Minimizing Energy Requirements for Polymer Processing by the Means of Supercritical Fluids

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Supercritical fluid-based technology has been largely proposed to produce materials with nanostructural properties. Namely, classical methods that use environmentally hazardous volatile organic solvents and chlorofluorocarbons for processing and synthesis of polymers are undesired due to the enormous increment of volatile organic solvents and chlorofluorocarbons emissions and also generation of aqueous waste streams. As carbon dioxide is quite soluble in many polymers, it can be used as a solvent or plasticizer. Dissolved CO_2 causes a considerable reduction in the viscosity of the molten polymer, a very important property for the applications like polymer modification, formation of polymer composites, polymer blending, microcellular foaming, particle production and polymerization. Properties of the obtained powder product like particle size, size distribution and morphology depend on phase equilibria and thermodynamic behaviour of the system, fluid dynamics, mass transfer and nucleation-growth kinetic. Phase equilibria and reaction kinetics, verification of process steps and design of process sequences to produce a product (energy) from raw materials are the main hindrances concerning SCF applications. Detailed investigations on the basic thermodynamic and transport data like phase equilibria, density, viscosity, dielectric constant and diffusion coefficient have to be carried out to obtain the data fundamental for the design of a process in order to fulfil consumer and economic requirements. One of the main industrial challenges is the adoption of sustainable technologies, development and scaling up of processes from an approach mainly focused on the performance towards a global comprehensive approach of the production process.

1. Introduction

Boosting industrial application of green chemistry and sustainable technologies, developing the tools for design, scale-up and implementation of emerging processes into industry is a goal that should be followed in the near future. This can only be successfully achieved through connection of research in emergent areas such as: i) best use of raw materials; ii) use of clean solvents; iii) use of energy and iv) production of minimal amount of waste. An overall concept of a processing plant where biomass feedstock is converted and extracted into a spectrum of valuable products, biofuels, biospecial chemicals and bioefficient materials, has commonly been termed as biorefinery. Great importance of this approach is derived from several benefits of renewable resources utilization: reduced dependence on imported fossil oil, reductions in greenhouse gas emissions, building on the existing innovation base to support new developments, a bio-industry that is globally competitive, development of processes that use biotechnology to reduce energy consumption and the use of renewable materials, sustainable development along the supply chain from feedstocks to products and their end-of-life disposal.

Using supercritical fluids (SCFs) as solvents in chemical processes means an advantage in many points of view. It has health, safety, environmental and also chemical benefits (Knez et.al., 2014). CO_2 has been proven to influence the physical properties of polymeric materials. SCFs can be easily removed from the product by depressurization since it is gaseous under atmospheric pressure. That means no solvent residues in the final product and consequently lower processing cost. The diversity of polymer properties makes polymers such as cotton, wool, rubber, Teflon, and all plastics widely applied in everyday life and also in industrial applications. As mentioned above, low cost, low density and ease of processing are just some of the advantages of polymers which make them highly applicable. But there is also a disadvantage, poor mechanical properties. This explains

the fact that polymers are highly investigated also in the fields of scientific literature in order to moderate this disadvantage.

Absorption of compressed gas in polymer matrices results in a wide spectrum of possible applications in the field of sustainable polymer processing, for instance production of fibres, micro-particles and foams, polymer impregnation, separation of gas mixtures through polymer membranes. Investigation of thermodynamic properties of binary systems polymer/CO_2 is a topic under an intense research (Tsivintzelis et al., 2016). Several modifications of polymers are taking place since CO_2 dissolution and polymer swelling can be expected. SCF addition reflects in modification of several physical properties of polymer, such as glass transition temperature, melting temperature, surface tension, and viscosity, which are changed depending on solubility of SCF in the polymer. Recently, different drug loaded nanoparticles are developed for tissue engineering applications. Scaffolds are produced by SC CO_2 drying of polymeric gels (Naddeo et al., 2016).

2. Aims

Environmental and social criteria are considered simultaneously during multi-objective optimization, in order to assess the trade-offs between the sustainability aspects (Čuček et al., 2012). The aim of our current research is to obtain data on phase equilibria, density, interfacial tension, viscosity and diffusion coefficient of systems containing supercritical fluids (such as CO_2) which significantly influence high pressure separation and formulation process. Figure 1 presents a flow-sheet of PGSS (Particles from Gas Saturated Solution) process. A binary system of a molten polymer (polyethylene glycol) and CO_2 was used as a model system to carry out the investigation. Our previous research reports on the solubility of CO_2 in PEGs of different molecular weights ranging from 1,000 to 100,000 over a pressure range up to 30 MPa at 343 K (Knez. Hrncic et al., 2014). In the field of polymeric foams, SC CO_2 is used as blowing agent. To obtain polymer or composite foams the substrate is saturated with SC CO_2, followed by rapid depressurization at constant temperature (pressure quench) (Tsivintzelis at al., 2016). This method takes advantage of the large depression of the glass transition temperature (T_g), usually determined by the means of DSC (Differential scanning calorimetry), observed for many polymers in the presence of dense CO_2 (Costeau et al., 2014).

Particle formation (PGSS)

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Dissolving fluids in molten substances

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Low viscosity and reduced surface tension

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Release of compressible fluid form the gas saturation solution

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Volume increase-Cooling

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Temperature decrease below the solidification temperature

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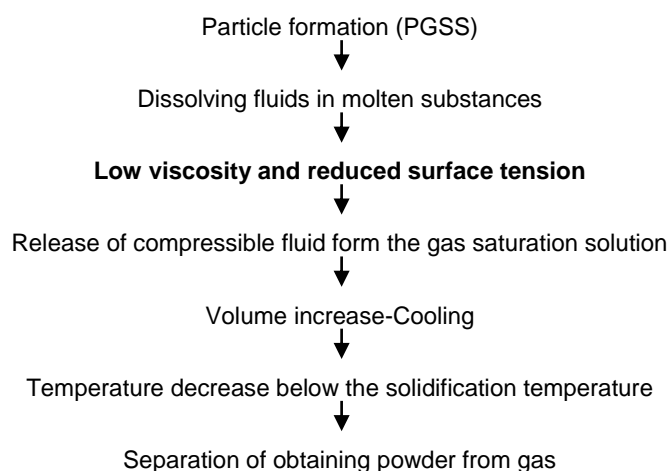
Separation of obtaining powder from gas

Figure 1: A flow-sheet of PGSS (Particles from Gas Saturated Solution) process.

SCFs can be used either as a solvent (RESS-Rapid expansion of supercritical solution), an antisolvent (GAS-Gas antisolvent crystallization) or a solute (PGSS-Particles from Gas-Saturated Solutions) in the processes of particle size reduction. Some of these applications already found applications in polymer processing branch. In PGSS process the substance (polymer) to be powdered must be converted into sprayable form by liquefaction/dissolution. This can be achieved by melting or dissolving of the substance in liquid solvent followed by saturation of the melt or solution with gas, where the formation of fine droplets after spraying through a nozzle are driven by reduced surface (interfacial) tension and low viscosity (Montes et al., 2013). These two parameters crucially influence economy of a micronization process. Basis for scale up and cost estimation for an industrial production are related to the production capacity and depend on the annual hours of operation and the amount of CO_2 required to generate 1 kg of powder Weidner has considered an economic evaluation of PGSS micronization plant with a capacity of 1.5 t/h (Figure 2). The process is featured by low operating costs, as low as 0.20 €, including investment, personal, consumables (incl. gas), maintenance and interest. Feasibility of a plant of that size it could be increased by installing a CO_2 recovery (Weidner, 2009). However, processing costs

can increase up to 1.2 €/kg in case of short processing time and high GTF (gas, used as a solvent, to feed) ratios. Low GTF ratios contribute significantly to reduce processing costs. For a plant with capacity of 1,500 kg/h, processing costs decrease from 1.2 €/kg to 0.4 €/kg at the same operation time. For a plant of the same capacity, extending processing time from 3,000 h/y up to 8,000 h/y can reduce operating cost for almost 50 %. In the frame of our research, volumetric method to measure density of single phase gas saturated solution of solid compounds at elevated pressures at isothermal conditions, validated by determining density of pure CO_2 at a temperature of 293 K, has been developed. Viscosity of binary systems of a sub or supercritical fluid and a compound (molten polymer) has been studied at isothermal conditions.
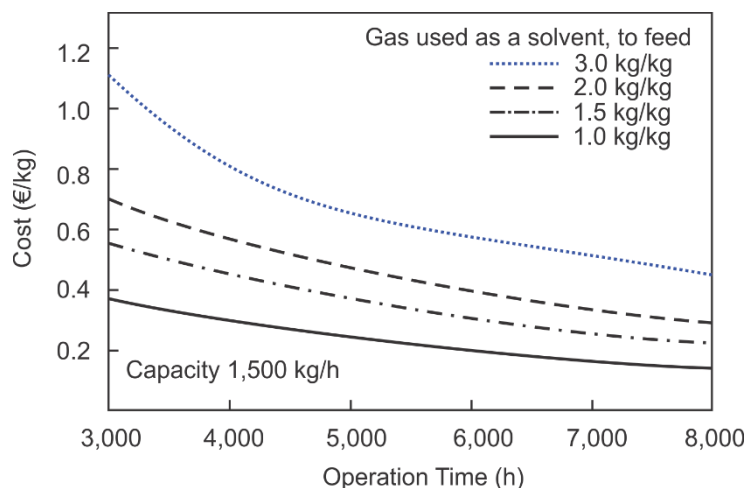

Figure 2: *Economic evaluation of PGSS micronization plant with a capacity of 1.5 t/h (Weidner, 2009)*

3. Methods

A brief explanation of the methods for determination of density (i), viscosity (ii) and interfacial tension (iii) of the binary systems is provided below:

(i) Determination of density of the binary systems: According to the external balance method, an amount of sample is placed into the chamber and saturated with gas at the desired conditions. The system is exposed to vigorous mixing at for a certain time period. Afterwards the sample is taken from the lower phase into a certain tube segment of a known volume and weight. As the main advantage, it is possible to employ the external balance method when a system does not qualify for the more accurate Magnetic Suspension Balance.

(ii) Determination of the viscosity of binary systems: A new method has been developed for the calculation of the viscosity of binary systems at moderate and elevated pressures. By the use of available experimental data and a simple viscosity mixing rule, results obtained previously for the viscosity of pure compounds have been extended to mixtures.

(iii) Capillary rise method for investigation of interfacial tension of the binary systems: An experimental setup to determine the interfacial tension and visualize the interfacial interactions phenomenon has been developed based on the capillary rise phenomena to allow measurements in two-phase systems comprising a liquid phase and a fluid phase in the gaseous, liquid, or SC state. Results obtained by conducting preliminary experiments on a model system by measuring interfacial tension between CO_2 and pure water show a good agreement with the ones found in the literature.

4. Results

Melting point temperatures (T_m) and melting enthalpies (ΔH_m) of the investigated PEGs are presented in Table 1. Measurements were performed by DSC1 at atmospheric pressure.

The effect of molar weight on the melting temperature cannot be unambiguously proved thus an increase in the molar mass of the polymer does not simultaneously mean an increase of the melting temperature. Some authors (Aionicesei et al., 2011) state that an increase of the melting point actually occurs due to an increase of the molar mass. Thus the average melting temperature (except PEG 1,000 and PEG 1,500) varies in the range from 430 K to 440 K, a temperature of 343 K is chosen as the working temperature. Melting enthalpies vary between 190 J/g up to 210 J/g, only in case of PEG 1,000 the enthalpy is much lower; about 125 J/g.

In case of PEG 15,000 melting point is observed at 429.75 K, a possible explanation is that polydispersion of polymer chain length influences the temperature of the melting point (Knez Hrncic et al., 2014).

Viscosity of CO_2 saturated solutions of polyethylene glycols (PEGs) of different molecular weight at different pressures and at a temperature of 343 K was measured using a high-pressure view cell. After saturating PEG 1,500 with 10 MPa of CO_2 pressure its viscosity decreases from 76.6 mPas to 2.24 mPas at 333 K. Further addition of CO_2 and increasing pressure result in even lower viscosity. Expectedly, highest viscosity reduction was reached at the highest investigated pressure; at 35 MPa viscosity of the system PEG 1,500/CO_2 is only 0.665 mPas (Figure 3). Interfacial tension of molten polymer polyethylene glycol in contact with SC CO_2 or argon was measured using capillary rise method (Kravanja et al., 2016). Interfacial tension decreases by increasing pressure, the effect of temperature is rather low.

Table 1: Melting temperatures T_m (K) and melting enthalpies ΔH_m for PEGs of different molecular weight (Knez Hrncic et al., 2014).

M (g/mol)	T_m (K)	ΔH_m (J/g)	ΔH_m (kJ/mol)
1,000	412.56	125.20	125.20
1,500	420.31	191.66	287.49
3,000	431.32	202.94	608.82
4,000	432.68	203.50	814.00
6,000	434.17	208.83	1,252.98
10,000	435.87	196.83	1,968.30
15,000	429.75	190.04	2,850.60
20,000	435.81	206.31	4,126.20
35,000	438.19	199.05	6,966.75
100,000	438.98	204.69	20,469.00

Viscosity, as one of the main factors that influences feasibility of polymer processing, sharply decreases with increasing pressure. After a certain pressure of about 20.0 MPa, the effect of pressure is less significant. Temperature variation has a significant effect on viscosity. With increasing temperature, a rapid reduction of viscosity can be achieved. However, that is not an optimal choice for viscosity reduction since it leads to polymer degradation. Indeed, in the pressure range up to 20.0 MPa, a relatively high impact of molecular weight on viscosity is observed; as expected, PEG of higher molecular weight has higher viscosity which decreases sharply with increasing pressure, the highest viscosity reduction is observed in case of saturation of PEG 10,000 with CO_2, followed by PEG 6,000. Such rapid viscosity reduction with increasing pressure of CO_2 is not observed for PEG 3,000 and PEG 1,500, probably due to the molecule structure; namely, higher mobility of polymer chains enables better absorption of gas molecules even at low pressure. Increasing pressure means increasing concentration of gas, which shows a tendency to enter inside the polymer and at the same time increases the volume of the sample. At pressures above 25.0 MPa, molecular weight of polymer does not exhibit an important impact on viscosity of the system after saturation with CO_2. The viscosity values are similar for all of the studied systems at the same conditions. After saturation with CO_2, PEGs with higher molecular weight still have slightly higher viscosity which is 4.5138 mPas for CO_2 saturated PEG 10,000 at a pressure of 20.3 MPa, but only 1.4112 mPas for CO_2 saturated PEG 1,500 at the same pressure. As viscosity decreases with increasing pressure, viscosity of PEG 10,000 in a system with CO_2 decreases to 1.6041 mPas at a pressure of 35.1 MPa and viscosity of PEG 1,500 in a system with CO_2 is only 0.6376 mPas at 35.3 MPa. Viscosity reduction of PEGs due to addition of CO_2 is directly dependent on the quantity of CO_2 dissolved in the polymer (Mukherjee et al., 2002). Since increasing pressure means increasing concentration of gas, which shows a tendency to enter inside the polymer; increase in volume of the sample also increases the solubility, (Tochigi at al., 2007). This is probably influenced by the plasticizing effect of CO_2 and by the hydrostatic effect of pressure. When polymers absorb CO_2, the molecules rearrange themselves towards a new equilibrium conformation (Knez Hrnčič et. al, 2014). For small gas concentrations, equivalent to low pressures, the plasticizing effect of CO_2 is reflected in a higher mobility of the polymer chains and therefore in increasing values of the diffusion coefficient. For high concentrations, however the hydrostatic pressure may play an important role by reducing the available free volume and leading to decreased diffusivity. The parallel fact is that diffusion coefficient is not largely dependent on the molecular weight of the polymer (Knez Hrnčič et al., 2014).
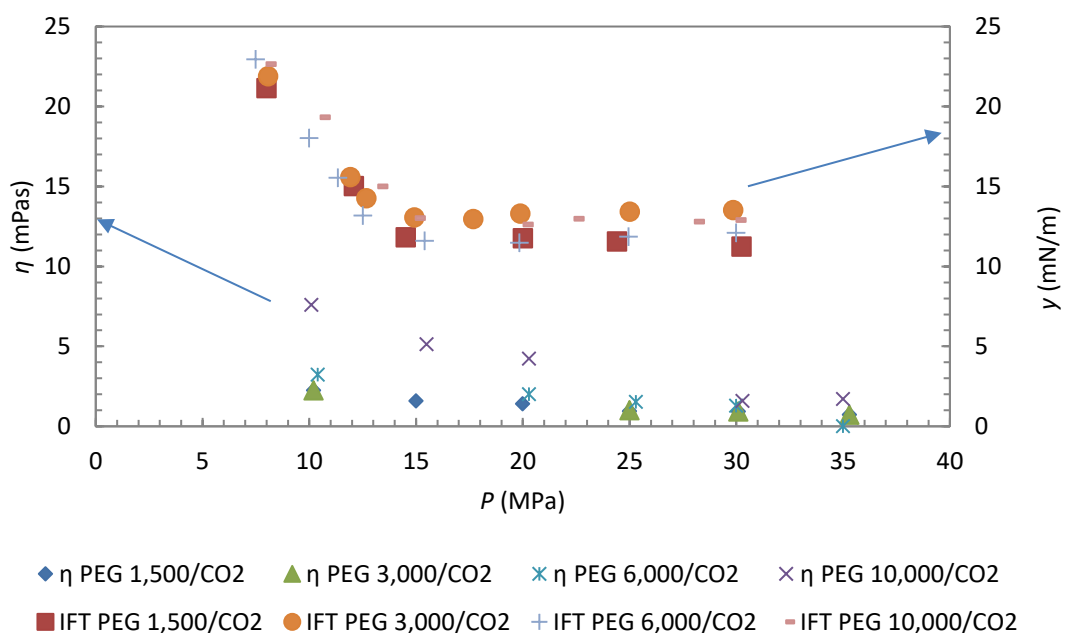
Figure 3: Relation between viscosity and interfacial tension for binary systems of PEG and CO_2 as two crucial parameters influencing the economy of a micronization plant (Kravanja et al., 2016).

Higher concentration of gas in the sample consequences in a lower viscosity. Consequently, viscosity decreases with increasing pressure for all of the studied systems, from approximately 2.7791 mPas at 10.1 MPa for PEG 3,000, which was the highest observed viscosity, to 0.6376 mPas at 35.3 MPa for PEG 1,500 as the lowest.

5. Conclusions

Processing of polymers with SCFs certainly has a bright future due to several beneficial effects considering ecological and economic feasibility. Substances are processed at lower temperatures as well, which is suitable in case of temperature labile compounds. CO_2 is overwhelmingly still the most frequently applied processing media in novel engineering concepts. These concepts comprise use of supercritical CO_2 as a swelling agent for polymers to enhance impregnation affinity of desirable substances. These substances are mainly bioactive compounds. Furthermore, CO_2 may act as a compressed fluid to obtain different polymer morphologies of pure polymers or composites.

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