

SUPERCRITICAL FLUID AIDED ENCAPSULATION OF PARTICLES

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The development of advanced encapsulated material with tailored characteristics for timed-release applications has been a long lasting challenge of polymeric material and application domain scientists. A new method for coating polymeric thin films on particles has been achieved by simultaneous nucleation of polymeric material out of a supercritical fluid, encapsulating the particles fluidized in the supercritical fluid, and further curing and binding the material coated on the particles. The prototype system uses carbon dioxide as the supercritical solvent, hydroxyl terminated poly butadiene (HTPB) as the polymer. The particles coated are sodium chloride crystals with a particle size range of 30-500 micron as well as Ammonium Nitrate. The film thickness were determined using FTIR and were as low as 0.2 micron; the characteristics of the encapsulated material were also studied using DSC (Differential Scanning Calorimeter), AFM, SEM and Transmission Electron Microscope (TEM).

INTRODUCTION

The development of advanced encapsulated material with tailored characteristics for timed release applications has been a long lasting challenge of polymeric material and application domain scientists. The implementation of success in new materials has been partially hindered due to a suitable processing technology till the advances in supercritical fluid aided material processing.

In the last ten years or so, there has been influx of new supercritical fluid aided material processing options for impregnation of porous matrices, formation porous material, coating/spraying of flat surfaces, encapsulation, extrusion, comminution nucleation of particles and drying.

The micro-encapsulation using supercritical fluids has been initiated for drug-polymer systems with limited success due to poor understanding of complex phenomena involved in co-nucleation of components. The RESS [1] (Rapid Expansion of Supercritical Fluid Solutions) process used for micro-encapsulation therefore has major limitations. Not only do the particles with desired particle size and shape have to be nucleated, but a uniform encapsulating material has

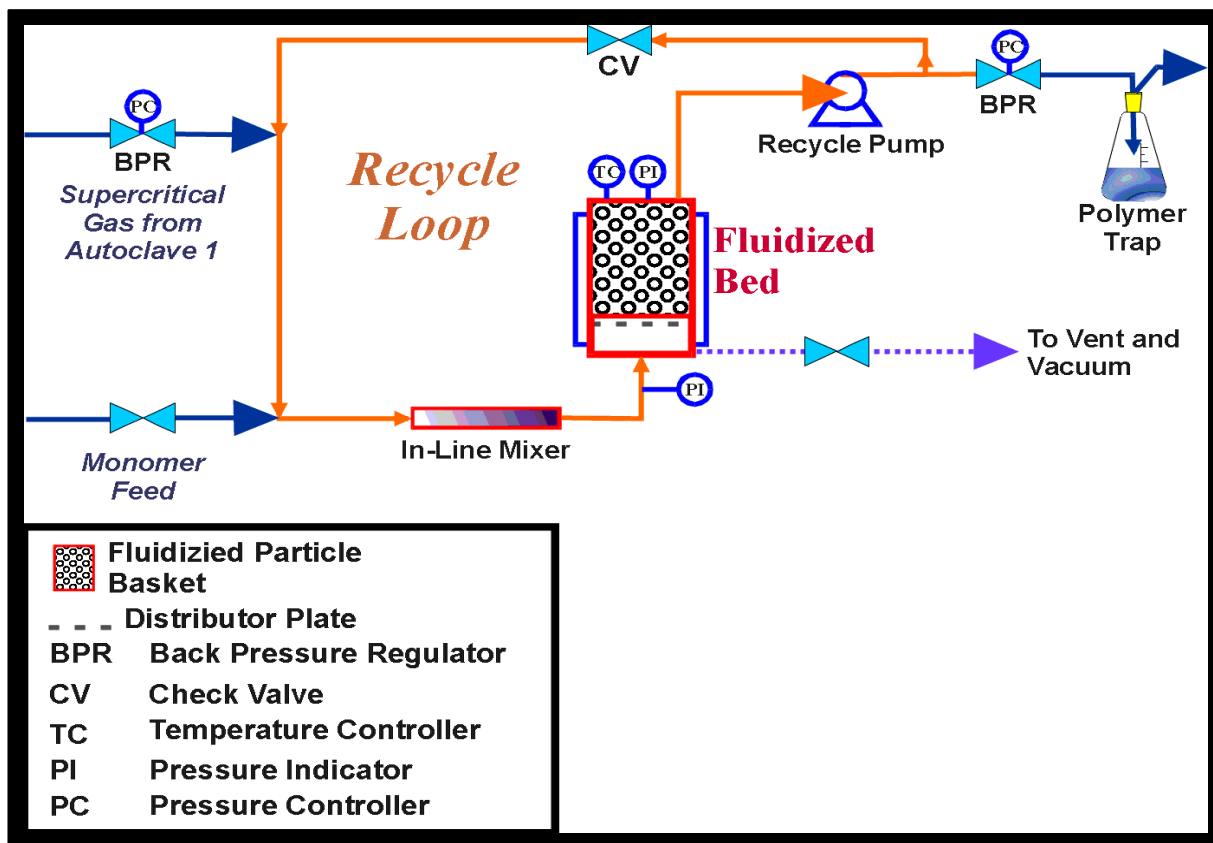


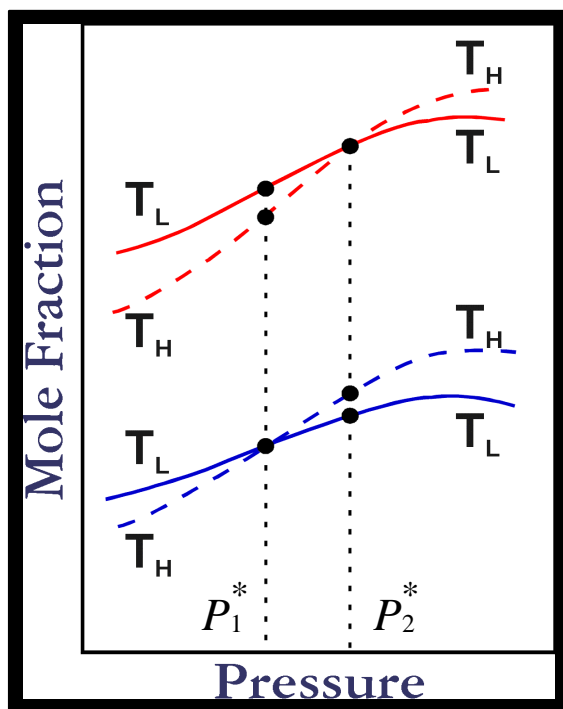
Figure 2. Expanded view of one the Encapsulation section.

The first vessel is used to store the compressed or pumped fluid under supercritical or near critical conditions. The bed of particles to be coated is placed in the second vessel (fluidized bed). This second vessel internals permit passage and fluidization of the supercritical fluid but no entrainment of the fluidized particles through the vessel. Furthermore, dead space as well as by pass are avoided. The vessel contains a device for distribution of the supercritical fluid prior to the fluidized bed and a thermocouple. Furthermore, the autoclave can be heated in a controlled fashioned.

Initially, the particles are fluidized with supercritical fluid that is recirculated through a recirculation pump in a closed loop. The loop is maintained at a low but supercritical temperature while the fluidized bed is controlled at a higher temperature at which solubility in supercritical fluid is less and at which polymerization occurs. Upon achieving successful fluidization, the liquid feed that contains a monomer/polymer, catalyst, and the curative is introduced into the

recirculation loop that is operating at a temperature that maximizes solubility (i.e. low but supercritical temperature). This highly solubilized material is introduced into the fluidized bed at its high solubilized state. The fluidized bed temperature induces reduction of the solubility resulting in the falling out of solution of the multipart pre-polymer system, with subsequent and simultaneous particle coating and inception of polymerization/curing. The operation continues in the recycle mode until satisfactory level of coating and curing is achieved. Then, the system is shut down through a procedure that avoids further polymerization and precipitation of the polymer.

RESULTS



The prototype system uses carbon dioxide as the supercritical solvent, hydroxyl terminated poly butadiene (HTBB) as the polymer, MDI (bifunctional isocyanate) as the curative, and tributyl tin dilaurate as the polymerization catalyst. The particles coated are salt (NaCl) and Ammonium Nitrate (AN) with a particle size range of 30-600 micron. The polymer is solubilized at supercritical pressures such as 1,100-2,000 psi and a temperature of range of 32-50 °C. The precipitation and curing temperature range is from 60-120 °C. One key future for synchronization of the solubilization and precipitation steps is to tailor the pressure to allow simultaneous precipitation of the pre-polymer, catalyst and the cross linking agent. In other words, one must pay due care for retrograde behavior shown in Figure 3.

Figure 3. Retrograde Behavior of Multiple Solutes

The film thicknesses were determined using FTIR and were as low as 0.2 micron. A micrograph of a select set of samples is shown in Figure 4, where the left top picture is the uncoated salt crystal and left bottom is the coated salt crystal. Furthermore, FTIR results confirmed preservation of stoichiometry of target particle polymer, indicating no fractionation of components during the SCF deposition process is observed. As can be further seen in Figure 5, which depicts the surface characteristics of the polymer encapsulant as observed through AFM, the coverage is quite uniform and pin free. SEM and AFM both confirmed the deposition of defect free, self-planarizing, encapsulating layer on the selected particulate materials.

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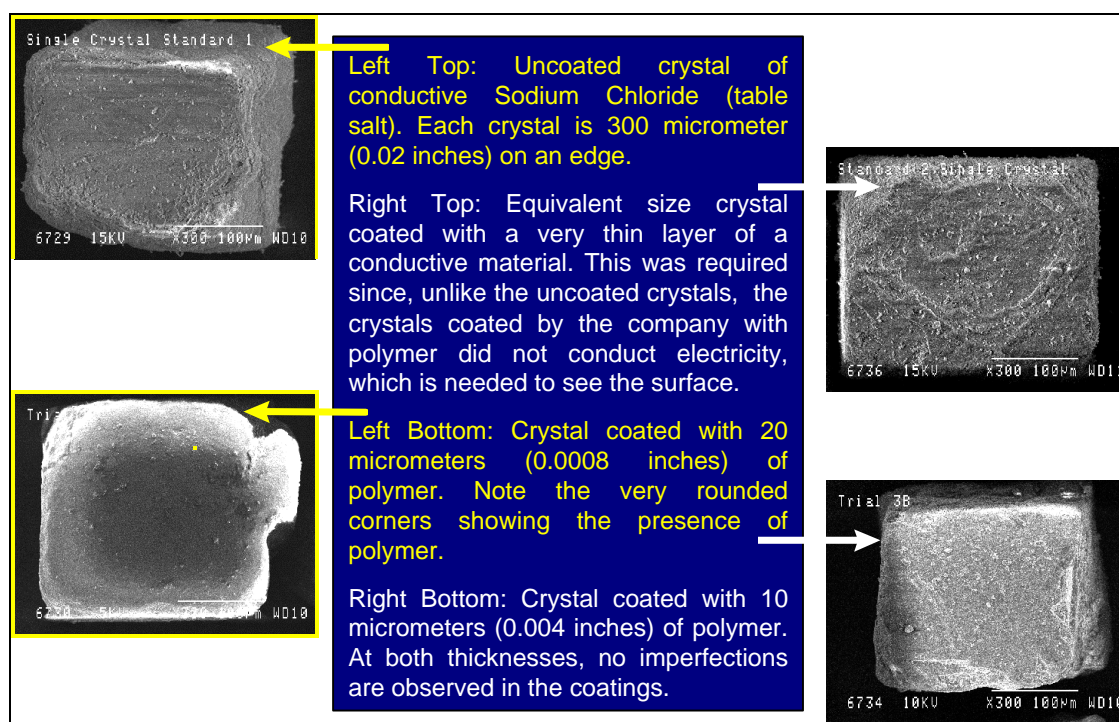


Figure 4. Micrographs of Coated Salt

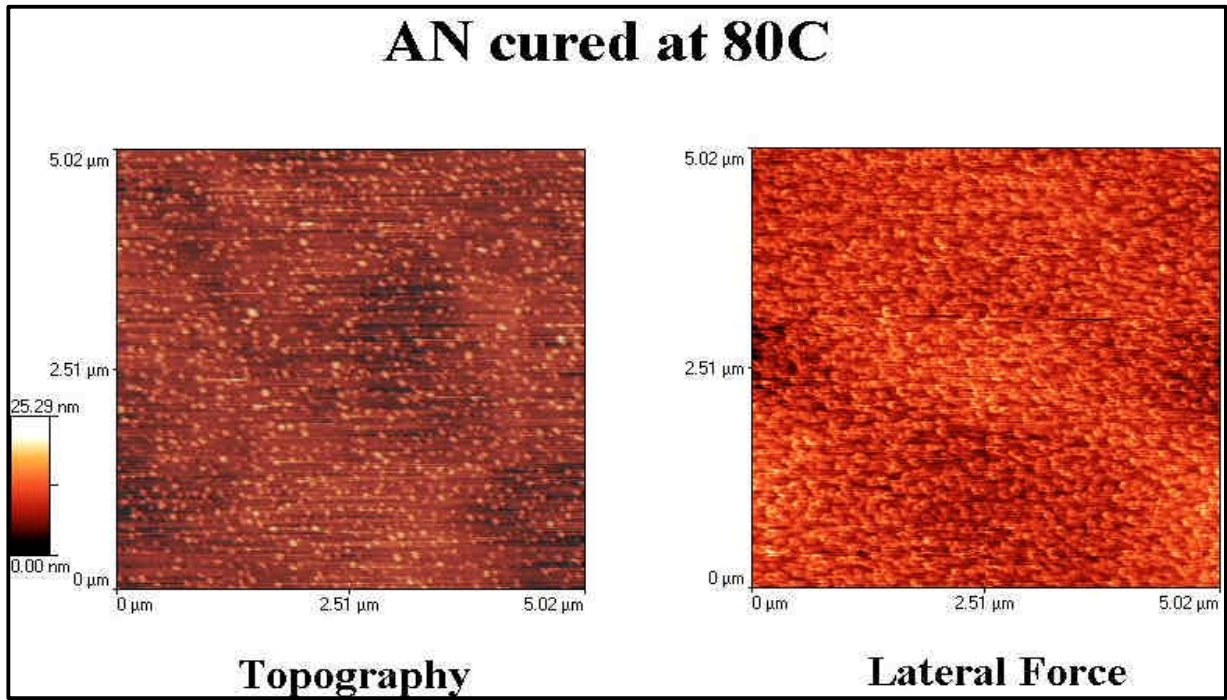


Figure 5. AFM Surface Image of a 1- μ m HTPB polymer deposition on a 600 nm Ammonium Nitrate (AN) Particle