

Deagglomeration and Dispersion of Carbon Nanotubes Using Microfluidizer® High Shear Fluid Processors

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ABSTRACT

For many carbon nanotube (CNT) applications, paramount performance can be achieved if the CNTs get deagglomerated, frequently shortened, and uniformly dispersed in liquid media. Microfluidizer high shear fluid processors were used successfully to disperse single- and multi- wall CNTs in various liquid media including polymer resins, organic solvents and water. Processing deagglomerated the CNTs and caused them to form networks inside the liquid media. Length reduction of CNTs was possible and controlled based on the processing conditions. During processing, CNTs detached from the catalyst substrate, facilitating purification. Finally, the electrical resistivity of polymer/CNT composites was measured as a function of CNT concentration. For samples processed with the Microfluidizer® processor, the volume resistivity of the composites decreased by seven orders of magnitude as the CNT concentration increased from 0.008wt% to 0.06wt%. There was no change in resistivity for the baseline samples.

Keywords: dispersion, carbon nanotubes, nanocomposites microfluidizer

1 INTRODUCTION

Deagglomeration and dispersion of carbon nanotubes (CNTs) in various media has been recognized as one of the major challenges in utilizing CNTs in commercial applications. For many CNT applications, paramount performance can be achieved if the carbon nanotubes get deagglomerated, frequently shortened and uniformly dispersed in media such as organic solvents, polymer resins, water, etc.[1-3]. Deagglomerated CNTs form networks, and such networks are responsible for enhanced strength and electrical conductivity of polymer composites containing CNTs.

Any method used to de-agglomerate CNTs should be efficient, economical, and scalable. Sonication is a method that is often used in lab scale to de-agglomerate and shorten the CNTs. This method does not scale up and may contaminate the CNTs with metal particles from the sonication probe. In addition, it may change the chiral properties of the nanotubes[3]. Functionalization of CNT surfaces to improve dispersion may be effective but does not solve the problem fully and is still in the research stage[2].

Microfluidizer high shear fluid processors have been used extensively for particle deagglomeration, dispersion and size reduction. Processing of multi-phase liquids takes place as the fluids flow at velocities of up to 500 m/s in microchannels of various geometries, thus exposing uniformly the liquids to high shear stresses. The process pressure and the channel geometry control the velocities inside the channels, and therefore the energy dissipation.

Microfluidizer processors were used to process various formulations of single- and multi- wall CNTs. These were dispersed in water, high viscosity mineral oil, polymer resins and organic solvents. Process pressures in the range of 41 to 158 MPa were used in which the CNT dispersion is forced through specially designed microchannels called interaction chambers. Carbon nanotube concentrations varied in the range of 0.008 to 1.9 wt%. The effect of processing was assessed using FESEM (Field Emission Scanning Electron Microscope) imaging, particle size analysis and bulk resistivity measurements.

2 EXPERIMENTAL APPARATUS

The Microfluidizer processor model M-110EH, equipped with two 'Z' type interaction chambers, was used to process the CNT dispersions. Figure 1 shows schematics of a 'Z' type microchannel design.

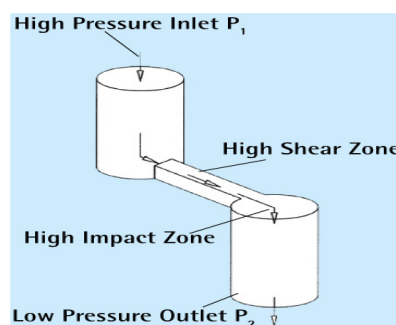


Figure 1: Schematic of a "Z" chamber. Copyright by Microfluidics, 2007.

Typically, the CNT bundles, dispersed in a liquid media, are forced through this type of configuration that has been specially designed to optimize shear. This consists of sharp turns and a very narrow rectangular cross-section; as small as 50µm across the smallest dimension. This combination is referred to as the interaction chamber.

Process scale up simply means adding multiple chambers or microchannels in parallel. Two interaction chambers were used in series for these experiments, the H30Z(200 μ m) and the G10Z(87 μ m).

The intensification of the process fluid involves the use of electro-hydraulics. An electric motor may drive a hydraulic pump, which in turn forces hydraulic fluid over the area of a piston. In all cases this piston is coupled to a plunger which forces the process fluid through the interaction chamber. The ratio of the areas or the piston to the plunger defines the amplification of pressure. This is schematically shown in Figure 2.

The premixes were obtained using either a Talboy 102 propeller stirrer, or an IKA T-25 shear mixer. The processed materials were analyzed using an Olympus BH-2 optical microscope and a Horiba LA-910 particle size analyzer. Samples were imaged by Hitachi S-4800, a Zeiss Supra™ 25 and Jeol JSM 6340F FESEMs. Volume resistivity testing was also conducted referencing ASTM-D257-99 using a Quadtech 1825 Tester.

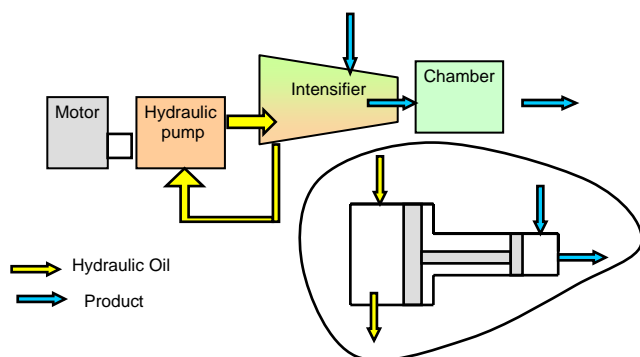


Figure 2: Principal of operation of a Microfluidizer processor. Copyright by Microfluidics, 2007.

3 PROCEDURE

The respective concentrations of the CNT dispersions were prepared by adding specific quantities (by weight) to the desired solvent or matrix material. Upon formulating, each dispersion mix of CNT was then stirred or shear mixed before addition to the reservoir of the Microfluidizer processor.

The test to de-agglomerate in a liquid media was such that all materials in the formulation were mixed well before processing. Table 1 shows a list of carbon nanotube formulations that were processed. Subsequently, they were analyzed by a combination of techniques, including optical microscopy, field emission scanning electron microscopy and particle size analysis.

The resistivity procedure involved first weighing the SWNTs (Single Wall carbon Nanotube) and then adding them to the Epon™ 862 [4-6] epoxy resin, which was preheated to approximately 40°C and was continuously being stirred in a water bath using a Talboy model 102

Sample	Solid Content	Nanotube Type	Dispersant
1	1.90 %	SWNT	mineral oil
2	0.38 %	SWNT	mineral oil
3	1.00 %	SWNT	Polymer resin
4	1.00 %	SWNT	Water
5	0.70 %	SWNT	Toluene
6	6.00 %	MWNT	Methanol
7	6.00 %	MWNT	Methanol
8	0.60 %	MWNT	Methanol
9	0.06%	SWNT	Epoxy resin

Table 1: Typical CNT formulations processed with the Microfluidizer

propeller mixer. Batches of up to 255mL were used at each SWNT concentration which were 0.008, 0.02, 0.04 and 0.06 wt%. The SWNT-resin mixture was then processed at 158 MPa for 1 pass using an H30Z (200 μ m)-G10Z (87 μ m) chamber combination. The temperature of the material exiting the processor was maintained between 45 and 57°C. This mixture was then combined with the curing agent (Epicure™ 3282) [4-6] within 5 minutes and allowed to cure in 4" x 4"x 1/8" moulds for 2 hours. The SWNT-epoxy tiles thus formed, were then allowed to finish curing in an oven at 120 °C for 4 hours.

4 RESULTS

4.1 Deagglomeration in Liquid Media

The effects of processing 0.38% SWNT carbon nanotubes dispersed in high density mineral oil can be seen in the FESEM images of Figure 3. The unprocessed nanotubes, Figure 3a, are densely packed and the individual nanotube strands are not discernable. After a single pass, individual long and thin tubes can be clearly seen; as in Figure 3b. The CNTs appear much more de-agglomerated and forming a network. They are also uniformly dispersed throughout the media. It is not clear that these are individual nanotubes or thin strands but their diameter appears to be fairly uniform.

Additional passes shorten such strands, without necessarily decreasing the diameter of the strands; as seen Figures 3c and 3d.

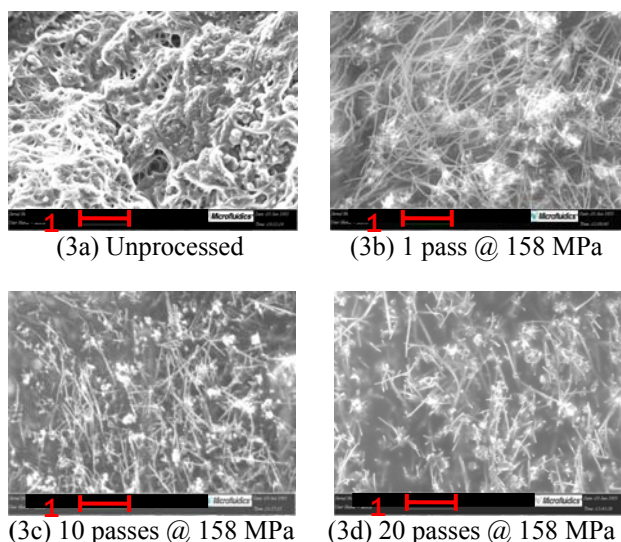


Figure 3: Images captured with an FESEM at 20,000x Magnification. Each picture corresponds to different number of passes through the Microfluidizer processor. Copyright by Microfluidics, 2007.

4.2 Length Reduction

Results were obtained using a laser scattering particle size analyzer for the samples that had water or ethanol as the diluent. One of the assumptions that the particle size analyzer makes is that the particles are spherical. Since the carbon nanotubes have an extremely high aspect ratio, the numbers that are reported may not necessarily correspond to any dimensions of the nanotubes themselves. These particle size distributions merely act as a comparison between unprocessed and processed samples. The particle size analysis of the MWNTs (Multi Wall carbon Nanotubes) are shown in Figure 4. The particle size data shown was measured using 60 seconds of sonication in the flow cell of the particle size analyzer.

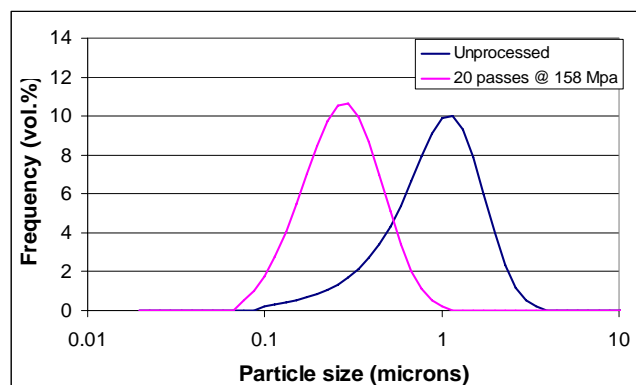


Figure 4: Particle size distributions of MWNTs dispersed in water before and after processing with the Microfluidizer processor. The median particle size went from 0.892 μ m down to 0.254 μ m after 20 passes at 158 MPa.

4.3 Impurity Stripping

Catalyst used during the reaction to form the CNTs becomes a residual impurity. After processing in the Microfluidizer processor, the residual catalyst that was entangled with the CNTs is broken and detached from the CNTs. This is shown in FESEM images of Figure 5.

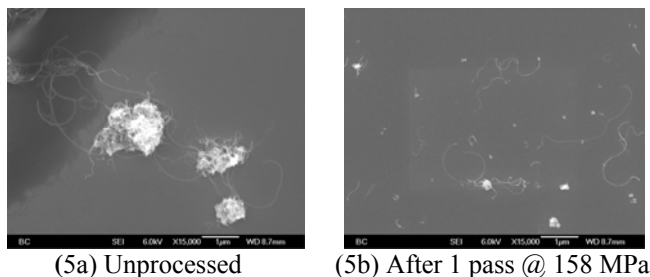


Figure 5: FESEM (20,000x) images of catalyst clumps being stripped from MWNTs (5a) before and (5b) catalyst impurity segregated after processing. Images provided by Nanolab Inc., Newton, MA.

4.4 Control Conductivity

A distinct change in appearance between the processed and unprocessed epoxy tiles is shown in Figure 6.

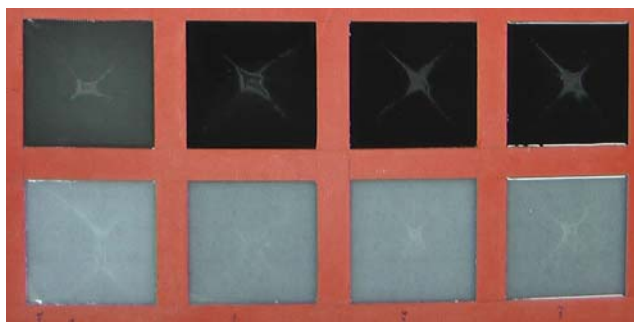


Figure 6: SWNT-Epoxy tiles during the initial curing state in the mold. Starting from the 1st column from the lower left, 0.008% at 0 and after 1 pass above, 2nd column 0.02% at 0 and 1 pass, 3rd column 0.04% at 0 and 1 pass and finally the 4th column 0.06% at 0 and 1 pass.

Comparisons of the unprocessed and the processed SWNT-epoxy systems are shown in Figure 7. A dramatic difference between the resistivity value measured both before and after processing, and also between the resistivity values measured at increased concentrations of SWNT. At 0.008 wt%, there was a 23% reduction in resistivity after processing. At 0.02 wt%, there was a 6 order of magnitude drop in resistivity when the volume resistivity dropped from 7.28×10^{15} ohm-cm down to 1.21×10^9 ohm-cm. Similarly at 0.04 wt%, there was a 7 order of magnitude drop in resistivity when the volume resistivity dropped

from 7.22×10^{15} ohm-cm down to 1.34×10^8 ohm-cm. At the maximum SWNT loading of 0.06 wt% there was also a large drop in resistivity from 7.16×10^{15} ohm-cm down to 2.35×10^8 ohm-cm. The electrical behavior exhibited suggests that the critical loading required for a significant change in resistivity lies between 0.008 wt% and 0.02 wt% of SWNT. It also suggests that beyond the critical loading, enhanced dispersion of the SWNTs, ultimately resulted in

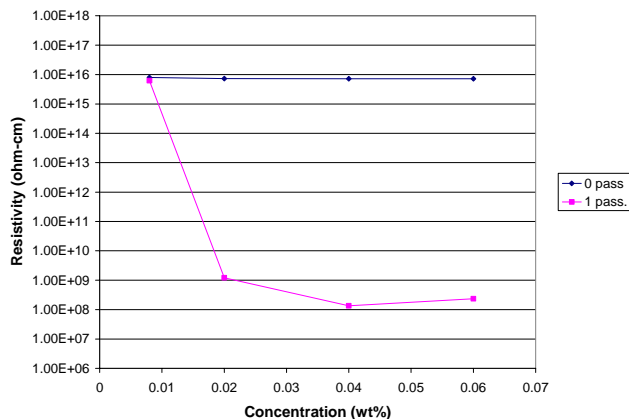


Figure 7: Resistivity vs concentration of SWNT after processing for 1 pass at 158 MPa using Microfluidics technology.

significant drops in resistivity. There was no significant change in resistivity for the SWNT-epoxy samples that were not processed with the Microfluidizer processor. The images of Figure 8 show the typical characteristics of the 0.06 wt% SWNT-epoxy specimen at a magnification of about 4,000x before and after processing with the Microfluidizer processor.

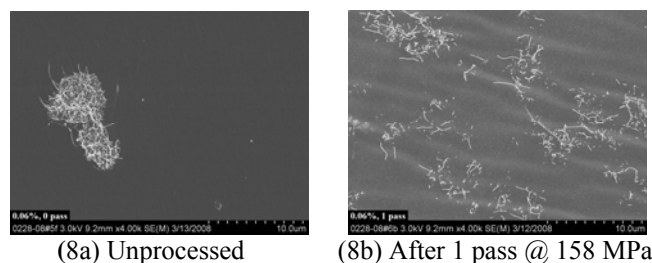


Figure 8: FESEM images of the 0.06 wt% SWNT-epoxy composites, (8a) before and (8b) after processing with a Microfluidizer processor.

These FESEM images suggest that for each concentration range, the SWNT clumps were dispersed by processing. This may have contributed to the enhanced conductivity of the SWNT-epoxy composite at loadings above 0.008 wt%.

5 SUMMARY

Microfluidizer technology was successful in de-agglomerating SWNT and MWNT, and creating stable suspensions of nanotubes in various liquid media. These

included polymer resins, organic solvents, mineral oil and water, with concentrations of carbon nanotubes varied in the range of 0.38-6%. Microscopy, both electron and optical, confirmed that the nanotubes were de-agglomerated to a large extent, and dispersed uniformly within the dispersion media in a single pass. Additional passes resulted in controlled length reduction of the nanotubes. A distinct advantage of Microfluidizer technology is that the amount of shear that is applied on the material can be easily varied, allowing the nanotubes to detangle and be shortened to the extent required by any application. Microfluidizer processor technology was successful in reducing the particle size distribution of the MWNTs' dispersion in all four of the diluents that were analyzed.

The Microfluidizer processor provided the dispersion necessary for enhanced electrical conductivity as well. There was no significant change in resistivity at the lowest SWNT loading of 0.008 wt%. Similarly, there was also no significant change in resistivity for the specimens with loadings above 0.008 wt% that were not processed with the Microfluidizer processor. If good dispersion is initiated, the critical loading level above which there is a significant drop in resistivity lies between 0.008 and 0.02 wt% for this SWNT-epoxy system. This was also observed by Andrews et al [4-6].

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