, and Concentration Processes	[27]
1995	Reactions at Supercritical Conditions: Applications and Fundamentals	[28]
1995	Vibrational Spectroscopy in Supercritical Fluids: From Analysis and Hydrogen Bonding to Polymers and Synthesis	[29]
1995	Innovations in Supercritical Fluids: Science and Technology	[30]
1995	Chain Polymerization in Inert Near- and Supercritical Fluids	[31]
1996	Supercritical Fluids as Solvents for Chemical and Materials Processing	[2]
1996	Polymers and Supercritical Fluids	[19]
1996	Polymer Synthesis and Characterization in Liquid/Supercritical Carbon Dioxide	[32]
1996	Supercritical Fluid Chromatography and Extraction	[33]
1997	Application of FTIR Spectroscopy to Supercritical Fluid Drying, Extraction, and Impregnation	[34]
1997	Polymerizations in Liquid and Supercritical Carbon Dioxide	[35]
1997	Carbon Dioxide as a Continuous Phase for Polymer Synthesis	[36]
1998	Separations and Materials Processing in Solutions with Dense Gases	[37]
1998	Fundamentals of Supercritical Fluids	[3]
1998	Thermodynamic Aspects of Supercritical Fluids Processing: Applications to Polymers and Waste Treatment	[38]
1998	Separations and Materials Processing in Solutions with Dense Gases	[37]
1999	Chemical Synthesis Using Supercritical Fluids	[4]
1999	Polymerizations in Dense Carbon Dioxide	[39]
1999	Phase Behavior of Polymers in Supercritical Fluid Solvents	[13]
1999	Polymerization in Supercritical Carbon Dioxide	[40]
1999	Fluides Supercritiques et Matériaux	[41]
1999	Supercritical Fluid Processing: A New Route for Materials Synthesis	[42]
1999	Enzymatic Catalysis	[43]
1999	Supercritical Enhanced Processing	[44]
1999	Supercritical Fluids in Separation Science: Dreams, Reality, and Future	[45]
1999	New Directions in Inorganic and Metal-Organic Coordination Chemistry in Supercritical Fluids	[46]
2000	Polymer Synthesis and Processing Using Supercritical Carbon Dioxide	[47]
2000	Supercritical Fluids for Sustainable Development	[48]
2000	Use of Supercritical Fluids for Different Processes Including New Developments: A Review	[49]

foaming of polymers, and changes in polymer morphology due to induced crystallization. The overall

effect of scCO₂ on glassy polymers is presented schematically below:



The plasticization of polymers is characterized by increased segmental and chain mobility and by an increase in interchain distance. The plasticizing effect of CO₂ is the result of the ability of CO₂ molecules to interact with the basic sites in polymer molecules, for example, the interaction between CO₂ and the carbonyl group in PMMA, which has been suggested to be of the Lewis acid–base type [50]. It has also been shown experimentally that such interactions between CO₂ and polymer functional groups reduce chain–chain interactions and increase the mobility of polymer segments [51]. Thus, increased mobility of the ester groups in PMMA was observed at 40°C when a PMMA film was subjected to scCO₂ at a pressure of to 10 MPa. In the absence of CO₂ mobility of the ester group is only observed when the PMMA is heated above its glass transition temperature (105°C). This example demonstrates how the effect of scCO₂ mimics the effect of heating the polymer. Evidence of CO₂-induced motion of phenyl rings in polystyrene has also been recently observed via NMR [52]. The spectroscopic evidence for interaction between CO₂ and polymers [50] provides molecular-level support for suggestions by Sanders *et al.* [53] and by Handa *et al.* [54] on the mechanism of CO₂-induced plasticization of PMMA. Spectroscopy also provides evidence [50] for the weak CO₂–fluorine interactions proposed by Shah *et al.* [55] and also detected recently via NMR [56, 57] in solutions of fluoroacrylates dissolved in scCO₂. These observations are significant in that increased mobility in glassy polymers can be achieved using scCO₂ at much lower temperatures than would otherwise be needed. Plasticization of polymers is accompanied by the swelling of the polymer matrix with a consequent increase in the free volume of the polymer. It is important to realize that the specific interactions discovered between CO₂ and polymers also explain the high solubility of CO₂ in many glassy polymers used in membrane applications [58]. This proposal is consistent

with the observation of Koros [59], who found that the increase in concentration of carbonyl or sulfone groups in various compounds, including several polymers, resulted in a corresponding increase in the solubility of CO₂ relative to that of CH₄; molecules of CH₄ lack the ability of CO₂ to form specific interactions with functional groups. Spectroscopic evidence of specific interactions between CO₂ and carbonyl groups in polymers has been supported by recent *ab initio* calculations for CO₂/poly(ethylene terephthalate) [60]. The solubility of CO₂ in polymers has been discussed in a number of recent publications [61–70].

CO₂-induced plasticization of polymers has been studied by a variety of methods including gas sorption and permeability [53, 71, 72]; polymer swelling [73, 74]; creep compliance [73, 75, 76]; ultrasonic measurements of Young's modulus [77]; indentation [78]; high-pressure DSC [54, 58, 79–82]; *in situ* FTIR spectroscopy [50, 51]; fluorescence [83]; NMR spectroscopy [52, 84]; X-ray diffraction [85]; dielectric relaxation [86]; dynamic mechanical response [87]; chromatography [88, 89]; molecular dynamics simulations [90]; and positron-annihilation-lifetime spectroscopy [91, 92].

The thermodynamics of polymer–gas mixtures, polymer–SCF interactions, and the theory of glass transition in polymers induced by SCFs and high-pressure gases has received much attention in recent years. Thus, Chow's analysis [93] of polymer plasticization was based on classical and statistical thermodynamics. It was assumed that polymer segments remain completely immobile below T_g , while small plasticizers (e.g., gas molecules) are able to move and fill the holes within the polymer matrix. This analysis is based on the assumption by DiMarzio and Gibbs [94] that the configuration entropy is zero at some second-order transitions. Chow demonstrated that his model provides a reasonable explanation for the reduction in T_g for polystyrene plasticized with high-pressure gases [75]. A similar approach was used by Barbari and Conforti [95], who

also reviewed recent theories of gas sorption in glassy polymers [96]. The Flory–Huggins lattice fluid theory developed by Sanchez and Lacombe [97, 98] and Panayiotou and Vera [99] appear to be particularly useful in applications to polymers plasticized with high-pressure gases and supercritical fluids. This theory has been developed further and was recently applied to plasticization of glassy polymers [70, 100, 101] and to modeling of solute partitioning between crosslinked polymers and supercritical fluid phases [102–104]. A comprehensive analysis of the molecular thermodynamic approach to predict the T_g reduction in polymer–supercritical fluid systems has also been reported [105]. A statistical thermodynamic approach was developed by Dong and Fried [106] to account for the mixing of polymers, small molecules, and holes, which are different in size. They conclude that plasticizing efficiency is largely determined by polymer–plasticizer interactions and plasticizer segment size. This approach shows that highly soluble CO_2 is expected to be a highly efficient plasticizer due its small size although its interactions with polymer are quite weak.

III. IMPLICATIONS OF CO_2 -INDUCED PLASTICIZATION OF POLYMERS

(i) Extraction and Drying

The use of SCFs in extraction and separation has been the focus of several recent reviews and books [45, 107–112]. Supercritical fluid extractions (SFE) is also the title of the “classic” book on supercritical fluids, which offers an excellent introduction to their properties and phase behavior [21]. A comprehensive review on the thermodynamics of supercritical fluid extraction [27] and a review of the applications of supercritical fluid chromatography [113] have been published in the Russian literature. Therefore, these topics will not be discussed in detail in this article.

The most common example of SFE is the use of scCO_2 for decaffeination of coffee. More than a hundred thousand tons of decaffeinated coffee are produced per year in the world using scCO_2 . Coffee beans are just a particular example of a much broader range of matrices used in supercritical extraction. Polymeric matrices represent one of the most important materials in which the advantages of supercritical fluids can be fully utilized. Thus, high diffusivity and low surface tension of SCFs combined with polymer plasticization and swelling considerably enhances the rates of the extraction of residual solvent, oligomer or monomer, or other unreacted species from polymeric samples. Analytical applications of supercritical fluid extraction from polymeric samples have been covered in a review article by Vandenburg *et al.* [109], while Dean [110] has discussed SFE in the context of other extraction techniques used in environmental analysis. *In situ* spectroscopic monitoring of SFE and drying has recently been reviewed [34]. Recent applications of SFE to

polymeric systems include the extraction of copper ions using scCO_2 -soluble chelating agents [114], the use of scCO_2 in a degreasing process in the leather industry [115], and the development of quantitative analysis of additives in polypropylene [116].

(ii) Impregnation and Dyeing

The interest in the supercritical fluid impregnation of polymeric materials stems from the opportunity to utilize SCF properties (high diffusivity, low surface tension, the ease of solvent recovery, etc.) for preparing new polymeric materials. The most commonly used supercritical fluids are solvents which can diffuse out of the polymer easily once the pressure is reduced to ambient values; thus, no solvent residues are left in the impregnated polymer sample. Pioneering reports by Sand [117] and Berens *et al.* [118] where the advantages of SCFs have been demonstrated to infuse or deposit solute molecules dissolved in an SCF into a polymer matrix exposed to such a solution. These works played an important role in stimulating interest in this area. Polymers which have been impregnated using scCO_2 include polystyrene [118, 119]; poly(methylmethacrylate) (PMMA) [50, 51, 118–122]; poly(vinyl chloride) (PVC) [118, 123]; polycarbonate [118, 119, 123–125]; polyethylene [117, 125–129]; poly(tetrafluoroethylene) (PTFE) [123]; poly(chlorotrifluoroethylene) (PCTFE) [123, 125, 130]; poly(4-methyl-1-pentene) (PMP) [125]; nylon [125]; poly(oxymethylene) [125]; poly(ethylene terephthalate) (PET) [131–136]; poly(dimethylsiloxane) (PDMS) [103, 104, 120, 137, 138]; and polyimides [139, 140]. Solutes used in impregnating polymers range from metal carbonyl complexes to organic dyes.

It is important to distinguish between two different mechanisms of supercritical fluid impregnation of additives into polymer matrices. The first involves the simple deposition of a compound soluble in an SCF into the polymer matrix. This happens when a polymer matrix is placed in the cell or vessel and is subjected to an SCF containing a solute; when the cell is depressurized, CO_2 molecules quickly leave the polymer matrix, leaving the solute molecules trapped inside the polymer matrix [126, 128, 129, 141–143]. This approach is particularly effective for solutes that are highly soluble in SCFs such as ferrocene [131], or when glassy polymer matrices are used [34], since the ability of scCO_2 to plasticize the polymer matrix for enhanced solute infusion is also beneficial.

A different mechanism applies to impregnation of compounds having very low solubility in the SCF phase. In such cases the high affinity of these solutes for certain polymer matrices can result in the preferential partitioning of a solute in favor of polymer over fluid [51, 119, 120, 131]. The high partition coefficient of polar dye molecules played a crucial role in the success of supercritical fluid dyeing [131, 133, 136, 144, 145].

Dyeing of polymeric materials with the use of supercritical fluids represents a particular but very important case of supercritical fluid impregnation. Supercritical fluid dyeing has been reviewed recently, and the first pilot plant has been built in Germany [133, 135, 146–148]. The interest in supercritical fluid dyeing is motivated by the environmental advantages since the use of supercritical fluid could replace water in dyeing processes. The ease of recovering an SCF simply by reducing the pressure of the solvent, and the possibility of using the SCFs repeatedly without needing to clean the solvent (since the dye will precipitate from SCF solvent once the pressure is significantly reduced) provides a strong argument for commercializing this process.

Supercritical fluid impregnation of organometallic compounds into polymer matrices has been reviewed [29]. Taylor and coworkers [139, 140] have extended this approach to produce polymer films with highly reflective metallized surfaces. Their work was motivated by potential applications of polymer films with highly reflective surfaces in aerospace devices. Polyimides with a highly reflective surface are particularly suitable candidates in such applications. With that in mind, Rosolovsky *et al.* [139] impregnated a number of polyimide films by infusing silver complexes (1,5-cyclooctadiene-1,1,1,5,5,5-hexafluoroacetylacetonato)silver(I), and then thermally curing those films at 300°C. This process resulted in the formation of a silver mirror on both polymer film surfaces. They established the nature of silver and its surface distribution on the surface and within the polymer film with the use of microscopy and surface analysis techniques. They also mentioned that the large number of carbonyl groups in the polyimides played a role in relatively large CO₂ solubility, thus allowing one to perform the infusion of the silver complexes from this solvent [139]. As noted above, the carbonyl functional groups in polymers may weakly interact [50] with CO₂ molecules, thus enhancing CO₂ solubility in polyimides. There are, of course, other factors that play a role in this process, such as the accessibility of these groups for CO₂, polymer free volume, and morphology; therefore, the effectiveness of CO₂-assisted infusion was not as great as the authors initially hoped as they detected that only a shallow surface layer was impregnated. It should be noted that if the authors of this work had increased the duration of this process and had done it at higher temperatures, one would have expected effective impregnation of the bulk of the polymer film. However, for creating materials with reflective coatings, the modification of the bulk of the material was not required.

Supercritical fluid impregnation of platinum complexes has been used for preparation of metal-containing nanocomposite materials. In the latter case, the reduction of the metal precursor impregnated into the polymer matrix (PMP and PTFE) led to the formation of metal clusters with size ranging from 10 to 100 nm [149]. The authors reported uniform distribution of

these clusters throughout the film. Popov *et al.* has used supercritical fluid impregnation of polyarylate (aromatic polyester) with copper(II) hexafluoroacetylacetonate, and studied tribological properties of the modified polymers. Copper oxide could be formed in the polymer matrix, and its presence presumably plays a role in improved tribological properties (such as wear resistance) of the treated polyarylate.

Supercritical CO₂ dissolved in glassy polymers significantly influences mass transport properties of solutes in the polymer matrix. Berens *et al.* [118] have shown that impregnation of solutes into polymers is accelerated in scCO₂-swollen polymers. Cotton *et al.* [150] reported an increase in diffusivities of additives in semicrystalline polypropylene in the presence of scCO₂. Dooley and coworkers observed an increase of 6 orders of magnitude for the diffusivity of ethylbenzene in polystyrene subjected to supercritical carbon dioxide [151]. Paulaitis and coworkers [152] used forced Rayleigh scattering to measure diffusion coefficients of azobenzene in polystyrene. They discussed the enhancement in solute diffusion in this system in the context of plasticization and subglass relaxations associated with local polymer dynamics. It has been shown that the enhancement in solute diffusion cannot be accounted exclusively for reduction of T_g in polystyrene, thus indicative that subglass transitions play a role. Moreover, they suggested that solute–CO₂ interactions may play a role in the process. This suggestion is consistent with the proposal by Kazarian *et al.* [51], who described the role of scCO₂ in a similar process as a “molecular lubricant.” This terminology was the result of comparing diffusion rates of DR1 between scCO₂-swollen PMMA and PMMA heated above its T_g . The temperature deviations of these experiments from T_g in both cases were similar, whereas the rates of diffusion in scCO₂-swollen PMMA were higher than those in the heated polymer [119]. However, it is not just the swelling of a polymer matrix that facilitates the mass transfer of dyes under these conditions. Indeed, it has been shown that the presence of CO₂ in the polymer matrix significantly enhances the diffusivity of water in polymers. Vincent *et al.* [121] compared the diffusion of water in CO₂-swollen PMMA with that of lyophilically swollen PMMA. It was concluded that free volume theory alone cannot describe the differences between the two systems. The presence of CO₂ in a swollen matrix seems to play a role in solute mass transport process, presumably by solvating solutes and, thus, facilitating the diffusion. Based on these observations and the fact that CO₂ is a relatively small molecule compared to most solute molecules (e.g., dyes), the action of scCO₂ was described as molecular lubrication [51, 131].

A recent report on diffusion of dyes in PET subjected to scCO₂ also indicate that polymer swelling and dye structure play a role in the mass transport mechanism under these conditions. By contrast, swelling was

not considered to play a role in another study of the kinetics of supercritical fluid impregnation [153]. Convective diffusion mechanism in mass transport of solutes within polymer matrices subjected to supercritical fluids has been recently discussed [154, 155].

Another type of surface modification of polymeric materials involves the grafting of a specific group onto polymer surfaces. This was achieved in the free-radical grafting of maleic anhydride onto poly(4-methyl-1-pentene) using scCO_2 as solvent [156]. Sparado *et al.* grafted maleic anhydride onto a polypropylene surface via γ -irradiation in an scCO_2 environment [157]. In this work the effect of scCO_2 -induced polymer swelling was utilized. The grafting of isocyanato-isopropyl groups onto semicrystalline poly(ethylene-co-vinylalcohol) using scCO_2 has recently been achieved [158].

One of the most interesting applications of supercritical fluid impregnation is the modification of polymers via the infusion of a monomer and an initiator into a CO_2 -swollen polymer matrix with subsequent polymerization of a monomer within the polymer matrix. Berens *et al.* [124] used scCO_2 to impregnate polycarbonate with poly(ethylene glycol) diacrylate and a photoinitiator followed by UV photolysis of the system under the ambient condition, which resulted in the reaction of acrylates within the matrix of polycarbonate. Watkins and McCarthy extended this approach to the synthesis of a variety of polymer blends by infusion of styrene monomer and an initiator into PCTFE, PMP, polyethylene, nylon 66, poly(oxyethylene), and bisphenol A polycarbonate [125]. Recently, this approach has been extended to combine impregnation and *in situ* polymerization for the systems including polycarbonate, PVC, and PTFE as polymer matrices; and styrene, methyl methacrylate, and methacrylic acid as monomers [123]. Polymerization within CO_2 -swollen polymer matrices has been achieved using azoisobutyronitrile as an initiator. As in other cases, scCO_2 acted as a plasticizer for enhancing diffusion of a monomer within scCO_2 -swollen polymer matrices. The authors have shown that PTFE has demonstrated the least ability to be modified by this technique due to its limited swelling capability. Muth *et al.* [123] have also shown that this approach can be restricted in some cases to a certain penetration depth, thus modifying surface layers but not the bulk of the polymer matrices. As in the works of Taylor and coworkers [139, 140], this could actually be an advantage in cases where only surface modification is required. Mandel and Wang [159] report using a solution of polymers diluted with scCO_2 for powder-coating applications. They report that Ferro Corporation has developed the so-called VAMP process used in the production of powder coatings, new polymers and polymer additives, and various biomaterials [159]. Formation of polymer powders by rapid expansion of solution with consequent precipitation, and the morphology of these powders, have also been reported [160]. Lee and Kander discuss applications of

SCF technology to high-performance polymers, in particular, to processing of PEEK and poly(phenylsulfones) [161]. Applications of supercritical fluids for coatings and impregnation of porous and fibrous substrates (e.g., polymer fibers, wood, composite and ceramic materials) with various chemicals are discussed in recent article [143].

Supercritical fluids have great potential in coating applications due to the reduction or elimination of volatile organic compound emissions during spray painting [162, 163]. Union Carbide has developed a process for spray coatings using scCO_2 as a solvent. Hay [163] has recently reviewed the process and its implications. This process is believed to have a number of advantages over the alternative approach in powder coatings such as improved film coalescence and quality of the coating. The coating materials are dissolved in scCO_2 and subsequently released through a specially designed nozzle from the spraying head as an atomized spray. It is reported that this process produces a highly uniform spray with a narrow droplet size distribution. Unfortunately, the solubility of many compounds used in coating systems is quite low in scCO_2 . Therefore, methanol or another organic cosolvent is usually added to an scCO_2 solution to increase the solubilities of these compounds. The alternative to the addition of cosolvents is the use of stabilizers in these processes similar to their use in dispersion polymerization reactions. It was shown that fluorinated acrylate polymers [164] may act as an effective stabilizer in such reactions. There are other stabilizers, such as block or graft copolymers, that could be used in dispersion polymerization or in mixtures for the supercritical fluid coating processes mentioned above. Thus, Hay [165] is developing dispersion coatings based on the concept of exploring suitable dispersion stabilizers. This would lead to the elimination of emissions of organic solvent in coating processes with environmentally benign technology. Applications of this technology range from polymer and paper coatings to leather and biomaterials.

Recently, Johnston and coworkers [166] reported the successful use of suspensions of poly(2-ethylhexyl acrylates) in scCO_2 formed by dispersion polymerization with a PDMS-based surfactant. These suspensions were sprayed through nozzles from 30 to 100 μm in diameter; the suspensions formed uniform circular films. Johnston and coworkers [166] studied various factors (nozzle size, spray duration, spray distance, fluid velocity, etc.) which may affect the quality and pattern of films obtained by this approach. They report that the spray pattern changed little as a function of nozzle size but changed significantly with spray distance and fluid velocity. They also pointed out that scCO_2 -induced viscosity reduction of the dispersed phase is crucial for producing fine droplets in the spray atomization process and for droplet coalescence and film formation on the surface. Johnston and coworkers [166] also compare their approach with other spray methods,

for example, with the mentioned Unicarb process and rapid expansion from supercritical solvent (RESS) process. They outlined a number of advantages of using suspensions for polymer coatings applications, and thus, further development and practical utilization of this approach is expected.

SCFs have recently been used for preparing polymer substrates with drugs. Scientists from 3M Company have recently developed an interesting modification for supercritical fluid impregnation of polymeric materials [167]. In their process, scCO_2 is used as an agent to enhance the diffusivity of water soluble solutes into various substrates by performing the process in water pressurized with scCO_2 .

(iii) Polymer Blends

Previous examples have demonstrated that SCF impregnation can be used to prepare polymer blends. This has been achieved by impregnating the monomer and initiator from an scCO_2 solution into a polymer matrix with subsequent polymerization of the monomer within the matrix. This route has led to the formation of polymer blends not easily obtainable by conventional methods. Thus, Muth *et al.* [123] prepared PVC containing poly(methacrylic acid) via scCO_2 impregnation and claimed that it would not be possible to form this system using mixing in a high temperature extruder. In fact, scCO_2 could probably be used to achieve the mixing of these components in an extruder at lower temperatures. This approach to polymer blending will be discussed later in this section. The properties of the polymer blends obtained via polymerization within the scCO_2 -swollen polymer matrices can be quite different from the properties of the same blends obtained by conventional technologies. Thus, Kung *et al.* [168] have recently reported a detailed study on the morphology and mechanical properties of polystyrene–polyethylene composites prepared via radical polymerization of styrene within scCO_2 -swollen high density polyethylene. They have shown that this scCO_2 -assisted process of blend preparation does not affect the crystalline structure of high-density polyethylene but does affect the spherulitic structure, and polystyrene was detected in spherulite centers, which implied that there is a lack of crystallinity there. Kung *et al.* [168] described this process as polystyrene forming a “scaffold” that reinforces the polyethylene spherulites. They demonstrated that this behavior results in a significant increase of modulus and strength improvement but with a penalty, namely, loss in fracture toughness.

The “tunable” solvent power of an SCF could add an extra dimension in which one could manipulate the properties of blends and composites obtained via this route. Therefore, it is important to understand the effect of scCO_2 on the phase behavior of polymer blends and the implications for their miscibilities. Walker *et al.* [169]

have applied *in situ* small-angle neutron scattering, UV–visible spectroscopy, and visual observation to study the effect of temperature and pressure of scCO_2 on the miscibility of low-molecular-weight polystyrene–polyisoprene blends. These authors studied a reduction in cloud point temperature for this polymer blend as a result of the plasticizing effect of scCO_2 . The polystyrene–polyisoprene system exhibits an upper critical solution temperature (UCST), and thus, the Flory–Huggins interaction parameter χ decreases with increasing temperature. Walker *et al.* have also used the Flory–Huggins theory to predict the phase behavior of the polystyrene–polyisoprene system. Their experimental study comparing CO_2 and nitrogen as plasticizing agents allowed them to decouple the plasticizing effect of CO_2 from effects due to hydrostatic pressures. This showed that hydrostatic effects cannot be neglected at high pressures for scCO_2 .

The effects of scCO_2 on cloud point temperature include studies of the polystyrene–cyclohexane system [170] and the demonstration of solvent-induced transitions in polystyrene–block–polyisoprene copolymers in the presence of CO_2 and ethane [171]. In the latter work, the authors also applied small-angle neutron scattering as did Walker *et al.* [169] to study the phase behavior of this system experimentally and Flory–Huggins theory to model it [171]. In related earlier work, the Flory–Huggins theory was used to model CO_2 sorption and dilation of polystyrene/poly(2,6-dimethyl-1,4-phenylene oxide) blend [172]. The interaction parameters for these systems were then used to calculate the enthalpies of mixing.

Specific interaction between carbon dioxide and polymer functional groups found via *in situ* spectroscopic studies [50] have broad implications for the processing of polymer blends. Thus, if CO_2 interacts differently with components of the polymer blend which have different molecular structures, it should have different effects on the glass transition temperature of each component of the blend. This could result in different plasticizing effects, thereby improving the mixing of these components. Indeed, Elkovitch *et al.* [173] and Lee *et al.* [174] have recently demonstrated that scCO_2 can assist in polymer blending in batch and continuous processes. Elkovitch *et al.* [173, 175] studied the effect of scCO_2 on blending in a PMMA–polystyrene system using a high-pressure batch mixer and a single screw extruder with an attached slit die rheometer to study the effect of added scCO_2 into these systems. The solubilities of CO_2 in PMMA and polystyrene at 20 and 13.78 MPa were ca. 5.8 and 3 wt %, respectively. These results are in accordance with the higher affinity of CO_2 for PMMA than for polystyrene [50, 58], a consequence of the specific interaction between CO_2 and carbonyl functional groups in PMMA being stronger than those between CO_2 and polystyrene. Therefore, a greater plasticizing effect will occur for the PMMA

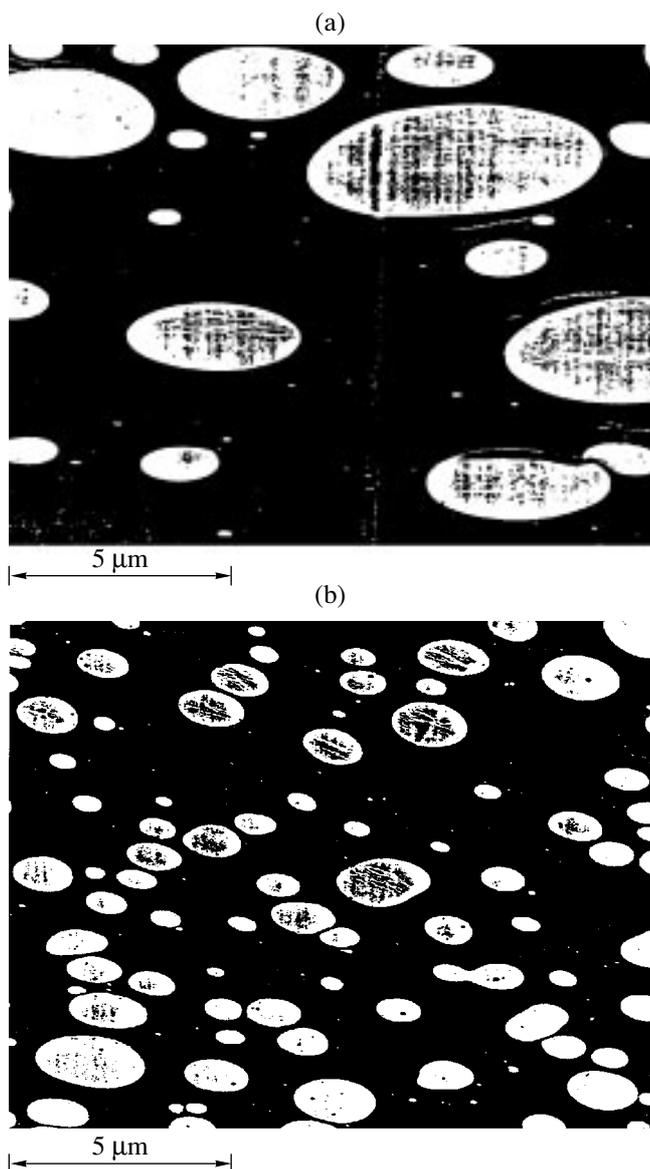


Fig. 2. TEM micrographs of blends of 25/75 PMMA/Polystyrene (a) without CO₂, (b) with CO₂. Reproduced with permission from [173] (*Polym. Eng. Sci.*, 1999, vol. 39, p. 2075) (Society of Plastics Engineers).

than for the polystyrene, which could lower viscosity of PMMA more than that of polystyrene. Indeed, Elkovitch *et al.* demonstrated a CO₂-induced viscosity reduction of PMMA of 70%, while that of polystyrene was 56% under identical conditions. These two polymers were then studied in a mixer to prepare a PMMA–polystyrene (25 : 75) blend, and the effect on addition of CO₂ into the batch mixer on blend morphologies is shown in Fig. 2. As can be seen from this figure, the addition of scCO₂ has a pronounced effect on the morphology of PMMA–polystyrene blend. The domains of the PMMA have been reduced in size and are more

evenly distributed as a result of scCO₂ addition into the system at 200°C. The authors explained this as the result of CO₂ lowering the polymer viscosity ratio and possibly affecting the interfacial surface tensions between these polymers [173]. They also used a single screw extruder to study the effects of CO₂ on the viscosity of polymer melts and a twin screw extruder to explore the possibilities of scCO₂-polymer processing in continuous operations [173]. The effects of added CO₂ into a twin extruder on the morphologies of 50/50 PMMA–polystyrene blends is shown in Fig. 3. The domain size of PMMA dispersed in polystyrene was reduced upon addition of CO₂.

The effects of added scCO₂ on the viscosities of polyethylene, polystyrene, and polyethylene–polystyrene blends has also been investigated in a twin screw extruder with a mounted wedge die [174, 176]. Researchers have also studied the effect of scCO₂ on polyethylene–polystyrene morphologies using twin and single screw extruders in tandem [177]. A metered amount of CO₂ was directly injected into the barrel of the extruder. The authors tried to ensure complete dissolution of CO₂ under the conditions of their experiments. It was found that the size of the dispersed polystyrene domains in the polyethylene–polystyrene blend decreased when 5% of CO₂ in polystyrene was injected, and no further increase was observed at concentrations of CO₂ up to 10 wt. %. A number of experimental difficulties associated with the extrusion setup were overcome in these elegant experiments:

- reduction of pressure fluctuation inside the barrel at the injection point of CO₂,
- prevention of injected CO₂ from leaking upstream,
- maintaining sufficient CO₂ pressure downstream,
- ensuring good mixing in the twin extruder by using an array of kneading disks.

The authors report experimental details and procedure and present micrographs of morphologies for polyethylene–polystyrene blends processed via this setup. They have found that this polymer system was foamed upon exiting the die of the extruder, and cell structures and the mechanism of formation are discussed [174]. This and earlier work by this group [178] has had an important impact on stimulating interest in SCF-assisted polymer processing (foaming, extrusion, blending) and will also be discussed below in the section on scCO₂-induced viscosity reduction for polymer processing.

(iv) Crystallization

The phenomenon of scCO₂-induced plasticization of glassy polymers has important implications for semicrystalline polymers. For example, scCO₂-induced plasticization may induce crystallization in certain polymers. This occurs in some polymers when CO₂-

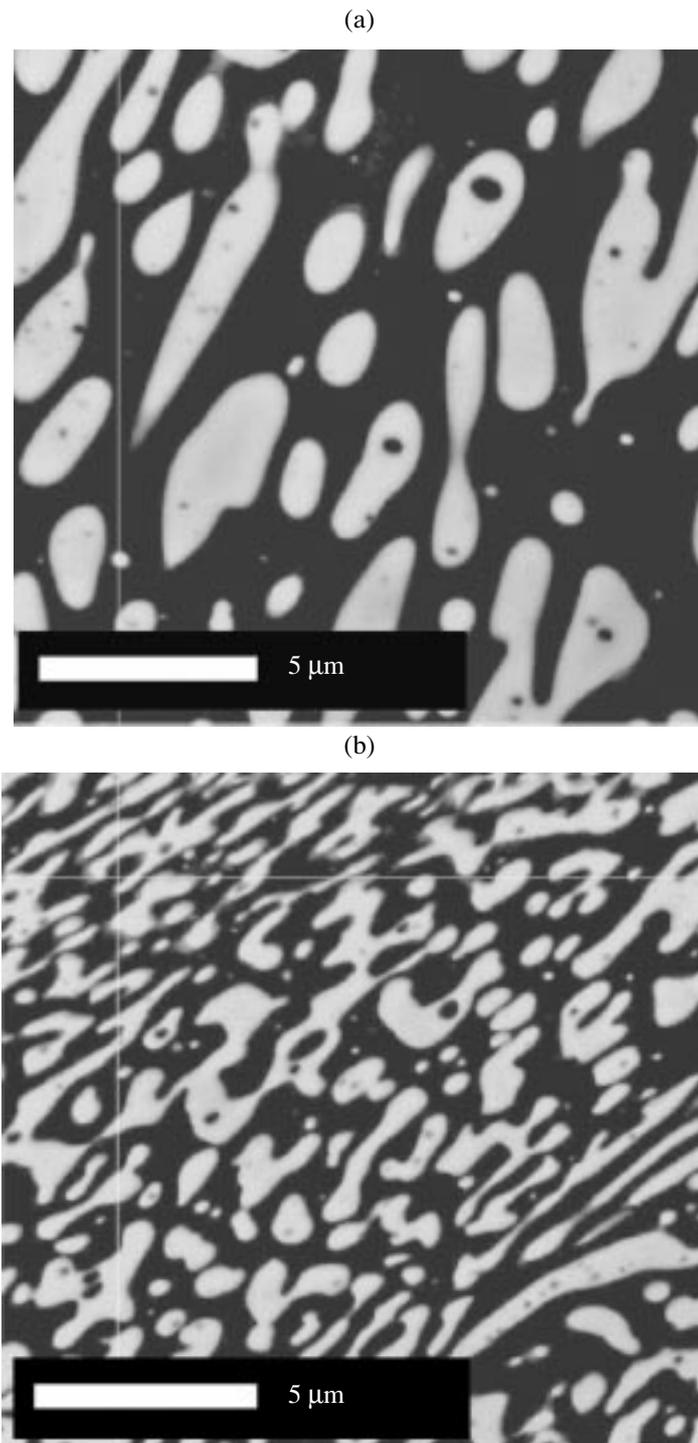


Fig. 3. TEM micrographs of blends of 50/50 PMMA/Polystyrene prepared from twin screw extrusion (a) without CO₂, (b) with CO₂. Reproduced with permission from [173] (*Polym. Eng. Sci.*, 1999, vol. 39, p. 2075) (Society of Plastics Engineers).

induced mobility of the polymer chains allows them to rearrange into kinetically favored configurations, thus forming crystallites. It was found that scCO₂ can change the degree of crystallinity in poly(ethylene terephthalate) [81, 179–183]. The interest in the mor-

phology of PET stems from the fact that PET-based materials are widely used in the production of soft-drink bottles and synthetic polyester fibers. The morphology and the degree of crystallinity in PET-based materials used in bottle manufacturing affects the gas

permeability of these products (crucial for CO₂-saturated drinks), while the morphology of PET-based fibers plays an important role in determining the mechanical properties of the fibers used in the textile industry. Moreover, the degree of crystallinity of polyester fibers may affect the ability of the polyester fiber to be dyed [131–134, 136, 144]. FTIR and FT-Raman spectroscopy have been applied [180] to elucidate morphology of PET processed with scCO₂. Combined efforts with other techniques (e.g., X-ray scattering, density measurements, DSC, etc.) are needed to reveal subtle aspects of morphological changes in PET processed with scCO₂. It is also important to compare polymer samples with different histories and molecular weights and samples polymerized with the use of different catalysts and containing different concentrations of terminal groups. Recently Brantley *et al.* [184] applied *in situ* near-IR spectroscopy to study the sorption of CO₂ into PET at elevated pressures. They found that CO₂ induced crystallization in initially amorphous PET films at 28°C and 50°C. However, they did not detect crystallization in PET at 0°C at pressures of CO₂ up to 175 bar. Apparently, the inherent mobility of PET chains was so low at these temperatures that even the presence of CO₂ did not induce crystallization [184]. It is important that the morphology of PET processed with scCO₂ could be different from the morphology of PET processed by heat or drawing [131, 180], and this gives a new approach to modifying the properties of these materials.

Relevant recent work has demonstrated that the drawing of PET fibers [185] subjected to sub- and supercritical CO₂ also induces crystallinity. It was shown that the draw ratio of the fibers drawn in subcritical CO₂ was 30% higher compared to fibers that were cold-drawn. However, the fibers treated in CO₂ had lower tensile properties at a given draw ratio in comparison to cold-drawn samples. Although the authors of the above work claimed that the studies of PET with scCO₂ were “essentially nonexistent”, the references provided in this review show that this is not the case. Unfortunately, Hobbs and Lesser [185] appeared to have overlooked prior work on polymers drawn under CO₂ made by Japanese researchers [186, 187]. These works demonstrated for the first time how the plasticizing effect of high-pressure CO₂ could facilitate the drawing of glassy polymers without heating. It was also shown that gas permeability in polystyrene samples oriented by CO₂-assisted drawing were higher compared to those in the hot-drawn samples, without the use of CO₂ as plasticizer. This was attributed to an increase in interchain distances in CO₂-processed polystyrene [187].

The SCF dyeing of polyester-based materials shows much promise in attempts to prevent pollution because it is an environmentally friendly process. It has been shown that scCO₂ can change the degree of crystallinity

in various polymers such as poly(phenylene sulfide) [188, 189], polycarbonate [190], poly(aryl ether ether ketone) (PEEK) [79], methyl-substituted PEEK [191], and syndiotactic polystyrene (sPS) [44, 192, 193]. The interest in sPS stems from its industrial importance. Morphology in this polymer is usually changed by heat, strain, or solvent. It was hoped that the effect of scCO₂ would resemble that of an organic solvent (such as toluene) but it would be much easier to remove CO₂ from the polymer once the process is complete. The “tunable” solvent power of scCO₂ provides an additional advantage in manipulating scCO₂-induced crystallization. Handa and coworkers have applied high-pressure DSC and X-ray diffraction to analyze the effect of scCO₂ on the morphology of syndiotactic polystyrene. They noticed that the crystallization process in sPS subjected to scCO₂ at 122°C, proceeds so fast that it is difficult to measure the kinetics of crystallization [193]. This is because, at high pressures of CO₂, the polymer achieves the maximum crystallinity before the temperature of the DSC can be stabilized. By contrast, *in situ* FTIR spectroscopy allows one to monitor this unusually fast crystallization process in real time. Thus, Kazarian and colleagues [194] have recently used *in situ* FTIR spectroscopy to analyze changes in the IR spectrum of sPS subjected to scCO₂. Dramatic changes in the IR spectra of sPS have been observed demonstrating the power of IR spectroscopy to reveal morphological changes induced by scCO₂ in polymers. The changes in the IR spectrum were followed as a function of time, allowing one to determine the type and kinetics of the induced crystalline form of sPS.

Supercritical CO₂ can also induce crystallization in polycarbonate films, and Gross *et al.* [195] have demonstrated this phenomenon in granules and beads of low-molecular-mass polycarbonate very recently. The CO₂-induced crystallization was studied as a function of molecular weight, CO₂ pressure, temperature, and time. These studies were related to solid-state polymerization of poly(bisphenol A carbonate) facilitated by scCO₂, and it was shown that the plasticizing effect of CO₂ which allows crystallization to proceed at low temperatures also suppresses side reactions, which lead to color body formation. No changes in the degree of crystallinity upon treatment with high-pressure CO₂ were observed in some polymers (e.g., poly(vinylidene fluoride) [196]). Crystallization of a linear aliphatic polyester from scCO₂ solution was reported by Stejny *et al.* [197], who observed that the packing of polyester chains in the ribbonlike lamellae was not of polyethylene type observed in crystal growth by conventional methods.

(v) Foaming of Glassy Polymers

Plasticization of glassy polymers with high-pressure gases of supercritical fluids plays an important role

in the formation of polymeric foams. Currently, a number of research groups in Western laboratories are studying the use of high-pressure gases in the production of microcellular polymers. Microcellular polymers have closed cells ca. 10 μm or less in diameter and a cell density of ca. 10^8 cells/cm³. These microcellular polymeric foams may have properties superior to those of unfoamed polymers, e.g., higher impact strength. Such polymeric materials have applications including insulation of lightweight materials, biomedical devices, and adsorbents. Russian scientists have made important contributions to the understanding of the chemistry and to developing the technology of polymeric foams. Pioneering studies on the foaming of glassy polymers with high-pressure gases or SCFs were carried out by Skripov and coworkers [77, 198–200].

If the polymer is subjected to high-pressure gas, and the pressure is suddenly decreased or the temperature is rapidly increased, the gas will try to escape from the polymer, causing antiplasticization. This rapid escape of gas can cause the nucleation and growth of bubbles within the polymer. Once a significant amount of gas escapes, the T_g of the polymer drops and, thus, “freezes” the foamed structure. Skripov’s work in this area began more than 30 years ago with studies of the solubility and diffusion of CO₂ in PMMA and then continued with the measurements of the mechanical properties (e.g., Young’s modulus) of PMMA saturated with CO₂. These studies provided the basis for further developing the theory of nucleation kinetics of bubble formation in gas-saturated PMMA. The theory of homogeneous nucleation proved to be a satisfactory approximation in describing the kinetics of bubble nucleation in a gas-saturated polymer. Skripov and Blednykh [200] believed that local regions of polymer containing elevated CO₂ concentrations serve as nucleation centers for bubbles.

Research on gas-assisted foaming of glassy polymers has since seen a significant increase in activity. Foaming of PMMA has also been studied by Goel and Beckman [201–203], while Kumar and coworkers have studied foaming in the polycarbonate–CO₂ system [204]. The importance of Kumar’s work is that it questioned the applicability of traditional theories of nucleation in explaining the cell density of foamed polycarbonate in the foaming temperature range 60–160°C [204, 205]. In another study, the effect of CO₂-induced crystallinity on the foaming of PET was demonstrated [181]. The work from Kumar’s group has recently been reviewed [206]. Detailed studies of the glassy polymer–CO₂ system by Wessling and coworkers [207] suggest that the nucleation mechanism underlying the foaming process is heterogeneous in nature. The significant advance made by Wessling and coworkers was that they were able to detect and explain the appearance not only of the porous structure in the polymer film after saturation with CO₂ but also of a dense layer next

to the porous layer. They provided a physical explanation and a mathematical model to predict the thickness of this dense layer. McCarthy and coworkers [208] have recently reported on microcellular polystyrene foams processed in scCO₂; they studied the effects of cell size and orientation on the yield stress. The recent article from the groups of McCarthy and Russell [209] reports the effect of the residual oligomer in polystyrene on its foaming with scCO₂, and they have shown that its presence affects the cell size in these foams. It was found that addition of low-molecular-weight oligomers to the polymer samples offers a way of controlling the cell structure in polystyrene foams formed by scCO₂. This work also questioned the ability of classical nucleation theory to explain the foaming mechanism in these systems, and the authors suggest a spinodal mechanism as an alternative route of cell formation [209]. Foaming of polypropylene has also been studied extensively [210, 211], with the most recent report by Liang and Wang [212], who highlighted the effect of temperature drop during depressurization of the polymer in equilibrium with high-pressure CO₂. High-pressure nitrogen has been used to foam polypropylene [211], polyethylene [213], and polystyrene [214]. The process of nucleation in the formation of microcellular foams was also discussed in a number of publications [215–217].

An interesting development in this field made recently by Handa and coworkers [218] was the preparation of a very fine structure of foamed PMMA with an average cell size of 0.35 microns and cell density of 4.4×10^{13} cells/g. The authors utilized the phenomenon of retrograde vitrification documented earlier by Condo and Johnston [76, 100]. Handa and Zhang [218] used the existence of a rubbery state at low temperatures to generate foams by saturating the polymer with CO₂ at 34 bar and at temperatures in the range –0.2 to 24°C followed by foaming at temperatures in the range from 24°C to 90°C. They demonstrated that the solubility of CO₂ in the polymer plays an important role in controlling cell density and cell size. Thus, the solubility of CO₂ at 34 bar and temperature of –0.2°C is 22.5 wt %, while at the same pressure but at 24°C, the solubility is just 7.9 wt %. The report of Handa and Zhang was the first to comment on the formation of ultramicrocellular foams at relatively low saturation pressures. Handa and Kumar [219] have also recently reported the analysis of foaming glycol-modified PET (PETG) with scCO₂. The process of scCO₂-assisted polymer foaming has also been coupled with polymer extrusion and is currently being commercialized by Reedy International Corporation [220].

Another approach to create microcellular materials was demonstrated recently by Beckman and coworkers [221]. First, they synthesized a number of chemicals soluble in scCO₂ or liquid CO₂. These chemicals comprise a number of “monomers” containing one or two

Table 2. Polymer systems foamed with the use of supercritical fluids

Polymer	References
Polymethyl (methacrylate) (PMMA)	[198, 200, 229], [201–203]
Polyethyl (methacrylate) (PEMA)	
Polycarbonate	[198, 204, 205], [230], [207]
Poly(ethylene terephthalate) (PET)	[181, 206]
Polystyrene	[231, 232], [208, 209]
Glycol-modified PET (PETG)	[219, 233]
Polyvinylchloride (PVC)	[206, 231]
Polypropylene	[210, 212]
Biodegradable polymers: polyester (polybutylene succinate); poly(lactide- <i>co</i> -glycolide) (PLGA);	[225–228]
Polyimide	[234]

urea groups and fluorinated “tail” groups that enhance solubility of these compounds in CO₂. When these compounds were dissolved in CO₂, their self-association led to the formation of gels. The removal of CO₂ via depressurization resulted in the formation of foams with cells with an average diameter of less than 1 μm. Beckman and coworkers reported that the bulk density reduction of these foams was 97% compared to the parent materials. They also argue that the phenomenon of gelation in CO₂ could be used to enhance the tertiary recovery of petroleum from aging fields and in coating processes. It should also be noted that gelation in scCO₂ has been reported in sol–gel polymerization in porous silica aerogel [222].

New applications of SCFs to polymeric foams include SCF extraction of chlorofluoroalkanes from rigid polyurethane foams [223], synthesis of conductive polypyrrole–polyurethane foams [224], and forty fold expansion of biodegradable polyester foams with supercritical carbon dioxide [225]. CO₂-assisted foaming of biodegradable polymers, such as poly(lactide-*co*-glycolide) (PLGA) copolymer [226], represents an exciting opportunity in the formation of sponge scaffolds for medical applications. Indeed, this approach was used to generate high-surface-area fibrillar scaffolds that were then used to generate liver tissue [227].

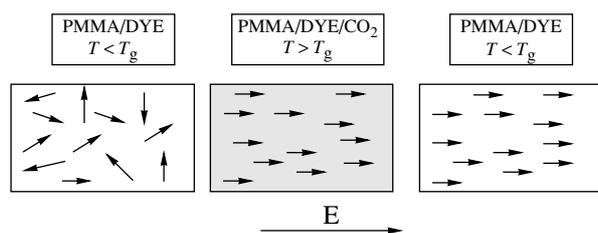
One of the most recent applications of using CO₂ for polymer foaming includes preparation of bioabsorbable polymer scaffolds for tissue engineering capable of sustained growth factor delivery. Thus, Mooney and coworkers [228] studied the effects of several processing parameters (such as polymer composition, molecular mass, and gas type) on preparing three-dimensional porous matrices from copolymers of lactide and glycolide (PLG). They demonstrated that crystalline polymers (polylactide and polyglycolide) did not produce

foamed materials via this approach, while gas treatment of amorphous copolymers produced matrices with porosity up to 95%. This work also demonstrated that only CO₂ among the other gases used (e.g., N₂ and He) created highly porous polymer structures in these copolymers [228] and explained this by the possible interactions between CO₂ and carbonyl groups [50] in PLG. Mooney and coworkers [228] also incorporated vascular endothelial growth factor into these porous matrices and studied its release in a controlled manner. This approach shows good potential in preparing scaffolds for tissue engineering. The polymers foamed with the use of high-pressure gases of supercritical fluids are summarized in Table 2.

(vi) Applications to Optical Materials

Plasticization of glassy matrix by supercritical CO₂ opens new opportunities in processing polymeric-based materials for optical applications. For example, azobenzene derivatives represent a class of molecules that are frequently used as dopants in NLO devices for second harmonic generation [235]. In order to produce such doped polymeric materials having an NLO effect, one needs to orient impregnated azobenzene chromophores. This orientation is usually achieved via poling at temperatures near the T_g of the polymer matrix. The ability of CO₂ to reduce the T_g of glassy polymers offers an exciting opportunity to perform such poling at room temperatures [236, 237]. Also, azobenzene derivatives can be isomerized by visible light [238–242]. Such photoisomerization induces a change in the refractive index of the system and, most importantly, can increase second harmonic generation. The mobility of the polymer chains and segments and its free volume play an important role in these processes. The key idea of CO₂-assisted orientation of NLO dopants within a

polymer matrix via electric poling at room temperature realized by Barry and Soane is presented in the schematic view below:



The picture on the left shows that the dipole orientation of the impregnated dopant molecules are initially distributed at random. When the polymer is subjected to supercritical CO_2 , the glass transition temperature is reduced below room temperature. An electric field is applied under these conditions and the dopant molecules are oriented as shown in the central picture. A reduction in CO_2 pressure followed by the removal of electric field results in “freezing” the dopant molecules in oriented states, since the matrix becomes glassy again as shown in the picture on the right. Barry and Soane demonstrated the feasibility of this approach studying the second harmonic generation on a glassy polymer containing an azo-dye. Presumably, the reduced thermal energy in an scCO_2 -plasticized polymer matrix assisted in better orientation of dye molecules than would have been achieved by poling at higher temperatures by heating the polymer.

IV. POLYMER PROCESSING

(i) Viscosity Reduction

One of the major factors that influence the processing of polymers is the effective viscosity of the bulk materials. For example, high viscosity is a major obstacle to the processing of high-molecular-weight polymers or complex mixtures of particles filled polymers or pastes. Usually this problem is solved by increasing the temperature and/or by the addition of plasticizing agents. However, increasing the temperature requires a higher energy consumption and may lead to thermal degradation. Added plasticizers usually remain in the product, thus affecting its properties and performance. On the other hand, the desired removal of some intrinsic plasticizers, such as fats from dough systems in food processing applications or organic solvents from ceramic precursor pastes, results in increased bulk and interfacial viscosity. The changes are nevertheless being driven forward by consumer and environmental concerns, and there is a need for improved technologies to accommodate the more stringent processing demands of these materials.

The use of SCFs to reduce the viscosity of polymers stems not only from the environmental advantages of some SCFs but also from the ability of SCFs to plasticize glassy polymers. As discussed above, this effect is

most significant in the case of scCO_2 . The plasticizing effect of scCO_2 on polymers reduces their viscosity, presumably due to the reduction of chain–chain interactions and increasing the interchain distance. CO_2 also weakly solvates the molecular segments of the polymer, thus acting as a “molecular lubricant”. Such action also contributes to viscosity reduction in the bulk. Very recently, these phenomena have been used in the extrusion of polyethylene–polystyrene blends and for foam extrusion of thermoplastic polyurethane elastomers and other polymers.

The polymer systems for which scCO_2 -induced viscosity reduction has been demonstrated include polymeric liquids (such as polysiloxanes), glassy polymers, and their blends. The studied polymer systems include polydimethylsiloxane [243–246]; poly(ethylene glycol) [247–251]; poly(ethylene glycol) nonylphenyl ether [252]; polystyrene [176, 253–257]; blends of polyethylene and polystyrene [174]; blends of polystyrene and PMMA [173]; polyurethane elastomers, binary mixtures of polystyrene and toluene [258, 259]; and biomaterials [260].

In another recent example, scCO_2 has been used for extrusion in the cooking of foods [261]. This work is important because it has shown the feasibility of combining SCFs with extrusion processing of starch-based materials. Therefore, the advantages of SCFs demonstrated for polymer processing were also anticipated for starch products [261]. The combination of supercritical extraction of fat with viscosity reduction may be particularly useful in food processing involving products as diverse as bakery products, chocolate, and egg yolk. In addition, the new SCF-assisted extrusion processes will facilitate the addition of flavors, colorings, and other additives to the process mixture without the use of organic solvents, because these substances are generally soluble in scCO_2 and can be impregnated into the matrix from a supercritical solution. The plasticizing effect may also be used to modify the properties of polymeric additives such as binders in the processing of ceramic pastes. Indeed, since some ceramic pastes are suspensions of solid particles in a polymer solution, the effect of scCO_2 on the polymer phase will modify the mechanical properties of the paste. Thus, the viscosity reduction of the polymer phase may result in lower extrusion or injection pressures, reducing the residual stresses and improved accuracy of formation. Moreover, once the processing of the ceramic paste is completed the polymeric binders and solvents have to be removed prior to sintering [262–264]. Clearly, scCO_2 may be used in polymer–ceramic composites to influence the processing rheology of these pastes, as well as in the supercritical fluid extraction and drying of the pastes.

Early work on the effect of scCO_2 in viscosity reduction involved studies on viscosity reduction for polydimethylsiloxane (PDMS) with dissolved CO_2 . Gerhardt *et al.* [243] demonstrated a reduction up to

60% in viscosity at 50°C and low shear rates. Careful studies of viscometric and volumetric behavior of PDMS/CO₂ solutions have also been reported [246]. The swelling of uncrosslinked PDMS induced by high-pressure CO₂ was measured and modeled using the Sanchez–Lacombe equation of state [256]. A detailed study of miscibility, phase separation, and volumetric properties of PDMS–CO₂ mixtures has recently been reported [266, 267]; Kiran and coworkers [268–270] also addressed a relevant and important phenomenon of pressure-induced phase separation in polymer solutions with SCFs. They studied the kinetics of this process and observed crossover from nucleation and growth to a spinodal decomposition mechanism [269].

Extensive recent studies on the effect of scCO₂ on polymer viscosity reduction involves poly(ethylene glycol)s (PEG) of different molecular weights ranging from 200 to 8000 g/mol. These studies are motivated by practical interest since PEGs are used in certain high-pressure applications as, for example, lubricating fluids for compressors or gas absorbents. The initial work on a PEG–CO₂ mixture was performed by Daneshvar *et al.* [251], who measured the high-pressure phase equilibrium of this system. They circulated both phases in a countercurrent mode and, assuming that equilibrium had been achieved, the composition of the phases was determined by taking samples from the system. Thus, the mass fraction of CO₂ dissolved in PEG was determined. It was shown that solubility of CO₂ in PEG decreases with an increase in temperature and increases with an increase in CO₂ pressure. The mass fractions of CO₂ dissolved in PEG (molecular weights from 400–1000 g/mol) were as high as 0.6 at pressures higher than 20 MPa. Unfortunately, attempts to reproduce these results have failed, indicating possible experimental errors in this initial work. Thus, Weidner *et al.* [247], Gourgouillon *et al.* [249, 250], and Lopes *et al.* [248] have found that solubilities of CO₂ in PEG under the same conditions are significantly lower than that reported by Daneshvar *et al.* [251]. They explained these discrepancies by suggesting that in previous experiments, the procedure allowed nonhomogeneous samples to be taken from a system which could have contained large amounts of CO₂ due to foaming. If this was the case it would, of course, had led to an overestimation of the CO₂ solubility. The effect of the added scCO₂ to the polymer solution on viscosity reduction is the prime objective for the design of scCO₂-assisted polymer processing. However, the correct interpretation of this effect requires, as rightly stated by Gourgouillon and Nunes da Ponte [249], a detailed knowledge of the solubility of scCO₂ in polymers. Therefore, these data were obtained for a CO₂–PEG system using a vibrating-wire viscometer and high-pressure equilibrium view cell. The authors estimated that the accuracy of their method was better than 5% of the mass fraction. They modeled their experimental results with the

Sanchez–Lacombe equation of state using a non-temperature-dependent interaction parameter. This modeling is in excellent agreement with the experimental results of Lopes *et al.* [248] and Weidner *et al.* [247]. They also noted that hydrogen-bonding chain–chain interactions, which would be more pronounced for low-molecular-weight PEGs, would affect the binary interaction parameter used to model a phase equilibrium for CO₂–PEG-200. The binary interaction parameter changes abruptly between 200 and 400 g/mol and increases smoothly for molar masses between 400 and 800 g/mol. The work of Nunes da Ponte and coworkers [249] form a good basis for further studying the effects of scCO₂ on the viscosity reduction in polymer systems. These studies are ongoing, and the paper by Wiesmet *et al.* [271] has just been published in which the authors measured and modeled the high-pressure equilibria in the systems of PEG–propane, PEG–nitrogen, and PEG–carbon dioxide. It was found that CO₂ dissolves much better in PEG than does propane or nitrogen. This result could have been anticipated given the fact that specific interactions between CO₂ and functional groups in polymers, discussed earlier in this review, affect the solubility of CO₂ in the polymers. Wiesmet *et al.* [271] have correlated their data for gas solubilities in polymers with the SAFT equation of state. Another interesting issue which could have been studied in the context of the effect of CO₂ is the effect of H-bonding on viscosity reduction in PEGs. This effect is related to the fact that PEG molecules can form H-bonding within (intramolecular) and between (intermolecular) polymer chains. As correctly mentioned in some of these articles, this effect will be more pronounced for low molecular weight PEGs, and self-association is dominant for these polymers. However, what has not been addressed or studied is the effect of dissolved CO₂ on the degree of H-bonding in PEGs. This effect will not only be a function of the molecular weight or temperature of the PEGs but could also be affected by the pressure (and density) of CO₂. Indeed, it is known that H-bonding is a function of the solvent density going from the gas phase through the critical point to the liquid-like densities [272]. It would be interesting to apply *in situ* FTIR spectroscopy to measure the effect of dissolved CO₂ on H-bonding in PEGs and, thus, to elucidate the contribution of this effect to the CO₂-assisted viscosity reduction in these polymer systems.

As mentioned above in the section on polymer blends, a single and twin extruders have been coupled with the injection of scCO₂ to study the effect of scCO₂ on polymer viscosity [177]. The measurement of the viscosity reduction is usually achieved by measuring the pressure drop in capillary die. Elkovitch *et al.* [173] used a single screw extruder with a three-quarter-inch screw coupled with the injection of scCO₂ into the barrel to measure the drop in polystyrene melt viscosity via an attached slit die rheometer. The injected scCO₂

reduced the viscosity of polystyrene by up to 60% at a processing temperature of 170°C. A twin screw extruder and a twin–single tandem extruder system [176, 177] have been utilized for experiments on processing polyethylene–polystyrene blends with scCO₂. Lee *et al.* [176, 177] have also demonstrated that the scCO₂-induced viscosity reduction of polystyrene was greater than that of polyethylene, and the viscosity reduction of the blend of these polymers was in between those of separate polymer solutions with scCO₂.

Rheological studies for mixtures of CO₂ with polystyrene and polypropylene have also been reported [254], and viscosity reduction for these systems were translated into a shift of T_g due to addition of CO₂ into polymer. Recent studies of polystyrene melts containing different dissolved supercritical and near-critical gases have been reported [253], where the authors interpreted the data in the framework of classical viscoelastic scaling theory.

(ii) The Use of Other SCFs in Polymer Processing

The use of SCFs other than CO₂ also has a broad range of applications, from enzymatic catalysis [43, 273–278] to “tuning” conformational [279] or tautomeric equilibrium [280]. Supercritical pentane [281] and methanol [282] have been used in the formation of cellulose fibers by rapid precipitation. Phase behavior of polymers in SCF solvents has recently been reviewed by Kirby and McHugh [13]. They provide data for a broad range of SCF solvent–polymer systems.

In this section, the application of SFCs for the recycling of polymers is briefly discussed. One of the applications of SFCs for polymer processing is their use to decompose PET. PET is a widely used material for manufacturing soft drink bottles due to its excellent processing and gas permeability properties. Supercritical methanol ($T_c = 513$ K; $P_c = 7.95$ MPa) has been used to decompose PET into monomers [283]. Supercritical methanol has some advantages over supercritical water in polymer recycling. As mentioned above, the critical parameters of methanol are lower than those of water, allowing reactions at milder conditions, thus simplifying operations. Therefore, Ozaki and coworkers [284] studied reactions of phenol resin in supercritical methanol by varying the temperature in the range of 300–420°C. They found that the conversion above 400°C was higher than 80%. The liquid product was found to include phenols, while analysis of the solid product showed a high concentration of carbon [284]. Among the uses of other supercritical fluids there is a patent on using ammonia to recycle polyamide [285].

It is more challenging to recycle thermosetting resins due to their highly crosslinked structure. However, the idea of using supercritical fluids for recycling used tires is very promising in terms of both economic and environmental benefits. Therefore, there is interest in

finding new ways to decompose and, possibly, recycle used plastic materials. Thus, Park *et al.* [286] report supercritical water oxidation to partially break down rubber materials of used tires. The use of batch and semicontinuous reactors for this process is discussed. The authors claim that these materials can be converted to chemicals such as alcohols, aldehydes, and ketones under certain experimental conditions [286]. However, characterizing the oxidation products still requires more work. German researchers report feasibility studies for using supercritical water for plastics recycling [287]. Applications of scCO₂ in polymer processing relevant to waste treatment have been discussed recently [288].

Preliminary results on the disposal of epoxy resin via this approach were encouraging, and Eyerer *et al.* [287] discuss the use of supercritical water for energetic materials (such as explosives or pyrotechnics), treatment of contaminated soil, plastics and additives, and other organic materials. Motivated by the need to cut the cost of hazardous waste treatment in Germany, they are currently setting up a prototype plant to explore and utilize these processes.

Hydrolysis and oxidation of epoxy resin in sub- and supercritical water has been studied in batch reactors [289]. This work is directly related to the treatment of nuclear waste since epoxy resins are used as coatings for materials in nuclear plants. Since these materials are considered to be radioactive waste, there is a need to find how these waste materials can be destroyed. Cansell and coworkers [289] have shown that hydrothermal oxidation at 410°C and 24 MPa resulted in the total destruction of epoxy resin, without formation of toxic by-products. These results are attractive for waste management in the nuclear industry, and therefore, this group of researchers plans to apply the same process to other uranium containing nuclear wastes.

V. OUTLOOK AND CONCLUDING REMARKS

The objective of this review is to stimulate further investigations into polymer processing with SCFs. It is hoped that the applicability and intrinsic advantages of SCFs in some areas of polymer processing have been made clear. The recent renaissance in the use of SCFs in chemical synthesis and materials processing has been driven by environmental concerns, and, therefore, one would expect an increase in research in this area. The use of SCFs, in particular scCO₂, which is an inexpensive and nontoxic solvent, should open a whole new dimension for the processing of polymeric materials difficult to process due to their high viscosity. For example, an important application of CO₂-induced polymer plasticization will be in processing injection-molded or extruded ceramic components. Indeed, if one views a ceramic paste as a suspension of solid particles in a polymer solution, then the effect of scCO₂ on the polymer phase will modify the mechanical properties of the paste. Thus, the viscosity reduction of the

Table 3. Recent and potential breakthroughs in the applications of supercritical fluids in polymer processing

Recent Breakthroughs in the Applications of Supercritical Fluids to Polymer Processing	Potential Breakthroughs in the Applications of SCF in Polymer Processing
<p>1. Structure/Properties and Characterization</p> <ul style="list-style-type: none"> ● Solubility of polymers in SCFs ● Models of SCF-induced polymers plasticization ● High-Pressure <i>in situ</i> methods for the characterization of polymer/SCF systems <p>2. Synthesis</p> <ul style="list-style-type: none"> ● Dispersion and emulsion polymerization ● Polymerization with CO₂ as solvent and reactant ● Polymerization in SCF-swollen polymer matrices ● Dendrimers <p>3. Surfaces and Interfaces</p> <ul style="list-style-type: none"> ● Cleaning with SCFs using surfactants ● Surface modification via impregnation ● Coatings (e.g., UNICARB process) <p>4. Materials</p> <ul style="list-style-type: none"> ● Polymer–metal composites ● Bone replacement materials ● Dyeing ● Foaming ● Impregnation of microporous materials ● Nanoscale casting using SCFs and lithography ● Gelation <p>5. Biopolymers</p> <ul style="list-style-type: none"> ● Food processing ● Biodegradable polymers ● Scaffolds for tissue engineering <p>6. Pharmaceutical applications</p> <ul style="list-style-type: none"> ● Production of protein powders ● Preparation of biodegradable microparticles ● Aerosol formation <p>7. Polymer extrusion</p> <ul style="list-style-type: none"> ● SCF-induced viscosity reduction ● SCF-assisted polymer blending <p>8. Recycling the polymeric materials</p>	<p>1. Structure/Properties, and Characterization</p> <ul style="list-style-type: none"> ● Development of novel <i>in situ</i> high-pressure techniques for polymer/SCF systems ● Theories of polymer solubility in SCFs <p>2. Synthesis</p> <ul style="list-style-type: none"> ● Combining ionic liquids and SCFs for two-phase mixtures polymer synthesis ● Novel hybrid systems <p>3. Surfaces and Interfaces</p> <ul style="list-style-type: none"> ● Novel SCF-soluble surfactants for coatings ● Novel SCF-soluble polymers for lithography <p>4. Smart materials</p> <ul style="list-style-type: none"> ● Processing of shape-memory polymers ● Metastable polymer systems ● Non-linear optical materials ● Chemical vapor deposition of new optical materials from SCF solutions ● Molecular imprinting ● Systems for controlled release <p>5. Biodegradable polymers for environmental, ecological applications and medical applications.</p> <ul style="list-style-type: none"> ● SCF-assisted processing of plastic wastes ● SCF-assisted processing of personal care products ● Extrusion of biodegradable polymers <p>6. Pharmaceutical applications</p> <ul style="list-style-type: none"> ● Formation of particles with complex morphology (e.g., multi-layer system) for controlled drug release ● SCF-impregnation of bio-active substances into biomedical or personal care products (e.g., contact lenses, tooth brushes, bone cements, etc.) <p>7. Polymer extrusion</p> <ul style="list-style-type: none"> ● Combining catalysis and SCF-assisted extrusion for polymer systems ● Extrusion of ceramic pastes ● Extrusion of food materials with simultaneous impregnation of fragrances and colorings <p>8. Converting polymer waste into useful materials</p>

polymer phase may result in lower extrusion or injection pressures, reducing the residual stresses and improving the accuracy of formation. Moreover, once the processing of the ceramic paste is completed, the polymeric binders and solvents have to be removed prior to sintering.

The application of supercritical fluids to polymers in pharmaceutical applications and in biomaterials processing is set to expand. These applications warrant a review on their own and have only been discussed briefly in this article. Any readers interested in learning more about these applications are referred to a number of relevant review articles [290–293]. Supercritical fluids offer opportunities for purifying proteins [293], producing micronic particles via rapid expansion [294] and antisolvent precipitation [295], creating protein powders [295], preparing liposomes encapsulating water-soluble compounds [296], and for aerosolization for fine powder generation and drug delivery [297]. The preparation of biodegradable highly porous scaffolds [228] that could be used for temporal templates in tissue engineering offer an opportunity to realize the potential of supercritical fluids in these applications. Some recent applications and potential breakthroughs in the area of supercritical fluid processing are summarized in Table 3.

The use of supercritical CO₂ as a solvent in polymerization reactions, which has not been discussed in this article, will continue to expand due to the environmentally benign nature of the solvent. The comprehensive reviews on this topic can be found in Table 1. This is a rapidly developing and changing field, and new developments appear frequently. Thus, the most recent reports on polymerization in CO₂ include the use of palladium catalyst in the polymerization of olefins [298], a report on the dispersion polymerization of acrylonitrile using a block copolymer as a stabilizer to produce sub-micron-size spherical polyacrylonitrile particles [299], and a report on the dispersion polymerization of 1-vinyl-2-pyrrolidone [300], the ring-opening precipitation polymerization of poly(D,L-lactide-co-glycolide) [301], and synthesizing linear poly(tetrafluoroethylene-co-vinyl acetate) [302]. SCFs have proved their applicability in polymer fractionation [303–305] and particle formation [47, 306–309]. The “tunable” properties of SCFs played a crucial role in these processes.

SCFs offer exciting opportunities for processing new advanced materials. Thus, recently, Ober *et al.* [310, 311] have demonstrated how scCO₂ could be used to facilitate the processing of new polymeric materials for imaging applications. Most recently, a process utilizing scCO₂ for fabricating 0.2 μm features the use of fluorinated polymers has been developed. In their study, the high solubility of fluorinated block copolymers in scCO₂ and the selectivity of scCO₂ to both polarity changes and the molecular structure of the polymer were used to develop an environmentally

friendly lithographic process which could be superior to that of aqueous-based systems. Since the microelectronics industry is aiming to miniaturize its products, one would expect that the practical utilization of the process described above would emerge in the near future.

The use of SCFs in electrochemical processes (e.g., electroreduction of CO₂ in liquid and supercritical mixtures of CO₂) [312] would require further studies of the interactions of polymer-coated microelectrodes with SCFs. In general, SCFs will play an increasingly important role in the production of high-value-added polymeric materials.

In summary, SCFs offer a marvelous opportunity for exciting research with a good potential for utilizing the results in industrially important processes for sustainable development in the new millennium.

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