

Enhancement of Dielectric Properties of PVDF Composites with MWCNT and GCNF Fillers

Chethan P.B.^{1,2}, Ganesh Sanjeev^{1,*}

¹Microtron center, Department of Physics, Mangalore University, Mangalagangothri, Karnataka, India

²Department of Physics, Atria Institute of Technology Bengaluru, Karnataka, India

Abstract

The paper discusses the role of multiwalled carbon nanotube (MWCNT) and graphitized carbon nanofibre (GCNF) in Polyvinylidene fluoride (PVDF) composites prepared by melt mixing method. Analytical studies were carried out using X-ray diffraction analysis (XRD) and Fourier transform infrared spectroscopy (FTIR) for understanding the role of fillers. Formation of β phase crystalline structure with a relative increase in β phase content is observed and is maximum at 5 wt.% of multiwalled carbon nanotube and graphitized carbon nanofibre. Scanning electron microscopy (SEM) analysis has revealed modifications in the surface morphology and the microstructure of the composites. The dielectric properties of the PVDF composites were studied from 20 Hz to 10 MHz and the addition of fillers is observed to significantly improve the dielectric properties of PVDF composites. It is established from the AC conductivity measurements that the conduction mechanism in the composites follows the correlated barrier hopping (CBH) model.

Keywords: Composites, dielectric properties, PVDF, β phase

*Author for Correspondence E-mail: ganeshsanjeev@rediffmail.com

INTRODUCTION

Polymer composites have been attracting the attention of scientific community due to their unique characteristics like easy processability, lightweight, flexibility and mechanical stability [1–3]. Therefore, these composites are extensively used in many applications like electromechanical systems, super capacitors, and electromagnetic interference (EMI) shielding, etc. [4–6]. The polymer-based composites can be developed by the addition of ceramic filler particles and conductive fillers. The inclusion of ceramic particles could improve the dielectric properties of polymer. However, high concentration of fillers limits the use of these composites for many industrial applications due to poor flexibility and higher bulk density. Compared to the polymer/ceramic composites polymer composites with conductive fillers lead to higher dielectric constant at low filler content and also maintain good mechanical properties and flexibility [7]. The conductive fillers like carbon nanotube and carbon nanofibre are widely used in the fabrication of polymer

composites due to their excellent dielectric properties, high aspect ratio, thermal, mechanical, and electrical properties [8, 9].

Polyvinylidene fluoride (PVDF) is a semi-crystalline thermoplastic engineering polymer known for its piezoelectric and pyroelectric properties [10]. It exhibits desirable characteristics such as chemical stability, flexibility, thermal stability, good mechanical strength, and it has relatively higher room temperature dielectric permittivity (7–13 at 1 kHz). These properties make the composite suitable for a wide range of applications as sensors, actuators, sound transducers, pyroelectric detectors, bio-medical devices and electromechanical devices [11–13]. PVDF has five different crystalline forms namely α , β , γ , δ and ϵ , respectively. Among these, the polar β phase has all-trans (TTT) planar zigzag conformation with dipole moments perpendicular to the chain axis which increases the polarity and hence PVDF possesses improved piezoelectric, pyroelectric, and ferroelectric properties [14, 15].

Widely used techniques for the preparation of polymer nanocomposites are the solution casting, melt mixing and *in-situ* polymerization [16]. The main objective of these methods is to achieve uniform dispersion of the filler in the polymer matrix because it directly affects the electrical, thermal, mechanical, and physical properties of the composite. The dispersion of fillers is a critical task and good dispersion is the key for achieving good and balanced electrical, thermal, and mechanical properties of the composites.

In this investigation, the PVDF composites were prepared by the melt mixing method [17]. This method is known for its simplicity, ease of processing and its main advantage is that it does not involve solvents and is free from contaminants. A large quantity of polymer composites can be prepared by this technique and it is considered as an efficient and effective technique for dispersion of carbon nanofillers into the commercial thermoplastic polymers [18, 19].

The present work focuses on the structure and dielectric properties of PVDF-MWCNT and PVDF-MWCNT-GCNF composites. The influence of these fillers on the crystal structure of the PVDF matrix and the formation of β phase has been investigated. The frequency dependent dielectric parameters like AC conductivity, dielectric constant, and loss tangent ($\tan\delta$), have been determined and the results are presented and discussed. Multiwalled carbon nanotube (MWCNT) is preferred conducting filler because it does not alter the density of the polymer matrix significantly in which it is incorporated but results in exceptional improvements in electrical, thermal, and mechanical properties. Therefore, MWCNT is blended with PVDF matrix to achieve multifunctional properties of the PVDF composites. Graphitized carbon nanofibre (GCNF), owing to its high surface to volume ratio imparts exceptionally good electrical, thermal, and mechanical characteristics to the PVDF matrix. Hence, MWCNT and GCNF were selected as fillers and were incorporated into the base PVDF matrix.

EXPERIMENTAL METHODS

Materials

The commercially available Polyvinylidene fluoride (PVDF), grade Kynar 301 F (with a density 1.77 g/cc, melting temperature 155–160°C and melt flow index of 2–6 g/10 min at 232°C under a load of 21.6 kg) was received from M/s Arkema, France. Uncoated MWCNT filler used had a mean outer diameter of 10–20 nm, length of 10–30 μm , purity of 97%. GCNF filler had a diameter \sim 200 nm, length of 10–30 μm , and purity above 90%. The fillers were procured from M/s Global Nanotech Co. India. The required amount of MWCNT was added to PVDF and mixed using Haake mixer. The operating speed of the mixer was 60 rpm and the temperature used was 220°C and the duration of mixing was 10 min. Under these conditions, it was possible to achieve uniform dispersion of MWCNT. The resulting PVDF-MWCNT mixture was then used for preparation of pellets. The laminates of the composites were prepared from pellets by compression moulding at 220°C. The thickness of the composites prepared was 0.5 mm. By following a similar procedure, and by adding the requisite amount of GCNF and MWCNT, preparation of PVDF-MWCNT-GCNF composites was undertaken. The composites fabricated are identified as shown in Table 1.

Measurement Methods

The X-ray diffractograms of the samples were recorded in the 2θ range of 10–50° with a scan speed of 0.02°/s, using Rigaku Smart Lab X-ray diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$) at 40 kV and 30 mA. Analysis of the functional groups of the composites was undertaken by using Fourier transform infrared spectroscopy (FTIR) with Perkin Elmer spectrum-GX FT-IR instrument. The samples were scanned in transmission mode in the wavelength range of 400 to 4000 cm^{-1} .

Table 1: Sample Designation.

Composites	Identification
Pristine PVDF	P
PVDF+3wt% MWCNT	PM3
PVDF+5wt% MWCNT	PM5
PVDF+3wt% MWCNT+3wt% GCNF	PMG3
PVDF+5wt% MWCNT+5wt% GCNF	PMG5

The surface morphology of the composites was analyzed using scanning electron microscope (SEM) model VEGA3 of TESCAN. A layer of gold was sputter-coated on the samples for SEM analysis.

The capacitance (C), dissipation factor ($\tan \delta$) and conductance (G) of the composites were measured using Wayne Kerr high-frequency LCR meter (model 6500 P), over a frequency range of 20 Hz–10 MHz. From the measured values of capacitance, the dielectric constant (ϵ_r) was determined.

RESULTS AND DISCUSSION

X-ray Diffraction Analysis

The X-ray diffraction (XRD) diffractogram of pristine PVDF, PVDF-MWCNT and PVDF-MWCNT-GCNF composites are shown in the Figure 1. Prominent characteristic peaks at $2\theta=17.7^\circ$, 18.5° , 20° and 26.7° are observed in pristine PVDF (composite P) indicating that the PVDF α -phase crystal has (100), (020), (110) and (021) reflections [11, 20]. With the addition of 3 wt.% of MWCNT to pristine PVDF, (composite PM3), there is a slight shift in the peak position with corresponding increase in the intensity. At 5 wt.% of MWCNT, (composite PM5), the diffractogram resembles that of PM3 but for reduction in the intensity of the peaks.

With the addition of 3 wt.% each of MWCNT and GCNF into the pristine PVDF, (PMG3) the diffraction peak is observed around $2\theta=20.8^\circ$. Though the peak at $2\theta=20.8^\circ$ appears in all the composites, it is relatively more prominent in PMG3, signaling the formation of β -phase with (110)/(200) reflections [11, 21]. The peak position at $2\theta=17.7^\circ$ seen in PMG3 vanishes in PMG5 due to the addition of 5 wt.% each of MWCNT and GCNF. The peak intensities of the PVDF composites with fillers at $2\theta=26.7^\circ$ are observed to decrease in comparison to that of the pristine PVDF (P). This result conclusively establishes that the relative β phase content in PVDF composites increases due to the addition of fillers.

According to the density functional theory (DFT) proposed by Shansheng Yu and

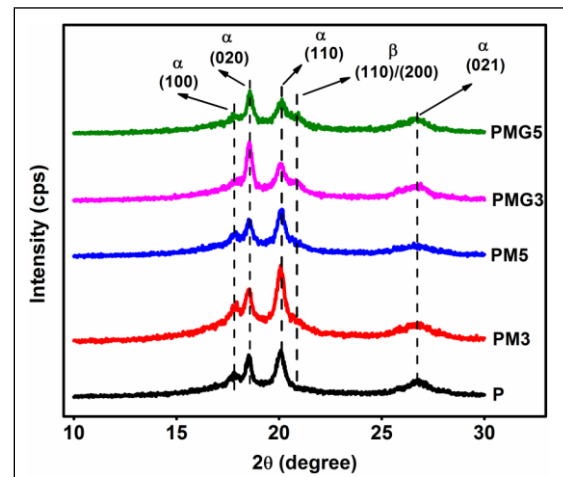


Fig. 1: X-ray Diffractograms of PVDF Composites.

coworkers [22], it is established that the TTTT and TGTG' chains of PVDF are absorbed by the CNT surface and the TTTT molecular chains in the process are more rigidly bound to the CNT surface rather than TGTG' molecular chains. The authors [22] have also reported that the more stable configuration is the one in which H atoms and CNT surface are oriented face to face. Thus, from the XRD diffractograms, it is concluded that in the PVDF composites with MWCNT and GCNF fillers, the TTTT type of molecular chains of PVDF are adsorbed significantly by the MWCNT and GCNF surfaces and therefore, the fillers act as nucleating agents to form the β phase crystals.

FTIR Analysis

The FTIR spectra of the PVDF composites in the region 400 to 1600 cm^{-1} is shown in Figure 2. The absorption peaks at 530 , 613 , 763 , 974 , 1148 , 1180 and 1381 cm^{-1} correspond to the α -phase, whereas the peaks at 511 , 840 and 1278 cm^{-1} represent the β -phase [23, 24]. From the Figure 2, it is observed that the transmittance of β -phase peak is enhanced by the addition of fillers and the α -phase peaks are considerably suppressed. The relative percentage of β -phase $F(\beta)$ in each of the composite is computed using the following equation [19, 25]:

$$F(\beta) = \frac{X_\beta}{X_\alpha + X_\beta} = \frac{A_\beta}{1.26A_\alpha + A_\beta} \times 100\% \quad (1)$$

Where, X_α and X_β are the crystalline mass fractions of α and β phases, A_α and A_β are the absorbance of the vibration bands at 763 and

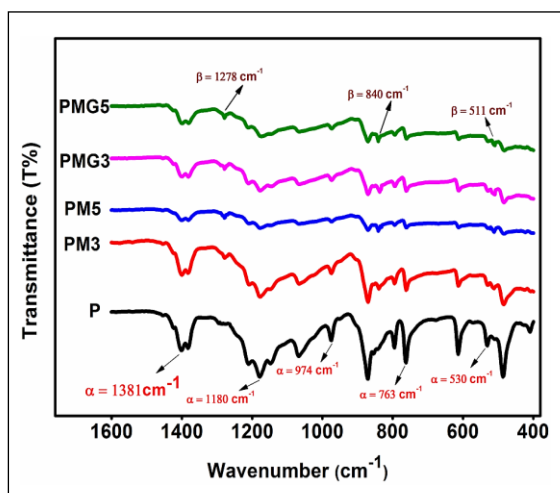


Fig. 2: FTIR Spectra of PVDF Composites.

Table 2: Relative Percentage of β-phase of PVDF Composites.

Samples	F(β)
P	27
PM3	38
PM5	40
PMG3	38
PMG5	41

840 cm⁻¹, respectively. The computed relative percentage of β-phase of the pristine PVDF and the PVDF composite with fillers are shown in Table 2.

From the results of Table 2, it is observed that with the addition of fillers, the β-phase content significantly increases in the PVDF composites. This evidently proves that the fillers help to enhance the formation of β-phase crystals. The maximum value of F (β) observed is 41% and it is seen in the case of PMG5 and this value would strongly influence the piezoelectric properties of the composite [26]. This fact is well complimented by the results of XRD. The addition of MWCNT and GCNF fillers help to reduce the α-phase of the pristine PVDF. Thus, the results of FTIR and XRD have both established that the combination of MWCNT and GCNF fillers help in generation of polar β-phase crystals with relative reduction in alpha phase.

A similar study on PVDF/MWCNT/Fe₃O₄ composites is reported by Tsonos and co-workers [27]. The authors have highlighted the

formation of β-phase crystal structure as due to the incorporation of conducting MWCNT (4 wt.%) and Fe₃O₄ (5-15 wt.%) fillers. In Table 2, the relative percentage of β-phase due to incorporation of MWCNT and MWCNT with GCNF of different wt.% are shown to highlight the role of fillers.

Surface Morphology

The effect of fillers on the microstructure of the composites has been analyzed using SEM. The microstructure of the pristine PVDF (sample P) shows dense layers of PVDF, having smooth surface with minimal presence of voids as shown in Figure 3(a). However, in PVDF composite with 3 wt.% of MWCNT (Figure 3(b)), it is observed that the filler particles are homogeneously dispersed and the surface appears to be modified in comparison to the pristine PVDF. With the increase in MWCNT loading to 5 wt.%, (Figure 3(c)) the microstructure of the PVDF composite is observed to completely change due to the presence of the filler. Formation of vast grainy aggregates is also observed at 5 wt.% of MWCNT.

In the SEM image of MWCNT-GCNF-PVDF composites (PMG3) shown in Figure 3(d), the fillers appear to be well dispersed, more evenly in the PVDF matrix and a grainy aggregates of the fillers are observed in the SEM micrograph. With increase in the percentage of the two fillers to 5 wt.% (PMG5), the presence of MWCNT dominates over that of the GCNF. This leads to inhomogeneous dispersion of fillers which destroys the uniformity of the PVDF matrix. This can be seen in SEM micrograph of Figure 3(e). Thus, PVDF composite shows better compatibility at the interface of the fillers and the host polymer but, the homogeneity of the matrix is influenced by the relative wt.% of the two fillers.

Dielectric Parameters

AC Conductivity

The variations in AC conductivity of neat PVDF, PVDF-MWCNT and PVDF-MWCNT-GCNF at room temperature (25±2°C), in the frequency range 20 Hz to 10 MHz is shown in Figure 4. The AC conductivity of pristine PVDF at 20 Hz is 5.07×10⁻¹³ S/cm and it increase with increase in frequency. The

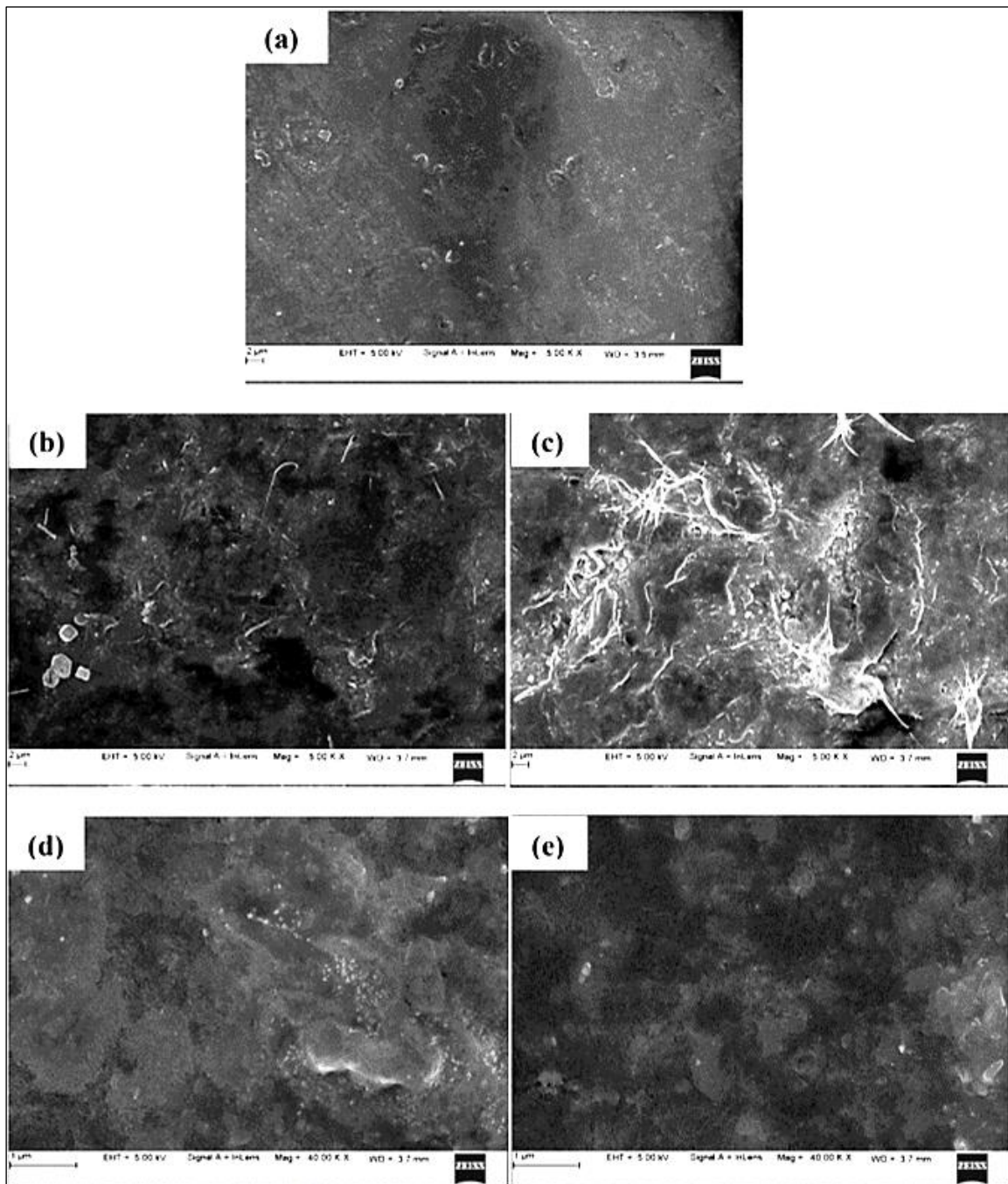


Fig. 3: SEM Micrographs of (a) P, (b) PM3, (c) PM5, (d) PMG3, (e) PMG5 Samples.

frequency dependence of the AC conductivity of the pristine PVDF is due to its insulating nature. With the addition of 3 wt.% of MWCNT, due to the influence of the relative wt.% of the filler, there is an improvement in the AC conductivity. Variations in σ_{AC} appear to be invariant from 20 Hz to 100 kHz and from 100 kHz to 10 MHz, a linear increase is observed like the variations in the pristine PVDF. With further increase in the wt.% of

MWCNT to 5 wt.%, there is a further improvement in the AC conductivity. However, the variations in σ_{AC} appear to be identical to that of PM3, and it remains invariant from 20 Hz to 100 kHz. From 100 kHz to 10 MHz, a linear increase is observed as seen in PVDF with 3 wt.% of MWCNT.

In PMG3 and PMG5, the difference in the AC conductivity over the entire frequency range is

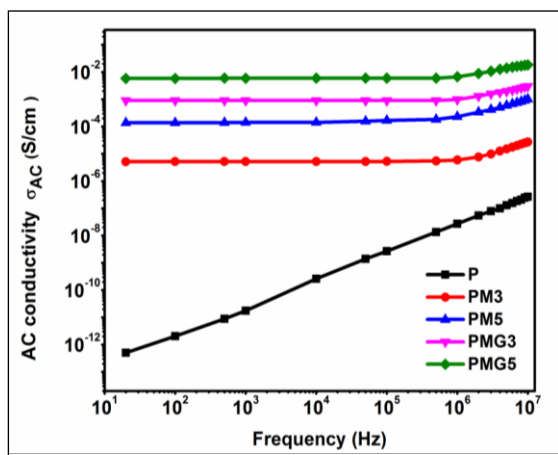


Fig. 4: Variation of AC Conductivity with Frequency of PVDF Composites.

observed to be minimal and the variations in σ_{AC} appear to be identical to that of PM3 and PM5. Further, the AC conductivity remains nearly invariant in the frequency range of 100 kHz and starts increasing above 100 kHz. Thus, it is observed that composites PM3 PM5, PMG3 and PMG5 differ in the variation of σ_{AC} with frequency in comparison to pristine PVDF. In all the composites a DC plateau is observed in the low frequency region and it increases with increase in frequency in the high frequency region (>1 MHz).

The σ_{AC} of PM5 is of the order of 10^{-4} S/cm over the measured frequency range (20 Hz–10 MHz) and a highest value of 1.01×10^{-3} S/cm is achieved at 10 MHz. A similar trend in variation of σ_{AC} is observed in PMG3 and PMG5. The highest value of σ_{AC} of the composites is 1.84×10^{-2} S/cm and it is observed in case of PMG5 at 10 MHz. It is important to note that the σ_{AC} value of 10^{-2} S/cm of PMG5 makes it suitable for electrical applications like electrostatic dissipation, electrostatic painting, and EMI shielding [28].

The charge transport mechanism in the composites can be explained using universal power law [29, 30] which is expressed as,

$$\sigma_{AC} = \sigma_{DC} + Af^n \tag{2}$$

Where, σ_{AC} and σ_{DC} are the AC and DC conductivities, respectively, f is the frequency of the applied electric field, A and n are the fitting parameters computed from the

Table 3: A and n Values of Composites.

Composites	A (S/m-Hz ⁻¹)	n
P	2×10^{-14}	1.02
PM3	3×10^{-11}	0.84
PM5	6×10^{-9}	0.74
PMG3	3×10^{-7}	0.56
PMG5	2×10^{-5}	0.41

empirical relation of Eq. (2). The value of exponent n is in the range $0 < n < 1$ and typical of hopping conduction mechanism. The value of n and A can be computed from the slope and intercept of the plots of Figure 4, which shows the variation of AC conductivity of the composites with frequency. The computed values of A and n for the different composites are tabulated in Table 3.

The variations in the exponent n emphasized the fact that the nature of the conduction mechanism differs in the composite. From the Table 3 it is observed that the exponent n decreases with the addition of MWCNT and GCNF fillers. This result clearly indicates that the conduction mechanism follows the correlated barrier hopping (CBH) model [31].

Dielectric Constant

The variations in the dielectric constant with frequency at room temperature in the range 20 Hz to 10 MHz is shown in the Figure 5. The dielectric constant of PVDF increases with the addition of fillers. As already discussed under XRD and FTIR analysis, the β -phase content significantly increases with fillers. The increased content of β -phase crystal enhances the polarity and it is the main reason for the increase in the dielectric constant [32] of the PVDF composites with fillers. The highest dielectric constant of 755 is observed in PMG5 and the lowest value of 178 is observed in PM3 which is ten times the value of neat PVDF. This result signifies that the MWCNT and GCNF are well dispersed in PVDF matrix and there is a formation of a network of nanocapacitance in the PVDF matrix due to the increase in the wt.% of fillers.

When a small amount of filler is added into the PVDF matrix, nanocapacitance structures are formed, resulting in an increase of the dielectric constant as compared to that of the

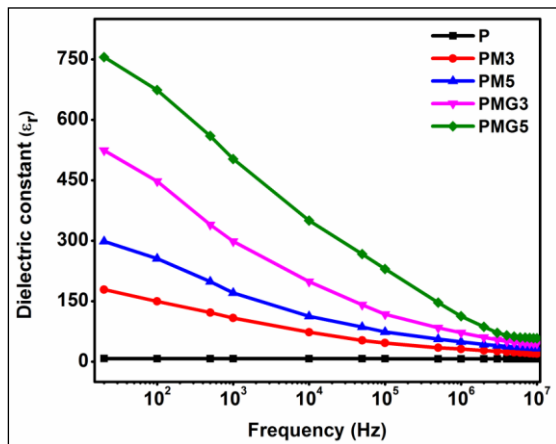


Fig. 5: Variation in Dielectric Constant with Frequency of PVDF Composites.

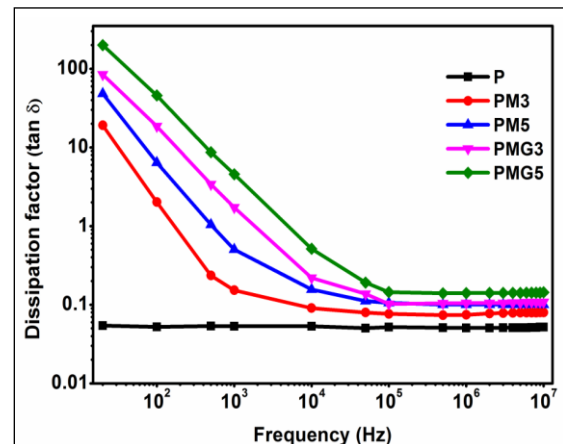


Fig. 6: Variation of Dissipation Factor with Frequency of PVDF Composites.

neat PVDF. Further Maxwell-Wagner-Sillars's (MWS) polarization phenomenon plays a very crucial role in improving the dielectric constant. The MWS effect is related to the free charge accumulation between the insulator and conductor interfaces. Due to the MWS effect, when current flows across the interfaces, charges are accumulated at the interface of the PVDF matrix and MWCNT fillers. Since the relaxation time of the PVDF is relatively higher than that of MWCNT, the charge carriers are blocked at the interfaces between the polymer and the fillers due to the MWS effect. This factor significantly contributes to the increase in the dielectric constant over the low frequency range [33]. With increase in frequency, the dielectric constant decreases because of the establishment of a conductive network within the composite which allows the flow of leakage current, which is otherwise blocked in the lower frequency range [34].

Dissipation Factor

The loss tangent ($\tan \delta$) variations with frequency of pristine PVDF, PVDF with MWCNT-PVDF and MWCNT-GCNF fillers is shown in Figure 6. The dielectric loss gives an indication about the energy dissipated by a material on application of AC voltage. For neat PVDF, the loss tangent remains invariant in the frequency range of 20 Hz to 1 MHz. Composite PM3 also shows identical $\tan \delta$ variations with frequency, but for marginal increase in the dissipation factor values. When the filler loading is increased, the loss tangent increases to relatively much higher levels.

The decrease in dissipation factor of the PVDF composites PM5, PMG3 and PMG5 with increase in frequency is attributed to the dipoles which get lesser time to orient themselves in the direction of the applied electric field. This effect is prominently seen in PVDF composite at filler loading above 3 wt.%. Further, the interfacial polarization and the long conductive network formed in the polymer matrix due to the addition of fillers results in higher dielectric constant and higher dissipation factor in the lower frequency range [35]. The higher values of dielectric constant and dissipation factor of PVDF composites with fillers are beneficial in the use of the composites for decoupling capacitor applications [4].

This study has established that addition of MWCNT and GCNF fillers would result in many advantages to the PVDF matrix to render the composite suitable for applications like sensing, static charge dissipation, energy storage, electric stress control and others.

CONCLUSIONS

In the present work, a series of PVDF-MWCNT and PVDF-MWCNT-GCNF composites were prepared using melt mixing method and their dielectric parameters are investigated. Based on the experimental results the following important conclusions are drawn:

- (i) XRD and FTIR analysis have shown that the inclusion of MWCNT and GCNF leads to the formation of β -phase in the

composites which is relatively the highest at 41% with 5 wt.% each of MWCNT and GCNF in PVDF.

- (ii) SEM analysis has shown that the distribution of MWCNT and GCNF fillers leads to significant changes in the surface morphology and the microstructure of the PVDF composites.
- (iii) The formation of β -phase crystals leads to the increase in the dielectric constant and AC conductivity which make the composites suitable for many electrical applications. At 5 wt.% of the filler loadings in PVDF, higher values of dielectric constant and dissipation factor are observed in the frequency range of 20 Hz–1 MHz. This is due to MWS interfacial polarization mechanism and the existence of nanocapacitance in the polymer matrix.
- (iv) The conduction mechanism in the composites follows the CBH model.

ACKNOWLEDGEMENTS

The first author gratefully acknowledges the support and help received from the Microtron Centre, Mangalore University Mangalagangothri, Mangalore, Karnataka, India, and the Nanodielectrics Laboratory of Sri Jayachamarajendra College of Engineering, JSS Science and Technology University, Mysore, Karnataka, India for undertaking this research work.

Conflict of Interest

The authors declare that there is no conflict of interest.

REFERENCES

1. Huang X, Jiang P. Core–Shell Structured High- k Polymer Nanocomposites for Energy Storage and Dielectric Applications. *Adv Mater.* 2014; 27(3): 546–54p.
2. Dang ZM, Zheng MS, Zha JW. 1D/2D Carbon Nanomaterial-Polymer Dielectric Composites with High Permittivity for Power Energy Storage Applications. *Small.* 2016; 12(13): 1688–701p.
3. You Y, Zhan C, Tu L, *et al.* Polyarylene Ether Nitrile-Based High- k Composites for Dielectric Applications. *Int J Polym Sci.* 2018; 2018: 1–15p. doi: 10.1155/2018/5161908.
4. Panwar V, Kang B, Park J, *et al.* Study of dielectric properties of styrene-acrylonitrile graphite sheets in low and high frequency region. *Eur Polym J.* 2009; 45: 1777–84p.
5. Sousa PM, Chu V, Conde JP. Mechanical properties of polymer/carbon nanotube composite micro-electromechanical systems bridges. *J Appl Phys.* 2013; 113: 134508 1–9p.
6. Verma M, Verma P, Dhawan SK, *et al.* Tailored graphene based polyurethane composites for efficient electrostatic dissipation and electromagnetic interference shielding applications. *RSC Adv.* 2015; 5: 97349–58p.
7. Yang K, Huang X, Fang L, *et al.* Fluoro-polymer functionalized graphene for flexible ferroelectric polymer-based high- k nanocomposites with suppressed dielectric loss and low percolation threshold. *Nanoscale.* 2014; 6: 14740–53p.
8. Shehzad K, Hakro A, Zeng Y, *et al.* Two percolation thresholds and remarkably high dielectric permittivity in pristine carbon nanotube/elastomer composites. *Appl Nanosci.* 2015; 5: 969–74p.
9. Chowdhury SA, Saha MC, Patterson S, *et al.* Highly Conductive Polydimethylsiloxane /Carbon Nanofiber Composites for Flexible Sensor Applications. *Adv Mater Tech.* 2019; 4(1): 1800398 1–10p.
10. Jaitanong N, Yimnirun R, Zeng HR, *et al.* Piezoelectric properties of cement based / PVDF/PZT composites. *Mater Lett.* 2014; 130: 146–49p.
11. Gregorio RJr. Determination of the α , β , and γ Crystalline Phases of Poly (vinylidene fluoride) Films Prepared at Different Conditions. *J Appl Polym Sci.* 2006; 100: 3272–79p.
12. Raun L, Yao X, Chang Y, *et al.* Properties and Applications of the β Phase Poly (vinylidene fluoride). *Polymers.* 2018; 10(228): 1–27p.
13. Xia W, Zhang Z. PVDF-based dielectric polymers and their applications in electronic materials. *IET Nanodielectrics.* 2018; 1(1): 17–31p.

14. Kabir E, Khatun M, Nasrin L, *et al.* Pure β -phase formation in polyvinylidene fluoride (PVDF)-carbon nanotube composites. *J Phys D: Appl Phys.* 2017; 50(16): 163002, 1–25p.
15. Shah D, Maiti P, Gunn E, *et al.* Dramatic Enhancements in Toughness of Polyvinylidene Fluoride Nanocomposites via Nanoclay-Directed Crystal Structure and Morphology. *Adv Mater.* 2004; 16: 1173–77p.
16. Haldorai Y, Shim J. In: Thomas S, Muller R, Abraham J, editors. *Manufacturing Polymer Nanocomposites.* Hoboken, New Jersey: John Wiley and Sons Inc. Publishing; 2016.
17. Georgousis C, Pandis C, Kalamiotis A, *et al.* Strain sensing in polymer/carbon nanotube composites by electrical resistance measurement. *Compos Part B-Eng.* 2015; 68: 162–169p.
18. Achaby MEI, Arrakhiz FZ, Vaudreuil S, *et al.* Preparation and Characterization of Melt-Blended Graphene Nanosheets–Poly(vinylidene fluoride) Nanocomposites with Enhanced Properties. *J Appl Polym Sci.* 2012; 127(6): 41577 1–8p.
19. Ke K, Potschke P, Jehnichen D, *et al.* Achieving β -phase poly(vinylidene fluoride) from melt cooling: Effect of surface functionalized carbon nanotubes. *Polymer.* 2014; 55: 611–19p.
20. Kriptomou S, Sovatzoglou S, Pandis C, *et al.* Effects of CNT inclusions on structure and dielectric properties of PVDF/CNT nanocomposites. *Phase Transit.* 2016; 89: 717–30p.
21. He L, Xia G, Sun J, *et al.* Unzipped multiwalled carbon nanotubes-incorporated poly (vinylidene fluoride) nanocomposites with enhanced interface and piezoelectric β phase. *J Colloid Interf Sci.* 2013; 393: 97–103p.
22. Yu S, Zheng W, Yu W, *et al.* Formation Mechanism of β -Phase in PVDF/CNT Composite Prepared by the Sonication Method. *Macromol.* 2009; 42: 8870–74p.
23. Boccaccio T, Bottino A, Capannelli G, *et al.* Characterization of PVDF membranes by vibrational spectroscopy. *J Membrane Sci.* 2002; 210: 315–29p.
24. Martins P, Lopes AC, Mendez SL. Electroactive phases of poly(vinylidene fluoride): Determination, processing, and applications. *Prog Polym Sci.* 2014; 39: 683–706p.
25. Gomes J, Nunes JS, Sencadas V, *et al.* Influence of the β -phase content and degree of crystallinity on the piezo- and ferroelectric properties of poly (vinylidene fluoride). *Smart Mater Struct.* 2010; 19: 065010 1–7p.
26. Wu CM, Chou MH. Polymorphism, piezoelectricity, and sound absorption of electrospun PVDF membranes with and without carbon nanotubes. *Compos Sci Technol.* 2016; 127: 127–33p.
27. Tsonos C, Pandis C, Soin N, *et al.* Multifunctional nanocomposites of poly(vinylidene fluoride) reinforced by carbon nanotubes and magnetite nanoparticles. *Express Polym Lett.* 2015; 9(12): 1104–18p.
28. Ramasubramaniam R, Chen J. Homogenous carbon nanotube/polymer composites for electrical applications. *Appl Phys Lett.* 2003; 83(14): 2928–30p.
29. Greenhoe BM, Hassan MK, Wiggins JS, *et al.* Universal Power Law Behavior of the AC Conductivity Versus Frequency of Agglomerate Morphologies in Conductive Carbon Nanotube-Reinforced Epoxy Networks. *J Polym Sci. Part B: Polym Phys.* 2016; 54(19): 1918–23p.
30. Arya A, Sadiq M, Sharma AL. Effect of variation of different nanofillers on structural, electrical, dielectric, and transport properties of blend polymer nanocomposites. *Ionics.* 2018; 24: 2295–319p.
31. Mansour SA, Al-ghoury ME, Shalaan E, *et al.* Dielectric Dispersion and AC Conductivity of Acrylonitrile Butadiene Rubber-Poly(vinyl chloride)/Graphite Composite. *J Appl Polym Sci.* 2011; 122: 1226–35p.
32. An N, Liu S, Fang C, *et al.* Preparation, and properties of β -phase Graphene Oxide/PVDF Composite Films. *J Appl Polym Sci.* 2015; 132(10): 41577 1–8p.
33. Yuan JK, Yao SH, Dang ZM, *et al.* Giant Dielectric Permittivity Nanocomposites: Realizing True Potential of Pristine Carbon Nanotubes in Polyvinylidene Fluoride Matrix through an Enhanced Interfacial Interaction. *J Phys Chem C.* 2011; 115: 5515–21p.

34. Li YJ, Xu M, Feng JQ, *et al.* Dielectric behavior of a metal-polymer composite with low percolation threshold. *Appl Phys Lett.* 2006; 89: 072902 1–3p.
35. Ram R, Rahaman M, Khastgir D. Electrical properties of polyvinylidene fluoride (PVDF)/multi-walled carbon nanotube (MWCNT) semi-transparent composites: Modelling of DC

conductivity. *Compos Part A-Appl S.* 2015; 69: 30–39p.

Cite this Article

Chethan P.B., Ganesh Sanjeev. Enhancement of Dielectric Properties of PVDF Composites with MWCNT and GCNF Fillers. *Journal of Polymer & Composites.* 2020; 8(3): 43–52p.