

HIGH PRESSURE MICRONISATION OF POLYMERS

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For production of particles with micron and submicron size, several methods using supercritical fluids are used in the recent time (HPC, RESS, GASR, GASP, SEDS, PCA, PGSS™, CPF). These methods will be compared in terms of their technological properties (mode of operation, gas consumption, pressure, volume of high pressure equipment, separation of solids from gas and liquid). A short review of application of above mentioned processes for micronisation of various substances will be given in the lecture

More in details a relatively new process for the formation of Particles from Gas Saturated Solutions (PGSS) will be presented. Special attention will be given to thermodynamic fundamentals of this process and technical application of PGSS process for production of powders from polymers.

Polyethylene, polyethylenewaxes, polyethyleneglycols and polyethyleneters were processed using PGSS process. The pre-expansion process pressures were between 100 bar and 300 bar and the pre-expansion temperatures were between 323K and 383K. The influence of process parameters and nozzle geometry on the particle size, particle size distribution and geometry of the particles were studied.

INTRODUCTION

Basic principle of the PGSS™ process [1,2]

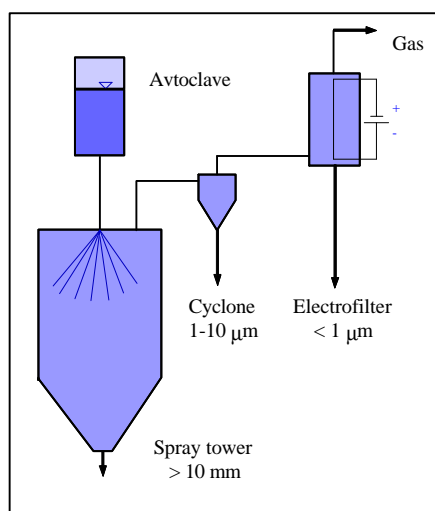


Figure 1: Scheme of the experimental equipment for PGSS

The solubility of gases or generally compressible media in liquids is usually much higher than the solubility of substances in the compressible media at the same conditions [3,4]. By dissolving the compressible media in a liquid the so-called gas saturated solution is formed. By expansion of such a solution in an expansion unit, e.g. a nozzle, the compressed medium is evaporated and the solution is cooled. Due to the cooling caused by the Joule-Thompson effect the temperature of the two phase flow after the expansion nozzle is lowered. At a certain point the crystallisation temperature of the substance to be solidified is reached. Thus solid particles are formed and subcooled.

A scheme of the equipment is presented in **Figure 1**.

CONCLUSION

PGSS™ of Polyethyleneglycols

Polyethyleneglycols (PEG's) are water soluble polymers, which are due to their physiological acceptance used in large quantities in pharmaceutical, cosmetic and food industry. The general formula of PEG's is $H(OCH_2CH_2)_nOH$, where n is the number of ethylene oxide groups. PEG is, like other polymers, a mixture of homologues where n varies between certain numbers. PEG's up to molar mass of 600 g/mol are liquid while those with higher molar masses are solid. PEG is usually manufactured as flakes but in some applications it is used as a powder, which is obtained by milling of flakes. Milling is possible for PEG's with molar masses between about 2000 g/mol and 10000 g/mol. PEG's of lower molar mass are too greasy and higher PEG's are too hard. Not only with respect to flexibility for different feedstocks, the new developed process - PGSS - is favourable for the generation of fine particles [5].

It was found that the solubility of CO_2 (expressed in weight percent) in PEG above a certain chain length is practically independent from the molecular mass of PEG and is influenced only by pressure and temperature of the system.

At low pressures the liquefaction temperature of PEG in presence of CO_2 slightly increases compared to the melting point of the pure PEG. This increase might be caused by a pressure effect or by solid transition of PEG induced by increasing pressure. Than a sharp decrease is observed. The liquefaction temperature passes a minimum and increases again.

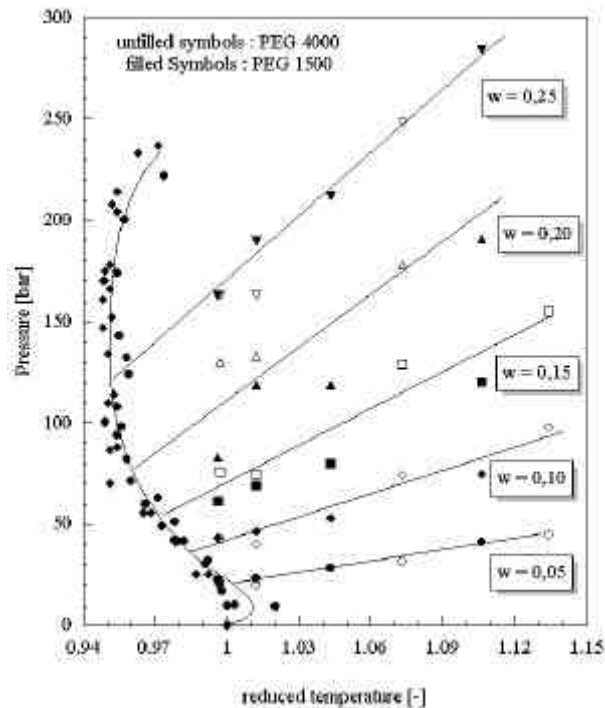


Figure 2: P-T_{red} diagram with melting point line and constant composition lines.

On a diagram (**Figure 2**) for the system PEG/CO₂ the expansion according to the PGSS-process is represented by the isoplethes (the composition does not change during the expansion). The gas saturated solution is established at pressures and temperatures which are on the right hand side of the liquefaction curve (S-L-V line). On the left hand side of the liquefaction curve solid PEG coexists with gaseous CO₂. The starting conditions have to be chosen in that way, that the end conditions after expansion are in the S-V region of the binary system.

For the production of fine dispersed PEG by expanding CO₂-saturated solutions a first assumption indicates that the starting conditions should be near the liquefaction curve in order to reach the solid-gas region after the expansion. An initial estimation can be performed by an energy balance which takes into account:

- enthalpies of CO₂ before and after expansion (e.g. from an T,S-diagram),
- enthalpies of PEG before and after expansion (e.g. from heat capacity of liquid and solid PEG),
- enthalpy of solution of CO₂ and PEG (e.g. derived from phase equilibrium data) and
- heat of crystallisation of PEG (from literature data or DSC).

The mechanical energy for the formation of new interface is, in most cases, two to three orders lower than the thermal energies and can therefore be neglected.

The experiments on PGSS of PEG were performed in a lab-scale plant with sample sizes of about 200 – 400 g powder and in a small pilot plant with sample sizes of 1 – 3 kg powder. Depending on the nozzles (orifices 0.4 / 0.5 / 1.0 mm, spraying angles 30° and 90°), the kinds of PEG (MW 1500/4000/8000/35000) and on pressure (100-250 bar) and temperature (45-70°C) three classes of particles were obtained: fibres, spheres and sponges as presented in **Figure 3**.

Spheres are obtained when the initial temperature is so high (approx. 30 K above the melting point), that the product is not completely powderous. Fibres are preferably obtained, when the molar mass of the PEG increases. The „normal“ configurations are the sponges.

From DSC measurements of fresh powders (some minutes old) it was derived, that the crystallinity is between 85 to 90%. Elder powders (1 - 6 weeks) have a crystallinity, which correspond to the conventional PEG's.

In the investigated pressure range the saturation pressure has almost no influence on the mean particle size and no influence on the bulk densities.

The diameter of the nozzle influences the mean particle size. A 1.0 mm nozzle gave particles between 350 – 500 µm, while 0.4 mm nozzle gave mean particles sizes of 170 – 370 µm.

The overall CO₂ consumption is in the range between 0.17 – 0.7 kg /1kg of powdered PEG.

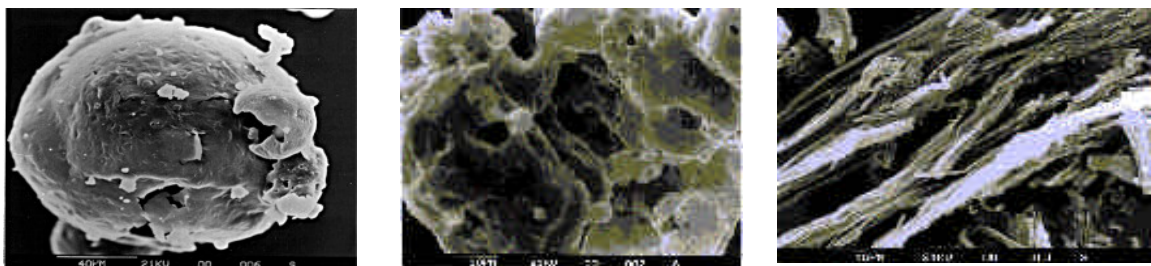


Figure 3: Shape of the particles of PEG obtained by PGSS™ process

PGSS™ micronisation of other polymers

On the enclosed **Figure 4** a gallery of REM photos of various PGSS™ processed polymers is presented. The materials were processed at various process conditions with various types of nozzles.

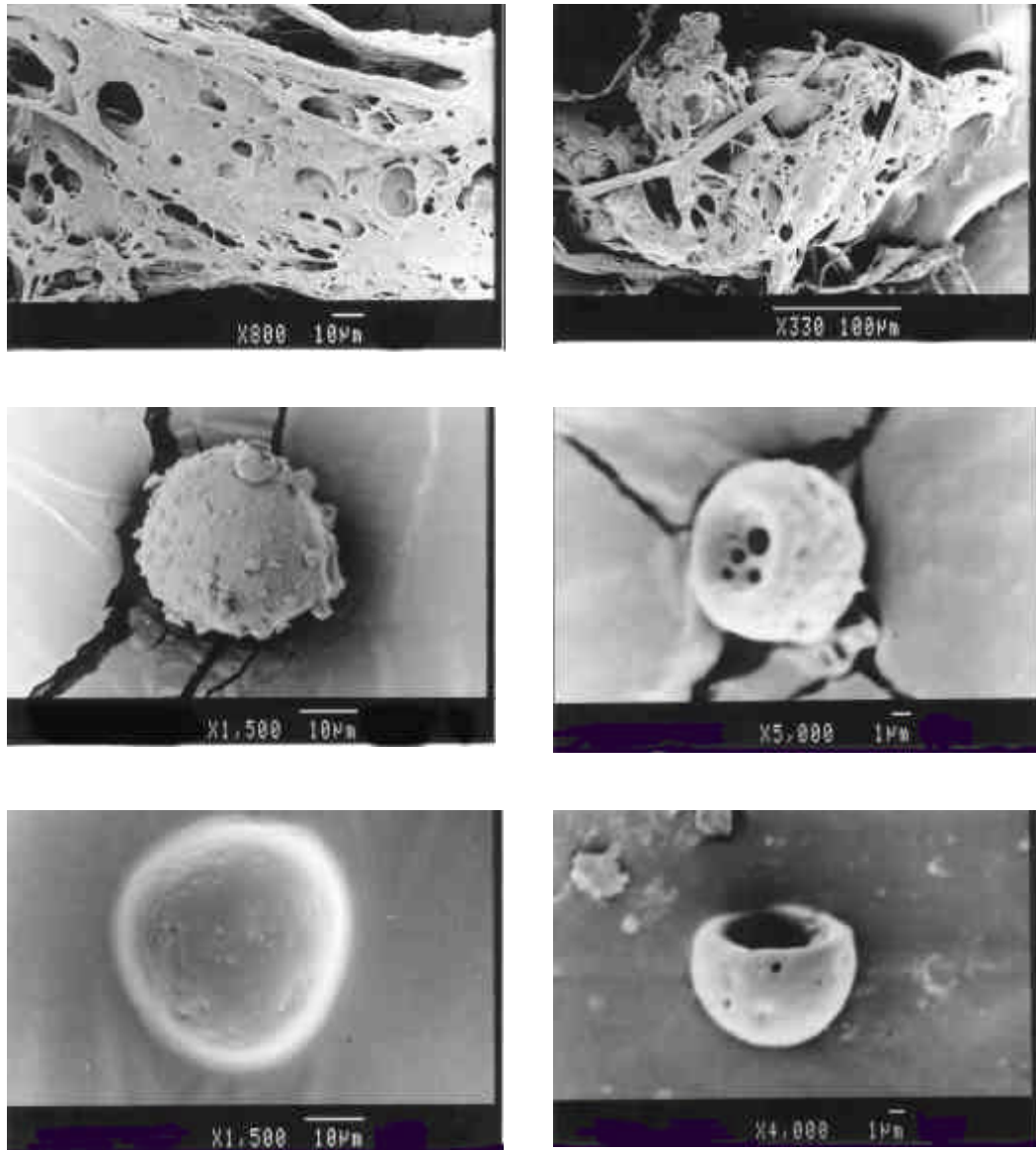


Figure 4: A gallery of REM photos of various PGSS™ processed polymers

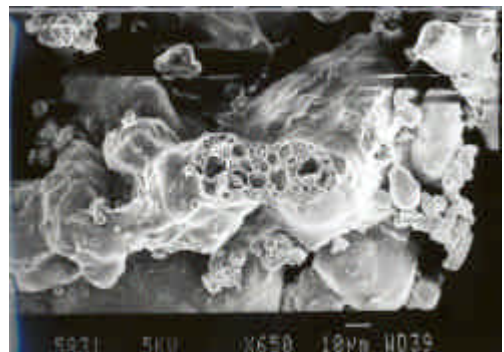
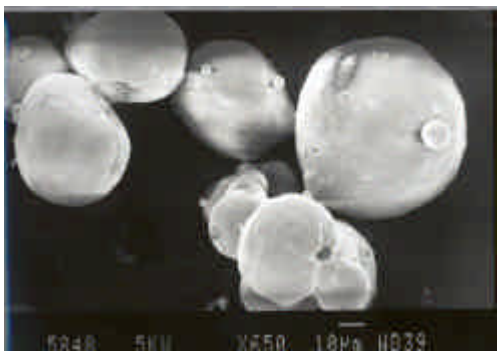
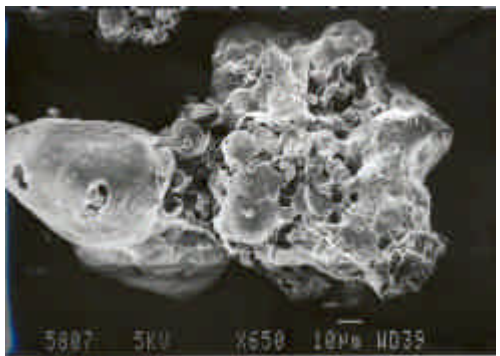
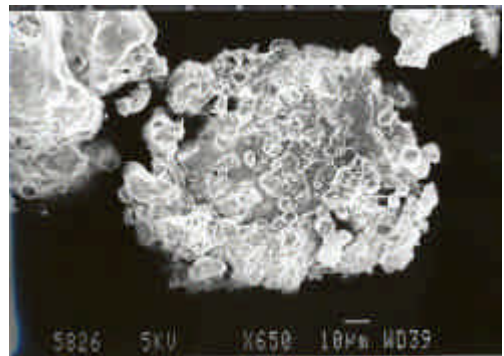
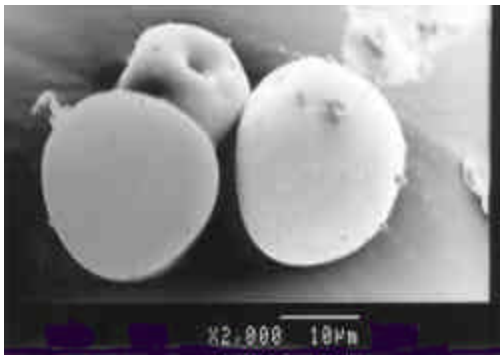
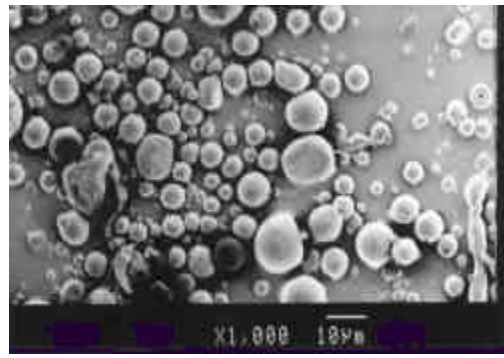
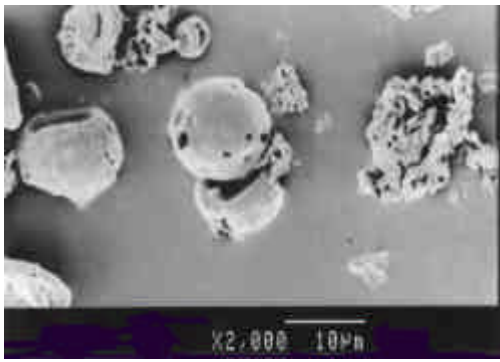


Figure 4: A gallery of REM photos of various PGSS™ processed polymers (continued)

Economy of the process

Based on the results from laboratory scale equipment and first production plants the basic economy of the process was calculated. The processing costs are between 0.15 and 0.60 Euro/kg (composition of costs: investment ~ 20%, personnel ~ 37% and operating ~ 43%) and vary based on the substances to be micronised, scale of the equipment etc.

The advantages of PGSS

The advantages of PGSS process over conventional methods of particle size reduction are numerous like: versatile process applicable for several substances, moderate pressures, low gas consumption, solvent-free powders, suitable for high viscous or sticky products, fine powders with narrow size distribution, different morphologies and easy scale-up.

Through the choice of the appropriate combination of solvent and operating conditions suitable for a particular compound, PGSS can eliminate some of the disadvantages of traditional methods of particle size redistribution in material processing. Solids formation by PGSS therefore shows a promising potential for the production of crystalline and amorphous powders with a narrow and controllable size distribution, thin films and mixtures of amorphous materials.

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