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POLYMER PROCESSING WITH SUPERCRITICAL FLUIDS: AN OVERVIEW

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1. Introduction

The first industrial process involving polymers and supercritical fluids (SCFs) was the free radical polymerization of ethylene: it was developed in the late 40s, and the first plants began to operate in the early 50s. In this process ethylene acts both as a reactant and as a solvent for the sinthesized polymer. The process is conducted at temperatures as high as 250°C (to increase reaction rate) and at pressures between 2000 and 2500 bar (to make sure that the reacting system is in a single phase to have a better control on the reaction). Besides this widespread diffused process, no attempts to develop applications involving polymers and supercritical fluids can be found in the open literature till the early 90s.

However, in these last years a lot of work has been performed in the field, which has also been reviewed in some papers [1, 2].

Mainly two motivations gave a push to the research:

- supercritical fluid technology can be profitably used to process substances of high value which need to be obtained at high purity and without any trace of solvent (examples are fine chemicals and pharmaceutical products). In particular, the supercritical fluid can be used as a cleaning agent (to extract any entrapped solvent from the product) or it can directly replace organic solvents in the process;
- supercritical fluids are more environmentally benign solvents than normal organics; the always more stringent exigency for an environmentally benign chemistry has further promoted the development of this field.

In particular, the most important applications are polymerization reactions, polymer fractionation and cleaning, polymer impregnation and dyeing, polymer recrystallization involving supercritical solvents or antisolvents.

This review is divided in two parts. In the first part a fundamental analysis on polymer-SCF systems is carried out. The possible kinds of binary phase diagrams are presented, and a qualitative interpretation on a molecular basis is given, which tries to explain the special behavior of a polymer-solvent system. The effect of swelling and sorption of a SCF in a polymer and the effect of pressure on the glass transition temperature are also analyzed.

In the second part, a number of applications of supercritical fluids for polymer processing is reviewed. The reader should pay attention on the fact that thermodynamic issues play a primary role to establish if these processes are feasible or not, and to optimize the operating conditions.

2. Thermodynamics of phase equilibria for polymer-solvent systems

2.1 Polymer-solvent systems phase diagrams

Two classes of binary P-T diagrams, which originate from type III and type IV diagrams for small molecules systems (according to the classification can describe the phase behavior for polymer-solvent binary systems by Scott and Van Konynenburg [3]).

Figure 1 shows the *P-T* diagram for a polymer-solvent system, which derives from the type III diagram for small molecules. The most important feature is the presence of a Upper Critical Solution Temperature (UCST) and a Lower Critical Solution Temperature (LCST). The UCST is the temperature at which two liquid phases critically merge if the system temperature is isobarically increased. The LCST is the temperature at which two liquid phases critically merge if the system temperature is isobarically decreased. At temperatures between UCST and LCST a single-phase region is found, while at temperatures lower than UCST and higher than LCST a liquid-liquid equilibrium occurs. Both the UCST and the LCST loci end at the intersection with the liquid-vapour (L-V) equilibrium line. In the two intersection points two liquid phases critically merge together with the appearance of a vapour phase. From these two intersections, two liquid-liquid-vapour (L-L-V) equilibrium lines originate. The high temperature one ends at a critical point where a liquid and a vapor phase merge to a single fluid phase in the presence of a second liquid phase. Note that both the L-L-V and L-V equilibrium lines are virtually superposed onto the vapour pressure curve for the pure solvent.

The reason of the appearance of a UCST curve is usually ascribed to energetic interactions between the two components. While dispersion forces are temperature independent, polar interactions and specific interactions such as hydrogen bonding are strongly temperature dependent, and become much more effective when temperature is lowered. Phase demixing occurs if the polymer and the solvent exhibit stronger polar and specific interactions with themselves than with each other, and when temperature is low enough to make this kind of interactions more effective than dispersion forces. On the other hand the reason for the presence of a LCST curve is ascribed to entropic effects. When the solution is heated, the expansion of the solvent is higher than that of

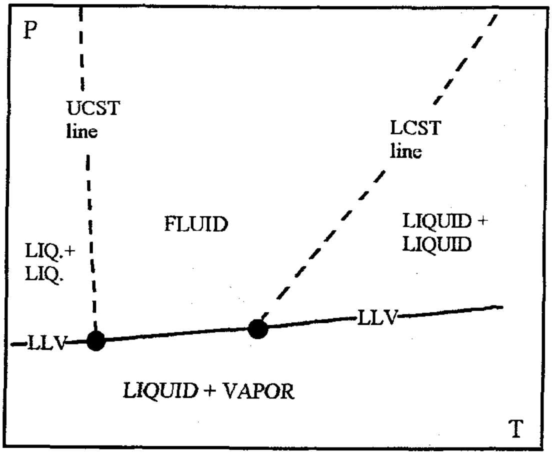

FIGURE 1
P-T diagram for a polymer-solvent system

the polymer, and its free volume becomes larger. To solubilize the polymer, the solvent has to completely surround it. This process causes a penalty in terms of entropy of mixing. Such a penalty becomes higher when the solvent free volume is higher, i. e. when the solvent is more expanded. Eventually, the unfavourable contribution to the entropy of mixing is so large that the free energy of mixing becomes positive and a phase separation occurs.

In Figure 2 a qualitative *P-T* diagram for a system polymer-SCF, derived from a type IV diagram for small molecules is reported. When the difference in size and intermolecular potential becomes larger, i. e. when we turn from a liquid organic solvent to a supercritical fluid solvent, the UCST and LCST curves become progressively closer, till they finally merge. The equilibrium curve reported in Figure 2 can be roughly interpreted as a combination of LCST-type transitions at high temperatures and UCST-type transitions at low temperatures. As suggested by its slope, on the low temperature side phase behaviour can be controlled and modified by varying temperature; on the high temperature side the same effect on phase behaviour can be achieved by varying pressure.

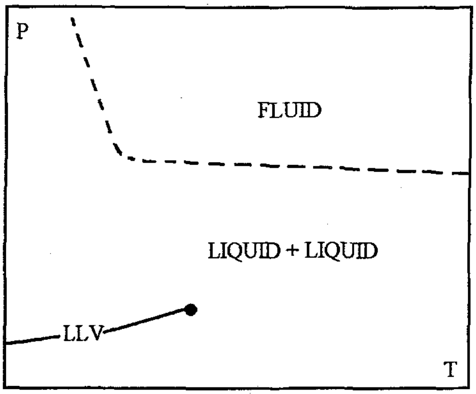

FIGURE 2
P-T diagram for a polymer –SCF system

Extensive measurements on polymer-organic solvent systems have been performed in the late 1960s and early 1970s by Patterson's group [4-6]. On the other hand, studies on polymer-SCF systems were started only in the 1980s, in the groups of Rätzsch [7-10] and Luft [11, 12].

In the last ten years a lot of work in this field has been performed in the groups of Radosz [13-21] and McHugh [22-27]. It is not the purpose of this chapter to review all the results obtained by the quoted researchers. It is important to note that all these results can be successfully placed in the thermodynamic framework described above.

Another important property of polymer-SCF systems is the ability of SCFs to dissolve to considerable extents into amorphous glassy polymers, causing the swelling of the polymer matrix. This fact can be exploited to increase the diffusion coefficients in the polymer [28], and to develop impregnation processes (this application is reviewed in a following paragraph). Swelling (i. e. volume increase of the polymer) and sorption (i. e. weight amount of the gas dissolved into the polymer) databases are quite narrow: available data are presented in Table 1. Swelling data are collected by measuring the extension of a polymer film as a consequence of pressurization with the SCF; the volume expansion is easily calculated from the linear extension if swelling is supposed to be isotropic. For sorption data, usually gravimetric methods are used: the most difficult task is to take into account the effect of the buoyancy, which is negligible at low pressures, but becomes important when the density of the SCF is increased. Accurate equations of state for pure fluids are used to calculate gas densities at a given temperature and pressure; swelling data are needed to calculate the volume of the rich polymer phase. The amount of dissolved gas exhibits an increasing trend at increasing pressures, till a saturation value is reached at pressures usually around 100 bar. When temperature is increased the saturation value of sorption is reached at a higher pressure. An example of sorption data is reported in Figure 3.

An important effect of gas sorption in a polymer is the plasticization effect, i. e. the depression in the glass transition temperature: the sorbed gas acts as a kind of "lubricant", making it easier for chain molecules to slip over one another and thus causing polymer softening. Measurements of glass transition temperatures at high pressure can be only indirect; in particular creep compliance [29,30] and differential scanning calorimetry [31,32] measurements have been performed, from which the value of glass transition temperature can be recovered. The measured depression reaches values as high as 60°C for poly(methyl methacrylate) and poly(styrene).

Recently, a new method has been developed for measuring the glass transition temperature [40] : it uses two Electron Paramagnetic Resonance techniques, and it has been shown to be effective also for polymer-SCF systems.

Some attempts can be found in the literature to model both the sorption of a supercritical fluid in a glassy polymer and the glass transition temperature depression induced by supercritical fluids.

Wissinger and Paulaitis [30] develop a model to correlate swelling and sorption in glassy polymers, based on the Panayiotou-Vera equation of state (a lattice-fluid equation) and on the concept of order parameters. Order parameters are additional variables that describe the thermodynamic state of a system. In the case of a glassy polymer described by a lattice equation two order parameters can be assumed: the fraction of holes in the lattice and the number of nearest-neighbor contacts between polymer segments on the lattice sites. To represent a glassy polymer order parameters are frozen in at the value they assume at the glass transition temperature. Above the glass transition phase equilibria calculations are performed simply by minimizing the Gibbs free energy of the system (i. e. by imposing isofugacity equations and using the equation of state to

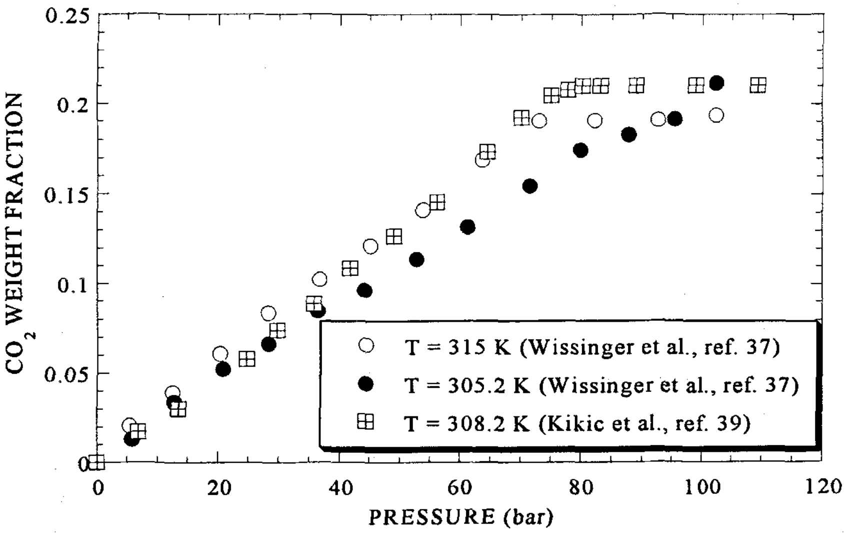

FIGURE 3
Sorption of CO_2 in PMMA at different temperatures

calculate fugacity coefficients). Under the glass transition the system is not at equilibrium, and this is accounted for by "freezing in" the order parameters at their glass transition value before imposing isofugacity equations. Good correlation of the swelling and sorption data above and below T_g are obtained, even if the model is not predictive, as it exhibits two binary interaction parameters.

In a further development of the model, Kalospiros and Paulaitis [41] use the glass transition temperature of the pure polymer to calibrate the value of the order parameter (fraction of holes in the lattice). This value is kept constant even if a swelling agent is added to the system: so the glass transition temperature depression induced by the SCF can be predicted.

A somehow similar model is developed by Condo et al. [42].They use the Sanchez-Lacombe equation of state (again a lattice-fluid equation) and to calculate the glass transition temperature they impose the Gibbs-Di Marzio criterion, which states that the entropy of the system is zero at the glass transition. Only the glass transition temperature of the pure polymer is needed to calibrate the energy parameter. The prediction of the glass transition temperature depression for the systems CO_2-PMMA and CO_2-PS is good. Moreover the model is able to predict a retrograde vitrification phenomenon (i.e. for some polymers at proper *P*, *T* conditions a decrease in *T* at constant *P* leads to a glass to liquid transition). This kind of behavior has been confirmed experimentally in a later paper[43].

2.2 Polymer-solvent systems phase behaviour: a qualitative interpretation

The purpose of this paragraph is to try to answer the question: "Why a polymer is (or is not) soluble in a (SCF) solvent?". It is our aim to show how the choice of the solvent and of the operating variables (temperature and pressure) affects the value of the Gibbs free energy of mixing for the polymer-solvent system.

The isothermal and isobaric free energy of mixing (ΔG_{mix}) for a polymer-solvent system represents the difference between the free energy of the mixture and that of the two components at the same temperature and pressure: if ΔG_{mix} is negative, the two components form a single phase upon mixing. For isothermal and isobaric mixing it can be written:

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} \qquad (1)$$

The enthalpic term (ΔH_{mix}) depends on the intermolecular interactions between solvent-solvent, solute-solute and solute-solvent segments. The entropic term (ΔS_{mix}) depends on the free volume difference between the solute and the solvent.

To explain the role of intermolecular interactions, approximate expressions are used in order to reveal the properties of the components that determine the strength of intermolecular forces[27, 44, 45].

Also non-polar molecules exhibit momentary dipole moments due to electron oscillation; they change direction and magnitude randomly, and they average to zero over a finite period of time, but they cause a net attractive force that can be described in terms of interaction energy by the following simplified expression:

$$\Gamma_{ij} = -C_1 \frac{\alpha_i \alpha_j}{r^6} \qquad (2)$$

where α is the polarizability of each component expressed in cm^3, *r* is the distance between the centres of mass of the molecules (or segments), and C_1 is a constant. The attractive forces between non-polar molecules are called dispersion forces, and the corresponding interaction energy is the dispersion energy. The dispersion energy is independent on temperature, and short-range. The polarizability is the key property to establish the strength of a non-polar solvent: within a given class of molecules, it generally increases with the size of the molecule.

Molecules can also exhibit permanent dipoles, whose direction and strength are functions of the molecular structure. Depending on mutual orientations, two dipoles can both attract and repulse each other. But if the mutual interaction is averaged on all possible orientations, a net attractive contribution is obtained. The following simplified expression can be written for the average dipole-dipole interaction energy:

$$\Gamma_{ij} = -C_2 \frac{\mu_i^2 \mu_j^2}{r^6 kT} \qquad (3)$$

where μ are the dipole moments of the components (in debyes), k is the Boltzmann constant, T is the temperature and C_2 is a constant. The attraction forces are again short range, and they decrease with increasing temperature; when temperature is high enough also a polar substance can exhibit non-polar behaviour, because the dipole-dipole interaction energy becomes negligible with respect to the dispersion energy. In this case the key molecular parameter is the dipole moment: polar interactions have a large effect on the potential energy between two molecules if the dipole moment is larger than 1.0 debye.

Molecules can exhibit also quadrupole moments, whose mutual interaction averaged on all possible directions give again a net attractive contribution; the simplified formula for quadrupole-quadrupole interaction energy becomes:

$$\Gamma_{ij} = -C_3 \frac{Q_i^2 Q_i^2}{r^{10} kT} \qquad (4)$$

where Q is the quadrupole moment. Also quadrupole interactions decrease when temperature is increased, but they are more short ranged than dipole interactions, so they are less effective. However, the solvent power of CO_2, the most commonly used supercritical fluid, is due to its large quadrupole moment.

Quadrupoles and dipoles can also interact between themselves; moreover, they generate electric fields that cause charge separation and polarize also non-polar molecules. Thus attractive interactions take place also between polar and polar-induced molecules, and can be taken into account as follows:

$$\Gamma_{ij} = -C_4 \frac{\mu_j^2 Q_i^2}{r^8 kT} - -C_5 \frac{\mu_i^2 Q_j^2}{r^8 kT} - C_6 \frac{\mu_j^2 \alpha_i + \mu_i^2 \alpha_j}{r^6} - C_7 \frac{Q_j^2 \alpha_i + Q_i^2 \alpha_j}{r^8} \qquad (5)$$

where the first two terms account for dipole-quadrupole interactions, the third one refers to dipole-induced dipole interactions, and the last one to quadrupole-induced quadrupole interactions.

In addition to physical forces, molecules can exhibit also chemical attraction forces, such as hydrogen bonding and electron donor-electron acceptor complexing. The most important differences between physical and chemical interactions are: chemical interactions can become saturated, while physical cannot, and the temperature dependence is much stronger for chemical interactions..

In every molecule that is able to hydrogen bond there is a certain number of hydrogen bonding sites: once they are all occupied, no more bonds will form. But if temperature is high enough, the Brownian motion of the molecules makes it difficult for them to reach the proper alignment to build a bond. Again, if temperature is high enough also a hydrogen-bonding molecule can behave like a non-polar molecule. Unfortunately, chemical forces are more difficult to quantify than physical ones, and no simplified expressions are available.

To determine if a polymer will dissolve in a given solvent, it is necessary to consider the balance of intermolecular attraction forces between solvent-solvent, polymer-polymer and solvent-polymer segments. The interchange energy of mixing can be written as:

$$E = \Gamma_{ij} - \frac{\Gamma_{ii} + \Gamma_{jj}}{2} \qquad (6)$$

If the strength of *ii* or *jj* interactions is higher than that of *ij* interactions, the polymer will not be dissolved. To maximize *ij* interactions it is necessary that *i* and *j* have similar characteristics, i. e. that they are both polar or non polar.

As an example it is interesting to compare the solubility of poly(ethylene) (PE, non polar) and poly(methylacrylate) (PMA, polar) in ethylene and CO_2. CO_2 is more polar than ethylene (quadrupole moment is $-4.3*10^{-26}$ $erg^{0.5}cm^{2.5}$ for CO_2 and $+1.5*10^{-26}$

$erg^{0.5}cm^{2.5}$ for ethylene), but it has a lower polarizability ($26.5*10^{-25}$ cm^3 against $42.5*10^{-25}$ cm^3). Non polar PE is soluble in ethylene, but not in CO_2 [27] because the higher polarizability of ethylene increases the dispersion interactions with PE, while CO_2 quadrupole moment does not interact well with non polar PE. On the contrary, polar PMA is soluble in CO_2 [27] but not in ethylene [46] because the high quadrupole moment of CO_2 interacts favourably with the dipole moment of polymers' repeat unit. Moreover, a weak electron donor-electron acceptor complex is likely to be formed between the carbonyl oxygen of PMA repeat unit and the carbon atom of CO_2 [47]. Another interesting example is the comparison between the PMA-CO_2 and PVAc-CO_2 systems. The structure of these two polymers is similar, the only difference being that the carbonylic group in PVAc is more far away from the main backbone. This makes it easier for CO_2 to interact with the carbonylic oxygen; indeed PVAc is soluble in CO_2 at 1000 bar, while PMA is soluble only at 2000 bar [27]. Analogous considerations can drive in the interpretation of sorption data of a dense gas in a glassy polymer: favourable physical and chemical interactions allow higher amounts of gas to be sorbed.

Besides the enthalpic term also the entropic one plays an important role. The solvent molecules have to surround completely the polymer in order to solubilize it. This represents a large entropic penalty for the solvent, which becomes higher when the difference between the free volumes of the solvent and the polymer is higher, i. e. when the solvent is more expanded. This explains why increasing the density of the solvent by increasing pressure leads to an increased solvent power. From the point of view of the polymer the free volume increases when the polymer is more branched, because it is more difficult for the polymer chains to align and pack. Also the glass transition temperature (T_g) is important. The higher the T_g, the higher the chain stiffness, which means a higher entropic penalty for the solvent. This fact can explain why PMMA is not soluble in CO_2 till 255°C and 2550 bar, while PMA is soluble in CO_2 at 150°C and 2000 bar [27]. The intermolecular interactions between both polymers and CO_2 are about the same, because the structural difference between them is little. On the other hand, PMA has a T_g of 9°C, while PMMA of 105°C, so the latter causes a much higher entropic penalty to the solvent due to its stronger chain stiffness. Also the selectivity of the SCF solvent on the molecular weight is based on an entropic issue. The higher the molecular weight of the polymer, the higher the degree of order needed for the solvent to solubilize it. As the molecular weight is increased, more pressure is needed for the SCF solvent in order to overcome this entropic penalty. By increasing pressure step by step, different oligomers can be selectively extracted.

Entropic penalty plays an important role also for the sorption of gases in glassy polymers. High chain stiffness makes it difficult for CO_2 to dissolve into the polymer, so a high T_g is unfavourable for gas sorption. Another negative factor is cross-linking, again because it prevents polymer chains from slipping making the whole structure more rigid.

3. Polymer processing with supercritical fluids

Before 1985 really little work had been reported in the open literature about polymers processing with supercritical fluids. However, since then a lot of papers have appeared in the field, mainly in the following areas:

- use of supercritical fluids as environmentally acceptable reaction media for polymerization reactions;
- supercritical fluid cleaning and purification of a polymer from monomers, solvents or other kind of impurities;
- polymer fractionation processes;
- special applications to obtain a particular structure, such as swelling, Gas Anti-Solvent recrystallization, polymer impregnation, fibres dyeing.

All of these processes are briefly described in the following paragraphs, and the most recent developments proposed in the open literature are presented.

3.1 Polymerization reactions in SCFs

The most important example in this field is the high pressure polymerization process to produce low density poly(ethylene) (LDPE). LDPE is obtained in tubular or CST reactors at temperatures over 200°C and pressures over 2000 bar, where ethylene acts both as a reactant and as the solvent. Downstream of the reaction section the LDPE-ethylene solution is expanded to a lower pressure (about 350 bar). The solvent strength of supercritical ethylene is lowered, and the polymer precipitates in a separator. After that, residual ethylene is recycled to the reactor. This process has been in operation since the early 1950's, with production rates as large as 150 to 250 million kg/yr of LDPE.

Besides this very important and widespread process, little has been done in the field of polymerization in a SCF environment until the early '90s. Starting 7-8 years ago some research groups (DeSimone, Beckman) carried out a number of studies on the use of supercritical CO_2 as the medium for polymerization reactions [48]. Perhaps the greatest motivation for this research comes from environmental issues. Usually polymerization reactions are conducted in volatile organic solvents, chlorofluorocarbons (CFC), and water solutions. After the reaction the waste streams need to be treated and purified, and the operations involved are expensive and time consuming. Moreover CFC solvents have been banned by the Montreal protocol in 1986. Supercritical CO_2 seems to be a possible answer to the requirement for environmentally benign solvents: it is readily available, non toxic, non flammable, inexpensive and environmentally acceptable. In addition, it exhibits unique solvent properties: at moderate pressures its density is similar to that of liquids, and it is able to dissolve a number of non-polar or slightly polar organic compounds; on the other hand viscosity and transport properties are intermediate between those of gases and liquids. The properties of supercritical CO_2 can easily be controlled and finely tuned by changing pressure and temperature, especially near the critical point.

Unfortunately, the dissolving power of CO_2 for polymers is negligible at low to moderate pressures. In particular only perfluoropolymers and silicones are soluble to an acceptable extent in supercritical CO_2 at relatively mild conditions [49]. Other polymers, such as poly(acrylates), poly(acetates), fluorinated and chlorinated polymers are soluble in CO_2 only at very high pressures (over 2000 bar), or they need a cosolvent. As a consequence homogeneous free radical polymerization in CO_2 can seldom be performed, and other methods need often to be used, such as precipitation polymerization and dispersion polymerization.

In the following paragraphs the results obtained with these three different techniques will be described and discussed.

3.1.1 Homogeneous free radical polymerization

The first homogeneous free radical polymerization in supercritical CO_2 has been reported by the group of DeSimone [50]. They successfully polymerized 1,1 dihydroperfluoroctyl acrylate (FOA) with supercritical CO_2 as the solvent at 60°C and about 200 bar. The reaction is started by an initiator, azobisisobutyronitrile (AIBN). Kinetic studies of the decomposition rate and efficiency of the initiator [51] lead to the conclusion that the decomposition rate is higher in benzene than in CO_2, probably because the higher dielectric strength of benzene stabilizes the transition state of the reaction. On the other hand, the efficiency of the initiator is higher in CO_2, because the better transport properties of CO_2 make it easier for the radicals to diffuse into the solvent bulk and thus to become active. The reaction was carried on for 48 h, with a yield of about 65%. Similar results can be obtained with a variety of other highly fluorinated acrylic monomers. It is also possible to sinthesize statistical copolymers of fluorinated monomers and conventional hydrocarbon-based monomers (methyl methacrylate, styrene). Even if the hydrocarbon polymers are almost insoluble in supercritical CO_2 at pressures and temperatures investigated, the copolymers can be sinthesized by homogeneous polymerization, because the perfluorinated component is able to keep the whole polymer in solution.

Another study was performed about the telomerization of tetrafluoroethylene (TFE) and 1,1 difluoroethylene (VF2) with perfluorobutyl iodide as the telomer [48, 52, 53]. Chain transfer is easy when TFE and VF2 are treated in normal hydrocarbons, because the fluorinated free radicals are able to extract hydrogen atoms from the solvent, thus stopping the reaction. On the other hand, CO_2 is completely inert towards TFE and VF2, and chain transfer is avoided. A very narrow polydispersity curve is obtained.

Finally fluorinated vinyl ethers and oxetanes (cyclic ethers) were polymerized in supercritical CO_2; the reaction was carried on in a single phase with a yield of about 70% and a narrow molecular weight distribution [54]

3.1.2 Precipitation polymerization

As already noted, only a few polymers can be solubilized in CO_2 at moderate pressure; for them a homogeneous polymerization is possible. If a polymer is insoluble in supercritical CO_2, heterogeneous polymerization techniques have to be used: among others, precipitation polymerization and dispersion polymerization have been attempted.

In precipitation polymerization the polymer, not soluble in the solvent, precipitates as soon as it forms. This technique has been tested for the copolymerization of tetrafluoroethylene (TFE) and perfluoro(propyl vinyl ether) (PPVE) [55]. The synthesis is difficult to perform in normal organic solvents, because the fluorinated free radicals are able to extract hydrogen atoms from nearly all hydrocarbons, precluding the formation of high molecular weight fluoropolymers. When the reaction is performed in supercritical CO_2, no chain transfer to the solvent is detected, and it is possible to obtain good yields and high molecular weight products.

Another example is the polymerization of vinyl and cyclic ethers in supercritical CO_2 [54]. Also in this case the yields were good, even if the average molecular weights were low and strongly dependent on initiator type.

Finally, acrylic acid has been polymerized in supercritical carbon dioxide, using AIBN as initiator [56]. Pressure range was 125 to 350 bar; high yields and high molecular weight polymers were obtained: the products were similar to those obtained from reactions carried out in conventional solvents.

Other attempts to perform precipitation polymerization did not give good results. The main problem is that the polymer precipitates (i. e. it goes out of the reacting environment) too early, thus causing low yields, low molecular weights and broad molecular weight distributions. Moreover, the polymer usually precipitates as a continuos network, while spherical particles would be more useful. A way is needed to make the reaction more stable and easy to control, in order to achieve higher yields and molecular weights. The problem can be solved by the addition of the stabilizer, which "builds a bridge" between the growing polymer chain and the continuos CO_2-rich phase containing the reactant. This is the basic idea of dispersion polymerization.

3.1.3 Dispersion polymerization

In the supercritical CO_2 dispersion polymerization process a stabilizer is used to form a stable polymeric colloid consisting of a "CO_2-phobic" dispersed phase containing the sinthesized polymer, and a CO_2–rich continuos phase. This procedure allows for the synthesis of high molar mass polymers in the form of micrometer-sized particles with a narrow size distribution. By using a proper stabilizer in a proper amount, a good control of particle size and particle size distribution can be achieved. A free radical dispersion polymerization starts in a one-phase, homogeneous system, because the monomer, the initiator and the stabilizer are all soluble in the polymerization medium (in our case supercritical CO_2). The sinthesized polymer is not soluble, and precipitates as "primary particles". These particles are stabilized by the stabilizer, which is able to surround them and to prevent flocculation and aggregation.

DeSimone et al. [57] reported the first successful dispersion polymerization in supercritical CO_2. They polymerized methyl-methacrylate (MMA) by using AIBN or fluorinated AIBN (F-AIBN) as initiators, and poly(FOA) as stabilizer. Poly(FOA) is a fluorinated acrylic polymer (see the paragraph about homogeneous polymerization) and is soluble in CO_2. The stabilization is due to a steric mechanism. The stabilizer molecules are adsorbed onto the surface of the dispersed phase (the growing poly(methyl methacrylate) chains). They contain an anchoring segment, i. e. the main backbone of poly(FOA) which has a hydrocarbon nature and interacts well with the growing PMMA particles, and stabilizing tails, i. e. the fluorinated tails of poly(FOA) which are soluble in the CO_2 continuos phase. Stabilizer molecules, which prevent aggregation and flocculation, thus surround a growing polymer particle, making the colloidal dispersion stable and allowing further growth of the polymer. In the paper quoted above very low yields and molecular weights are obtained if no stabilizer is added. The addition of 4% stabilizer at T=65°C and P=200 bar is enough to reach yields of 90% molecular weights of 300000, and to obtain the sinthesized polymer as spherical microparticles. At the end of the reaction the stabilizer can be removed by washing with CO_2, and a pure polymer is finally obtained. Hsiao [58] carried out a more-in-depth study of the same reaction. It is shown that the poly(FOA)-CO_2 system exhibits LCST phase behavior, with a very high solubility of the polymer in CO_2. The polymer is produced in the form of spherical particles.

In another study [59] MMA was polymerized by using a poly(dimethylsiloxane) (PDMS) macromonomer as a stabilizer. The macromonomer has an acrylic functionality on one side, so it can also take part in the polymerization reaction. High yields high molecular weights and spherical particles are obtained. Lepilleur and Beckman [56] report similar results for MMA.

With the same technique poly(styrene) can be sinthesized [49, 61]. In this case poly-FOA is not a successful stabilizer, probably because the anchoring to the growing polymers is not effective enough. As alternative stabilizers block copolymers of styrene and FOA [62], or styrene and DMS have been used with good results. It seems that the styrene blocks provide a good anchoring and stabilizing action, while the FOA or DMS blocks keep the stabilizer solubilized in the CO_2 continuos phase. High yields and molecular weights can be obtained by properly tuning the operating conditions.

More recently poly(styrene) has been synthesized with a siloxane based macromonomer as a stabilizer [63, 64]: again good results have been obtained.

Synthesis of poly(2,6-dimethylphenylene oxide) in carbon dioxide was also proposed [65]. An amine needs to be used as initiator: low molecular weight amines and polymeric, CO_2-soluble amines were used. The latter should act also as stabilizers, leading to higher yields. In fact experiments showed that the stabilizing effect of polymeric amines was negligible. The most effective stabilizers were block copolymers of FOA (soluble in CO_2) and styrene (in which the sinthesized polymer is soluble). High yields could be obtained, even if molecular weights were quite low.

The inverse emulsion polymerization of acrylamide performed by Adamsky and Beckman [66] is similar to the dispersion polymerization. They used a surfactant with a polar head (an amide) to interact well with water, acrylamide and AIBN (the initiator), and a fluorinated tail which is soluble in CO_2 and forms the emulsion between the reacting mixture and CO_2. High yields and molecular weights can be obtained.

It is not easy to understand the effect of operating parameters on yield, average molecular weight, and polymer particles diameter, also because different authors seems to obtain different results.

If the stabilizer concentration is under a certain limit (which is a characteristic value of each reaction) the stabilizing effect is not strong enough, leading to a precipitation polymerization rather than a true dispersion polymerization. In this case, yields and number average molecular weights are low, and particles are not regular [49, 57, 58, 59, 61, 63]

When the concentration of stabilizer is increased the mean particle diameter decreases and more uniform particles are obtained [49, 57, 58, 59, 63]. Moreover, the yield and the number average molecular weight usually increase [58, 59, 61, 63]. If the molecular weight of stabilizer is increased, larger polymer particles are obtained [57]

In the synthesis of poly(styrene) it is necessary to use a copolymer as a stabilizer, and in this case also the relative amount of anchoring and stabilizing segments is effective. Canelas et al. [49] found that an increase in both the anchoring and the stabilizing segments length leads to lower particle diameters and particle size dispersity. If the stabilizing segment becomes too large with respect to the anchoring segment, a strong decrease in yields and number average molecular weights is found, together with higher particle size dispersity [61]. On the other hand, when the stabilizing segments are short enough, high yields and molecular weights are obtained; when the anchoring segment is increased, particles becomes larger and more monodisperse [61].

As the concentration of the initiator is increased, a lower number average molecular weight is obtained [49], probably because the higher amount of initiator causes the formation of a greater number of polymer chains which as a consequence have to be shorter.

When the monomer concentration is increased, higher number average molecular weights and larger diameters are obtained [58]. This is probably due to the fact that the solvent power of the reaction medium towards the polymer is increased when the monomer concentration is enhanced; phase demixing occurs later, and fewer and more stable nuclei are formed. This leads to larger particles with a wider particle size distribution.

Finally the effect of pressure needs to be evaluated. If pressure is too low, the solvent power of CO_2 towards the stabilizer is not enough to obtain a uniform and stable dispersion [57]. A low pressure causes also a smaller conversion rate [64]. If pressure exceeds a certain limit (which is different for each reaction) a stable dispersion is obtained which leads to high yields and little particles. Some authors find that increasing pressure above this limit leads only to little variation in the product with no apparent trends [58]; other authors find an increase in the molecular weight when pressure is increased [61].

An interesting study has been recently carried on to understand which is the mechanism the nucleation and subsequent phase demixing and dispersion formation [64]. The particle number density varies rapidly at the very beginning of the reaction, it approaches early its final value, and then it remains constant and the only effect of reaction is to cause particles growth. The average particle diameter and particle number density are monitored as a function of time by means of turbidity measurements. As the particle number density goes through a maximum before reaching its final value, a mechanism involving two following steps is proposed. In the first one (nucleation) a large amount of nuclei is formed in a short time, leading to the maximum in the particle number density curve; in the second one these very little nuclei become unstable, and cause coagulation and flocculation until a smaller number of stable nuclei is obtained. From now on no new particles are formed any more, and the reaction leads only to particles growth.

3.2 Polymer cleaning with SCFs

The basic idea driving SCF polymer cleaning is simple: the SCF is flowed through the matrix to be purified, and its solvent capacity allows the solubilization of non-polymeric impurities, but not of the polymer matrix. Supercritical fluids are usually more selective compared to normal organic solvents, and should be able to extract only the impurities without affecting the matrix. Moreover, it is enough to decrease pressure to separate the supercritical solvent from the impurities after the extraction. One problem has to be carefully considered: the plasticization effect occurring when an amorphous polymer is contacted with a supercritical fluid can damage the polymer matrix. In order to avoid this, proper operating conditions need to be selected.

Among others, the application of this technique is under development for the following materials: polymers used in the food industry [67], pharmaceutical compounds [68], fibres [69,70]. The process can be applied not only to polymers, but also to a wider variety of substances: metal parts, both mechanical and electronical [71-73] and ceramic materials [74].

Breivik et al. [75] use supercritical CO_2 to clean poly vinyl chloride from residual anionic emulsifier and volatile components. Both are drastically reduced if methanol is used as a modifier to increase the solubility of the polar emulsifier in the supercritical solution.

Also the degreasing of sheepskins by supercritical CO_2 has been reported [76]. Depending on the type of sheepskin, the maximum extractable fat with SCF cleaning can be higher or lower than the traditional one.

Dense CO_2 has been proposed to clean NBR (an acrylonitrile-butadiene copolymer) and PET (poly(ethylene therephthalate)) from additives used in the synthesis process and residual reagent traces [67]. For both polymers, purification can be achieved in a short time at a satisfactory level simply by tuning pressure and temperature. The most difficult task is connected with the fact that the polymer absorbs CO_2 and swells. Enough free volume is needed in the vessel to allow polymer swelling. Moreover, after the cleaning process decompression needs to be slow enough to avoid damages to the polymer structure, which could reduce impermeability.

Supercritical CO_2 has been used also to remove residual solvent from a controlled drug release system [68]. In such a system the drug needs to be carried into a matrix, which is usually a biocompatible polymer. At the conditions generated inside the human body the polymer swells and allows the drug to diffuse out. To carry the drug into the matrix an organic solvent is used as the swelling agent. The drug is solubilized in it; when the solution contacts the matrix the solvent is able to swell it and the drug easily diffuses into the pores. The following step is the solvent removal. Usually vacuum drying is applied, but this treatment can damage the drug if high temperatures are needed. Supercritical fluid extraction can be useful in this case, because of its milder temperature conditions. Obviously the solubilities of both the solvent and the drug need to be measured, and the operating conditions (temperature and pressure) need to be set in order to maximize the solubility of the solvent without dissolving also the drug. It is important to take into account that the presence of the solvent can increase the solubility of the drug in the supercritical fluid (cosolvent effect). The quoted authors claim to be able to reduce the solvent amount from 1500 to 20 p.p.m. without removing any drug.

Finally, it is possible [69] to remove ε-caprolactam from nylon-6 with supercritical CO_2, and the removing rate is faster when temperature and pressure are increased. The removal of spinning and finishing oil from fibres (PET, nylon-6 and nylon-66) was performed with supercritical CO_2 [70]. The extraction efficiency is high for all the fibres (more than 90% of the oil is successfully extracted). The tensile properties are similar to those obtained with the normal water cleaning process.

3.3 Polymer fractionation processes

When a polymerization reaction is performed, it is usually difficult to obtain a monodisperse product with a desired molecular weight. But a number of applications need polymers at a well-defined molecular weight and with a proper molecular weight distribution. As an example, if a polymeric material has to be extruded, a little amount of low molecular weight product is usually necessary to increase the fluidity of the system (it acts as a lubricant). Normal organic solvents are often not effective in the fractionation of polymers of different molecular weights. At normal conditions the solubility of a polymer in an organic solvent is governed by energetic interactions, such as dispersion forces, dipole-dipole interactions or complex formation. If a polymer-solvent pair exhibits good energetic interactions, the polymer can be dissolved regardless its molecular weight. In a polymer-SCF system the phase behaviour is governed also by entropic interactions, i. e. the free volume differences between the polymer and the solvent. Qualitatively speaking the solvent molecules need to condense around the polymer in order to solubilize it, and this causes a large entropic penalty for the solvent. Of course the larger the polymers chain (high molecular weight polymers) the higher this penalty. To overcome this penalty, it is necessary to increase pressure in order to reduce the free volume difference between solvent and polymer. As soon as pressure is increased, higher molecular weight fractions become soluble, and it is possible to fractionate the polymer by tuning pressure.

To choose the proper solvent for a certain polymer, some straightforward principles are usually adopted. In the first paragraph of this chapter qualitative considerations on the phase behaviour of polymer-SCF systems are reported, which can be helpful to make a good choice. Moreover, a large data bank on the solubility of polymers in supercritical fluids is now available [45]. The most important point is that the polymer needs to exhibit good physical (and also chemical, such as complex formation) interactions with the solvent.

To perform the separation process, two procedures can be used [45]: the Isothermal Decreasing Pressure Profiling (IDPP, used above all in the industrial practice) and the Isothermal Increasing Pressure Profiling (IIPP, used at a laboratory level).

The IDPP process (represented in Figure 4) is performed in a multiple sequential pressure reduction system, with a certain number of extraction/separation vessels. The liquid polymer is pumped to the first vessel (extractor) at the top. The supercritical fluid enters at the bottom, and dissolves the polymer to a certain extent depending on the operating temperature and pressure. The solution leaving the extractor is then expanded to a lower pressure in the first separator, where the higher molecular weight oligomers are forced to precipitate. The remaining stream is further expanded in subsequent separation vessels, which results in further separation by molecular weight. The molecular weight distribution of each fraction can be extremely narrow if the pressure decrease between two different stages is small. Of course the lower the pressure jumps, the lower the amount of each fraction. In this case, different runs at subsequent decreasing ranges of pressure are needed to fractionate completely the polymer.

On a laboratory scale the IIPP process (represented in Figure 5) is more useful. An amount of polymer is charged in a high-pressure vessel, and the supercritical solvent is passed through the system at sequentially increasing pressure levels. After the extraction the solution is expanded and the extracted polymer precipitates in a collector. A low pressure is used at first, and the extraction is continued until the extraction rate drops down markedly and no more polymer is collected. Then the pressure is raised, the

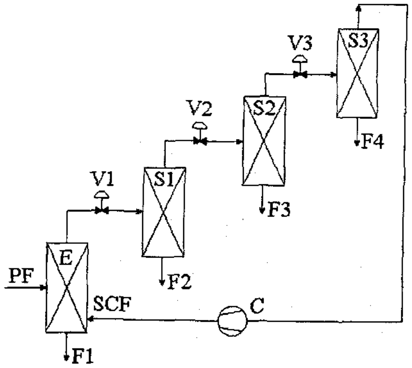

FIGURE 4
Isothermal Decreasing Pressure Profiling polymer separation process (PF: polymer feed; SCF: supercritical fluid feed; C: compressor; E: extraction vessel; S1, S2, S3: separation vessels; V1, V2, V3: regulation valves; F1, F2, F3, F4: fractions (F1 heavier, F4 lighter)

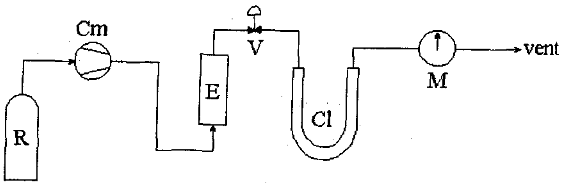

FIGURE 5
Isothermal Increasing Pressure Profiling polymer separation process (R: reservoir; Cm: compressor; E: extraction vessel; V: regulation valve; Cl: U-tube collector; M: dry test meter

collection vessel is changed and a new polymer fraction is sampled. The sequence is repeated until all of the polymer is dissolved (or until the maximum operating pressure for the apparatus is reached).

Examples of polymer fractionation following these principles are presented [45]. Among others, data on fractionation of poly(ethylene), poly(ethylene-co-methyl acrylate), poly(siloxanes), other silicone polymers, perfluoroalkyl polyether, poly(styrene), poly(isobutylene) are presented.

A different concept is used by Super [77] and Altland [78] for the purification of mixed plastic waste streams, in which different polymers are mixed together in a thermoplastic mixture and need to be separated. Separation is obtained by floatation. The waste stream is charged into a vessel, then the vessel is pressurized with near critical CO_2, SF_6, or a mixture of both. Pressure is gradually increased, till the various components of the thermoplastic mixture are sequentially floated according to their densities. It is important to know that the polymers involved (polyethylene, polypropylene, polystyrene, polyvinyl chloride and polyethylene terephthalate) are not altered either physically or chemically by the supercritical floating agent.

3.4 Special applications

With "special applications" we indicate some new operations and techniques developing mainly in the field of material processing. Some of them allow to obtain particular properties in a polymeric material (polymer swelling, recrystallization processes like the rapid expansion of a supercritical solution and the precipitation with a supercritical antisolvent). Others are used to load a polymeric matrix with other compounds of interest (impregnation of a bioerodible matrix with a drug, material coating and textile dyeing).

In the following paragraphs all of these special applications will be briefly described and summarized.

3.4.1 Polymer swelling

The swelling of an amorphous polymer induced by a supercritical fluid is a well-known phenomenon; surprisingly, the experimental data base is still quite narrow (all the data available at present are reported in Table 1 . When an amorphous polymer is contacted with, for example, dense CO_2 at room temperature and moderate pressures (70 to 100 bar), the sorption of CO_2 can be as high as 20 wt%, thus leading to a swelling of about the same percent level.

Polymer swelling can be exploited to obtain microcellular foams [79]. In this work a poly(styrene) foam is obtained by pressurizing the polymer with N_2 or CO_2, and then suddenly releasing pressure, in order to obtain bubble nucleation in the bulk. The higher the pressure drop, the higher the nucleation rate, and the smaller the cell diameter. If the

TABLE I

Available data base on sorption and swelling of polymers with dense gases

Polymer	Gas	T range (°C)	P range (atm)	Reference
PMMA PEMA	CO_2	30-80	0-20	[33]
PMMA	CO_2	41.8-68	0-300	[34]
PVB	CO_2, N_2, Ar	25-70	0-50	[35]
PC	CO_2	35	0-65	[36]
PC, PMMA, PS	CO_2	33-65	0-100	[37]
PVC, PC, PMMA, PVA	CO_2	25	0-65	[28]
PS, PMMA, PVD, PI copolymers	CO_2	35	0-100	[38]
PMMA, biocompatible pol.	CO_2	35-45	0-120	[39]

PMMA: poly(methyl methacrylate); PEMA: poly(ethyl methacrylate); PVB: poly(vinyl benzoate); PC: poly(carbonate); PS: poly(styrene); PVC: poly(vinyl chloride); PVA: poly(vinyl acetate); PVD: poly(vinyl pyridine); PI: poly(isoprene)

polymer is heated for a certain time after releasing pressure, cell diameter can grow significantly, because of the expansion of the gas trapped in the cells.

Another important consequence of dense gas sorption in an amorphous polymer is the plasticization effect. The glass transition temperature can decrease significantly upon pressurization [80]. The lower viscosity of the polymer can be exploited during manufacturing it (for example in extrusion processes).

The swelling effect can be exploited also to impregnate a polymer matrix with additives. Sand [81] patented a technique to charge biocompatible polymers with drugs. The polymer is swelled with a dense gas, thus inducing larger pores that increase the diffusivity into the matrix and allow the drug to migrate into it. Then, pressure is suddenly released and the gas can diffuse easily out of the polymer. The heavy drug diffusivity is much lower, so that it remains trapped in the finally unswollen matrix. Perman [82] presents similar process. The substrate to be impregnated is suspended in water, which contains in solution the substance to be charged. The mixture is exposed to supercritical CO_2, which is able to solubilize in water and into the polymer matrix, thus swelling the polymer. The solute dissolved in water diffuses rapidly into the swollen matrix; once the impregnation is completed (this is determined by experimental trial) pressure is released, the supercritical fluid diffuses out and the solute remains inside the matrix. Several variables affect the impregnation process. Increasing pressure and temperature leads to a faster impregnation of the matrix. Higher solute concentrations in water lead to a higher substrate loading at equilibrium. Finally, amorphous polymers are loaded much more easily than semi-crystalline or cross-linked polymers, because the latter are more difficult to swell.

3.4.2 Precipitation processes

Polymers produced in form of microspheres are useful in several applications. They can be used as stationary phases in chromatography columns, in order to maximize the exchange area and to make the columns more efficient. A large area per unit volume leads to a better efficiency also for adsorbent media and as catalyst supports. A relatively new application for biopolymers is to use them as the base for controlled drug delivery systems. For this purpose, polymer microspheres need to be charged with a drug; if a uniform dispersion of the drug inside the polymer is obtained, the drug is slowly and uniformly delivered to the organism as the polymer is degraded.

The most important recrystallization processes involving supercritical fluids are the Rapid Expansion of a Supercritical Solution technique (RESS) and the Supercritical AntiSolvent recrystallization technique (SAS).

3.4.2.1 RESS technique

In the RESS technique (first proposed by Krukonis [83], and represented in Figure 6) the solute of interest needs to be solubilized in a SCF. The supercritical solution is then expanded through a nozzle, the solvent power of the SCF dramatically decreases and the solute eventually precipitates. This technique is clean, because the precipitated solute is completely solvent free. Unfortunately most of heavy substances and almost all

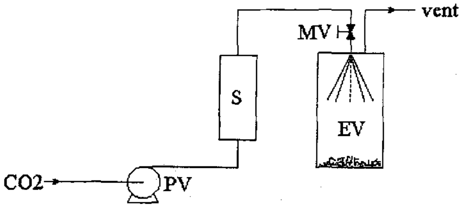

FIGURE 6
Experimental apparatus for the RESS technique (PV: volumetric pump; S: saturator; MV: micrometering valve or nozzle; EV: expansion vessel)

polymers exhibit little or no solubility in SCFs, thus making this technique of little interest for practical applications. RESS was widely studied during the late 80s and early 90s, and in this period some papers appeared which explored the application of the technique to polymeric materials. Lele and Shine [84] precipitated poly(methyl methacrylate) poly(styrene-*b*-methyl methacrylate) and poly(caprolactone) from supercritical solutions with chloro-difluoro-methane. They obtained various particles morphologies and sizes. A lot of work in the field was performed in Debenedetti's group [85-88]. In particular they performed the RESS technique on bioerodible polymers (poly(L-lactic acid), poly(D,L- lactic acid)), and were able to precipitate them as microspheres with a narrow size distribution curve, and to co-precipitate the polymers together with a drug (lovastatin) and a heavy aromatic compound (pyrene). They obtained a uniform distribution of the drug inside the polymer matrix. In this case the solubility of the polymers was considerable, because their molecular weight was quite low (less than 10000); but RESS cannot be used with high molecular weight polymers, because of their negligible solubility in supercritical fluids. It can be concluded that RESS has a little interest from a practical point of view for processing polymers: indeed in the last years much less can be found in the literature about this technique.

3.4.2.2 SAS technique

In the SAS technique [89] (represented in Figure 7) a SCF (antisolvent) is added to a solution of the solute of interest with an organic solvent. The antisolvent is miscible with the solvent but immiscible with the solute. When pressure is increased, its solubility in

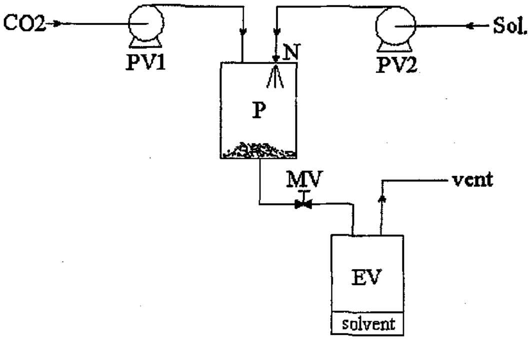

FIGURE 7
Experimental apparatus for the SAS technique (PV1, PV2: volumetric pumps; N: nozzle; P: precipitation vessel; MV: micrometering valve; EV: expansion vessel)

the liquid phase also increases; at a certain pressure, the solvent capacity of the mixed solvent towards the solute becomes low enough to trigger solute precipitation. Because of the high level of supersaturation, the production of small particles with a narrow size distribution curve is expected. The solvent can be extracted by exploiting its solubility in the SCF (even though such a solubility is low), and a dry and pure solute can be obtained. SAS can be used much more widely than RESS, because for all the substances of interest (heavy solids, polymers) a number of good organic solvents are available, and SCFs are usually highly soluble in them. Moreover, the operating conditions are milder: pressure rarely overcomes 100 bar and temperature is close to room temperature.

SAS can be carried on in batch and semi-continuos modes.

In the batch SAS process (proposed by Gallagher et al. [89]) an amount of solution is charged in the precipitation vessel, and then pressure is increased by adding the antisolvent (usually CO_2). When, as a consequence of the increasing pressure, enough antisolvent has entered the liquid phase, the solvent capacity is lowered and the solute precipitates. After precipitation, when the final operating pressure is reached, the antisolvent is flowed through the vessel, in order to strip the residual solvent. When the solvent content has been reduced to the desired level, the vessel is depressurized and the solid product can be collected.

In this mode of operation the only driving force is the antisolvent effect, because the evaporation of the solvent during the pressurization (which could help precipitation) is usually negligible. The supersaturation depends strongly on the pressurization rate (i. e. on how fast is the dissolution of the antisolvent into the liquid phase). To obtain a narrow size distribution curve it is essential to reach a uniform mixing of the antisolvent in the liquid phase. Usually the antisolvent bubbles through the liquid, and a good distributor is important to obtain a uniform dispersion of little bubbles of gas within the continuos phase. On the other hand this mode of operation is very simple.

In the continuos mode [90] the liquid solution and the antisolvent are fed continuously into the precipitator. This allows to reach steady state conditions, and to have a better control on operating variables and on particle shape and diameter. To maximize the driving forces, the operation is usually carried out in co-current mode, to ensure that the original liquid solution is in contact with pure antisolvent at the beginning of the precipitator. To obtain small and uniform particles it is necessary to create a uniform distribution of small liquid droplets in the continuos gas phase. The smaller the droplet diameter, the higher the exchange area, the faster the mass transfer. Precipitation is based on two driving forces: the dissolution of the antisolvent in the liquid phase and the evaporation of the solvent. Due to the contribution of evaporation, a higher supersaturation level is expected with respect to the batch mode, and smaller particles should be obtained. If the ratio between the gas and liquid flow rates is high (greater than 50, depending also on how volatile is the solvent) the solvent can be completely evaporated, and only one phase (plus the solid) is present in the precipitator. This way of carrying on the process has been proposed by Dixon et al. [91] and is called Precipitation with a Compressed Antisolvent (PCA). If the ratio between the two flow rates is lower, two phases coexist in the precipitator.

The injection device of the liquid solution plays a key role. This is designed to produce the liquid jet break-up and the formation of droplets as small as possible, to maximize the exchange area and the mass transfer rate. To obtain this, high values for the Weber numbers are needed, i. e. high velocity for the liquid through the nozzle: a small nozzle diameter is suitable.

A multiple nozzle assembly has also been used [92] to co-precipitate a drug (para-hydroxybenzoic acid) in a biocompatible polymer. The drug solution was delivered into the precipitator through the inner nozzle, the polymer solution through the middle one, and the antisolvent (CO_2) through the outer. A uniform dispersion of the drug in the polymer matrix was obtained.

Reverchon [93] has reviewed the results of SAS recrystallization performed over a lot of different substances. In this work attention is paid only to applications to polymeric materials.

Bleich et al. [94] and Gao et al. [95] treated several biopolymers: poly(L-lactide) (PLA), poly(β-hydroxybutyric acid) (PHB), poly(DL-lactide) (PDLA), poly(GL-lactide) (PGLA). Bleich et al. were able to precipitate PLA and PHB, while PDLA and PGLA remained solubilized in the liquid phase and were extracted from the precipitator. They performed also co-precipitation experiments with PLA plus a drug. A fast initial release of the drug was observed, so it was concluded that a large amount of drug was located on the surface. Gao et al. precipitated PLA both in continuos and discontinuos mode, and obtained different shapes (films, fibres, spherical particles) depending on experimental conditions. Co-precipitation with PLA and a drug was also performed [96]: the drug loading of the resulting microspheres was low. Probably a large amount of drug was extracted in the gas phase, with the liquid solvent acting as a cosolvent.

Randolph et al. [97] precipitated L-PLA from a methylene chloride solution with a semi-continuos SAS process, and studied the effect of operating conditions. At constant temperature and pressure below 75 bar a gas and a liquid phase are present in the precipitator; the slow drying of the droplets, leads to the fromation of a polymer film. If pressure is increased over 75 bar CO_2 and methylene chloride become fully miscible, and a single phase is present in the precipitator. This leads to a faster mass transfer of CO_2 into and solvent out of the droplets thus causing the formation of microspheres. When pressure is increased larger particles are obtained probably because of lower mass transfer rates. Higher temperatures at constant density lead to slightly larger particles. The effect of polymer concentration in the solution is almost negligible, while higher solution flow rates lead to larger particles, probably because the higher solvent concentration reduces its mass transfer rate into the gas phase.

Some co-precipitation experiments were also performed [98, 99]. As the drugs to be impregnated were ionic compounds, they exhibit very little solubility in methylene chloride. To increase this solubility hydrophobic ion-pairing (HIP) was used. The hydrophilic ion is paired with a oppositely charged hydrophobic surfactant, which makes it much more soluble in low-dielectric organic solvents. SAS co-precipitation experiments were then performed, leading to good incorporation results. The drug release was linear with $t^{0.5}$: it is concluded that the kinetic of release is controlled by diffusion through the polymer matrix.

Benedetti et al. [100] studied the micronization of polymeric hyaluronic acid methyl ester (HYAFF-11, a biodegradable polymer) from dimethyl sulfoxide (DMSO). They obtained sub-micron spherical particles by operating in a batch mode. Co-precipitation results were poor, because the drug precipitated on the surface of the microspheres. This is probably due to the different precipitation pressures of the drug and the polymer matrix. The drug is much more diluted in the starting solution, so its precipitation pressure is expected to be higher, and it precipitates as a coating on the polymer microspheres already formed.

Yeo et al. [101, 102] tested aromatic polyamides (aramids) and modified aramids; Johnston's group [91, 96, 103-105] performed the precipitation of poly(styrene), ethyl cellulose and poly(methyl methacrylate) from toluene solutions, and poly(acrylonitrile) from dimethyl formamide solutions. By varying the process mode (batch or continuos) and the operating parameters they were able to produce fibres, balloons and microspheres.

Bertucco et al. [106] presented some experiments on drug encapsulation. A suspension of the solid drug was realised. The idea was to precipitate the polymer around the drug acting as a nucleation centre. In fact, a partial encapsulation was obtained at low polymer concentration, while at high concentrations the particles aggregated during the precipitation.

It can be concluded that it is possible to precipitate polymers and that different operating conditions lead to different morphology of the precipitated particles. Co-precipitation is more difficult, both because drugs usually exhibit a non negligible solubility in the antisolvent, which is enhanced by the cosolvent effect of the liquid solvent, and because the precipitation pressure for the drug is higher than that for the matrix polymer, leading to a polymer coating rather than a true co-precipitation.

The effect of operating variables on the morphology of the precipitated polymer is difficult to establish, and at the moment it is impossible to propose a single model of the mechanism for particle formation that correlate all the available information, also because experimental results are often contradictory.

Polymers are usually precipitated as microspheres, fibres or networks. In the batch process spheres or spherulitic structures are usually obtained. In semi-continuos process, the solution exiting the nozzle undergoes to strong friction, which leads to a preferential orientation in the growing particles and thus to fibres formation. This effect is enhanced when the starting solution is enough concentrated and viscous, because the jet is stable and jet break-up is more difficult. The stress caused by friction forces polymer chains to align axially, leading to the precipitation of fibres [91]. The formation of networks and balloon-like particles is usually ascribed to the agglomeration of smaller particles (nanospheres [100, 107]). Such an agglomeration is due to the plasticizing effect of the mixture solvent-antisolvent on the precipitated polymer. It is unlikely that an amorphous polymer precipitates as a pure substance, because both solvent and antisolvent are soluble in it. What truly precipitates is a polymer–rich phase (examples on the phase behaviour of systems polymer-solvent–antisolvent are presented in [108, 109]). The solvent and antisolvent dissolved in the polymer decrease its glass transition temperature (T_g). If this becomes lower than the operating temperature, particles become sticky and agglomerate. Bodmeier et al.[96] experimented the effect of compressed CO_2 on a number of polymers, and showed that sometimes it is enough a moderate CO_2 pressure (70 bar) at room temperature to cause agglomeration. To avoid this, it is necessary to operate at a lower temperature. Another promising way [110] is to add a stabilizer to the CO_2. The referred authors used poly(1,1 dihydroperfluoroctyl acrylate) (polyFOA), which is soluble in CO_2 at mild conditions and acts as a surfactant towards poly(methyl methacrylate) (PMMA), the polymer to be precipitated. Poly(FOA) chains can surround the precipitated microspheres of PMMA and prevent their agglomeration.

Recently some new applications of SAS to polymers were proposed. White and Knutson [111] were able to separate poly(L-lactic acid) and poly(D,L-lactic acid) from a solution of both in chloroform using CO_2 as the antisolvent, and exploiting the fact that the precipitation pressures of the two polymers are different. Selective precipitation can be achieved by selecting for the operating pressure a value between the precipitation pressures of the two polymers. Finally Luna-Barcenas et al. [112] experimented the co-precipitation of two polymers (poly(styrene) and poly(isoprene)) to obtain blends. Mechanical agitation is very important to obtain the precipitation of both polymers: without agitation it is impossible to precipitate PI. In this case an unfavourable thermodynamic behavior (PI is too soluble in the expanded liquid phase) is overcome by increasing mass transfer rates (i. e. by stirring).

3.4.3 Impregnation and dyeing of a polymer matrix

We choose to incorporate these apparently different processes in the same paragraph, because the principles are almost the same.

The idea is to dissolve the solute to be charged in the polymer in a SCF, and then to flux the supercritical solution on the polymer matrix. The supercritical fluid swells the matrix, and the solute splits between the solution and the matrix itself according to a partition coefficient that is a function of the thermodynamic properties of the system. This technique can be applied, for example, when a biocompatible polymer needs to be charged with a drug, or when a fiber needs to be dyed. The process is feasible only if the active substance (drug or dye) is soluble in the supercritical fluid, if the polymer is swollen by the supercritical solution, and the partition coefficient is favourable to charge the matrix with enough active principle.

At the moment information on partition coefficients are very scarce. Shim and Johnston [113, 114] measure the partition coefficient for toluene between supercritical CO_2 and silicone rubber by means of supercritical fluid chromatography.

Eckert et al. [115] use a spectroscopic approach to measure the partition coefficients for dyes between CO_2 and PMMA, and for cosolvents between CO_2 and PDMS. They show that if the partition coefficient for the dye is large enough, a good dyeing can be obtained even if the solubility of the dye in the supercritical fluid is low. The partition coefficient for isopropanol between PDMS and CO_2 decreases rapidly when pressure is increased. If pressure is high enough the cosolvent is not absorbed in the polymer matrix. This fact is important because the presence of a cosolvent can affect the interactions between the matrix and the solute to be charged.

Alessi et al. [116] study the effect of operating parameters on the impregnation of cross-linked poly(vinyl pirrolidone) (PVP) with different drugs (Ketoprofen, Piroxicam, Nimesulide, three anti-inflammatory). The solubility of the different drugs in supercritical CO_2 is of the same order of magnitude. Some sorption measurements have demonstrated that supercritical CO_2 is able to solubilize into the polymer, so it can be used as a carrier fluid for the drug. Even if the solubility of the drugs in CO_2 is similar, they interact differently with the polymer, thus leading to different levels of impregnation. Also the use of different PVPs (physically or chemically cross-linked) leads to different impregnation results. Finally increasing temperature causes a better impregnation, probably because the solubility of the drug in CO_2 is higher.

Another application of polymer swelling is in wood-polymer composite manufacture [117]. A way to improve mechanical properties of wood is to impregnate it with a monomer (and sometimes with a polymer initiator), and to run a free radical polymerization reaction inside the porous structure of the wood: in such a way a wood-polymer composite is produced. Supercritical CO_2 has been successfully used as a carrier fluid: it dissolves the monomer and the initiator, then the supercritical solution is flowed through the wood matrix, and the heavy components split between the gas and the matrix itself. The required amount of monomer inside the wood can be reached by tuning operating conditions.

Further problems need to be taken into account in the case of dyeing. Again it is necessary to have a good solubility of the dye in the supercritical fluid, a large polymer swelling and a favourable partition coefficient. Moreover, good fastness to washing and light is needed, that is the dye must be resistant to washing with water and to light exposure. The traditional dyeing process is performed with water as the solvent. The dye is solubilized in water, and the fibres are soaked in the bath. Some kind of fibres (above all the artificial ones) becomes dyed with good fastness properties simply when the fibres are contacted with the dyeing solution. In other cases (for example wool, silk, and natural fibres) the so-called mordant dyeing is necessary. The yarn is first treated with a metal, and the metal exchanged fiber (mordanted fiber) is contacted with the solution containing the dye. The dye forms a complex with the metal on the surface of the fiber, and is trapped there. Depending on the metal and the ligand (dye) different colours can be obtained. All of these processes have to deal with the problem of wastewater purification and elimination, which adds a lot of costly steps to the process itself. Moreover, in conventional dyeing a lot of dispersing agents and surfactants need to be used, which again must be purified and recovered. Finally a drying process is necessary.

The supercritical fluid dyeing process can overcome almost all of these problems. Supercritical fluids have superior mass transfer properties compared to liquid solvents, due to their lower viscosities and higher diffusivities. They have very low surface tension, which enables easy penetration into the fibres. The dissolved dye can be separated and recovered by simple expansion: the dye can be recycled, and waste problems are completely eliminated. Finally the drying process is not necessary.

Bach et al. [118, 119] investigate the dyeing of synthetic fibres (poly(propylene) (PP), poly(ethylene therephthalate) (PET), poly(amide6.6), (PA6.6)) in CO_2 and CO_2 plus cosolvents, and compare the results with those obtained with water. The dyeing results for PP are better in CO_2 than in water. PP is non-polar, and its affinity to water is very low, thus causing the presence of a large amount of unfixed dye on the surface of the fiber. For PET and PA6.6 similar results are obtained with water and CO_2. On the other hand the dye uptake of the fibres is always higher for water than for CO_2. The fastness properties are usually better for the CO_2 processed fibres. The dye uptake can be substantially increased when a cosolvent is added to CO_2, but the presence of a cosolvent can affect the shrinkage, the crystallinity and the mechanical properties of the fibres.

Akgerman et al. [120] reports on the dyeing of wool with mordant dyes and supercritical CO_2. In the first step the metal ions are adsorbed or ion-exchanged to the fibres. Then the fibres are contacted with the dyeing supercritical solution, and the dye reacts with the mordanting ion on the fiber surface. To obtain good results in the complexing reaction and so in the dyeing it is important that wool is processed with about 30% moisture, in order to have the mordanting metal in ionic form.

Colombo et al. [121] studies the impregnation of cellulosic materials with dyes and other natural products (aromas, essential oils). Dyebility of cellulose is low, because the polymer is in a glassy state and the interaction between the dye and the polymer chain is difficult. To overcome this problem, cellulose was treated with poly(ethylene glycol), a plastifying agent. When the treated cellulose is contacted with CO_2, it turns to the rubbery state, which is more favourable for dye-fibres interactions. Unfortunately when pre-treated cellulose is processed with CO_2 no dyes fixation is achieved, leading to poor washing and light fastness.

4. Conclusions

Polymer processing with supercritical fluids can offer the opportunity of producing materials with peculiar properties. Most of the applications described are still on the laboratory or pilot plant scale and further investigation is needed for the industrial scale application.

The adoption of the new technology can be justified if the properties are completely different and if it is impossible to process the polymer using traditional solvents. It is necessary to remember that supercritical solvents cannot be considered as the normal and the only solution to the problems of polymer processing.

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