

DEVELOPMENT OF ENCAPSULATED MICROSPHERES FROM A MULTIPLE-COMPONENT, RAPIDLY EXPANDING SUPERCRITICAL SOLUTION FOR SENSING APPLICATIONS

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Rapid expansion of supercritical solution (RESS) is a well-recognized technique for the production of microparticles and/or microspheres. RESS precipitates have attracted growing interest for various applications ranging from coatings, to particle encapsulation as well as the formation of composite structures. Our main interest in this process is directed to finding innovative solutions that address performance problems in chemical and biological sensors. By the production of a multi-component sensor material, it may be possible to improve specific sensor performance parameters including sensitivity, selectivity and shelf life. In this paper, we present our preliminary results on the development of encapsulated nano- and micro-particles, as well as nano-composite materials, which will then form the basis of an advanced sensor. For this purpose, mixtures of 2,5-distyrylpyrazine (DSP), a fluorescent monomer, and either diethyl p-phenylenediacrylate (EPA), or DAIKIN FM-300, a fluorinated polyacrylate (FAA) in supercritical chlorodifluoromethane (F-22), have been investigated as model systems.

INTRODUCTION

The versatile processing method known as Rapid Expansion of Supercritical Solutions (RESS) has been used to produce films, fibers, and particulate morphologies of a variety of materials including ceramics, polymers, and pharmaceutical or organic compounds [1-4]. More recently, RESS has been used as a novel route to solvent-free production of composite microparticles primarily for the purpose of controlled/targeted drug delivery. The interest in composite particles is not limited to the pharmaceutical industry. A wide range of materials, including adhesives, agrochemicals, live cells, active enzymes, flavors, fragrances, and inks were also studied as possible core substances via RESS and other supercritical particle design techniques [5]. The shell materials have primarily consisted of natural and synthetic organic polymers. In some studies fats and waxes were also used [5]. Our main interest in nano-composite and encapsulated particles is aimed at improving specific performance parameters for chemical and biological sensors including sensitivity, selectivity and shelf life.

Although RESS is a versatile processing technology, it does have limitations, e.g. the solute(s) need to be dissolved in the supercritical solvent. In order to overcome these limitations and improve encapsulation efficiency, modified RESS processes have been previously tested. Co-solvents were used to improve solute solubility in supercritical fluids [6-7]. Also, it has been shown that a non-solvent can be used as a co-solvent in order to reduce product agglomeration [8-9]. Co-precipitation was studied where two supercritical solutions, each carrying only one of the solutes, were mixed immediately before the nozzle [7]. To obtain suspended final products, a supercritical solution was rapidly expanded into a liquid

solution [10-13]. For encapsulation via coating, the expansion unit was designed as a fluidized bed for the core particles, and the supercritical carrier solvent delivered the shell material over the fluidized core particles during rapid expansion [14-16]. Another coating based encapsulation was achieved through rapidly expanding a supercritical solution of the shell material with the core material suspended in that same solution [17]. Different nozzle geometries were tested for improved encapsulation efficiency, and further control over particle morphology [18-19]. Conventional RESS, on the other hand, has not been thoroughly investigated for multicomponent systems. The only study on rapid expansion of a multiple component supercritical solution, was reported by Kim et al [20]. Even though most of these studies did not report successful encapsulation results, they serve as reference guides for improved processes, and contribute to this challenging and interdisciplinary research area.

Previously, our research group has studied single-component particulate polymer coatings for miniature sensor applications. This previous work not only showed RESS is a suitable technique to produce particulate sensor coatings, but also identified requirements and limitations for them to satisfy the needs of miniature sensors [21]. In this paper, we investigate the possibility of producing nano- and micro-scale composite particles from a multi-component, rapidly expanding supercritical solution or suspension, i.e. “a conventional RESS process”, for the advancement of sensor applications.

MATERIALS AND METHODS

I - Materials

The solvent used in this study, chlorodifluoromethane (F-22), was purchased from DuPont. The DSP monomer, 2,5-distyrylpyrazine, was synthesized by the method of Hasegawa et al [22]. The DSP monomer has a yellow color and a melting point of 223 ± 1 °C (toluene). The EPA monomer, diethyl p-phenylenediacrylate, was synthesized by modifying the general method described by Grinev et al [23]. After the reaction was completed, water was added 3:1 by volume to the reaction solution. EPA (68%) was obtained as a white powder after precipitation for about 0.5 hr and filtration. The melting point of the monomer was 97 ± 1 °C (ethanol). Fluoroalkylacrylate (FAA) polymer was from Daikin Industries, Ltd. FAA has a glass transition temperature of 80-90 °C according to the manufacturer. The polymer was used as received without any further purification.

II - Methods

The RESS apparatus for this multiple component system, shown in Figure 1a, is basically the same as the set-up used for the single component system [24]. Both solutes are loaded in the vessel together, dissolved in the supercritical solvent, and sprayed through a metal capillary nozzle (100 μ m inner diameter) as a mixture keeping the concentration constant by means of a floating piston incorporated into the vessel. The RESS apparatus can be controlled at temperatures and pressures to 200 °C and 500 bar, respectively. The automated coating stage was used to control the exposure time in order of seconds to produce thin coatings compatible with miniature sensor technology. The RESS conditions were chosen using single-component phase behavior studies as a qualitative guide. In order to ensure complete dissolution of both the core and the shell material, the total concentration of solutes in the supercritical fluid solvent was maintained at no more than what has been tested for the individual components previously. The relative concentration of each solute is defined as another processing variable. The single component solubility data for solutes used in this study were obtained using a modified phase monitor from Supercritical Fluid Technologies

[24], shown in Figure 1b. This variable-volume view-cell can operate up to 200 °C and 750 bar. Phase behavior data was collected by visual observation of the solution upon depressurization at isothermal conditions. Photosensitive monomers, DSP and EPA, were handled and tested at conditions filtering UV and white light by using special cut off filters, transmitting light with wavelength longer than 570 nm.

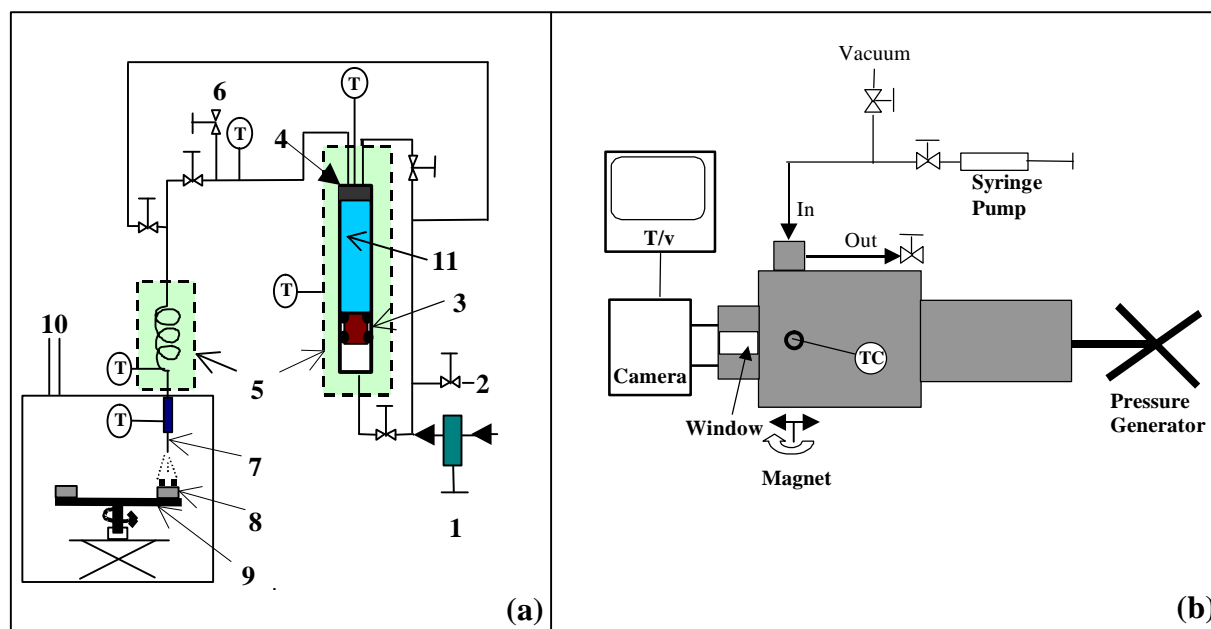


Figure 1 : a) Schematic Diagram of the RESS apparatus

1 - syringe pump; 2 - vacuum inlet; 3 - floating piston; 4 - filter; 5 - furnace; 6 - vent; 7 - nozzle; 8 - substrate; 9 - adjustable height rotation table; 10 - exhaust, 11 - polymer side.

b) Schematic Diagram of the Phase Monitor

RESULTS AND DISCUSSION

Single-component phase behavior data was obtained for all three components used in this study. For comparison purposes, the single component phase behavior data for the two solutes co-precipitated from a common solvent, are plotted together in Figure 2. The cloud point curve showed that FAA has a linear trend with a positive slope illustrating good solubility of the polymer in supercritical as well as liquid F-22. Solidification of FAA was not observed even at temperatures as low as 60 °C. EPA has a flat profile at 60 bar within the temperature range of interest. DSP also has a flat profile at 120 bar for temperatures higher than 100 °C, and goes through solidification (crystallization) at temperatures below that.

The single-component phase behavior data was used only as a qualitative guide, to design the RESS experiments. For the DSP-FAA system, the total solute concentration was 0.15 wt%, 10% of which was DSP. For the DSP-EPA system, the total solute concentration was 0.07 wt%, 10% of which was again DSP. In the RESS experiments for both systems, the preexpansion conditions were chosen well in the one-phase fluid region, and expanded into atmospheric conditions. RESS preexpansion temperatures were varied from 110 to 130 °C, and pressures from 275 to 483 bar.

For all systems, we were able to obtain uniform, less than micron size, particles required for sensor technology. Figure 3 represents a typical SEM image of the formed morphologies. The particle size of the composite DSP-FAA and DSP-EPA precipitates, in general, were less than 500 nm.

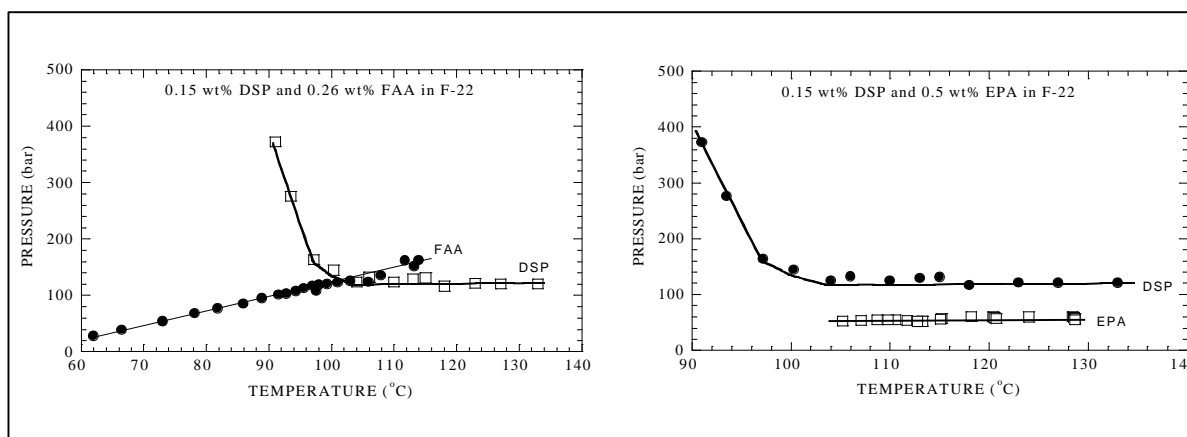


Figure 2 : Single Component Phase Behavior Data

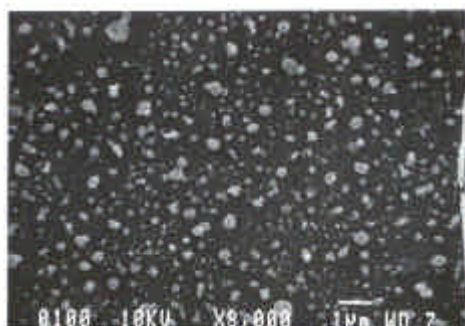


Figure 3 : A general look at the RESS precipitates. (DSP-FAA particles produced at 110 °C & 275 bar)

The EPA-DSP particles were produced via RESS and polymerized by UV light. For the EPA-DSP system, we have fully and partially encapsulated particles, and composite structures as shown in Figure 4. This system needs to be further investigated to optimize the RESS conditions for better control over the final product. The FAA-DSP precipitates after RESS were exposed to a contrasting vapor. The contrasting vapor had no effect on the FAA component, but induced crystallization of DSP. This vapor treatment process is beyond the scope of the present paper and will be described in detail in a separate publication. After the treatment, the particles were exposed to UV light to polymerize DSP monomer within FAA matrix. Analysis of AFM and SEM images of morphologies developed at different RESS conditions revealed that the hyper-expansion pressure at give expansion temperature led to the smaller size precipitates, but did not change the particle structure.

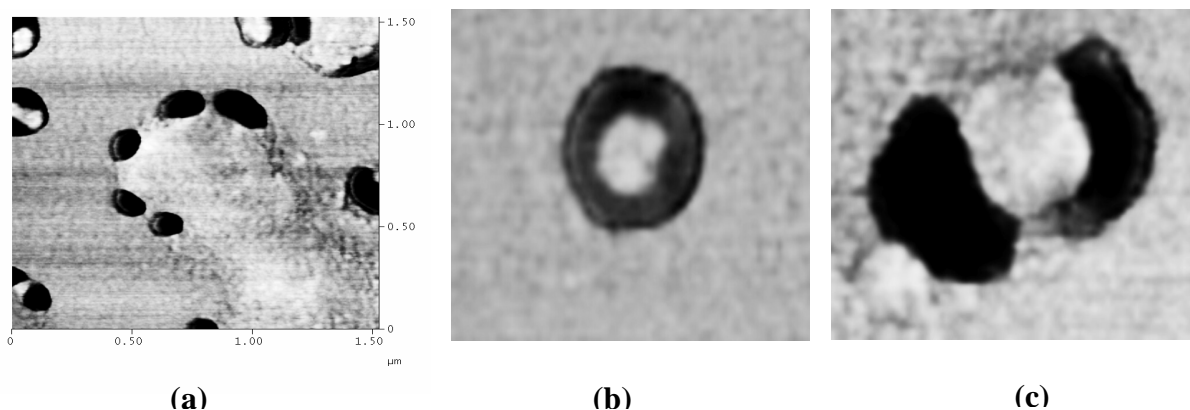


Figure 4 : DSP-EPA precipitates obtained via RESS at 130 °C and 345 bar. The dark regions shown in these AFM phase images are DSP, and the light ones are EPA. (a) Composite structure, (b) Full encapsulation, (c) Partial encapsulation.

RESS precipitates developed at pre-expansion temperatures below 120 °C exhibited two-phase composite structures with no well-defined continuous phase of either component. Successful encapsulation was reported for FAA-DSP mixture at RESS conditions given in Figure 5. These structures were composed of alternating layers of DSP and FAA. The nucleation process for the formation of these interesting structures must be investigated further, but these preliminary results suggest that the nanoscale DSP crystals are completely encapsulated with the FAA polymer and then agglomerated to form a nanocomposite with exhibiting both crystalline and non-crystalline features.

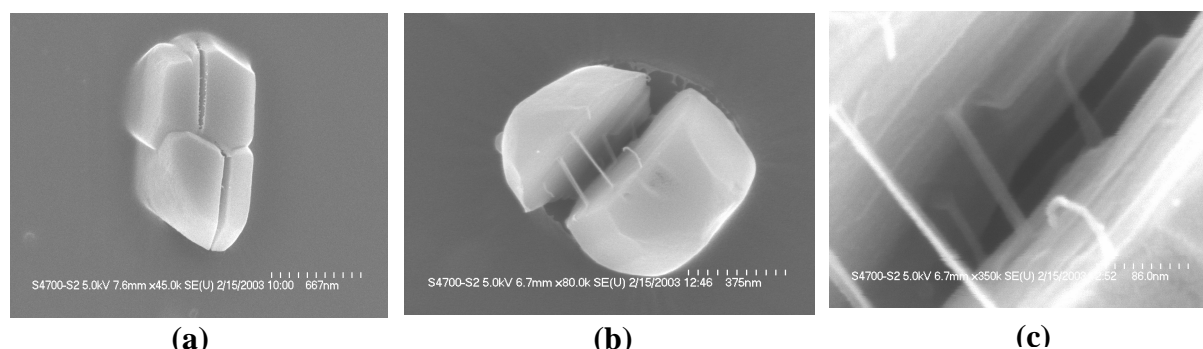


Figure 5 : DSP-FAA precipitates obtained via RESS at 120 °C and 483 bar. The crystalline structures in these SEM images are DSP, the coat and the fibers are FAA.

(a) DSP crystals coated in FAA agglomerated together, (b) A nanoparticle cracked open showing its cross-sectional structure, (c) The blow up of (b) shows the alternating layers throughout its cross-sectional surface.

CONCLUSION

The rapid expansion of two solutes from the common supercritical solvent was investigated to develop nano-scale particles compatible with miniature sensors. It was determined that the structure of the RESS precipitates depends strongly on the processing conditions and can range from segregated materials to blends as well as encapsulated particles.

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