Deagglomeration and Mixing of Nanoparticles

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A major problem in utilizing nanoparticles is that they are highly agglomerated and if used directly in a bulk composite, they often lose their high-surface area due to grain growth or unavailability of the high surface area where it matters. This NIRT project focuses on mixing of two (or more) nano-constituents at nano-scale in an environmentally benign manner. In well-mixed nano-particles at nano-scale, the loss of high surface area is prevented, and unique and special properties can be achieved due to the interactions of different phases at their interfaces in a nano-composite. Thus the ability to achieve nano-mixing can open up innovative ways to improve performance of drugs, biomaterials, catalysts and other high-value-added materials.

The main objective of this project which involves an interdisciplinary team of researchers at four Universities is to address the overall problem of nano-particle de-agglomeration, mixing and characterization. The research tasks include; measurements of the degree of de-agglomeration as a result of applying de-agglomerating forces, investigation of several different environmentally benign nano-particle mixing methods, as well as nano-mixing characterization techniques, and to develop a fundamental understanding of the de-agglomeration and mixing of two or more species of nano- particles through complimentary continuum and molecular dynamics modeling.

Our studies have shown that most nano-particle agglomerates are rather large (typically ~100-400 μm), extremely porous (ε~0.99), and have a hierarchical fractal structure consisting of sub-agglomerates or aggregates at a number of different length scales, down to individual nano-size particles. Our estimates indicate that their fractal dimension is about 2.6, which is close to the theoretical value of 2.5 for diffusion-limited aggregation (DLA), although their structure could differ from DLA. It is clear that whether mixing can be achieved depends on the ability to de-agglomerate down to a given size-scale, and different methods of de-agglomeration would produce mixing at different scales.

Several mixing/deagglomeration methods, ranging from low energy (fluidized bed) to very high energy (rapid expansion from supercritical suspensions- RESS) are examined for different candidate powders. Although direct measurement of the level of de-agglomeration by a given method is rather difficult because the powders quickly re-agglomerate, one can get an idea of the extent of de-agglomeration from the level of mixing of two nano-particle constituents. Typical results of the mixing homogeneity at micron scale [2, 3] are shown for various methods in Figure 1. Here, nano-powders of alumina (Al_2O_3) and silica (SiO_2) (size ranging from 15-30 nm) are mixed and from a SEM/EDX analysis of the mixture samples, the average atomic ratio and its variation (shown as the error bar) for different mixing methods are calculated. The mixing methods from left to right in Figure 1. are: mixing in a magnetically assisted fluidized bed [4] for 1 hr and 3 hrs, respectively, stirring in supercritical fluid (at about 100 rpm) at pressures of 1300 and 200 psi, respectively, mixing by magnetically assisted impaction mixing (MAIM) [3] for 15 minutes and 60 minutes, respectively, ultra-sonication for 10 minutes in a supercritical fluid at 25

watts and 85 watts, respectively, and mixing by RESS [2, 3] from an initial pressure of 1500 psi and 1000 psi, respectively.
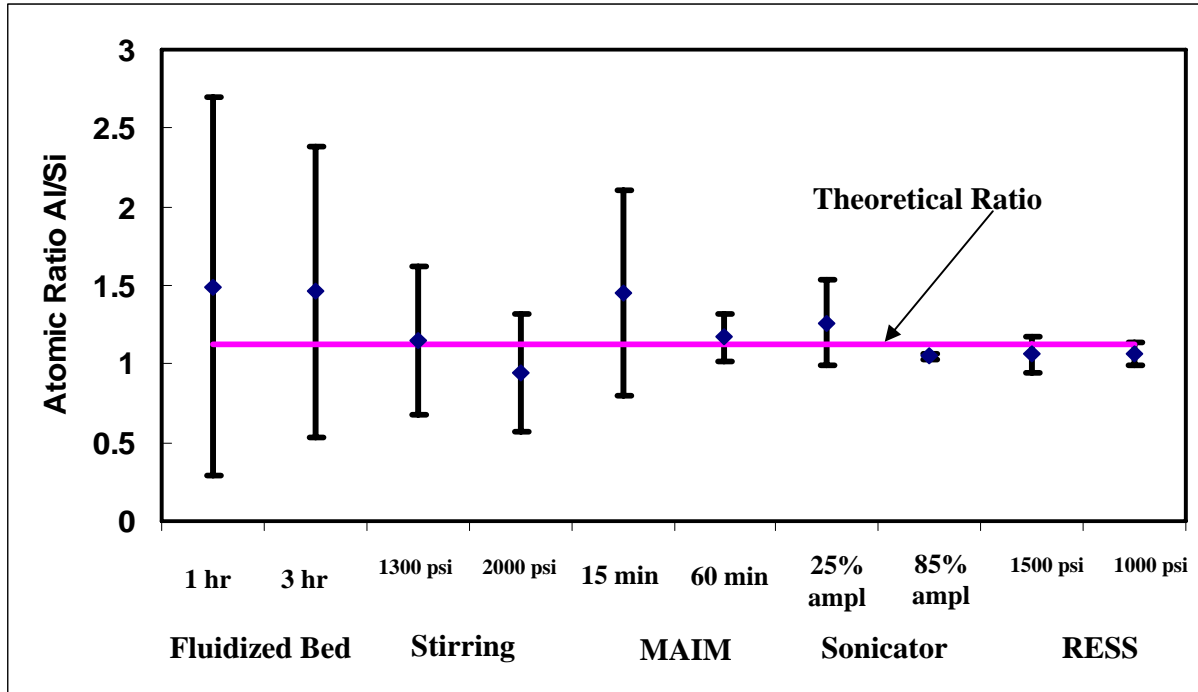

Figure 1. Typical mixing results from 5 different environmentally benign methods.

As can be seen, nano-particle de-agglomeration and subsequent mixing gives better results for sonication and RESS. The ability to de-agglomerate nano-scale materials using RESS is further illustrated by considering a very difficult material to mix such as carbon nanotubes (CNT). Figure 2 shows large, tight bundles of original CNTs (size of about 10-20 microns) that are de-agglomerated by RESS to 1 micron and smaller, even down to individual nanotubes. In fact, the ultrasonication method cannot achieve such strong de-agglomeration for CNTs; see, for example, Figure 3 showing mixtures of CNTs with silica (SiO$_2$) and titania (TiO$_2$), respectively indicating that while silica was embedded within the CNT bundles, the bundles could not be de-agglomerated as effectively as by RESS.
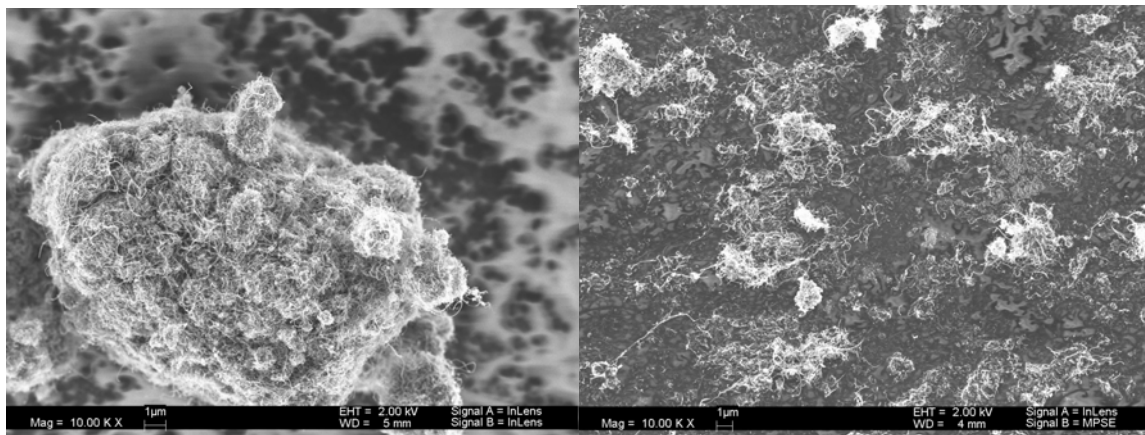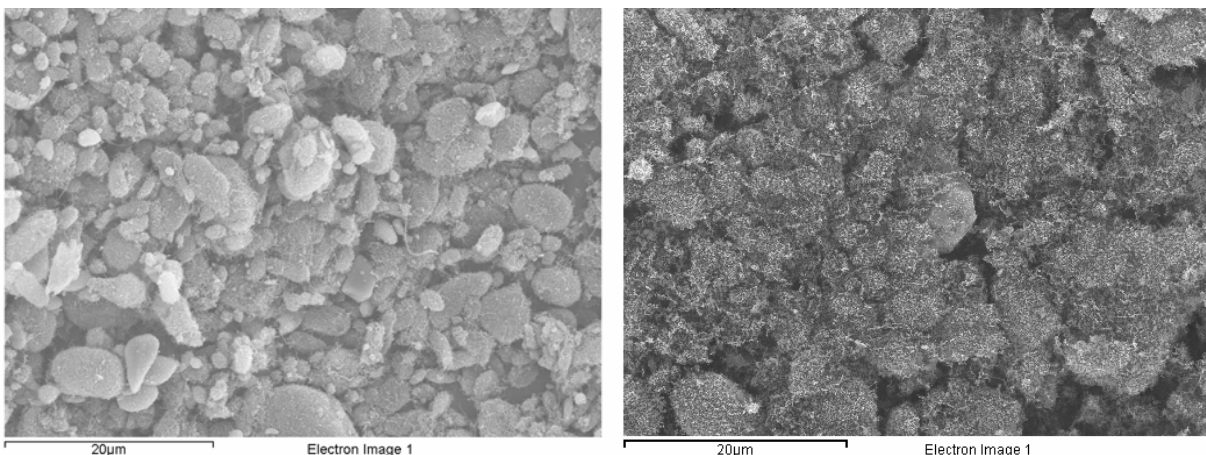

Figure 2. CNT bundles before and after RESS de-agglomeration (both images are at the same magnification.

Figure 3.Carbon nano-tubes (CNT) mixed with titania (TiO$_2$, left) and silica (SiO$_2$, right) using sonication (70 watt) indicating that while CNT bundles are smaller than their original size, they are not de-agglomerated as effectively as under RESS.

The experimental work has produced a wealth of information that is forming the basis of our multi-scale simulation efforts, led by the Princeton and Rutgers groups. Our goal is to develop a fundamental understanding of the nature of the agglomerate break-up under various conditions to help with scale-up of the mixing processes.

The NJIT group and the Auburn group are working jointly on nano-particle mixing experiments. While the Auburn group is focusing on the use of sonication within the supercritical fluid as well as using it in addition to RESS at the exit, the NJIT group is working on other mixing methods. During the next year, Auburn and NJIT will jointly work on pharmaceutical nano-mixing applications. The Princeton group is leading the effort on continuum and DEM modeling with the assistance of the Auburn group and the NJIT group. The Rutgers group is developing molecular dynamics simulations to understand the strength and break-up of the agglomerates of several candidate materials, and provide information necessary for the larger length scale simulations that are being done at Princeton.

References

[1] For further information about this project email **dave@adm.njit.edu**
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