ALIGNMENT AND GRAPHITE CRYSTAL PACKING FOR HIGH STRUCTURAL PERFORMANCE OF CNT NANOCOMPOSITES

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ABSTRACT

Buckypaper is comprised of a random CNT network, and as the CNT network becomes more aligned, properties of the resultant composites are able to increase to levels desirable for structural composite applications. In this research the CNT network is aligned using a mechanical stretching technique with the assistance of resin systems to achieve 60-80% stretching strain. TEM, SEM, and Raman analyses are used to characterize the packing and alignment degree of the CNT networks. SEM images display the microstructure evolution in the CNT network as the stretch ratio or strain increases from 0% to 80%. As the CNT network is stretch from 0% to 60% strain, SEM images show an apparent increase in alignment, and as the network is further stretched to 80% it can be seen that the waviness of the aligned network decreases. TEM images suggest increased alignment and packing on the nanoscale level. As the stretch ratio increases along with the alignment degree, the nanotubes become more densely packed and a graphite crystal structure becomes apparent. Aside from visual verification of the alignment degree, the effect of mechanical stretching on alignment degree has been quantitatively proven to be effective through use of Raman spectroscopy. Raman spectroscopy measurements show that as the material is stretched and the network plastically deforms, the surface nanotubes become more highly aligned and show a polarized response in the direction of alignment. The resulting best fit curve can then be obtained to find Raman intensity versus orientation angle and consequently calculate the degree of alignment. Using the data acquired in this manner, it was found that at a 60% stretch ratio, 80% of the CNTs became aligned along the stretch direction. At an 80% stretch ratio, more than 90% of the CNTs became aligned along the stretch direction. High degree of alignment and crystal packing of CNTs are essential to achieve high mechanical performance.

1 INTRODUCTION

Carbon nanotubes (CNTs) possess multifunctional properties that are widely desired such as high mechanical [1–5], thermal [4–6], and electrical properties [2, 5, 10, 12]. However, due to the random orientation of the CNT network and low concentration of CNTs that are used in composite applications, the high properties of CNT composites are not able to be reached.

To overcome the randomness in the CNT networks, there has been much work previously completed that has increased the alignment degree of the CNT networks and thereby increased the properties as well. These methods of alignment include using argon gas flow to create flow induced alignment [11], growing the CNT forest using chemical vapor deposition and plasma enhanced chemical vapor deposition to obtain natural growth orientation [12–14], as well as melt processing methods to achieve alignment via shear flow [15]. One of the more successful methods that has been used to increase the alignment degree is through mechanical stretching [1-3, 5, 11, 19, 20]. The CNTs are able to be stretched through application of tensile forces to align the individual CNTs within the network. This method has proven useful not only through the success in increased alignment of the CNT network and through increased properties, but also due to the simplicity and scalability of the method.

The increase in degree of alignment is able to be seen and characterized with several different methods. Qualitative characterization can be accomplished through use of scanning electron microscopy (SEM) and transmission electron microscopy (TEM). SEM and TEM allow for visualization of large changes in the degree of alignment and can also help to determine the surface quality of the aligned CNT network. However, after a certain point in the stretching process the increase in alignment is not as notable by optical methods. To be able to accurately characterize and attribute an alignment fraction to the stretched CNT network more quantitative methods must be implemented.

A simple method that is used to quantitatively characterize the degree of alignment in is Raman spectroscopy. Raman has been shown to give an accurate estimate of the degree of alignment of CNTs within the network [5, 12, 21–23]. Although Raman is only able to measure a small area of the sample at one time, it has been assumed to be representative of the entire sample. For this reason, Raman spectroscopy was used in conjunction with SEM and TEM to accurately characterize the degree of alignment of CNT networks at various stretch ratios.

2 EXPERIMENTAL

Randomly oriented carbon nanotube sheets, provided by Nanocomp Inc, were used to conduct testing. The CNT sheets were treated with CYCOM 5250-4 resin and EPON 862 liquid epoxy. The viscosity of the resins are easily changed with heat to assist as a lubricant during the stretching process. The sheets were stretched using a mechanical stretching method previously developed [23] to achieve stretch ratios or strains between 0% (randomly oriented) and 80%.

After the stretching process, the samples were washed to remove the resin. Characterization was then completed on the samples using several different methods. Visual characterization was completed through SEM using a JEOL F7401 field emission microscope. TEM images were taken using the JEM-ARM200cF (A Sub-Angström Cs Corrected Transmission/Scanning Transmission Electron Microscope from JEOL) at 80 kV to study in detail the nanostructures and CNT/CNT and CNT/resin interfaces. The TEM samples were prepared by peeling and cutting the failure areas from failed tensile specimens and placing them on TEM mesh grids.

A Renishaw inVia micro-Raman system using a 785 nm excitation wavelength diode laser. Laser power used was 0.5 mW with a 50× magnification objective lens. Polarized Raman spectra were obtained in the VV configuration. Measurements were taken between the preferred axis and the VV polarization vector.

3 RESULTS AND DISCUSSION

3.1 SEM CHARACTERIZATION OF ALIGNED CNT NETWORKS

SEM was completed on samples stretched between 0%, randomly aligned samples, to 80% stretched samples using the mechanical stretching technique. As shown in Figure 1, as the stretch ratio increases the CNT network can be seen to change from a random orientation of the CNTs to having a more aligned, and ordered orientation. Additionally, as has been noted in previous research [23], after a 60% stretch ratio has been reached the change in alignment is less noticeable, however it is evident that the CNTs are less wavy in nature. This lowered waviness is attributed to self-assembly of the CNTs within the network as well as sliding between the CNTs.

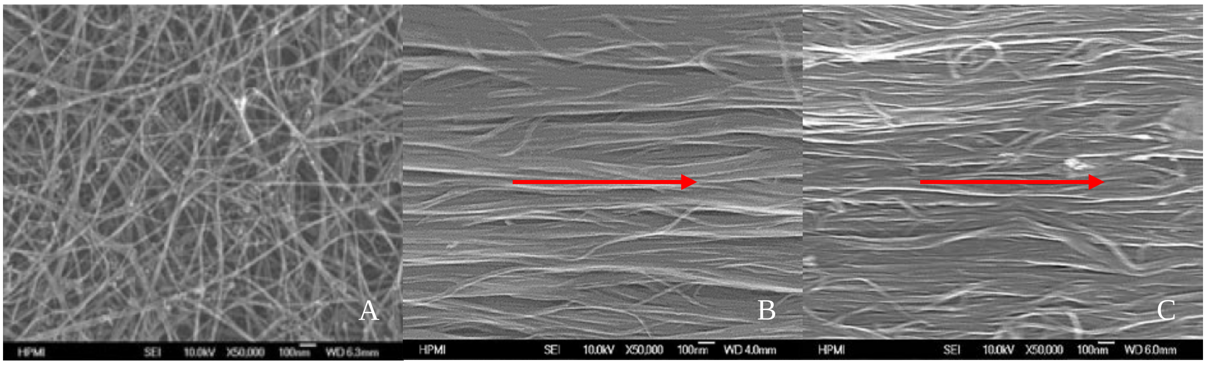

Figure 1. SEM images of (A) 0% stretched, randomly oriented buckypaper,(B) 60% stretched buckypaper with BMI resin treatment and (B) 80% stretched buckypaper with BMI resin treatment, arrows indicate stretch direction.

3.2 TEM CHARACTERIZATION OF ALIGNED CNT NETWORKS

TEM analysis was also conducted on cross sectional areas of the aligned samples between 0% and 80% stretch ratios. Similar patterns to SEM were noticed, as the stretch ratio increased the alignment direction is also seen to increase along the stretched direction. This is noticed through the fact that the CNTs are perpendicular to the image, indicating that the CNTs have become aligned along the stretched direction. The density of the CNT network also increases with the increase in stretch ratio. As the stretch ratio increases more CNTs are aligned along the same direction, and therefore more CNTs are able to be packed into a smaller area, through deformation, to form local crystal packing as shown in Figure 2. Different degrees of CNT deformation from ideal circular cross-section shapes to flattened or dog-bone shapes are co-existing.

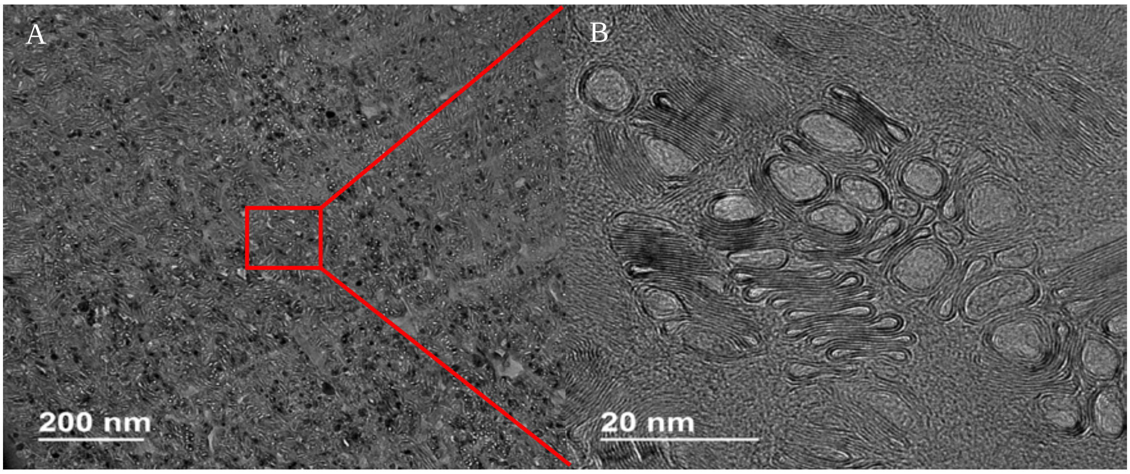

Figure 2. TEM images of CNT network at 80% stretch ratio at lower (A) and higher (B) magnification.

3.3 RAMAN SPECTROSCOPY CHARACTERIZATION OF ALIGNED CNT NETWORKS

Although SEM and TEM are both excellent tools for visual observations of CNT alignment development during stretching, after a point the amount of increase in alignment is difficult to qualitatively characterize through images alone. Raman spectroscopy was implemented to quantitatively characterize the degree of alignment of the CNT network. Raman measurements were taken in 10° increments between 0°, or along the aligned and stretch direction, and 90° perpendicular to the stretch direction, Figure 3 (A).

G-band Raman scattering intensity is highly dependent on the orientation of the CNT network with respect to the polarization vectors from the excitation laser beam. To obtain a distribution function that allows for insight into the CNT degree of alignment a polarized laser beam is used and measurements are taken between the preferred axis and the VV polarization vector [15]. The G-band Raman intensity of aligned CNTs is proportional to $\cos^4\theta$, where θ is the angle between the CNT axis and the incident excitation polarization. Due to the anisotropic nature of the optical absorption of the CNT network, there is an orientation dependence of the penetration depth. This can be described using a correction factor $f\text{abs} \approx 1/(\cos\theta + K\sin\theta)$, where K is the ratio between the nanotube absorption coefficient for polarizations perpendicular to the tube axis and nanotube absorption coefficient for polarizations parallel to the nanotube axis. Since the CNTs are axially symmetric, the distribution function has a Gaussian cylindrical symmetry.

For thin CNT sheets (~45 micrometers thick) a 2D model was used by neglecting the anisotropic optical penetration depth, the Raman intensity data can then be fitted to the following function, which calculates the deviation from 100% aligned CNT sheets:

$$I(\phi, f, \sigma) = A\int_0^{\pi/2}\left[\frac{1-f}{\pi} + \frac{\pi}{\sigma\sqrt{\frac{\pi}{2}}}e^{-\frac{2(\theta-\phi)^2}{\sigma^2}}\right]\cdot\frac{cos^4\theta}{\cos\theta + K\sin\theta}d\theta \qquad (1)$$

where f is the aligned fraction, and σ is the Gaussian standard deviation. The two orthogonal measurements that are taken parallel and perpendicular to the alignment direction give a ratio dependent on both f and σ, seen in Figure 3 below. Even with Raman data taken at many θs, σ is found by fitting the deviation from $\cos^4\theta$ law which necessitates very accurate intensities. Therefore, a 2D distribution function was used to describe the CNT degree of alignment which we can then use to generate a best fitting curve of the Raman intensity versus the orientation angle of the CNTs as shown in Figure 3 (B).

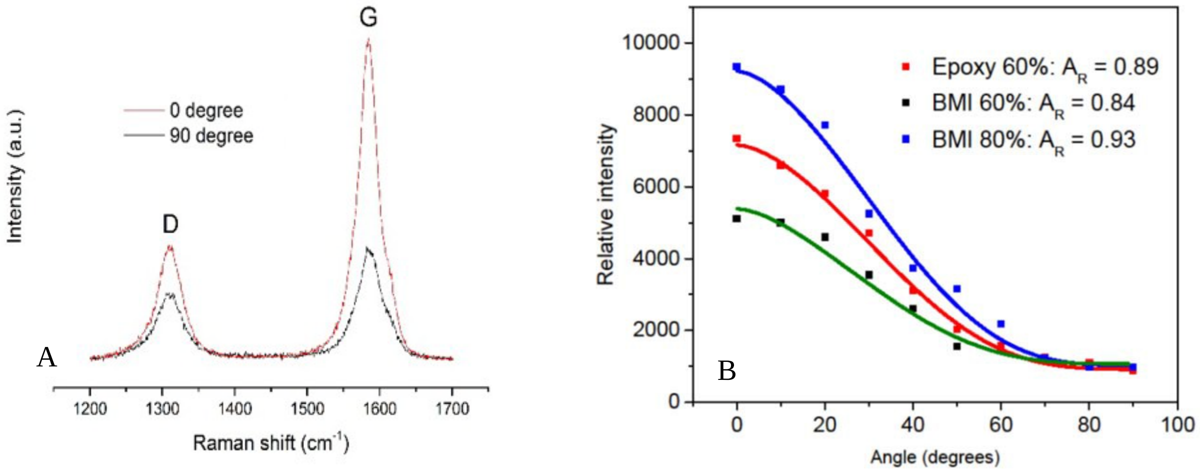

Figure 3. (A) Alignment Fraction analysis: Raman fitting results for all cases as a function of angle with respect to the alignment direction (B) the BMI treated 60%-stretched samples taken with orientation parallel (0 degree) and perpendicular (90 degree) to the laser polarization vector

Using Equation (1) above, the degree of alignment is calculated as the CNT sheet is stretched from a random orientation to 80% stretch ratio. The alignment degree rapidly increases as the stretch ratio increased from 0% to 60% stretch, from 60% to 80% stretch the alignment degree increased a marginal amount, depicted in Figure 4 below. At 60% stretch ratio over 80% of the CNTs became aligned within the network. As the stretch ratio continues to increase to 80%, the CNT degree of alignment increased to over 90% alignment.

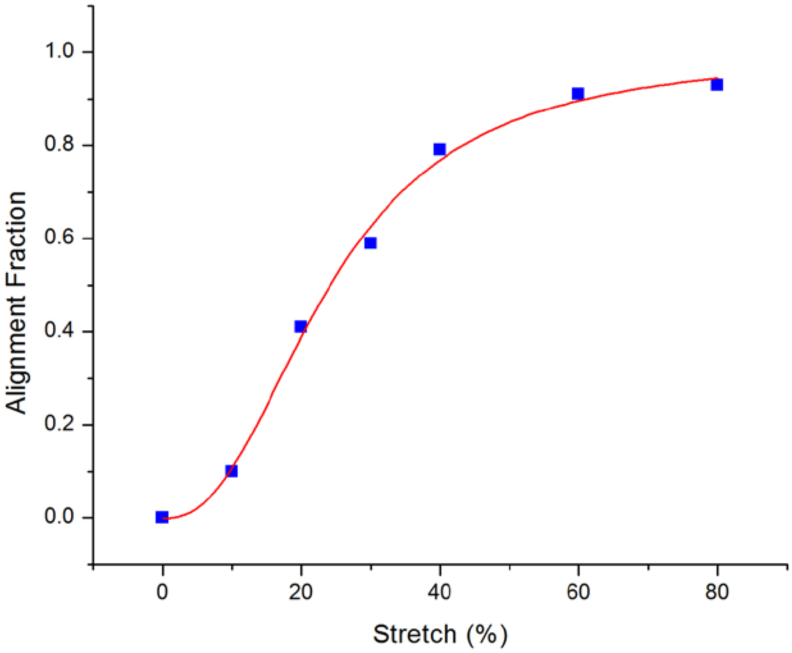

Figure 4. Alignment fraction based on Raman spectroscopy

However, due to the Raman scattering being greater in the weakly absorbing transverse orientation, where θ=90°, I(90°) is greatly overestimated compared to the value of I(0°). This means that σ is overestimated and that *f* is underestimated. Raman intensity is much less sensitive to out-of-plane than in-plane misalignment when polarized measurements were completed in-plane.

4 CONCLUSIONS

Raman spectroscopy is a useful tool in quantitatively characterizing the degree of alignment as the CNT network changes from a randomly oriented network to a highly aligned network. However, after a 60% stretch ratio is reached there are diminishing returns on the increase in alignment. At an 80% stretch ratio, the sample can achieve 90% degree of alignment. Additionally, a drawback of Raman is that it tends to overestimate the degree of alignment in the sample. Therefore, although Raman is a suitable means of determining degree of alignment Raman measurements may necessitate adjustments during testing that lowers the measured degree of alignment to account for the overestimation. A supplementary method to be used in conjunction with Raman spectroscopy is wide angle x-ray scattering (WAXS) can be used in conjunction with Raman spectroscopy. Since WAXS underestimates the alignment degree when compared to Raman spectroscopy, it may be used to counter the overestimation from Raman spectroscopy in future research.

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