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Dispersion evaluation, processing and tensile properties of carbon nanotubes-modified epoxy composites prepared by high pressure homogenization

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ABSTRACT

In this paper, high pressure homogenization (HPH) served as the main dispersion method for making carbon nanotubes (CNTs)-modified composite materials. A new quantitative approach was proposed to evaluate the dispersion of CNTs in epoxy resin by combining microscopic images with maximum likelihood estimation theory. The results were in good agreement with those obtained from optical observation and ultraviolet–visible (UV–vis) absorbance measurement. Moreover, the dispersion process specific to HPH processing was analyzed with the aid of the proposed approach. The changes of the morphologies and lengths of CNTs in HPH were illustrated. It was found that, in the first few cycles, the lengths of CNTs fell significantly and the entanglements remained severe. In the following cycles, individual CNTs were gradually separated from agglomerates and the lengths experienced a slow decline. After homogeneous dispersion, the transverse tensile properties of CNTs-modified carbon fiber reinforced epoxy composites (CFRP) got obviously ameliorated.

1. Introduction

Since being discovered by Iijima [1], carbon nanotubes (CNTs) have attracted wide attention. Owing to their exceptional mechanical, electronic and thermal properties [2–5], numerous research efforts were devoted to modifying composites with CNTs. CNTs-modified composites offer tremendous potential for the next generation of high performance materials, because of the dramatic improvement in various aspects of properties, with minor weight penalty. Despite of broad prospects, the application of CNTs in real products is still in the early stage of realization, which is mainly due to two interrelated factors: lack of homogeneous dispersion and lack of sufficient interfacial adhesion [6–8].

Unlike in thermoplastics, the dispersion of CNTs in thermosets, i.e. epoxy resin, was far from satisfactory. To separate individual CNTs from agglomerates and stabilize them in epoxy resin, plenty of processing techniques have been developed. CNT functionalization [6], ultrasonication [9], three-roll milling [10] and HPH [11] were among the most prevalent dispersion methods. These would help to achieve homogeneous dispersion, but inevitably cause mechanical damage to CNTs as well. Meanwhile characterization techniques, such as Raman spectroscopy [12], UV–vis spectroscopy [13], electron microscopy [14,15], etc. have been applied to compare the dispersion quality. They encompassed morphological measurements over length scales in the micrometer down to nanometer range [16]. The aforementioned spectroscopy and microscopy were restricted to characterize the dispersion of CNTs in solvent and cured composite, respectively. Most of them were time-consuming and complicated. Therefore, a quicker and more convenient approach to characterize the dispersion of CNTs in liquid resin is necessary. Optical microscopy is such an ideal technique with the merits of real-time monitoring and high feasibility in the lab.

However, qualitative characterization, like optical observation, is subjective and easily guided by the observer's expectations. Quantitative characterization, by contrast, can help to realize the better control and optimization of the dispersion process. So far many researchers [16–19] have tended to make rough comparisons through optical images. The potential of optical microscopy has not been fully tapped.

Besides, the influence of CNT dispersion on the mechanical properties of modified system has been investigated by many previous works. Recently, Gupta [16] found that a combination of HPH processing and planetary shear mixing could yield a better disper-

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sion of nanotubes in epoxy. As for sonication, Gkikas [9] reported the relation among dispersion, processing durations and mechanical properties. Furthermore, Chen [20], Gojny [21], Zhou [22] also suggested that the mechanical properties increased continuously with low CNT content (usually below 0.5% weight fraction of CNTs to epoxy resin), but began to degrade at higher CNT content, which can be attributed to the uneven dispersion of CNTs and the more manufacturing defects caused by high viscosity of CNTs/epoxy mixture. So far experimentally achieved mechanical properties of CNTs-modified epoxy composites have failed to match theoretical expectations [23].

In this study, two prevalent processing techniques, ultrasonication and HPH, were used to exfoliate CNTs. A new quantitative approach was proposed to evaluate the dispersion quality of CNTs in liquid resin. The dispersion process specific to HPH processing was analyzed with the aids of the proposed evaluation approach, scanning electron microscopy (SEM) and atomic force microscopy (AFM). The effect of dispersion on the transverse tensile properties of CNTs-modified CFRP was studied systematically.

2. Experimental

The carboxyl-functionalized multi-wall carbon nanotubes were purchased from Chengdu Organic Chemicals Co. Ltd, China (Fig. 1). They are specified with average inner and outer diameters of 8 and 15 nm respectively, lengths up to 50 μm, carboxyl content about 2.56 wt% and carbon purity exceeding 95%. Bisphenol-A-based epoxy resin, anhydride-based curing agent and tertiary amine-based accelerating agent (100:80:1 weight ratio) were supplied by Nanya Electronic Materials Co. Ltd, China. T300 unidirectional carbon fiber fabric was supplied by Rayonchi Inc., USA with 3 K in tow size and 160 g/m^2 in areal weight.

A high-pressure homogenizer microfluidizer M-110P (Microfluidics, USA) and an ultrasound machine SK2210HP (frequency 59 kHz, Kudos Ultrasonic Instrument Co. Ltd, China) were used to disperse CNTs in ethanol. For HPH processing, CNTs were first premixed with ethanol (3 mg:1 ml, 6 mg:1 ml, 9 mg:1 ml for 0.3, 0.6, 0.9 wt% of CNTs to keep the consumption of ethanol consistent), then the solutions passed through the interaction chamber working at different pump pressures (103, 138, 172 MPa) for different circulation passes (5, 10, 20, 40, 60 cycles). When microfluidizer pumped CNT solutions toward the interaction chamber, strong turbulence, impact and shear force were applied to reduce the size of agglomerates. Extending cycles could provide continuous energy

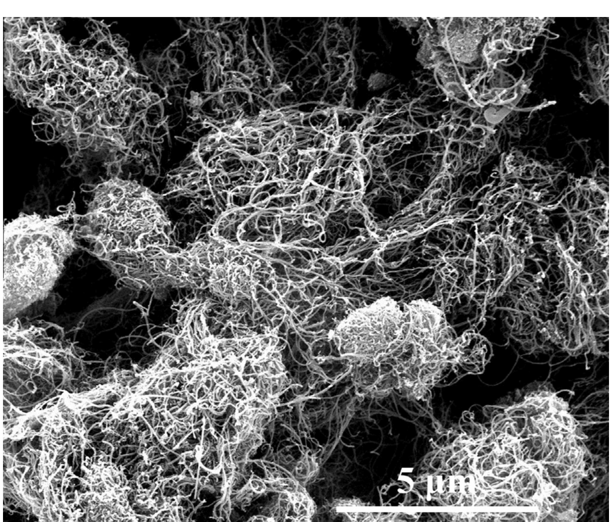

Fig. 1. Micrograph of the spaghetti-like CNTs used in this study.

input, which was necessary to overcome surface energy. For ultrasonication processing, the solutions were prepared at 100 W of output power in a water bath for different time (0.5 h, 2 h).

Epoxy resin was added to the CNT solution and stirred at the speed of 1000 rpm and the temperature of 60 °C for 2 h. After removal of ethanol in a vacuum oven at 80 °C for 24 h, CNTs/epoxy resin was mixed with curing agent and accelerating agent. The obtained resin system was stirred at 1000 rpm for 0.5 h and degassed for 2 h. Fourteen layers of carbon fiber fabric were laid up to fabricate CFRP. On each layer, the CNTs-modified resin was poured and spread out. Then a hand roller was used to help the impregnation of the fabric and squeeze out the excess resin. The impregnated plies were cured in a hot-press machine at 120 °C for 2 h with a pressure of 1.2 MPa. Their nominal fiber volume fraction was approximately 60%, and the voids content was found negligible.

A UV–vis spectrophotometer UV-1800PC (Mapada, China) was used to evaluate dispersion state of CNTs in ethanol. The solutions were diluted to a ratio of 0.1 mg:1 ml and the absorbance was measured at a specific wavelength of 260 nm. AFM (Multimode 8, Bruker Co., Germany) was used in tapping mode to investigate the effect of HPH processing on the lengths of individual CNTs. To obtain individual CNTs, test solutions were prepared with the addition of 1 wt% Triton X-100. Before measurements, the solutions were also diluted to a ratio of 0.1 mg:1 ml and Triton X-100 was removed. A 10XB-PC optical microscope (Shanghai Optical Instrument Factory, China) was used to observe a drop of CNTs/epoxy resin between two glass slides. Quantitative evaluation of dispersion state was carried out with the aids of image analysis softwares (MATLAB and MiVnt). Transverse tensile tests of unidirectional CNTs-modified CFRP were performed according to ASTM D3039 using a testing machine, supplied by Wance test equipment Co. Ltd, China. Specimens were in dimensions of 175 mm × 25 mm × 2 mm. The tests were carried out at a crosshead speed of 2 mm/min. SEM (Quanta 200 FEG system, FEI Co., USA) was used to observe the morphologies of the tensile fractured surfaces of CFRP.

3. Results and discussion

3.1. Analysis scheme

Fig. 2 revealed the optical image of epoxy resin with 0.3 wt% of CNTs prepared by hand-mixing for 15 min. The presence of black CNT agglomerates could be clearly observed. To obtain a wide visual field as well as a high resolution, nine (3 × 3) images were taken at 200 times magnification and stitched together in sequence. The optical image was converted from 24-bit red–green–blue color format into 8-bit grayscale one (Step A in the following MATLAB code), which meant that instead of three color components, the grayscale information of each pixel was extracted for later processing by MiVnt. This conversion greatly simplified image analysis and shortened computation time. In theory, the values of the grayscale could range from 0 (completely black) to 255 (completely white). But in practice, epoxy resin seemed gray rather than white from the image, so the grayscale of epoxy resin was unlikely to reach 255. And the grayscale of CNT agglomerates was usually between 0 and that of epoxy resin. Although the light illuminance was set to basically the same when taking pictures of each sample, the brightness of epoxy resin differed more or less from one another. To evaluate the dispersion quality under the same background, a threshold was defined for the gray histogram of each image (Step B). As shown in Fig. 2, once beyond a certain grayscale threshold, the number of pixels fell to almost zero. This threshold was regarded as the grayscale of epoxy resin, and selected manually on the basis of the corresponding gray