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Abstract: Electrospray deposition (ESD) required a dispersing agent that could form a stable suspension of solution for carbon nanotubes (CNT) deposition on the carbon fiber (CF). The N-methyl-2-pyrrolodone (NMP), dimethylformamide (DMF) and tetrahydrofuran (THF) solvents were investigated for dispersion of CNT. Based on the optical observation, zeta potential and UV-Vis spectroscopy, all findings indicate that the CNT dispersed in NMP has better dispersion and higher stability. Analysis by extreme high-resolution field emission scanning electron microscope (XHR-FESEM) shows the CNT was homogeneously distributed and covered the entire surface of the CF.

Keywords: carbon nanotubes, N-methyl-2-pyrrolodone, electrospray deposition

1. Introduction

Since their discovery in 1991, carbon nanotubes (CNT) have generated tremendous interest in most areas of science and engineering because of their remarkable chemical and physical properties [1-5]. CNT have indeed been made ideal candidates for advanced composite reinforcement materials as a material that combines excellent mechanical, thermal and electronic properties [6-8]. In addition, CNT have also been widely used to hybridize with carbon fiber (CF) as reinforcement in polymer composites [9-10]. CF reinforced polymer composites are widely used in the field of aerospace, marine engineering, military and wind power infrastructure due to their outstanding performance, such as high specific strength, high-temperature resistance and corrosion resistance [11]. One of the methods used to hybridize CNT and CF is the electrospray deposition method (ESD) [12]. This method required liquid as a medium for deposition of CNT on the surface of the CF.

It is commonly believed that pristine CNT unable be dispersed directly because of their high aspect ratios and strong van der Waals interactions, while CNT surface modifications are needed to disperse CNT homogeneously [13]. Based on these commonly accepted perspectives, various surface modification or side wall functionalization techniques such as covalent bonding, surfactant coating, and polymer wrapping have been developed [14-20]. However, these methods are time-consuming, complex, and will result in the significant damage to the CNT structure and properties. Historically, pristine CNT without surface functionalization have been identified to be substantially debundled and relatively stable dispersed in certain organic solvents, such as N-methyl-2-pyrrolodone (NMP) [21-23].

In this study, ESD method was used for pristine CNT deposition on the CF surface. Various solvents have been tested for CNT dispersion, such as NMP, dimethylformamide (DMF) and tetrahydrofuran (THF). Appropriate solvents are selected on the basis of suspension stability, solvent type, performance, zeta potential and UV-Vis spectroscopy for the ESD process. The aim of this research is to identify the best solvent for dispersion and deposition of CNT on the surface of CF using the ESD method.

2. Experimental

2.1 Materials

Multi-walled CNT with a length of 10-30 μm, an inner diameter of 5-10 nm, an outer diameter of 20-30 nm and a Woven CF with a thickness of 0.3 mm, a density of 1.76 g/cm³ were purchased from Sky Spring Nanomaterials Inc., Houston, TX, USA and Toray Industries Inc., Chuo-Ku, Tokyo, respectively. NMP, DMF and THF solvents were purchased from Sigma-Aldrich, St. Louis, MO, USA.

2.2 Dispersion of CNT

CNT dispersions in different solvents with a concentration of 0.5 mg / mL were produced using a sonicator (Q700, Qsonica, Melville, CT, USA) at a frequency of 50 kHz for 5 hours. The samples were then placed in the vials for further testing.

2.3 Characterization of CNT dispersion

The dispersion and stabilization of CNT were first investigated by optical observation of sedimentation. Then, the CNT dispersion was characterized by using Zetasizer Nano Instrument (Model: Nano ZS ZEN3600, Malvern, UK) to obtain zeta potential analysis. After that, UV-Vis spectroscopy was performed to investigate the stability of CNT in solvent over a week. In this test, the CNT dispersion was characterized by UV-Vis spectrophotometer (Model: Cary 50 Conc, Agilent technologies). The samples were filled into quartz cuvette and placed in the part between detector and UV-Vis light. The UV–Vis absorption spectra were recorded between 200 nm and 800 nm.

2.4 Preparation and characterization of CNT deposited on CF

The CNT dispersion with the highest stability and good dispersion was used to deposit CNT onto the CF surface using the ESD method to form hybrid CF-CNT. The equipment consists of a stainless steel needle and a roller steel platform as a ground electrode. The precision high voltage power supply is connected to the stainless-steel needle. The needle is fitted to a 20 ml syringe and the syringe is mounted to a precision syringe pump. Woven GF with dimension of 20 cm x 30 cm attached to the roller steel platform. The CNT dispersion with a flow rate of 0.02 ml/min was applied throughout the process with an applied voltage of 15 kV and spray duration of 15 minutes. On completion of the spray process, the CF was left to dry for 24 hours, and the spray process was repeated on the opposite side. After that, an extreme high-resolution field emission scanning electron microscope (XHR-FESEM) (Model: FEI Verios 460L) was used to analyse the morphology of the hybrid CF-CNT.

3. Results and discussion

3.1 Stability of CNT in various types of solvent

3.1.1 Optical Observation

The preparation of the CNT dispersion is very important for deposition of CNT on the CF using ESD method. This is due to the ESD method required liquid as a medium to deposit CNT to CF. Solvents such as DMF, NMP and THF have been used to disperse CNT since it is difficult for the water to disperse pristine CNT without any functionalization. In order to determine the best solvent for preparation of CNT dispersion, the stability of the CNT in the solvent need to be investigated. The

stability of the CNT in solvent is a useful indication of its dispersion quality, as CNT usually tend to re-agglomerate into bundles and sedimentation with time in an unstable solvent. High dispersion quality of the CNT had less agglomeration and it took a long time for sedimentation to occur. The optical observation on the CNT agglomeration and sedimentation of the CNT in the solvent is a simple approach to evaluate the dispersion quality of CNT. Although this optical observation could not determine the absolute quality of CNT dispersion, it was well suited for comparative studies where only relative information was obtained and compared under the same circumstances from samples tested. The stability study of the CNT in DMF, NMP and THF solvents was done using sonication and optical observation based on the sedimentation time. The digital photographs of vials of the CNT dispersed in DMF, NMP and THF solvents taken after sonication, one hour, one day and one week are shown in Fig. 1.
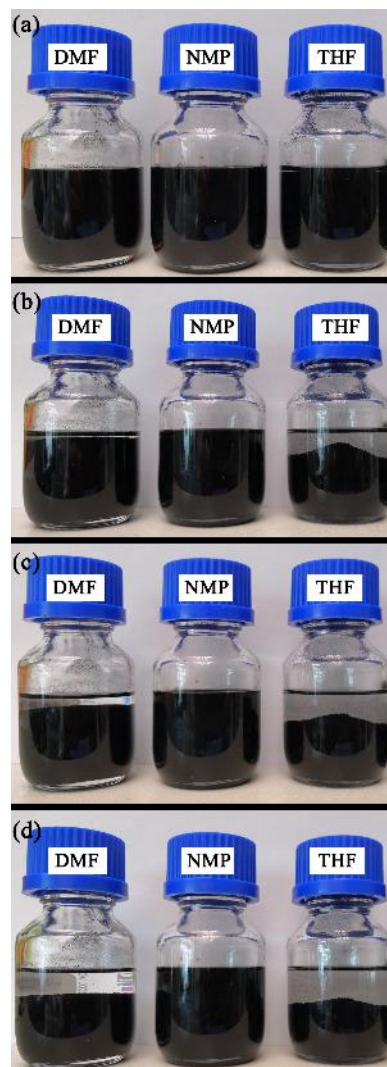
Fig. 1: Digital photographs of CNT dispersed in DMF, NMP and THF solvent. Pictures were taken after (a) sonication, (b) one hour, (c) one day and (d) one week.

From the observation, the CNT dispersed in DMF slightly aggregated after one hour and sedimentation started in a day. For the CNT dispersed in THF, the CNT sedimentation is very fast and most of the CNT settle down in the dispersion after one hour. This can be clearly seen the sedimentation of CNT at the bottom together with the upper clear solvent. In contrast, the stable black and uniform dispersion of CNT dispersed in NMP are clearly visible. The CNT dispersed in NMP remain stable and shows no aggregation or sedimentation after one week. Based on the observation, this proves that NMP is the best solvent for dispersing CNT while the THF is the poorest solvent for dispersing CNT in the present investigation solvent. In addition, this indicates that pristine CNT without any physical wrapping or chemical functionalization can be well-dispersed and relatively stable in solvent such as NMP. This is due to the polarity of the solvent that helps the CNT to disperse well.

3.1.2 Zeta Potential

Zeta potential is one of the useful techniques to determine the stability of the CNT in the solvent as the optical observation could not determine the absolute stability of the CNT in the solvent. Fig. 2 shows the zeta potential of CNT dispersed in DMF, NMP and THF solvents. Based on the result, it demonstrates the CNT dispersed in DMF, NMP and THF solvents have zeta potential value of -15.2 mV, -31.9 mV and -1.7 mV, respectively. The negative value of zeta potential for all types of solvents indicates the surface charge of CNT is negative. All solvents give a similar negative zeta potential because the DMF, NMP and THF are categorized as polar aprotic solvents (without O-H or N-H bonds) and served as Lewis base as shown in Fig. 3.
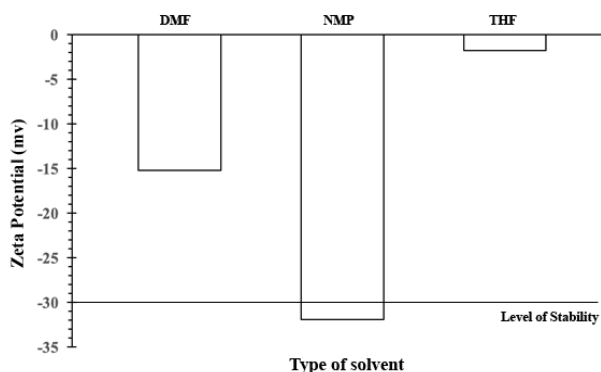

Fig. 2: Zeta potential of CNT dispersed in different types of solvent.

The NMP and DMF show higher zeta potential as compared to THF due to the presence of nitrogen in their chemical structure. Besides that, NMP and DMF also have higher dipole moment as compared to THF as referred to Table 1. The reason behind such higher dipole moment of the NMP and DMF is due to the participation of the nitrogen lone pair electron to resonance structure of the

NMP and DMF to form a positive charge on the nitrogen and negative charge on oxygen [24]. This high dipole moment causes a higher repulsive force between the CNT and prevents the CNT from agglomeration. Thus, it will lead to higher stability of the CNT in solvents [25].
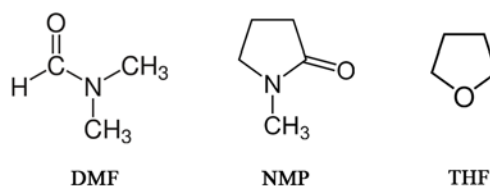

Fig. 3: Chemical structure of DMF, NMP and THF.

Table 1. The dipole moment of DMF, NMP and THF [26].

Solvent	Dipole Moment
DMF	3.86 D
NMP	4.09 D
THF	1.75 D

Table 2 shows the stability of suspension in relation to zeta potential. Based on the table, the value of zeta potential higher than -30 mV can be considered to have sufficient repulsive force. Thus, the zeta potential value -31.9 mV of CNT dispersed in NMP resemble the moderate stability and indicates the CNT was dispersed individually without aggregation. Meanwhile, the zeta potential value -15.2 mV of CNT dispersed in DMF indicates incipient instability and the zeta potential value -1.7 mV of CNT dispersed in THF indicates maximum aggregation and flocculation. This zeta potential result was consistent with the previous optical observation. The optical observation after 1 hour shows most of the CNT settle down in the THF solvent, the CNT slightly aggregated in DMF solvent and the CNT remains stable in NMP solvent. The NMP shows the highest stability of CNT dispersion followed by DMF and THF may be due to the NMP, which possess the highest dipole moment among these solvents. Although, the zeta potential value of CNT dispersed in NMP only slightly exceeds the level of stability, it is suitable for electrospray deposition process as long the CNT is not aggregate and settles down in syringe during the process. For the CNT dispersed in DMF and THF, it not suitable for electrospray deposition due to the aggregation and sedimentation of the CNT can lead to the jammed at the syringe nozzle.

Table 2. Stability of suspension in relation to zeta potential [27].

Stability characteristics	Average zeta potential in mV
Rapid coagulation or flocculation	From 0 to ±5
Incipient instability	From ±10 to ±30
Moderate stability	From ±30 to ±40
Good stability	From ±40 to ±60
Excellent stability	More than ±61

3.1.3 UV-Vis spectroscopy

UV-Vis spectroscopy is another useful technique and widely used to characterize the CNT in solvents. As the CNT is dispersed, the solvent becomes darker and absorbs more light and therefore, the maximum absorbance can be used to determine the quality of dispersion. The Beer-Lambert law is commonly used to measure the quality of CNT dispersion by relating the absorbance intensity to the concentration of the CNT in the solvent at a specific wavelength [28]. Fig. 4 shows UV-Vis spectrum analysis of the CNT dispersed in DMF, NMP and THF solvents after sonication, one hour, one day and one week. As is well known, each solvent has a UV cutoff wavelength. Generally, the UV-Vis spectrum below the UV cutoff wavelength becomes noise because the solvent itself absorbs all of the light. Since the CNT peak in this study appeared at around 230 nm, the presence of the CNT peak was only visible in the CNT dispersed in THF due to the lower UV cutoff of THF at 212 nm while the UV cutoff of DMF and NMP are 268 nm and 285 nm, respectively.

The presence of CNT peak at around 230 nm is similar to other researchers, which reported the presence of CNT peak in the range between 200 nm to 260 nm. Jiang et al. reported the presence of CNT peak at 253 nm [29], Yu et al. reported the presence of CNT peak at 260 nm [30] and Grossiord et al. reported the presence of CNT peak at 235 nm [31]. Due to the high UV cutoff of DMF and NMP solvents that exceed the CNT peak at 230 nm, the quantitative study using Beer-Lambert law to investigate the concentration of CNT in solvents could not be calculated. It is therefore impossible to provide a direct quantitative comparison between DMF, NMP and THF solvents owing to the CNT peak absence in DMF and NMP solvents. Although quantitative comparisons between DMF, NMP and THF solvents could not be made using this UV-Vis spectroscopy test, the qualitative comparison could be made by observing the change of absorbance intensity over time.

Lou et al. reported that the change of absorbance intensity over time is proper for the qualitative study to investigate the stability of CNT [32]. Usually, the CNT dispersion with good stability has a small change of absorbance intensity over time. From the result, the CNT dispersed in NMP shows the smallest change in absorbance intensity over time, followed by CNT dispersed in DMF and CNT dispersed in THF. This shows that CNT dispersed in NMP has the greatest stability compared to DMF and THF.
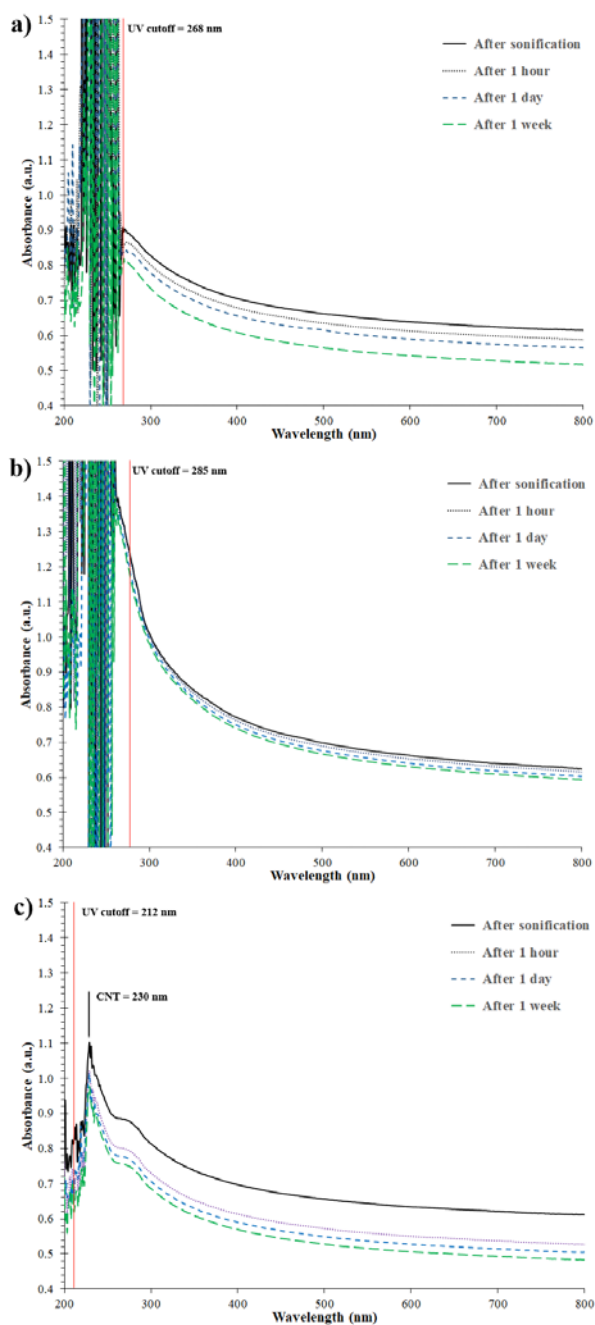
Fig. 4: UV-Vis spectrum of the CNT after sonication, one hour, one day and one week dispersed in (a) DMF, (b) NMP and (c) THF.

The ability to monitor CNT dispersion in the solvent enables to detect early-stage quality issues and prevent the problem during ESD process. Based on the optical observation, zeta potential and UV-Vis spectroscopy, all result demonstrates the CNT dispersed in NMP has good dispersion and higher stability. Thus, CNT dispersed in NMP was chosen for the electrospray process to deposit CNT on the CF to form the hybrid CF-CNT.

3.2 Distribution of CNT deposition on the CF

3.2.1 FESEM analysis

The surface morphology of the hybrid CF-CNT was characterized by FESEM. Fig. 5 shows the FESEM images of the hybrid CF-CNT. It was observed that the CNT was homogeneously distributed and covered the entire surface of the CF. As is well known, the CNT tends to agglomerate due to the strong Van der Waals force. Interestingly, the CNT dispersed in NMP managed to properly deposit the CNT on the CF surface without forming any agglomeration. Thus, based on the observation, the NMP solvent is capable of preventing the agglomeration of the CNT and is suitable for the deposition of the CNT on the CF surface by using the electrospray method. In addition, CNT dispersed in NMP also operates well on electrospray without CNT jammed in the syringe nozzle compared to other solvents due to agglomeration.
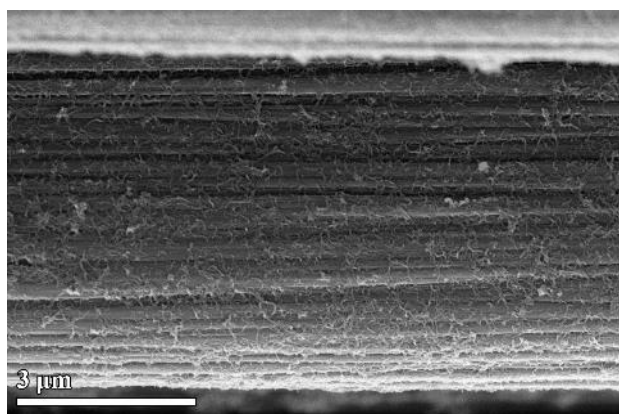

Fig. 5: SEM images of hybrid CF-CNT.

4. Conclusion

This investigation confirms that the NMP is suitable as a solvent for electrospray deposition to deposit CNT on the CF as compared to DMF and THF. Based on the optical observation, the NMP is the best solvent for while the THF is the poorest solvent. The zeta potential analysis also shows that CNT dispersed in NMP has a higher zeta potential value of more than -30 mV, which can be considered to have sufficient repulsive force. Furthermore, UV-Vis analysis also indicated that the CNT dispersed in NMP has the greatest stability compared to DMF and THF. Based on these results, this proved that pristine CNT without any physical wrapping or chemical functionalization could be well-dispersed and relatively stable in solvent such as NMP. Finally, analysis by FESEM shows the CNT was homogeneously distributed and covered the entire surface of the CF.

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