PURIFICATION AND SIMULTANEOUS MICRONIZATION OF POLYMERS BY SUPERCRITICAL ANTISOLVENT PRECIPITATION

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ABSTRACT
One of the most important environmental concerns for the polymer industry is to produce new products with near-zero residual monomer content. A new process based on supercritical CO_2 has been successfully tested for the extraction of the residual monomer and the simultaneous micronization of the polymer. The process has been tested on a pilot-scale plant. The reduction of methyl methacrylate (MMA) in PMMA is described as a representative model system. The polymer is dissolved in its monomer until a dilute homogeneous solution is formed; than the resulting solution is sprayed in a vessel where supercritical-CO_2 is delivered at constant pressure and temperature. CO_2 acts as an antisolvent for the polymer and as a solvent for the monomer that is removed from the polymer. The results show that it is possible to produce micro and nanoparticles with a very low solvent residue in one process step. It is also shown that it is possible to modify the particle dimension in a wide range of dimension by changing the operating pressure and/or temperature.

INTRODUCTION
One of the major drawbacks of polymerization techniques (bulk, emulsion, dispersion) is the difficulty to obtain complete monomer conversion at standard processing conditions. This difficulties result in the presence of relatively large amounts of residual monomer in the final product of the polymerization process. For health, safety and environmental reasons, it is desirable to reduce the residual monomer content in commercial polymers. Some techniques for residual monomer removal are already used. In general, the available methods are based on two concepts: 1) conversion, or 2) extraction of residual monomer.

The first method requires the introduction of extra chemicals that have to be subsequently removed and additional post-polymerization steps. Extraction methods are performed using high temperature steam that can cause problems of polymer stability. Moreover, steam extraction is an energy consuming process. These techniques have specific characteristics that have been discussed by Kemmere et al. [1].
Since legislation on levels of residual monomer in consumer products is expected to become more severe in the near future, there is considerable room for improvement of the existing techniques.

Supercritical CO_2 (SC-CO_2) is an interesting alternative for residual monomer removal because it is an excellent extraction medium for a variety of monomers [2]. Indeed, many monomers have a relatively high solubility in SC-CO_2 whereas the solubility of the corrisponding polymers is very reduced or negligible. In addition, small changes in pressure and temperature can tune solubility, diffusion in SC-CO_2 and viscosity. The extraction of

liquids from solids cannot be performed using conventional apparatus as a packed tower since the polymer will precipitate inside the tower. In this case a SC spray extraction has to be adopted [3]. The pre-conditions to apply spray extraction are: the liquid solvent has to be very soluble in SC-CO_2, whereas, the polymer has to be not soluble. A SC-spray extraction process consists of a precipitation vessel charged with SC-CO_2 and in which the SCF continues to flow where a spray of the liquid solution is continuously injected. If the process conditions have been properly selected, the liquid is rapidly dissolved in the SCF, whereas the solid precipitates at the bottom of the vessel. One of the key steps in this process is the spray formation. The scope of this operation is to produce a very large liquid surface due to the formation of small liquid droplets. The large surface between the liquid and SCF strongly enhances the solubilization of the liquid phase in the supercritical medium and reduces the time required for the complete elimination of the liquid phase. For this reason the process is performed at conditions at which the liquid is completely soluble in SC-CO_2.

Moreover, SC-spray techniques have emerged as promising methods for precipitating polymer particles from solution while near solvent-free particles are produced [4].
The aim of this work is to provide a new method [5] for producing polymer microparticles whereas the polymer is purified from its monomer by a one-step integrated process. The method is based on the concepts of SC-spray extraction and of the supercritical antisolvent (SAS) precipitation process. The experiments have been performed on a pilot scale plant using PMMA that has been chosen as a model system since its processability by SAS was previously successfully demonstrated.

MATERIALS AND METHODS

MMA purity 99.0% and PMMA (MW=100K) were bought from Aldrich. Carbon dioxide (purity 99 %) was supplied by S.O.N., Italy.
The powder collected was observed by a scanning electron microscope (FE-SEM) (model LEO 420). Samples were covered with 250 Å of gold using a sputter coater (Agar model 108A).
MMA residue in the PMMA latex was measured using a gas chromatograph interfaced with a flame ionization detector (GC-FID) and coupled to a headspace sampler. Solvent residue was separated using a fused-silica capillary column 30 m length, 0.25 mm internal diameter, 0.25 mm film thickness. Head space conditions were: equilibration time 30 min at 110 °C; pressurization time 50 s; loop fill time 70 s. Head space samples were prepared in 10 mL vials filled with 10 mg of PMMA dissolved in acetone.
The pilot plant used in this study consists mainly of a CO_2 storage vessel, a precipitator, a liquid separator, two pumps, and a heat exchanger. The water-jacketed precipitator has an I.V. of 5.2 dm^3 and a L/D ratio of 9.4. The liquid solution and SC-CO_2 are fed to the chamber through a tube-in tube injection system. The generation of small liquid droplets is ensured by the presence of a 0.5 mm nozzle fitted on the tip of the internal tube. In the semi-continuous operation SC-CO_2 and the liquid solution are continuously delivered to the precipitator through an injection device. The precipitation process continues for several minutes until the flow of the liquid solution is stopped, while SC-CO_2 continues to flow in the chamber to wash up the SC-solution formed by the solvent and the antisolvent. A more detailed description of the plant can be found elsewhere [6]. The washing of the precipitator with the antisolvent is of great importance for the success of the process. Indeed, the condensation of the liquid solvent in the precipitator can cause the partial resolubilization of the solid modifying its morphology and increasing the solvent residue. The time required for the elimination of the liquid solvent

down to a fixed percentage, can be calculated by writing a mass balance around the precipitator under the hypothesis of a CSTR behavior [7].

EXPERIMENTAL RESULTS AND DISCUSSION

Among others SC-spray processes, SAS precipitation is a sound choice for polymer particle formation. In this process SC-CO_2 is used as the antisolvent for precipitating the polymer that is dissolved in an organic solvent. From a thermodynamic point of view, SAS process must satisfy the following requirements: the polymer must be soluble in the organic solvent at the process temperature and it must be insoluble (or sparingly soluble) in the SC-CO_2; the solvent must be completely miscible with the SC-CO_2 at the operating conditions. After the precipitation of the solute, the organic solvent and the antisolvent can be removed from the precipitator and recovered. The mixing the organic solvent with SC-CO_2 creates a supersaturation that is the driving force for the polymer nucleation. From this point of view, SAS process can be regarded both as a micronization and a solvent removal process. In this work this concept has been applied in the special case of the removal of a monomer from a polymer where the monomer is also the solvent and SC-CO_2 is the antisolvent used to precipitate the polymer.

Prior to attempting purification of the polymer, the process conditions (p, T) required to solubilize the monomer with SC-CO_2 were determined. According to literature data [8] the system MMA-CO_2 exhibits type-I phase behavior and the mixture critical point at 40°C is located at 7.82 MPa and 0.961 CO_2 mole fraction. Thus, operating at 40 °C and above 7.82 MPa a homogeneous supercritical mixture MMA-CO_2 is formed. Moreover, these experimental conditions are consistent with those required for SAS precipitation of polymers [9, 10].

Precipitation of the polymer was attempted dissolving PMMA in MMA at 1, 2.6 and 5.3 w/w %. Polymer concentration is one relevant variable in controlling the morphology of SAS precipitates [10]; indeed, varying the PMMA concentration in MMA we obtained a large change of polymer macrostructure and microstructure. Figure 1 shows PMMA fibers formed from a 5.3 w/w % solution at 43 °C and 12 MPa. The surface is composed by very small microparticles oriented along the flow direction. In contrast, operating at 1 and 2.6 w/w % solution at the same T and p conditions, a powder is obtained composed of very small microparticles. Figure 2 shows a SEM image of these microparticles. The primary particles are very small (below 100 nm), regular in shape and have a fairly monodisperse distribution. The microstructure is an open network where the particles are partially agglomerated but have not coalesced into larger particles. The macrostructure is open, loosely connected and subject to collapse when mechanically crushed. The agglomeration is caused by the plasticization of the polymer due to a depression in the glass transition temperature (Tg) when it is contacted with high pressure CO_2. The reduction of Tg is a thermodynamic effect due to intermolecular interactions between CO_2 and the polymer. In the case of PMMA the -dT/dP can be higher than 1 [11].

MMA residue in the PMMA powder was analyzed at the end of the precipitation by gas chromatography as described in the materials and method section. The MMA residue is a function of the washing time and of the extraction time. Indeed, at the end of the precipitation, when the solution delivery is stopped, SC-CO_2 continues to flow in the precipitator chamber to remove the MMA. The washing time is the time required to wash the chamber for the residual content of MMA. In a typical experiment the washing time has been set to about 70 min, calculated as the 98% of the total time required to completely eliminate

MMA from the chamber in the hypothesis of CSTR behavior. To completely extract the MMA entrapped in the PPMA powder it is necessary an extra time that has been evaluated empirically in about 30 min. Preliminary results show a near-zero MMA content.

Figure 1. SEM images of PMMA powders generated by the SAS precipitation at 43 °C, 12.0 MPa, 5.3 wt% solution of PMMA in MMA.
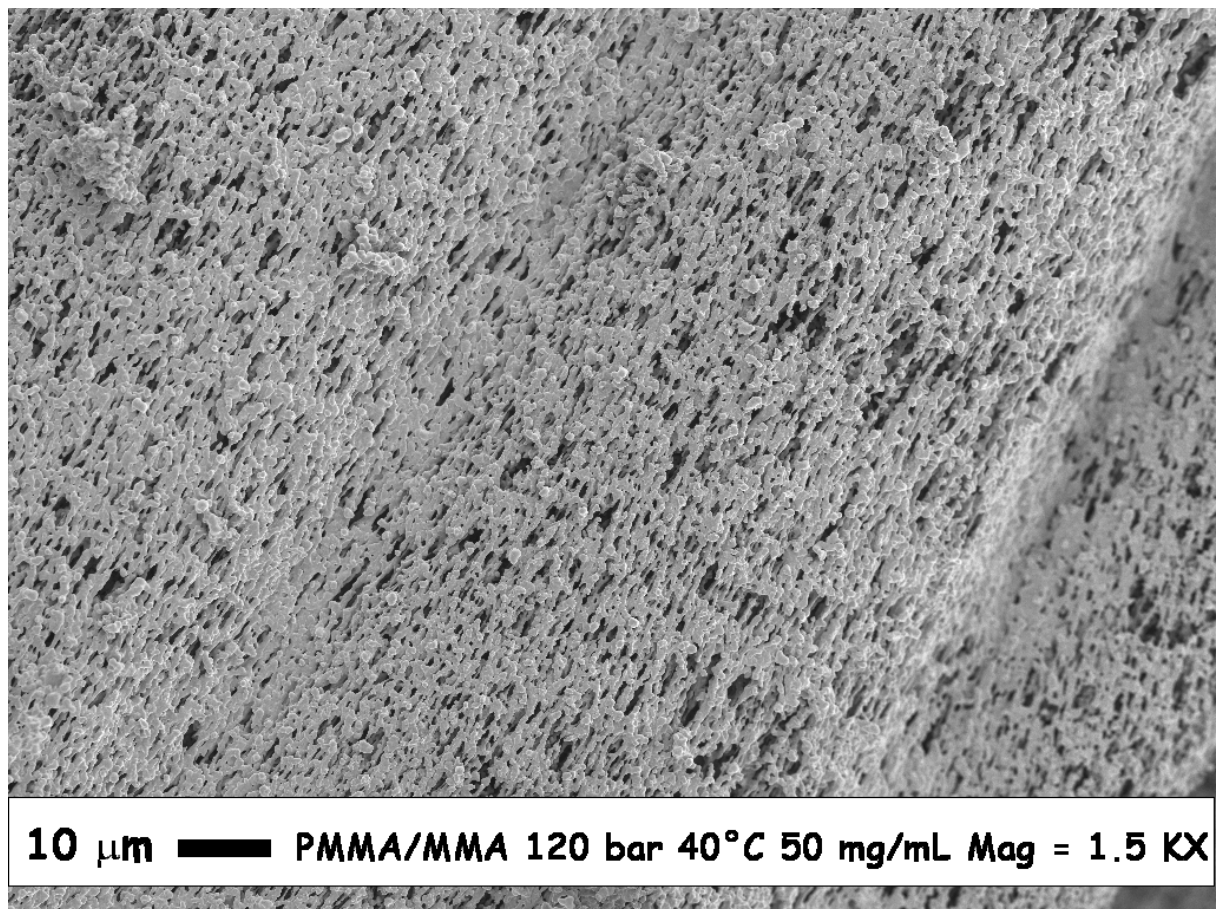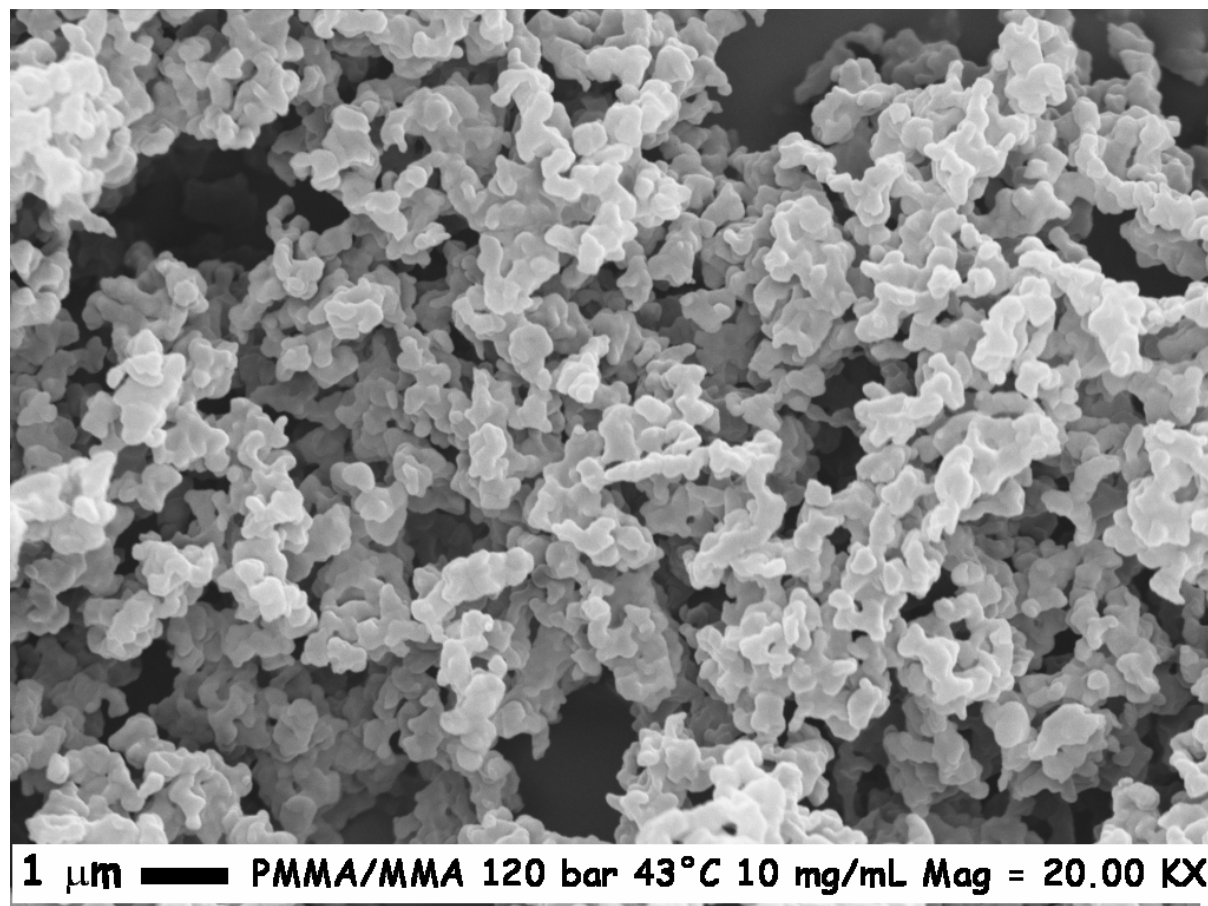
Figure 2. SEM images of PMMA powders generated by SAS precipitation at 43 °C, 12.0 MPa, 1.0 wt% solution of PMMA in MMA.

CONCLUSIONS

SC-spray extraction can be used to purify and simultaneously precipitate PPMA from MMA as a fine powder. At the end of the process microparticles of PMMA with near zero MMA residue can be obtained. The process proposed can be applied to a variety of systems Polymer/Monomer. The prerequisite is the solvency of the liquid monomer in SC-CO_2 and the insolubility of the polymer in SC-CO_2. The process could be also applied to remove from the polymer other residual chemicals used in the polymerization process (i.e. surfactants, initiators and organic solvents residue).

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