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Electrophoretic Deposition (EPD) of Multi-Walled Carbon Nanotubes (Mwcnts) Onto Carbon Fiber (CF) Fabric

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Abstract: The Fiber Reinforced Polymer Composite (FRPC) has been widely employed in structural applications. However, adding nanoparticles such as multi-walled carbon nanotubes (MWCNTs) can be used to improve the composites' mechanical properties substantially. The purpose of this study is to investigate the stability of MWCNTs in distilled water (DW) and dimethylformamide (DMF). Electrophoretic deposition (EPD) was chosen as the method for depositing MWCNTs onto carbon fiber (CF) fabric because of the advantages of simple equipment and inexpensive cost. Thus, the effect of voltage and deposition time were examined to attain the ideal condition for the EPD of MWCNTs onto CF fabric. The stability of dispersed MWCNTs in various dispersing mediums was explored as the importance of the MWCNTs to remain stable in the medium is essential to achieve homogeneous deposition. The UV-Vis and colloidal stability test revealed that MWCNTs dispersed in DMF have greater stability than DW. Scanning Electrode Microscopy (SEM) images exhibited that 10 minutes and a 20 V voltage were the optimal conditions for the deposition of MWCNTs onto CF fabric.

Keywords: Electrophoretic deposition, colloidal stability, multi-walled carbon nanotubes

1. Introduction

Fiber reinforced polymer composite has been extensively used as a primary load-bearing structure in the aerospace industry. Carbon fiber (CF) is widely used as a fiber component in a composite due to its low densities and superior mechanical properties [1,2]. The previous researcher reported that the fiber is used to improve the performance of polymer composite in the form of fatigue performance, strength, and specific stiffness. However, the interfacial and compression properties of the fiber-reinforced polymer composite are dependent on the interface between the fiber and the matrix [3]. For a continuous fiber-reinforced composite, the interface between the fiber and matrix is critical as it acts as a bridge that transfers load between the fiber and the matrix through shear flow, therefore, it is challenging for composites with high interfacial shear strength to transfer stress for reinforcement purposes [4]. However, the advancement of technology has introduced a hierarchical structure to improve the interfacial strength of fiber composite [5]. Among several nanomaterials available, carbon nanotubes (CNTs) have been introduced into conventional fiber composite due to their remarkable thermal and electrical properties, and outstanding modulus and strength [6].

Direct mixing, electrophoretic deposition (EPD), chemical vapour deposition (CVD) growth coating, and dip coating are some of the methods utilized to integrate nanofillers. EPD has proven to be useful for depositing CNTs onto fiber surfaces, probably due to its low cost, ease of use, uniformity of deposits, microstructural homogeneity, and lower electric potential requirements [7]. In the field of carbonaceous materials, EPD is attracting interest for controlling

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individual nanoparticles in colloidal suspensions to develop sophisticated nanostructured coatings and nanoscale films with superior characteristics.

In this paper, the influence of voltages and deposition times on MWCNTs suspension stability in distilled water (DW) and dimethylformamide (DMF) medium were examined to get a uniform deposit of MWCNTs on the CF surface. The behaviour of MWCNTs dispersed in DW and DMF suspensions were evaluated in terms of suspension stability in the presence and absence of voltages. UV-Vis (ultraviolet-visible) spectroscopy was used to confirm the findings. The relationship between voltage and deposition time was explored further and confirmed with the MWCNTs deposition morphology on the CF fabric surface.

2. Experimental

2.1 Materials

As-received MWCNTs (average diameter of < 8 nm, length of 5-20 µm, and purity of > 95 wt% (MWCNTs) were used in this study and purchased from Skyspring Nanomaterials, Inc., USA. The commercial plain-woven CF (530-C) was supplied by Fiber Glast Developments Corporation, USA. MWCNTs and CF fabric were used as the reinforcements for the composites. Dispersing mediums used were distilled water (DW) and N-Dimethylformamide (DMF). DMF was supplied by Merck Sdn. Bhd.

2.2 Electrophoretic Deposition Process

The EPD experimental arrangement consisted of a power supply (BK1672, Taiwan), multimeter (Fluke 115, USA), glass deposition bath, and two electrodes (Figure 1). For the EPD process, MWCNTs suspension of 0.05 mg/mL was prepared by dispersing MWCNTs in DW and DMF, respectively. The MWCNTs suspension was sonicated using a Kudos SK2200H bath ultrasonicator for 3 hours to form a stable suspension. The bath ultrasonicator has a power consumption of 100 W and an operating frequency of 53 kHz. Both stainless steel and CF (with a dimension of 78 mm x 13 mm) were immersed in the EPD cell containing MWCNTs suspension and were fixed parallel at a distance of 1.5 cm. The EPD was performed at numerous voltages (5 V to 30 V) and deposition times (0 to 30 minutes) to generate optimal conditions. The deposited CF was removed from the EPD cell and dried at room temperature for 1 day followed by drying in the oven at 150°C for 24 hours.

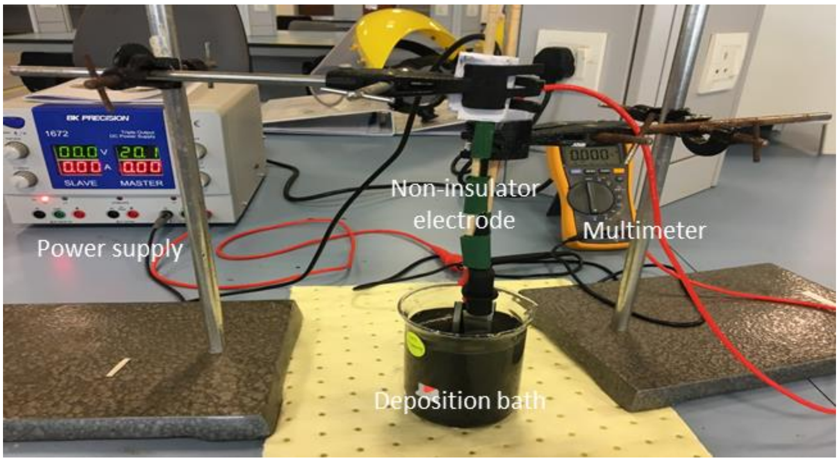

Fig. 1 - Experimental set-up for EPD process

2.3 Characterizations

The surface morphology of the MWCNTs and the deposited MWCNTs on the CF were observed using the Scanning Electron Microscope, SEM (JEOL JSM-6390LA). Before imaging, the deposited CF rectangular samples (1 cm × 1 cm) were sputtered with a thin layer of gold coating to avoid electrostatic charging. The UV–Vis spectrophotometer (SHIMADZU UV-1800) with UV–Vis absorption spectra between 200 and 800 nm were performed to evaluate the stability of ultrasonicated MWCNTs suspension. The supernatant of MWCNTs suspension was employed to acquire a detectable transmission during the measurements. Fourier Transform Infrared, FTIR (Shimadzu IRAffinity-1S) is used to study the nature of MWCNTs surface group after sonication and deposition of MWCNTs onto CF surface.

3. Results and Discussion

3.1 Colloidal Stability

Figures 2 and 3 show the colloidal stability of the MWCNTs dispersed in DW and DMF, respectively. Before sonication, the MWCNTs were observed floating on the surface of the DW and DMF. This observation is probably related to the nature of the pristine MWCNTs that are randomly oriented and heavily agglomerated due to their high aspect ratio and strong Van der Waals interaction between CNTs. Figures 2 (b) and 3 (b) show the condition of dispersed MWCNTs immediately after sonication. In this state, the dispersion of the MWCNTs was optimum, which is shown by the opacity of the MWCNTs dispersed in the solvent [8-10]. The finding showed that MWCNTs dispersed in DW (Figure 2) slowly agglomerated 10 minutes after the sonication and the precipitation gradually proceeded with time. The strong Van der Waals forces and inherent hydrophobic nature of the MWCNTs prevent the interaction of MWCNTs with DW that is a polar solvent [11,12]. However, higher opacity was observed for MWCNTs dispersed in DMF (Figure 3) and this proved that the MWCNTs are fully dispersed. In the case of the DMF as a solvent, the opacity of the suspension has no apparent changes, proving that the MWCNTs are stable for a longer period as reported by previous work [13].

Figure 4 shows the EPD process for MWCNTs dispersed in DW and DMF, respectively. Figure 4 (a)-(d) shows the behaviour of MWCNTs dispersed in DW at different voltages (5-30 V) and a constant time of 5 minutes. The result revealed that at a lower voltage, there is no obvious gas evolution was observed. However, apparent gaseous bubbles were detected at the electrodes as the voltage was increased to 30 V (Figure 4 (d)). This confirms a previous study stated that at higher voltage, electrolysis of water occurred on the surface of the electrodes and may cause a reduction of quality in deposited samples [11]. Therefore, further investigation was performed at a fixed voltage of 20 V and at various deposition times (10 to 30 minutes). As shown in Figure 4 (e)-(g), the findings show that the longer the deposition time of EPD, the more gas bubbles forms at the electrode. This observation exposed that the electrolysis of water can be prevented using a low voltage (20 V) and shorter deposition time (10 minutes). Similarly, when the MWCNTs dispersed in DMF at 20 V and deposition time of 10 minutes (Figure 4 (h)), the suspension retained a uniform black colour with no visible development of gaseous bubbles. This shows that the use of DMF suspension can reduce the electrolysis gas revolution [7,9].

Fig. 2 - Colloidal stability of MWCNTs dispersion in DW (a) before sonication, and stability of MWCNTs after 3 hours sonication at; (b) 0 minutes; (c) 10 minutes; (d) 20 minutes; (e) 30 minutes; (f) 40 minutes; (g) 50 minutes; (h) 1 hour; (i) 3 hours; (j) 7 hours; (k) 1 day

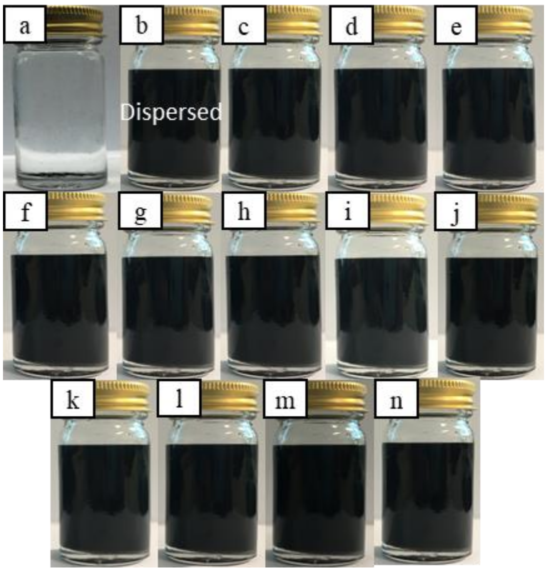

Fig. 3 - Colloidal stability of MWCNTs dispersion in DMF (a) before sonication, and stability of MWCNTs after 3 hours sonication at; (b) 0 minutes; (c) 10 minutes; (d) 20 minutes; (e) 30 minutes; (f) 40 minutes; (g) 50 minutes; (h) 1 hour; (i) 3 hours; (j) 7 hours; (k) 1 day; (l) 1 week; (m) 2 weeks; (n) 3 weeks

3.2 Ultraviolet-Visible Spectroscopy

Figures 5 and 6 shows UV-Vis absorption spectra of MWNCTs dispersed in DW and DMF, respectively after sonication. The absorbance of MWCNTs dispersed in DW (Figure 5) was maximum at 264 nm wavelength immediately after sonication (t = 0 minute) and steadily decreased from UV to near IR wavelength. After sonication, the absorbance intensity of MWCNTs suspension steadily reduces with time, which is consistent with colloidal stability. This demonstrates that the ultrasonication process generates enough energy to disrupt the Van der Waals forces between MWCNTs. Thus, causes bundled and agglomerate MWCNTs to be dispersed into an individual nanoparticle. As time increases, the suspension gradually agglomerates, and precipitation progress with time. This is due to the hydrophobic nature of MWCNTs and Van der Waal's forces to overcome the sheer force between the MWCNTs which initially prevented interaction with DW. Figure 6 shows UV-Vis absorption spectra of MWCNTs dispersed in DMF. The highest absorbance after sonication (t = 0 minute) is at approximately 300 nm. There was no decrease of intensity at week 1 and this observation shows that MWCNTs dispersed in DMF are stable for several weeks [13]. Previous studies report that individual MWCNTs are more absorptive in the UV-Vis range of wavelengths between 200 and 800 nm [14], while agglomerated MWCNTs are rarely active in the UV-Vis region because charge carrier tunneling between MWCNTs inhibits photoluminescence [15].

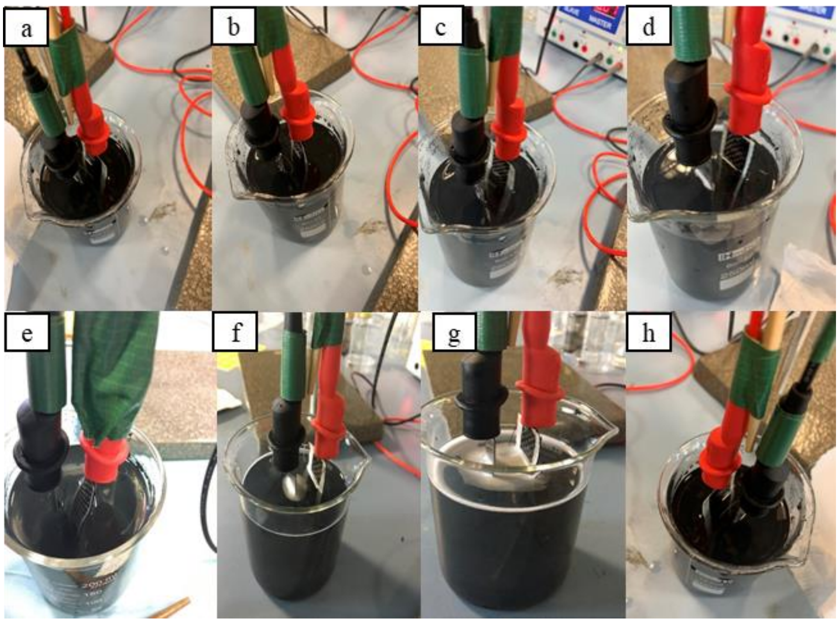

Fig. 4 - Colloidal stability of MWCNTs dispersed in DW during EPD at a constant time of 5 minutes at a voltage of (a) 5 V; (b) 10 V; (c) 20 V; (d) 30 V, and a constant voltage of 20 V at deposition time of; (e) 10 minutes; (f) 20 minutes; (g) 30 minutes, and; (h) colloidal stability of MWCNTs dispersed in DMF at a voltage of 20V and deposition time of 10 minutes

3.3 Fourier Transform Infrared (FTIR)

Figure 7 shows FTIR spectra of pristine, and sonicated MWCNTs. This characterization is performed on infrared wavelengths between 4000 to 500 cm-1 [16]. Pristine MWCNTs (Figure 7 (a)) show no significant peak whereby it suggests that MWCNTs are fully inert and there are no functional groups during characterization. Figures 7 (b) and (c) show that the sonication process causes slight changes in the spectra of MWCNT. The peak at 3393.90 cm-1 which is a characteristic of O-H stretching is more pronounced in Figure 7 (b) and peaks at 2359.04 cm-1 and 2362.90 cm-1 for Figure 7 (b) and (c) respectively which is characteristic for absorption of the C=C group. This may be due to a functional group or defective site created during the sonication process. Whereby the previous study shows that there is a tendency to form defects if MWCNTs were to be sonicated for a long time [17]. Figure 8 shows FTIR spectra of as received CF and deposited CF where the wavelength used to characterize this sample is between 4000 to 1000 cm-1. The spectra for as received CF showed a peak at 3736.28 cm-1 which is assigned to O-H stretching (Figure 8 (a)). Deposited CF showed peaks at 2941.57 cm-1 and 1714.79 cm-1 which indicated the presence of C-H stretching and C=O deformation. According to previous studies, the stretching of the C=O region in deposited CF compared to as-received CF shows that there is carboxyl formed due to the presence of CNTs on the surface of CF fabric as a result of the EPD process [18]. This shows that EPD is suitable to deposit CNTs onto CF fabric to enhance the surface roughness of the CF used to fabricate FRP with better adhesion with the polymeric matrix.

3.4 Morphologies of Deposited CF

SEM was used to observe morphologies of MWCNTs, as received CF, and deposited MWCNTs onto CF fabric where the effect of voltages and deposition times were investigated (Figure 9 and Figure 10). It is reported that CF has weak adhesion with the polymeric matrix and has a higher tendency to cause fiber and matrix debonding [19]. Therefore, deposition of MWCNTs onto CF can be regarded as improving the surface roughness of the CF and also improving the overall CF matrix compatibility and overall mechanical properties of composite [9]. Figure 9 (b) and (c) shows SEM images of as-received CF. The surface of the CF is smooth with parallel grooves along the axis of CF.

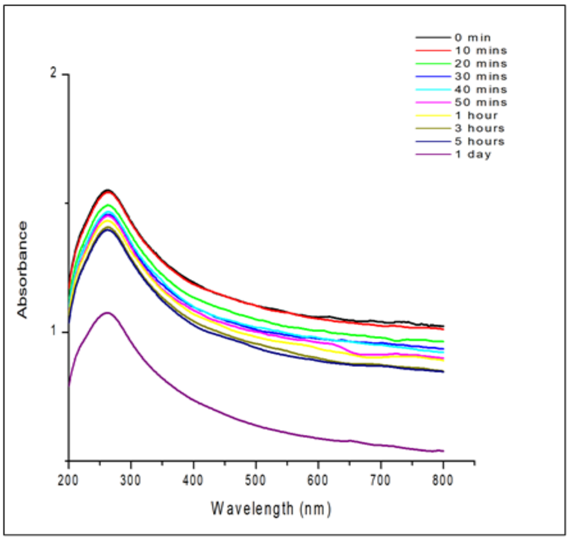

Fig. 5 - UV-Vis spectra of MWCNTs dispersed in DW (after sonication) as a function with time

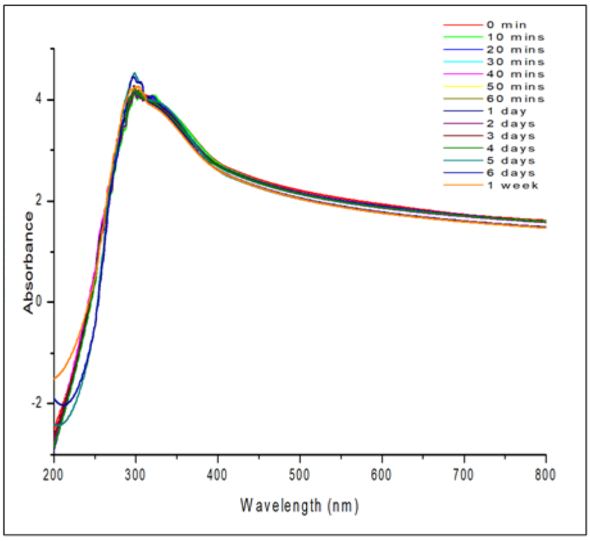

Fig. 6 - UV-Vis spectra of MWCNTs dispersed in DMF (after sonication) as a function with time

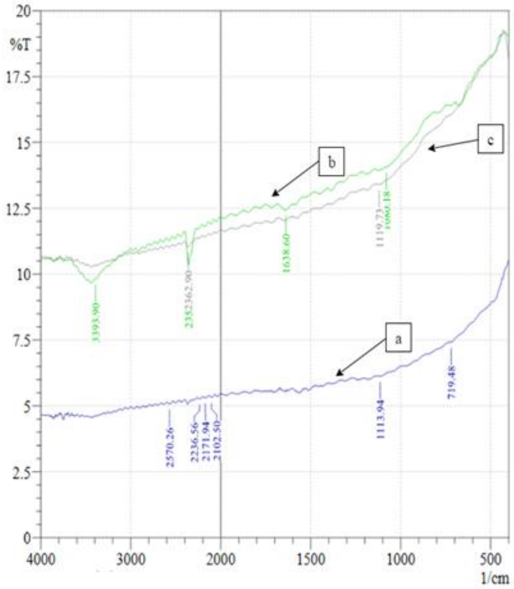

Fig. 7 - FTIR spectra of (a) pristine MWCNTs; (b) MWCNT sonicated in DMF, and (c) MWCNTs sonicated in DW

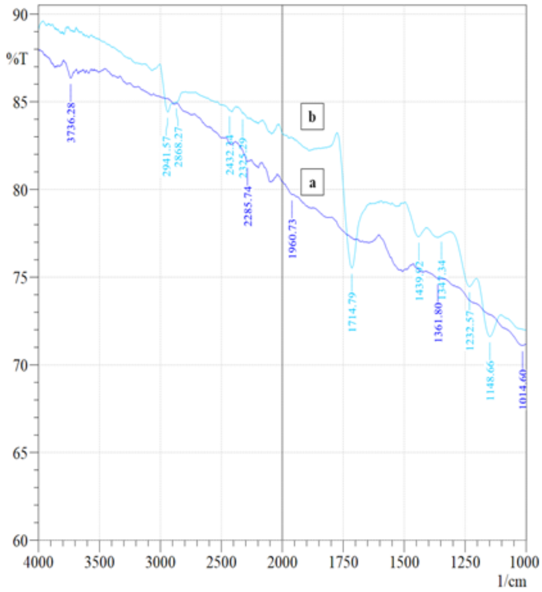

Fig. 8 - FTIR spectra of (a) as received CF and; (b) deposited CF

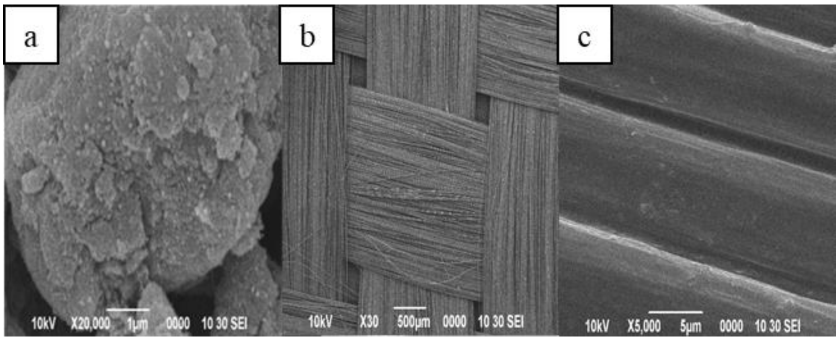

Fig. 9 - SEM images of (a) MWCNTs; (b) and; (c) CF (magnification of 20 Kx, 30x, and 5 Kx)

Deposited CF in Figure 10 shows a rougher surface with MWCNTs adhering randomly on the surface. SEM images of Figure 10 (a) - (n) shows that there is a gradual increase in deposition of MWCNTs onto the surface of the CF (with an increase of voltage from 5 to 30 V at a constant time of 5 minutes). Figure 10 (a) - (d) shows that there is a large area of CF are not covered with MWCNTs, while Figure 10 (e) - (n) shows that the deposited MWCNTs are gradually greater. This suggests that the bath ultrasonicator used was not sufficient to fully break the van der Waals bonding between the MWCNTs to allow homogenous deposition onto the surface of the CF [9]. Figure 10 (i) - (l) shows the deposition of MWCNTs into the surface of CF with a constant voltage of 20 V at a variable time of 10 to 20 minutes. The SEM images show deposition of MWCNTs which cover the surface of the CF and they are gradually increased and thickens with time. However, the formation of the pinhole was observed on the surface of the deposited CF (Figure 10 (l)), which is due to the formation of gas bubbles on the surface of the suspension during EPD (Figure 4 (f)). This observation confirms the previous study that stated that the gas evolution causes the air bubbles formed to be entrapped within the deposit [7]. The SEM images reveal that the deposited MWCNT-DMF onto CF (Figure 10 (n)) showed a slightly uniform distribution with the CF surface almost completely covered as compared to deposited MWCNT-DW onto CF (Figure 10 (j)) probably due to better dispersibility and stability of MWCNTs in DMF.

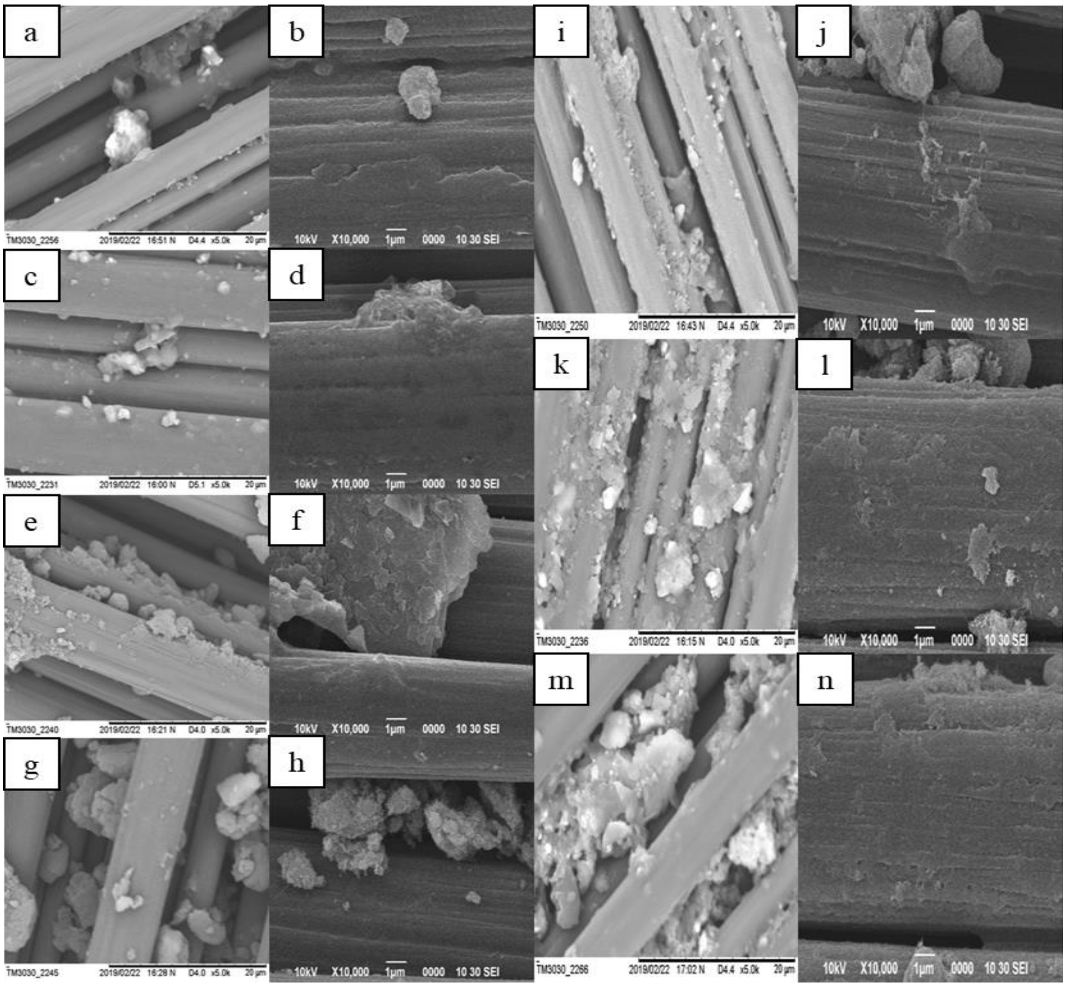

Fig. 10 - SEM images of deposited MWCNT-DW ((a)-(l)) and MWCNT-DMF; ((m) and (n)) onto CF surface at a fixed time of 5 minutes with numerous voltages of 5 V, 10 V, 20 V and 30 V (magnification of 5 Kx for (a), (c), (e) and (g) and magnification of 10 Kx for (b), (d), (f) and (h)), fixed voltage of 20 V with several deposition times of 10 and 20 minutes (magnification of 5 Kx for (i), (k), and (m) and magnification of 10 Kx for (j), (l), and (n))

4. Conclusion

This investigation confirms that the colloidal stability of MWCNTs dispersed in a medium is affected by the types of mediums used. MWCNTs in DMF are much more stable than in DW after sonication. This investigation can be further confirmed by UV-Vis spectra of the colloidal suspension. EPD is proven to be an excellent method of depositing MWCNTs onto CF surface as FTIR spectra show stretching of C=O bond on the surface of CF which proves the existence of MWCNTs on its surface. The MWCNTs have better stability if dispersed in the organic solvent than an aqueous solvent. For MWCNTs dispersed in DW, high solubility and dispersed are shown in the first 10 minutes after sonication. The behavior of stability of MWCNTs in DW was affected by voltage and deposition time. The optimal condition for deposition of MWCNTs onto CF was at 20 V and 10 minutes. This is sufficient for the deposition of MWCNTs onto CF before the particles fully sediment. The higher voltage and longer deposition time have shown that bubble formation at the surrounding of the electrode during EPD is not favourable due to the formation of pinholes caused by entrapped bubbles and therefore will reduce the mechanical property of FRP.

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