Effects of solvent ratio on the encapsulation of carbon nanotubes/Arthrospira platensis composite within electrospun poly(methyl methacrylate) nanofiber

Satisvar Sundera Murthe¹, Mohamed Salleh Mohamed Saheed¹, Veeradasan Perumal², Norani Muti Mohamed¹, ², Mohamed Shuaib Mohamed Saheed¹, ², a

¹Department of Fundamental and Applied Sciences, Universiti Teknologi PETRONAS, 32610 Seri Iskandar, Perak, Malaysia
²Centre of Innovative Nanostructures and Nanodevices (COINN), Universiti Teknologi PETRONAS, 32610 Seri Iskandar, Perak, Malaysia

Corresponding author: a) shuaib.saheed@utp.edu.my

Abstract. In recent times, oil spills have plagued oceanic bodies across the globe and has caused catastrophic consequences to the marine ecosystem. As such, this study focuses on developing an oil sorption material capable of removing oil efficiently from water. Electrospinning technique was employed to create biomimetic nanofibers containing carbon nanotube/Arthrospira platensis with PMMA as a base polymer. The composite is vital to fabricate the biomimetic nanofibers as it produces well-defined nanofibers and gives the nanofibers unique configurations for oil sorption. The properties of electrospun nanofibers were examined using FT-IR spectroscopy and X-ray diffractometer. Besides that, the properties of nanofibers were examined through thorough FESEM analysis. Better barrier and morphological properties were obtained for composite nanofibers than for pure polymer nanofibers.

INTRODUCTION

Due to exponential population growth, the demand for oil production has increased tremendously. Intrinsically, oil spill has become a potential risk during oil exploration and transportation [1]. The marine oil spills which occur due to a plethora of factors cause severe damage to the aquatic ecosystem and leads to acute water pollution [2]. The current technologies utilised for oil spill remediation in marine environments can be categorised into four main classes, namely, physical, thermal, biological and chemical [3]. Conventional oil remediation methods that fall into categories described earlier can be sub-categorised into methods such as chemical dispersion, skimming, bioremediation, ultrasonic separation and flotation have flaws such as low efficiency, low reliability, high cost and may cause secondary pollution [2,4]. Regrettably, the common methods applied in oil remediation currently are unable to conform to the ideal oil spill remediation mechanism characteristics [5]. In recent times, physical sorption has been suggested as an efficient mechanism for oil spill remediation which is capable of fulfilling the ideal oil remediation criteria [1]. The electrospinning technique has emerged foremost as this technique is able to fabricate nanofibers which can absorb oil spill through physical sorption with high efficiency [4]. Electrospinning allows various conditions to be fine-tuned to prepare absorbents with advantages such as being in the nanoscale, have nanostructured geometries, possess selective wettability and reduced manufacturing costs. Nanofiber absorbent materials are highly desirable for oil spill absorption because of its capacity for complete
collection and removal of oil spill from the contaminated water body [6]. Nanofiber polymers have been shown to absorb oil spills effectively. However, there are limitations to using nanofibers composed of pure polymers. Nanofiber absorbents composed of pure polymers experiences a reduction in nanofiber strength and resiliency after oil absorption which leads to poor reusability. One method to overcome these flaws are by reinforcing the nanofiber with other materials that are durable, elastic and able to withstand mechanical stress during absorption and be oleophilic to be able to absorb oil by themselves [4].

Tandemly, CNT based composites have been researched extensively to probe its capabilities as an effective oil sorption material. Despite this variety of research, a novel research niche exists as biomimetic CNT based composites have not been incorporated into nanofibers to function as sorbents for oil spill remediation have not been explored. Previous study have shown that biomimetic hybrids have high and fast sorption capacities as well as good selectivity, high thermal stability, low density, and excellent recyclability for oil remediation [7]. A highly possible candidate material to be combined with CNT to form biomimetic composite is the blue-green algae Arthrospira platensis (AP) as evidenced by a study. Algae have been heavily studied for its capability as heavy metal adsorbents, yet its potential as an oil sorbent has only been studied once. The algae sorbent in that particular study yielded a maximum sorption rate in the range of 12-14 g/g for diesel and lubricating oil. The algae biomass can be utilised for the development of low cost sorbents and the biomass can be easily mass produced [8]. As with CNTs, AP biomass have also been regularly used in tandem with polymers. On the other hand, AP composite based nanofibers are yet to be made for oil spill remediation and this presents an opportunity to fabricate AP based biomimetic nanofibers which contains polymethyl methacrylate (PMMA) and CNTs for the removal of oil from water.

**EXPERIMENTAL**

**Methods**

The AP/CNT composite was synthesised by hydrothermal process. The AP utilised were produced commercially and were carefully removed from the packaging capsule. One gram of AP was weighed and added in 40ml of distilled water. The mixture was heated at 100°C for 10 minutes and subsequently cooled down to room temperature. Then, 4ml of glutaraldehyde was added into the mixture and stirred with a magnetic stirrer for one hour. 0.1g of untreated CNT was then added to the mixture which is then dispersed thoroughly through ultrasonication for two hours. The mixture was then heated in a Teflon container at 180°C for 12 hours. Subsequently, the container was left to cool to room temperature and the pH was adjusted to 7 thereafter by adding distilled water. The composite was obtained by filtering the mixture in a vacuum filter and was dried at 80°C in an oven.

The nanofibers were fabricated through electrospinning. 9% of PMMA was dissolved in acetonitrile: ethanol in a 4:1 ratio and was electrospun with a voltage of 25kV, collector-syringe distance of 15cm, drum rotating speed of 1300rpm and pumping speed of 0.8ml/H. The electrospinning solvent was then changed to acetonitrile and dimethylformamide (DMF). The ratio of acetonitrile: DMF was varied in ratios of 6:4, 7:3, 8:2 and 9:1. 9% of PMMA was dissolved into the electrospinning solvent and was electrospun with a voltage of 25kV, collector-syringe distance of 15cm, drum rotating speed of 1300rpm and pumping speed of 0.8ml/H. Next, the acetonitrile: DMF ratio of 6:4 was prepared and 6% of PMMA was added into the electrospinning solvent. The PMMA was dissolved in the electrospinning solvent using a magnetic stirrer. The solution was then electrospun with a voltage of 25kV, collector-syringe distance of 15cm, drum rotating speed of 1300rpm and pumping speed of 0.8ml/H. The nanofiber formed on the aluminium foil was peeled off, collected and dried in the oven at 80°C.

The procedure was repeated with slight alteration by using acetonitrile: DMF ratio of 6:4 with 6% PMMA and 1% of AP was added into the solvent and electrospun with a voltage of 25kV, collector-syringe distance of 15cm, drum rotating speed of 1300rpm and pumping speed of 0.8ml/H. The process was repeated again with yet another alteration to the process described earlier by substituting the AP with the CNT/AP composite. The nanofiber formed on the aluminium foil was peeled off, collected and dried in the oven at 80°C. All the nanofibers that were formed were later viewed under a Scanning Electron Microscope to reveal detailed images of the nanofiber structures. AP and the CNT/ AP composite was also viewed under the scanning electron microscope to inspect the structures in lucid detail. Fourier Transform Infrared Spectroscopy was then utilised to identify the presence of various function groups in AP, AP embedded PMMA nanofiber, CNT and CNT/AP. Finally, three samples consisting of AP, CNT
and AP/CNT composite was submitted for X-Ray Diffraction (XRD) analysis to study crystallinity and material orientation of the sample.

RESULTS AND DISCUSSION

The various intricacies and minute details were analysed very thoroughly through SEM. In Figure 1 (a), the dried AP were clumped due to the heating process during spray drying which binds them closely to one another. The AP clumps were in various sizes ranging from 11μm to 37μm as the algae were stacked together. In Figure 1 (b), individual AP in the composite can be seen clearly as it was hydrated during hydrothermal process and was ultrasonicated to separate it into its individual components. The curved shape of the AP stems from its original structure before dehydration where it possess a spiral configuration. During spray drying, the spiral structure of the AP is broken leaving the dried AP with its curved structure. This however, does not affect the functional capabilities of AP as its functional capabilities is not dependent of it spiral structure. The conglomeration of AP is held by CNT as evident from the SEM images. The CNT attaches itself to AP due to the crosslinking effect of glutaraldehyde and hydrothermal process. It must also be noted that the size of CNT is smaller than that of the AP by multiple magnitudes.

Figure 1 (c) reflects the structure of the nanofiber with 9% of PMMA in acetonitrile: DMF solution of 6:4 configuration. The nanofibers formed had a knotted appearance and were bundled together. As visible in the images, the nanofibers were not well formed and were tied together in nanofiber superstructures. The high voltage necessary for the electrospinning of the concentrated PMMA polymer reduces the whipping effect in electrospinning drastically. Moreover, there is a higher electrostatic attraction between the individual nanofibers as the PMMA is of high molecular weight. The bundling also prevented the complete evaporation of the electrospinning solvent which also led to the agglomeration of the nanofibers as the solvent evaporation happens after the nanofibers are deposited on the rolling drum. This is evident from the size of individual nanofibers which ranges from 250nm to 450nm. The nanofiber bundle superstructure on the other hand has a range of between 1μm to 5μm. In Figure 1 (d), the individual structure of the 7:3 is less pronounced that those of the nanofibers in Figure 1 (c). The nanofibers also exhibit agglomeration of nanofibers to some degree similar to those in 6:4 configurations. The nanofibers are bundled irregularly in large sizes with the smaller individual nanofibers measuring around 1.5μm. The nanofibers also exhibit a highly twisted and convulsed configuration indicating instability during electrospinning.

The nanofiber electrospun in 8:2 acetonitrile: DMF as seen in Figure 1 (e) showcase no characteristics of nanofibers at all. The product collected on the rotating drum were in the form of strips and small branches at some areas. The branches albeit being in ribbon morphology they cannot be classified as nanofibers. Besides that, the nanofibers in Figure 1 (f) which were electrospun from an acetonitrile: DMF ratio of 9:1 did not exhibit any nanofibers. The structures that were formed were strips that was sprayed from the electrospinning syringe and not even minor branches were formed. The nanofibers in Figures 1 (e) and 1 (f) represent solvent ratios that are unsuitable for electrospinning PMMA. The higher percentage of acetonitrile utilised to electrospin the nanofibers in Figures 1 (e) and 1 (f) reduces the capability of PMMA to form nanofibers. The acetonitrile: ethanol with the ratio of 4:1 was replaced with acetonitrile: DMF as ethanol which has a low boiling point evaporates the solvent as soon as the electrospinning solution leaves the syringe. This causes nanofiber yarns to form and block the tip of the syringe preventing nanofibers to be formed. In order to overcome the problem, DMF was chosen as a secondary solvent as it has a relatively high boiling point. The PMMA electrospinning was done with different ratios to discover the ratio that is best suited for the electrospinning of high molecular weight PMMA.
Upon reviewing the various nanofiber morphology produced from the set of solvent ratios, the acetonitrile: DMF with a ratio of 6:4 was determined to be the best ratio for electrospinning and thus the ratio was utilised to electrospin the PMMA. However, the concentration of the PMMA was reduced from 9% to 6%. This is to reduce the viscosity of the solution used for electrospinning. Figure 2 (a) portrays the images of the acetonitrile: DMF with a ratio of 6:4 and 6% of PMMA. The nanofibers formed highly resembled twigs from trees. Interestingly, the nanofibers formed exhibited rigid structures and sharper bends uncommon to nanofibers. However, this oddity can be explained by the high molecular weight of the nanofiber which contributes to its stiff structures. Upon closer inspection, the nanostructures bear a resemblance to tree branches. The shrivelled up structure arises from the evaporation of the solvent from the nanofibers from the relatively large nanofibers. The nanofiber sizes range from 650 nm to 1 μm. The large size of the nanofibers can also be attributed to the high molecular weight of the PMMA. It is also of note that the nanofibers appear to be pinned down on places where the nanofibers overlap. This is because of the rigid structure of the nanofibers prevent the smooth layering of nanofiber on top of each other and hence appears to bend down rigidly.
As seen in Figure 2 (b), the nanofibers formed are markedly different than the nanofibers in Figure 2 (a) despite the fact that only one addition was made to the nanofibers in Figure 8. The nanofibers in Figure 2 (b) were electrospun with the similar configuration of acetonitrile: DMF solvent with a ratio of 6:4 and 6% of PMMA. However, 1% of AP was added to the solution to form a suspension. The nanofibers that were formed on the rotating collector were found to be mostly aligned with the direction of the rotation of the drum. Despite the alignment, the nanofibers formed were not uniform in size and were highly erratic. These can be attributed to the uneven distribution of the suspension during electrospinning which leads to the highly skewed size distribution in the nanofibers. The Figure also shows numerous nanofibers being split away from the parent nanofibers into branches. This is due to the unevenly charged solution due to addition of AP which then breaks of into smaller dimensions. The size of the nanofibers range from 45nm to 515nm which indicates uneven electrospinning. Last but not least, the nanofibers in Figure 2 (c) was electrospun in the same conditions as the nanofibers in Figure 2 (b) except the AP was replaced with the AP/CNT composite with the same weight percentage. The resulting product are nanofibers with uniform configurations and random distribution across the collecting drum due to the whipping effect. The nanofibers with composite show well-formed cylindrical nanofibers with highly uniform sizes. The improved nanofibers are due to the presence of CNTs which allow the uniform charging of the solution throughout the nanofibers. The nanofibers are ranged from 300nm to 600nm which indicates a healthy distribution of sizes across the collecting drum. The even distribution of the composite throughout the nanofiber also allows even oil sorption to take place and allows high sorption capabilities.

Fig. 2: (a) Acetonitrile: DMF 6:4 / 6% PMMA (inset: low magnification image showing branch like structure), (b) Acetonitrile: DMF 6:4 / 6% PMMA / 1% AP (inset: low magnification image showing highly aligned nanofibers), (c) Acetonitrile: DMF 6:4 / 6% PMMA / 1% AP-CNT (inset: low magnification image showing highly uniform nanofibers)

The FTIR analysis was used for the evaluation of the functional complexes in the materials is shown in Figure 3 (a). The FTIR analysis of the AP in the infra-red spectrum shows a frequency range from 3500–3200 (s,b) cm⁻¹ which represents the O-H stretching vibration and presence of alcohols, phenols. The next frequency ranges from, 3000–2850 cm⁻¹ peaks which represents the C-H stretching vibration presence of alkenes and the frequency which ranges from 3300–2500 cm⁻¹ peak represents aliphatic O-H stretching vibration presence of carboxylic acids. The next set of peaks 1680–1640 cm⁻¹ are present in the –C=C– stretching vibration present in the alkenes while the frequency ranges from 1550–1475 cm⁻¹ peak are present in the N–O asymmetric stretching vibration present in the nitro compounds. The next frequency ranges from 1320–1000 cm⁻¹ C-O stretching, O-H bending vibration presence of alcohols, carboxylic acids, esters, ethers which is followed by the frequency ranging from 1300–1150 cm⁻¹, presence of C–H wag (–CH2X) stretching presence of alkyl halides and the peak range 1250–1020 cm⁻¹ present in C–N stretching, presence of aliphatic amines as well as the peak value representing 910–665 cm⁻¹ present in N–H symmetric stretching vibration primary, secondary amines [9]. The FTIR analysis of CNT shows that the largest peak dwells in the range of 3280–3675 cm⁻¹ and 1640–1600 cm⁻¹ bend, which attest to O–H groups of adsorbed water or covalently bonded functional groups that might have occurred during the CNT purification process. The peaks also appear in the range of peak at 2800-2900cm⁻¹ that corresponds to the C-H asymmetric and symmetric stretching vibration, derived from long alkyl chain which reveals the stability of carbon nanotube suspensions in the aqueous phase.
The appearance of peak at 1532-1560cm\(^{-1}\) elucidates the existence of C=C. The 1300–1000 cm\(^{-1}\) region may be assigned to the O=O vibration mode of ester, ether, phenol or carboxyl groups, but it is difficult to clearly assign the peaks in this region because of the absorption bands overlap from many oxygen-containing ones [29–31]. The FTIR of the composite agrees with the FTIR results of both AP and CNT. This can be seen in the range of 3280–3675 cm\(^{-1}\) and 1640–1660 cm\(^{-1}\) bend which indicates the presence of O-H and is similar to CNT. Similar to AP, the peaks are prominent in the 3000–2850 cm\(^{-1}\) region where it showcases its C-H stretching vibration presence. One sharp peak can be seen in a similar region as AP in the range of 1680–1640 cm\(^{-1}\) that indicates C=C.

Next, X-Ray diffraction analysis that was done to reveal the crystallinity and material interactions is shown in Figure 3 (b). The graph line for AP is characterised by a black line. It is of note that, as AP is an organic compound, there are no known phases for it. The CNT compound exhibits its significant peak at 28° and is characterised the red graph line. The composite on the other hand which is characterised by the blue line has the characteristics of both CNT and AP the peaks as given a broad peak.

![Fig. 3: (a) FTIR analysis, (b) XRD analysis](image)

**CONCLUSION**

The AP/CNT composite was fabricated by crosslinking with glutaraldehyde through hydrothermal process to produce a hybrid material with novel characteristics for oil sorption. These composite materials were then encapsulated within PMMA nanofibers through electrospinning with the aim of efficiently removing oil from water. The combinatorial properties of each material which has its own oil sorption capacity produces unique oil retention properties in its biomimetic complex. Furthermore, the distinctive structure of the composite was an important criterion for the fabrication of functional nanofibers.

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