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Quantitative evaluation of carbon nanotube dispersion through scanning electron microscopy images

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ABSTRACT

A comprehensive method that quantitatively characterizes the dispersion state of carbon nanotubes (CNT) was proposed to improve the preparation of CNT-filled composites. CNT/polymer composites with different dispersion and distribution states were prepared, and the microstructures of these composites were obtained. Two indices representing the global and local randomness of CNTs were extracted through quantitative image analysis.

1. Introduction

Since the discovery of carbon nanotubes (CNT) by Iijima [1], numerous studies have been conducted to obtain CNT-filled composites with optimal physical, electrical, thermal, and mechanical properties [2–5]. This optimization has enabled the application of CNT-filled composites in various fields [6,7]. Given that the properties and microstructures of composites are strongly correlated, improving the dispersion state of CNTs, as well as the interfacial bonding between CNTs and polymeric resin, is crucial in enhancing the property of CNT/polymer composites [8–10]. The homogenization of CNT dispersion states improves the electrical conductivity and mechanical properties of the original polymer matrix [11]. However, the homogenization of CNT dispersion states remains a challenge that is yet to be resolved in the field of composite material research [12].

CNTs dispersed in matrixes can be characterized by using two methods, namely, the direct and indirect methods. The direct method includes morphological analysis, whereas the indirect method involves mechanical, electrical, and thermal analyses [13]. The direct method employs transmission electron microscopy, scanning electron microscopy, or X-ray diffraction and is more reliable compared with other methods. Although quantitative measurements have been conducted to understand the physical structural arrangement of CNT particles, limited quantitative measurements have been performed by direct methods. Therefore, this study employs two indices to assess the degree of positional randomness of nanoparticles.

Spatial disposition and nanoparticle arrangement are common problems in the field of nanotechnology. Positional randomness can be divided into two different levels: global and local randomness. Global randomness indicates the positional arrangement of particle groups, whereas local randomness indicates the positional arrangement of individual particles inside each particle group. The spatial arrangement of particles can be described in terms of distribution and dispersion, as explained above [14].

Few studies quantitatively analyze particle dispersion in terms of global and local randomness. For instance, Liu [15] divided a specimen image into several grids and calculated the number of particles in each grid. However, Liu failed to consider the size of particles. Therefore, Liu's study cannot determine the degree of particle dispersion, but can only determine whether particle distribution is homogenous. Another disadvantage of the statistical method of Liu is that the calculation error of this method largely depends on mesh size and number of particles. In another study, Sul et al. [14] utilized molecular dynamics analogy to calculate a new index that considers positional randomness. Although this index reflects both global and local randomness, this index cannot express particle distribution and dispersion respectively.

Considering the above research bottlenecks, this paper proposes a comprehensive method for quantitatively characterizing the dispersion state of CNTs. Two indices were defined and calculated on the basis of scanning electron microscopy (SEM) imaging. The first index reflects particle distribution and global randomness, whereas the second index reflects particle dispersion and local randomness. Several image analysis techniques, such as filtering, binarization [16] and morphology processing, were also adopted to extract CNT information from raw SEM images. The proposed

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method provides a comprehensive approach of characterizing the dispersion degree of nanoparticles.

2. Experimental

The CNTs used in this study, which were supplied by Showa Denko K. K., Japan, had average diameters of 80 nm and had lengths ranging from 5 to 15 μm. The CNTs were synthesized by chemical vapor deposition. Epoxy resin (EP44, supplied by Wuxi Resin Corporation, China) was selected as the polymer matrix. The hardener (AB-HGA) was obtained from Anbang New Materials Company in Jiaxing, China. The CNTs were purified in a 3:1 mixture of 65% H_2SO_4/HNO_3 for 30 min at 100 °C to remove impurities such as amorphous carbon, graphite particles, and metal catalysts. Afterward, the acid-treated CNTs were blended homogenously with dispersant TX100 (polyoxy ethrlene nonyl phenyl ether) [17,18]. The mixture was subsequently stirred for 18 h by using 35 mL of deionized water. The epoxy resin and hardener were added to the suspension and stirred for 10 min. The suspension was kept at −55 °C for 2 h and placed under vacuum at 80 °C for 48 h. Further details of the procedures are available in previous studies [19,20].

3. Analysis scheme

The dispersion degree of CNTs were evaluated by image processing and index calculation. During image processing, an SEM image with gray level ranging from 0 to 255 was manipulated by using matrix laboratory (MATLAB). The raw SEM image was processed using histogram equalization to enhance image contrast. The resulting image was filtered to remove noisy points. Accordingly, binarization was applied on the image to convert its format into black and white (binary). The image was then eroded and dilated to eliminate remaining small image noise. The areas of particles marked in the image were separated from the area of background pixel points to prepare for the extraction of dispersion index.

It is noticed that the proposed method works under the assumption that the states of nanoparticle distribution and dispersion are consistent throughout the bulk of the material under investigation. The method makes an analysis of the dispersion state, just considering the global and local randomness in the image.

The distribution index was identified by dividing the image into several grids. The particle area in each grid, as well as the standard deviation of the particle area per grid, was calculated. The distribution index reflects particle distribution, which is uneven in the image.

The dispersion index was obtained by calculating the equivalent radius of each dispersed phase particles. This index can be expressed as follows:

$$R = \sqrt{\frac{S}{\pi}} \tag{1}$$

where S is the area of each particle. The dispersion index was calculated based on particle size distribution:

$$M(R) = CR^{-p} \tag{2}$$

where $M(R)$ represents the number of particles that are larger than the equivalent radius R of the selected particles; C is constant; p is the parameter of the particle size distribution, which is simply the dispersion index. $M(R)$ and R can be calculated based on the information obtained from the processed image. The width of the particle size distribution decreases with decreasing p, thereby denoting that particles do not substantially agglomerate.

4. Results and discussion

A quantitative analysis in view of positional randomness, specifically, global and local randomness, was conducted. On the basis of homogenization mechanisms, suitable mixers were arranged and employed to ensure that all matrix particles are well dispersed and are uniformly distributed.

Reference images were used in evaluating the method proposed in this study, thus verifying the feasibility of the proposed method. Scenario A, B, and C in Fig. 1 illustrates the effect of the different degrees of dispersion and distribution. The bottom images in each column are the results obtained after marking the original image. It is obviously found by intuition that Scenario A possesses the best dispersion and distribution, and C has the worst dispersion and distribution.

Fig. 2 shows the dispersion and distribution indices for each scenario. The dispersion index increases with the deterioration of particle agglomeration. Moreover, the decrease in the distribution index can be attributed to the depravation of the positional arrangement of particles, that is, a handful of particles concentrate on a certain corner, with few particles in the remaining areas of the region. As the amount of agglomeration expands, the state of dispersion becomes poor, and the dispersion index consequently drops. Meanwhile, a monotonic increase in the distribution index becomes evident as the positional arrangement of particles becomes more uneven. This finding indicates that the results of the proposed image analysis scheme are in good agreement with the visual assessment. The proposed approach successfully obtains information regarding the dispersion state through the utilization of the two indices. The two indices did not produce any error and captured different aspects of the dispersion degree because only one representative image was used for the calculation of each case.

The designed image processing system was applied on the actual images of CNTs dispersed in polymer matrix. Fig. 3(a) and (b) shows the transformation of images undergoing image-processing procedures, which include binarization and erosion/dilation. In order to facilitate calculation of area of each particle, the CNTs were marked under the condition of 8 connected region by using different colors. The different colors mean different connected regions, and it is also represent different CNTs particles. The dispersion index was calculated by using Eqs. (1) and (2), whereas the distribution index was obtained by using the method shown in Section 3.

Fig. 4 shows the values of the two indices obtained. Fig. 4(a) shows that the value of the dispersion index decreases when CNT agglomeration increases from local to see. Fig. 4(b) shows that the value of the distribution index increases when the CNT concentration in one region changes from global to see. Results of dispersion quantification are in a satisfactory agreement with

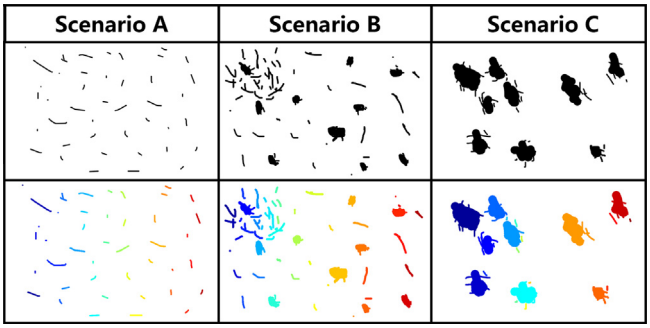

Fig. 1. Three different particle dispersion and distribution states in a matrix: well distributed and well dispersed (Scenario A); mediocrely distributed and mediocrely dispersed (Scenario B) and poorly distributed and poorly dispersed (Scenario C).