Systematic exploration of electrospun polyvinylidene fluoride (PVDF)/multi-walled carbon nanotubes’ (MWCNTs) composite nanofibres for humidity sensing application

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Abstract
In this paper, the electrospinning technique was used to obtain multi-walled carbon nanotubes (MWCNTs) supported on electrospun polyvinylidene fluoride (PVDF) nanofibres (NFs) (PVDF/MWCNTs), a composite-based mat of NFs. The surface morphology of the PVDF/MWCNTs NFs was analysed by a field effect scanning electron microscope. The thickness of the NFs mat varies with the time and concentration of MWCNTs. The contact angle (CA) measurement shows that 2.5 wt% of MWCNTs in NF mat shows 61° CA which suggests the hydrophilic nature of the prepared NF mat. Fourier transform infrared and Raman spectroscopy revealed the implantation of MWCNTs in PVDF matrix and side wall attachment with polymer chain. X-ray diffraction and FTIR studies show that as the MWCNT content increases, the $\alpha$-phase in PVDF decreases, indicating that MWCNT has a strong effect on phase transformation. Consequently, the NFs show an almost linear capacitive response. They showed that the high-capacitive changes in PVDF/MWCNTs’ NFs are achieved at 2.5 wt% MWCNTs’ addition at different humidity levels. The sensitivity of the PVDF/MWCNTs’ (2.5 wt%) NF mat-based capacitive sensor exhibits high sensitivity $\sim 0.71$ pF/%RH. Hence, PVDF/MWCNTs’ NFs perform attention-grabbing properties for the humidity sensing application.

1. Introduction
Electrospinning is a method of producing fibres with nano-sized diameters. The produced electrospun fibrous mats have several distinct properties, including high mechanical strength, large surface area, adaptability to different shapes, low flow resistance and high porosity. Electrospinning fibres are used in a variety of applications, including filtration, catalysis and capacitor sensor [1–8]. Figure 1 illustrates the electrospinning set-up, which is made up of three major components: a collector, a syringe pump and a power supply.

In this method, an external electrical force is subjected to a polymer solution to fabricate polymeric fibres. The diameters of the electrospun fibres range from micrometre to nanometre. Different process parameters influence the electrospun fibres’ diameters, such as polymer solution concentration, magnitude of the applied voltage, gap distance between the collector and the tip of the needle and polymer flow rate, which affects the fibres’ deposition time [9–12]. An electrically charged jet of the polymer solution is ejected and it discharges towards the oppositely charged electrode. After reaching the surface of the collector, the polymeric NFs become neutralized and get collected at the collector as dry NFs. Its fine structure, large surface area, controllable thickness of the nanofibrous mat and a variety of materials make it a crucial contender as the framework of sensing materials. Polyvinylidene fluoride (PVDF) is a pyroelectric and piezoelectric semi-crystalline thermoplastic and electro-active polymer. It has advantages, including good chemical and mechanical stability, high thermal stability, stable in high electric field and high mechanical elasticity. These significant properties have made PVDF a promising material for many different applications, including batteries, actuators, super-capacitors and transducers in the field of electronic engineering. In humidity sensing, the hydrophilic/hydrophobic feature of the sensing films is directly connected to the device sensitivity and response/recovery time [13]. When comparing hydrophilic and hydrophobic polymers, Lin et al. [14] found that water molecules in hydrophilic polymers had a lower diffusion coefficient due to stronger hydrogen bond interactions. The hydrophilic polymer is more sensitive than the hydrophobic polymer, according to the researchers.
Carbon nanotubes (CNTs) can be differentiated by the number of walls that compose their structure (SWCNTs, DWCNTs and MWCNTs), the inner and outer diameters, and the factors that influence their weight and density. Due to the CNT’s excellent electrical properties, it is a promising contender among the all electrically conductive fillers for the development of conductive polymeric composite [15]. A slight quantity of CNTs with uniform dispersion can produce a well-organized conductive network in the insulating polymer matrix with a high aspect ratio. Several researchers have investigated the electrical properties of polymeric with multi-walled carbon nanotube (MWCNT) or single-walled carbon nanotube (SWCNT) composites. Aguilar et al. [16]
studied that the electrical conductivity of CNT/polymer composite film will be stimulated when the clustering of CNT contents are adjacent to the percolation threshold. Li et al. [17] conducted experimental studies on the electrical properties of MWCNTs/epoxy composites. Electrical characteristics of polymer increase with the addition of the CNTs within PVDF. CNT has a significant impact on the properties and technical significance of PVDF. MWCNTs, in particular, have attracted the attention of researchers because it causes phase changes in PVDF from α-phase to β-phase. As a result, MWCNTs improve the piezoelectric, electrical and dielectric properties of PVDF, as well as its mechanical and thermal properties. However, most experiments use multi-walled carbon nanotubes (MWNTs), which are much simpler to spread into polymers than single-walled carbon nanotubes (SWNTs) [18]. PVDF/MWCNT composite nanofibres (NFs) can also be used for the NFs breathing mask that allows comfortable germ-free breathing by blocking the entry of bacteria and viruses. Bacteria cannot enter into these NFs because the pore area is smaller than that of the bacteria, so NFs can be used to protect them from bacteria and viruses, while allowing air molecules to move through them [19,20]. Nanocomposite has a wide range of applications, including sensors, actuators, super-capacitors, transducers and nanogenerators [21–23]. Zhaofei et al. used electrospun polymer NFs (PVDF and PU) doped with metal nanoparticles and MWCNTs for H₂O₂ and glucose electrochemical sensors [24]. Soumyaranjan prepared PVDF piezoelectric films with N-Methyl-2-pyrrolidone and changed the films with piezo-resistive CNTs as well as carbonic and sulphonic acid-functionalized CNTs [25]. PVDF and carbonic acid-functionalized CNT had a higher saturation current of 2.7 mA, whereas bare PVDF in nanomagnetic particles had a lower value of 0.0087 mA.

However, the effect of the concentration of MWCNTs in the PVDF/MWCNTs composite NFs for humidity sensing applications has not been broadly reported. Thus, in the present work, we aimed to modify the hydrophobic PVDF NFs to hydrophilic NFs to improve its humidity sensing properties. The nanocomposite of the PVDF has been prepared using MWCNTs with different amounts. MWCNTs were used as an additive in PVDF/MWCNTs’ composite NFs-based humidity sensors to improve porosity, sensitivity and linearity. Surface morphology, thermal stability, structural properties and the electrical response of the NFs mat have been studied. We have also studied the effect of humidity on the capacitive response of pure and PVDF/MWCNTs’ composite NFs. The hydrophilic PVDF/MWCNTs NFs sensing mat-based capacitive sensors showed improved humidity sensing response when compared to the hydrophobic PVDF NFs mat sensor. Pure PVDF and composite NFs were prepared with different filler contents (1 wt% and 2.5 wt%) by the electrospinning method. The capacitive response of samples was measured after moisturizing them in different levels of relative humidity (RH) (35–80%RH).

2. Experimental details

2.1. Materials

MWCNTs (diameter 20–60 nm; purity 95%; procured from Chengdu Organic Chemicals Co. Ltd., China) and PVDF (average Mw ∼ 275,000) and N, N-dimethylformamide (DMF) were purchased from Aldrich, chemical co. for preparing NFs by electrospinning.

2.2. Preparation of PVDF/MWCNTs’ composite polymer solution

The composite electrospinning polymer solutions were prepared in three major steps. First, 15 wt% of (PVDF was dissolved in a solvent mixture of acetone and DMF (acetone 80 wt%; DMF 20 wt%) to prepare the pure polymer solution. To obtain homogenous polymer solution, the pure polymer solution was subjected to continuous magnetic stirring for 8 h at 80°C. Second, the raw MWCNTs (20 mg) were heated at 450°C for 2 h in the air to remove the carbonaceous residue. The MWCNTs were dispersed in DMF to eliminate the agglomeration by conducting ultra-sonication for 2 h in DMF. The obtained solution was diluted with distilled water and filtered using Whatman filter paper. The MWCNTs on the filter paper were washed and rinsed thoroughly with distilled water and dried at 50°C for 12 h. Finally, the obtained MWCNTs were added to the PVDF solution to make a final solution with MWCNTs with a mass ratio of 1 and 2.5 wt%, respectively. After the addition of MWCNTs, the mixed solution was stirred for 2 h to obtain a homogenous solution. Then the solution was dispersed by ultrasonic for 1 h, to ensure the MWCNTs could uniformly disperse in solutions.

2.3. Synthesis of composite nanofibres

The pure PVDF and PVDF/MWCNTs’ composite solutions were loaded to a nozzle/syringe with a stainless-steel spinneret (inner diameter 0.72 mm). It was connected to the positive electrode of a high-voltage DC power supply generating a constant voltage ranging from 0 to 30 kV. In this experiment, 25 kV voltage was applied. The fabricated aligned NFs were deposited on a rotating drum used as the collector. This rotating drum was connected to the negative electrode of the DC power supply. The distance (working distance) between the spinneret and the collector was 18 cm. All experiments were conducted at room temperature. The obtained NFs mat samples were heated at 60°C for 12 h to form many mesoscopic joints of NFs and then unpeeled from the aluminium foil. Mats of composite
NFs are elastic and very flexible, so they can be used for flexible device fabrications and applications.

2.4. Characterization

A field-emission scanning electron microscope (JEOL, MA, USA) was used to study the morphology of the samples at 2 kV acceleration voltage. For the investigation of the morphology of PVDF NFs and its interactions with the MWCNTs, Fourier transform infrared (FTIR), using the smart ATR-FTIR model “Nicolet iS 10” (Thermo Fisher Scientific, MA USA) equipped with the specular reflectance. The range of scanning was 400–3500 cm\(^{-1}\) and the samples were placed on the top of the spectrophotometer. Raman spectra of the pure PVDF and the PVDF/MWCNTs NFs were obtained on a Micro-Raman Spectrometer (LabRAM, HORIBA JY, New Jersey, USA) at 532 nm laser excitation. The laser power density was 25 mW. The Raman spectrum was from 500 to 4000 cm\(^{-1}\) wavenumber. The NFs mats were analysed by X-ray diffraction (XRD) (Ultima IV, Rigaku, Tokyo, Japan) for their crystalline behaviour. XRD results were obtained at room temperature with a Copper K\(_{\alpha}\) radiation source (\(\alpha = 0.154\) nm) operated at 30 kV. The X-ray diffractograms were recorded in the scan range (2\(\theta\)) of 1–60° at the scan speed of 1° min\(^{-1}\) using a step size of 0.05°. A DTG-60H (Shimadzu, Tokyo, Japan) Thermogravimetric analyser (TGA) was used for the thermal analysis and stability of NFs’ samples with a heating rate of 10°C/min and nitrogen flow rate of 20 mL/min. The temperature range for the analysis was set between room temperature and 650°C. A static contact angle (CA) was measured to investigate the NF mats’ surface wetting property (hydrophobic/philic) (Biolin Scientific, Attension theta flex, Finland). The capacitance of the pure PVDF and composite NFs mat sensor was measured by the LCR metre (LCR-816 GW INSTEK, Taiwan) at different RH levels.

3. Result and discussion

3.1. SEM analysis

The morphology of the electrospun nanofibrous mats with different concentrations of MWCNTs was investigated here. Figure 1 shows the aligned fibrous PVDF NFs with MWCNTs loaded with 1 and 2.5 wt%. It can be observed that the composite NFs have a large diameter compared to pure PVDF NFs shown in Figure 1. The PVDF/MWCNTs’ composite NFs have a randomly oriented structure, as shown in Figure 1. The diameter of NFs increases with an increase in the addition of MWCNTs. With the addition of more MWCNTs, conductivity would also increase. With the increase in MWCNTs, it prefers to agglomerate due to the strong van der Waals force.

A critical analysis of the images reveals that MWCNTs were very well dispersed with PVDF in the solution. The MWCNTs are PVDF-coated and uni-axially oriented with PVDF NFs, as shown in Figure 1(b–d). The NFs contain MWCNTs; this confirms the presence of MWCNTs inside the PVDF NFs and also some MWCNTs coated by PVDF. The high alignment of MWCNTs along the NF can be attributed to the synergistic effect of the electric field. Due to the rapid stretching of the solution jet, shear forces are produced during the electrospinning and PVDF chains due to nanoscale confinement [26]. From Figure 1(a,c), it is manifested that the diameter of composite NFs has increased because the MWCNTs are implanted within the PVDF NFs.

3.2. FTIR spectroscopic analysis

FTIR has been used to recognize the different functionalities present on the surface of our material. The IR vibrational bands at 761 cm\(^{-1}\) (skeletal bending) and 793 cm\(^{-1}\) (CH\(_2\) rocking) are related to \(\alpha\)- phase PVDF. With the addition of MWCNTs, it acts as a nucleating agent during the crystallization process to stimulate the \(\alpha\)- to \(\beta\)-phase transformation in PVDF and induce charge accumulation at the interface [26,27]. In Figure 2, the peaks at 1070, 1177 and 1403 cm\(^{-1}\) are related to the vibration of C–C (stretching), C–F (stretching) and C–H (distortion), respectively. The characteristics band at 761 cm\(^{-1}\) is nominated to the \(\alpha\)-phase modification, while 873 cm\(^{-1}\) to the \(\beta\)-phase modification of PVDF.

Here, a blue shift observed at 873 cm\(^{-1}\) confirms the phase transformation due to the addition of MWCNTs. This reveals that a strong interfacial interaction happens in MWCNTs and PVDF matrix when increasing the concentration of MWCNTs. This is because of a skin-tight affection of the PVDF chains on the sidewalls of MWCNTs through concentrated F-C bonding [28].

Figure 2. FTIR spectra of Pure PVDF NFs (a); PVDF/ MWCNTs (1 wt%) NFs (b); PVDF/MWCNTs (2.5 wt%) NFs (c).
Soumyaranjan et al. observed similar types of FTIR spectra for PVDF/MWCNTs composites [25]. The intensity of the PVDF representative bands gradually increased, suggesting that a large percentage of PVDF is coated on the sidewalls of MWCNTs. The enhancement of β-phase with increasing MWCNT concentration due to a higher electric field during NFs manufacturing process, as well as the increasing amount of MWCNTs in the composite NFs, is shown in Figure 2 [29].

3.3. Raman spectroscopic analysis

Raman spectroscopy was used to investigate the influence of MWCNT concentrations on the structure of PVDF. The peaks and shifts can be used to confirm the intercalating of polymer chains with MWCNTs and the integration of MWCNTs into the polymer matrix.

Figure 3 displays the Raman spectroscopic analysis of pure PVDF and PVDF/MWCNTs’ composite NFs. The D-band (disorder mode) at 1255 cm$^{-1}$ and G-band (tangential mode) at 1559 cm$^{-1}$ correspond to sp$^3$ and sp$^2$ hybridized carbons, respectively [30]. A shift in D- and G-bands, as shown in Figure 3(b,c), leads to higher wavelengths with a concentration of MWCNTs in composites. This shift can be related to the interaction between MWCNT and PVDF, due to the electron affinity of the fluorine [28,31].

3.4. XRD analysis

The XRD analysis of pure PVDF and its composites nanofibres in the range of 10° < 2θ < 60° are shown in Figure 4. PVDF exists in at least four different crystalline forms: α-, β-, γ- and δ-phases. The α-phase is the most common and stable of the four polymorphs, while the β-phase is the most notable for a variety of applications.

The PVDF NFs showed crystalline peaks at 18.6° and 20.2° peaks of the PVDF polymer’s α-phase crystal. XRD peaks at 26.5° and 40.6° confirm the presence of MWCNTs in composite NFs [32]. As shown in Figure 4(b,c), the

![Figure 3. Raman spectra of Pure PVDF NFs (a); PVDF/ MWCNTs (1 wt%) NFs (b); PVDF/MWCNTs (2.5 wt%) NFs (c).](image1)

![Figure 4. XRD graph of Pure PVDF NFs (a); PVDF/ MWCNTs (1 wt%) NFs (b); PVDF/MWCNTs (2.5 wt%) NFs (c).](image2)
addition of MWCNTs to PVDF solution results in the formation of a diffraction peak at 26.5° in addition to the β-phase of PVDF. Levi et al. [33] reported that the addition of MWCNTs followed by sonication to the formation of the β-phase in PVDF. MWCNTs are responsible for the peak at 2θ = 26.5°. The addition of MWCNTs to the PVDF results in a significant increase in intensity and shift in peak at 20.6, as seen in the XRD analysis, which is directly attributed to the β-phase transformation.

3.5. TGA analysis

Thermograms for PVDF and MWCNTs/PVDF composite NFs are shown in Figure 5. As can be seen from the data, all the samples have an almost identical thermal pattern and excellent thermal stability. TGA graph of pure PVDF NFs indicates temperature stability up to 450°C.

As the temperature rises, a loss of nearly 80% is observed at 510°C, due to the degradation of the polymer backbone and decomposition of the 80% of PVDF NFs. Related trends are observed in the composites of PVDF/MWCNTs, as shown in Figure 5(b,c). The degradation of the PVDF, as well as the degradation of the C–C bonds and C–F bonds of the PVDF and MWCNTs, results in a steady mass loss of up to 80%-85% [34,35]. Minor temperature variation is found in composite samples during full deterioration after 500°C. These temperature changes may be due to the occurrence of phase change (α-β transition) as the MWCNTs are also embedded in the PVDF NFs [32].

3.6. Contact angle

A constant volume of DI water was dispensed on the surface of NFs mats and a built-in programme was used to measure the CA. The NF mat’s interaction angle, as seen in real time, is shown in Figure 6. The CA of pure PVDF NFs was 103.7°, which makes it hydrophobic. The PVDF/MWCNTs (1 wt%) composite NFs’ CA was 89°, as shown in Figure 6(b), which indicates that the addition of MWCNTs in the PVDF polymer enhanced the surface wettability of the composite NFs and, therefore, it became hydrophilic. Further addition of MWCNTs (2.5 wt%) in PVDF composite decreased the CA to 61°. This decrease indicates the improved hydrophilicity of the surface. We know that PVDF and MWCNTs are normally hydrophobic in nature. We assume that when the NF mat is dried at 60°C, all solvent crusts are removed and the MWCNTs’ open ends become reactive, forming tight bonds with PVDF fluoride ions resulting in the formation of hydrophilic composite NF mats [36].

3.7. NFs mat humidity sensing tests

The sensing principle of NFs’ mat is based on the change in dielectric constant of the mat when water vapour is absorbed in fibrous mats. RH was generated for this sensing experiment using the saturated salt solution. We tested our samples to observe changes in capacitance with RH at temperature above 20°C. The saturated salt solution was kept in a sealed chamber (desiccator) with an NF sensing electrode. The size of the chamber was 0.09 cu. ft and could hold vacuum up to 24 h. A commercial humidity sensor (Model Thermo Pro TP50 digital hygrometer) was placed in the sealed chamber to monitor real-time RH level inside the chamber. The equilibrium values of RH of the saturated solution of several salts used are listed in NBS Circular 512 [37,38].

The RH in equilibrium with the saturated salt solution is given by the following equation:

\[ RH = \frac{e_d}{e_a} \times 100, \]

Figure 5. TGA graph of Pure PVDF NFs (a); PVDF/ MWCNTs (1 wt%) NFs (b); PVDF/MWCNTs (2.5 wt%) NFs (c).

Figure 6. CA measurement of Pure PVDF NFs (a); PVDF/ MWCNTs (1 wt%) NFs (b); PVDF/MWCNTs (2.5 wt%) NFs (c).
where $e_d$ is the vapour pressure of pure water at the dew point temperature, and $e_a$ is the vapour pressure of pure water at the ambient temperature [34,37].

The NF mats were placed in between the two aluminium electrodes to investigate the performance of pure PVDF NFs and PVDF/MWCNTs' composite NFs at different RH levels from 35% to 80%. It is used as a parallel plate capacitor, as shown in Figure 7. After that, the samples were placed inside vacuum desiccators at room temperature. All samples were moisturized at each level of %RH for 6 h. The capacitance of NFs’ sensing mats was measured by an LCR meter at 1 kHz frequency. The RH level inside the humidity chamber was increased from 35%RH to 80%RH.

Figure 8 shows the capacitive response of NFs to RH changes. It has been observed that RH influenced the dielectric properties of NFs’ mat. We observed that capacitance saturated after 2 min at each level of RH. Nearly linear capacitive responses were observed in all samples. The energy stored in a parallel plate capacitor is given by the following equation:

$$ W = \frac{1}{2} CV^2 = \frac{1}{2} \varepsilon_0 \varepsilon_r \frac{A}{d} V^2 $$

(2)

where $C$, $V$, $\varepsilon_r$, $\varepsilon_0$, $A$ and $d$ are the capacitance, the voltage, the relative dielectric constant, the permittivity of vacuum, the surface area of the plate and the distance between plates, respectively.

The capacitance for different samples was varied at a different level of %RH. The capacitance of pure PVDF mat sensor showed the highest capacitance 35pF at 80% RH. The responses of composite NFs sensing mats were very fast in comparison to pure PVDF. The highest capacitance measured for PVDF/MWCNTs’ composite NFs of 1 wt% MWCNTs and 2.5 wt% MWCNTs concentration addition to PVDF reached up to 53pF and 68pF at 80% RH, respectively. The addition of MWCNTs into the PVDF solution has resulted in a high degree of sensitivity in new hydrophilic NFs with different oxygen functional groups. From Figure 8(b,c), we can see that PVDF/MWCNTs composites’ NFs samples have a higher capacitive response than the pure PVDF (Figure 8(a)). The maximum difference in capacitance value for PVDF/MWCNTs’ composite NFs is at 2.5 wt% MWCNT addition when the sensor is exposed to lower to higher humidity levels.

Sensitivity is defined as the change in capacitance for a 1% change in relative humidity, and it is measured by determining capacitance at two distinct RH levels and divided by the percent RH change.

$$ \text{Sensitivity} = \frac{\Delta C}{\Delta \text{RH} \%} $$

(2)

The sensitivity of NF mat sensors observed 0.24 pF/% RH, 0.5 pF/% RH and 0.71 pF/% RH for pure PVDF, 1 wt% MWCNTs and 2.5 wt% MWCNTs, respectively, as shown in Figure 9. Comparison of the sensing properties’ sensors reported previous is shown in Table 1. The sensitivity of the hydrophilic PVDF/MWCNTs NFs sensors were higher compared to that of hydrophobic Pure PVDF NFs sensors at room temperature.

The humidity sensitivity of the sensor, as shown in Figure 10, is very low at various humidity ranges from 40% to 80%, suggesting that the capacitance of the
sensor is stable at humidity. This is due to the CNT-PVDF composite NF dielectric layer’s stability at various humidity levels, as confirmed by holding a certain nanostructures pre- and post-drying.

This confirms that the addition of MWCNTs improves the response of the composite NFs, making it faster and higher. The individual MWCNTs existing in the insulating matrix may work as a nano-capacitor. The number of such nano-capacitors increased with the increase in MWCNTs amount leads to the increase in total capacitance [43,44]. Hence, the PVDF/MWCNTs’ nanofibrous mats can be used as capacitive humidity sensors.

4. Conclusion

In this paper, we demonstrate the possibility to fabricate a humidity sensor based on PVDF/MWCNTs’ nanofibrous mats produced by the electrospinning method. The PVDF phase transformation from $\alpha$- to $\beta$-phase in composite NFs’ mat is confirmed by FTIR, TGA and XRD. The CA was measured 61° for the 2.5 wt% MWCNTs-based NF mat. The influence of hydrophilic MWCNTs on the morphology and humidity sensing properties of the PVDF/MWCNTs composites’ NFs were investigated in 35–80% RH atmosphere. PVDF and PVDF/MWCNTs samples were used as capacitive humidity sensing electrodes. Capacitance was measured from 25 to 68 nF with an increased humidity level in the chamber. The sensitivity of the PVDF/MWCNTs (2.5 wt%) NF mat-based capacitive sensor exhibits high sensitivity $\sim 0.71\text{pF}/\%\text{RH}$, while for the PVDF NFs mat is 0.24pF/%RH. A good response of PVDF/MWCNTs NFs’ mat as a humidity sensor attained was produced using the electrospinning method. It was observed that composite NFs show a good response in increasing the concentration of MWCNTs. The PVDF/MWCNTs’ NFs mat can be used as the capacitive humidity sensor. But to attain a good response time, better sensitivity and repeatability need improvement in the design of humidity sensor.

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