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Research Article

Characterization and Alignment of Carbon Nanofibers under Shear Force in Microchannel

Jinshan Yang,[1] Shaoming Dong,[2,3] David Webster,[4] John Gilmore,[4] and Chengying Xu[1]

[1] *Department of Mechanical Engineering, Florida State University, Tallahassee, FL 32310, USA*
[2] *State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China*
[3] *Structural Ceramics and Composites Engineering Research Center, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China*
[4] *Department of Mechanical and Aerospace Engineering, University of Central Florida, Orlando, FL 32816, USA*

Correspondence should be addressed to Chengying Xu; cxu@fsu.edu

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This work presents a novel method to align CNFs by using shear forces in microchannels. Effect of two different microchannel sizes (1 mm × 0.1 mm and 1 mm × 0.2 mm) on CNFs alignment is investigated. SEM images of CNFs preform display significant alignment by both microchannels, which can be interpreted using a second-order alignment tensor and a manual angle meter. In the second-order alignment tensor description, an elongated ellipse can signify high degree of alignment in the direction of the major axis. When the microchannel size is 1 mm × 0.2 mm, the lengths of major and minor axes of the ellipse are 0.982 to 0.018. An angle meter manually shows that 85% of the CNFs are aligned in the direction between 60° and 90° when the microchannel is 1 mm × 0.2 mm. Both methods can demonstrate that better alignment of CNFs can be obtained using the 1 mm × 0.2 mm microchannel.

1. Introduction

One-dimensional carbon materials such as carbon nanotubes (CNTs) and carbon nanofibers (CNFs) have attracted extensive interest due to their superior properties such as high strength and modulus, high aspect ratio, and excellent electrical and thermal conductivity [1–4]. It has initiated much research on the utilization of these one-dimensional materials as unique and superior reinforcements in polymer, ceramic, and metal composite material systems [5–10].

In actual applications, however, CNTs and CNFs composites have failed to display their full potential and the measured properties have fallen far below the theoretical predictions. Obstacles, such as uneven dispersion and lack of alignment, are central to this failure [11, 12]. They can cause low loading and poor interfacial bonding between the matrix and these one-dimensional reinforcements. The properties of CNTs and CNFs are significantly better along the long axis direction in comparison to those displayed in the radial direction. Utilization of their enhanced properties depends on the directional axes of these one-dimensional materials. Aligning CNTs or CNFs along the long axis direction is critical to optimizing their remarkable properties [13].

In the past decades, several methods have been investigated to align CNTs or CNFs. Some researchers focus on aligning CNTs directly during the synthesis process by CVD to create a CNTs array or forest [14, 15]. CNTs fibers can be spun directly from the CVD synthesis zone [16]. The aligned CNTs films or sheets obtained using this spinning method have significant impurities, however, as CNTs with different diameters and chiralities (as well as the catalysts) are mixed together [17]. Another method involves dispersing CNTs in a solvent and using magnetic field, gas flow, electrical field, shear flow in liquid polymer matrix, or mechanical force techniques to prepare aligned CNTs sheets [18–22]. Most of these solvent-based methods are low-cost (except for the magnetic field method), yet the need for improved surface uniformity and preparation speed, among other concerns, provides ample motivation to develop and refine new methods to prepare aligned CNTs or CNFs films.

In this paper, we detail the development of a novel and low-cost method to align CNFs by shear force in microchannels to prepare large CNFs films. This method can create uniform, thickness-controlled CNFs films, as well as other one-dimensional materials such as CNTs, on a large scale to take full advantage of these one-dimensional materials in high performance composite materials. The effect of microchannel size on the alignment of CNFs is analyzed with the help of a second-order alignment tensor description and a manual angle meter method.

2. Materials and Methods

Commercial carbon nanofibers (PR-19, Pyrograf Products, Inc., USA) with a diameter of ~100 nm and a length of 30–100 μm were used in our research and poly(sodium 4-styrenesulfonate) (average M_w ~ 70000, Sigma-Aldrich Co. LLC, USA) was used as the surfactant for dispersing CNFs in water. CNFs were mixed with poly(sodium 4-styrenesulfonate) in a mass ratio of 1 : 2 and the concentration of CNFs in water was controlled to 1 mg/mL. The mixture was ultrasonicated by a high intensity sonicator (Q500, Qsonica, LLC, USA) for two hours to prepare CNFs suspension.

In this technique, our alignment system was specifically designed and built using a microchannel to control the suspension as it flows through the nozzle. A schematic diagram of the platform design used to prepare the aligned CNFs preform was shown in Figure 1(a). The CNFs suspension was placed into a syringe and a programmable syringe pump (NE-1000, New Era Pump Systems, USA) was used to accurately control the flow rate of the suspension and the volume of the CNFs suspension dispensed. CNFs alignment was achieved by the shear stress generated during the suspension flow through the microchannel. The microchannel was expected to have great impact on the alignment of CNFs, so the effect of small microchannel sizes (1 mm × 0.1 mm and 1 mm × 0.2 mm) on CNFs alignment was investigated. The channel design was shown in Figure 1(c). This CNFs suspension was laid layer-by-layer to create preform samples of varying thicknesses, as shown in Figure 1(d). Each layer overlapped the previous layer in an offset pattern to enable the preform to maintain its structure as unified single piece.

The microstructure of CNFs preforms was analyzed by scanning electron microscopy (SEM, Zeiss ULTRA-55 FEG, Carl Zeiss SMT AG Company, Germany). The CNFs alignment state was described by one distribution function, in which the second moments can be referred to as the alignment tensor. The degree of CNFs alignment was also measured manually with an angle meter.

3. Results and Discussion

In the research, we propose the development of a simple and novel technique to create preforms with aligned CNFs. Several factors can be modified to obtain the optimized condition to prepare the aligned CNFs preforms, such as the microchannel size, flow speed, and the channel move speed controlled by the motor. The flow speed and channel move speed are set to 10 mL/min and 100 mm/s separately to study effect of the microchannel on CNFs alignment. As shown in Figure 1(b), the channel design consists of two parts, a larger pipe milled by a computer numerical control (CNC) machine and a small microchannel milled by micromachining. The top port of the large pipe is the inlet for the CNFs suspension, which can flow through the big channel and out the bottom port into the microchannel. The microchannel is expected to have a big impact on the alignment of CNFs.

Figure 3(a) shows the optical image of the CNFs preform with the filter paper. After they were dried in an oven, the preforms were peeled off from the filter paper. Samples 1 and 2 meanthe CNFs preforms prepared by 1 mm × 0.1 mm and 1 mm × 0.2 mm microchannels separately. Figure 2 shows the SEM images of CNFs within three preform samples created under different conditions (random state through vacuum process; aligned by the 1 mm × 0.1 mm microchannel; and aligned by the 1 mm × 0.2 mm microchannel). It can be found that the microstructures of the random-state CNFs preform reveal large spaces between nanofibers and many aggregations, while the CNFs preform samples prepared by utilizing the 1 mm × 0.1 mm and 1 mm × 0.2 mm microchannels exhibit denser CNFs networks with more evenly dispersed CNFs possessing clearly noted alignment. In characterizing the alignment state of CNFs, it is assumed that each CNF is uniform in length and diameter and that the CNFs preforms have the same microstructures at the base and the surface so that the characterization of CNFs alignment from the surface can be extended to the entire preform.

One distribution function can be used here to describe the CNFs alignment state, in which the second moments can be referred to as the alignment tensor. More details can be found in included references [23, 24]. As shown in Figure 3(b), the alignment state of each CNF can be characterized by a unit vector $\vec{P}$ placed in the direction along its length. In this research we applied the alignment tensor in the xy plane ($\varphi = 90^\circ$), where p_i and p_j are the components of the vector along the coordinate directions x and y separately; and $\langle a \rangle = \langle p_i p_j \rangle$, in two dimensions $p_1 = \sin\theta$ and $p_2 = \cos\theta$. These relationships can be derived in (1) as each alignment angle of the CNFs is experimentally measured from the SEM images. The parameters of alignment tensor are based on the measurement of the CNFs in the gridded zones in SEM images statistically. In the calculation, the SEM images of CNFs preforms are gridded into multiple zones and CNFs preforms are assumed to have the same microstructures from the base to the surface. Consider the following:

$$\begin{aligned} a_{11} &= \frac{1}{N}\sum_{n=1}^{N}\sin^2\theta_n, \\ a_{12} &= \frac{1}{N}\sum_{n=1}^{N}\sin\theta_n\cos\theta_n, \\ a_{22} &= \frac{1}{N}\sum_{n=1}^{N}\cos^2\theta_n. \end{aligned} \tag{1}$$

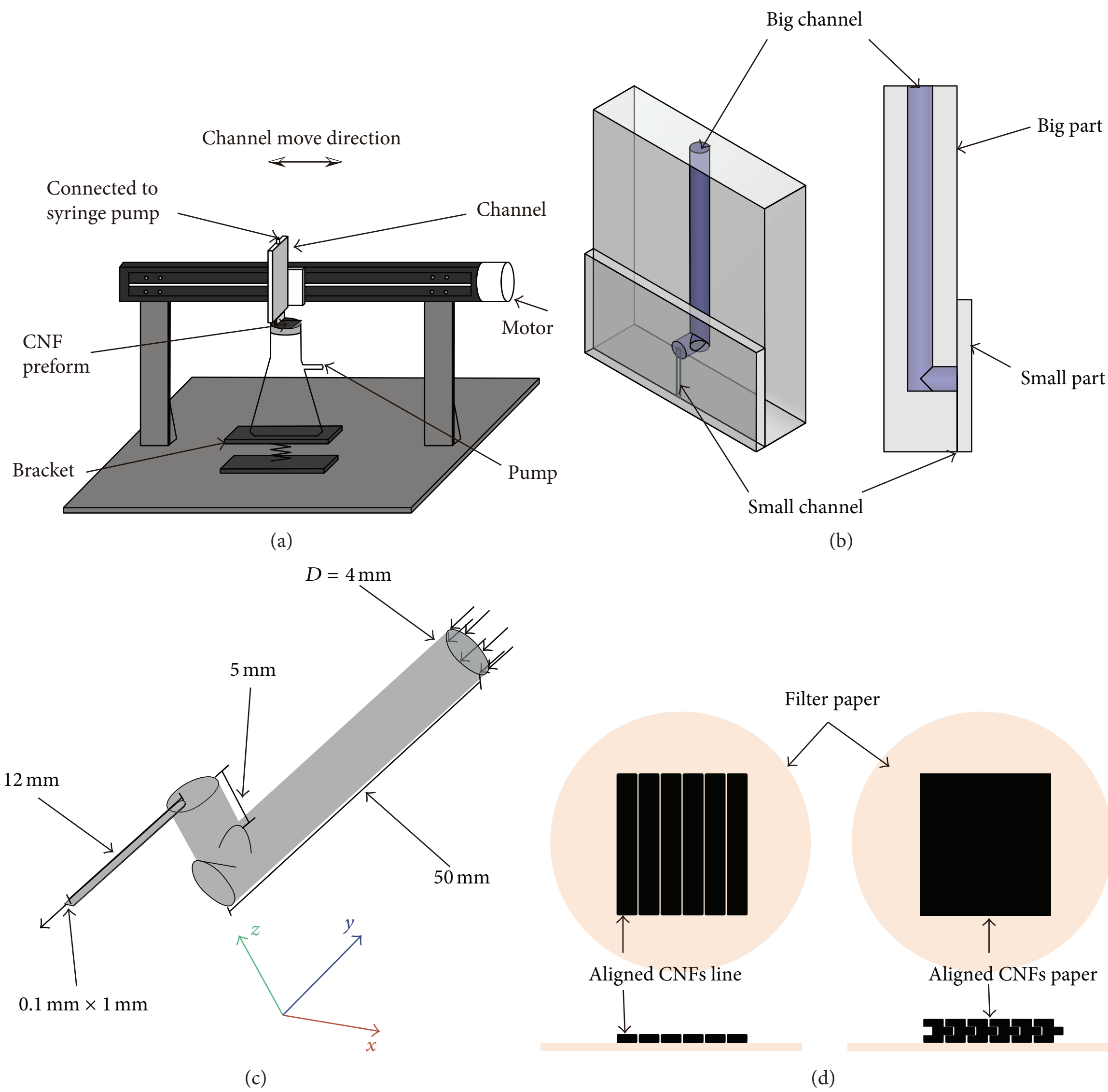


Figure 1: CNTs alignment design: platform, channel, and architecture. (a) Schematic diagram of the platform design used to prepare aligned CNFs preform; (b) channel design with two different pieces, big part has a drilled-cylinder nozzle ($\Phi = 4$ mm) and small piece is milled to form the microchannels (1 mm × 0.1 mm and 1 mm × 0.2 mm); (c) pipe and microchannel sizes; (d) layering pattern of aligned CNFs suspension within preform.

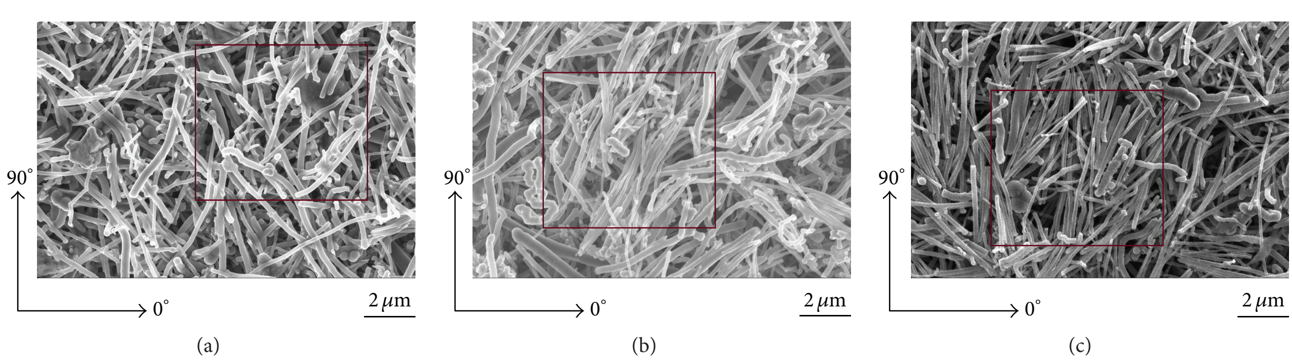
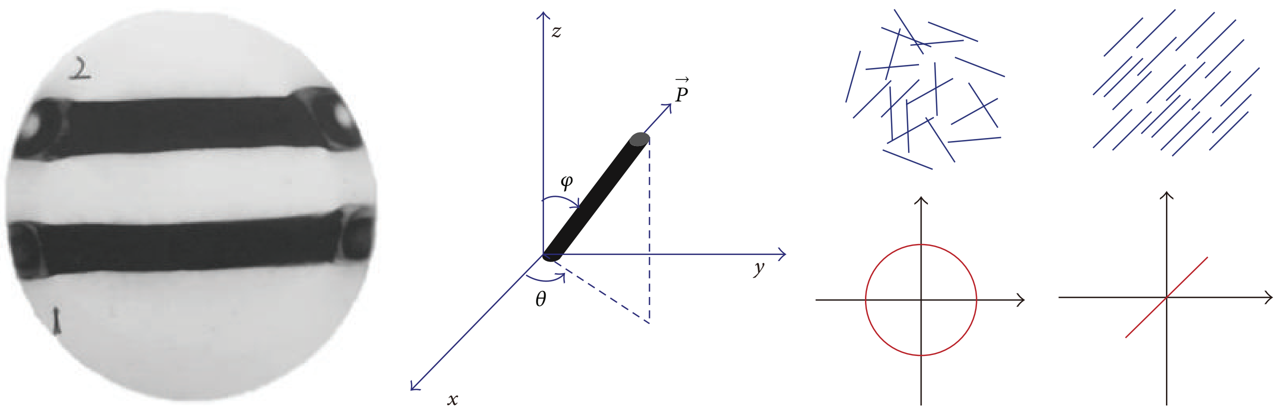
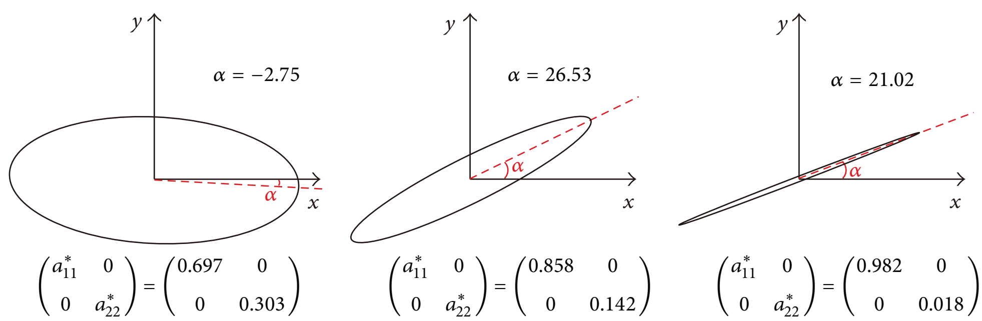


Figure 2: SEM images of CNFs preforms prepared under three different conditions: (a) random state by vacuum filtration process; (b) alignment state by a 1 mm × 0.1 mm microchannel; (c) alignment state by the 1 mm × 0.2 mm microchannel.



(a) (b) (c)

Figure 3: (a) Aligned CNFs sample with the filter paper; (b) definition of orientation of a single carbon nanofiber in a Cartesian coordinate frame; (c) two extreme cases: completely random and perfectly aligned.



(a) (b) (c)

Figure 4: Ellipse to characterize the alignment state of CNFs: (a) random state by vacuum filtration process; (b) alignment state by a 1 mm × 0.1 mm microchannel; (c) alignment state by the 1 mm × 0.2 mm microchannel.

The principal values of the second-order alignment tensor can be found by diagonalizing it from $\langle a \rangle$ to $\langle a \rangle^*$. As shown in (3), a_{11}^* and a_{22}^* are the lengths of major and minor axes of the ellipse. In this equation, α is the angle of major axis rotated from horizontal axis x and can be derived from (2) [25]. Therefore, in the ellipse, the major axis represents the preferred orientation of CNFs in the region and an elongated ellipse can signify higher degree of alignment in the direction of the major axis, whereas a circle signifies no particular preference of orientation:

$$\tan 2\alpha = \frac{2a_{12}}{a_{11} - a_{22}}, \tag{2}$$

$$\begin{pmatrix} a_{11}^* & 0 \\ 0 & a_{22}^* \end{pmatrix} = \begin{pmatrix} \cos\alpha & \sin\alpha \\ -\sin\alpha & \cos\alpha \end{pmatrix} \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} \begin{pmatrix} \cos\alpha & \sin\alpha \\ -\sin\alpha & \cos\alpha \end{pmatrix}^T. \tag{3}$$

The SEM images can be gridded into multiple zones and an ellipse is drawn to graphically represent the alignment of the CNFs, in which the components of the alignment tensor in two dimensions can be used to draw the ellipse. As shown in Figure 3(c), two extreme cases can be found: completely random and perfectly aligned [25].

Figure 4 is a graphical representation of the CNFs alignment state within three preform samples. For the random-state CNFs, the lengths of the major and minor axes of the ellipse are 0.697 and 0.303, respectively. In the preforms created under the two microchannel conditions, the lengths of the major and minor axes of the ellipse are 0.858 to 0.142 for the 1 mm × 0.1 mm microchannel and 0.982 to 0.018 for the 1 mm × 0.2 mm microchannel. This increased ratio of major axis length to minor axis length, graphically illustrated by an elongated ellipse, indicates better CNFs alignment along the major axis direction of the ellipse. As evident in Figure 4, the greater degree of CNFs alignment is achieved through the 1 mm × 0.2 mm microchannels.

The degree of CNFs alignment in the SEM images can also be measured manually with an angle meter. Figure 5 plots the quantity distribution of CNFs at specific degrees of angle (0° to 30°; 30° to 60°; 60° to 90°; 90° to 120°; 120° to 150°; and 150° to 180°). In the preforms created through the two microchannels, CNFs alignment can be achieved in the direction between 60° and 90°. The sample from the 1 mm × 0.1 mm microchannel exhibited less alignment with only 55% of CNFs distributed in the alignment direction between 60°

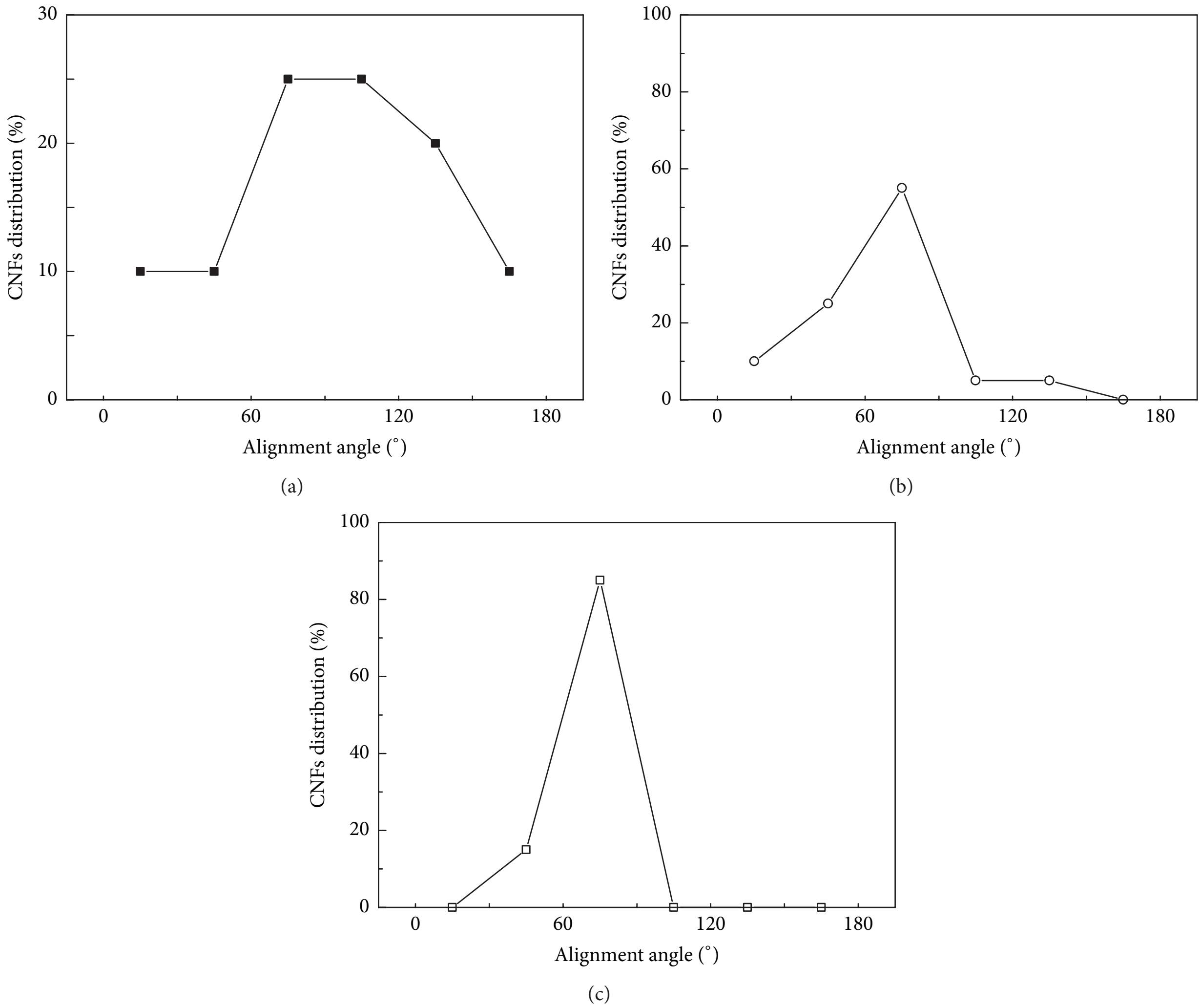


Figure 5: Quantity distribution of CNFs at specific degree (0° to 30°; 30° to 60°; 60° to 90°; 90° to 120°; 120° to 150°; and 150° to 180°). (a) Random state by vacuum filtration process; (b) alignment state by a 1 mm × 0.1 mm microchannel; (c) alignment state by the 1 mm × 0.2 mm microchannel.

and 90°. When the microchannel size was increased to 1 mm × 0.2 mm, more than 85% of CNFs aligned between 60° and 90°.

Experimental results indicate that better CNFs alignment can be obtained through the 1 mm × 0.2 mm microchannel. Shear force applied on the CNFs particles as they flow within the pipe induces alignment of CNFs along the flow direction and the microchannel functions in dispersing CNFs uniformly.

4. Conclusions

In summary, we develop a novel method to align CNFs which suggest profound implications for future studies in this area. The effect of microchannel size on the degree of alignment is studied. The microstructural information obtained from SEM images is interpreted using a second-order alignment tensor and a manual angle meter to describe the CNFs alignment. In the second-order alignment tensor description, the lengths of major and minor axes of the ellipse are 0.982 to 0.018 as the microchannel size is 1 mm × 0.2 mm, meaning that CNFs can be aligned along the major axis direction of the ellipse and the degree of the alignment of CNFs increases with larger channel size. The degree of CNFs alignment measured manually with an angle meter shows that 85% of CNFs aligned using the 1 mm × 0.2 mm microchannel in the direction between 60° and 90°. Both characterizations demonstrate that better CNFs alignment can be obtained by the 1 mm × 0.2 mm microchannel.

Competing Interests

The authors declare that they have no competing interests regarding the publication of this paper.

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