Dispersion and Distribution Analysis of Carbon Nanotubes in Liquids

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***Abstract*— Carbon Nanotubes exhibits extremely high and unique mechanical properties when they dispersed and aligned properly. Since the discovery of single walled and multi-walled carbon nanotubes (SWNT and MWNT), in the early 1990s, the exceptional mechanical properties have motivated a wealth of research. The synthesis of Carbon Nanotube's (CNT's) by effectively aligning and dispersing in fluids is a challenging task.**

Production processes for carbon nanotubes often produce mixtures of that are self-associate into aggregates. Aggregated nanoparticles often need to be dispersed into fluid suspensions in order to develop materials that have unique mechanical characteristics. This paper reviews the physical (mechanical) methods of dispersing nanotubes in liquids and analysis of nanotube distribution.

***Keywords*— Carbon Nanotube, Disperssion, Aggregates.**

1. INTRODUCTION

Nanoparticles are generally considered to be a number of atoms or molecules bonded together with a radius of <100nm. A nanometer is 10-9nm or 10Å. These are aggregates of atoms between 1 and 100nm viewed as a subdivision of a bulk material, and of dimension less than the characteristic length of some phenomena. Nanoparticles, Nano plates, Nanowires and Nanotubes have lateral dimension 1 – 100 nm[1]. Nanowires and nanotubes exhibit novel physical, electronic and optical properties due to

- Two dimensional quantum confinement
- Structural one dimensionality
- High surface to volume ratio

The nanoparticles can be fabricated by using Top-down and Bottom-up approaches. Carbon is responsible for creating the most diverse variety of compounds. It has more allotropes than any other element. The most recent additions to this list are fullerenes and nanotubes. Nanotubes can be produced through a homogeneous sonochemistry process. The reaction is very fast and takes place at the ''hot spot'' created right at the tip of the sonication probe, where the temperature is thought to reach over 5000K.

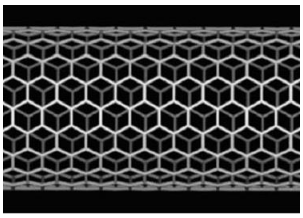

Fig. 1. A part of Nanotube

Production techniques includes Chemical, Lithography, Evaporation, Vapour deposition, Milling, Plasma, Ion bombardment etc.

Properties of Carbon Nanotubes[4]:

- The transport properties of carbon nanotubes are high compared to many solids.
- Percolation theory suggests that highly conductive, high aspect ratio solids could produce three-dimensional networks with high transport properties. The thermal and electrical conductivities of single nanotubes are thought to be higher than graphite.
- CNTs have the combination of remarkable mechanical properties like strength, very high aspect ratio, very high thermal conductivity and unique electrical properties.
- All nanotubes are expected to be very good thermal conductors along the tube, exhibiting a property known as "ballistic conduction".
- CNTs can be metallic or semiconducting and offers amazing possibilities to create future Nano electronic devices, circuits, and computers.

Challenges to Use Nanotubes:

- Purification and separation of nanotubes by chemistry and morphology.
- Uniform and reproducible dispersion.
- Orientation of these solids in liquid and melt phases.

This review discusses physical (mechanical) methods with emphasis on the morphology of their carbon nanotubes products. References are provided for the effects of milling, ultrasonication, high shear flow, functionalization and dispersant systems on morphology of carbon nanotubes and their interactions in the fluid phase.

2. DISPERSION METHODS

To produce a suspension of independent, separated nanotubes that then can be manipulated into preferred orientations in one-dimensional (fiber), twodimensional (flat sheet), or three-dimensional (bulk solid) objects dispersion science and technology is used.

There are two different approaches to nanotube dispersion:

1.**Mechanical (or physical) methods:** Mechanical dispersion methods, such as ultrasonication, separate nanotubes from each other, but can also fragment the nanotubes, decreasing their aspect ratio during processing.

2.**Chemical methods:**Chemical methods use surfactants or functionalization to change the surface energy of the nanotubes, improving their wetting or adhesion characteristics and reducing their tendency to agglomerate in the continuous phase solvent. However, aggressive chemical functionalization, such as using neat acids at high temperatures, can digest the nanotubes.

3. MECHANICAL (OR PHYSICAL METHODS)

Various mechanical methods of separating nanotubes into preferred orientations in liquids are discussed in this paper.

a) Ball Milling:

Ball-milling has been used to narrow the length and diameter distributions and to open the nanotubes for improved sorption capacity for gases. It has also been observed that a large amount of amorphous carbon is created, which clearly indicates that the tubes are damaged in different ways and that ball-milling is a destructive method. The creation of amorphous carbon introduces a high surface area, which is a more likely explanation to the increased storage capacity than the introduction of open tube ends would be.

Ball-milling has also been used in an attempt to intercalate lithium in SWNTs, creating compounds to be used in batteries. Li-intercalated graphite and carbonaceous materials are commercially used in Li-ion batteries. The intercalation involves electron donation from the alkali metal to the nanotube.

b) Grinding:

Rubbing is more destructive than any other method. The process introduces cuts and bends in SWNTs, but no change in storage capacity is observed. A less damaging method is chemically cutting SWNTs by grinding them in a fluid (a- or b-cyclodextrin) using mortar and pestle. MWNTs can be hand-ground with mortar and pestle. The MWNTs were mixed with a small amount of toluene, creating a thick paste. The paste was ground for approximately an hour, with no further addition of toluene.

Grinding produced significant defects in the MWNTs. Much of the mechanical energy goes into complete breaks of the tubes, new defect sites are continuously generated on the tube surface.

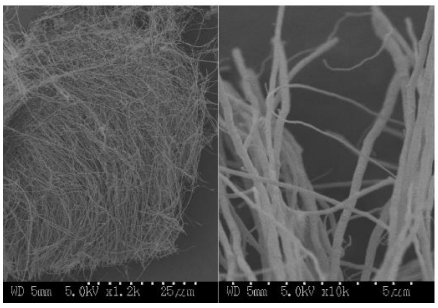

Fig. 2. Lengths of nanotubes before grinding

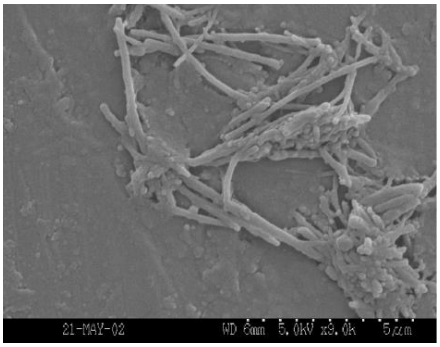

Fig. 3. Lengths of nanotubes after grinding

c) Shear Mixing:

In this method shear force is applied to pull agglomerates apart. Narrow passages with relatively high rates of flow, are required to generate high shear; in a lot of cases, rotor and stator construction is used. Carbon nanotubes were dispersed into synthetic oil, four centistokes poly with the aid of a non-ionic dispersant. The test fluid is pumped through a small-clearance diesel-injector nozzle, which provides both turbulent and localized shear. The viscosity profile of the nanotubes is very similar to that of the cylindrical particle suspensions, indicating that at certain point the carbon nanotubes can be treated as high-aspect ratio cylindrical particles.

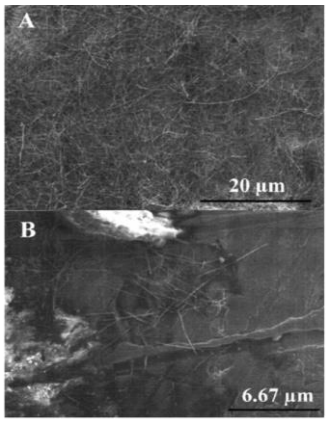

Fig. 4. SEM images of nanotubes before and after shear mixing.

d) Ultrasonication:

Ultrasonication of carbon nanotubes in solvents such as alcohols is a common technique for dispersing samples for electron microscopy. One way to improve the dispersion of nanotubes is to shorten the tubes. The shorter tubes are less likely to entangle and arrange into aggregates.

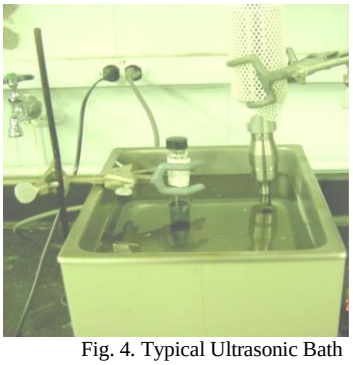

Fig. 4. Typical Ultrasonic Bath

Ultrasonication is an extremely common tool used to break up nanotube aggregates during purification, mixing, and other types of solution processing techniques. One example is ultrasonication with diamond crystals, a method that reportedly destroys the SWNT bundles but not the tubes. Raman-spectra show typical SWNT peaks even after 10 hours of treatment with this method. Ultrasonication creates expansion and peeling or fractionation of MWNT graphene layers. So MWNTs would not only get shorter, but actually thinner with time. In some cases, ultrasonication can be used to remove impurities. Ultrasonication disperses solids primarily through a bubble nucleation and collapse sequence.
There are two major methods for delivering ultrasonic energy into liquids,
1. Ultrasonic Bath.
2. Ultrasonic Horn.

Bath Ultrasonication

Multiwalled carbon nanotubes will be dispersed in toluene by using an ultrasonication bath (a frequency of 55 Hz).The MWNTs had initial dimensions of L¼450 nm, Di¼2.9 nm and Do¼25 nm, respectively. Water in the ultrasonication bath promots uniform energy distribution. The MWNT loading was 0.1 wt.%, and samples from the bath after 5, 10, 15, 20, and 25 min will be analyzed by using SEM. The measured of MWNT lengths are plotted cumulatively. The log-normal models are also presented in the differential form in Fig. 5 and the model parameters are presented. The differential curves clearly show the loss of larger tubes at longer sonication times.

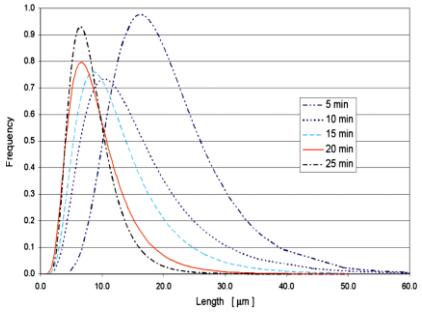

Fig. 5. Normal density function for MWNT lengths

Ultrasonication Horn

In this method, tips of ultrasonic wands oscillate at a fixed frequency with variable power being applied to the fluid phase. The rapid oscillation of the wand tip produces a conical field of high energy in the fluid. The solvent within this conical field undergoes nucleated boiling and bubble collapse, which is the primary mechanism by which ultrasonic energy disperses materials. The volume fraction of nanotubes in the suspension affects the solid surface per fluid volume. Dispersion of 0.1 wt.% dispersion of MWNTs in toluene were treated with an ultrasonication horn. Data will be collected and modeled in the same manner as “Bath Ultrasonication”.

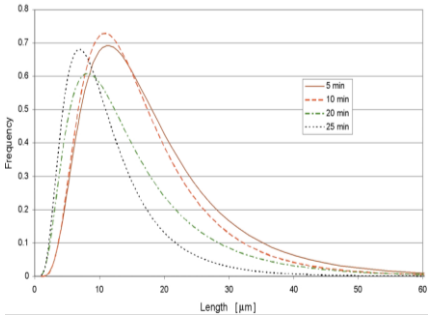

Fig. 6. Normal density function for MWNT lengths

4. ANALYSIS OF NANOTUBE LENGTH DISTRIBUTIONS

Mathematical functions have been used to model the particle size distributions of comminution processes. These functions include empirical models as well as probability density functions.

As particles are fragmented and broken during processing, their length distributions change as do the model coefficients that describe the distributions.

Probability density functions are particularly useful if they provide a good fit to particle size distributions since the moments of the distributions can be used in kinetic rate models that predict the change in the length distributions with time.

Gel permeation chromatography of polymers yields complete differential distributions that provide rich information on the fragmentation process.

A key assumption of these models is that one fragmentation event occurs in the chain (or particle or nanotube) at a time.
Typical Particle Fragmentation Distributions are,

- As the materials fragment to smaller sizes, less of the applied energy results in fragmentation and more is lost through particle motion, particle compression, particle flexing, and other mechanisms.
- A simple kinetic rate model based on binary fragmentation that can describe these phenomena is:

$$-\frac{dL}{dt} = kL^b$$

Where, L is a characteristic material length, t is time, k is a rate constant, and b is the exponent that describes the change in fragmentation rate with length.
Gaussian distributions are often assumed to represent particle size distributions.

Size Distribution Measurement and Analysis

- It is possible to measure nanotube size distributions using Scanning Electron Microscope and optical microscopy.

Transmission Electron Microscope is not useful for size distributions except when very short (<100 nm) tubes are present.

- Fitting a differential distribution accurately might require as many as one thousand data points and is practical when digital imaging software can be applied to the problem.
- An alternative is, determine the probability density function coefficients of cumulative particle size distributions for 50–100 nanotubes. This approach reduces the instrument time for length measurements and often provides sufficient accuracy for engineering models of the fragmentation process.
- The differential probability density function has two fitting parameters, the standard deviation of the distribution, s, and the logarithmic mean, m.

$$f(\ln(L)) = \frac{1}{\sigma \cdot \sqrt{2\pi}} e^{-\frac{1}{2}\left(\frac{\ln(L)-\mu}{\sigma}\right)^2}$$

5. REFERENCES

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