



Clean polymer synthesis and processing using scCO_2

Andrew Cooper from Liverpool University in the UK describes how scCO_2 (supercritical carbon dioxide) is proving to be a valuable green alternative to conventional solvents in polymer synthesis and processing

Concern over volatile organic solvent emissions and the generation of aqueous waste streams has prompted a number of chemists and chemical engineers to seek new, cleaner methods for polymer synthesis¹ and polymer processing.² The use of supercritical carbon dioxide (scCO_2) has attracted particular attention in both of these areas for the following reasons:

- CO_2 is non-toxic, non-flammable, chemically inert, and inexpensive
- Supercritical conditions are easily obtained: $T_c(\text{CO}_2) = 31.1^\circ\text{C}$; $P_c(\text{CO}_2) = 73.8$ bar (Figure 1)

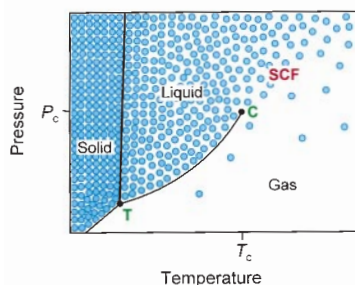


Figure 1 Schematic phase diagram for CO_2 showing the supercritical region

- The solvent may be removed by simple depressurisation
- The density of the solvent can be 'tuned' by varying the pressure
- Many polymers become highly swollen and plasticised in the presence of CO_2

On the other hand, the use of supercritical fluids requires elevated pressures and relatively specialised equipment, and these considerations must be balanced carefully with the perceived advantages for a given application. However, there are many recent examples which suggest that the benefits of using CO_2 as an alternative solvent might warrant the

additional complexity associated with supercritical fluid technology, at least for certain applications. The aim of this article is to highlight some of these areas.³

Polymer synthesis

Much of the pioneering work in the field of polymer synthesis using scCO_2 has been carried out by Professor J. M. DeSimone and colleagues at the University of North Carolina at Chapel Hill (UNC), USA.⁴ In 1992, this group showed that it was possible to synthesise amorphous fluoropolymers in CO_2 under relatively mild conditions by homogeneous solution polymerisation.⁵ Since the only other solvents for these polymers tend to be chlorofluorocarbons (CFCs), the use of CO_2 represents a much cleaner route to materials of this type. However, with the exception of certain amorphous fluoropolymers and polysiloxanes, the vast majority of polymers show negligible solubility in CO_2 under practicable conditions ($<100^\circ\text{C}$, <100 bar). Hence, a number of research groups have studied the synthesis of polymers by heterogeneous polymerisation in scCO_2 (*i.e.*, under conditions where the resulting polymer is not soluble in the supercritical solvent). In 1994, DeSimone demonstrated that it was possible to synthesise polymers such as poly(methyl methacrylate) (PMMA) in CO_2 by dispersion polymerisation using specially designed, CO_2 -soluble surfactants.⁶ Since dispersion polymerisation is usually carried out in solvents such as hydrocarbons or C_1 - C_3 alcohols, the use of CO_2 has potential to reduce organic solvent usage. These techniques have recently been extended to the synthesis of a range of materials, including water-dispersible polymer powders⁷ and well-defined cross-linked microspheres (Figure 2).⁸ Water-dispersible powders are useful because they can be transported dry, thus saving on transport costs, while cross-linked microspheres are

very important in applications such as chromatographic separations and polymer-supported synthesis.

The use of scCO_2 for the synthesis of porous polymers is an area of great interest, particularly since conventional processes tend to be solvent intensive and can generate materials containing organic solvent residues which may be difficult to remove. Carbon dioxide has allowed the 'solvent-free' preparation of polymeric materials with pore sizes spanning a very broad range, from microcellular foams down to macroporous resins (Figure 3) and mesoporous/microporous aerogels.⁹

In the UK, several academics are investigating aspects of the use of CO_2 for polymer synthesis, including groups in Nottingham, Cambridge, and Liverpool.¹⁰

Polymer processing

Carbon dioxide has been used in a wide range of polymer processing applications, the most established of which are polymer fractionation and extraction.¹¹ Both of these techniques exploit the variable density which is associated with supercritical fluid solvents. More recently, there has been much interest in the use of CO_2 for the infusion or 'impregnation' of molecules into

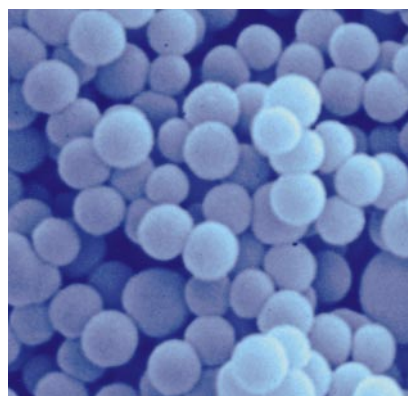


Figure 2 Cross-linked polymer microspheres synthesised in scCO_2 , average diameter = 410 nm, see ref. 8

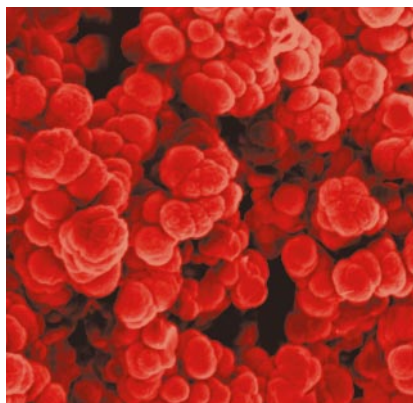


Figure 3 Internal structure of a porous polymer monolith synthesised using $scCO_2$, average pore size = $7.8 \mu m$, see ref. 9(b)

polymeric materials. From an environmental perspective, a particularly exciting technique is disperse dyeing using $scCO_2$.¹² In this approach, the dye molecule has very low solubility in CO_2 (e.g., mole fractions of 10^{-5} – 10^{-6}). However, because the dye molecules partition preferentially into the polymer phase, significant quantities of dye can be loaded into the polymer in a relatively short period.¹³ In addition to using a clean solvent, very little dye is actually dissolved in the fluid at any given time, thus minimising dye loss and environmental burdens.

Another exciting processing technique is the Vedoc Advanced Materials Process or 'VAMP', which was recently

commercialised by Ferro Corporation (Cleveland, OH).¹⁴ This process utilises the fact that CO_2 is a good plasticising agent (i.e., it can cause polymers to soften and flow, even at low temperatures). The method has been applied successfully to low-temperature processing of a range of composite materials, particularly polymer-pigment formulations for use as powder coatings. Other important methods for polymer particle formation include rapid expansion from supercritical solutions (RESS) and a range of antisolvent precipitation techniques.¹⁵ Supercritical CO_2 has also been exploited for the solvent-free application of protective fluorinated coatings¹⁶ and for dry-cleaning,¹⁷ the latter of which has already shown real commercial promise.

Finally, carbon dioxide has been viewed as a potential solvent for microlithography. At present, the semiconductor industry produces millions of gallons of organic and aqueous waste effluent every year, all of which requires treatment. Supercritical solvents offer the possibility of simpler separations and recycling, and new processes are under evaluation which use CO_2 as the solvent, both in the spin-coating stage and also in the development step.¹⁸

Conclusions

Carbon dioxide has great potential as an alternative solvent for polymer synthesis and processing. The drive to use CO_2 is especially strong in the case of processes which use volatile organic solvents. However, there may also be cases where CO_2 is a viable substitute in aqueous processes, particularly if separations are simplified by the use of a supercritical solvent. A major breakthrough in the acceptance of this technology would be the generation of novel polymeric materials that are difficult or even impossible to obtain without the use of supercritical fluids. Whilst this may be a challenging goal, the rapid growth of this area over the last few years suggests that we will see future developments in the use of CO_2 for the synthesis and processing of progressively more advanced materials.

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- 3 This short article is based on a full-length review which will appear in the *Journal of Materials Chemistry*: A. I. Cooper, *J. Mater. Chem.*, 2000, **10**, in press.
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Biography

Andrew Cooper obtained his PhD at the University of Nottingham, working with Professor Martyn Poliakoff in the area of organometallic chemistry. He then spent two years (1995–1997) as an 1851 Research Fellow at the University of North Carolina at Chapel Hill, USA, working with Professor Joseph DeSimone on the development of novel dendritic surfactants for extractions using CO_2 as the solvent (Cooper *et al.*, *Nature*, 1997, 389, 368). From 1997 to 1999, he held a Ramsay Memorial Research Fellowship at the Melville Laboratory for Polymer Synthesis in Cambridge, UK, working with Professor Andrew Holmes on polymer synthesis using supercritical CO_2 (Cooper *et al.*, *Macromolecules*, 1999, 32, 2156). He was appointed as a Royal Society University Research Fellow at the University of Liverpool, UK, in January 1999.