Study of the Dispersion and Electrical Properties of Carbon Nanotubes Treated by Surfactants in Dimethylacetamide

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In this study, the effects of sodium dodecyl benzene sulfonate, polyvinylpyrrolidone, sodium dodecyl benzene sulfonate/polyvinylpyrrolidone, and Triton X-100 on the dispersion of 0.1 wt\% carbon nanotubes in dimethylacetamide are reported. Sedimentation results show that except for sodium dodecyl benzene sulfonate, all the surfactant-assisted carbon nanotube solutions have visually-stable dispersions for at least two months, and even the samples without a surfactant gave no obvious deposition. UV-Vis spectra of the dispersions with and without acid-treatment proved that the carboxyl group attached to the carbon nanotubes positively improves the dispersion effect. The states of aggregation of carbon nanotubes treated by different surfactants are distinctive, and the electrical properties of carbon nanotubes are strongly related to these states of aggregation. The best dispersing and stabilizing effect was found in the sodium dodecyl benzene sulfonate/polyvinylpyrrolidone sample, which also gave the lowest resistance ($2.15 \times 10^4 \Omega$ at 20 V) among all the surfactant-treated stable suspensions.

Keywords: Surfactant, Multiwalled Carbon Nanotubes, Dispersion, Electrical Properties.

1. INTRODUCTION

Since carbon nanotubes (CNTs) were first reported in 1991,\textsuperscript{1} they have attracted the attention of large numbers of researchers from all over the world because of their unique electrical,\textsuperscript{2} thermal\textsuperscript{3} and mechanical properties.\textsuperscript{4} Despite the potential application of CNTs, poor dispersion in both aqueous and non-aqueous solutions is still a considerable challenge for their separation and assembly. During the past decade, several approaches have been successfully adopted in trying to disperse CNTs in aqueous systems.\textsuperscript{5-9} Among all the dispersion methods, surfactant-assisted dispersion\textsuperscript{10-13} is attractive because it is easy and economical, which makes it suitable for an industrial process. However, research studies on different surfactants stabilizing CNTs in organic solvents are limited.\textsuperscript{14-16} A study on the stabilization of CNTs in organic solvents with the help of surfactants is significant to the aim of finding a suitable surfactant which is effective to create a stable dispersion of CNTs in the synthesis of polymer/CNTs composites, especially for \emph{in-situ} polymerization.

Dimethylacetamide (DMAc) is a water-miscible, high boiling point solvent which is commonly used as an excellent polar solvent in organic chemistry; in addition, it is widely used as a solution for fibers and in the adhesive industry. However, to our knowledge, there are no studies reported on the effect of a surfactant in this solution. In addition, almost all previous research studies about dispersion have concentrated on singlewalled CNTs (SWNTs), and few studies about multiwalled CNTs (MWNTs) have been reported. Nevertheless, MWNTs have many advantages compared with SWNTs, such as being cheaper, easier to handle and with larger quantities of product. Moreover, the MWNTs are dispersed better in solution than SWNTs which can be bundled easily. If the SWNTs bundles cannot be effectively broken up, their mechanical reinforcement in composites will be affected by the slip between individual SWNTs. Meanwhile, the properties of MWNTs are also not weaker than those of SWNTs. For example, Kim et al.\textsuperscript{3} obtained a thermal conductivity of 3000 W/m·K by measuring an individual MWNT, which...
is higher than that of aligned SWNT. The resistance of individual disordered multiwalled carbon nanotubes measured by Tsai et al.\textsuperscript{17} was almost the same order of magnitude as that of a SWNT\textsuperscript{2}. Therefore, research concerning the dispersion of MWNTs in organic solutions is significant for the practical application of MWNTs in reinforced polymer composites.

The electrical properties of CNTs are strongly related to the method of treatment and depend strongly on the state of aggregation of CNTs. It is therefore worthwhile to examine the conductivity of CNTs treated with different surfactants. Moreover, CNTs generally exist in matrices as networks and other states of aggregation, especially, if the surfactants are left in the matrices. The electrical properties of macro-aggregation of such structures with a surfactant are a vital guide for the subsequent manufacture of CNT films or composites. Unfortunately, very few studies have focused on the electrical behavior of these aggregate structures of CNTs, and to our knowledge, no surfactant-treated conductivities of states of aggregation have yet been reported.

In this study, the aging sedimentation, aggregation, dispersion, and electrical properties of MWNTs treated with various surfactants in DMAc were investigated. The dispersion effects of CNTs with and without acid-treatment were also compared and it was found that acid-treatment was helpful for the dispersion of CNTs in DMAc. The states of aggregation of CNTs treated with different surfactants are different, and the electrical properties of CNTs treated with surfactants are strongly related to these states of aggregation.

### 2. MATERIALS AND EXPERIMENTAL PROCEDURES

#### 2.1. Materials

Multiwalled CNTs (grown by chemical vapor deposition with a purity of 95%, a diameter of about 60 nm and length of about 2 μm) were provided by ShenZhen Nano Tech. Port Co., Ltd (China). The surfactants-sodium dodecyl benzene sulfonate (SDBS, 90%, TianJin FuChen Chemical reagents Co., Ltd), polyvinylpyrrolidone (PVP, PVP10-500G, Sigma-Aldrich), Triton-X100 (TX100, 98%, International Lab USA), and solvent DMAc (99.5%, International Lab USA) were used as received.

#### 2.2. Preparation of CNTs Dispersions

As-received CNTs were purified with hydrochloric acid (37 wt%) under ultrasonic agitation (BRANSON B5210E, 47 kHz) for 1 hour at room temperature with the aim of removing metallic impurities (denoted as CNTs-1). Then the purified CNTs were refluxed in concentrated HNO\textsubscript{3} (67 wt%) at 70 °C for 9 hours, thereby leaving carboxylic acid groups on the CNTs (denoted as CNTs-2). All the CNTs solutions were made in DMAc with a CNT concentration of 0.1 wt%; the detailed components of each sample are listed in Table I. The sample #8 and #9 (without surfactant) were employed to study the dispersion effect of CNTs with and without acid-treatment. After mixing CNTs into the solvent, all the samples were treated in an ultrasonic bath for 1 hour at room temperature to achieve a visibly stable dispersion (Fig. 1(a), 0 hour) and then samples were sealed and kept at room temperature to incubate for one month. The as-prepared samples were not filtered or centrifuged, which meant that large tangles of CNTs still existed in the solutions.

#### 2.3. Electrical Property Measurements

To prepare the electrical measurement samples, 0.4 ml CNTs suspensions which had been ultrasonically treated for 3 minutes were dropped on 1.0 × 2.5 cm rectangular glass substrates and dried on a hotplate at 80 °C. Coplanar gold electrode patterns were sputtered on these samples with the help of a shadow mask with a separation of the...
electrodes of around 20 μm. I–V curves of the samples were measured by a two-probe station at room temperature using a Keithley 236 source meter unit controlled by a computer. The results were obtained by running the program at least three times until the data were stable.

2.4. Characterization of the Dispersions and Microstructures

Light microscope images of the suspensions were captured by an Olympus BX60F5 optical microscope. UV-vis absorptions of 8# and 9# samples after 1 month incubation (0.2 ml suspensions were diluted to 4 ml) are measured with a Perkin-Elmer UV/Vis/NIR spectrometer (Lambda19) with 0.5 nm steps. All the absorption spectra were background subtracted, to account for the solvent and surfactant. The states of aggregation of CNTs were obtained by using a scanning electron microscopy (SEM Philips, XL40 with an energy dispersive X-ray spectroscopy (EDX) attachment) on the same samples as for the I–V measurements. Transmission electron microscopy (TEM) samples of SDBS, SDBS/PVP and PVP treated CNTs were prepared by directly dropping the ultrasonically-treated suspensions onto copper grids with a carbon film and were characterized by a Philips CM20 TEM.

3. RESULTS AND DISCUSSION

3.1. Sedimentation and Supposed Schematics of the Dispersions

Test photographs after aging for 144 hours for all the samples are presented in Figure 1(a). The SDBS solution shows an obvious deposition, while, the other samples retained a good dispersion even after two months, neither depositing nor separating into layers. The concentration of CNTs was 0.94 mg/ml and the concentrations of surfactants were 4.7 mg/ml (1#–5#) and 2.8 mg/ml (6# and 7#), respectively (see Table I). According to the results, SDBS has proved to be incompatible with DMAc, even though it has shown extraordinary properties in dispersing 20 mg/ml CNTs in water. Normally, a surfactant should form a micelle (in an aqueous solution) or a reversed micelle (in an organic solution) above the critical micelle concentration (CMC), however, the evidence of SDBS forming a reversed micelle in DMAc has not been found. An additional test in a dilute 1 mg/ml SDBS/DMAc solution was made, and the suspension seemed turbid under ultrasonication, while the deposition of SDBS was found after stopping ultrasonication, which means SDBS cannot dissolve in DMAc. Moreover, the SEM results discussed latter in Section 3.6 proved the existence of the SDBS particles. The micro-SDBS particles were formed after the ultrasonic treatment and were adsorbed on the CNTs. Van der Waals forces made the micro-particles accumulate into packages on the surface of CNTs which resulted in sedimentation (as illustrated in Fig. 1(b) top). Furthermore, SDBS particles aggregated by themselves and the unequal adsorption onto CNTs also increased the speed of sedimentation. We have established that SDBS is not suitable for dispersing CNTs in DMAc.

SDBS/PVP treated CNTs in a water dispersion have been reported in Ref. [18], which proved that PVP and SDBS have a good synergistic effect in forming a suspension of CNTs, even though the actual mechanism of this synergy is not completely understood. In our case with SDBS/PVP, smaller amounts of SDBS might not aggregate into packages and the micro-SDBS particles played a role as anchors which enhance the wrapping and wall-direction alignment of the PVP molecular chain (as illustrated in Fig. 1(b) middle), which improved dispersion effect between CNTs.

In the case of PVP, the molecular chain of the PVP adsorbed and wrapped on the CNTs (as illustrated in Fig. 1(b) bottom) randomly, however, the wall-direction chain alignment effect as will SDBS/PVP may not have occurred:

TX100, which has an aromatic ring head group, should be helpful for CNT dispersion as established in an aqueous solution. However, because the suspensions without a surfactant were also stable, the effect of an aromatic ring cannot be clearly demonstrated by this simple dispersion and aggregation test. Moreover, the amounts of surfactant needed for dispersions cannot be clearly given at this stage; further research is needed, which will be reported later.

It should be emphasized that the above schematics (Fig. 1(b)) do not suggest that the suspensions are stable or unstable, but rather that the level of interaction among the surfactant, solution and CNTs, and all the suspensions, except for SDBS, have a homogeneous appearance for at least two months. Furthermore, it is worth mentioning that CNTs without a surfactant, both CNTs-1 and CNTs-2, were stable, which proved that DMAc is an excellent solvent for the dispersion of CNTs. The improved dispersion of CNTs in DMAc may be explained by the polar character of DMAc, which structurally contains an optimal geometry of the alkyl amide group for interaction with CNTs. Thus, hydrophobic CNTs are wetted by the organic solvent and some bundles become separated by the DMAc molecular structure. Strano et al. have described the dispersion mechanism of a surfactant on the basis of a “zipping” model, and assumed that the surfactant molecules absorbed on CNTs keep the CNTs from aggregating with the help of an ultrasonic treatment which provides a strong shearing force between the CNTs. From the above analysis, an organic solution system is definitely different to an aqueous system, and Hasan et al. proposed that there is a “competitive” process of the adsorption of surfactant and solvent molecules on CNTs, which is helpful for stabilizing dispersions of CNTs.
3.2. TEM Images of CNTs Treated by SDBS, SDBS/PVP and PVP

In order to characterize the morphology and the diameters of CNTs, CNTs treated with SDBS, SDBS/PVP and PVP were chosen as TEM samples. The TEM images in Figure 2 show that all the three samples gave clear profiles, and the diameters of the CNTs range from about 20 nm to 70 nm. Irregular surfaces were found in the SDBS sample, which means some SDBS particles may have been adsorbed on the walls of the CNTs. However, the chemical analysis from EDS (which is not shown here) could not establish the existence of sodium or sulphur. It is believed that because the amounts of sodium and sulphur are below the detection limit of the instrument. It is also found that the end structures of CNTs were destroyed and some CNTs were broken into shorter lengths because of the acid refluxing and ultrasonic treatment.

3.3. Light Microscope Observations of Aggregation

In order to uncover the real situation in the solutions, the suspensions were observed immediately after 15 minutes of ultrasonic treatment by putting drops on glass slides and after leaving samples aggregated on glass slides for 1 hour. Two surfactant solutions are compared in Figure 3. The SDBS system showed strong aggregation (Figs. 3(a, b)), however, the SDBS/PVP system only gave a few small aggregates, and their round shape results from the wettability of the system with the help of PVP. After one hour, the boundary of CNTs within the SDBS system is clearer and the color is darker, which means CNTs aggregated more strongly than before. However the aggregates in the PVP/SDBS sample were still small and only a few new aggregates were seen. Light microscope images revealed that although there were no visible particulates in the PVP/SDBS solution, small level of aggregation were still present and new aggregates occurred. The solutions should be metastable and tend to deposit with time, while this sedimentation time might be very long.

3.4. UV–Vis Spectra of CNTs Solutions With and Without Acid-Treatment

Although the sedimentation tests in Section 3.1 could not show the dispersion difference between sample 8# and 9#, the UV-Vis absorption spectra in Figure 4 show obvious differences. In Figure 4, the peaks around 661 nm, 1347 nm, 1429 nm and 1546 nm in the acid-treated CNTs (9#) result from semiconducting tubes which correspond to the transitions between symmetric Van Hove peaks in the CNTs density of states, however, these peaks almost disappear in the sample without acid-treatment (8#), which proved the enhancement of dispersion affected by acid-treatment. The carboxyl group attached on the CNTs after acid treatment positively improves the dispersion effect. Moreover, compared with references, the peaks in our study are broader; we attribute this broadening to the existence of large tangles in the solution because these samples were not centrifuged. The fewer tangles and CNTs bundles the stronger absorbance signal. Normally, the UV-Vis peaks of CNTs should exhibit absorption characteristic of both metallic and semiconducting tubes absorption, but the peaks from absorption by metallic tubes between 400 and 600 nm are absent in our case, which means our CNTs mostly existed in the semiconducting state. Another factor is that the diameter of these CNTs is too large to give a pronounced metallic effect.
3.5. The $I$–$V$ Properties of CNTs Treated by Various Surfactants

The $I$–$V$ plots of CNTs treated with different surfactants are shown in Figure 5. The resistances of CNTs-1 (8#, without surfactant), CNTs-2 (9#, without surfactant) and CNTs-2 treated with SDBS, PVP, SDBS/PVP and TX100 at 20 V are $7.41 \times 10^2$ $\Omega$, $7.52 \times 10^3$ $\Omega$, $7.98 \times 10^2$ $\Omega$, $1.13 \times 10^6$ $\Omega$, $2.15 \times 10^4$ $\Omega$ and $8.68 \times 10^5$ $\Omega$, respectively. Large currents were found in 8# and the CNTs-2 with SDBS-treated sample, which means that the individual CNTs were connected strongly with each other and many pathways were provided for the current, not only

![Fig. 3. Light microscope images of suspensions immediately after 15 minutes of ultrasonic treatment (a, c), and after leaving aggregated on glass slides for 1 hour (b, d) dispersed by SDBS (a, b) and SDBS/PVP (c, d).](image)

![Fig. 4. UV-Vis absorption spectra of CNTs (with and without acid-treatment) in the DMAc solution.](image)

![Fig. 5. The $I$–$V$ plots of CNTs treated with different surfactants (Inset: $I$–$V$ plots of PVP and TX100 samples).](image)
along the axis of the CNTs but also from wall-to-wall interactions. In addition, by comparing the 8# and 9# samples, it proved that the acid treatment indeed destroyed the electrical property of CNTs which made the current carrying capacity of CNTs-2 almost ten times lower than that of CNTs-1. Almost all the samples showed good ohmic behavior, while the inset graph of Figure 5 indicates that the electrical properties of the samples treated with PVP and TX100 showed downward facing curves which depended on the measurement voltage. This might originate from the non-uniform distribution of the area of the surfactant after solution distillation (shown by the SEM results). Berliocchi et al.\textsuperscript{23} also believed that a non-uniform charge distribution induced a regime of space-charge limited current and a curved $I-V$ behavior.

The SDBS samples gave a higher electrical current carrying capacity than that of the CNTs-2 samples, which was attributed to a contribution of the conductivity from the remnant SDBS particles on the CNTs. The current carrying capacity of the sample treated with SDBS/PVP was higher than that of the samples treated with TX100 and PVP, because the CNTs in the SDBS/PVP can form

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**Fig. 6.** SEM micrographs of different surfactant-dispersed suspensions (a) 1# SDBS, (b) EDS of SDBS, (c) 2# PVP, (d) 3# PVP/SDBS, (e) 4# TX100, and (f) 9# CNTs-1 (see Table 1 for sample details).
CNT networks and moreover, SDBS absorbed on CNTs plays a role in bridging which strengthens the connection between neighboring CNTs and allows the electrical current to pass through different CNTs easily by wall-to-wall contact. Meanwhile, the polymer surrounding CNTs in the sample treated with TX100 and PVP decreased the capability of charge movement, which makes the current passing through them very small, and the conductivity was also affected by the continuity of the polymer film.

3.6. SEM Images of CNTs Treated with Various Surfactants

To work out the relationship between the architecture and the electrical properties, 1#, 2#, 3#, 4# and 9# suspensions (see Table I) were selected to investigate the aggregated states of CNTs captured by SEM (Fig. 6). Compared with the other samples, we observed the strongest aggregation of CNTs in the SDBS sample (Fig. 6(a)). Besides CNTs, large massed aggregations were found in the microscope, and EDS (Fig. 6(b)) showed the existence of sodium in the large mass aggregations, which further proved the assumption that SDBS particles aggregated together by themselves and encouraged the deposition. The ragged edges indicated that SDBS is a type of non-wetting particle in the amide solvent. The CNTs treated by SDBS/PVP (Fig. 6(d)) showed an excellent break up of aggregates effect, which proved the dispersion schematic in Figure 1(b). The networks formed after distilling the solution had looser network structures and no strong bundles could be seen. Nevertheless, there were no clear CNTs figures found in the PVP (Fig. 6(c)) and TX100 (Fig. 6(e)) samples, the surfactants surrounded and adhered on the CNTs, and then polymer/CNTs films formed (pointed to by arrows in Fig. 6(e)). In particular in PVP, a continuous polymer matrix film was built up, and only slight CNTs agglomerates could be seen (pointed to by arrows in Fig. 6(c)), which is agreement with the results of the electrical measurements (the PVP sample gave a lower current than the TX100 sample). The circular “hillocks” in the PVP sample should be PVP particles; the round shape indicates that they originate from a separation out of the solution during the drying process and this non-uniformity induced the obvious downward I–V curve for the PVP treated sample. Furthermore, we found the CNTs-1 sample without surfactant treated (Fig. 6(f)) are strongly aggregated, but some CNTs seem also to be separated, and these images of CNTs are clear. The results of the states of aggregation study matched with the electrical properties, and explained the conductivity of the various CNTs samples very well.

4. CONCLUSIONS

In summary, sedimentation results showed that all the CNTs treated with surfactants, except for the case of SDBS, give visibly-stable dispersions for at least two months; even samples with no surfactant showed no obvious depositions. DMAc has been proved to be an excellent solvent for dispersing CNTs, by comparison with water, because there is a “competitive” balance of the adsorption of surfactant molecular chains and solvent molecules which helps in stabilizing the CNTs in solution. Although the sedimentation tests gave no clear effect of the carboxyl groups on the dispersion of CNTs, the UV-Vis spectra proved that the carboxyl group attached to the CNTs positively improve the stabilizing effect. The states of aggregation of CNTs treated with different surfactants are different, and the electrical properties of CNTs are strongly related with these states. The acid treated CNTs with the aid of SDBS/PVP showed the best de-bundling capability and looser network structures were found in the SEM, and this sample also gave the lowest resistance (2.15 × 10² Ω, at 20 V) among the surfactant-treated stable suspensions. SDBS/PVP is an optimal choice among these surfactants considering the dispersion characteristics and electrical properties.

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References and Notes

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