

## Development and evaluation of environmentally benign techniques for polymer film coating of fine particles

*Baohua Yue, Jun Yang, Jose Quevedo, Rajesh Dave\*, Chien-Yueh Huang, Robert Pfeffer  
New Jersey Center for Engineering Particulates (NJCEP)  
New Jersey Institute of Technology, Newark, NJ 07104*

### Abstract

Film coating of fine particles (5-20 microns) by polymers has a wide range of industrial applications, yet few techniques are commercially available that are environmentally friendly. In this study, four different techniques are considered with an ultimate goal of developing a reliable technique that is scaleable and is also environmentally friendly. Two of these techniques are fluidization based; magnetically assisted fluidization, and rotating bed or centrifugal bed fluidization. The other two techniques are based on utilizing supercritical fluids, one is a supercritical antisolvent (SAS) process, and the other is an in-situ polymerization process done within a supercritical fluid medium. Several types of fine powders ranging from a few microns to about 20 microns are considered, including energetic material simulants, metal powders, and drug materials. Various polymers are also considered as coating materials, including biodegradable polymers as well as commercial polymers. Electron micrography techniques (FESEM and TEM) are used to characterize the particles before and after coating. It is shown that all of these techniques are capable of coating fine particles, but each one has a different set of advantages and disadvantages. Relative merits of these methods are discussed, including the possibility for their scale-up, and feasibility for use in film coating of energetic materials.

**Keywords:** Encapsulation, Film-Coating, Fine Particles, Magnetic Fluidization, In-situ Polymerization, Rotating Fluidized Beds, Supercritical CO<sub>2</sub>, SAS.

### Introduction

Particle surface properties can be tailored for specific physical, optical, electronic, chemical, and biomedical applications by proper film coating<sup>1</sup>. As an important industrial process, polymeric particle coating are widely used in chemical and pharmaceutical industries. Polymer coating often serves as a barrier for protection and controlled release purposes. Conventionally, it is usually done by wet coating methods such as pan coaters and a variety of fluidized bed coaters, or by wet-chemistry based techniques such as sol-gel process, emulsification and interfacial polymerization. However, wet coating methods have become less desirable recently because of environmental concerns over the resulting waste streams and VOC emissions. These concerns have stimulated great interests in environmentally benign techniques for polymer coating of fine particles. Among the environmentally friendly processing methods, dry coating and supercritical processing are two of the promising alternative approaches.

**Dry Particle Coating:** In dry particle coating process, submicron-sized guest particles are coated onto larger, micron-sized host particles to achieve desired properties. Different than in wet particle coating process, the guest particles are brought into direct contact with the host

---

\* Corresponding author. Tel: +1-973-596-5860; Fax: +1-973-642-7088.  
E-mail address: dave@adm.njit.edu.

particles through the application of mechanical forces. Since the guest particles are very small, van der Waals interactions are strong enough to keep them firmly attached to the host particles. After coating, either a discrete or continuous coating of guest particles can be obtained depending on the operating conditions, including processing time, weight fraction of guest to host particles and particle properties [Fig. 1.]. Continuous coating can consist of either a particle layer (monolayer or multilayer), which is porous, or a continuous film coating, which is generally non-porous. While continuous coatings are generally preferred, the ability to create discrete coatings has some unique advantages. For example, in some applications, a coating may be required to change a specific surface property, but a complete shielding of the underlying core particle is undesirable<sup>2</sup>.

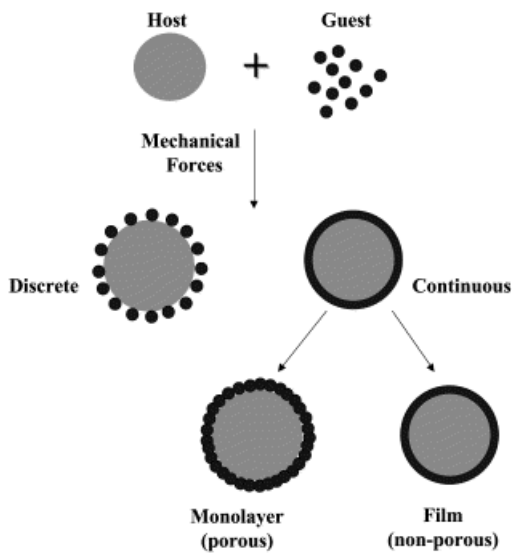


Fig. 1. Schematics of dry particle coating.

MAIC method uses a magnetic field to accelerate and spin larger magnetic particles mixed in with the core and guest particles promoting collisions between the particles and with the walls of the device [Fig. 2.]. There are several unique features of MAIC that makes it advantageous as a dry particle coating device<sup>3</sup>. Firstly, the MAIC can coat soft organic host and guest particles without causing major changes in the material shape and size. Secondly, although there is some heat generated on a microscopic level due to the collisions of particles, there is negligible heat generation on a macroscopic level and hence no increase in temperature of the material during processing by MAIC. This is desirable when processing temperature sensitive powders such as pharmaceuticals. Lastly, the device can be operated both as a batch and continuous system making it versatile in the amount of material it can process.

In a rotating fluidized bed, the host and guest powder mixture are placed into the -

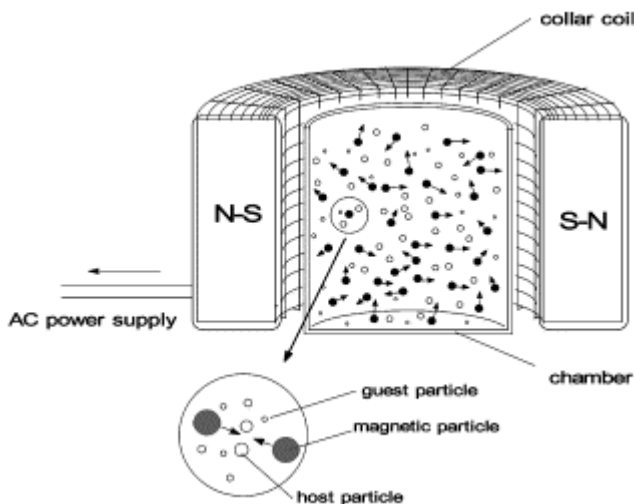


Fig. 2. Schematic of the MAIC process.

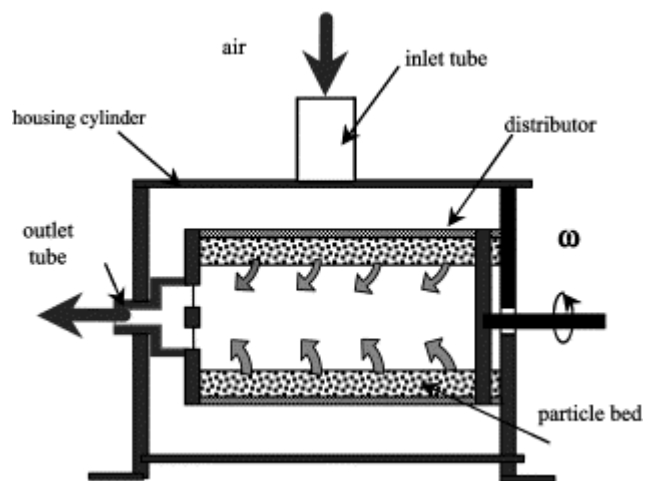


Fig. 3. Schematic of the rotating fluidized bed coater.

rotating bed and is fluidized by the radial flow of gas through the porous wall of the cylindrical distributor [Fig. 3.]. Due to the high rotating speeds, very high centrifugal and shear forces are developed within the fluidized gas–powder system leading to the break-up of the agglomerates of the guest particles. Moreover, the very large flow of air needed to fluidize the particles at high rotating speeds and the motion of bubbles when operating the bed above minimum fluidization conditions creates strong mixing and hence good coating is achieved. For example, at "100 g's", the minimum fluidization velocity can be 2 orders of magnitude greater than in a conventional "1 g" fluidized bed. The RFBC has another advantage over a conventional fluidized bed in that very small host and guest particles belonging to Geldart group C can be easily fluidized by increasing the rotating speed<sup>4</sup>. The RFBC also has the capability of being operated in a continuous mode.

Supercritical fluid processing: There has been a continuing growth of interest in replacing conventional organic solvents with environmentally friendly supercritical fluids in chemical processes. Among them, supercritical carbon dioxide (scCO<sub>2</sub>) emerged as an excellent candidate due to its superb characteristics and properties: it is inexpensive, nontoxic, nonflammable, readily available, easily recycled, and as a solvent, it possesses both gas-like diffusivities and liquid-like densities and solvencies. Successes in applying scCO<sub>2</sub> as a solvent or processing medium have been found in various areas from the well-established supercritical extraction and separation to the relatively new engineered particle formation<sup>5</sup>.

One of the recent interesting applications is coating of particles with polymers via a supercritical antisolvent (SAS) process<sup>6</sup>. The SAS process is based on the principle of SC CO<sub>2</sub> induced phase separation in which the solute precipitates due to a high super-saturation produced by the mutual diffusion of organic solvent into SC CO<sub>2</sub> and vice versa when an organic liquid solution comes into contact with SC CO<sub>2</sub>. An important feature of the SAS process is that the organic solvent can be almost completely removed by simply flushing with pure CO<sub>2</sub>. Thus, dry particles are produced after a CO<sub>2</sub> extraction step (flushing) following feeding of the organic solution.

The procedures for SAS coating are: (1) prepare a polymer solution by using a cosolvent, like acetone; (2) charge powders to a high pressure tank and then pump CO<sub>2</sub> until to reach to the supercritical state; (3) deliver the polymer solvent into the tank by using a small nozzle. Since there is a big difference between the solvency of polymer inside the cosolvent and the supercritical CO<sub>2</sub>, the polymer will precipitated out quickly from the cosolvent and deposit on the surface of charged powders to form film coating. The stirring of the powders is helpful to get a homogeneous coating; (4) dry the cosolvent by using supercritical CO<sub>2</sub>. The supercritical CO<sub>2</sub> was slowly vented to ambient atmosphere to get rid of the dissolved cosolvent. The schematic diagram of the SAS coating device is shown in Fig. 4.

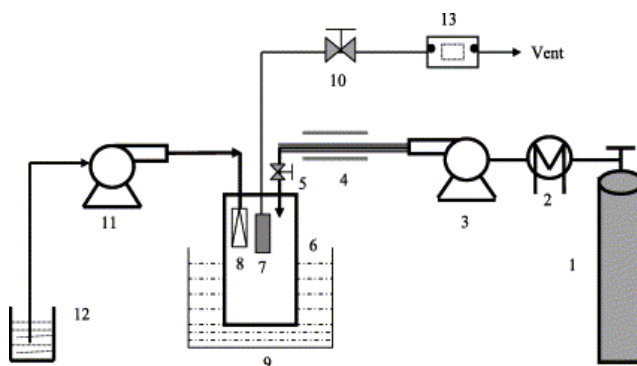


Fig. 4. Schematic diagram of SAS process for particle coating.

Recently, a novel coating process based on in-situ polymerization in supercritical CO<sub>2</sub> was developed<sup>7</sup>. The particle surface coating is achieved by polymerization induced phase separation. After reaching certain molecular weight, polymers precipitate out from the CO<sub>2</sub> onto particle surface and form a coating layer. Due to the initially homogeneous distribution of monomers, complete surface coverage was obtained and the coating has high uniformity. The coating thickness and surface morphology can be relatively easily controlled by varying reaction parameters, such as monomer to particle mass ratio, pressure, and temperature etc.

## Results and Discussion

In this work, Dechlorane Plus 515<sup>®</sup> (DCR) are used as host particles. These particles have an average size of 10 $\mu$ m with broad size distribution [Fig. 5.]. They are commonly used as fire retardant and in this case as a stimulant of certain energetic material.

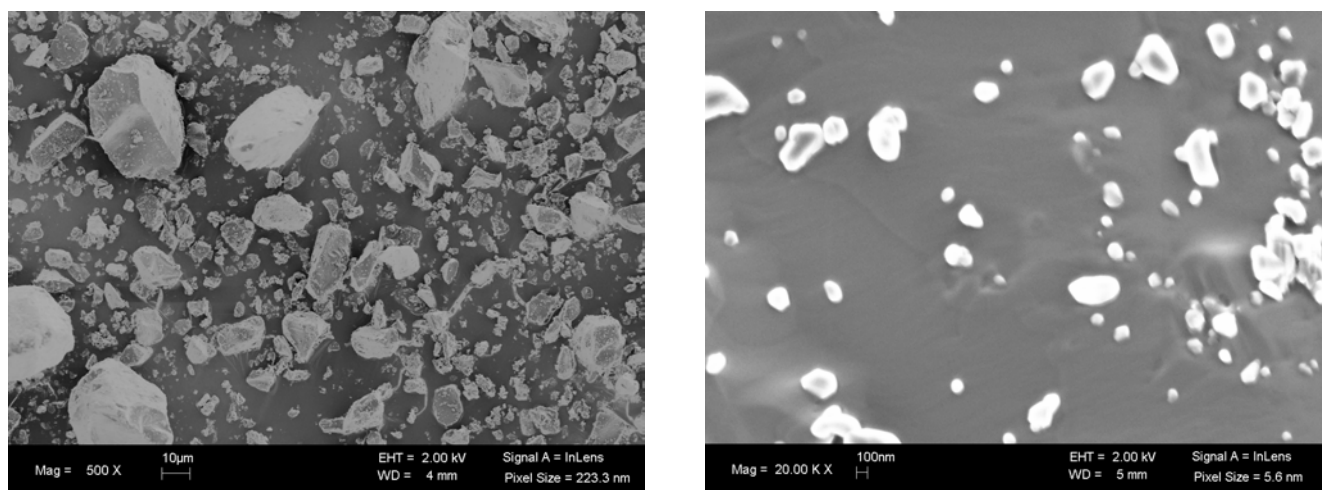


Fig. 5. SEM micrographs of uncoated DCR particles and surface feature.

**Dry Coating Results:** The RFB coating is based on the success of fluidization of the DCR particles. According to Geldart theory, these fine particles are group C particles and cannot be fluidized under normal vertical fluidized bed because the weight of the powder is very small but interaction force (mainly contributed from van der Waals force) is very strong. However, the high speed rotating will largely increase the centrifugal force of the fine powders (depends on the rotating speed), which acts like increase the “weight” of the powders. Under certain conditions, the fine group C particles will act as group A particles and will be fluidized very well. When the powders fluidized, a prepared polymer solution will spray to the fluidized bed. Fluidized gases extract the solvent and leave the polymer deposited on the particle surface to form coating. Hydroxypropyl Cellulose (HPC) is used as the coating polymer. Omnitex fluidized bed (Nara Machine, Japan) is used for the coating device.

Shown in Fig. 6. are micrographs of DCR particles coated with RFB process. A total of 240 g of DCR and 32.91 g HPC were processed at 80G. No obvious agglomeration before and after processing was observed. The DCR surface was uniformly covered by tiny polymer particles. The SEM images also indicate that the film coating may formed first, and then covered by tiny polymer particles which was possibly formed by the drying of HPC polymer solutions droplets.

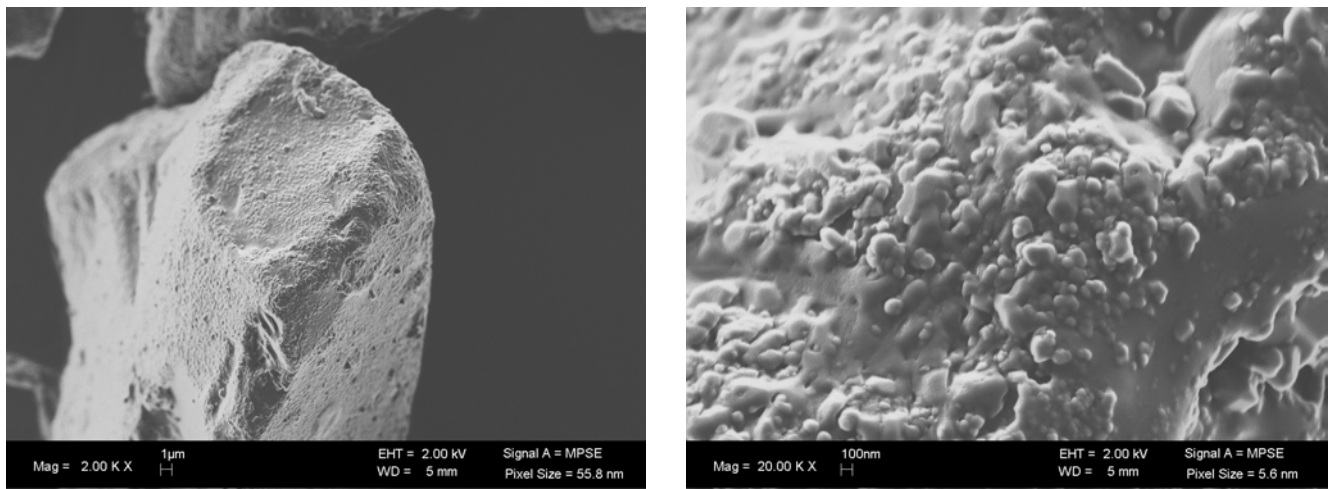


Fig. 6. DCR particles after dry coating, the second micrograph shows the detailed surface morphology.

Coating with SAS process: The SAS experiments were conducted at relatively low pressure (1500psi) and temperature (35°C). The major component of the coating material used is polyurethane. As indicated in Fig. 7., there are no obviously differences between particle's size and shape before and after processing. Smooth film coating with complete surface coverage was obtained. The coating effect is heavy dependent on the addition amount of polyurethane paint. The advantages of the SAS coating include: environmental benign, inert atmosphere; the disadvantage for this process is the drying process is hard to control and excessive polymer will lead to particle agglomeration.

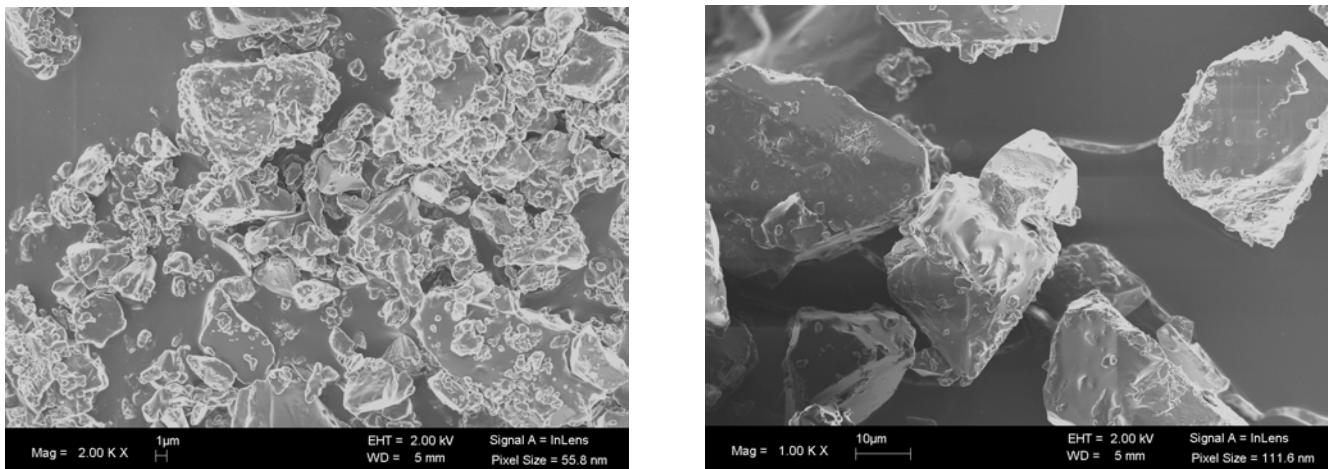


Fig. 7. DCR particles after SAS coating, the second micrograph shows thin and smooth surface film coating.

Coating with in-situ polymerization in SC CO<sub>2</sub>: Compared to SAS process, higher pressure (>2500psi) and temperature (65°C) are needed in order to achieve high polymerization yield. Coating thickness and morphology can be controlled by varying reaction parameters, including pressure, monomer to DCR ratio etc. Shown in Fig. 8 are DCR coated with formed PMMA at different MMA/DCR mass ratios.

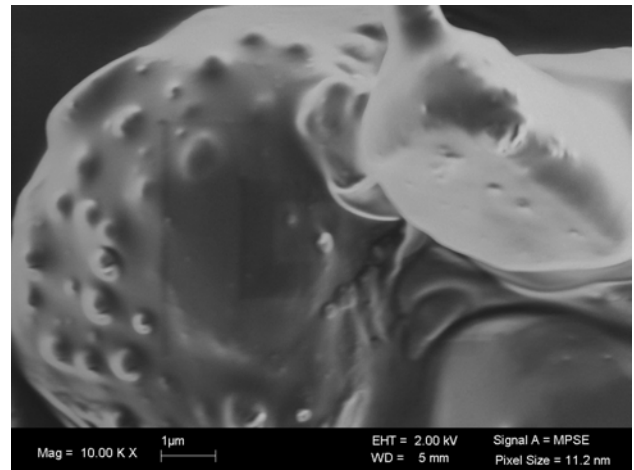
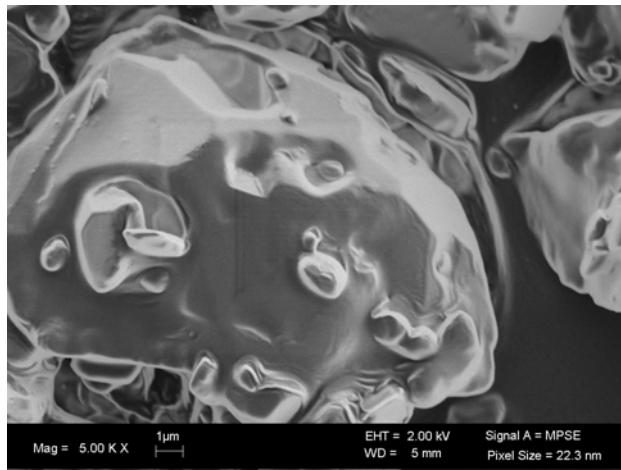
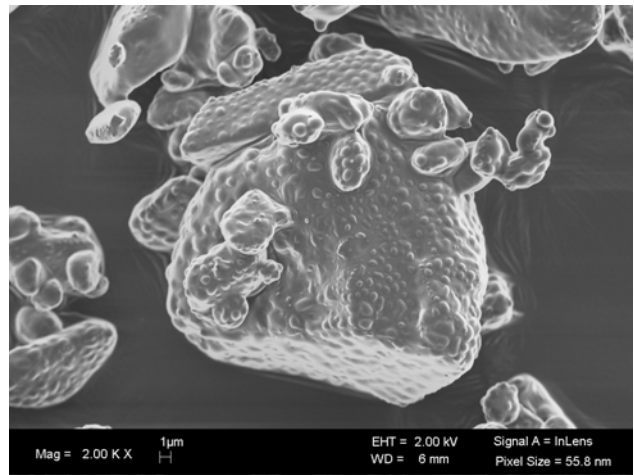
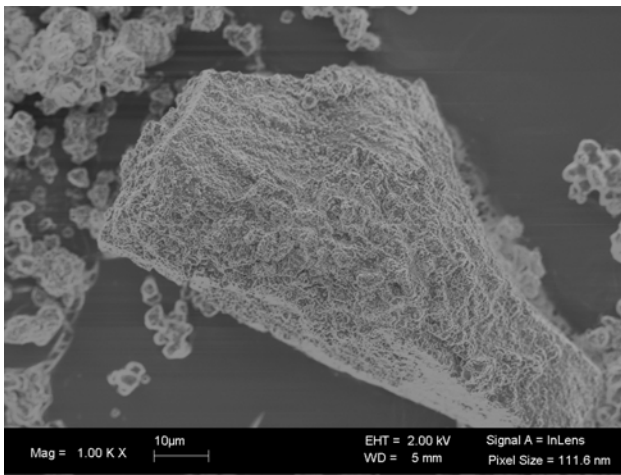


Fig. 8. Clockwise: SEM micrographs of coating morphology at four DCR/MMA ratios: 1/2, 1/1, 2/1 and 5/1.

The in-situ polymerization based coating was also successfully applied for some drug particle coating<sup>8</sup>. Shown in Fig. 9. are hydrocortisone particles coated with common pharmaceutical excipient poly (1-vinyl-2-pyrrolidone).

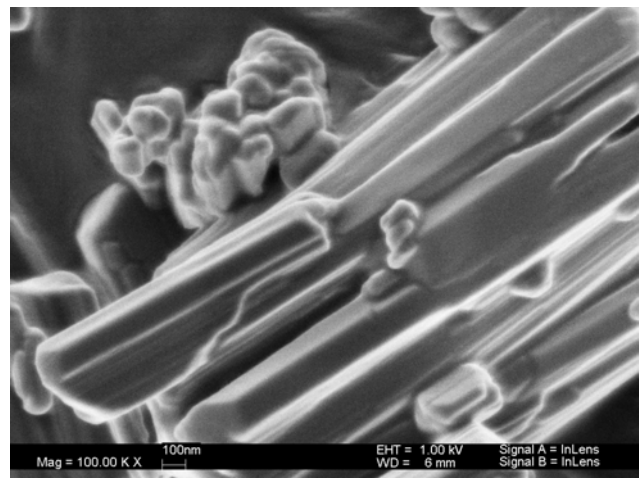
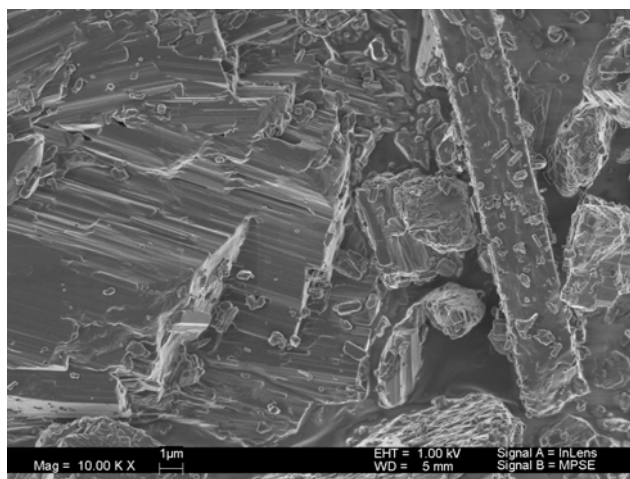


Fig. 9. Hydrocortisone particles before and after coating.

## Conclusions

We have demonstrated that fine particles coating can be carried out in environmentally friendly methods. Both dry particle coating and supercritical fluid processing were proven to be promising alternative to the conventional wet coating methods. No or minimum organic solvents were consumed in these processes. Simple down stream processing and product collection add to the environmental benefit. Successful film coatings were investigated with different polymers and host particles. The coating properties, such as thickness and surface morphology, can be controlled by varying operation conditions. All the methods studied here have advantages and disadvantages, so proper process should be chosen based on specific requirements.

## Acknowledgements

The authors would like to thank the National Science Foundation for financial support through Grant # CTS-9985618. An NSF MRI Grant # CTS-0116595 allowed NJIT to build a new electron microscopy facility which was used extensively throughout this research.

## Reference:

1. M. Naito, A. Kondo and T. Yokoyama. *ISIJ Int.* 33 (1993), 915.
2. R. Pfeffer, R. N. Dave, D. Wei and M. Ramlakhan. *Powder Technology*, 117 (2001), 40.
3. M. Ramlakhan, C.Y. Wu, S. Watano, R.N. Dave and R. Pfeffer. *Powder Technology* 112 (2000), 137.
4. G.H. Qian, I. Bagyi, R. Pfeffer, H. Shaw, J.G. Stevens, *AIChE Journal*, 45 (1999), 1401.
5. S. D. Yeo, G. B. Lim, P. G. Debenedetti, H. Bernstein, *Biotechnol. Bioeng.* 41 (1993), 341.
6. Y. Wang, R. Dave, R. Pfeffer, *Journal of Supercritical Fluids*, 28 (2004), 85.
7. B. Yue, J. Yang, Y. Wang, C. Y. Huang, R. Dave, R. Pfeffer, *Powder Technology* In Press.