The impedance characterization of Carbon Nanotubes - Fumed Silica Poly (vinyl alcohol) Composites

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Abstract. Carbon Nanotube (CNT) was grown on the surface of fumed silica via chemical vapor deposition (CVD) method. In this work, silica acted as a site that holds CNT together, which prevents further agglomeration during composite processing. Iron catalyst at different loading (7.5 wt. % up to 25 wt. %) was introduced via impregnation method to synthesize CNT at 1000°C, under methane flow. Floating catalyst method was used where ferrocene (2.5 wt. % and 5 wt. %) was used as starting reactants together with toluene at 760°C. The reaction time was set at 1 hour for both methods. It was later confirmed via SEM images that the floating catalyst method is more suitable to produce a large amount of CNTs. The sample synthesized via floating catalyst method at both 2.5 wt.% and 5 wt. % ferrocene was later used to prepare composites. Composite films of the particles in poly (vinyl alcohol) (PVOH) were cast and their TEM images show that the dispersion is indeed uniform. From impedance measurement, it was found that the particles synthesized via floating catalyst method were found to form an electrically-conductive percolated network with percolation threshold of 1 wt. %, obtained via percolation equation.

1. Introduction

Carbon nanotubes (CNTs) are multifunctional fillers that impart enhanced mechanical [1], electrical [2], and thermal [3] properties to polymer composites. Electrically-conducting composites have found wide application in areas ranging from aerospace to electronics. However, the majority of nanotubes available on the bulk scale are entangled, making them difficult to disperse into a polymer matrix [4]. Among the approaches used to improve the dispersion of CNTs in polymer matrices include chemical functionalization, in situ polymerization, and enhanced physical blending [4].

Grafting of CNTs onto substrates such as fibers [5-7] and micro particles [8-10] offers an alternative approach to tackle the issues associated with dispersion in a composite matrix, as well as additional benefits (hybrid effects) provided by these dual-filler systems. One approach to obtain such hybrid systems is the direct growth of nanotubes on the supporting fibre or particle. Studies have shown that fibers of carbon [5], silica [6], and alumina [7] acted not only as sites for CNT growth, but also as a substrate carrier to disperse CNTs into polymer matrices. Direct growth of CNTs on silica particulate substrates has been reported [8, 11-13]. The growth of aligned CNT on alumina particles

(μAl_2O_3) has also been studied and a low percolation threshold and a high thermal conductivity were achieved in an epoxy matrix [9]. CNT grown on spherical stainless steel particles were reported to give improvements in the tensile strength and Young's modulus of polyurethane composites [10].

Polyvinyl alcohol (PVOH) has been widely used as a media to study the dispersion of CNT [14-16]. Shafer and Windle assessed the effectiveness of chemically treated CNTs as conductive filler in PVOH and reported a percolation threshold of 5-10 wt. % [14]. On the other hand, Kilbride *et al.* [15] achieved a lower percolation threshold value of 0.005 wt. %, in their non-treated arc discharge CNT – PVOH composite. Although Kilbride *et al.* [15] did not contrast their findings with Shaffer and Windle [14], this difference in percolation is thought to be due to the types of CNTs used. Without treatment, both CVD and arc discharge produced CNTs are tangled in nature. In contrast to that, the treated, hydrophilic CNTs form an individual dispersed fibre, which is not favourable for the formation of conductive pathway in PVOH.

In this study, CNTs were grown on fumed silica nanoparticles by Chemical Vapor Deposition (CVD) method. Two methods were performed to introduce catalyst into the system which is via iron impregnation and also via floating catalyst where the ferrocene was co-flown together with toluene during reaction. In the floating reaction, the ferrocene formed in-situ within the iron catalyst particles.

2. Experimental

2.1 Synthesis and the characterization of the CNT-Fumed Silica

In this section, the procedures taken to grow the CNTs on the fume silica substrates via Chemical Vapor Deposition method were described. As shown in figure 1, the morphology of the fume silica can be described as highly agglomerated nanostructured particles. There were two approaches in introducing catalyst into the system was taken, which were impregnated catalyst and floating catalyst.
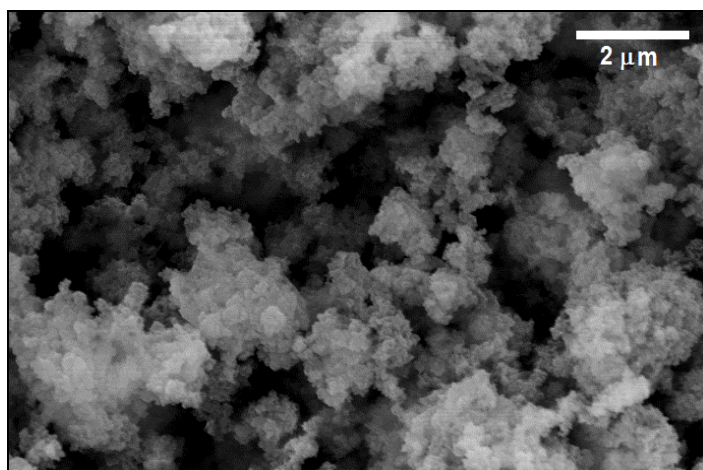

Figure 1. The typical FESEM images of the fumed silica before the growth of CNT

In the case of catalyst introduced via impregnation, the fume silica was first coated with Iron (III) nitrate $Fe(NO_3)_3$ in acetone solution to achieve 7.5 wt.%, 10 wt.%, 15 wt.%, 20 wt.%, and 25 wt.% catalyst loading. The catalyst was dispersed throughout the fumed silica via the assistance of sonic tip with 10% amplitude, held for 10 minutes. The particles were then left to dry overnight in fume cupboard. The pre-coated particles were then placed with the heating zone of the furnace catalysts. The CNTs were grown under the flow of methane, hydrogen and argon for 1 hour at 1000°C.

The CNTs were also grown on the surface of fumed silica via floating catalyst method. In this approach, the mixture of ferrocene–toluene was injected into the furnace during reaction at a rate of 0.4 ml/min. The loading of ferrocene was kept at 2.5 wt. % and 5 wt. %. The reaction temperature and time was kept at 760°C and 1 hour, respectively.

The Scanning Electron Microscope (SEM) imaging was performed for all samples in determining the effects of reaction conditions on the yield of CNTs. An adhesive carbon disc on a pin stub was lightly pressed in the nanoparticles. The sample was then coated with gold using sputter coater to enhance the sample imaging. Philips XL 30 FEG SEM was used to view the morphology. Based on the results obtained, the sample obtained that yield the highest density of CNT was selected for further impedance investigation.

2.2 Synthesis and characterization of PVOH – CNT-Fume Silica
The preparation of the thin films can be described as follow. 80 mg of the hybrid particles from the selected sample was added into 20 ml of 2 wt. % PVOH aqueous solution (PVOH$_{(aq)}$). The particles were dispersed in the solution by magnetic stirring for 20 minutes at 80°C. 10 ml of this solution was then transferred to a plastic mould and left to dry to yield a thin PVOH film with 20 wt.% hybrid particle loading. Another 10 ml of (PVOH(aq)) was then added to the remaining solution, in which the process was repeated further to yield solution containing 10 wt. % dispersed hybrid particle loading. This process was stopped until the final dispersion containing 0.04 wt. % hybrid particles loading. All the thin films were left to dry in fume cupboard up to 5 days. To prevent water uptake, the dried samples were kept in dessicator for 2 days before performing impedance measurement.

The impedance characterization was performed using an Impedance Analysis Interface/NumetriQ PSM 1735, with a frequency ranging from 1 Hz to 1 MHz. The rectangular thin films (~ 30 mm x 10 mm) were cut and placed on glass slides. Silver paint was applied to both ends of the films to act as electrodes which were connected to the instrument by crocodile clips. At least five measurements were taken for each film sample to ensure the results reproducibility.

3. Results and Discussion
Figure 2 shows the typical SEM images of the particles synthesized via catalyst impregnation, CVD method. From the images, it can be seen that CNTs started to grow with catalyst loading as low as 7.5 wt. % Fe (figure 2a), with the amount seemed to increase as the catalyst loading was further increased. The diameter of the CNTs also seemed to be increased as the amount of the catalyst increased, implying a bigger initial catalyst nucleation before growth took place [17-19], based on the growth mechanism as suggested by Baker [20]. Although more catalysts were introduced (up to 25 wt. %), this attempt failed to result in the higher density of CNT formation. It can be concluded from figure 2 that catalyst impregnation fails to results in the formation of high amount of CNTs under the specified reaction conditions.
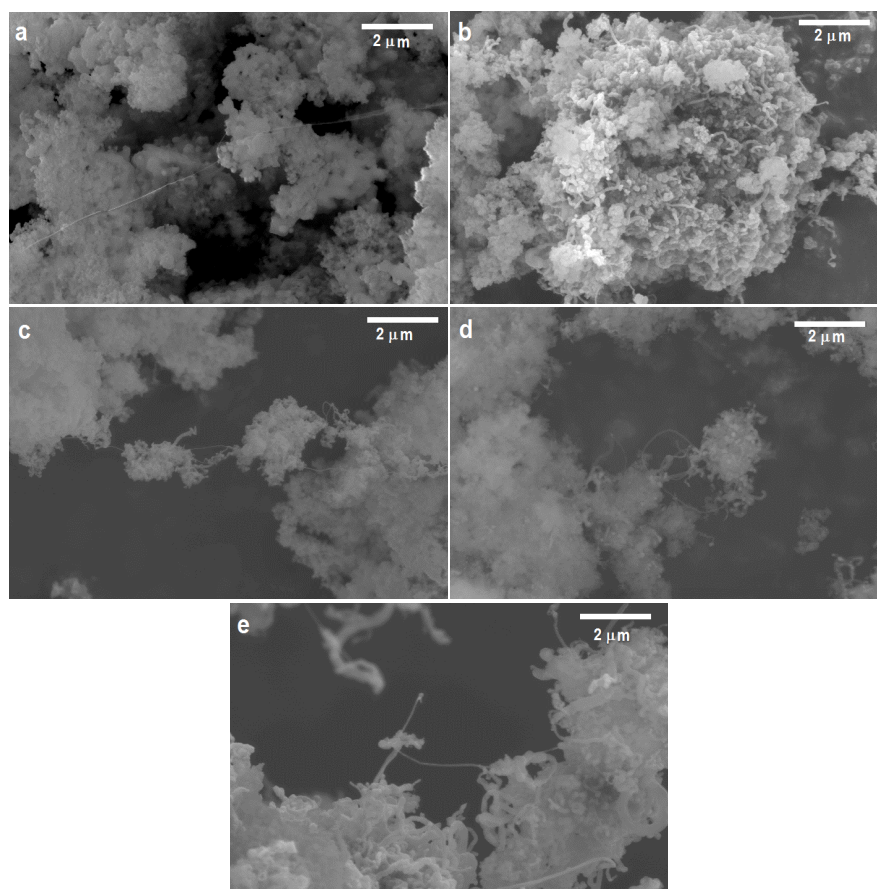
Figure 2. Typical SEM images of the hybrid particles via Fe(NO$_3$)$_3$ catalyst impregnation CVD method; with the following Fe loading; (a) 7.5 wt. %, (b) 10 wt. %, (c) 15 wt. %, (d) 20 wt. %, and (e) 25 wt. %.

As the pre-coated catalyst method did not seem to work, further effort in synthesizing CNT on the fumed silica substrate was performed via floating catalyst CVD method. Figure 3 shows the typical SEM images of the hybrid particles obtained. It can be seen that high density of CNTs were obtained via this method although the ferrocene loading employed was as low as 2.5 wt. %. As the loading was further doubled to 5 wt. %, tremendous improvement in the CNT yield could be observed. The efficiency of this floating catalyst method in enhancing the growth of CNTs was also reported previously on spherical micron silica gel [2], spherical alumina substrate [21], silica fibers [6], just to name a few.
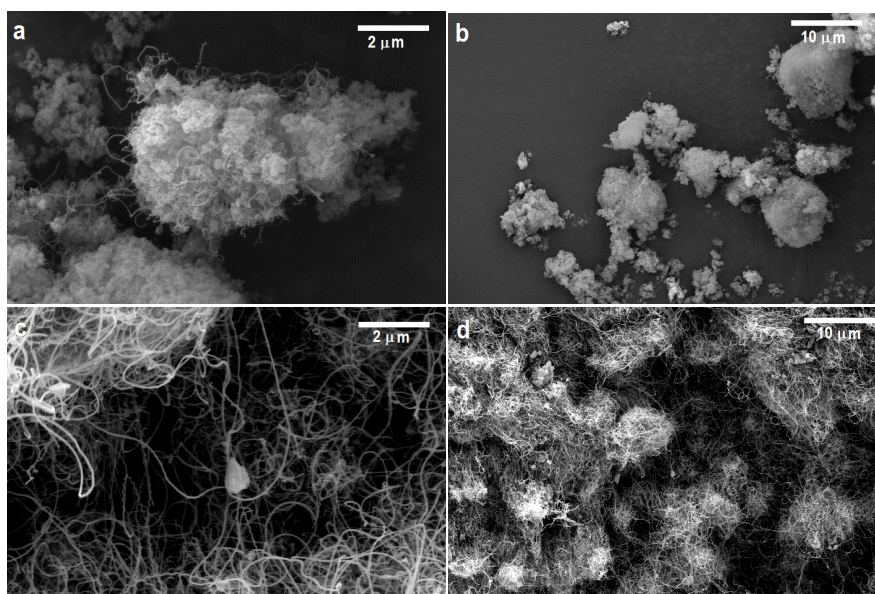
Figure 3. Typical SEM images of the hybrid particles synthesized via floating catalyst CVD with ferrocene concentration of 2.5 wt. % (a & b) and ferrocene concentration of 5 wt. % (c & d).

The particles synthesized via floating catalyst CVD were later selected for further electrical impedance investigation, as the condition with floating catalyst method yielded CNT with the high density (figure 3). The specific conductivity of the particles in poly (vinyl alcohol) films was measured using impedance spectroscopy and the results were summarized in figure 4 and 5.

Figure 4 shows a log-log plot of the film's conductivity as a function of frequency. In the case of the films containing particles synthesized from 2.5 wt. % ferrocene, the conductivity values of the films increased more than two orders of magnitude when loading is doubled from 2.5 wt. % to 5 wt. % (figure 4a). These values were recorded at frequency less than 10 Hz, as it is close to the dc condition [22, 23]. It can also be observed that for samples less than 5 wt. %, the resistance was constant until 10Hz after which it raised by three orders of magnitude as frequency increased up to 10^4 Hz, indicative of an increase in the capacitive component, compared to higher loadings. Figure 4b shows the impedance pattern for films containing higher CNT density (produced from 5 wt. % ferrocene). It can be seen that the conductivity values of the films for all loadings above 0.625 wt. % are generally higher than those containing particles synthesized from 2.5 wt. % ferrocene (Figure 4a). This simply implied that higher CNT density contributes to the higher values of the composite's conductivity.
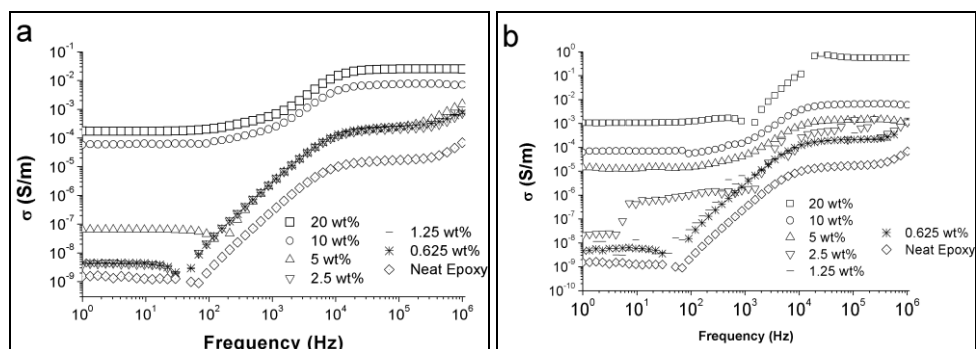

Figure 4. Log-log plot of the film's conductivity as a function of frequency for films containing hybrid particles synthesized with 2.5 wt. % ferrocene (a) and 5 wt. % ferrocene (b).

Figure 5 shows the relation between the film's conductivity as a function of particle loading for both cases. Samples were also made with 0.04, 0.08, 0.16, 0.32 wt % loading and all these were found to be insulating within the limits of the analyzer. As such, the values were not shown on these figures. In the case of films containing particles synthesized with 2.5 wt. % ferrocene, the significant increase in conductivity is overserved upon increasing the particle loading from 5 wt. % to 10 wt. % (figure 5b). This indicated the formation of a conductive network of particles above 5 wt. % loading. In the case of films containing particles synthesized with 5 wt. % ferrocene, the advancement in conductivity was observed to occur above 1.25 wt. %, implying the formation of percolated conductive network.

The critical percolation threshold can be determined from the percolation scaling law; $\sigma = \sigma_0 (p - p_c)^t$; where σ is the conductivity, σ_0 is a constant, p is the particle loading, p_c is the critical loading, and t is a constant. The transition from insulator to conductor occurred at p_c. The constant t defines the dimensionality of the filler forming percolated network; i.e. $t \sim 1.33$ for 2D and $t \sim 2.0$ for 3D [24]. The values of p_c equals to 4.9 and 1.2 are calculated from the films synthesized from 2.5 wt. % ferrocene amd 5 wt. % ferrocene, respectively. As the 5 wt. % sample containing higher CNT, the critical loading needed to achieve percolated network is definitely lower. Both films yielded the t values approximately equals to 2, indicating formation of 3-dimensional conductive network, as confirmed by the SEM images (figure 3).
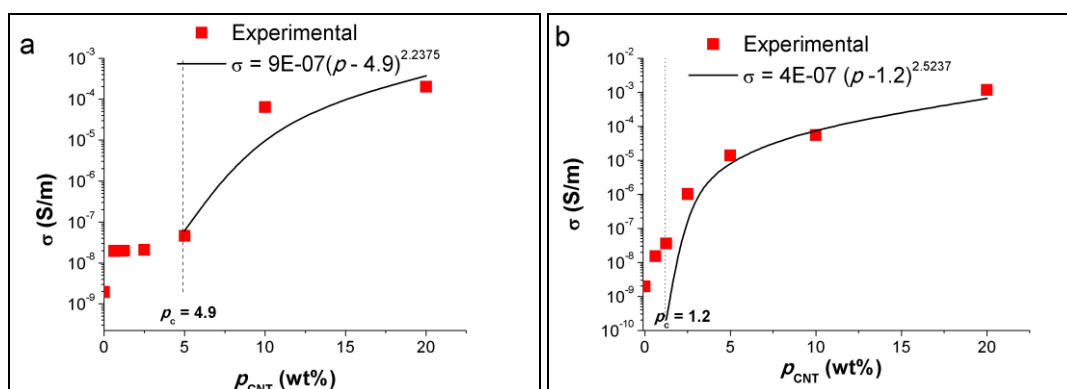

Figure 5. Semi log conductivity of the films as a function of weight loading for particles synthesized with 2.5 wt. % ferrocene (a) and 5 wt. % ferrocene (b). The equations showed the corresponding fitted percolation equations for each particle.

4. Conclusions
In conclusion, CNTs were successfully grown on the surface of fumed silica. The catalysts were introduced via both impregnation and floating catalyst method. The silica acted as to hold the CNTs and to prevent them from forming bundles during composites processing. This study presented a simple approach in controlling bundle formation during CNT-polymer processing. Its ability in forming a conductive network at low p_c demonstrated the efficiency of grafting CNT in fumed silica. The values of t obtained from percolation scaling law indicated that the network formed was in 3-dimensional.

5. References

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