Review

Polymer–supercritical fluid interactions

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The role of the interactions in systems containing polymers for the definition of operative conditions in the supercritical fluid processing is reviewed. The approaches used for the study of the behaviour of polymers in presence of supercritical fluids are considered also in the case of mixtures containing more than two components. The attention is focused mainly on the thermodynamic properties of the systems.

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**1. Introduction**

The use of supercritical fluids in polymer processing technologies includes polymerization, fractionation, foaming, dyeing/impregnation, encapsulation and micronization. In this context, particular attention has been paid to carbon dioxide as supercritical fluid due to its molecular structure. It is non-toxic, non-flammable, chemically inert and inexpensive.

Many recent developments have arisen out with the use of CO2 as a new reaction solvent. Novel construction of CO2-phillic catalysts and surfactants has allowed both traditional and new reaction pathways to be explored. Studies have shown that CO2 used as a solvent can offer a “green” alternative for carrying out many processes often with significant improvements in selectivity, conversion, or rates [1–3].

Other applications carried out in a fluid phase include several of the particle generation technologies wherein material is dissolved in CO2 or in an organic solvent and precipitated from that solution via a pressure or solvent composition change [4]. It is notable that a variety of morphologies are attainable over a wide size range. Particle generation is certainly an area of intense inquiry and is receiving attention primarily from the pharmaceutical and biotechnology industries, although there are significant polymer and inorganic material applications of these techniques. In the applications addressed so far, the common feature has been a fluid phase solvent in which compressed CO2 is a major (if not the predominant) component. In these applications one may take advantage of proximity to critical points and of the divergent thermodynamic properties in those regions. There is also another range of composition that is an active area of research and this arises from the dissolution of compressed CO2 into a condensed phase. Dissolved CO2 causes a considerable reduction in the viscosity of molten polymer due to an increase in free volume. Moreover, it alters physical properties of polymers such as density, diffusivity...
and swollen volume. Therefore, it has tremendous potential as a plasticizer in polymer processing, which is generally carried out at high temperatures.

For the rational design and optimization of all these processes the knowledge of solubility, diffusivity, density, and permeability is essential. The behaviour of the polymeric systems in presence of a supercritical fluid depends strongly on several parameters: the chemical nature of the polymer and its physical state (such as \( T_g \), degree of crystallinity, degree of crosslinking, and chemical structure), the properties of the pure supercritical fluid (molecular structure, critical point), the nature of the interactions between the SF and the polymer, and obviously the external temperature and pressure.

The second aspect of the polymer thermodynamics, the description of systems containing a gas or a supercritical fluid dissolved in the polymer, is receiving much more attention in these last years due to the special behavior of these systems. In particular the modulation of the glassy state and the glass-to-rubber transition have attracted intensive research interest \([5–9]\).

In the last years polymer processing was the subject, of general reviews \([1,2,10]\) and of reviews on their use for particular applications \([4,11,12]\).

In this work the different aspects related to the description of the properties of systems containing a polymer and a supercritical fluid will be discussed with reference to the different technological processes.

2. Experimental methods

The experimental methods used to obtain information on the behaviour of systems containing polymers differ on the basis of the particular property measured. It is possible to distinguish the methods in two large classes depending on the concentration level of the polymer present in the mixture.

The mixtures in which the solvent concentration is prevalent can be constituted simply by a polymer dissolved in a supercritical fluid (binary mixture). In this case phase equilibria studies refer to the determination of cloud point of the mixture in order to establish the miscibility limits. Byun et al. measured recently \([13]\) the bubble-point, dew-point and critical-point; cloud-point curves are obtained with a high pressure, variable-volume cell.

The ternary systems studied are often of interest in the application of supercritical fluid technology for particle production. In the case of anti-solvent processes it is interesting to know the influence of the polymer properties on the phase equilibrium of supercritical fluid - organic solvent binary system. In this way it is possible to determine the region of the phase space in which a homogeneous or heterogeneous mixture is present. In all the different versions of antisolvent production of particles as pointed out recently by Yeo and Kiran \([4]\), the process consists in modifying the operating parameters in order to exit from homogeneous region and to enter in the heterogeneous region. Also in this case variable volume cells are used to determine mainly the demixing pressures at different operative temperatures for synthetic mixtures of the ternary system. These data, if determined for mixtures in which two different polymers are present, are of extreme interest also for understanding the effect of operating parameters in the case of high pressure solution blending of two different polymers \([14]\). This process was studied in the case of poly (methyl methacrylate) and poly \((\epsilon\)-caprolactone\) polymers using acetone + \( \text{CO}_2 \) mixed solvents. The presence of the first polymer strongly influences the melting and crystallization behaviour of the poly \((\epsilon\)-caprolactone\). The blend of the two polymers requires higher pressures and temperatures for the solubilization compared to the solutions of the individual component polymers.

The experimental methods used for the study of polymer rich mixtures are more varied depending on the particular property under investigation. The investigation of the properties of these systems seems simplified by the fact that normally one phase is essentially given by the pure supercritical fluid (and this is true only for binary polymer-SF systems). From a practical point of view the presence of the fluid in the polymer rich phase determines the modifications of different properties and, depending on the technological process under investigation, the experimental method used can be very different.

Also the basic experiment of the determination of the solubility of the sub critical or supercritical solvent in the polymer can be done with different methodologies if the polymers are above or below their melting point and below or above their glass transition temperature.

Above the melting point for low viscosity polymers where mixing is relatively easy the experimental methods used for normal phase equilibria determination with sampling, for analysis of both phases can be used. In the case of polymers below melting point, when the solubility of the supercritical fluid in the polymer rich phase must be determined, the experimental methods basically do not need the sampling of the two phases for analysis.

In the pressure decay method \([15]\) the quantity of the gas absorbed by the polymer is determined from the difference between the amount of gas present before and after equilibration with the polymer. For these evaluations, corrections for the swelling of the polymer and a very accurate equation of state for the gas phase are needed. Also the system volume is selected such that a very small reduction in the amount of the gas phase will produce a marked pressure reduction.

In the gravimetric method, the weight difference between the initial polymer sample and the polymer sample after the contact with the supercritical fluid is measured with a sensitive microbalance. The method requires an accurate equation of state and an estimate (or experimental measurement) of the swelling of the polymer phase to account for the buoyancy correction. The swelling is generally determined by measuring the change in one or more dimensions of a polymer sample \([16,17]\).

An experimental set-up with an electronic microbalance inside a pressurized equilibration cell was used by different authors \([1]\) but, due to the microbalance operating conditions, it is not suitable for measurements at high temperatures (often not higher than 125 °C).

A magnetic suspension balance (MSB) apparatus \([18,19]\). is also used to determine \( \text{CO}_2 \) solubilities in several polymers \([16,17]\). In this case the weight difference is determined by measuring the force required to suspend a sample enclosed in a pressure vessel without having contact with the microbalance. An electronically controlled magnetic suspension coupling transmits the signal to the microbalance. Also in this case the swelling of the polymer must be incorporated in the solubility calculations to account for the buoyancy correction but this is facilitated by the possibility of measuring in situ the density of the fluid.

Other experimental methods are suggested for the measurement of the sorption and of the swelling of polymers. A quartz crystal microbalance represents also a very accurate method for the measurement of the sorption. The method is based on the piezoelectric effect of an AT-cut quartz crystal. The vibrational motion of the crystal under the influence of an alternative electric field is registered. The maximum deformation is exhibited at a given frequency, the resonance frequency which depends on the mass \([20]\). The crystal is coated with a well adhered film of the polymer under investigation and when the mass of the specimen varies due to the absorption the resonance frequency changes. The experimental method requires very short equilibration time and presents a
good accuracy but it cannot be used at temperatures and pressures higher than 180 °C and 60 bar respectively [8].

Different studies [21,22] show that FTIR spectroscopy is not only a powerful tool for the study of interactions of the polymer with supercritical carbon dioxide but also that using a modified ATR-IR accessory it is possible to measure directly and simultaneously the sorption and the swelling of the polymer [23]. The method requires the deposition of a polymer film on the surface of a diamond crystal mounted in a heating plate connected with the temperature controlling system. From the comparison of the spectra of the polymer without and with carbon dioxide and of the pure carbon dioxide the swelling and the sorption data are obtained [24]. Characteristic absorption bands are measured for carbon dioxide (at 660 and 2338 cm−1) and pure polymer. Increasing the carbon dioxide pressure, a decrease of the polymer absorption band, due to the reduction of the polymer density, and an increase of the intensity of the characteristic band intensity for CO2 (at 2338 cm−1) can be observed. The swelling of the polymer is calculated from the variation of the area of the characteristic polymer band with the carbon dioxide pressure. The sorption data are evaluated from the variation of the height of the 2338 cm−1 band taking into account also the polymer swelling.

Since in these last methods the preparation of a polymeric film is a prerequisite the type of polymers that is possible to investigate with these techniques is limited.

In Table 1 a comparison is made of sorption data for the system Polystyrene–CO2 at 35 °C. The sorption data agree rather well at lower to moderate pressures, except for the data of Shieh and Liu [28], due to a short time of equilibration. The discrepancies between sorption data are not generally ascribed to the different experimental method used but often to the experimental set-up. The larger deviations at higher pressures are probably due to the buoyancy effect and the swelling estimation.

The swelling of polymers exposed to supercritical carbon dioxide is also a key property that receives continuous attention from different researchers so that various methods for the measurement have been proposed. The most common and simple method is based on the optical observation of the swelling but the measurement of the small increases in polymer dimensions is always difficult. For thin polymer films the swelling data measured depends also on the positioning of the film (horizontal or vertical) in the cell.

Other methods proposed are neutron reflectivity [29] and the already mentioned high pressure FTIR imaging proposed by Kazarian and Chan [30]. Recently [31] high pressure nuclear magnetic resonance, already used to investigate reactions [32] in supercritical fluids, was proposed for the real-time measurement of the polymer dimensions upon swelling. The method is very accurate and produces also information on the polymer chain dynamics; one example can be the information on chain mobility by measurement of NMR relaxation times of the polymer protons as a function of carbon dioxide. The method was applied to the measurement of the swelling of cross-linked poly(dimethylsiloxane) and semicrystalline linear low-density poly(ethylene).

Table 1
| Sorption data (gr. CO2/100 gr. of polymer) in Polystyrene at 35 °C. |
|-----------------|-------|-------|-------|-------|
|                 | P (bar) |       |       |       |
|                 | 25     | 50    | 75    | 150   |
| Wissinger and Paulaitis [25] | 3.8    | 7.8   | 11.6  |       |
| Zhang et al. [26] | 3.4    | 5.6   | 5.7   |       |
| Shim et al. [27] | 4.2    | 7.9   | 14.2  | 17.7  |
| Shieh and Liu [32 °C] [28] | 0.7    | 2.0   | 3.8   | 5.2   |
| Pantoula and Panayiotou [8] | 4.0    | 8.3   |       |       |

In Fig. 1 swelling data for the system CO2/PMMA measured by different researchers are compared. In this case the agreement is better than in the case of the sorption data reported in Table 1. It is necessary to remind that in all these comparisons the polymers are often only namely the same but they can differ for the molecular weight or molecular weight distribution. A very interesting comparison is presented by Duarte et al. [35] for a biocompatible polymer.

Sorption of carbon dioxide has been measured on biocompatible acrylate copolymer by using a gravimetric method, the transmission IR spectroscopy and the ATR-IR spectroscopy as shown in figure 2. There is a good agreement between all the three methods at low pressures (up to 50–60 bar). The gravimetric approach provides slightly higher values for the sorption compared to in situ IR spectroscopy. These discrepancies can be due to the fact that in the gravimetric method the polymer samples are weighted outside of the high pressure cell after a rapid depressurisation and the amount of carbon dioxide present in the polymer is evaluated from the data analysis using diffusion equations.

The CO2 induced plasticization has an important impact on many polymer-processing operations and for that reason the measurements of the variation of the glass transition temperature is also a consistent method for the characterization of the interactions between polymer and supercritical fluid. In literature, mechanical and thermal techniques have been used to investigate the plasticization of polymers by supercritical fluids. The mechanical determinations are based on the change of the polymer creep compliance at the glass transition state [13,36]. The thermal technique utilizes high pressure calorimeters to determine the glass transition temperature (Tg). The advantage of this technique is related to the gas pressure that is maintained constant during the experimental measurement, avoiding any possible desorption of the gas.
Ever not high. Measurements of T_g and Handa [38], Pantoula and Panayiotou [8], O’Neill et al. [40], Wissinger and Paulatis [41].

The high-pressure partition chromatography, modification of the Inverse Gas Chromatography (IGC) technique, was also used for the study of the plasticization effects of carbon dioxide on polymers [1,37,38]. Interlaboratory reproducibility of these measurements is however not high. Measurements of T_g depression performed by different researchers and using the same method differ even for the same polymer.

In Fig. 3 the glass transition temperatures at different carbon dioxide pressures are reported for polystyrene (PS). The data are obtained by using different methods (IGC) [8], high pressure calorimetry [40], creep compliance measurements [41], differential scanning calorimetry [38]). Discrepancies are evident even for data obtained at relatively lower pressures: possible explanations are the ambiguities in the pure polymer properties, that is whether or not they are actually the same polymers.

3. Evaluation of interactions – simulation

Several studies explore the interactions between polymer and carbon dioxide. Fourier transform infrared spectroscopy [21] was extensively used for the determination of the interactions between carbon dioxide and the different groups contained in the polymer molecule. For example it was found that polymers containing carboxyl groups act as electron donors and show specific interactions with carbon dioxide as electron acceptors rather than as electron donors. The specific interactions between carbon dioxide and the dipole of the C–F bonds or fluorine can explain the observed good solubility in polymers containing fluorine atoms.

Computational studies were performed for the evaluation of interaction strengths in polymer–carbon dioxide systems [42,43]. Discontinuous molecular dynamics simulations were performed assuming that the polymer is a freely jointed square-well chain and that the solvent molecules (carbon dioxide) are hard spheres or square-well spheres. The study is limited to model carbon dioxide densities in the supercritical or liquid regions. In both hard sphere and square-well solvents the interaction energy between polymer and solvent strongly influences the polymer solubility. Increasing the packing factor increases the capacity of the solvent to dissolve the polymer only if the segment–solvent interactions exceeds a critical value. If weak segment–solvent attractions are present the increases of packing factor have a limited effect on the solubility. At low values of the packing the polymer is not more soluble in the hard sphere solvent if the value of the interaction energy between polymer segments and solvent increases. The assumption of hard sphere model for the solvent allows observing only UCST behaviour, instead, depending upon the interaction strengths and chain length, both UCST and LCST behavior are observed when the solvent is modeled as square-well sphere. The conclusion is that it is necessary to account for the solvent–solvent attraction to investigate LCST versus UCST behavior in supercritical carbon dioxide. The simulation studies were also extended to surfactant carbon dioxide systems in order to understand the behavior of such surfactants in supercritical carbon dioxide. It is necessary to remember that the presence of surfactants is essential to dissolve some polymers in supercritical carbon dioxide [43].

4. Macroscopic modeling

Modern thermodynamic EOS theories for polymer/solvent systems are essential to understanding and predicting polymer/CO_2 systems behavior. In all these theories, phase equilibria of pure components or solutions are determined by equating chemical potentials of a component in coexisting phases.

The commonly used EOS models for polymer/CO_2 systems are conveniently considered in three categories based on cubic EOS, lattice theory and off-lattice theory. In the following a brief discussion is presented reporting more details on some equation of state models.

4.1. Cubic equations of state

Cubic equations of state are currently used for phase equilibria calculations due to their simplicity. Peng–Robinson equation [44] is the most popular cubic equation used for low molecular weight and also for mixtures containing polymers:

\[ P = \frac{RT}{v-b} - \frac{a}{v(v+b)+b(v-b)} \]  

(1)

Calculations with this equation require the knowledge of pure component parameters (a and b related to critical properties) and almost one binary interaction parameter. The binary parameter is normally evaluated by correlating binary experimental data. Pure component parameters (critical temperature, critical pressure and acentric factor) are known or easily evaluated for low molecular weight compounds but their values must be obtained by fitting volumetric properties in the case of the polymers. For these compounds they loose any physical meaning and they must be considered simply as characteristic parameters of the equation. Examples of calculations using Peng–Robinson EOS for different binary and ternary systems containing commercial biodegradable polymers and copolymers poly(ε-caprolactone), poly(ε-caprolactone), poly(ε-caprolactone-co-butylene adipate)) and high pressure fluids are reported by Arce and Aznar [45] and Byun and Mc Hugh [46].

4.2. Lattice fluid theory

In the lattice theory the polymer molecules are ordered according to a lattice structure and the presence of holes on the lattice accounts for the change of volume. The theory reduces to the Flory–Huggins theory at low temperatures. Various equations of state based on lattice model approach are proposed. All these theories used three pure component characteristic parameters P^*, T^* and \rho^* or \nu^* defined as:

\[ T^* = \frac{\epsilon^*}{k_b T} \quad P^* = \frac{\epsilon^*}{\nu^*} \quad \rho^* = \frac{M_{WP}}{(RT^*)} \]  

(2)

where r is the number of lattice sites occupied by a molecule, and the equation is expressed in terms of dimensionless reduced
variables such as reduced temperature $T_\text{r}$, reduced pressure $P_\text{r}$ and reduced density $\rho_\text{r}$:

$$T = \frac{T}{T_\text{c}}, \quad P = \frac{P}{P_\text{c}}, \quad \rho = \frac{\rho}{\rho_\text{c}}$$

(3)

The most popular model is the Sanchez and Lacombe [47,48] EOS (SL):

$$\bar{p}^2 + \bar{P} + \bar{T} \left[ \ln(1 - \bar{\rho}) + \left( 1 - \frac{1}{\bar{T}} \right) \bar{\rho} \right] = 0$$

(4)

Extension of the equation to mixtures needs the knowledge of a binary interaction and adjustable parameter which is introduced into equation for the calculation of the characteristic mixture temperature

$$T_\text{mix}^* = \frac{e_\text{mix}^*}{k}$$

(5)

where the mixing rule for $e_\text{mix}^*$ is:

$$e_\text{mix}^* = \frac{1}{v_\text{mix}^*} \sum_i \sum_j \psi_i \psi_j e_i^* v_i^* \psi_j^* v_j$$

(6)

and the cross term

$$e_y^* = \sqrt{e_x^* e_y^*} (1 - k_y)$$

(7)

where $k_y$ is an adjustable parameter and $\psi_j$ are the volume fractions of component $i$ and $j$ respectively.

The mixture parameter $v_\text{mix}^*$ is calculated from the pure components characteristic volume without the introduction of further binary parameters.

The model was extensively used for the correlation of experimental phase equilibrium data for binary and ternary systems [49,50]. A modified SL equation of state [51] is used in [52] for the modeling of high pressure phase equilibria in systems linear low density polyethylene (LLDPE)–n-hexane–ethylene. Also in this case, as in [50], the LLDPE–ethylene binary interaction parameters were adjusted to the ternary cloud point data. In this way the equation of state gives an almost quantitative prediction of the ternary bubble point and the liquid–liquid–vapor boundary curves.

Significant improvement of the classic SL equation is obtained by accounting for the non-random distribution of free volume and for highly specific forces, like hydrogen bonding, between neighboring molecules [53,54]. The modified model is known as the quasi-chemical hydrogen-bonding (QHCB) model [55] and gives better results for mixtures. A further modification of the previous model was recently proposed by using a new combinatorial term derived from Staverman model and by introducing a generalized non-randomness factors: the model is known as non-random hydrogen-bonding (NRHB) model [56]. The NRHB model for non-hydrogen bond pure components has three characteristic parameters: the average interaction energy per segment of molecule $e_i^*$, the average segmental volume, $v_i$, and the number of segment per molecule, $r_i$, that are calculated from pure component vapor pressure and volumetric properties for normal fluids and for polymers from PVT data of the melt. In the case of hydrogen bonding fluids three additional parameters, the energy, the volume and the entropy of hydrogen bond, are needed. The non hydrogen bond parameters are calculated on the basis of spectroscopic data or from ab initio quantum mechanics calculations.

In the case of mixture the corresponding parameters $\epsilon^*$, $\nu^*$ and $r$ are obtained through combining and mixing rules containing a binary interaction parameter.

The corresponding scaling parameters for the temperature $T^*$, pressure $P^*$ and density $\rho^*$, are interrelated as:

$$\rho^* = \frac{M_w}{\rho \nu} \quad \text{and} \quad \epsilon^* = R \rho^* = P^* \nu^*$$

(8)

where $M_w$ is the molecular weight. A molecular shape factor $s_i$ is defined as the ratio between the surface $q_i$ and the volume $r_i$.

The equation of state in terms of reduced quantities (already defined for the Sanchez–Lacombe equation of state) for the mixture is:

$$\bar{P} + \bar{T} \left[ \ln(1 - \bar{\rho}) - \bar{\rho} \left( \sum_i \psi_i \frac{l_i}{r_i} \right) \right] - \frac{z}{2} \ln \left(1 - \bar{\rho} + \frac{2}{3} \bar{\rho} \right) + \frac{z}{2} \ln \Gamma_0^* = 0$$

(9)

where $l_i = z/2(r_i - q_i) - (r_i - 1)$ and $z$ is the coordination number of the lattice where molecules are assumed to be assembled. $\Gamma_0^*$ is a factor for the non-random distribution of empty sites around an empty site.

In deriving the equation for the chemical potential [8] two other pure component parameters are defined: $\Gamma_{ir}$, that is a factor for the non-random distribution of molecular segment around a central molecular segment and $\delta_i$, characteristic quantity of the fluid $i$ that takes into account the flexibility and the symmetry of the molecule. The non-random parameters are calculated from the other quantities already defined and depend specifically on the value of $\epsilon^*$. The flexibility parameter is calculated from the knowledge of the rotational conformations per main-chain bond and the flex energy [57–59].

The new model was applied successfully to the calculation of equilibrium data at low and high pressure also for mixtures containing polymers.

4.3. Off lattice fluid

Lattice fluid equations of state are based on molecular considerations but the real fluids exist in a real space and are not contained in a lattice. The off lattice equations of state take into account, even more explicitly than the NRHB model, the effect of density on rotational and vibrational motions in addition to the translational degrees of freedom. Perturbed hard chain theories are extensively applied for the development of different equations [60,61]. In particular PHSC equation [61] and SAFT equation [62,63] are useful for the description of systems containing polymers. The basic idea in the development of such models is to consider that the Helmholtz energy or the compressibility factor can be expressed as sum of the contributions derived from the different interaction forces:

$$z = 1 + z^{\text{hs}} + z^{\text{disp}} + z^{\text{chain}} + z^{\text{assoc}}$$

(10)

where $z^{\text{hs}}$ term is the reference term for the hard sphere contribution of repulsive forces, $z^{\text{disp}}$ is the contribution for the dispersion forces interactions and is derived from the results obtained by computer simulation, $z^{\text{chain}}$ is the contribution for the interactions between segments and finally $z^{\text{assoc}}$ is the contribution for the hydrogen bond association. The SAFT equation was applied for the description of properties of polymer solutions at elevated pressure [64,65].

Modifications of the SAFT equations were also proposed, namely for example the so-called PC-SAFT [66,67]. An interesting comparison between the performances of cubic, lattice fluid and PC-SAFT equations was presented in [45] for the correlation of experimental data for different binary and ternary systems containing biopolymers and supercritical fluids. The comparison is made on the basis
of the capacity of the different models to calculate the cloud point pressure. The PC-SAFT equation shows the lowest pressure deviation (0.85%), SL 2.86% and PR EOS the highest deviation in pressure (4.84%). In all these cases one temperature dependent binary interaction parameter is used. The simple cubic equation of state model is not able to take in account the molecular structure of the polymer and this is very important in the case of complex molecules as polymers and copolymers. Moreover in many cases the SL equation of state can be preferred respect to the equations of state based on SAFT for its simplicity.

Common feature or common difficulty for all the models is the calculation of the pure component equation of state parameters by fitting liquid pure component PVT data. If no PVT data are known for the pure polymer, group contribution or other predictive methods must be used [68,69].

The description of the properties of polymer solutions and polymer melts when the appropriate thermodynamic model is chosen is not presenting problems different from those that it is possible to have in the modeling of phase equilibria for mixtures containing low molecular weight compounds. The situation is different when it is necessary to model polymers close to the glassy state or below the glass transition temperature. It is well known that the sorption of supercritical fluids in the polymers, the swelling of the polymeric matrix and the modification of the glass to rubber transition characterized by the glass transition temperature are the main peculiar aspects presented by these systems and have been often investigated.

For the solubility of gases and vapors in glassy polymers, the dual-mode sorption model was often utilized [70,71]. It is an empirical model in which the parameters must be evaluated for each polymer gas system at each temperature independently.

Starting from Sato et al. [72], who model solubility data using the SL EOS, Doghieri and Sarti [6] describe the sorption of gases and vapors in glassy polymers using the SL model and an internal variable, the polymer density, to represent the non equilibrium of the structure (NELF model).

The difference with the classical phase equilibrium calculations with the SL EOS is the introduction of an order parameter, the polymer density, for the description of the non equilibrium state of the glassy polymer.

The evaluation of the pseudo-equilibrium solubility of a vapor phase in a given polymer at given temperature and pressure, is performed by coupling the equilibrium equation in terms of chemical potentials with the evolution equation for the order parameter given by the following expression:

\[
\frac{d\rho_2}{dt} = f(T, p, \omega_1, \rho_2)
\]  

where \(\rho_2\) is the density of the polymer phase at the given temperature and pressure when the weight percent of the supercritical fluid in the polymeric phase is \(\omega_1\).

The evolution equation can be substituted by directly measured values of the polymer density, if available. Recently the NELF model was slightly modified [73] to include the possibility of evaluating the pseudo-equilibrium polymer density through a linear variation with the pressure [74] and the glass transition temperature with Chow theory [75].

The plasticizing effect of the supercritical fluid is an important evidence of the dissolution in the polymer. The glass transition temperature of polymers can be estimated by combining the Lattice-Fluid and the Gibbs–DiMarzio theories [76]. The Gibbs–DiMarzio criterion for mixtures assumes that the mixture entropy (not the entropy of pure polymer) is zero at the glass transition.

As equation of state the well-known Sanchez–Lacombe lattice fluid has been originally used. The equilibrium condition is given by equating the chemical potential of the pure solvent in the fluid phase and the one of the same component in the polymer rich phase.

Fig. 4 reports as an example the sorption isotherm calculated following the NELF and the Condo approaches for the case of the system polymethylmethacrylate–carbon dioxide. Both models are able to reproduce the experimental data: very good agreement is obtained with the Condo approach.

Recently [8] very interesting results are obtained substituting the SL equation of state with the NRHB model.

In Fig. 3 the glass transition temperatures calculated using the SL and NRHB models are compared with the experimental data. For the lower pressure the two models give similar results. Both models are able to predict the appearance of a retrograde vitrification phenomena but for different values of the pressure.

5. Concluding remarks and impact of the theories on technological aspects

The different technological applications of supercritical fluids can take advantages from the understanding of the basic interactions between the different components. This fact is well recognized [4] but a lot of work is still required.

In the applications of supercritical fluids for particle technologies using the antisolvent processes family as pointed out in [4] it is necessary to well establish the borders between the regions where the system is represented as a homogeneous phase or an heterogeneous phase. The problem is that information is needed not for a binary system but almost for a ternary system polymer–SF–organic...
solvent. These data are very scarce and only few experimental determinations on the effect of the presence of a polymer or heavy solute on the phase equilibria of the binary system SF–organic solvent are performed.

In the preparation of porous scaffolds phase inversion using the supercritical fluid as antisolvent the characteristics of the structure obtained depend on the thermodynamic properties [77,78] of the ternary systems as in the particle production processes. In particular in the case of semicrystalline polymers (as for example poly(l-lactide) [79]) the final structure is controlled through the competition between liquid–liquid and solid–liquid demixing processes.

In the impregnation processes [80] the polymer is charged with a third component (drug, additive) using the supercritical fluid as carrier. The process can operate statically or dynamically when the supercritical fluid is pre-saturated with the additive. Recently [81–85] interesting results are obtained with different drug and carriers. The process can operate statically or dynamically when the supercritical fluid is pre-saturated with the additive. Recently [81–85] interesting results are obtained with different drug and carriers.

In these processes the knowledge of the interactions in the ternary system is of great importance but generally not perfectly determined. Unfortunately only the behavior of the binaries polymer–SF and additive–SF are generally known. The study of the ternary system is normally very difficult as a consequence of the fact that the additive component is often a heavy component (drug with high molecular weight). Simulation studies must be very useful in this area in order to avoid the experimental difficulties and to understand the effect of the operative parameters on the process [86].

Extrusion processes of polymers take advantage of the modification of the polymer properties induced by the supercritical fluid. Recently the applications of pressurized gases to hot melt extrusion have received increasing attention and different applications of this technology were described in the literature [87–89]. Also in this case the ternary system involves polymer–supercritical fluid–heavy component (drug) as in the impregnation processes. The lack of thermodynamic data for these systems still represents a problem but it is necessary to remember that in the implementation of the supercritical technology the interactions influence dramatically transport properties modifying substantially the possible operative process conditions.

References
