Percolation threshold of multiwall carbon nanotube-PVDF composite for electromagnetic wave propagation

Noorhana Yahya, Surajudeen Sikiru, Amir Rostami, Hassan Soleimani, A’fza Shafie, Bilal Alqasem, Saima Qureishi and Menaka Ganeson

Abstract
Advanced physical properties of conductive polymers fibre composites have attracted the attention of material scientists. Here, we produced a polymer fibre composite with aligned multiwall carbon nanotube (MWCNT) of different weight fractions, ranging from 0.25 wt% to 1.5 wt%. At 1.5 wt% additive, a conductor-non-conductor transition occurs that is percolation threshold. This effect enhances the electrical conductivity of polymer composite from 0.050 S m$^{-1}$ to 326.250 S m$^{-1}$. Electrically conductor polymer composite will be highly preferred to fabricate radio frequency antennas, due to their unique physical and mechanical properties. We evaluated the performance of the polymer composite antenna and observed the percolation effect in electromagnetic wave propagation of the composite antenna. Far-field radiation of 1.5 wt% MWCNT-polymer antenna was 0.728 V m$^{-1}$, whereas the maximum far-field result of the antennas made by lower MWCNT concentrations was 0.102 V m$^{-1}$. Adopting the mechanical properties of PVDF composite, the composite-based RF antenna can be used in robust environments, such as high pressure high temperature oil reservoirs.

1. Introduction

Polymers without additive generally exhibit very low conductivity at room temperature [1]. However, their conductivity can vary by adding an additive to change the charge carrier density on the polymer backbone. The conductivity of those polymers varies depending on the additive concentration [2, 3].

MWCNT has received highlights and preferences for many industrial applications due to their high mechanical strength, excellent electrical and thermal conductivity [4–8]. These attributes had made them as an exceptional material for nanocomposites preparation. However, the inert characteristic of MWCNT’s inert nature has a drawback on poor solubility and forms unstable interfacial interactions with polymer fibre [9].

Currently, different researchers have been made effort on exploring various performance of carbon nanotube (CNTs) at high temperature and high pressure due to their good thermal properties. Hence, dielectric properties of carbon materials at high temperature have been significant studies. Moreover, it was reported by Wei-Li Song et al the dielectric properties of multiwalled carbon nanotubes/silica_MWNTs/SiO2 at the range of 8.2–12.4 GHz at X-band frequency [10].

Among various conducting polymer composites including polypyrrole (PPy) [11], polyaniline (PANI) [12], polythiophene (PT), poly (3,4-ethylenedioxythiophene) (PEDOT), trans-polyacetylene, and poly(p-phenylene vinylene) (PPV) [13], Poly (vinylidene fluoride) (PVDF) displays premier characteristics. PVDF is a fluoropolymer comprising of the monomer unit CF$_2$–CH$_2$ unlike other polymers. Additionally, it is a polymorphic, semi-crystalline polymer showing at least four crystal phases at different processing conditions [14–16]. It has an exceptional chemical stability and a large dipole moment of 9.8 × 10$^{-30}$ cm, perpendicular to the polymer chain. This results in piezo-, pyro-, and ferroelectric characteristics due to a polar crystal phase it can build [17–21]. PVDF is able to retain high concentration of MWCNTs and creates excellent conducting networks of nanotube to enhance the effectiveness of electromagnetic interference shielding [22].
Advance electromagnetic (EM) and thermo-physical properties of conductive polymer fibers are of the highest interests of researchers and industry players. Studies concentrated on DC and radio frequency (RF) behavior of conductivity, shielding effectiveness, propagation properties of carbon based composite fibers, both theoretically and experimentally [9, 23, 24]. Different applications on shielding effectiveness and conductivity of carbon fiber composites have been explored and advanced materials have been developed for RF antenna propagation, spacecraft solution. It was then stirred with spinneret ori

Despite various use of antennas, their applications can be narrow down to three major categories: (i) aerospace, (ii) ground-based [27–29], and (iii) oceanic and sub-marine applications [30–32]. Rigorous studies on advanced material based antennas have started since 1970s, where DeLoach et al [33] invented an electrically conductive graphite fiber antenna. Using non-conventional materials for antennas spread out to different applications, such as offshore deep hydrocarbon exploration [34], enhanced oil recovery [35], fabrication of flexible and optically transparent dipole antenna [36]. Polymer composite has high conductive and good mechanical strength, this make it a good substance for antenna propagation [37–39].

This work aims on finding the critical value of MWCNT additive that causes a significant shift in electrical conductivity of the fabricated polymer composite. On the other hand, we investigated dependence of electrical conductivity of the polymeric mixture on weight fraction of the conductive additive.

In this research we synthesized MWCNT, using chemical vapour deposition (CVD) method, and used different volume fractions of it to fabricate and characterise conductive PVDF fiber composite. Furthermore, we measured complex permittivity of the fabricated composites at X-Band frequency [40, 41]. Using these data, we calculated electrical conductivity of each composite to determine percolation threshold. These approaches lead us to validate the fabricated composite fibre as an RF dipole antenna.

2. Experimental details

PVDF pellet was purchased from sigma-Aldrich (63103) St and used as received. Louis USA with 99% purity without further purification. 1-methyl-2-pyrrolidinone (NMP) reagent plus of 99% purity was also purchased from Sigma-Aldrich international Corporation. Specifications of commercial polymer are as follow: Mw: 99.13 g mol$^{-1}$, Mp: −24 °C (lit), bp: 202 °C (lit), bp: 81 °C–82 °C/10 mmHg, Fp: 1.4 (lit), Vapour pressure: 0.2 gmmHg (20 °C) and assay 99%.

2.1. Synthesis of multi-wall carbon nanotube through CVD Method

High temperature technique ranging from 800 °C–1200 °C to synthesis MWCNT. Ferrocene and methanol were the catalysts. 6 g of ferrocene were dispersed into 500 ml of methanol and it was sonicated for about 1 h before placing it for production. Figure 1 shows the schematic diagram of CVD system.

We fabricated PVDF polymer fibers composite using solvent induced phase separation through the spinning machine. Then we dissolved PVDF pellet in N-methyl-2-pyrrolidinone (NMP) followed by using electric stirrer at temperature between 60 °C–80 °C, until the solution became homogeneous. Then we dispersed 0.25 wt%, 0.5 wt%, 1.0 wt% and 1.5 wt% of MWCNT into different containers of 30 g of ethanol before adding it to dope solution of PVDF, respectively. Then the dispersed MWCNT was added to 200 ml of polymer dope solution. It was then stirred with spinneret orifice diameter of 6.0 mm, to stir it at 300 rpm. It was degassing to remove created bubbles during stirring for about 45 min. All the prepared polymer solutions were clear and homogeneous at room temperature. Water was used as the external coagulant. The take up velocity was (8–9 m min$^{-1}$) and the air gas range was from 5 to 25 cm.

2.2. Simulation on RF application

We modelled the composite based dipole antenna via COMSOL Multiphysics® [42] and compared the performance of each antenna made by different volume fractions of MWCNT. Generated wavelength at the dipole’s operated frequency in free space is 30 cm. Therefore, antenna length, obtained by $l = \lambda/2$, is 15 cm. We defined impedance boundary condition [43] for the antenna, which indicates a finite conductivity on the surface of the antenna. For surrounding environment we applied perfectly matched layer (PML) boundary condition [44], that absorbs the outing radiated wave.

Electric permittivity, magnetic permeability and electrical conductivity are parameters that elaborate in radiation ability of each material. We obtained these parameters experimentally and manually defined them in the simulation model as the antenna’s material.

We introduced different mesh sizes in the system, due to small diameter of the antenna in comparison with the environment. Thus, finer mesh size was defined for the antenna, whereas normal mesh size was defined for the environment.
2.3. Instruments
We characterized the synthesized MWCNTs and polymer fiber by different techniques. Raman Spectroscopy (Horiba Jobin HR800 Raman Spectroscope instrument), provides distinctive information about vibrational and electronic properties of MWCNTs, and identifies materials through the characteristic’s vibrations of certain structures.

Furthermore, Field Emission Scanning Electron Microscope (Zeiss Supra 55/55 VP FESEM Model) is to observe the morphology and minute details on surface topography, assisted with Energy Dispersive x-ray (EDX) to study the elemental structure of the MWCNTs. Transmission Electron Microscopy (TEM), Hitachi H7100 model is to study the morphology and the compositional characterization, and also to determine the number of nanotube walls and the dimension of CNTs. Anton Paar Tu1-C-PTD200 Rheology Viscometer is to determine the viscosity of the polymer composite with the addition MWCNTs in different weight percentages. Moreover, we used Differential Scanning Calorimetry Q2000 for differential scanning calorimetry Analysis. DSC analysis is broadly used for investigating the polymeric material to determine their thermal transition and stability. This technique can show polymer degradation by lowering of expected melting point [46]. Keysight ENA E5071C Network Analyzer was used for electric permittivity and magnetic permeability measurements.

3. Results and discussion

3.1. Morphology and elemental analysis of MWCNTs
The FESEM image (figure 2(a)) shows the structure, length and the orientations of MWCNTs. The morphology analysis shows the chain like structure of MWCNTs oriented in different directions. The average diameter of MWCNTs is from 47.95 nm to 100 nm.

EDX elemental analysis (figure 2(b)) indicates the presence of elemental carbon. Table 1 displays EDX quantitative analysis. Where, elemental carbon weight per cent and atomic per cent represent the maximum elemental values, indicating 49.63% and 59.39%, respectively.
Figures 2(c) and (d) display TEM images of the MWCNTs. We can clearly observe the continuous chain like structure as we reported in FESEM image as well. The sample consists of MWCNT with a hollow internal channel bearing at the tip. Figure 2(d) shows the structural details of a thicker multiwall tube. The outer diameter of the nanotube is 35 nm while the inner diameter is 14 nm. Fringes are obviously visible representing the diameter of MWCNTs composed of different walls. Figure 2(e) represents the electron diffraction pattern of MWCNTs. There are four diffraction peaks that give four indices. The (0002) index is the dominant plane that represents the highest intensity.

3.2. Crystallinity of carbon nanotube polymer fiber
Raman peaks are not significant for the polymer composite with MWCNT concentration of 0.25 wt%. Therefore, here we discuss the Raman band shift of the higher MWCNT concentrations.

Figure 3 identifies D Raman band of carbon nanotube and polymer fiber composite, from 1340–1366 cm$^{-1}$. This band is activated in the first order scattering process of Sp2 carbons by the existence of in-plane substitution heteroatoms, vacancies, grain boundaries or other defects [47].

We observed the G-band and its second order overtone, G$'$-band (also called the 2D band), in the 1570–1590 cm$^{-1}$ and 2600–2700 cm$^{-1}$ regions, respectively. The Raman shift of G-band confirms C-C vibrational model [47]. The D-band scattering consists of one-elastic and one-inelastic scattering process, in which the elastic scattering arises from defects (such as vacancies, impurities and hetero-atoms) in the crystal. On the other hand, the G$'$-band is due to two-inelastic scattering process, in which the two emitted phonons possess vectors of $+\mathbf{q}$ and $-\mathbf{q}$, respectively [45]. The momentum constant is therefore automatically preserved in...
the G′-band scattering and no defect is required to observe the G′-band. The Raman peak wavelength shift at each MWCNT concentration were illustrated in table 2.

### Table 2. Raman band shift of MWCNT in PVDF composite.

| MWCNT wt% | D-band (cm \(^{-1}\)) | G-band (cm \(^{-1}\)) | G′-Band (cm \(^{-1}\)) |
|-----------|----------------------|----------------------|----------------------|
| 0.25      | 1122                 | 1429                 | 2938                 |
| 0.5       | 1366                 | 1588                 | —                    |
| 1.0       | 1346                 | 1573                 | 2685                 |
| 1.5       | 1340                 | 1571                 | 2680                 |

3.3. Thermal stability of the carbon filler using differential scanning calorimetry (DSC) analysis

We used DSC Q2000 at the heating rate of 10 °C and flow of 50 ml nitrogen gas for DSC analysis. From figure 4 we observe that the composite is free of void, also it indicates that both the fiber and the matrix behave as perfect linear elastic materials and there is perfect bonding between the fiber and the filler which show the stability of the materials. DSC results indicate that there is significant improvement in thermal stability of the polymer fiber composite with the incorporation of MWCNT ranged from 0.25 wt% to 1.5 wt%. However, the composite material shows both endothermic and exothermic reaction.

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3.4. Rheology graph (at 80 °C) for four polymer dope solution with different weight percent of MWCNT
All nanomaterials display high viscosity at low shear rate and reduce to a low viscosity with high shear rate, due to the occurrence of the number of particles, resulting in increasing interactions between particles which then leading to an overall increase resistance with fluid layer. Nanomaterials show Newtonian behaviour with an increase in shear rate where the interaction between particles becomes weaker and is broken down.

Rheology viscometry result shows the concentration of the carbon nanotube alter the viscosity of the dope solution, it was captured that the increase in temperature leads to decrease in viscosity. Higher concentration of MWCNT results in higher viscosity of carbon nanotube polymer fiber, as displayed in figures 5(a) and (b) for 0.25 wt%, 0.5 wt%, 1.0 wt%, and 1.5 wt%. Therefore, 1.5 wt% shows the highest viscosity due to the highest concentration of MWCNTs.

3.5. Permittivity and conductivity theory for two phase composite
For a composition of a non-conductor background material with a conductor phase, assume \( \varepsilon^* \) and \( \sigma^* \) as complex permittivity and conductivity, respectively. Equation (1) indicates relation between permittivity and conductivity of the composite [48].

\[
\varepsilon^* = \frac{1}{j\omega\varepsilon_0} \sigma^* = \varepsilon' - j\varepsilon'' = \varepsilon' + j\varepsilon'', \quad \sigma = \omega\varepsilon''\varepsilon_0.
\]

where, \( j = \sqrt{-1} \) is complex number, \( \omega \) is angular frequency, \( \varepsilon' \) and \( \varepsilon'' \) are real and imaginary parts of complex permittivity respectively, \( \varepsilon_0 \) is permittivity of free space, and \( \sigma \) is electric conductivity.

We used Network Analyser at X-band range to measure the dielectric properties (\( \varepsilon' \) and \( \varepsilon'' \)) of carbon polymer fiber composite with different concentration of carbon nanotube. Figures 6(a) and (b) display real and imaginary parts of complex relative permittivity, respectively. The weight fraction of 1.5% represents the highest \( \varepsilon' \) and \( \varepsilon'' \), where percolation threshold occurred. From equation (1) we obtain the conductivity of polymer composite, \( \sigma(\omega) \), as a function of frequency given by

\[
\sigma = \omega\varepsilon''\varepsilon_0.
\]

We observed a significant change in behaviours and magnitudes of \( \varepsilon' \), \( \varepsilon'' \), and \( \sigma \) at 1.5 wt% of MWCNT. Figures 6(a) and (b) represent the real and imaginary permittivity in X-band frequency, for different weight percentages of MWCNT. Introducing 1.5 wt% of MWCNT, real permittivity of PVDF increased from 2.19 to 32.81, and growth of imaginary component of permittivity was from 0.18 to 469.48. We obtained frequency dependent electric conductivity using equation (2), as displayed in figure 6(c).

For further discussion, this is worthy to represent the complex permittivity of background and additive phases using equation (1) as below:

\[
\varepsilon_b^* = \frac{1}{j\omega\varepsilon_0} \sigma_b^* = \varepsilon_b' + j\varepsilon_b'', \quad \sigma = \omega\varepsilon''\varepsilon_0.
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\]
where, $\phi$ is volume fraction of additive material. We can also obtain the conductivity of the composite as

$$\frac{1}{\sigma^*} = \frac{1}{\sigma_b^*}(1 - \phi) + \frac{1}{\sigma_a^*}\phi.$$  

(6)

Simplifying equations (5) and (6), we obtain

$$\varepsilon^* = \frac{\varepsilon_b^*}{\varepsilon_a^* + \phi(\varepsilon_b^* - \varepsilon_a^*)},$$

(7)

and

$$\sigma^* = \frac{\sigma_b^*}{\sigma_a^* + \phi(\sigma_b^* - \sigma_a^*)}.$$ 

(8)

Equations (7) and (8) determine permittivity and conductivity of a two phase mixture with respect to the parameters of each phase and the volume fraction of the conductive additive phase. From these equations, it is clear that percolation occurs for both permittivity and conductivity at the same threshold. This is represented in our results, as well. Figures 6(a) and (b) for real and imaginary permittivity, show the same percolation threshold as the conductivity of the polymer composite (figure 6(c)). On the other hand, linear relation of imaginary part of permittivity with electrical conductivity in equation (2), can be observed by comparing figures 6(a) and (b).

Figure 5. (a) Viscosity versus temperature and (b) Viscosity versus shear rate; for MWCNT with polymer dope solution with ratio of 0.25 wt%, 0.5 wt%, 1.0 wt%, and 1.5 wt%.

Figure 6. (a) Viscosity versus shear rate; for MWCNT with polymer dope solution with ratio of 0.25 wt%, 0.5 wt%, 1.0 wt%, and 1.5 wt%.
The periodic responses of $\varepsilon'$ and $\varepsilon''$, at 1.5 wt% of MWCNT, might be due to the dispersion and orientation of the additive MWCNT phase, at the higher concentration. However, both $\varepsilon'$ and $\varepsilon''$ experience a significant percolation at this additive concentration.

We also plotted electric conductivity of the polymer composites versus different weight percent of MWCNTs, at a certain frequency, i.e. 11.0 GHz (figure 7). As represented in figure 7 and table 3, percolation threshold occurs near 1.5 wt% of MWCNT concentration which is the main cause for the exponential growth of conductivity. From the curve fitting result we obtain the exponential behaviour of conductivity at percolation threshold, as obtained:
Where, $s$ is the conductivity of mixture as a function of weight fraction, and $x$ is weight percent of MWCNT, $A (= 0.129 \text{ S m}^{-1})$, and $b (= 17.87)$ are driven curve fitting coefficients. Increase in conductivity of PVDF at this certain frequency is from 0.053 to 180.200 S m$^{-1}$, whereas for entire X-band frequency, the conductivity growth is from 0.050 to 326.250 S m$^{-1}$. We can conclude that, we observed a low percolation at critical concentration of 1.5 wt%.

As mentioned before, the mechanism is about using MWCNT as electrically conductive phase in a non-conductor PVDF phase. Distribution of MWCNT in PVDF fiber is mainly random. At a critical weight fraction of a random distribution of conductive and non-conductive phases, percolation threshold transition occurs. Conductivity of the mixture can be obtained by equation below [50]:

$$\sigma(x) = Ax^b,$$

where, $\sigma (x)$ is the conductivity of mixture as a function of weight fraction, and $x$ is weight percent of MWCNT, $A (= 0.129 \text{ S m}^{-1})$, and $b (= 17.87)$ are driven curve fitting coefficients. Increase in conductivity of PVDF at this certain frequency is from 0.053 to 180.200 S m$^{-1}$, whereas for entire X-band frequency, the conductivity growth is from 0.050 to 326.250 S m$^{-1}$. We can conclude that, we observed a low percolation at critical concentration of 1.5 wt%.

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$$\sigma(p) = \sigma_t (p - p_c)^\beta,$$  \(9\)

where, $\sigma (p)$ is conductivity of the mixture, $\sigma_t$ is conductivity of the conductive additive, $p_c$ is percolation threshold, $p$ is any value larger than percolation threshold, and $\beta$ is the spatial dimension constant. This is obvious that for $p \leq p_c$, $\sigma (p)$ becomes zero. We can conclude that, the obtained curve fit of equation (9) follows the same trend as the theoretical value of conductivity represented by equation (10).

It can be concluded that, for an inhomogeneous composite, the transport of the charge carriers occurs on some of the passages that are remarkably lower resistive than the other passages. Thus, highly resistive passages are dominating the conduction of the system. Percolation is a proven theory to investigate the complex permittivity and conductivity of a conductive-poor conductive composite. The percolation theory indicates that real and imaginary parts of permittivity experience significant changes upon increasing a small amount of conductive additive, in the vicinity of the percolation threshold. The conductivity also experiences the percolation effect (equation (10)), due to its direct proportionality to the imaginary part of permittivity (equation (1)). Different parameters can affect the conductivity (and imaginary part of permittivity), such as concentration, shape, and orientation of the additive phase, and the operating temperature [48, 51].

### 3.6. RF antenna evaluation

We proposed PVDF based electric dipole antenna for RF applications. As reported, MWCNT additive enhances electrical conductivity of the PVDF composite. We modelled dipole antennas based on properties of PVDF composites at each MWCNT concentration. In this simulation, we investigated the effect of the concentration of
MWCNT additive in performance of a 15 cm dipole antenna, which produces wavelength of 30 cm, and evaluated it at percolation threshold. Figures 8(a)–(d), display electric field propagation pattern of PVDF dipole, with different concentrations of MWCNT additive. The electric field response represents a promising radiation for 1.5 wt% of MWCNT.

Figures 8(e)–(g) reveal the quantity of far field electric field response. They represent polar radiations in xy and yz planes, and magnitude versus offset graphs, respectively. Nevertheless, percolation threshold effect is clearly distinguished, since electric field magnitude using the dipole with 1.5 wt% of MWCNT, is one order in magnitude greater than that of the lower MWCNT concentrations.
Figures 8(e) and (f) are indications of the directivity of the antenna. The polar radiation patterns indicate that the radiation of the composite based dipole antenna in all directions are equally well. This is the omnidirectional behaviour of a dipole antenna. The directivity formula is given by equation (11).

\[
D = \left[ 4\pi \int_0^{2\pi} \int_0^\pi |F(\theta, \varphi)|^2 \sin \theta d\theta d\varphi \right]^{-1}
\]

Where, \(F\) represents the average radiated power over all directions. \(\theta\) is zenith angle and \(\varphi\) is azimuth angle.

Table 4 represents the obtained directivity value from the simulation model for the composite-based dipole with 1.5 wt% of MWCNT, at specific zenith and azimuth angles.

| \(\theta\) (deg) | \(\varphi\) (deg) | \(D(\theta, \varphi)\) | \(D(\theta, \varphi)\) (dB) |
|-----------------|-----------------|------------------|-----------------------------|
| 90.0            | 0.0             | 1.68             | 2.26                        |

Table 5 represents the far field magnitude of electric component generated by different dipoles made of various MWCNT concentrations in PVDF composite.

| MWCNT wt\% | 0.25 | 0.5 | 1.0 | 1.5 |
|------------|------|-----|-----|-----|
| E field (V m\(^{-1}\)) | 0.102 | 0.100 | 0.044 | 0.728 |

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Table 5 represents far field response of PVDF dipole antenna, made of different MWCNT concentrations.

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The directivity value is at the same range of a half-wave dipole antenna (i.e. 1.64, or 2.15 dB) [52–54]. Such an antenna can be used in robust oil and gas reservoir environment, due to its mechanical strength, omnidirectional behaviour, and relatively high directivity value.

Table 5 represents far field magnitude of electric component generated by different dipoles made of various MWCNT concentrations in PVDF composite.

From simulation results, we reported that far field radiation of the PVDF antenna with 1.5 wt% of MWCNT additive (i.e. 0.728 V m\(^{-1}\)), is significantly higher than the generated field by dipoles with lower MWCNT weight percent.

Figure 9 displays the return loss of PVDF composite dipoles. The results for the dipole antennas made of composites with 0.25, 0.5, and 1.0 wt% of additive, do not represent a promising behaviour of S11 parameter versus frequency. Whereas, from S11 graph of the composite antenna consist of 1.5 wt% of additive, we observe that there are two significant peaks, at 10 dB and 7 dB for 0.8 GHz and 2.6 GHz, respectively.
4. Conclusion

We extruded PVDF carbon composite by spinning techniques with diameters in range of about 50–100 nm. Based on the X-band measurement of Network Analyser, MWCNT loading of 1.5 wt% displayed percolation threshold showing electrical conductivity of 326.250 S m⁻¹, which is four orders in magnitude larger than the lower MWCNT loadings. We observed the same effect for relative permittivity, where it changed from 2.10 for pure PVDF to 32.81 for the composite with 1.5 wt% of MWCNT additive.

According to the significant conductivity shift at 1.5 wt% of MWCNT concentration, we suggested to use the new PVDF composite as a material of a dipole antenna, for RF applications. We evaluated the performance of antenna using COMSOL Multiphysics® simulation, and represented that the desired dipole antenna performs promisingly. The antenna with electromagnetic properties of PVDF composite with a MWCNT loading of 1.5 wt%, radiates electric field of 0.728 V m⁻¹ in far field range.

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