ENVIRONMENTALLY BENIGN NANO-MIXING BY SONICATION IN HIGH PRESSURE CARBON DIOXIDE

Ganesh P. Sanganwar[a] and Ram B. Gupta[a]
Alexandre Ermoline[b], James V. Scicolone[b], and Rajesh N. Dave[*]

[a]Department of Chemical Engineering, Auburn University, Auburn, Alabama 36849, USA.
[b]New Jersey Center for Engineered Particulates, New Jersey Institute of Technology, Newark, NJ 07102-1982, USA.
[*] Corresponding Author: Email: dave@njit.edu, Phone: (973)-596-5860, Fax: (973)-642-7088

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Abstract

Due to the increased use of nanocomposites, mixing at nanoscale has become important. Current mixing techniques can be classified into: (a) dry mixing (mechanical mixing), and (b) wet mixing. Dry mixing is in general not effective in achieving desired mixing at nanoscale, whereas wet mixing suffers from different disadvantages like nanomaterial of interest should be insoluble, has to wet the liquid, and involves additional steps of filtration and drying. This paper examines the use of pressurized carbon dioxide having high density and low viscosity to replace the liquids (e.g., n-hexane, toluene). Ultrasound is applied to the suspension of nanopowders in gaseous and supercritical carbon dioxide where high impact collisions during sonication help mixing and the final mixture is obtained by simple depressurization. The method is tested for binary mixture of alumina/silica and MWNT (multiwalled carbon nanotubes)/silica. The effects of sonication intensity and pressure on the degree of mixing are studied. Comparative study is also done with liquid n-hexane as a mixing media. Quantitative characterization (e.g., mean composition standard deviation, intensity of segregation) of mixing of alumina/silica is done with energy dispersive x-ray spectroscopy, and that of MWNT/silica is done using field emission scanning electron microscopy. Results show that mixing in carbon dioxide at higher ultrasound amplitudes is as good as in liquid n-hexane, and the final mixed product does not contain any residual media as in the case of liquid n-hexane.

Introduction

Nanoparticles offer unique properties due to their small size and high surface area (Lines, 2007 and Roco, 1999). Unfortunately, the high surface area of particles causes them to agglomerate due to high interparticle van der Waals attractions (Kurkela et al., 2006), making them lose some of their unique properties. The agglomeration can be avoided by adding spacer material (Werth et al., 2003), but it is important to have spacer particle around each nanoparticle to preserve its properties. Hence, it is most important to mix nanoparticles of different materials effectively. Mixing of solid particles is widely practiced in various industries including pharmaceutical, food, cosmetics, fertilizers, pigment, detergent, animal feed, etc. Recent increase in the popularity of nanocomposties, nanocatalyst and nano-pharmaceuticals demands effective mixing of nanoparticles, which often poses challenges due to the small size. Often processes of mixing involve the breaking of micro-agglomerates and then subsequent mixing with other (inert) nano material to prevent preferential agglomeration of same material particles. Nanomixing can also be achieved by simultaneous production of different nanoparticles in same reaction chamber (e.g. titania/silica by flame aerosol synthesis or, flame synthesis of metal and oxide nanoparticles) for nanocomposite applications. However, there are many situations when simultaneous production is not possible, and the separately produced particles must be mixed. Various methods of nanoparticles mixing for such cases are introduced and compared by Wei et al. (2002) and Yang et al. (2003). It was shown that the rapid expansions of suspension of particles and wet mixing in n-hexane with ultrasound show better performance than other methods (e.g., magnetically assisted impact mixing, and stirred mixing). Mixing of nanoparticles with sonication in liquid medium involves cavitation and intense agitation of liquid due to ultrasound propagation. Organic liquids, such as n-hexane, are suitable for insoluble inorganic material also those which wet the n-hexane for better result. Therefore for organic material, n-hexane is not a good choice of solvent. In addition, the wet mixing using a solvent involves additional steps of filtration and drying. In this work, we propose to replace n-hexane by carbon dioxide. Carbon dioxide is an environmentally benign, inert, non toxic, non flammable, inexpensive, low viscosity fluid along with comparatively higher molar density. These unique properties of high pressure carbon dioxide help in propagation of ultrasound. Pressure amplitudes created during propagation of ultrasound cause particles to be put into oscillatory motion media particles suspended in high pressure CO_2. This involves motion of particles from a region of high pressure (compression) to low pressure (rarefaction), which induces collisions of particles with each other resulting into breakage of loose agglomerates and mixing of dissimilar particles. The final mixture is easily separated from CO_2 by depressurization. Also material does not have to wet the media; hence this method can be applied to a wide range of material mixtures. Here, the method is tested for binary mixtures of alumina (Al_2O_3) and silica (SiO_2), along with multiwalled carbon nanotubes (MWNT).

Mixing of silica/alumina was studied quantitatively by energy dispersive x–ray spectroscopy (EDS). Intensity of segregation of mixture was taken as criteria for degree of mixing. The qualitative analysis of mixing of MWNT with silica was carried out using field emission secondary electron microscopy (FESEM), because of the distinct difference in size and shape of component particles.

Experimental

Materials

Bone dry CO_2 (Airgas) and HPLC grade n-hexane (Fischer Scientific Inc.) were used without any pretreatment. Also alumina (Al_2O_3, Aeroxide Alu C), silica (SiO_2, Aerosil R972) nanopowders (Degussa Inc.) and multiwalled carbon nanotubes (Cheap Tubes Inc.) were used as received.

Mixing in gaseous and supercritical CO_2

Figure 1 shows the schematic diagram of experimental setup used for mixing powders in carbon dioxide. It consists of compressed carbon dioxide gas cylinder, chiller, piston pump (Thar Technology) for pumping CO_2, preheater, ultrasonic processor (Sonics and Materials Inc.) producing ultrasonic waves at a frequency of 20 kHz with maximum power capability of 600 W, and a 120 ml stainless steel mixing vessel heated by heating tape. The ultrasonic processor consists of three major components: an ultrasonic power supply, a transducer, and a horn with 0.75 inch tip diameter. Temperature and pressure inside the mixing vessel were measured with a thermocouple and a pressure gauge, and tape heating was controlled by temperature controller. To prevent the loss of powders during the vessel depressurization, a filter (Fischer Scientific Inc.) at the top exit of the vessel was installed.

The ultrasonic processor is designed to deliver constant amplitude (61 μm at 100% amplitude settings for a horn used in these experiments), i.e. it automatically adjusts power to maintain constant amplitude during the operation. All experiments were conducted at constant amplitude, and power was monitored.

Nanopowders in weight ratio of 1:1 (100 mg: 100 mg) were loaded into a stainless steel vessel and then carbon dioxide was introduced. The horn was immersed into the vessel, so that only 100 ml of its volume was available for mixing. Vessel pressure was maintained within ±3.5×10^5 N/m^2 and ±0.1 °C at the start of each experiment. Then vessel was heated with the heating tape to 45 °C in all experiments. After reaching desired pressure and temperature in the vessel, ultrasound was applied for 10 min at particular amplitude to cause mixing. After mixing, the vessel was slowly depressurized to prevent carryover of particles with CO$_2$. Further loss of particle was prevented using filter at the top exit of the vessel. After complete depressurization, vessel was opened, and powder was collected for analysis.

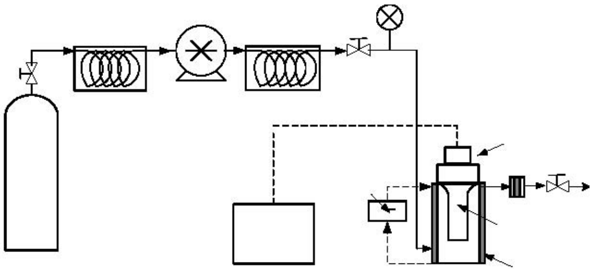

Figure 1. Schematic diagram of the experimental setup for mixing nanopowders in carbon dioxide.

Mixing in liquid n-hexane

The same ultrasonic processor, described above, was used in experiments with mixing in n-hexane. Ultrasound was applied to suspension of powder mixture (100 mg: 100 mg) in 100 ml n-hexane contained in beaker. To prevent loss of n-hexane, as temperature increases during sonication, the beaker was kept in an ice bath so that temperature during experiments stayed in the range from 5 to 10 ◦C. After the application of ultrasound for 10 minutes, suspension was filtered and the powders were collected and dried in an oven at 80 ₒC for 12 hours.

Mixture Analysis

In case of silica/alumina, quantitative analysis of degree of mixing was performed using energy-dispersive X-ray spectroscopy (EDS) of a field-emission scanning electron microscope (JEOL 7000F and Leo 1530 VP) equipped with x-ray detector from Princeton Gamma Tech. For analysis, mixed powder samples were compressed into wafers of about 1 mm thickness and 13 mm diameter using a die (International Crystal Laboratory Inc.) in mechanical press (Fred S. Carver) with the loads of 5-8 tons applied for 4 minutes. Two representative areas of size 21.94×16.46 µm were selected on the pellet surface, and in each area atomic composition at 20 randomly selected points (each spot size is of ~1 µm; i.e., 3×3 pixels, each pixel of 0.35 µm) was obtained with EDS. As a measure of degree of mixing, the intensity of segregation, parameter, introduced by Danckwerts, 1952, was used:

$$I = \frac{\sigma^2}{\bar{a}\bar{b}} \quad (1)$$

Where, $\bar{a}$ and $\bar{b}$ are average concentrations of silica and alumina respectively and while σ^2 is the variance. Intensity of segregation is a variance of concentrations in a mixture normalized by the variance in completely segregated unmixed powders. Thus in case of complete segregation of two components, the index of segregation is 1. On the other hand, since the volume spotted by EDS (an order of microns) technique is much higher than primary particle size (tens of nanometers), i.e. the size of the smallest units of mixture, the index of segregation for a perfect

Results and Discussions

SiO_2/Al_2O_3 System

Figure 2 shows results of EDS analysis for alumina/silica produced at various amplitudes both in supercritical (at 21×10^5 N/m^2 and 55×10^5 N/m^2) CO_2, as well as in liquid n-hexane (1.00×10^5 N/m^2). Figure 2(a) shows the results as a function of amplitude which is a controllable variable, while Figure 2(b) shows the same results but plotted as a function of power which cannot be directly controlled. For the mixture considered, the intensity of segregation generally decreases with amplitude, and at high enough amplitudes, as was already noted, the difference in intensity of segregation between different mixtures becomes almost indistinguishable. For the case studied here, at low pressure 21×10^5 N/m^2, the increase of amplitude doesn’t have any considerable effect on mixing quality at low amplitudes, with significant drop of intensity of segregation at 50% amplitude. At higher pressures, no significant difference of intensity of segregation was observed for silica/alumina system (Figure 2(a)). In fact, at 10% amplitude, pressure does not have a pronounced effect on intensity of segregation at all pressures considered here. Therefore, the main influence of pressure for this system is that at high pressures, the highest degree of mixing is observed already at 30% amplitude, while for the low pressure higher amplitude, 50%, is required to obtain the same mixing quality. Mixing in n-hexane shows better results at low amplitudes than in CO_2. A high degree of mixing has been obtained for alumina/silica sonicated in n-hexane even at low amplitude of 10%. At higher amplitudes mixing in CO_2 becomes as good as in hexane at least in the limits of our EDS resolution (lateral resolution of a micro-meter).

Capabilities of our mixture characterization method are limited in the sense that the volume of sample analyzed as well as lateral resolution with EDS is large (the order of microns) compared to primary particle sizes (tens of nanometers). Therefore, for powders mixed at nanoscale, intensity of segregation that reflects the compositional non-homogeneity, first, would not differ much for different mixtures, and, second, can even sometimes be so small that it becomes comparable with the uncertainties of determination of composition at each point by EDS. This fact was also pointed out in Wei et al. (2002) and Yang et al. (2003) indicating that another method of higher “resolution” is needed to resolve the question if we could achieve even higher mixing beyond 50% amplitude. Next, another interesting system is analyzed because the two constituents of the mixtures can be easily identifies at nano-scale using FESEM imaging.

(a) (b)

SiO_2/MWNT System

Qualitative analysis of mixing of MWNT/silica was done with field emission scanning electron microscopy (FESEM. Mixing of powders was carried in supercritical CO_2 (90×10^5 N/m^2, 45 °C) and n-hexane at different amplitudes.

Figure 3 represents the images for the products of sonication of MWNT with silica at 90 bar and 45 °C and different sonication amplitudes. Figure 3 Error! Reference source not found.(a) shows two typical types of agglomerates found in the mixture after sonication. One is an agglomerate of SiO_2, and the other represents a bundle of carbon nanotubes with silica agglomerates of both submicron and micron sizes distributed on the surface and inside the MWNT bundle (Figure 3(b)). Apparently, some deagglomeration of nanoparticles and partial mixing with carbon nanotubes occurred at this amplitude, but large amounts of silica still form separate agglomerates with the size in the range of tens of microns. Figure 3(c) shows a typical MWNT bundle observed at 30% amplitude mixing. No essential difference in size compared with the original, unprocessed MWNT bundles was observed, which means that sonication did not lead to any significant deagglomeration of MWNT. At the same time no individual silica agglomerates were found in this mixture. The high magnification image of the surface of MWNT-silica bundle in Figure 3(c) is somewhat similar to the one observed at 10%, except higher degree of particle deagglomeration and their more uniform distribution among nanotubes were observed in this case. No differences between mixing with 30 and 50% amplitudes could be resolved by the SEM image analysis.

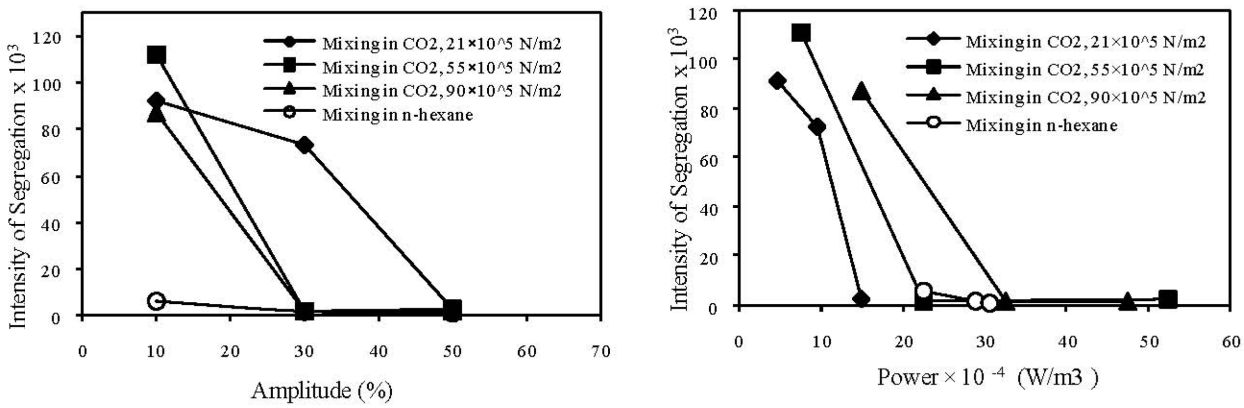

Figure 2. (a) Effect amplitude on intensity of segregation for silica/alumina at various pressures in CO_2 and n-hexane and (b) intensity of segregation versus average power consumption per unit volume (of carbon dioxide or n-hexane) for silica/alumina mixture. (Lines are drawn only for visual guidance).

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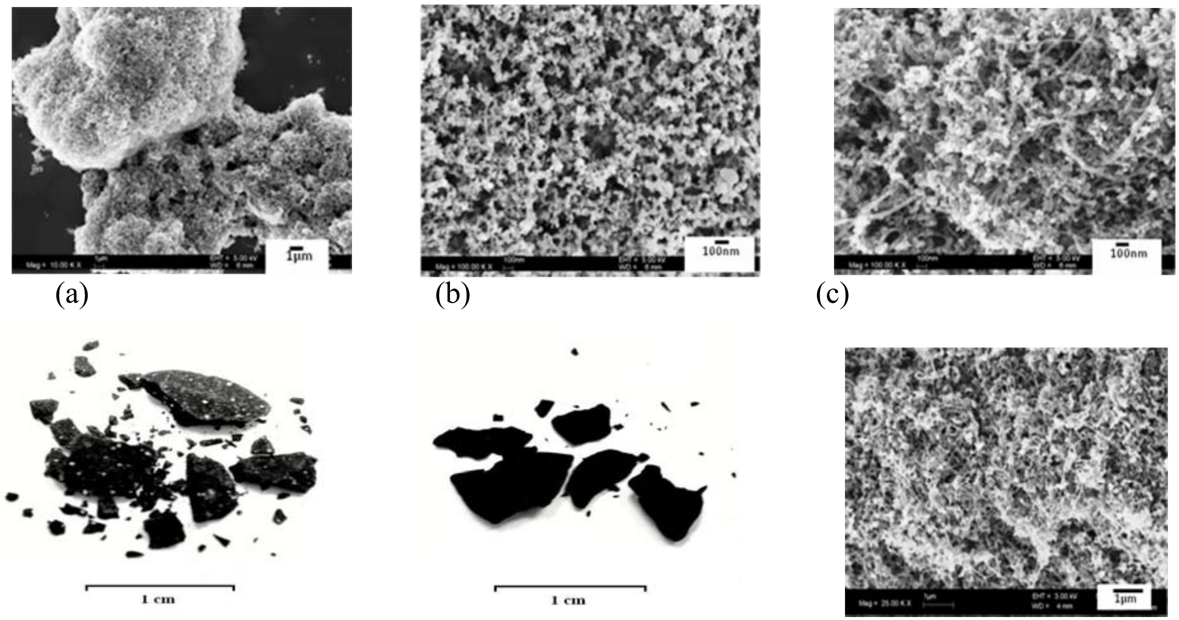
Product of mixed nanopowders in n-hexane has a distinctively different morphology compared with those obtained in CO_2. Figure 3 (d) & (e) is a photograph of MWNT - silica mixed in n-hexane that reveals the chunky nature and flaky shape of the particles in the very broad size range from microns up to centimeter. In case of MWNT-silica mixture, clear distinct white color silica nanoparticle agglomerates can be detected visually in the mixture produced at 10% amplitude (Figure 3(d)), while at 30% amplitude and higher, only dark colored mixture can be seen (Figure 3(e)). High magnification SEM image of the flakes (Figure 3(f)) produced at high amplitude show the distinct differences in the surfaces of the flakes. At 10% amplitude, large amount of nanoparticles are distributed on the surface forming some kind of matrix into which the MWNT are embedded, while in case of 50% amplitude the surface consists mostly of MWNT among which small agglomerates are dispersed. At low amplitude mixture the MWNTs have some preferred orientation, which, probably, can be explained by alignment of nanotubes in ultrasonic field in the direction of the wave propagation. In case of 50% amplitude MWNT are distributed more chaotically without any preferential orientation.



(a) (b) (c)

(d) (e) (f)

Figure 3. SEM images mixtures produced by sonication in CO_2 at $90\times10_5$ N/m_2 and liquid n-hexane: (a) Overview of MWNT – silica agglomerates produced by sonication at 10% amplitude. Two types of particles were observed: silica agglomerates: silica agglomerates and MWNT – silica bundles; (b) Close-up view of MWNT-silica agglomerate represented in (a); (c) Overview of a typical MWNT-silica bundle produced by sonication at 30% amplitude; (d) Photograph of particles obtained by mixing of MWNT with silica in n-hexane at amplitudes at 10%; (e) Photograph of particles obtained by mixing of MWNT with silica in n-hexane at 10% amplitude ; (f) Close-up of flake surfaces obtained by sonicating MWNT with the powders in n-hexane at 50% amplitude.

Conclusion

The use of supercritical fluids as a replacement of liquid solvent in wet sonication mixing process is examined for the purpose of nano powder mixing. In the wet mixing process, nanomaterial of interest should be insoluble, has to wet the liquid, and the final nanomixed product needs to be filtrated and dried. In addition, flammability and the residual solvent are major concerns when organic liquids (e.g., n-hexane, toluene) are used. Replacement of the organic solvent by supercritical CO_2 removes many of such drawbacks. From results it appears that ultrasonic mixing, carried in high pressure carbon dioxide involving high impact collisions between particles/agglomerates and against rigid surface (horn surface and vessel walls), were enough to deagglomerate particles and mix them as well. These high impact collisions seem to achieve similar results as through work done by cavitation (in liquid n-hexane) phenomenon which breaks the micro-agglomerates. The high impact collisions (among particles and against rigid wall and horn) are possible due to high molar density and low viscosity of carbon dioxide. High amplitude (30-50%) gave good results at various selected molar densities (pressure) of carbon dioxide. Degree of mixing/homogeneity for selected nanopowders was fairly constant at different selected pressure ranges for high ultrasound amplitude (50%). Nanomixing ⊵ CO_2 for silica/alumina is as good as in n-hexane. But in the case of CO_2, mixed powder is free of organic solvent and the powder recovery is simpler.

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