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Dielectric Analysis of PVDF-CNF Conductive Polymer Nanocomposite for EMI Shielding Application

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Abstract
Carbon based Nano fillers polymer nanocomposites are the advance polymer materials used in electrical device applications. Among them carbon nanofibers are highly preferred because of their high aspect ratio, long fiber range, high contact surface area, higher electrical conduction with uniform dispersion property. In the present work we have developed a thin (PVDF-CNF) conductive polymer nanocomposite by solvent casting technique. Here we have focused on understating the dispersion effect on electrical conductivity and for electromagnetic interference (EMI). The developed conductive polymer nanocomposite showed uniform dispersion with higher conductivity and higher dielectric properties. The newly developed composite has significant applications in the field of sensor and shielding.

Keywords- Conductivity, Dielectric, Electromagnetic Shielding, Polymer Nanocomposite.

1. Introduction
Advance conductive polymer materials are the future soft electronic device materials. Poly (vinylidene fluoride) PVDF is one of the most prominent electroactive polymer material for the sensor applications (Hammes and Regtien, 1992; Luo and Hanagud, 1999; Wang et al., 2003; Gu et al., 2005; Prasad et al., 2018; Rathi et al., 2018). It is highly appreciated because of its piezoelectric, high permittivity, extraordinary pyroelectric properties with high physical properties of chemical stability, strength (Fonseca et al., 2006) and shows high dielectric constant of 7 to 13 Hz (Collins et al., 1992; Kumar et al., 2001). Further enhancement of dielectric properties is highly appreciated for various applications such as strain sensors (Shahinpoor and Mojarrad, 2000), charge storage device (Collins et al., 1992), robotic arms, artificial muscles (Kumar et al., 2001) etc. To enhance the dielectric effect of the polymers, conductive fillers are added to the polymer matrix which shows high dipole moment and increases overall dielectric properties of the polymer nanocomposite (Hammes and Regtien, 1992; Prasad et al., 2019).

Past studies showed that different types of fillers are added to increase the dielectric properties such as carbon Nano fiber (CNF), graphene and its oxides, carbon black (CB), carbon single wall carbon Nano tubes (SWCNT), multi wall carbon Nano tubes (SWCNT), metal particles

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and ceramics (Sumita et al., 1991; Wong and Bollampally 1999; Becerril et al., 2008; Cipriano et al., 2008; Hernández et al., 2009; Kim et al., 2010; Zhu et al., 2010) as per the usage of application. Adding of fillers in the insulator polymer matrix above a certain level leads to the leakage current. (Shen et al., 2007) in his study found that if the dielectric enhancing fillers are added above 50wt %, it increases the dielectric properties but also leads to loss of mechanical strength and flexibility of the nanocomposite. Among all the carbon-based Nano fillers CNFs show advantage over others because of their low cost, long fiber length, Nano sizes, high aspect ratio and easy functionalization ability (Wang et al, 2005; Al-Saleh and Sundararaj, 2009). The CNF forms conductive network in the insulator PVDF polymer matrix to form mini capacitors for improving dielectric constant (Ahmad et al., 2006; Sun et al., 2010) of the polymer nanocomposite. For getting higher dielectric properties the filler materials with higher dielectric constant which can store more charge while maintaining the minimum loss. (Li et al., 2006) in his work added CNT to the PVDF matrix which increased the dielectric constant but also increased the dielectric loss nearly around 10 in the form of leakage current due to higher number of connecting channels. The leakage current is induced in the polymer matrix as the conductive network facilities the charge delocalization at microscopic level. Therefore, the high delocalization of charges leads to the formation of high conduction and the material acts as highly conductive with nearly no change in the polarity due to which no change is observed in the dielectric constant at higher frequencies. Therefore, it becomes important to study the dielectric behaviour of the material while maintaining the minimum tangent loss in the form of leakage current. Researchers in past applied techniques of coating on the filler elements for reducing the dielectric loss, as the coated filler material with shells reduces the charge leakage by creating a barrier in between the fillers (Qi et al., 2005).

In the present study we have incorporated CNF as conductive filler element with the PVDF insulator polymer matrix to form conductive polymer nanocomposite using the solvent mixing technique. Firstly, the PVDF was dry mixed with CNF followed by adding to DMF solution. The obtained solution then poured and dried to get dry thin conductive polymer membrane of 40 μm thickness. On dry mixing the CNF got covered by the PVDF to some extent to create a barrier between the filler elements to reduce the dielectric loss. CNF was added in varying concentration of 5, 10 and 15 wt.%. For measuring the dielectric properties of the obtained conductive polymer nanocomposite impedance analyser (E4900A) in the frequency range of 20 Hz to 1 MHz at room temperature. The developed conductive polymer Nano-composite showed higher dielectric constant with lower dielectric loss and increased AC conductivity with the increase of CNF wt.%.

2. Experimental

2.1 Materials

The conductive PVDF-CNF nanocomposite was developed using solvent casting technique. Here the Poly (vinylidene fluoride) PVDF was taken as a polymer matrix material supplied by Sigma Aldrich USA having density of 1.79 g ml^{-1} and molecular weight (M_w) = 534,000).

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Carbon Nano fiber (CNF) having fiber length of 20 to 100 mm with average diameter range of 120 nm was taken as the conductive filler for improving the dielectric properties. N, N dimethylformmamide (DMF) with M_w of 236.29 was taken as solvent for making the PVDF-CNF solution.

2.2 Fabrication Technique of Conductive Polymer Nanocomposite (CPNC)

The CPNC membranes were fabricated using solvent mixing and casting technique. Figure 1 shows the schematic diagram of the PVDF-CNF composite membrane. Firstly, the PVDF was mixed with CNF in different ratios of 5, 10, 15 wt% and dry mixed for about 2 hours at temp of 50 ^oC as shown in Figure 2 (a). After the dry mixing DMF was added as solvent to the heterogeneously mixed powder to form a total solution of 10 wt% shown by Figure 2 (a). The obtained heterogeneous solution was then stirred using magnetic bed over hot plate magnetic stirrer by maintain the speed of 500 rpm for 4 hours and heated to 60 ^oC as shown in Figure 2 (b). After 4 hours the obtained heterogeneous mixture was poured on to a glass petridish followed by heating at 70 ^oC to completely evaporate the solvent to form dry thin CPNC membrane. Figure 2 (c) shows the process drying. On drying the CPNC membrane was clipped off from the petridish and cooled at room temperature and shown in Figure 2 (d) followed by cutting in various shapes for characterisation.

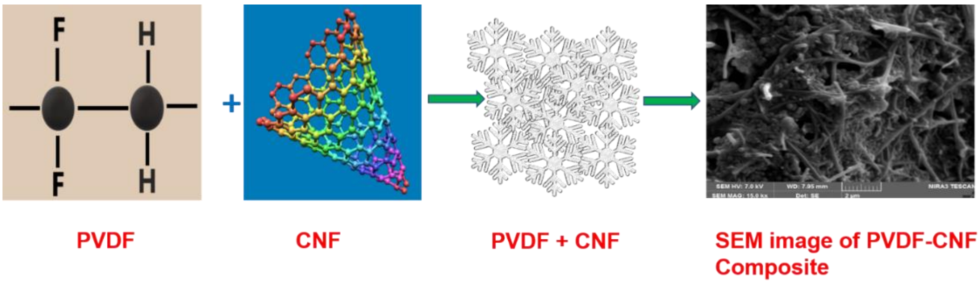

Figure 1. Schematic diagram of PVDF/CNF nanocomposite

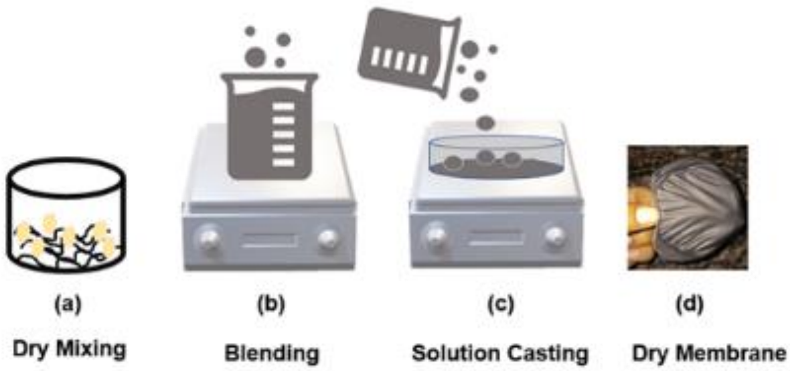

Figure 2. Fabrication technique of PVDF/CNF nanocomposite

Before taking the measurement the samples were coated with the silver paste on both sides.

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3. Measurements

The dispersion of conductive filler was observed using Field Emission Scanning Electron Microscopy (FESEM) MIRA3b TESCAN, USA. For characterization of micrographs, the samples were first dipped in liquid nitrogen for around 3 min and then fractured. The fractured ends were gold sputtered and the measurements were taken at different resolution.

The dielectric properties were measured using E4900A impedance analyzer supplied by the Key sight technologies in the frequency range of 20 Hz - 1 MHz. The characterization of CPNC samples were done using the stainless steel parallel plate probes of circular shape having diameter of 20 mm shown in Figure 3. The dielectric parameters such as dissipation factor $tan\delta$ and capacitance C were directly obtained using E4900A impedance analyzer. The dielectric constant was calculated using the formula shown by equation (1). Where in equation ε' is the dielectric constant, C is the capacitance l thickness of the samples, ε_0 is the dielectric permittivity of free space (ε_0 = 8.85 x 10^{-12} Fm^{-1}) and A is the cross-sectional area of the composite sample in cm^2.

$$\varepsilon' = \frac{L \times C}{A \times \varepsilon_0} \quad (1)$$

Figure 3. E4900A Impedance analyser for dielectric analysis

The AC electrical conductivity (σ) was calculated using equation (2), showing (ω) as the angular frequency.

$$\sigma = \omega \times \varepsilon' \times \varepsilon_0 \times \tan\delta \quad (2)$$

The Shielding effectiveness (SE) was calculated by simply adding the absorption, Reflection and refraction which is given by equation where A_{dB} is the absorption loss in dB, R_{dB} is the reflection loss due to electric field in dB, and C_{dB} is the refraction correction factor for electric field in dB and shown by Figure 4. And given by equation (3)

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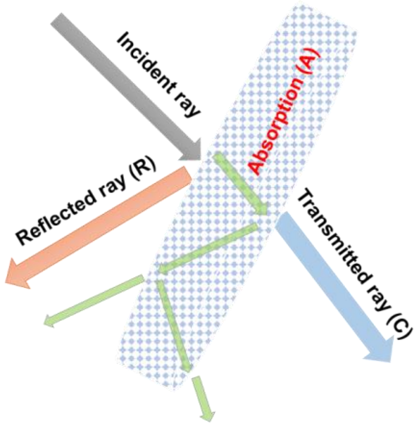

Figure 4. Schematic diagram of the shielding effectiveness

$$S_{\mathrm{dB}} = A_{\mathrm{dB}} + R_{\mathrm{dB}} + C_{\mathrm{dB}} \quad (3)$$

Absorption of the conductive shield is calculated by formula shown in equation (4). Here t is the thickness of sample, f is the frequency and σ shows the conductivity of conductive nanocomposite shield.

$$A_{dB} = 131\mathrm{t}\sqrt{(f \times \mu \times \sigma)} \quad (4)$$

Reflection (R) of the Nano conductive shield is calculated by the formula shown in equation 5. Here the reflection is dependent on the mismatch of incident wave and the impedance of surface.

$$R_{dB} = 168 - \log_{10}\frac{f \times \mu}{\sigma} \quad (5)$$

The internal refraction is represented by the correction factor C shown by equation. Here η^1 shows the intrinsic impedance and η^0 is the free space impedance of nanocomposite film. The internal refraction occurs due to the multiple reflections inside the plane of nanocomposite membrane. This internal reflection shows a very negative effect on the shielding efficiency. It can be reduced by maintain the thickness of composite greater than the skin depth. h0 is the impedance of free space and h1is the intrinsic impedance of shielding film (Rathi et al., 2018).

$$C_{dB} = 20 \times \log_{10} [1 - \left(\frac{\eta^0 - \eta^1}{\eta^1 - \eta^1}\right) \times exp^{\,-2yt}] \quad (6)$$

4. Result and Discussion

4.1 Surface Morphology

The CNF were heterogeneously distributed in the polymer composite matrix. The CNF concentration in the PVDF-CNF matrix was set 5, 10 and 15 wt.% respectively. The SEM

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micrographs in Figure 5 clearly shows the uniform dispersion of CNF in the PVDF matrix. The PVDF acts as an inner barrier to restrict the connecting network of CNF to bypass each other. The fibers of CNF are aligned upright in the form of tubes as shown in Figure 5 (a, b, c). These tubes form the conductive network for the transportation of charge.

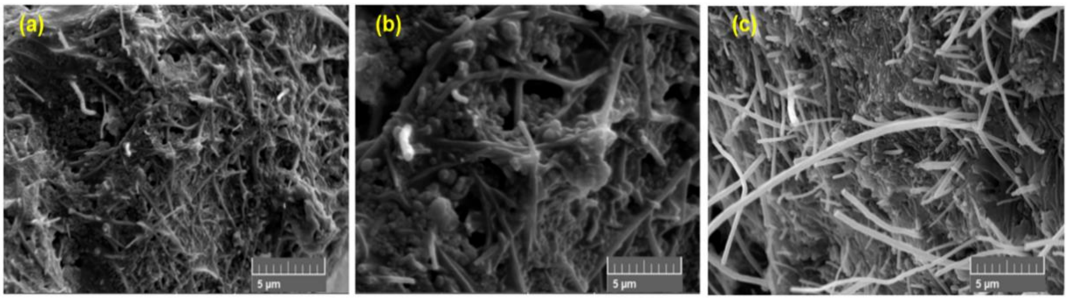

Figure 5. Shows the SEM images showing the heterogeneously mixed PVDF-CNF polymer composite

If CNF was added in higher quantities, it leads to high conductivity with loss of mechanical strength and higher dielectric loss as there occurs high leakage charge due to higher number of charge carriers. Figure 5 shows the SEM micrographs of the PVDF-CNF composite which are uniformly dispersed and are upright in the form of tubes. The uniformly dispersed filler concentration (CNF) at some extent effects the dielectric properties of the nanocomposite.

5. Dielectric and Shielding Effectiveness Analysis

The AC conductivity and the dielectric properties of the PVDF-CNF (95/5), PVDF-CNF (90/10) and PVDF-CNF (85/15) nanocomposite with varying concentration of CNF are characterized with the help of impedance analyser at room temperature in the frequency range of 20-Hz to 1MHz. The samples were cut in circular shape having diameter of 20mm. Silver paste was applied on both surfaces of the CPNC membrane before characterization to capture data efficiently as the charge gets accumulated near to silver paste because of its high conductivity. The silver paste was dried, and the measurements were taken by sandwiching the composite in between the parallel plate.

The measured data was transferred to the origin 8.5 software and the graphs were plotted. From Figure 6 it can clearly be depicted that with the increase CNF content there is increase in dielectric constant. The increased dielectric constant is not only the function of CNF particles but also because of the uniform dispersion of CNF by solvent casting technique in the PVDF polymer matrix. As per the Maxwell Wanger Sillars polarization mechanism (Tang et al., 2012) the dielectric constant of the nanocomposite film is not only enhanced by the conductive filler particles but rather governed by Maxwell Wanger Sillars interfacial interaction (Rathi et al., 2018). Figure 6 (a) shows the relation between dielectric constant and the frequency range of 10^4 to 10^6. As the percentage of CNF is increased in the PVDFCNF (95/5), PVDF-CNF (90/10) and PVDF-CNF (85/15) composite, the dielectric constant also increased. Similarly, in Figure

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6 (b) the relation between dielectric loss and the frequency shows that the dielectric loss has also increased in the PVDF-CNF (95/5), PVDF-CNF (90/10) and PVDF-CNF (85/15) composite, by increasing the conductive fillers, but very minor increase is there. Figure 6 (c) shows that the conductivity of the sample has increased for the PVDF-CNF (95/5), PVDF-CNF (90/10) and PVDF-CNF (85/15) composite. The method of calculating has been previously discussed in section 3.2. The SE depends on the absorption loss, reflection loss, and correction factor, which were calculated using equations (4) to (6). Total value of SE of PVDF-CNF is shown in Figure. 6 (d).

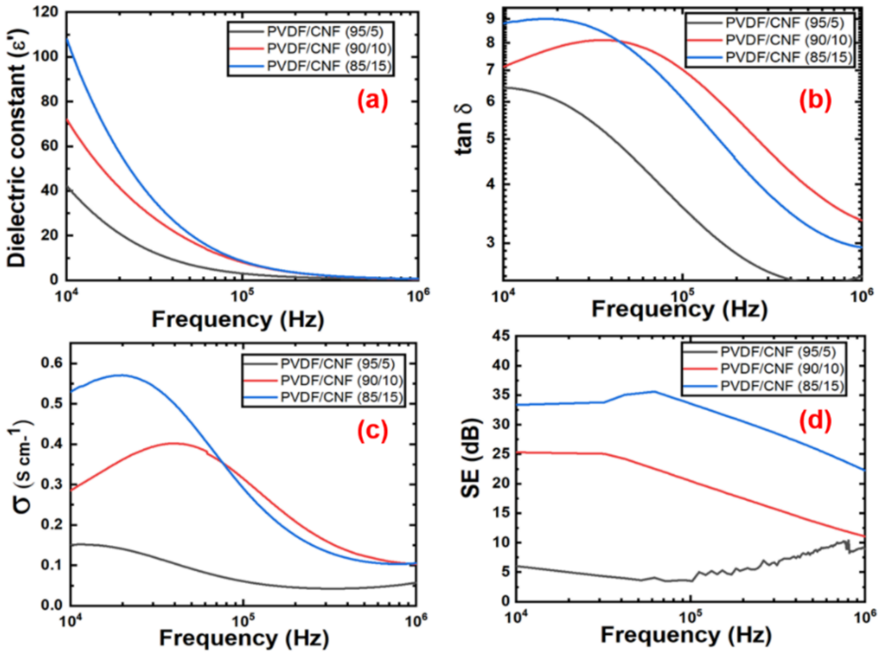

Figure 6. Shows the (a) dielectric constant vs frequency (b) dielectric loss frequency (c) conductivity frequency (d) shielding effectiveness

The value of SE increased with CNF content and decreased with frequency, except the fluctuation in value of 5 wt % of CNF filled composite. The composite having 15 wt % of CNF content depicted highest value of SE. The high value (36 dB) at 100 KHz was obtained for 15 wt % of CNF filled PVDF-CNF conducting polymer composite.

6. Conclusion

In this research, we have developed inexpensive PVDF-CNF composites using dry mixing and solvent casting method for dielectric and EMI shielding analysis in the radio frequency range. The ε^0 , tanδ, and σ increased with increasing CNF content. The PVDF-CNF composite with 15 wt % of CNF filled PVDF composite attained highest value of the ε^0 , tanδ and σ. The high value (36 dB) at 100 KHz was obtained for 15 wt % of CNF filled PVDF-CNF conducting polymer composite. However, samples of 5 wt % and 10 wt % CNF show satisfactory EMI shielding results for whole radio frequency region (10Hz - 1MHz).

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