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Characterization of orientation state of carbon nanotubes in shear flow

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Abstract

To characterize and understand carbon nanotube (CNT) orientation state in thermoset composite processing, we surface treated multi-walled carbon nanotubes (MWNT) and suspended them in vinyl ester resin. The surface treatment prevented clustering of the nanotubes and maintained homogeneously separate nanotubes in the suspension ensuring good dispersion quality. The suspension was subjected to shear flow in a micro channel, a nano channel and across a micro cylinder. transmission electron microscope (TEM) was employed to characterize the position of the nanotubes at various locations in the suspension. Second order orientation tensor description was used to describe the MWNT orientations in these flow fields in the 2-D plane. The degree of MWNT alignment was found to increase with increasing shear. However, we did not observe near perfect alignment, as one would expect in case of short fiber suspensions. Although MWNTs diameter is of the order of nanometers, we show by an order of magnitude analysis that Brownian motion is not significant. The MWNT orientations are maintained even after the shear force is discontinued.

Keywords: Orientation; Multi wall carbon nanotube; Vinyl ester

1. Introduction

Recently, great effort has been devoted to the synthesis and characterization of carbon nanotubes, due to the very high aspect ratio and promising physical properties for many applications. They are fullerene-based structures that can be viewed as a single sheet of graphite rolled into a cylinder of several microns in length and few nanometers in diameter [1–7]. The nanotubes can exist in two forms: multi-walled and single-walled. The multi-wall carbon nanotubes (MWNT) were the first to be discovered. They consist of concentric cylinders placed around a common central hollow area with a constant separation between the layers close to the graphite interlayer spacing (0.34 nm). Each individual cylinder can be characterized by a different helicity and has diameter ranging from 2 to 25 nm and length of several microns. The single walled carbon nanotubes (SWNT) were synthesized in 1993 when it was found that the addition of metals such as cobalt to the graphite electrodes in the arc evaporation method resulted in tubes with single layer walls [5]. A single wall nanotube is close to an ideal fullerene fiber and consists of a single cylinder extending from end to end with a narrow distribution in diameter range (1–2 nm). In 1991, Iijima [8] discovered CNT while inspecting the material deposited on the cathode during the arc-evaporation synthesis of fullerene. Since the invention of a large-scale synthesis method by Ebbesen and Ajaian in 1992 [9], systematic investigations and attempts have been made to understand their chemical structure, to improve their synthesis techniques and to analyze their relationship between structure and properties.

Carbon nanotubes (CNT) exhibit Young's modulus and tensile strength as high as 1 TPa [10] and 200 GPa [11], respectively, in addition to high thermal and electrical conductivities [12–14]. High aspect ratio, excellent mechanical, thermal and electrical properties make CNT a preferred candidate to manufacture high performance and conductive composites. Preliminary work in this field has shown some promise [14–21]. Sandler et al. found very low content of MWNT (about 0.005 wt%) made epoxy conductive [19]. As for enhancement of mechanic properties, Safadi et al. [20] mixed 2.5% of MWNT into polystyrene and obtained 100% improvement of its tensile modulus.

One way to manufacture polymer CNT composites, is to

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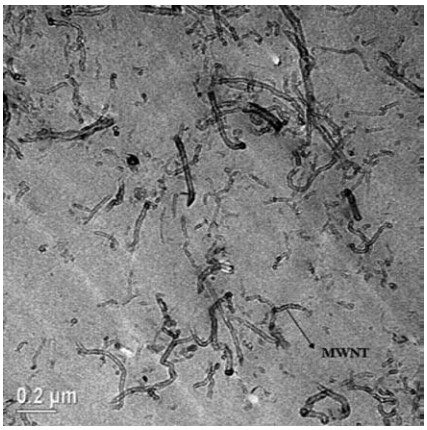

Fig. 1. TEM image of homogeneously separate oxidized MWNT (OMWNT) dispersed in vinyl ester.

inject the polymer suspension containing CNT into a mold cavity or force it through a die to form the shape of interest. The suspended CNT will connect with the resin and change orientation due to flow induced shearing of the suspension. The final composite microstructure will depend on how CNTs distribute, disperse and orient. There are four important parameters that describe the suspension characteristics: CNT dispersion, concentration, aspect ratio and orientation. Good dispersion of the CNT in the polymer matrix is a significant challenge in fabrication of CNT reinforced composites because the CNT, in their manufactured state, cluster together in any suspension due to the strong van der Waal's forces at that scale [22]. However, CNTs need to be dispersed homogeneously in the matrix so that the composite has uniform properties and can efficiently transfer load during structural excitation [15–18,21]. CNT concentration and CNT aspect ratio determine how easily CNTs can move and interact with each other to build inter connecting network, which can transfer heat and electrons faster to enhance composite thermal and electrical properties. Similar to short fiber-reinforced composites, CNT orientation state determines the anisotropic functionality of CNT composites. Thostenson et al. [18] found if MWNTs are orientated in one direction, storage modulus improved by 49%, compare to 10% in random orientated MWNT/PS composite. Liang et al. also found much higher electrical conductivity in aligned SWNT buckypaper than for the random case [23].

Hence, CNT orientation state plays a crucial role in defining the internal micro structure which will influence the composite physical and mechanical properties. In this paper, we explore two issues, (i) measurement of orientation state of CNT in flowing suspensions, (ii) quantification and correlation of the orientation state to the degree and amount of total shear undergone by the suspension. Unlike short fiber suspensions, as CNT cannot be seen by naked eye, the measurement techniques involve use of TEM.

1.1. Representation of orientation state

Before one can predict the orientation of these nanotubes in flow, one should be able to characterize and describe the orientation state. To represent the orientation state, one could use the orientation tensor description which has been successfully used to describe the orientation state of short fibers [24–26] and liquid crystal polymers [27].

However, one must measure the direction of each CNT to calculate the moments of the orientation distribution function in any given region. Due to the scaling difference between short fibers and CNT, it is more difficult to characterize CNT orientation state. The diameter of short fibers is of the order of 10 μm while CNT diameter is in the range 1–20 nm. Short fibers can be observed directly under optical microscope [28] and hence one can digitize their direction easily. But with CNT, no optical microscopy will be able to detect them. Thus other techniques, more commonly used with polymers, have been adopted to characterize CNT orientation state indirectly. Jin et al. used X-ray diffraction pattern to characterize alignment of CNT caused by stretching a polymer sample [29]. Haggenmueller et al. [30], Wood et al. [31] and Bhattacharyya et al. [32] applied Raman spectroscopy to determine the degree of CNT alignment in polymers. Hobbie et al. [33] created and developed a polarized optical measurement of CNT orientation state in sheared MWNT/water suspensions. Although X-ray, Raman spectroscopy and polarized light diffraction are helpful, they provide indirect results and no one has validated or calibrated these results with direct measurements of CNT orientation angles in the sample.

Our approach will be to characterize CNT orientation state by microtoming the composite. Transmission electron microscope (TEM) provides a way to observe CNT positions directly inside a composite sample. This is accomplished by slicing a thin section of thickness 80–200 nm from the composite sample and observing under TEM. Transmission of light permits one to detect all the CNTs present inside the section as shown in Fig. 1. This will allow one to measure the orientation angle of each nanotube and use the tensorial description to characterize the CNT orientation state.

A more fundamental challenge is to understand how the CNT orientation state changes as the suspension is made to flow through various ducts, channels and into molds. To process CNT composites one has to mix them with a polymer resin and inject or compress the suspension into molds or through dies to form them into various shapes. Shear is the dominant mechanism during such flows. We expect, just as in case of short fiber suspensions, that shear flow will align the CNT in the direction of shear. Shear flow induced CNT orientation is reported by others as well [18,34]. However, not much work has been done to quantify the orientation state as a function of the shear rate and total shear. A possible promising application is to create new functional and high performance hybrid composites by

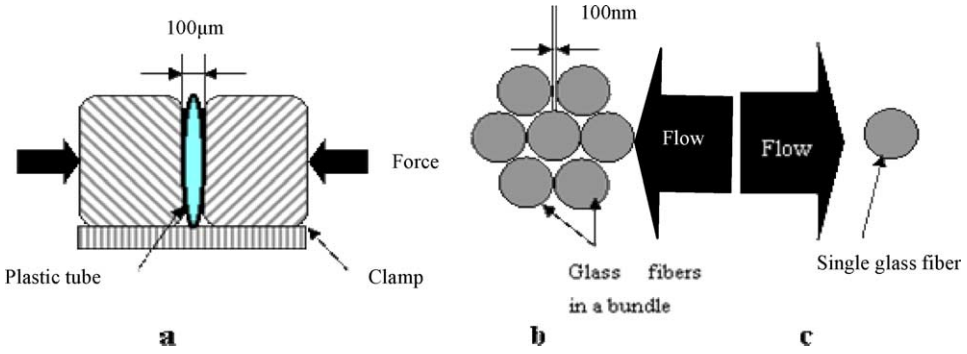

Fig. 2. (a) 100 μm micro channel created by clamping a plastic tube, (b) 100 nm nano channel formed by gap between glass fibers in a tow, (c) flow of OMWNT suspension across a cylinder (glass fiber).

adding small amounts of CNTs to a thermoset resin such as epoxy or vinyl ester and injecting the suspension into a glass or carbon fiber perform [22]. Naturally, one can expect more complicated flow fields to be generated during such hybrid composite processing which will affect CNT orientation field. Hence, the need to understand how CNT orientation state changes during flow.

An important question is the relationship between the degree of shear and the alignment of CNTs. Also, after the shear is discontinued and before suspension solidifies or cures, will Brownian motion and CNT relaxation randomize the orientation state and to what extent? Unlike short fibers, one cannot automatically neglect Brownian motion due to the much smaller scale of the nanotubes. Finally, the approach to address nanotube flexibility on the orientation state will be explored.

To address these questions, we characterized the CNT orientation state in three flow fields, all of them exhibiting certain degree of shear (i) flow in micro channel, (ii) flow in nano channels and (iii) flow across a micro cylinder. These are central flow fields we expect to encounter during fabrication of CNT/thermoset polymer composites and hybrid glass fiber/CNT/polymer composites [22]. The challenge is how to freeze the orientation state of the nanotubes without allowing the nanotubes to relax or recoil. Thermoset resins were used as suspending fluid to cure the composite which was examined under TEM (JEM 2010f) to characterize the CNT orientation state. To quantify the CNT orientation state, we measured the average angle of each CNT seen in the TEM image and used second order orientation tensors to describe the CNT orientation state. To test the effect of Brownian motion and nanotube relaxation time scale, we cured one sample in less than five minutes which froze the CNT orientation state quickly, preventing it from being disturbed by the Brownian motion or any other relaxation mode and compared it with a slow cured sample which took over 24 h to freeze the nanotube orientations. The change in the CNT orientation state should allow us to gauge the importance of the Brownian motion and CNT relaxation. Simple theoretical analysis was used to estimate the effect of Brownian motion.

2. Experimental

2.1. Preparation of carbon nanotube suspension

For economic reason, we used multi-walled carbon nanotube (MWNT) for our suspensions. The MWNT made by CVD (>95%) were purchased from the ILJIN nanotech Company, Korea. The diameters of the nanotubes were of the order of 10–20 nm and the length was between 10 and 15 μm, but after surface treatment, the length reduced to about 1 μm. The resin used was vinyl ester called Derakane 441–400 from Dow Chemical Company.

To separate and homogeneously disperse MWNT, its surface was oxidized [22,35,36]. First, 300 g of MWNT were refluxed in a mixture of concentrated nitric acid and sulfuric acid (1:3) 120 ml at 140 °C for 30 min and oxidized MWNTs (OMWNTs) were washed with water until neutral pH value was obtained. These OMWNTs were mixed with acetone and pulsated in ultrasonic water bath for 30 min. Next, vinyl ester was added and the suspension was mechanically stirred at 1000 rpm until the acetone evaporated. Hardener may be added to the well dispersed suspension to cure and freeze the microstructure of the composite. Fig. 1 showed the homogeneously separate MWNTs dispersed in vinyl ester under a high resolution TEM.

2.2. Carbon nanotube orientation in channels

To investigate the role of shear force on the alignment of nanotubes, we generated Poiseuille flow by forcing OMWNT/vinyl ester suspension to flow into micro and nano channels. The micro channel was created by clamping a plastic tube into a 100 μm gap (Fig. 2(a)). The OMWNT/vinyl ester suspension was injected into the gap. Nanochannels were created by gaps between 15 μm diameter glass fibers in a hexagonal arrangement within a fiber tow [22]. The channel was of the order of 100 nm as shown schematically in Fig. 2(b). When the suspension impregnates into the glass fiber tow, it wicks into these nano channels. After the suspension was injected into the micro

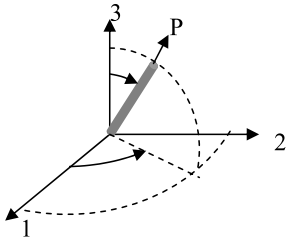

Fig. 3. Definition of the orientation of a single fiber in a Cartesian coordinate frame.

or nano channel, it was cured quickly to freeze the OMWNT orientation, reducing the influence of the Brownian motion and relaxation of nanotubes from disturbing the orientation created by the shear flow. The solid sample was sliced into very thin sections of about 100 nm thickness and observed under TEM. When the matrix contains glass fiber, it makes the cutting procedure very difficult. This is a tedious microtoming exercise but it did allow for the first time, to observe directly the CNT orientation state in hybrid glass fiber/OMWNT/polymer composite samples.

2.3. Carbon nanotubes orientation around a cylindrical fiber

Hybrid composites are manufactured by placing glass or carbon fiber performs in a mold and injecting a thermoset resin containing nanotubes to fill the spaces between the fibers. As the CNT suspension enters the mold, it has to flow across cylindrical fibers of the perform to occupy the empty spaces between them. Thus, it is important to understand flow of CNTs across cylindrical fibers. We would expect the carbon nanotubes to change orientation as they flow across a cylindrical fiber. We used a vinyl ester suspension containing well dispersed CNT with diameters of the order 10–15 nm to flow across a single glass fiber of diameter around 15 μm, changing the orientation state of the nanotubes (Fig. 2(c)). The OMWNT/vinyl ester suspension is cured before observing their orientation state under TEM. To compare with short fiber behavior, we also made short carbon fiber suspension flow across a cylinder. The carbon fiber diameter was about 15 μm and the diameter of cylinder was about 15 mm. This allowed us to draw a similarity between the nanotubes suspension flow around a fiber with flow of short fiber suspensions across a cylinder, where the ratio of the fiber diameter to the cylinder diameter is roughly of the same order as the nanotube diameter and the glass fiber diameter. Orientation state of OMWNT was observed and quantified under the TEM and was compared with orientation of short fibers flowing across the cylinder.

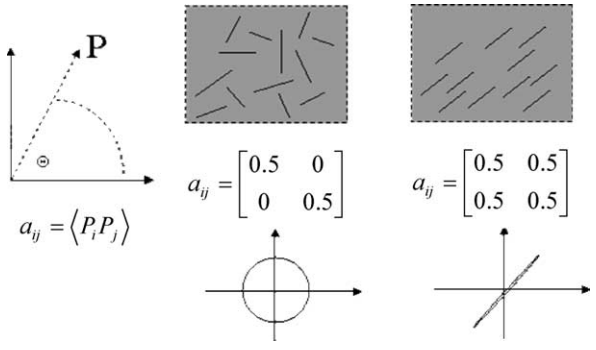

Fig. 4. Illustration of second order orientation tensor and use of an ellipse to graphically represent the orientation state in a planar region.

2.4. Orientation state description

Orientation of each carbon nanotube can be characterized by a unit vector **P** placed in the average direction of its length as shown in Fig. 3. However, as there will be many fibers or nanotubes at a selected location as shown in Fig. 1, it will be important to use a description that will embody many different directions.

The most basic description is the probability distribution function. If we consider a small region from the suspension we would expect to see many fibers with different orientations. The probability distribution will give us a measure of the state of fiber orientation at that location. Thus one can define $\phi(\theta,\Psi)\sin\Psi \mathrm{d}\Psi \mathrm{d}\theta$ describe the probability of a fiber being orientated between the specific angles θ and $\theta+\mathrm{d}\theta$ and angles Ψ and $(\Psi+\mathrm{d}\Psi)$ (Fig. 3). Here, $\sin\Psi \mathrm{d}\Psi \mathrm{d}\theta$ is the increment in area on the surface of the unit sphere.

The distribution function must satisfy two conditions. First, one end of the fiber is the same as the other end. Thus, φ must have the property of periodicity,

$$\varphi(\theta,\psi) = \varphi(\theta+\pi, \pi-\psi) \tag{1}$$

The other condition arises from the physical reality that all fibers have some direction, so the integral of the distribution function over all directions can be normalized to be unity.

$$\int_0^{2\pi}\int_0^{\pi} \varphi(\theta,\psi)\sin\psi \mathrm{d}\psi \mathrm{d}\theta = 1 \tag{2}$$

One can also carry out orientation averaging of any function. The orientation average of any function $g(\theta,\Psi)$ is given as

$$\langle g \rangle \equiv \int_0^{2\pi}\int_0^{\pi} \varphi(\theta,\psi) g(\theta,\psi)\sin\psi \mathrm{d}\psi \mathrm{d}\theta \tag{3}$$

Thus $\langle g \rangle$ is the average of g over all directions, weighted by the probability distribution function.

One can also use the second moments of the probability distribution function to describe the fiber orientation state in a selected region. The second moments are called orientation tensors and are defined as

$$\langle a \rangle = \langle p_i p_j \rangle = \oint p_i p_j \varphi(P) \mathrm{d}P \tag{4}$$

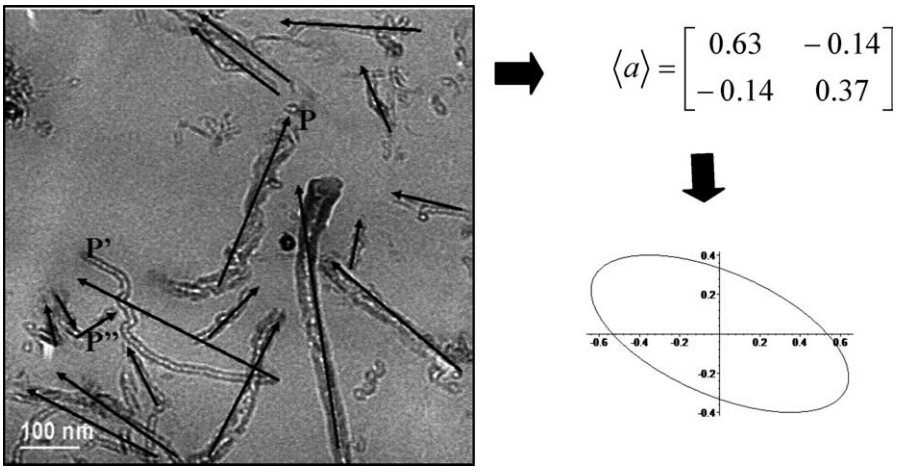

Fig. 5. Characterization of MWNT orientation state in one TEM image by second order tensor and ellipse.

here **P** is the unit vector along the length direction of the fiber or the tube. P_i and P_j are components of this vector along the coordinate direction. Details of this description can be found in [24–26].

In this paper, we applied the orientation tensor in the 2-D plane. Thus in two dimensions, as seen from Fig. 4 $p_1 = \sin\theta$, $p_2 = \cos\theta$

It is evident that the tensor is symmetric, and therefore,

$$a_{ij} = a_{ji} \tag{5a}$$

Also as probability function is normalized, therefore

$$a_{ii} = 1 \tag{5b}$$

We adopted this description from fibers to characterize a two dimensional MWNT orientation state.

To experimentally measure the components of the orientation, each orientation angle of the nanotubes was measured in the TEM image. If the TEM image contained N carbon nanotubes, a_{ij} in that region is given by [37]

$$a_{ij} = \frac{1}{N}\sum_{k=1}^{N} p_i^k p_j^k \tag{6}$$

From Fig. 4, one can note that if one used Eq. (6) to measure the components of the orientation tensor as shown for two extreme cases of random orientation and for aligned orientation, the values of the various components will be given as shown in the two matrices. Note that due to symmetry ($a_{12}=a_{21}$) and normalization ($a_{11}+a_{22}=1$), only two of the four components in two dimensions are independent.

2.5. Graphical representation

One can use the components of the orientation tensor in two dimensions to draw an ellipse to describe orientation state graphically. From the TEM image, we associate a vector with the average direction of each nanotube. Using Eq. (6), we can calculate the a_{ij} components. Next, we find the principal values of the second order orientation tensor by diagonalizing it from $\langle a \rangle$ to $\langle a \rangle^*$ using Eq. (7)

$$Q^* A^* Q^T = \begin{bmatrix} \cos(\theta) & \sin(\theta) \\ -\sin(\theta) & \cos(\theta) \end{bmatrix} \begin{bmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{bmatrix} \begin{bmatrix} \cos(\theta) & \sin(\theta) \\ -\sin(\theta) & \cos(\theta) \end{bmatrix}^T = \begin{bmatrix} a_{11}^* & 0 \\ 0 & a_{22}^* \end{bmatrix} = \langle a \rangle^* \tag{7}$$

The diagonal components of $\langle a \rangle^*$, a_{11}^* and a_{22}^* will be the length of major and minor axes of the ellipse. In rotation matrix $\langle Q \rangle$, θ is the angle of major axis rotated anticlockwise from horizon axis X. Therefore, in the ellipse, the major axis represents the preferred orientation of nanotubes in the region. The value of the major and minor axes of the ellipse represents the degree of orientation in that direction [25]. Thus an elongated ellipse will signify higher degree of alignment in the direction of the major axis, whereas a circle will signify no particular preference of orientation [24] as shown in Fig. 4.

The experimental procedure used to characterize MWNT orientation state is as follows. We first have to obtain the TEM images of the frozen composite to be able to clearly see the MWNTs and their orientations. Two issues need to be addressed before one can report the orientation state. First is to account for the MWNT length distribution. The length distribution may be due to the various lengths of available nanotubes. However, because MWNT may be cut short during microtoming for TEM, the length in the TEM image may not represent the real length. Hence, we normalize each single MWNT to $|P| = \sqrt{p_1^2 + p_2^2} = 1$ so as to not influence the orientation state due to the MWNT length effect. The other issue is the flexibility of MWNT. In Fig. 5, we can see most MWNT are curved. If the curvature of one MWNT is small, we draw an approximate P to represent the major direction vector of one curved MWNT, as shown by P and P' in Fig. 5. In case of large curvatures, we divide it into more than one direction vector, as shown

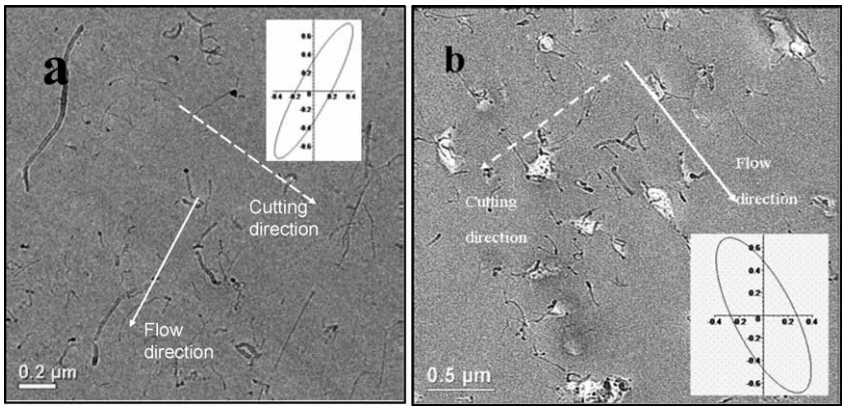

Fig. 6. TEM of oxidized MWNT near the edge of the micro channel: sample (a), suspension cured within 5 min sample (b), suspension cured after 24 h after the flow was discontinued.

by P'' in Fig. 5. Thus in Fig. 5, we calculate the orientation state $\langle a \rangle$ for the picture presented and also draw the ellipse to represent the orientation state and show the TEM image for comparison purposes. From the ellipse, one can gauge the preferred fiber orientation direction and the magnitude of this alignment.

3. Results and discussion

3.1. MWNT orientation in micro channels and Brownian motion effect

Oxidized MWNT/vinyl ester suspension was injected into a 100 μm channel creating Poiseuille flow with high shear along the walls of the channel. The flow rate was about 20 mm/s. The flow in the channel could be approximated as a 2-D Poiseuille flow between two parallel plates, and the maximum shear rate is given $\gamma = 6U/h$, where U is the average flow rate and h is the distance between the two plates. In this channel flow, h is the separation between the plates. We could estimate that the maximum shear rate was about $1000\,s^{-1}$. Once the channel is filled with the suspension, the flow stops and there is no more shear on the nanotubes. The question is will the orientation near the wall created by the shear remain unperturbed or will the Brownian motion or other relaxation mode tend to randomize it? To answer this question, we created two different samples: sample (a) in which the curing of the resin was accomplished within 5 min from the injection stage, freezing the orientation state of the nanotubes and sample (b), which was allowed to stay in the liquid state in quiescent state for 24 h before curing it. The purpose of slow cure was to evaluate if the Brownian motion and relaxation would disturb and randomize MWNTs orientation if we allow Brownian motion sufficient time to affect MWNT orientation after the shear was discontinued. Fig. 6 shows the orientation state of MWNTs in the two samples. Both samples show that most of the nanotubes are aligned as depicted by the elongated ellipse. The elongated ellipse suggests that there is significant alignment of MWNTs in the shear direction. This is consistent with what we would expect with rigid short fiber suspended in a viscous fluid. There is no clear difference between the orientation states in the two samples. This suggests that at the nano scale, Brownian motion has no significant effect on randomizing the orientation state, and we do not observe any MWNT relaxation at least on the scale of a day. While preparing the TEM sample, a diamond knife was used to cut the sections and this could align some of the MWNTs along the cutting direction. To eliminate such noise caused by diamond knife cutting procedure, the cutting direction we chose was perpendicular to the flow direction.

To estimate the Brownian motion effect theoretically, we conducted an order of magnitude analysis. As shown by a schematic in Fig. 7, Brownian motion is caused due to the random bombardment from suspension fluid molecules on MWNT. The single MWNT may be considered as a long rod, in constant collision with vinyl ester molecules. Brownian motion would be significant if MWNTs move extensively and randomly due to collisions with the vinyl ester molecules. Two factors can downplay the role of Brownian motion: (i) if the mass of MWNT molecule is too large compared to vinyl ester molecule, and (ii) if the

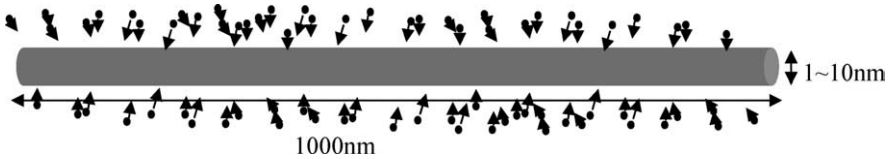

Fig. 7. Schematic of Brownian motion caused by bombardment of suspension fluid molecules on the surface of MWNT.

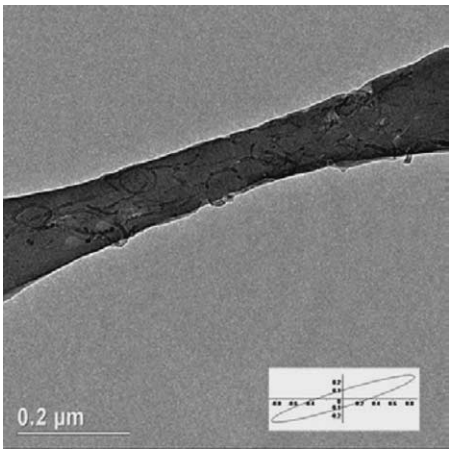

Fig. 8. TEM image of MWNT orientation in 100 nm channel: most MWNTs were aligned along the flow direction. The ellipse below represents the orientation state of the nanotubes. More nanotubes are aligned in the direction of the flow in the nano channel than observed in a micro channel.

surface of MWNT is comparatively large which will make the bombardment frequency on MWNT surface very high and collision effects on an average could cancel each other.

The mass of average vinyl ester molecule can be derived from mole mass, usually of the order of 1000 g/mol [38]. Dividing it by the Avogadro's number 6.02×10^{23}, the average mass of a vinyl ester molecule is of the order of $M_v \approx 10^{-21}$ g.

The mass of average MWNT molecule can be derived from its density. Considering the average size of MWNT used in our experiments was $D=10$ nm in diameter and $L=1000$ nm in length with average MWNT density is $\rho=2.6$ g/cm^3 [39]

$$M_{\mathrm{MWNT}} = \rho\pi\frac{D^2}{4}L \approx 10^{-16}\ \mathrm{g}$$

Based on the law of momentum conservation

$$M_v V_v = M_{\mathrm{MWNT}} V_{\mathrm{MWNT}} \tag{8}$$

We can easily note that

$$\frac{V_{\mathrm{MWNT}}}{V_V} = \frac{M_V}{M_{\mathrm{MWNT}}} \approx 10^{-5} \tag{9}$$

From mean velocity equation of molecules in fluid [40]

$$\bar{V}_v = \sqrt{\frac{8kT}{\pi m}} \tag{10}$$

where k is Plank constant, T is temperature, m is molecule mass, we can estimate the mean velocity of vinyl ester molecules to be of the order $\bar{V}_v \approx 3$ m/s. Because the mass of M_{MWNT} is too large as compared to M_v and as $\bar{V}_v$ is small, movement of a MWNT due to a collision with a vinyl ester molecule will be insignificant.

Turning to bombardment frequency, we can start from gas molecule velocity distribution function, known as Maxwellian equation f in [41].

$$f = \frac{N}{(2\pi kT/m)^{2/3}}\exp\left(-\frac{V_x^2+V_y^2+V_z^2}{2kT/m}\right) \tag{11}$$

where N is number of molecules per unit volume, V_x,V_y,V_z are velocity components. Number of molecules F that are incident on unit area per unit time is given by [39]

$$F = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{0}^{\infty} V_z f \mathrm{d}V_x \mathrm{d}V_y \mathrm{d}V_z = \frac{NkT}{\sqrt{2\pi mkT}} \tag{12}$$

Frequency p of vinyl ester molecules hitting on MWNT wall per unit time is going to be of the order

$$p = FS = F(\pi DL) \approx 10^{12}/\mathrm{s} \tag{13}$$

Considering in liquid case, p may be 2 order smaller, $p\sim10^{10}$.

Because the wall surface of a MWNT is large compared to the vinyl ester molecule, the frequency of vinyl ester molecules striking the Nanotube wall is very high, of the order of 10^{10}. This will cause on an average for all collisions to cancel each other and net effect on moving the MWNT will be negligible.

Thus, due to the mass difference between vinyl ester molecule and the MWNT, and due to the large surface area of the MWNT, Brownian motion effect on MWNT is not significant even on the nano scale. This is in agreement with result of MWNT alignment observed in Fig. 6. Moreover, MWNT aligned orientation state did not change 24 h after the shear was discontinued suggesting that Brownian motion does not play a significant role in the dynamics of nanotube motion and orientation.

3.2. MWNT orientation in nano channels

The nano channel is about 100 nm, which is formed by gaps between glass fibers in a glass fiber bundle. It was found that only homogeneously separated oxidized MWNTs could impregnate into such small nano channels created by the gap between the hexagonally packed glass fibers [22]. As in a micro channel, shear flow is generated substantially when MWNT suspension flow through these nano gaps or channels. MWNTs did align in the flow direction due to the shear force in nano channels, as shown in Fig. 8. The flow rate was about 2 mm/s, thus the maximum shear rate was about $10^5\ \mathrm{s}^{-1}$. Comparing Fig. 8 with the alignment obtained in a micro channel as shown in Fig. 6, the degree of MWNT alignment in a nano channel was much higher than in a micro channel. This may be attributed to the higher shear rate in the nano channel ($10^5\ \mathrm{s}^{-1}$) than in micro channel ($10^3\ \mathrm{s}^{-1}$) and the fact the nanotubes are flexible so one would not expect tumbling effect that one observes for short rigid fibers near a wall [42].

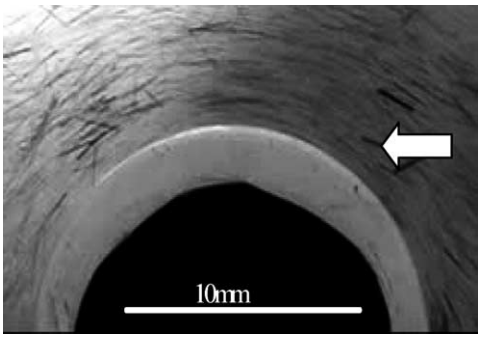

Fig. 9. Photo of short carbon fiber suspension flow around a cylinder. The black lines are carbon short fibers.

3.3. Flow across a cylinder

When MWNT suspension flows across a cylinder, in this case a single glass fiber, shear flow around the cylinder would also affect MWNT orientation. We cured the flowing suspension along with the glass fiber and used TEM to characterize 32 regions along the circumference of the fiber. In each region we measured the orientation angle of every nanotube we could see and calculated the second order orientation tensor for each region. These values are represented by ellipses in Fig. 10. It can be seen from the figure that most of the orientation is in the circumferential direction as most of the shearing takes place in that direction. This is similar to short fibers flowing past a cylinder as shown in Fig. 9. The similarity between MWNTs alignment on nano scale and short fibers alignment on micro scale confirms the influence of shear on orientation. The flexibility of the nanotubes will definitely cause quantitative deviations from the near perfect orientation state we would expect from short rigid fibers however it is clear that shear does play a dominant role in the alignment of the carbon nanotubes (Fig. 10).

4. Conclusions

We were able to create carbon nanotubes suspension that had homogeneously separated MWNTs dispersed in the

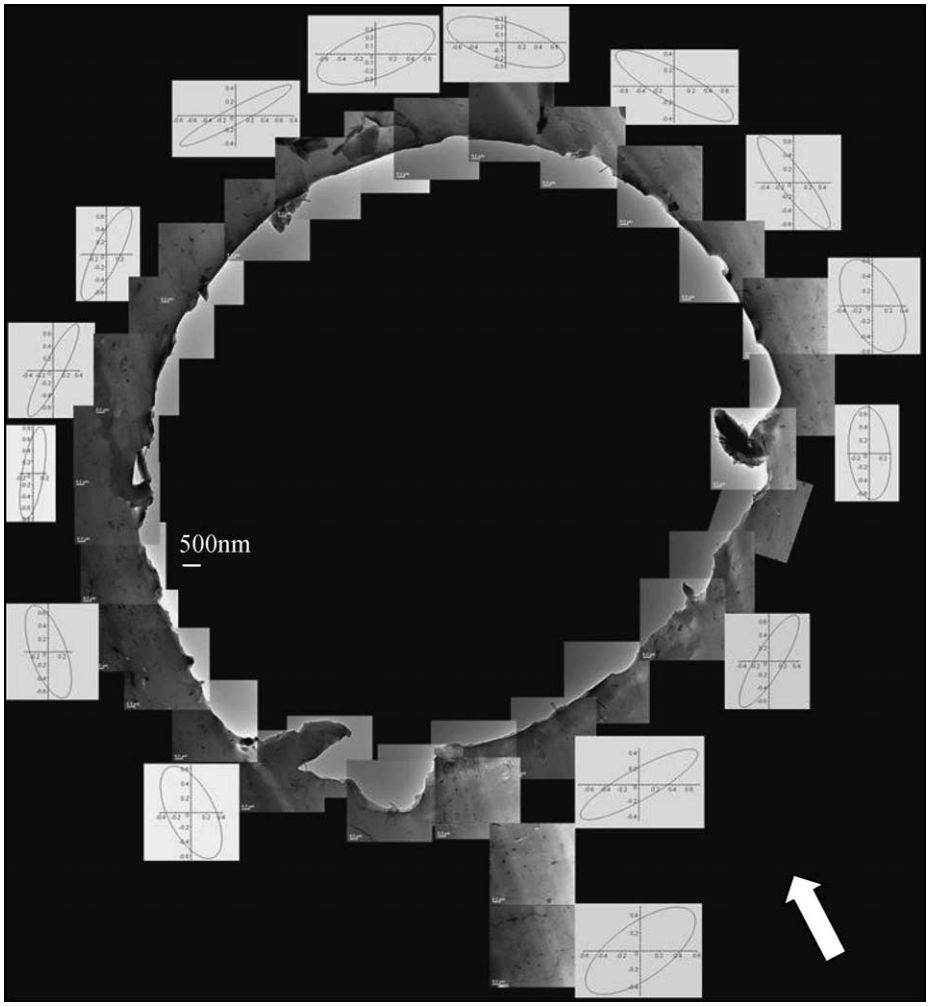

Fig. 10. TEM image of MWNT suspension flowing across and around a single glass fiber. Orientation ellipses indicate that MWNT preferred orientation were along the circumferential direction.

suspension to address the role of shear on orientation of these tubes. We used vinyl ester as the suspending fluid and were able to freeze the samples and observe the MWNT orientation states in shear flow and quantitatively characterize MWNT orientation state using TEM. Second order orientation tensors were used to quantify the orientation state of the nanotubes at a selected location. It was observed that shear forces do align MWNTs in the flow direction. The extent of alignment of MWNTs was a function of the shear rate. This was demonstrated by characterization of MWNT orientation in shear flow in a micro channel, nano channel and across a cylinder. There are similarities between MWNTs alignment and short fiber alignment in shear flow despite order of magnitude difference in scaling. The similarity should prove useful when developing models to describe the dynamics of carbon nanotube motion in shear flows. The Brownian motion was not found to have a significant effect to randomize MWNT orientation nor was any MWNT relaxation observed after the shear force was discontinued.

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