SFE541: Polymer Applications using Supercritical CO2

Introduction

Supercritical fluids have unique properties for the enhanced processing of polymeric materials. The ability of supercritical carbon dioxide to swell and plasticize polymers is critical to the extraction, impregnation and modification of polymeric materials. In addition, polymer plasticization reduces polymer viscosity and shear stresses.

Supercritical carbon dioxide (scCO2) is the most widely used supercritical fluid for polymer processing. CO2 is inexpensive, nontoxic, and nonflammable and has a relatively low critical point. In addition, CO2 is a gas under ambient conditions which makes for easy removal from polymeric matrices. This avoids the costly processes of drying or solvent removal from processed polymers.

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.

This review enumerates the many applications of supercritical fluids for polymer processing.

Equipment

Applied Separations Supercritical Extraction Equipment SFE Basic, SFE 2, SFE 4, Helix, Pilot and Production Plants.

Applications

(Locate the appropriate reference for detailed procedures)

Extraction of Polymers

The low surface tension and high diffusivity of SC CO2 combined with polymer plasticization increases the rates of the extraction of soluble monomers, oligomers, and other unreacted species from polymeric matrices.

Drying of Polymers

Most organic solvents are readily dissolved in SC CO2 and are easily extracted from a polymer matrix leaving no residual solvents in the dried polymer.

Impregnation of Polymers

Supercritical CO2 is a solvent which can dissolve and carry small MW nonpolar compounds into a polymer and then precipitate the dissolved compound in the polymer by a reduction in pressure of the supercritical fluid. The CO2 gas can then easily diffuse out of a polymer once the pressure is reduced to ambient. In addition, there are no solvent residues left in the impregnated polymer sample.

Polymers which have been impregnated using scCO2 include:

- Polystyrene
- poly(methylmethacrylate) (PMMA)
- poly(vinyl chloride (PVC)
- polycarbonate
- polyethylene
- poly(tetrafluoroethylene) (PTFE)
- poly(chlorotrifluoroethylene) (PCTFE)
- poly(4-methyl-1-pentene) (PMP)
- nylon
- poly(oxymethylene)
- poly(ethylene terephthalate) (PET)
- poly(dimethylsiloxane) (PDMS)
- polyimides

Solutes used in impregnating polymers range from metal carbonyl complexes to organic dyes to Alpha -Tocopherol.

Polymer Blends

SCF impregnation can be used to blend different polymer species. Monomers and initiators dissolved in a supercritical solution can partition into a different polymer matrix with the subsequent polymerization of the monomer within the matrix. The formation of unusual polymer blends may be achieved using this method.

Dyeing of Polymers

Dyes typically have poor solubility in supercritical CO2. Therefore, the supercritical CO2 dyeing of polymers uses a different mechanism to impregnate polymers than the previously described impregnation method.

Usually, the dye molecule has a greater affinity for the polymer matrix and only a slight solubility in supercritical CO2. In this situation, the dye preferentially partitions from the supercritical fluid into the polymer fibers.

Crystallization of Polymers

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- induced mobility of the polymer chains allows them to rearrange into kinetically favored configurations, thus forming crystallites

Foaming of Glassy Polymers

Plasticization of glassy polymers with high-pressure supercritical fluids plays an important role in the formation of polymeric foams. 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 anti plasticization. This rapid escape of gas can cause the nucleation and growth of bubbles within the polymer. Once a significant amount of gas escapes, the *Tg* of the polymer drops and, thus, “freezes” the foamed structure.

Examples of foamed polymers

Polymethyl (methacrylate) (PMMA)
Polyethyl (methacrylate) (PEMA)
Polycarbonate
Poly(ethylene terephthalate) (PET)
Polystyrene
Glycol-modified PET (PETG)
Polyvinylcloride (PVC)
Polypropylene
polyester (polybutylene succinate)
poly(lactide-*co*-glycolide) (PLGA)
Polyimide

Polymer Melts

Supercritical CO2 is quite soluble in many molten polymers, but as described previously only a few high molecular weight polymers are very soluble in supercritical CO2.

The main obstacle in processing high molecular weight polymers is high viscosity. This problem may be overcome by increasing the temperature or by the addition of solvents to the polymer melt. Unfortunately, high temperature may increase polymer decomposition and solvent addition creates problems associated with separation and recovery of solvents from the polymer mix.

Supercritical CO2 is a good replacement for organic solvents in handling highly viscous polymer melts. The dissolution of CO2 in a polymer causes its plasticization even at low temperatures. The plasticization is evidenced by a decrease in the glass transition temperature or melting point of the polymer which in turn results in a reduction in the viscosity.

Thus, the use of CO2 allows for the processing of polymers at low temperatures and polymer degradation is avoided.

Many of the above examples describing the processing of dry polymers with supercritical CO2 may be replicated by dissolving supercritical CO2 into a melted polymer as an alternative operation. These include: polymer modifications ,polymer blends, polymer foaming, and particle formation.

Conclusion

In summary, supercritical fluids offer a solution to many problems associated with the processing of polymers and polymer melts; including polymer extraction, drying, impregnation, blending, dyeing, crystallization and foaming without the use of toxic solvents.

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