Polymer melt micronisation using supercritical carbon dioxide as processing
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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2005

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):

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Chapter 1

Supercritical carbon dioxide as a green solvent for processing polymers

Supercritical fluids are well established as a processing solvent in various polymer applications such as polymer modification, formation of polymer composites, polymer blending, microcellular foaming, particle production and polymerization. As carbon dioxide (CO₂) is quite soluble in many polymers, it can be used as a solvent or plasticizer. Apart from an inert nature and easily attainable supercritical conditions, gas-like diffusivity and liquid-like density in the supercritical phase allow replacing conventional, often noxious, solvents with supercritical CO₂. Dissolved CO₂ causes a considerable reduction in the viscosity of molten polymer, a very important property for the applications stated above. In this chapter, solubility and viscosity measurement studies and various particle production methods which use supercritical CO₂ have been discussed. Finally, the purpose of the thesis and its contents have been discussed.
1.1. Introduction

Polymers have become an inseparable part of daily life. Not only the synthesis but also the processing of polymers has been given a major attention. Processed polymers are used for particular applications in particular forms as foam or blend or powder. For example, powder industries such as paint, toner and drug always seek for the solutions that provide particles of micron or nano size with a narrow particle size distribution.

There are classical methods that use environmentally hazardous volatile organic solvents (VOC) and chlorofluorocarbons (CFC) for processing and synthesis of polymers. Due to the enormous increment of VOC/CFC emissions and also the generation of aqueous waste streams a number of chemical engineers and chemists have already been looking for new and cleaner alternatives. One of these methods is the use of supercritical fluids as a processing solvent. A supercritical fluid is defined as a substance for which both pressure and temperature are above the critical values, Fig. 1.1.

Though a supercritical fluid doesn’t contain two phases such as gas and liquid, it possesses the properties of both gas and liquid. The special combination of gas-like viscosity and liquid like-density of supercritical fluid results in it being an excellent solvent. The density of supercritical fluid can be tuned easily by small changes in pressure. It has successfully been used as a solvent in the processing of polymers such as blending, microcellular foaming and particle production, in
Chapter 1: Supercritical carbon dioxide as a green solvent for processing polymers

1.2. Supercritical carbon dioxide

One of the supercritical fluids, which can be used, is carbon dioxide (CO$_2$). Supercritical CO$_2$ is a clean and versatile solvent and a promising alternative to noxious organic solvents and chlorofluorocarbons. It has attracted particular attention as a supercritical fluid in the synthesis as well as processing areas for polymers due to the following properties:

(a) CO$_2$ is non-toxic, non-flammable, chemically inert, and inexpensive. A large amount is available as a by-product from NH$_3$ and ethanol industries and refineries.
(b) Supercritical conditions are easily achieved: $T_c = 304$ K and $P_c = 7.38$ MPa.
(c) The solvent may be removed by simple depressurization.
(d) The density of the solvent can be tuned by varying the pressure.
(e) Many polymers become highly swollen and plasticized in the presence of CO$_2$. Moreover, the use of supercritical CO$_2$ doesn’t create a problem with respect to the green house effect as it is being conserved during the processes.

CO$_2$ is a good solvent for many non-polar (and some polar) molecules with low molecular weight [5]. It is a very poor solvent for most high molecular weight polymers under readily achievable conditions. Very few polymers have shown a good solubility in pure CO$_2$ under mild conditions like certain amorphous fluoropolymers and silicones [4,6-10]. Though the solubility of most polymers in supercritical CO$_2$ is extremely low, the solubility of supercritical CO$_2$ in many polymers is substantial.

The concentration of dissolved CO$_2$ in polymer mainly depends on the processing temperature and pressure. Now, the question arises is the dissolved CO$_2$ beneficial from a processing point of view? The dissolved CO$_2$ causes a considerable reduction in viscosity due to increase in a free volume of polymer. Thus, less energy is consumed during the process. The dissolved CO$_2$ also alters the other physical properties such as reduction in density and increase in diffusion coefficient. Therefore, it has a tremendous potential as a plasticizer in polymer processing.

1.2.1. Solubility of CO$_2$ in polymers

The knowledge of gas solubility in molten polymers is crucial for the commercial success of supercritical-polymer processes. The dissolved supercritical CO$_2$ in molten polymers alters most physical properties of the polymers like the viscosity, density, diffusivity and swollen volume. A lot of attention has been paid to the situations where polymers are dissolved in
supercritical CO₂. Only a limited part of this concerns molten polymers, the most likely form for processing. The reviews by Cooper [1] and Tomasko et al. [2] cover extensive information on the various applications of supercritical CO₂ to polymer synthesis and processing. Recently, Kendall et al. [3] have nicely reviewed polymerizations in supercritical CO₂.

In general, an increase in pressure increases the solubility of a gas in a solvent. The same law is applicable also to a polymer and CO₂. The density of CO₂, which is a strong function of temperature and pressure plays a vital role in deciding its solubility in a polymer. However, the quantity of CO₂ dissolved in different polymers also differs depending on the available chemical groups. A difference in the solubility can be explained with the specific intermolecular interaction between CO₂ and the chemical groups available in the polymers.

Several studies have been carried out to reveal the interactions between a polymer and CO₂. CO₂ does not have a dipole moment due to its structural symmetry. However, a quadrupole moment and Lewis acidity contribute to its solubility in a polymer. Using FT-IR spectroscopy Kazarian et al. [11,12] have given spectroscopic evidence of the Lewis acid-base interactions between CO₂ and a polymer. They used the bending mode rather than the stretching mode of CO₂ as it is much more sensitive to the Lewis acid-base interaction. The splitting of the bending mode of CO₂ signified the interaction between CO₂ and the polymers. The possible interactions of CO₂ with different chemical groups are shown in Fig. 1.2.

![Fig. 1.2. Weak interactions of CO₂ with different chemical groups: a) ether, b) carbonyl, and c) aromatic ring](image)

Fortunately in the last decade, various experimental methods for solubility measurements at elevated temperatures and pressures have been made available in the literature. These are applied to both solid (below glass transition temperature or melting point) as well as molten (above glass transition temperature or melting point) polymers. An overview of various methods and their applications to various polymer-CO₂ systems are given in Table 1.1 [13-29].
Table 1.1. Sorption studies of various supercritical CO$_2$-polymer systems (N.R.: not reported)

<table>
<thead>
<tr>
<th>Method</th>
<th>Polymers/CO$_2$</th>
<th>Press. (MPa)</th>
<th>Temp. (K)</th>
<th>Features of equipment</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure decay</td>
<td>PMMA</td>
<td>13.78</td>
<td>293, 473</td>
<td>N.R.</td>
<td>[13]</td>
</tr>
<tr>
<td></td>
<td>PS</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phase separation</td>
<td>PEG 400, 600, 1000</td>
<td>1-15</td>
<td>313, 323</td>
<td>373 K 35 MPa</td>
<td>[14]</td>
</tr>
<tr>
<td>Phase separation</td>
<td>PDMS</td>
<td>1-26</td>
<td>323, 353, 373</td>
<td>N.R.</td>
<td>[15]</td>
</tr>
<tr>
<td>Pressure decay</td>
<td>PS</td>
<td>1-20</td>
<td>373, 453</td>
<td>N.R.</td>
<td>[16]</td>
</tr>
<tr>
<td>Pressure decay</td>
<td>PP, HDPE</td>
<td>1-17</td>
<td>433, 453, 473</td>
<td>N.R.</td>
<td>[17]</td>
</tr>
<tr>
<td>Phase separation</td>
<td>PEG 1500, 4000, 8000, 35000</td>
<td>2-30</td>
<td>316-373</td>
<td>N.R.</td>
<td>[18]</td>
</tr>
<tr>
<td>Phase separation</td>
<td>PEG 200, 400, 600</td>
<td>3-26</td>
<td>313-348</td>
<td>423 K 50 MPa</td>
<td>[19]</td>
</tr>
<tr>
<td>Phase separation</td>
<td>PEG 200, 1500, 4000, 8000</td>
<td>5-30</td>
<td>323-393</td>
<td>423 K 50 MPa</td>
<td>[20]</td>
</tr>
<tr>
<td>Piezoelectric-quartz sorption</td>
<td>PVAc, PBMA</td>
<td>1-10</td>
<td>313, 333, 353</td>
<td>N.R.</td>
<td>[21]</td>
</tr>
<tr>
<td>Chromatographic</td>
<td>PMMA</td>
<td>1.5-9</td>
<td>236-453</td>
<td>N.R.</td>
<td>[22]</td>
</tr>
<tr>
<td>Chromatographic</td>
<td>PDMS</td>
<td>1.5-10</td>
<td>308-393</td>
<td>N.R.</td>
<td>[23]</td>
</tr>
<tr>
<td>High-pressure optical cell</td>
<td>PDMS</td>
<td>13.8-27.8</td>
<td>303, 323, 343</td>
<td>N.R. 50 MPa</td>
<td>[24]</td>
</tr>
<tr>
<td>Gravimetric</td>
<td>PBS, PBSA</td>
<td>1-20</td>
<td>308-393</td>
<td>523 K 35 MPa</td>
<td>[25]</td>
</tr>
<tr>
<td>Gravimetric</td>
<td>PVAc, PS</td>
<td>1-17.5, 1-20</td>
<td>313-373, 373-473</td>
<td>523 K 35 MPa</td>
<td>[26]</td>
</tr>
<tr>
<td>Gravimetric</td>
<td>PPO, PPO/PS</td>
<td>1-20</td>
<td>373, 427, 473</td>
<td>523 K 35 MPa</td>
<td>[27]</td>
</tr>
<tr>
<td>Gravimetric</td>
<td>LDPE/TiO$_2$</td>
<td>1-15</td>
<td>423, 448, 473</td>
<td>N.R.</td>
<td>[28]</td>
</tr>
<tr>
<td>Gravimetric</td>
<td>PPO, PPO/PS</td>
<td>1-15</td>
<td>423-473</td>
<td>523 K 35 MPa</td>
<td>[29]</td>
</tr>
</tbody>
</table>
Chapter 1: Supercritical carbon dioxide as a green solvent for processing polymers

The modelling of solubility data is as crucial as experimental measurements for understanding of the processes. It is an inexpensive way compared to the experiments. Thermodynamics plays a vital role here. Phase equilibria of pure components or solutions are generally determined by equating the chemical potential of a component in the existing phases. The theories used for the thermodynamics are the lattice, the cubic equation of state (EOS) and the off-lattice.

Among the theories above, the lattice theory has frequently been used. According to this theory, polymer molecules are ordered in a lattice structure with holes (represent free volume). The lattice fluid theory doesn’t require separate parameters to account for the flexibility of the molecule. The lattice fluid theory can be used to calculate heat and volume of mixing, lower critical solution temperature and enthalpic and entropic components of the chemical potential. The lattice fluid theory reduces to the Flory-Huggins theory at low temperatures. The EOS, a molecular lattice theory of classical fluids based on a well-defined statistical mechanical model, has been presented by Sanchez and Lacombe [30-31]. A detailed description of several versions of this model that extends the basic Flory-Huggins theory can be found in the literature [32-34].

1.2.2. Viscosity reduction

The processing of high molecular weight polymers is not an easy task. High viscosity is a major obstacle in processing a high molecular weight polymer. An option is the processing of a polymer at elevated temperatures since viscosity decreases with increasing temperature. But at elevated temperatures degradation of polymers is an important concern. In addition, it consumes a large amount of energy. The use of organic solvents can avoid this problem by reducing the viscosity of polymers at low temperatures. Nevertheless, emissions of the solvents into the environment, the separation of the solvents, and the reactive nature of the solvents are the major problems.

An alternative to this option is the use of supercritical CO2 as a plasticizer or a solvent for viscosity reduction in various processing. The dissolved CO2 causes plasticization at a low temperature. This plasticization is due to the reduction in the glass transition or melting point of a polymer [35-39]. Plasticization is generally referred to the reduction in viscosity due to the dissolved gas [40]. In this way, the processing of polymers can be carried out at low temperatures and hence, the degradation of polymers can be avoided. An increased attention has been given to understand the rheological properties of various polymer-CO2 solutions.

Capillary/wedge/slit die extrusion rheometers have been modified and reported for high pressure rheological measurements for various polymer-CO2 systems.
Chapter 1: Supercritical carbon dioxide as a green solvent for processing polymers

by several research groups [41-48]. In addition to an extruder, a static mixer has been used to form a single phase solution. A pressure drop along the die has been used for viscosity calculations. The results show that the viscosity decreases with increasing concentration of CO\(_2\). Though the solubility of CO\(_2\) increases with pressure, the viscosity increases at high pressures due to reduction in the free volume (hydraulic pressure effect). A large pressure drop can lead to phase separation if the concentration of supercritical CO\(_2\) is above the solubility limit at the final pressure and temperature. However, such devices are mostly useful when the concentration of CO\(_2\) is far away from equilibrium. This concentration limitation can be overcome by using drag-driven devices. Since the pressure is constant during measurements, it allows carrying out measurements at or near equilibrium concentrations of CO\(_2\). The viscosity measurement using a drag-driven device, a magnetically levitated sphere rheometer (MLSR), has been reported for the low viscosity polymer [49].

The viscosity curves (shear viscosity (\(\eta\)) vs shear rate (\(\gamma\))) for various concentrations of CO\(_2\) in a molten polymer are usually of a similar shape as those of a pure molten polymer. The curves obtained at different concentrations can be shifted (scaled) to the curve obtained from a pure polymer. This curve is known as the master curve. Extensive research has been done for theoretical viscosity prediction of polymer-CO\(_2\) solutions using the free volume theory [50-51].

1.3. Supercritical CO\(_2\) in the production of micron-size particles

Milling, grinding, crystallization and spray drying are the particle formation methods commonly used in the coating, toner and drug delivery industries. Narrow particle size distribution, solvent recovery and avoiding the emissions of VOCs are the major challenges associated with these methods. In addition, milling and grinding are not suitable for thermally instable and low glass transition temperature or melting point compounds due to the frictional heat dissipated during processes. Therefore, the industries have been looking for new technologies, which would provide micron size particles with a narrow particle size distribution using as small as possible quantity of VOC. This has motivated chemical engineers as well as chemists to apply a supercritical technology rather than classical methods. The supercritical technology utilizes the solubility of supercritical CO\(_2\) in a polymer or vice versa.

In the last decade, the research on particle production using supercritical CO\(_2\) has rapidly been growing. Various methods already exist that use supercritical CO\(_2\) as a solvent or anti-solvent. Recently, these methods have been broadly reviewed [52]; rapid expansion of supercritical solutions (RESS), gas anti-solvent crystallization (GAS), supercritical anti-solvent precipitation (SAS), precipitation by compressed anti-solvent (PCA), solution enhanced dispersion
by supercritical fluid (SEDS) and particles from gas saturated solutions (PGSS). To have a brief idea over the listed methods, a comparison of all of them is summarized in Table 1.2. Moreover, a brief introduction has been provided for most commonly used supercritical methods.

Table 1.2. The comparison of various supercritical methods

<table>
<thead>
<tr>
<th>Process</th>
<th>RESS</th>
<th>GAS/SAS/PCA</th>
<th>SEDS</th>
<th>PGSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas quantity</td>
<td>Discontinuous</td>
<td>Semicontinuous</td>
<td>Continuous</td>
<td>Continuous</td>
</tr>
<tr>
<td>Gas quantity</td>
<td>High</td>
<td>Medium</td>
<td>Medium</td>
<td>Medium</td>
</tr>
<tr>
<td>Organic solvent</td>
<td>Absent</td>
<td>Present</td>
<td>Present</td>
<td>Absent</td>
</tr>
<tr>
<td>Pressure</td>
<td>High</td>
<td>Medium</td>
<td>Medium</td>
<td>Low</td>
</tr>
<tr>
<td>Separation of gas</td>
<td>Easy</td>
<td>Easy</td>
<td>Easy</td>
<td>Easy</td>
</tr>
</tbody>
</table>

1.3.1. Rapid expansion of supercritical solution

The rapid expansion of supercritical solution (RESS) method utilizes a dramatic change in the dissolving power of a solvent, when it is rapidly expanded from a supercritical pressure to a low pressure. After expansion, the solvent exist as a gas that makes the collection of the resulting particles (solute) much easier.

RESS is based on crystallization or precipitation of a solute in order to facilitate the powder production. The method can generally be used if the solubility of a solute (polymer) in supercritical CO$_2$ or another appropriate fluid is high. Fig. 1.3 represents a schematic drawing of the RESS method. A fluid is pressurized and heated to ascertain the supercritical conditions needed for the process and passed through an extractor containing a solute in order to form single phase solution. Following this, the solution is depressurized over a nozzle to atmospheric pressure. The rapid depressurisation leads to nucleation of the solute caused by the lowering of the solvation power and therefore particles are formed. After the depressurization, CO$_2$ turns into the gas phase and is purged out of the collecting device.
1.3.2. Supercritical anti-solvent methods

Supercritical anti solvents methods are applicable to materials whose solubility in a supercritical fluid is very low. In these methods, a supercritical fluid is used as an anti-solvent. The operating principle is the same for all supercritical anti-solvent methods.

A schematic drawing of the precipitation with a compressed anti-solvent (PCA) method, one of the anti-solvent methods, is shown in Fig. 1.4. A solute is first dissolved in a solvent and then, exposed to a supercritical fluid in order to generate particles. The selected solvent has a good affinity for the supercritical fluid. The solvating power of the solvent is reduced after the exposure to CO$_2$ and the solution becomes supersaturated with the solute. Consequently, the precipitation of the solute takes place and micron size particles are formed. The nozzle through which the supercritical fluid is added is an important factor in order to control the morphology and size of the particles. At the end of the process, the precipitator is washed with the anti-solvent to remove the solvent completely.
1.3.3. Particles from gas saturated solution

Unlike RESS, a gas is dissolved in a solute under sub- or supercritical conditions in the particles from gas saturation (PGSS) method. A schematic drawing of the PGSS method is shown in Fig. 1.5. A solution is formed by saturating a solute with a gas. The gas-saturated solution possesses a low viscosity due to an increase in free volume. Moreover, the interfacial tension between the gas and the liquid phase is lowered as the surface tension of the gas in the supercritical state is zero. These properties ease the expansion of the solution. The solution is then expanded over a nozzle from a supercritical pressure to ambient pressure. It causes a supersaturation of the gas and an intense expansion of the nucleated gas bubbles leads to explosion of the molten material into fine particles. The particles are solidified due to the cooling effect of an expanded gas.

The method has been patented by Mandel et al. [53] and Weidner et al. [54]. Very few polymers have been processed using PGSS in a batch and continuous mode. In a batch mode a solution is formed using a stirrer while in a continuous mode a static mixer is used to saturate a molten polymer with a gas. The batch process has been applied for the generation of powder of poly(ethylene glycol) [55]. Conventional coating systems like acrylic coatings, polyester-epoxy systems and low-melting polyester coatings have been produced using a continuous process [56].
1.4. Selection of a method for the production of polymer particles

Different morphologies and particle sizes have been produced using different methods for several polymers [52]. The selection of a method is dependent on several factors such as the solubility of CO₂ in a polymer, solubility of the polymer in CO₂, solubility of CO₂ in a solvent and solubility of the polymer in a solvent and amount of solvent. Since the anti-solvent methods use organic solvents, a last preference may be given to these methods. RESS and PGSS are most preferable methods as they do not use an organic solvent. In case of RESS and PGSS, the major difference between them is the solubility term. In RESS, a polymer is dissolved in a supercritical fluid while in PGSS a supercritical fluid is dissolved in a polymer. Using CO₂ as a supercritical fluid, RESS is only applicable to very few polymers due to low solubility of many polymers in supercritical CO₂. PGSS is a better choice as it utilizes the solubility of supercritical CO₂, which is high in several polymers. However, the method has yet not been tested for different polymers of high viscosity and may require some modifications.

1.5. Purpose and outline of the thesis

This thesis mainly focuses on the production of particles using CO₂ as a supercritical fluid for different polymers such as polyester resins and poly (ethylene glycol) (PEG), and aspects relevant to the process such as solubility, viscosity and processing parameters. The polyester resins and PEG in particle form are used in toner and drug delivery applications. The particle size, the
particle size distribution and the morphology are the important properties of the particles depending on the applications. In a drug delivery application, PEG particles are generally used for encapsulating a drug where a release rate of the drug is dependent on the properties of the particles. It is possible to generate particles with different properties by tuning process conditions using supercritical CO\textsubscript{2} as a solvent or plasticizer, which allows a good control over the release of the drug. Moreover, the absence of an organic solvent in the supercritical CO\textsubscript{2} assisted process is the major advantage in the production PEG particles containing a drug. In a toner application, polyester resins are generally used due to their low melting point or glass transition temperature and hydrophobic nature. The resins are always mixed with colour pigments in order to have a desired colour prior to the production of particles. In this application, the particle size and size distribution play a very important role in determining the texture of the film and adhesion of the film to the surface as shown schematically in Fig. 1.6. A smooth film is obtained when the particles of a small size and with a narrow particle size distribution are used. Moreover, a better adhesion of the film to the surface is also achieved.

![Fig. 1.6. A schematic representation of the effect of the particle size on the film formed using a) big particles with a broad particle size distribution b) small particles with a narrow particle size distribution](image)

In this thesis the PGSS method has been adopted for low viscous PEG and modified for a high viscous polyester resin based on propoxylated bisphenol (PPB) in order to produce micron size particles. The PGSS method has already been reported for the production of micron size particles for a few polymers. Viscosity reduction caused by the dissolved CO\textsubscript{2} plays a vital role in the production of particles using PGSS. The higher the dissolved amount of CO\textsubscript{2} in a polymer the higher is the reduction in the viscosity of the polymer. For this purpose, knowledge of the solubility of CO\textsubscript{2} in a polymer is essential a priori. The solubility of CO\textsubscript{2} varies from one polymer to another depending on the available chemical groups. Chapter 2 discusses the relationship between the solubility of CO\textsubscript{2} and the strength of the interactions between polymers and CO\textsubscript{2}. Fourier transform infrared spectroscopy (FT-IR) has been used as a screening tool for the selection of the polymers to be processed. As the FT-IR study gives only qualitative information, Chapter 3 investigates the solubility of CO\textsubscript{2} in the polymers experimentally using a gravimetric method. In order to incorporate the buoyancy correction, a requisite in gravimetric measurements,
the swelling of the polymers using an optical cell has been measured separately.  
**Chapter 3** also describes the modelling of phase equilibrium data using Sanchez-Lacombe equation of state, which can be used for interpolating and extrapolating the solubility data at different processing conditions. **Chapter 4** describes a batch PGSS process for the production of particles from PEG of different molecular weights. In this chapter, flow and solidification models, and the effect of various parameters such as temperature, pressure, nozzle diameter and molecular weight have been studied in detail. Like PEG, shear viscosity data in the presence of dissolved CO₂ for PPB is not available in the literature. In **Chapter 5**, a model based on the free volume theory has been applied to predict the reduction in the viscosity of PPB which appeared to be considerable. The PGSS method has been tested for the particles production of PPB. It has not been possible to produce particle of PPB using PGSS mainly due to its very high viscosity compared to PEG. The method has been modified in terms of the amount of CO₂ used. **Chapter 5** also discusses the results obtained from scouting particles production experiments, which have been carried out using a continuous set up in which CO₂ and polymer have been mixed together in a Kenics type static mixer. It is possible to produce particles from the high viscous polymer melt by modifying the PGSS method. To overcome practical limitations of the set up, a gear pump and a SMX static mixer for higher through put and a better mixing, respectively, have been introduced. **Chapter 6** describes a detailed engineering study of the continuous production of polymer particles using the modified set up for various processing conditions. The effect of various parameters such as temperature, pressure, gas to polymer mass ratio, core-slot width and nozzle diameter on the particle size, shape and particle size distribution has been studied. **Chapter 6** also discusses the solidification model and the dimensionless analysis model to determine the contribution of various parameters. Finally, a technological assessment by comparing the modified method with the traditional methods, prospects of supercritical CO₂, and conclusions with future outlook of the thesis work have been discussed in **Chapter 7**.  

**References**


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Chapter 1: Supercritical carbon dioxide as a green solvent for processing polymers


