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Automated Dispersion and Orientation Analysis for Carbon Nanotube Reinforced Polymer Composites

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Abstract

The properties of carbon nanotube (CNT)/polymer composites are strongly dependent on the dispersion and orientation of CNTs in the host matrix. Quantification of the dispersion and orientation of CNTs by microstructure observation and image analysis has been demonstrated as a useful way to understand the structure-property relationship of CNT/polymer composites. However, due to the various morphologies and large amount of CNTs in one image, automatic and accurate identification of CNTs has become the bottleneck for dispersion/orientation analysis. To solve this problem, shape identification is performed for each pixel in the filler identification step, so that individual CNT can be exacted from images automatically. The improved filler identification enables more accurate analysis of CNT dispersion and orientation. The obtained dispersion index and orientation index of both synthetic and real images from model compounds correspond well with the observations. Moreover, these indices help to explain the electrical properties of CNT/Silicone composite, which is used as a model compound. This method can also be extended to other polymer composites with high aspect ratio fillers.

1. Introduction

Carbon nanotube (CNT)/polymer composites have emerged as a new class of functional materials for aerospace [1], energy storage [2, 3], electronic [4, 5] and other industries because of the superior properties such as high specific modulus and strength, high electrical and thermal conductivity and low coefficient of thermal expansion. However, it is well-known that the unique properties of CNT composites are significantly dependent on the dispersion and orientation of CNTs in the host matrix. For example, Zhao et al. demonstrated that improving the dispersion of CNTs could increase the Young's modulus by 30% at the same loading [6] while Khare and Burriss showed that even increasing the filler

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loading would sometimes deteriorate the modulus instead of enhancing it if CNTs were agglomerated [7]. Cheng et al aligned the CNTs by mechanical stretching and achieved a 22 fold and 2 fold improvements in Young's modulus and tensile strength, respectively [8]. Deng et al. found that the dispersion and orientation of CNTs indeed were the two crucial parameters to determine the reinforcement of the CNT/rubber composites [9]. Although intensive efforts have been made to achieve a good control of dispersion and orientation of CNTs during the composite preparation [10, 11, 12, 13, 14], an objective and accurate method is lacking to quantify the quality of dispersion and orientation.

In prior studies, some researchers characterized the dispersion and orientation of CNT fillers by the change in certain physical properties [10, 15, 16, 17, 18]. Unfortunately, these methods suffer from the fundamental limitation that the measured physical properties are usually the average value over large volumes, and as a result they cannot represent the local situation of an individual CNT. Another drawback of such indirect measurements is the interference of factors other than CNT dispersion or orientation. Especially in the case of composites with a loading level near the percolation threshold, a slight difference in filler loading could lead to orders of magnitude change in electrical conductivity, dielectric constant and viscosity even if the filler dispersion is kept constant [19, 20].

Another approach to characterize the dispersion and orientation of CNTs in polymer composites is to use the direct observation from microscopes and subsequent analysis of the obtained images. Techniques from image analysis have been employed in a number of previous studies [21, 22, 23, 24, 25, 26], and these approaches partially address the limitations of interpretation from physical properties. However, as has been pointed out by previous authors [24, 27], the bottleneck of these methods lies in the correct identification of CNTs from the obtained images. There are several challenges associated with CNT identification from the images: 1) The background brightness may be highly heterogeneous, resulting from noise in the imaging device and the spatial differences in the electrical conductivity/topology. The inhomogeneous background makes it difficult to find a universal threshold to separate the CNTs from background. 2) As high-aspect-ratio fillers, CNTs exhibit different morphologies from dots to tubes of different lengths, depending on their orientation relative to the observation plane. They can no longer be simplified as points, as in the case of particulate fillers [27], because such simplification will inevitably lose some key information present in the original image, such as orientation. Besides identification of their positions, there is an additional challenge to identify their shapes and dimensions.

Because of these challenges, previous researchers have opted to make simplistic assumptions in their analysis. For example, in most reports it was assumed that the CNT was uniformly brighter in the images, so that a global threshold [21, 23, 24, 26] or even the gray-scale image intensity values [22] could be applied to extract the CNTs. Unfortunately, this assumption is not always valid and manual picking is often performed to compensate for the unsatisfied identifications made by this automatic process [24]. Evidently, manually picking out the CNTs is time-consuming, tedious and subjective. Another issue is that researchers ignored the different morphologies of CNTs in the image and assumed that the CNTs were all perpendicular to the imaging plane, and their cross sections then appeared as dots in the images [21]. Approaches based on this assumption lose the ability to perform dispersion and orientation analysis spontaneously.

In the present study, we address the challenges of CNT identification by measuring the tube-shape characteristics with Hessian matrices for each pixel in the image. With this shape recognition function, the identification of CNTs no longer relies on the brightness assumption, and thus the result is much more accurate. In addition, a fully automatic pipeline for the CNT/polymer composite image analysis can be established by measuring the

(dis)-similarity in dispersion and orientation between the extracted CNTs and an ideally uniform dispersion/ orientation. The developed technique enables convenient Quantification of dispersion and orientation of CNT fillers and is of great use to correlate the microstructure of CNT/polymer composites with their processing conditions and their properties.

2. Method

The CNT dispersion and orientation analysis includes two steps: the automatic detection of CNTs and estimation of dispersion and orientation. These two steps are detailed below.

2.1. CNT detection

The tubular shape of the CNTs can be characterized by the Hessian of a gray-scale image. Mathematically, the image intensity can be regarded as a 2-dimensional (2D) function $I(x, y)$. Furthermore, near the location (x, y) , the function $I(x, y)$ can be written using the Taylor expansion as:

$$I(x+\Delta x, y+\Delta y)=I(x, y)+(\Delta x, \Delta y)\nabla I(x, y)+(\Delta x, \Delta y)H(x, y)\begin{pmatrix} \Delta x \\ \Delta y \end{pmatrix} \quad (1)$$

where $\nabla I(x, y)$ is the image gradient and $H(x, y)$ is the Hessian matrix. In this Taylor expansion, the eigenvalues of $H(x, y)$ at each point reveal the shape of the object around that pixel [28]. This is illustrated in Figure 1.

It can be seen that a tubular object in the image may be characterized via a large eigenvalue and a small eigenvalue of the Hessian matrix, while a spherical shape gives rise to two eigenvalues of similar magnitude. Note that, although in the above examples that the objects are brighter than their surroundings, this discussion can be also applied to the case where objects are darker than the background by simply taking the absolute value of the eigenvalues. With this observation, an indicator function V for the tubular object is defined as:

$$V(x, y)=\exp\left(-\frac{\alpha\lambda_1^2}{\lambda_2^2}\right)(1-\exp(-\beta(\lambda_1^2+\lambda_2^2))), \quad (2)$$

where λ_1 and λ_2 are the two eigenvalues at the position (x, y) with the order $|\lambda_1| \geq |\lambda_2|$. As a result, the closer the function value $V(x, y)$ is to 1, the more likely (x, y) is on a tubular object in the image. Therefore, with such processing, the original intensity image $I(x, y)$ is converted to a “tubular measuring image” $V(x, y)$. The CNT regions in the image can then be obtained by thresholding the $V(x, y)$ function. In this work, the threshold is fixed at 0.2 for all the images and the performance has been quite consistent.

Furthermore, the centerlines of the CNTs are extracted by using the morphological thinning operator [29]. Essentially, the regions containing the CNTs are “eroded” until the remaining region has a width of one-pixel. In order to mitigate the variations resulting from the implementation, we use the morphological operation function *bwmorph* in Matlab®.

After these operations, the CNTs are extracted and are represented as an image $B(x, y)$, with pixel values of zero or one. If $B(x, y) = 1$ for the position (x, y) , that means at least one CNT passes through this point, whereas $B(x, y) = 0$ indicates no CNT passes through.

2.2. CNT dispersion/orientation analysis

2.2.1. Spatial dispersion computation—In the step above, all the CNTs in the $B(x, y)$ image have been identified. However, the $B(x, y)$ image only provides the information whether any CNT passes through a certain pixel; it does not answer the question regarding which particular CNT passes through this pixel location. In order to estimate the dispersion of the CNTs, we first identify each single CNT in the $B(x, y)$ image computed above.

To answer this question, for each pixel in $B(x, y)$ with value 1, the 8 neighboring pixels are checked to see if they have value 1. If one neighboring pixel has value 1, then it is grouped with the original pixel as a connected component. This process repeats until no neighboring pixel has the value 1. As a result, all the pixels from the same CNT are grouped into one connected component and pixels from different CNTs form different connected components. After this step, we obtain an image $L(x, y)$ where pixels belonging to the same CNT are marked with a label distinct from all the other CNTs. Consequently, if we denote the total number of CNTs in the image as M , then the location of the j -th CNT in the image is given by pixels: (x_j, y_j) such that its label $L(x_j, y_j) = j$.

Consequently, in order to determine the spatial dispersion of the CNTs, we take the center of the mass (CoM) of each CNT as the representative of its spatial location. That is, for the j -th CNTs, its CoM, (u_j, v_j) , is computed as the average position of all the pixel locations with the same label j . As a result, we have M CoMs $(u_1, v_1), \dots, (u_M, v_M)$ representing the locations of the M CNTs.

Consider now that these M CoMs are the realizations of a random variable R ; then, the dispersion of the CNTs can be evaluated by measuring how R differs from a uniformly-distributed random variable, denoted by U . Mathematically, we write the probability density function (PDF) of R as $p_R(x, y)$ and the PDF of U as $p_U(x, y)$. The objective of comparing R and U can be formulated as measuring the difference between two functions $p_R(x, y)$ and $p_U(x, y)$. To that end, a widely used distance metric in the space of functions is adopted to define the dispersion $d(R; U)$ as follows:

$$d(R, U) = \int_{\Omega} (p_R(x, y) - p_U(x, y))^2 dx dy, \quad (3)$$

where the integration is carried out on the image domain Ω .

One question that remains is how to obtain p_R from the CoMs. This is the PDF estimation problem in the field of pattern recognition and *kernel density estimation* is one of the most employed techniques [30]. Essentially, the p_R is estimated as the sum of several Gaussian functions (called kernels), each centering at a sample point:

$$p_R(x, y) = \frac{1}{2N\pi\sigma^2} \sum_{i=1}^N e^{-\frac{(x-x_i)^2 + (y-y_i)^2}{2\sigma^2}}, \quad (4)$$

where (x_i, y_i) is the location of pixel which has CNTs passing through, and the standard deviation σ of the Gaussian function can be adjusted for the image size and magnification.

With the above computation, the smaller (the closer to zero) $d(R, U)$ value obtained, the more uniformly the CNTs are distributed. On the contrary, the more non-uniformly the fillers spread, the larger the obtained d value will be.

2.2.2. Orientation estimation—In addition to the spatial dispersion, the orientations of the CNTs also play an important role in determining various properties of the CNT-based composites. In order to estimate the orientation of the CNTs, we first identify each single

CNT in the $B(x, y)$ image. This can be achieved from the label image $L(x, y)$ computed above. In $L(x, y)$, the pixels in the same CNT are given the same label, whereas different CNTs have different labels.

Then, for each CNT, the pixel locations of this CNT are extracted and a line section is fitted to them. Mathematically this is a linear regression problem: Denote the points in the j -th CNT as $\{(x_i, y_i) : i = 1, \dots, N_j\}$. Then, we find the slope k_j and intercept b_j (the intercept is not used for the orientation estimation) for the j -th CNT with the minimum fitting error E_j :

$$E_j(k_j, b_j) = \sum_{i=1}^{N_j} (k_j x_i + b_j - y_i)^2 \quad (5)$$

Then, naturally, the angle θ_j of this CNT is

$$\theta_j = \tan^{-1}(k_j) \quad (6)$$

After the orientation angle for each CNT is computed, we get an array of angles $\theta_i, i = 1, \dots, M$. The histogram of the distribution of the θ_i 's is then computed, which gives the distribution of the CNT orientations. This distribution clearly shows which angles the majority of CNTs are aligned at. In the meantime, a further step can be performed to give a more quantitative analysis in a similar fashion as those in the dispersion analysis. The different angles of CNTs in an image can be viewed as the realizations of a random variable A . By comparing it with a uniform distribution on the range of -90° to 90° , we give a single-valued index for the orientation distribution of the CNTs. Again, the closer the obtained orientation index is to zero, the more randomly the CNTs are oriented. In contrast, a larger orientation index suggests alignment of CNTs in the matrix.

2.3. CNT-based model compound preparation and characterization

CNT/silicone composites with a filler loading of 15 wt.% were used as the model compound to verify the developed method and to correlate the obtained dispersion and orientation indices with composite processing conditions and their electrical properties. CNTs (Chengdu organic chemicals Co. Ltd.) are 10–20 μm by length and 50 nm by diameter. Silicone resin (SR) is a peroxide-curable methyl phenyl silicone gum provided by Rockbestos-Surprenant Cable Co. The dry CNTs were dispersed in SR by three roll mill (Torrey hills technologies LLC.) over various times. The dispersion level was set by the number of rolling cycles; the initial ten cycles of mixing were used to incorporate all the CNT fillers into SR. After mixing, the samples were pressed into a Teflon mold and cured for 1 hr at 180 $^\circ\text{C}$ under 1.6 MPa pressure. Fractured surfaces of the cured specimens were obtained in liquid nitrogen. Three fractured surfaces per specimen were imaged and analyzed to give the average dispersion/orientation index. SEM observation was conducted in LEO 1530 FE-SEM with an acceleration voltage of 15kV. Samples for electrical measurements were prepared by embedding two Ni coated Cu wires into the composite before curing. Then the electrical resistance was measured by a fluke 289 RMS multimeter after curing. Although the two-point measurement scheme includes the resistance of wires and contacts, this added resistance is negligible compared to the resistance of the composite films.

The vertically aligned CNTs (VACNTs) composite was used as an extreme case to test the orientation index. It is prepared by infiltrating the VACNTs with low viscose monomers. The details were described in our previous work [31].

3. Results and Discussion

In this section, the proposed algorithm is first validated on both synthetic images and real SEM images in terms of the correct identification of CNTs from images, dispersion Quantification and orientation Quantification. Then, it is demonstrated that the algorithm is able to correlate the CNT dispersion and orientation with the processing conditions and the electrical properties of the model compounds.

3.1. Experiments on synthetic images

In the first test, as shown in Figure 2, the proposed method is applied to synthetic images. Four synthetic images are generated to represent four different situations: 1) uniform dispersion and alignment (Figure 2a); 2) uniform dispersion and random orientation (Figure 2e); 3) non-uniform dispersion and alignment (Figure 2i); 4) non-uniform dispersion and random orientation (Figure 2m). Specifically, in Figure 2a and 2e, the CNTs are placed on a uniform grid whereas in Figure 2i and 2m, the CNTs are made to concentrate in the top-left 2/3 corner. On the other hand, the orientations of the CNTs in Figure 2a and 2i are controlled to be normally distributed around 30° with a standard deviation of 10° . In contrast, the CNT orientations in 2f and 2n are uniformly distributed from -60° to 60° . In all of the cases, the intensity of the background is simulated to vary gradually to mimic the inhomogeneous background present in real images.

The method identifies the CNTs in the synthetic images, which are shown in red color in the second column. As can be seen, in spite of severe background inhomogeneity, all the CNTs can be correctly identified. The third column shows the dispersion density function with the dispersion indices on the top-right corner. From this, it is verified that the dispersion index correctly characterizes the spatial dispersion of the CNTs. That is, the more uniformly the CNTs are distributed, the smaller the dispersion index is. Finally, in the fourth column, the distribution of the CNT orientations and their orientation indices are displayed. The alignment can be easily identified by the much larger orientation index.

3.2. Experiments on SEM images

3.2.1. CNT identification—In addition to synthetic images, the proposed technique was applied to a total of 81 SEM images of model compounds (details given in Section 2.3). These images include compounds prepared with different conditions and observed at different magnifications. As shown in Figure 3, the CNTs are extracted from the images and marked as red threads. The figures show that our method works robustly for various magnifications from 7k to 20k.

3.2.2. CNT dispersion analysis—To test the accuracy of the dispersion analysis, the images of one well-dispersed composite sample (Figure 4(a)) and one barely dispersed sample (Figure 4(d)) were analyzed using the proposed dispersion index. Despite the same filler concentration, in Figure 4(d), the CNTs were seriously agglomerated, leaving some blank polymer part; in contrast, the good dispersion in Figure 4(a) was illustrated by the even dispersion of CNTs over the whole field of view. The calculated dispersion index of Figure 4(a) is 5.32 while the dispersion index of Figure 4(d) is 15.70, which agrees well with the visual observation. Therefore, the dispersion index reasonably represents real dispersion situations.

3.2.3. CNT orientation analysis—Similarly to the dispersion analysis verification, two extreme cases of orientation, namely a VACNT-based composite and a random CNT-based composite were used to show the effectiveness of the orientation index. Figure 5 shows the images of the two samples and the histogram of their statistic distribution at different

directions. The calculated orientation of VACNT-based is 0.065 and that of the random CNT-based composite is 0.04. The VACNT orientation index is much larger than the random CNTs, which well represents the orientations of the two samples.

3.3. Experiments on model compounds

After validating the proposed dispersion and orientation methodology, we now consider a model compound prepared with different mixing intensities.

3.3.1. Dispersion analysis—Figure 6(a) shows the calculated dispersion indices as a function of rolling intensity. A significant decrease of dispersion index occurs in the first five rolling cycles, indicating a substantial improvement of dispersion at the beginning. Further rolling did not show a significant effect, as the slightly increased dispersion index may result from the statistical fluctuation of data. A final dispersion index as low as 6.78 can be achieved after intensive mixing of 400 rolling cycles. The general trend of a decreasing dispersion index with mixing agrees with our/common observation that a longer mixing time would result in better filler dispersion. A detailed analysis of the decreasing rate determines that 5 to 10 rolling cycles are enough for a good dispersion, which makes it possible to avoid the damage to the polymer chain or CNT fillers induced by fierce mechanical manipulation.

3.3.2. Orientation analysis—Due to the insufficient filler identification technique, only a few previous studies are able to characterize both the CNT dispersion and orientation analysis [24]. In our algorithm, the orientation index can be obtained simultaneously with the dispersion index, as shown in Figure 6(b). The first 5 rolling cycles also contribute to the randomization of orientation of CNTs, as indicated by the decreased orientation index. However, after 100 cycles, the substantial increase in the orientation index was observed, suggesting the alignment of CNTs by the strong and consistent shear force from the roll milling.

3.3.3. Correlation with electrical properties—After the dispersion and orientation indices of samples prepared with various mixing intensities are obtained, they may be used to predict the properties of the obtained composites. In the present study, the electrical properties were measured as an example.

Due to the high aspect ratio and possible alignment in the premixing stage, all the obtained composites show anisotropic properties. As shown in Figure 7, the resistivity measured in direction 1 is at least one order of magnitude smaller than the resistivity measured in direction 2. Therefore, direction 1 is more likely the direction in which the CNTs are aligned. The resistivity ratio further decreases with rolling cycles, especially after 100 cycles. This may result from the CNT alignment by shear forces during rolling as demonstrated by the orientation index analysis [32]. In addition, it is found that the standard deviation of resistivity ratio decreases with rolling cycles: the standard deviation is 0.04 without rolling while after 50 cycles, it is lower than 0.004. It is assumed that a better dispersion by intensive mixing is one important contributor to the reduced deviation. According to the dispersion index analysis, the dispersion improves with longer mixing time. A better dispersion quality could enhance the reproducibility and reduce the variation between parallel specimens. Therefore, after 50 cycles, the standard deviation is dramatically reduced. Above all, using the proposed image analysis technique, one can fully disclose the distribution and morphology of CNT fillers in the composites, which will be very useful to explain and predict various properties of the composites.

3.3.4. Discussion on the CNT orientation—Sometimes CNTs exhibit wavy or curved shape in the composite. This can be seen in both the original images and the detected CNTs

in Figures 3, 4, and 5. However, during the quantitative correlation between orientation of CNTs and the material properties, one has to define a certain value to represent the orientation of the curved CNT. To solve this problem, in this work we use the line fitting technique which find the “major axis direction” of the curved CNT, the distribution of which has been correlated with the rolling cycles and electrical properties.

Nevertheless, it is also realized that in some cases the “major axis direction” may have some limitations. For example, it was found that the reinforcement in CNT/rubber composites is strongly dependent on the persistence length; i.e., the more straight shape CNTs exhibit, the higher the persistence length and the better reinforcement [9]. When we use the major axis direction to represent each CNT in the orientation analysis, we lose the information of how tortuous the CNTs are. Therefore, we are unable to correlate the mechanical properties change induced by the persistence length evolution with the current dispersion and orientation analysis.

One possible solution to this problem is to further utilize the wellness of the fitting: when finding the major direction using line fitting, we can measure the wellness of such fitting. The more tortuous a CNT is, the worse it can be fit by a line. Therefore, by measuring quantities such as R^2 coefficients, such wellness can be estimated. Consequently, for those highly tortuous CNTs, either a scheme similar to [9] can be adopted by cutting the CNTs to smaller but more linear section; Or we can use higher order polynomial to model the shapes of the CNTs. Evidently, such analysis will lose the concept of “orientation”. Therefore, a combination of the orientation analysis and the tortuousness of CNTs is preferred for problems such as the reinforcement of CNT/polymer composites.

3.4. Running time

For an image of size of 1024 by 768 pixels, the identification of the CNTs takes an average of 0.3 seconds. The subsequent line segment fitting for all the CNTs and orientation computation takes 7.9 seconds on average. The fast automatic computation of the proposed technique will allow high throughput analysis of the images of CNT-based composites or other fiber reinforced composites.

4. Summary

We have developed an image analysis technique that can automatically and accurately analyze the CNT composite images. First, CNTs with different dimensions and shapes are automatically extracted from the SEM images by shape recognition function. Furthermore, under the statistics inference framework, the spatial and orientational dispersion of the extracted CNTs are computed, respectively, as spatial dispersion index and orientational dispersion index. The obtained indices will be of great help to optimize processing conditions and predict the properties of these composites.

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Figure 1. The intensity patterns and the eigen vectors of the Hessian matrix. The lengths of the vectors indicate the magnitudes of the eigen values. (a) Small bright blob in the image gives to two large eigen-values. (b) Large bright blob furnishes to two small eigen values. (c) Tubular shape corresponds to one large and one small eigen values.

Figure 2. Test on synthetic images. First column: four synthetic images. Second column: identified CNTs in red. Third column: CNT dispersion density functions and the dispersion index. Fourth column: the CNT orientation distribution and orientation index. See text for detail.

Figure 3.

The extraction of the CNT in the SEM images of model compounds prepared at various mixing intensity. The red threads in the images indicate the CNT identified by the proposed algorithm. The identification algorithm works well for various magnifications from 7K to 20K.

Figure 4. Validation of the dispersion analysis by comparing the dispersion of two CNT/SR composites. (a) The original image of a well mixed sample. (b) Identification of the CNTs in the image of (a). (c) The PDF of the image in (a). The inserted numbers are the calculated dispersion index. (d) The original image of a barely dispersed sample. (e) Identification of CNTs in the image of (d). (f) The PDF of the image in (d). The inserted number represent the dispersion index.

Figure 5.

Validation of the orientation analysis by comparing the dispersion of two CNT/SR composites. (a) The original image of a VACNT/SR sample. (b) Identification of the CNTs in the image of (a). (c) The histogram of the orientation distribution of image in (a). The inserted number is the calculated orientation index. (d) The original image of a random CNT/SR sample. (e) Identification of CNTs in the image of (d). (f) The PDF of the image in (d). The inserted numbers are the calculated the dispersion index.

Figure 6. The calculated (a) dispersion indices and (b) orientation indices of CNT/SR composites prepared at different rolling cycles.

Figure 7.
The ratio of the resistivity measured at direction 1 over the resistivity measured at direction 2.