PRODUCTION OF POLYMER PARTICLES USING SUPERCRITICAL CARBON DIOIXDE AS A PROCESSING SOLVENT IN AN EXTRUDER

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The high solubility of supercritical carbon dioxide (CO_2) in various molten polymers is utilized in a variety of polymer processes, where it replaces various organic solvents. In addition, CO_2 has attracted particular attention as a supercritical fluid because of its non-toxic, nonflammable, chemically inert, inexpensive nature and easily achievable supercritical conditions (T_c= 31 ^{0}C P_c= 73.8 bar). One of the processes, to which supercritical CO_2. This melt micronisation process is carried out in an extruder. The high viscosity material is mixed in an extruder, a traditional mixer for viscous materials, with supercritical CO_2. This gas-molten polymer solution is then expanded through a nozzle having a micronsize-diameter hole. The high-pressure difference between the upstream and the downstream and the micronsize hole of a nozzle cause the choking of a subsonic flow. This choked flow results in a supersonic expansion. This expansion leads to micronsize particles due to a release of the solution from the elevated to the atmospheric pressure. The cooling of the gas, due to a sudden expansion, vitrifies the molten polymer particles. A much narrower particle size distribution is obtained using this method than possible with traditional milling processes. Various factors such as the pressure, temperature, flowrate, and nozzle diameter play a crucial role in PGSS process. However, the research in this field, PGSS, is rapidly growing due to its various applications in paint and toner industries.

INTRODUCTION

The enormous increment of organic solvent emissions and the generation of aqueous waste streams have led a number of chemists and chemical engineers to seek new cleaner methods for polymer processing. One of these methods is the use of supercritical fluids in the particle production process, particles from gas saturated solutions (PGSS). A supercritical fluid (SCF) may be defined as a substance for which both pressure and temperature are above the critical values. The special combination of gas like viscosity and liquid like density of supercritical fluids results in its use as an excellent tuning solvent in the processing of molten polymer [1-3].

One of the supercritical fluids, which can be used, is CO_2. Supercritical CO_2 is a clean and versatile solvent, and a promising alternative to noxious organic solvents. It has attracted particular attention as a supercritical fluid in the processing areas for polymers due to the following properties:

i. CO_2 is non- toxic, nonflammable, chemically inert, and inexpensive
ii. Supercrtical conditions are easily obtained: T_c = 31 ^{0}C ; P_c = 73.8 bar
iii. The solvent may be removed by simple depressurization
iv. The density of the solvent can be tuned by varying pressure
v. 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. Although CO_2 is a good solvent for many non-polar (and some polar) molecules with low molecular weight, it is a very poor solvent for most high molecular weight polymers under readily achievable conditions (< 100 ^{0}C, < 1000 bar). The only polymers shown to have good solubility in pure CO_2 under mild conditions are certain amorphous fluoropolymers and silicones [4]. However, although the solubility of most polymers in supercritical CO_2 is extremely low, the solubility of supercritical CO_2 in many polymers is substantial. Therefore, it has a tremendous potential as a plasticizer in polymer processing. However, the research in this field, PGSS, is rapidly growing due to its various applications in paint and toner industries. In this work we have concentrated the application of supercritical CO_2 in the production of polymer particles using an extruder. PGSS process in an extruder is an integration of various parameters as shown in the block diagram in Figure 1.

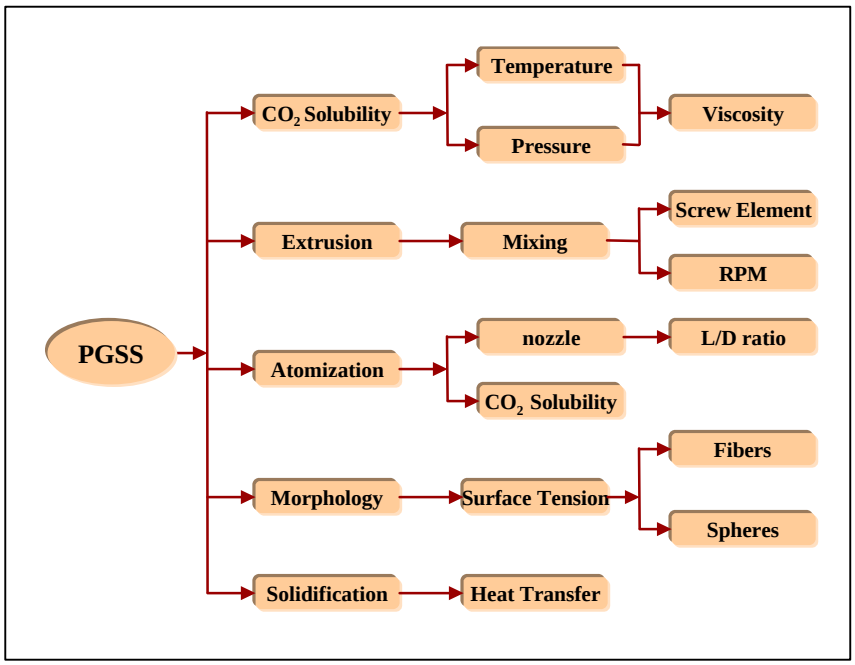

Figure 1 : A PGSS process using an extruder

THE EXPERIMENTAL SET UP:

Concerning the process, we focus on the extruder as the equipment to be used for the particle production with a PGSS process. Due to high viscosity of various polymers, the sorption of supercritical CO_2 in molten polymers is always diffusion-controlled in the absence of proper mixing. The good mixing action provided by the extruder for high viscous materials will be used to overcome these diffusion limitations of polymer-supercritical CO_2 systems. The schematic diagram of the experimental set up is shown in Figure 2. The twin screw counterrotating extruder is presently chosen due to its leakproof arrangement. The designed disc creates a high pressure in the front of the disc (left hand side of the disc) due to molten polymers in order to prevent the leakage of CO_2. Whereas, the high-pressure at the die is achieved using a micron size nozzle. Various zones in a twin screw counterrotating extruder

are shown in Figure 3. During the process, CO_2 is pumped in a partially filled zone, a low-pressure zone, where it is mixed with the molten polymers and the polymer solution is expanded through a nozzle.

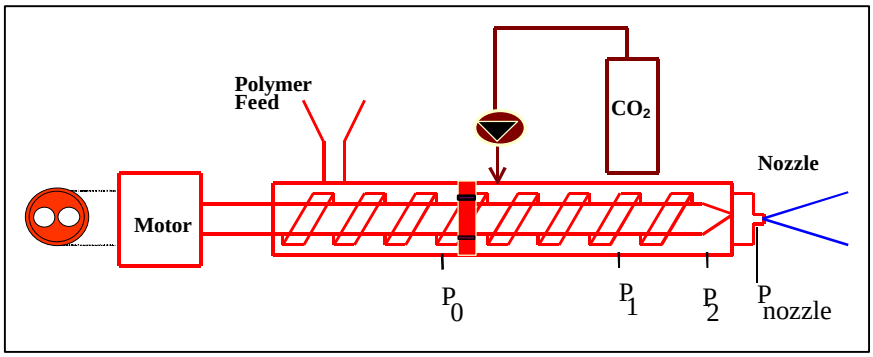

Figure 2 : A schematic diagram of the experimental set up of PGSS process

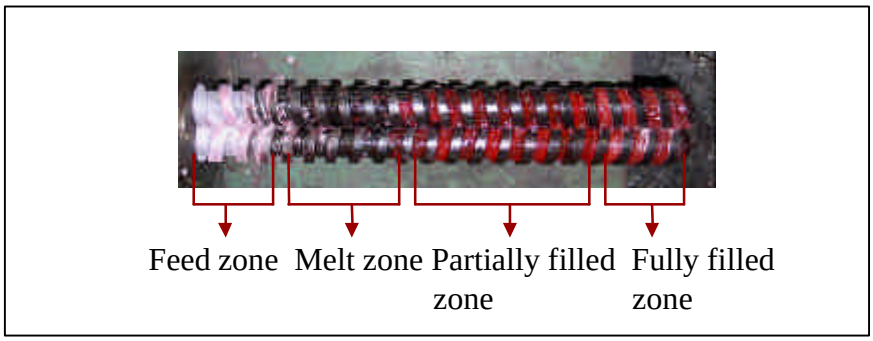

Figure 3 : Various zones in a twin screw counterrotating extruder

SOLUBILITY AND PGSS RESULTS:

The knowledge of phase equilibrium data of the gas-molten polymer systems in order to design and develop the PGSS process is essential. A useful compendium on the solubility of polymers in supercritical fluids is available because of its relevance to the fractionation of polymers. However, only a limited amount of data on the solubility of supercritical CO_2 in liquid polymers is existing, despite its applications in a variety of polymer processes. Only a few experiments were carried out to determine the solubility of supercritical CO_2 in the polymer melt (polyester resin) at the elevated temperatures and pressures due to the mixing limitations of the solubility apparatus. These experiments show the pressure-temperature behaviour of a polymer solution at a particular concentration of supercritical CO_2. The result of experiments with 5-wt % supercritical CO_2 in the polymer melt is shown below in Figure 4.

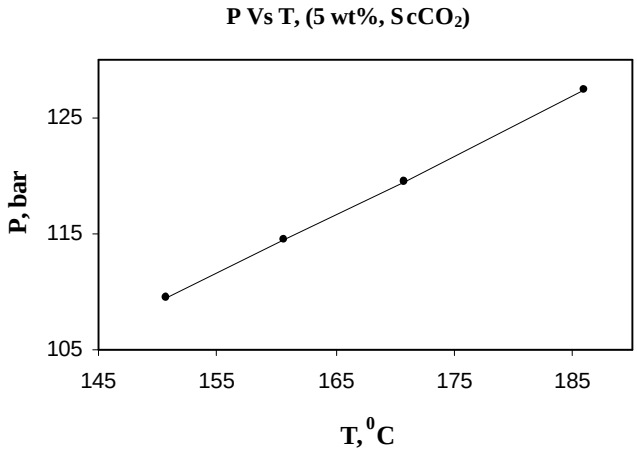

Figure 4 : Solubility curve, pressure-temperature, P120

The polyester resin melt is processed in a twin screw counterrotating extruder in the presence of CO_2. However, submicron-size fibers were obtained as a result of expansion through the nozzle, Figure 5. A narrow particle size distribution was obtained as shown in Figure 6. The pressure at the nozzle, P_{nozzle} , in an extruder is always higher than the pressure at the positions 1 and 2 shown in Figure 2. In this case, the pressure at the nozzle is calculated considering only the molten polymer, which was found greater than P_c. However, $P_{nozzle} > P_c$ is assumed and its (P_{nozzle}) value is not presented in this case as a reduction in viscosity due to the dissolved CO_2 is not known . A variety of experiments has yet to be carried out in order to optimize the processing conditions since the experiments described here were just exploratory experiments. However, much better results can be expected at high pressures ($P_{nozzle} >> P_c$) as the solubility of carbon dioxide in molten polymer increases with the pressure.

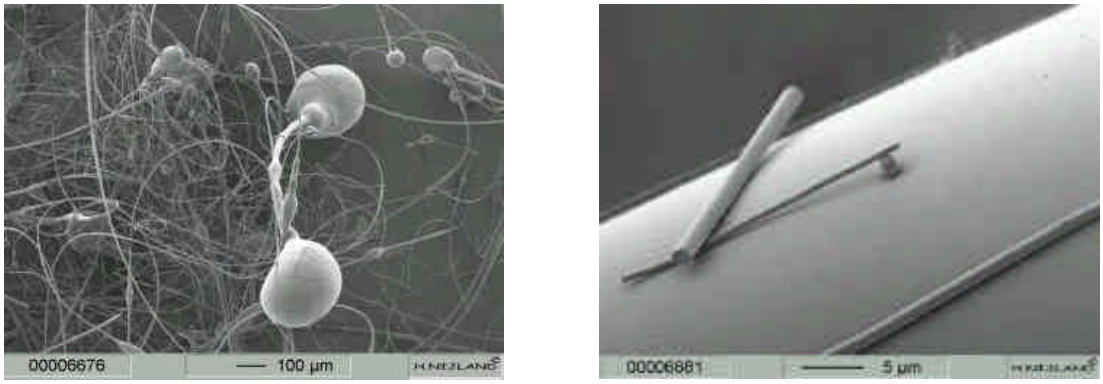

Figure 5 : Fibers P120 (P_2 = 60 bar, $P_{nozzle} > P_c$, T = 140 ^{0}C, L/D (nozzle) = 2 and feed = 2 kg/hr)

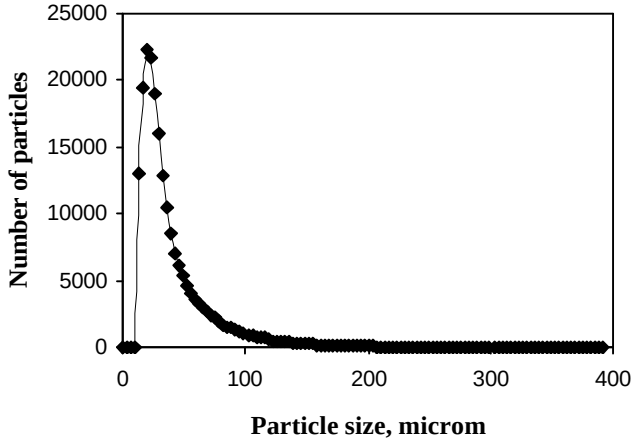

Figure 4 : Particle size distribution, P120 (P_2 = 60 bar, $P_{nozzle} > P_c$, T = 140 ^{0}C, L/D(nozzle) = 2 and feed = 2 kg/hr)

CONCLUSIONS:

PGSS using an extruder is a promising process for viscous materials. Submicron-size particles (fibers) are obtained using this process. A narrow particle size distribution and an easy separation of the solvent are achieved. An increase in pressure increases the solubility of carbon dioxide in the molten polymer. However, particle size can further be reduced at elevated pressures.

FUTURE WORK:

Various polymers have yet to be processed in the presence of supercritical carbon dioxide using an extruder. Effects of various parameters such as pressure, temperature, feed rate (polymer as well as carbon dioxide), RPM and screw elements arrangements (extruder) and length/diameter ratio of a nozzle on the PGSS process using an extruder will be determined in order to optimize the process.

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REFERENCES

[1] KNEZ Z., AND NOVAK Z., WEIDNER E., European Patent 0,744992, **2000**
[2] KNEZ Z., WEIDNER E., R. STEINER, High Pressure Chemical Engineering, Ph. Rudolf von Rohr and Ch. Trepp, **1996**, p. 223
[3] BLATTER K., PETERMANN M., REKOWSKI V., WEIDNER E., Chem. Eng. Technol., Vol. 24, **2001,** p.529
[4] MCHUGH M. A., KRUKONIS V. J., Supercritical Fluid extraction, butterworth-Heinemann, stoneham, MA, 2nd edn., **1994**