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Microarticle

Attenuation of ultrasound reflects orientation of carbon nanotubes in aqueous dispersion

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ABSTRACT

Ultrasound attenuates when propagating through aqueous dispersions of carbon nanotubes. We established a significant difference in the ultrasound attenuation frequency spectra for the nanotubes oriented either along or across the ultrasound beam. This effect can be used for calculating geometrical and rheological properties of nanofiber materials dispersed in liquids.

1. Introduction

Properties of liquid materials with dispersed non-spherical nano-objects depend strongly not only on their size, but on the objects' aspect ratio as well. There are not many analytical methods that can yield information of the aspect ratio for such objects. One of the most promising methods is ultrasound attenuation spectroscopy. This is a versatile tool for characterizing concentrated suspensions and emulsions [1], without diluting them. While the ultrasound attenuation has been extensively theoretically described and successfully applied for the determination of the size of spherical nano- and micro-particulates in suspensions, its applications to non-spherical nano-objects are limited. There are only a few theoretical and experimental studies describing the interaction of ultrasound with non-spherical objects in liquids [2–6]. These preliminary tests confirmed that ultrasound attenuation depends on the aspect ratio and orientation of non-spherical objects and, therefore, can be used for their characterization.

However, this effect has never been studied with enforcing particular orientation of the said objects. This idea was suggested in the paper [5], but has never been realized in practice, as far as we know. Modern acoustic spectrometers offer a simple way of orienting non-spherical objects in liquids by means of hydrodynamic flow. We take advantage of this feature and apply this method to such novel highly asymmetrical nano-objects as carbon nanotubes. This is the subject of this study.

2. Experimental

A 0.1% aqueous dispersion of single wall carbon nanotubes bundles with average number diameter of 8.1 ± 2.4 nm and length of 1.7 ± 0.1 μm, stabilized by sodium dodecyl sulfate (0.9%) was used in the experiment. Ultrasound attenuation of the dispersions was measured by acoustic spectrometer DT-1202 (Dispersion Technology, USA). The cylindrical measurement cell is equipped with a moving acoustic receiver and a stationary acoustic transmitter. The transmitter generates acoustic pulses at different frequencies from the range of 1–100 MHz. These pulses attenuate while passing through the dispersion. The receiver measures the intensity of these attenuated pulses. Software converts this intensity into the attenuation coefficient α according to the algorithm presented in the book [1].

The distance b between the transmitter and the receiver varied in the range of 0.3–8 mm with an average speed U of 1.3 ± 0.2 mm/s, determined by the specified receiver movement distance, measured by the acoustic spectrometer controller, and the movement time, measured by a stopwatch.

The motion of the acoustic receiver creates a hydrodynamic flow within the measuring cell. This flow orients carbon nanotubes differently depending on either closing the gap between the transmitter and receiver, or opening it. Next section describes this effect in detail.

3. Results and discussion

The measurements of ultrasound attenuation were made while either increasing (Fig. 1A) or decreasing the gap between the

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acoustic transmitter and the receiver (Fig. 1B). In both cases, a change in the gap causes an axisymmetric flow characterized by axial V_z and radial V_r components of the flow velocity. Such a flow leads to the preferential nanotube orientation determined by the direction of the receiver movement.

In the case of the decreasing gap (Fig. 1A), there is a decelerating axial flow of the dispersion $\left(\frac{\partial V_z}{\partial z} < 0\right)$ and an accelerating radial centrifugal flow of the dispersion out of the gap $\left(\frac{\partial V_r}{\partial r} > 0\right)$. Both of these processes make the nanotubes orient perpendicular to the axis of the measurement cell, or the ultrasound beam direction.

The deceleration of the axial flow and the acceleration of the radial flow of the dispersion are characterized by the average axial and radial flow velocity gradients:

$$\left\langle \frac{\partial V_z}{\partial z} \right\rangle \approx -\frac{U}{b}, \quad \left\langle \frac{\partial V_r}{\partial r} \right\rangle \approx \frac{U}{2b} \tag{1}$$

In Eq. (1) the velocity gradients are proportional to the speed of the receiver motion U and inversely proportional to the size of the gap b.

On the contrary, when the gap increases (Fig. 1B), there is an accelerating axial dispersion flow after the moving receiver and a decelerating radial centripetal dispersion flow. These processes make the nanotubes preferentially orient along the ultrasound beam direction. Components of the flow are characterized by the same Eq. (1), but with the negative speed: $U < 0$.

Cylindrical objects align along the flow direction in the accelerating flows [7], and an average speed of their evolution $\dot{\phi}$ is determined by the flow velocity gradient [8]:

$$\dot{\phi} = -\frac{3}{2}\frac{\partial V_x}{\partial x}\sin(\phi)\cos(\phi) \tag{2}$$

For the rate of the receiver movement of 1.3 mm/s the average values of the velocity gradients for accelerating and decelerating flows in accordance with Eq. (1) are equal to $0.7\ \mathrm{s}^{-1}$ for radial flow and $1.4\ \mathrm{s}^{-1}$ for the axial flow with a sign determined by the receiver movement direction. Using these data in the Eq. (2) the nanotubes' rotation angles to the flow direction are equal to 23° and 40° for the radial and the axial portions of the flow, respectively. As some of the nanotubes are acted upon consequently by the rotating forces on both portions of the flow, the total angle of their evolution can be estimated as the sum of the obtained angles, i.e. 63°. In other words, the nanotubes will be forced to orient perpendicular to the ultrasound beam when the gap closes and parallel to the beam when the gap opens. The maximum deflection angle of nanotubes from the perpendicular or parallel state, respectively, will be 27° (Fig. 1).

The frequency spectra of the ultrasound attenuation in the aqueous nanotubes dispersion with an orientation preferentially either parallel or perpendicular to the direction of the ultrasound beam are shown in Fig. 2. It is seen that these frequency spectra depend on orientations significantly in both shape and amplitude. The attenuation coefficient for the preferentially perpendicular orientation of the nanotubes monotonically increases with frequency. It becomes significantly higher than the attenuation coefficient for the parallel orientation at frequencies above 15 MHz. On the contrary, the frequency dependence of the attenuation coefficient for the parallel orientation of the nanotubes is a curve with a minimum at the frequency of 20 MHz, which may indicate the competition of different mechanisms of the ultrasound attenuation.

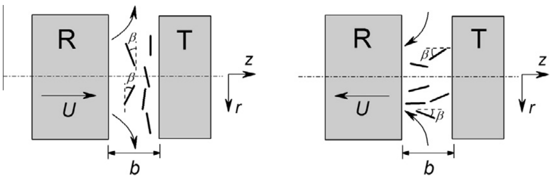

Fig. 1. Scheme of the experiment. (A) The acoustic receiver (R) moves toward the transmitter (T) with speed U, squeezing the nanotube dispersion out of the gap b. (B) The receiver moves away from the transmitter. Curved arrows in the gap show accelerating flows that orient the nanotubes perpendicular or parallel to the ultrasound beam with a maximum deflection angle β.

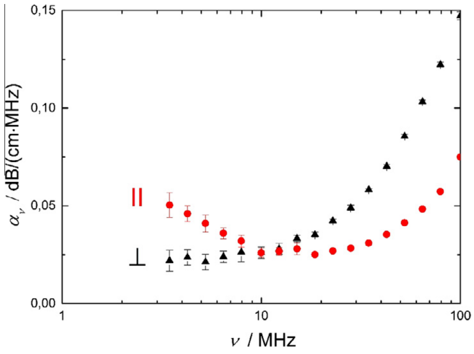

Fig. 2. Ultrasound attenuation spectra for aqueous dispersion of carbon nanotubes oriented preferentially perpendicular ($\perp$) or parallel ($\|$) to the ultrasound beam direction (average of seven measurements, attenuation spectra in water is subtracted).

There is a theory by Habeger [3] that describes these mechanisms. According to this theory attenuation should depend on the geometry of the dispersed objects (aspect ratio) and on their rheological properties. We suppose, that the application of the theory for fitting measured attenuation frequency spectra (raw data) with additional measurements of reference materials with different aspect ratios, validated by atomic force microscopy or transmission electron microscopy, would allow extracting information regarding geometrical properties of the cylindrical objects dispersed in liquid.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.rinp.2015.11.005.

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