University of North Carolina Asheville
Journal of Undergraduate Research
Asheville, North Carolina
December 2018

Rheological Characterization of DNA-Stabilized Boron Nitride Nanotubes

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Abstract

Boron nitride nanotubes (BNNTs) are an emerging nanomaterial with promising properties. Several applications of BNNTs include new flame retardant materials and elevated temperature corrosion protection for aerospace applications. BNNTs have a 1D tubular nanostructure, and are inherently noncytotoxic, mechanically robust, and have extraordinary chemical and thermal stability. The purpose of this project was to rheologically characterize BNNTs in aqueous DNA solution in order to predict their rigid rod behavior at semi-dilute concentrations. Rheology is the study of the flow of matter, and using rheology data to calculate rigid rod behavior can have theoretical liquid crystalline phase behavior implications. Due to BNNTs' inability to be dispersed in water (as BNNTs are hydrophobic), DNA was selected as an effective stabilizing agent for BNNTs in solution. Three types of DNA-wrapped BNNT dispersions were prepared for rheological analysis, and the excess unbound DNA was removed via a precipitation method. Our rheology results show Newtonian behavior for all three samples (indicating that they were in dilute regimes), where the steady shear viscosity of each type of sample remained constant as a function of shear rate. Future work will focus on the rheology of DNA-BNNT dispersions at varying concentrations in order to determine the distribution of average aspect ratio (length to diameter ratio) of BNNTs in the dilute regime, and also predict the rigid rod behavior of BNNTs in the semi-dilute regime.

1. Introduction

Boron nitride nanotubes (BNNTs) are an emerging nanomaterial with promising properties. Several applications of BNNTs include new flame retardant materials and elevated temperature corrosion protection for aerospace applications. BNNTs have a 1D tubular nanostructure, and are inherently noncytotoxic, mechanically robust, and have extraordinary chemical and thermal stability.[1]

Although nanotubes (both boron nitride and carbon) are grown from a base structure in specific ways, a useful way for visualizing the different types of nanotubes is shown below in Figure 1. One can picture either a graphene (hexagonal carbon) sheet or a hexagonal boron nitride sheet, and then imagine "rolling it up" to form a nanotube. The way that the atoms of the nanotube are arranged (or "rolled up" in the diagram below) causes the nanotube to possess electronic or optical properties specific to its arrangement. Nanotubes can also be multi-walled, which affects the nanotubes' properties as well.

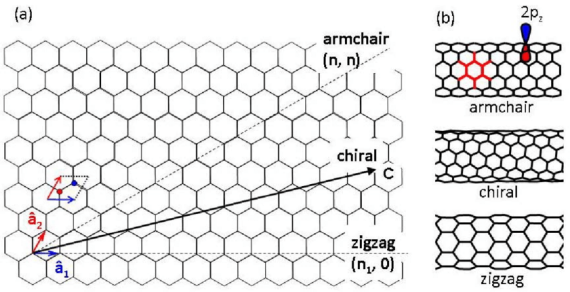

Figure 1.[2] The "Rolling" of a Graphene Sheet. a) Diagram of visualizing the different ways a hexagonal sheet can be rolled up; b) different orientations of the atoms and what different organizations can look like in nanotube form.[1]

The purpose of this project was to rheologically characterize BNNTs in aqueous DNA solution in order to predict their rigid rod behavior at semi-dilute concentrations. Rheology is the study of the flow of matter[3], and using rheology data to calculate rigid rod behavior can have theoretical liquid crystalline phase behavior implications. The liquid crystalline phase is a phase that falls between the solid and liquid states, where the molecules align themselves into semi-lattice structures, yet seem to remain in aqueous form to the naked eye.[4] There are various types of liquid crystals, depending on the orientation of the molecules in solution. BNNT liquid crystals have yet to be observed, although carbon nanotube liquid crystals have been well-studied.

Viscosity (η) is a rheological property that quantitatively defines a material's resistance to flow. Viscosity can be calculated with the following equation:

$$\eta = \frac{F/A}{\frac{dv_x}{dz}} \tag{1}$$

where viscosity is the ratio of the shearing stress, F/A, to the velocity gradient, dv_x/dz.

Due to BNNTs' inability to be dispersed in water (as BNNTs are hydrophobic), DNA was selected as an effective stabilizing agent for BNNTs in solution. DNA wraps around the BNNTs, making the hybrids hydrophilic, allowing the tubes to be dispersed in water for further purification and analysis.

Three types of DNA-wrapped BNNT dispersions were prepared for rheological analysis; each of which, are purified using a different process. First, the precipitated "bulk" samples were tip sonicated and precipitated with polyethylene glycol (PEG) in order to make the tubes crowd with one another, therefore making the excess unbound DNA extractable. Second, precipitated supernatant samples were tip sonicated, centrifuged, and also precipitated with PEG. Third, the membrane-filtered supernatant samples were centrifuged, then filtered through a membrane in order to remove debris and excess unbound DNA.

2. Methodology

The analytical balance was tared with a piece of wax paper for each sample. 1.0mg of the BNNT cotton was weighed in each 1.5mL tube. 75µL of GT_{20} DNA, 100µL of 1M NaCl stock solution, and 825µL of deionized H_2O were added to each tube using 10-100µL and 100-1000µL micropipettes. The samples were wrapped with parafilm, then bath sonicated at 23ºC for 1 hour. Each sample was tip sonicated for 1 hour in a tightly packed ice bath.

For the precipitated bulk samples, xµL of 50% polyethylene glycol (PEG) stock was added to achieve 6% mass by PEG of the samples, along with xµL of 10M NaSCN to attain 1M NaSCN concentration. The samples were placed in the fridge and were allowed to precipitate overnight. The samples were centrifuged twice for 25 minutes then 15 minutes at 17,000g and 19ºC; this time, all of the supernatant was collected and discarded. The pallet of BNNT-DNA hybrids was dispersed with ¼ the volume of the original sample (250µL) in DI H_2O in order to concentrate the sample 4x. The vortex mixer was used to completely disperse the pallet into the solution. All of the precipitated bulk samples were pooled together at the end of the process, in order to create one large precipitated bulk sample.

For the supernatant samples, each tip sonicated sample was evenly split into 9 (1.5mL) tubes using a 100µL micropipette. The samples were centrifuged for 90 minutes at 17,000g and 19ºC. 70-80µL of supernatant was collected

from each of the 9 tubes (in the same tube), then set aside and refrigerated until all of the supernatant was collected. All of the supernatant was mixed together, then split evenly amongst 1.5mL tubes that were designated for either precipitation or membrane filtration.

Precipitated supernatant samples were also precipitated with xμL of 50% PEG until 6% mass by PEG was obtained, along with xμL of 10M NaSCN until 1M NaSCN concentration was obtained as well. After being refrigerated overnight, the samples were centrifuged twice for 25 minutes then 15 minutes at 17,000g and 19°C; this time, all of the supernatant was collected and discarded. The pallet of BNNT-DNA hybrids was dispersed with ¼ the volume of the original sample (either 630μL or 720μL depending on if 70μL or 80μL of supernatant was collected originally) of DI H_2O in order to concentrate the sample 4x. The vortex mixer was used to completely disperse the pallet into the solution. All of the precipitated supernatant samples were pooled together at the end of the process, in order to create one large precipitated supernatant sample.

Membrane filtered samples were additionally filtered through a 30kDa centrifuge membrane. 500μL of the supernatant was placed into the membrane filtration cells, then the samples were centrifuged for 20 minutes at 17,000g and 19°C. 100μL of DI H_2O was added to the membranes after centrifugation, then a micropipette was used to "pump" and wash the BNNT-DNA hybrids on the surface of the membrane with the water. The samples were centrifuged for 20 minutes again, and the process was repeated 2-3 times. After the final washing, in order to achieve 4x concentration of the samples, 125μL of deionized water was added to the filtration cell, then repeatedly "pumped" in order to remove and re-disperse the BNNT-DNA hybrids from the surface of the membrane. All of the membrane filtered supernatant samples were pooled together at the end of the process, in order to create one large membrane filtered supernatant sample.

Samples were prepared for analysis in the UV-Visible spectrophotometer by diluting 3μL of the precipitated and membrane-filtered supernatant dispersions with 97μL of DI water, while 1μL of the bulk sample was diluted with 399μL of DI water due to the higher concentration of tubes in the bulk sample (the sample was out of the range of the spectrophotometer otherwise).

Samples were prepared for rheology by the graduate student Venkat, who handled the proper assembly of the MCR 302 rheometer, loaded the samples, and lowered the cone plate onto the samples. A cone plate with a diameter of 50mm was used to rheologically analyze the samples, and 1.5mL of each sample type was used per each run. Samples were reused various times due to the amount of time that sample preparation required. Since the samples were non-Newtonian fluids, a decent amount (between 30-45 minutes) of "rest" time was required between each sample after a run of a specific rheological measurement. All samples were ran at 10°C.

3. Data and Analysis

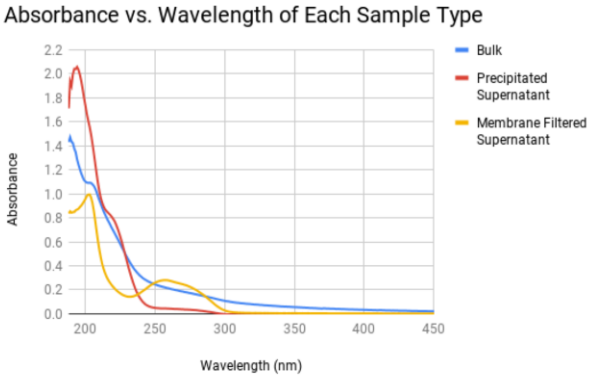

Figure 2. Absorbance Spectra for Each Sample Type. Beer's Law, $A = \varepsilon lc$, was used to calculate the concentration of the tubes in each sample type. The extinction coefficient, ε, was calculated by Venkat in a series of separate lab experiments. 205nm corresponds to the exact absorbance of DNA-BNNT hybrids, while 190nm corresponds to BNNT debris/impurities.

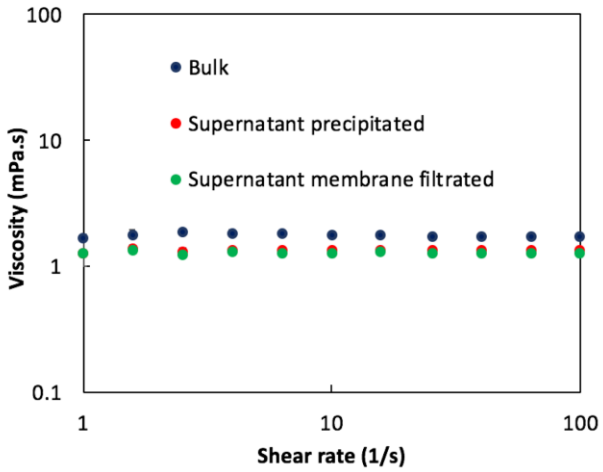

Figure 3. Rheology Data at 10°C. As the shear rate increased, the viscosity remained constant for each sample type, which is the key behavioral characteristic of a Newtonian fluid. Since the sample solutions were non-Newtonian, this means that the samples were in the dilute regime, as they behaved similarly to Newtonian fluids.

In Figure 2, the calculated extinction coefficient of 11.121 mL/mg·mm was used to determine the following concentrations of tubes for each sample type: 5.8287 mg/mL for the bulk sample, 1.2780 mg/mL for the precipitated supernatant sample, and 0.8300 mg/mL for the membrane filtered supernatant sample. The absorbance peak between 240-290nm for the membrane filtered supernatant sample corresponds to the broad absorbance spectra of free DNA; this should not be in the sample, therefore, this indicates a lab error occurred at some point throughout the purification process. Although the absorbance of the bulk sample seems to look lower than the absorbance of the precipitated supernatant sample, the concentration of the bulk sample is actually much higher, as the bulk sample was diluted 400x to be within the detectable range of the spectrophotometer.

In Figure 3, the viscosity remained constant for each sample type, despite the shear rate continuously increasing. Although the samples were non-Newtonian fluids, constant viscosity at different shear rates is a characteristic of Newtonian fluid behavior[5], implying that the samples were too dilute to behave as non-Newtonian fluids. Water (a Newtonian fluid) has a viscosity of 1 mPa·s, and each sample type had a viscosity that is higher than 1 mPa·s; this indicates that BNNT-DNA hybrids were present in the solution (a valid worry when working with nanomaterials), which increased the viscosity of the fluid. The bulk sample had a higher viscosity than both the precipitated supernatant and membrane filtered supernatant samples, due to the higher concentration of BNNT-DNA hybrids in the bulk sample than the other two samples.

4. Conclusion

The rheology results showed Newtonian behavior for all three samples (indicating that they were in dilute regimes), where the steady shear viscosity of each type of sample remained constant as a function of shear rate. Future work will focus on the rheology of DNA-BNNT dispersions at varying concentrations in order to determine the distribution of average aspect ratio (length to diameter ratio) of BNNTs in the dilute regime, and also predict the rigid rod behavior of BNNTs in the semi-dilute regime. This project was necessary in order to conclude BNNT properties that would be useful for creating BNNT liquid crystals, which would display optical properties of the BNNTs that may be useful for several applications in the chemical engineering industry. Since there is little known about BNNTs, there was a lot of trial and error during the experimental process, of which was a useful step towards actually creating BNNT liquid crystals.

5. Acknowledgements

The author wishes to express their appreciation to the NSF for the REU Grant #1659641, Venkateswara Rao-Kode, Miroslav Bogdanovski, Fjorela Xhyliu, Niyousha M. Shafie, and Jiarui Yan.

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