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Study of Optical, Structural, Thermal and Dielectric Properties of Poly(vinylidene diflouride)/Cuprous Oxide Polymer Nanocomposites

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Herein, a development of cuprous oxide (Cu_2O)/polyvinylidene difluoride (PVDF) polymer nanocomposite (PNC) films by solution casting route is reported. The nanocomposite films were characterized using UV-visible spectroscopy, Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), thermogravimetric analysis (TGA) and LCR meter. Formation of a broad band near 465 nm for polymer nanocomposite suggests that Cu_2O nanoparticles are present in the film. Some of the vibrational bands of PVDF were slightly shifted from their original position and the intensity of some bands were found to increase in presence of nanoparticles. Such features reveal that some interaction occurs between PVDF and Cu_2O nanoparticles. Scanning electron microscope (SEM) images show that the nanoparticles are interconnected to each other through PVDF polymer chain. Crystalline nature of Cu_2O nanoparticles in the film was confirmed from XRD pattern. Thermogravimetric analysis shows that thermal stability of neat PVDF has increased in presence of nanoparticles. The neat PVDF showed dielectric constant value of 8 at frequency 100 Hz, while that of 1 wt% Cu_2O doped PVDF polymer nanocomposite has exhibited dielectric constant value ~175 at the same frequency.

Keywords: Polymer nanocomposites, Poly(vinylidene diflouride), Cuprous oxide; Optical, Dielectric properties.

INTRODUCTION

Electroactive polymer like poly(vinylidene difluoride) (PVDF) is widely used as an energy harvesting polymeric material since its piezo-electricity was discovered by H. Kawai [1]. Scientific community showing interest on PVDF owing to its novel and exceptional optical, electrical and magnetic properties [2-4]. But for the application in the field of organic electronics, a polymer should possess improved mechanical, thermal and electrical properties. In order to improve these properties in a polymer, requisite amount of nanofillers in the form of metal, metal oxide, carbon, *etc*. are added [4,5]. We have chosen cuprous oxide (Cu_2O) nanoparticles to develop polymer nanocomposites (PNCs) because of its possession of some important properties like low band gap p-type semiconductor, high surface-to-volume ratio, execution of excellent catalytic, sensing, anti-fouling activity [6-10]. There are various methods are available to develop polymer nanocomposites. Cao and Xiao [11] have prepared Cu_2O/PVA/chitosan composite films *via* a one-step liquid phase precipitation-reduction method and tape casting process. Their characterization results suggested that Cu_2O particles were 200-300 nm in diameter. They reported that composite films exhibits efficient photocatalytic activity for decolourization of X-3B dye under visible light irradiation. PVA-Cu_2O composite has been prepared *via* chemical reduction method using PVA-Cu(II) complex as precursor [12]. It is reported that prepared polymer nanocomposites exhibits excellent antibacterial activity agents against Gram-positive bacteria (*B. thuringiensis*) and Gram-negative bacteria (*E. coli*).

Bhavanasi *et al.* [13] have reported enhancement in the piezoelectric energy harvesting performance of PVDF in bilayer films of poled poly(vinylidene fluoride-trifluoroethylene) [PVDF-TrFE] and graphene oxide (GO). According to their report, bilayer film exhibited superior energy harvesting performance with a voltage output of 4 V and power output of 4.41 μW cm^{-2} compared to poled PVDF-TrFE films without nanofillers. In PVDF-GO PNC films, enhanced voltage and power output is due to the combined effect of factors like electrostatic contribution from graphene oxide, residual tensile stress, enhanced Young′s modulus of the bilayer films. The presence of space charge at the interface of PVDF-TrFE and graphene oxide films is arising from the uncompensated polarization of PVDF-TrFE. They also reported that higher Young′s modulus and dielectric constant of graphene oxide led to the efficient transfer of mechanical and electrical energy. Kumar *et al*. [14] have synthesized iron oxide (Fe_2O_3) by a chemical precipitation method and then used oxide particles as filler in PVDF-HFP based copolymer electrolyte to develop PNCs for dye sensitized solar cell applications. Their Fe_2O_3 doped PVDF-HFP polymer electrolyte showed an ionic conductivity of 6.36×10^{-4} S/cm and diffusion coefficient as 1.02×10^{-4} cm^2/s. They used this PNC film for dye-sensitized solar cell fabrication. The power conversion efficiency was reported as 3.62 % with the enhancement of 2.1 times when compared to pure PVDF-HFP electrolyte. Zhao *et al*. [15] have blended with poly PVDF with graphene oxide and copper oxide (Cu_xO) nanofillers to develop a novel highly antifouling composite membranes *via* phase inversion process.

In this article, a development of PVDF/Cu_2O PNCs *via* a solution casting route is discussed. The Cu_2O nanoparticles were synthesized as reported [6,7] and then nanoparticles were added to PVDF solution to develop polymer nanocomposite (PNC) films. The developed polymer nanocomposite films were then characterized using UV-visible, FTIR, XRD, TGA thermogram, SEM and dielectric plots.

EXPERIMENTAL

Development of PVDF/Cu_2O polymer nanocomposites (PNCs): Cu_2O nanopowders in different amount were added to a fixed volume of poly(vinylidene difluoride) (PVDF) solution (3 g/L) taken in a beaker and stirred with the help of magnetic stirrer to get nanocolloid/nanofluid. Five samples of nanofluids consisting of different amount of Cu_2O nanoparticles with PVDF solution in dimethyl formamide were prepared. In order to develop PNCs, nanofluids were filled in petri dishes and then placed in an oven maintained at 50 ºC for 5 h in order to remove the solvent completely. Then, the films were carefully taken out from the petridish and kept in desiccators for their characterizations.

Characterizations: The optical absorption spectra of films were studied in the 200-900 nm regions by a UV-visible spectrometer (Perkin-Elmer Lambda 750 spectrophotometer). The FTIR data studied in this work were measured in the 4000 to 400 cm^{-1} region of the vibrational frequencies using Perkin-Elmer FTIR Spectrometer (Spectrum 65). The crystalline structures of nanoparticles were analyzed in terms of wide angle XRD by using an X-ray diffractometer (PHILIPS model PW-1710). The nanocolloids were casted on the surface of silicon substrate and placed in a sample holder in the diffractometer in order to measure the diffractogram from flat surfaces of the sample. The diffraction data were recorded using a filtered monochromatic radiation of CuKα of wavelength $\lambda = 0.15405$ nm through a Ni filter. Scanning electron microscopic (SEM, Oxford model Leo1550 VP SEM) images of selective samples of PNC films were also characterized. The samples were coated with a thin film of gold by a sputtering method to provide a conductive surface during the measurements. The images were taken at an accelerated voltage in the 2-10 kV range. Thermal measurements were done with a thermal analyzer of Perkin-Elmer model DT-40, Shimadzu Co. Japan. The electrical properties of Ag-PVA polymer nanocomposites of the free-standing films were measured. The variations of the dielectric constant (ε) and the dielectric power loss (tan δ) with a function of frequency (*f*) (varied in the 100 Hz to 5 MHz range) were measured at room temperature using a HIOKI 3532 50LCR HiTESTER LCR meter. Moreover, electrical resistances of these samples were studied as a function of temperature in the range of 60-350 K. A four-probe method has been employed to make the contacts between the sample and the electrodes.

RESULTS AND DISCUSSION

UV-visible analysis: The UV-visible optical absorption spectra in the 200-900 nm region were studied to verify the formation of Cu_2O nanoparticles in the PVDF-Cu_2O polymer nanocomposite (PNC) films at room temperature. The UV-vis spectra of six PNC solid samples consisting of (a) 0.0, (b) 0.1, (c) 0.2, (d) 0.3, (e) 0.5 and (f) 1.0 wt. % Cu_2O nanoparticles are shown in Fig. 1a. Two absorption bands in the spectrum for samples b-f were observed. One weak band is observed at 196 nm from the PVDF polymer [16,17], while another broad band near 460 nm is ascribed to surface plasmon resonance (SPR) band [6,7]. For neat PVDF no band is observed beyond 200 nm. Behera and Giri [6,7] have reported SPR band at 455 nm for this oxide nanoparticles. From Fig. 1a, it is also observed that with increasing the Cu_2O-content, the intensity of SPR band is increased due to presence of a large number of nanoparticles. Also, SPR band (Fig. 1b) is shifted to higher wavelength side (*i.e.* red-shift) with increased contnets in Cu_2O nanoparticles due to increase in the cluster size of nanoparticles [16,18].

As Cu_2O nanoparticles content increases in the composite film, relative number of PVDF molecules decreases and this causes the size of cluster to increase. The intensity of band near 196 nm is also increased with increasing nanoparticles content. It suggests that nanoparticles helped PVDF polymer to absorb UV light strongly in this region [18]. Execution of this characteristic by the PNC film is a good sign and may be a prospective candidate to be used as UV-shielding material.

FTIR analysis: The FTIR spectra of five films consisted of (a) 0.0, (b) 0.1, (c) 0.2, (d) 0.5 and (f) 1.0 wt. % Cu_2O NPs are shown in Fig. 2. A band at 3350 cm^{-1} is from O-H stretching vibration, whereas the bands at 3020 and 2925 cm^{-1} are due to C-H stretching vibrations. The bands at 1400 and 1175 cm^{-1} are asscribed due to C-F stretching and CH_2 bending vibration occured at 1430 cm^{-1}. The bands at 1450, 1175 and 675 cm^{-1} bands are due to polymeric chain defect [15-19]. In the presence of Cu_2O nanoparticles, it is observed from the spectra that intensity of some of the band has increased drastically. Some band even shifts towards shorter wavelength (*i.e.* blue shift) from their original position. Increased in band intensity and also shifting of band clearly suggests that some interaction occurs between Cu_2O nanoparticles and F-atoms of PVDF polymer [6,7]. A band near 640 cm^{-1} is found, which ascribed to Cu-O stretching vibration in Cu_2O nanoparticles [6,7,15,19]. No such band was found for neat PVDF film. Hence, it is suggested

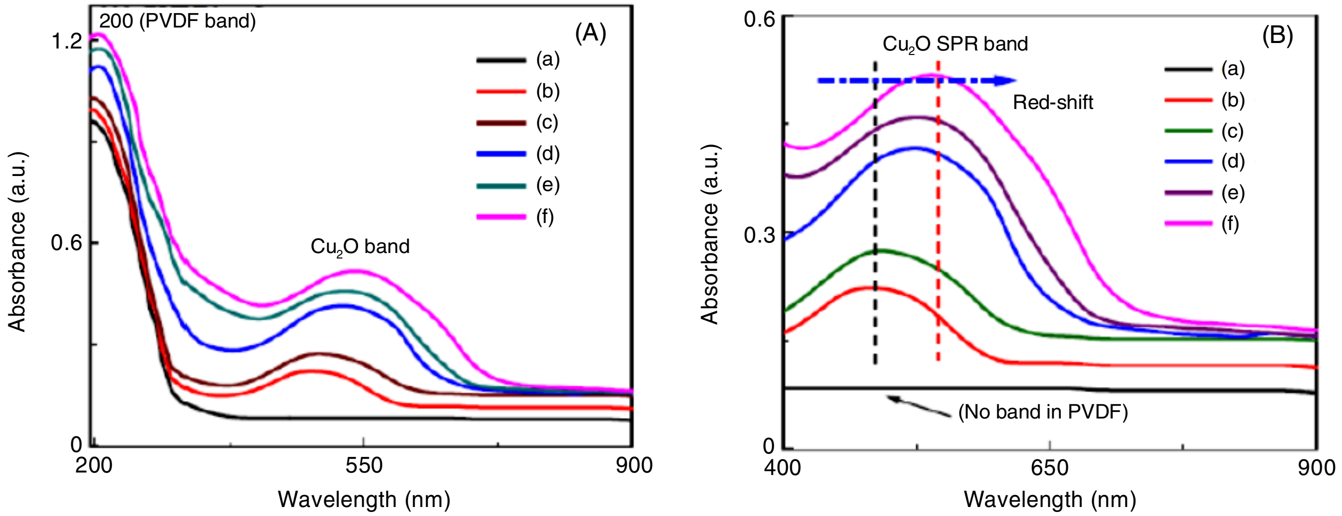

Fig. 1. (A) UV-visible spectra of PVDF-Cu$_2$O polymer nanocomposites consisting of (a) 0.0, (b) 0.1, (c) 0.2, (d) 0.3, (e) 0.5 and (f) 1.0 wt % Cu$_2$O NPs and (B) shows only SPR bands

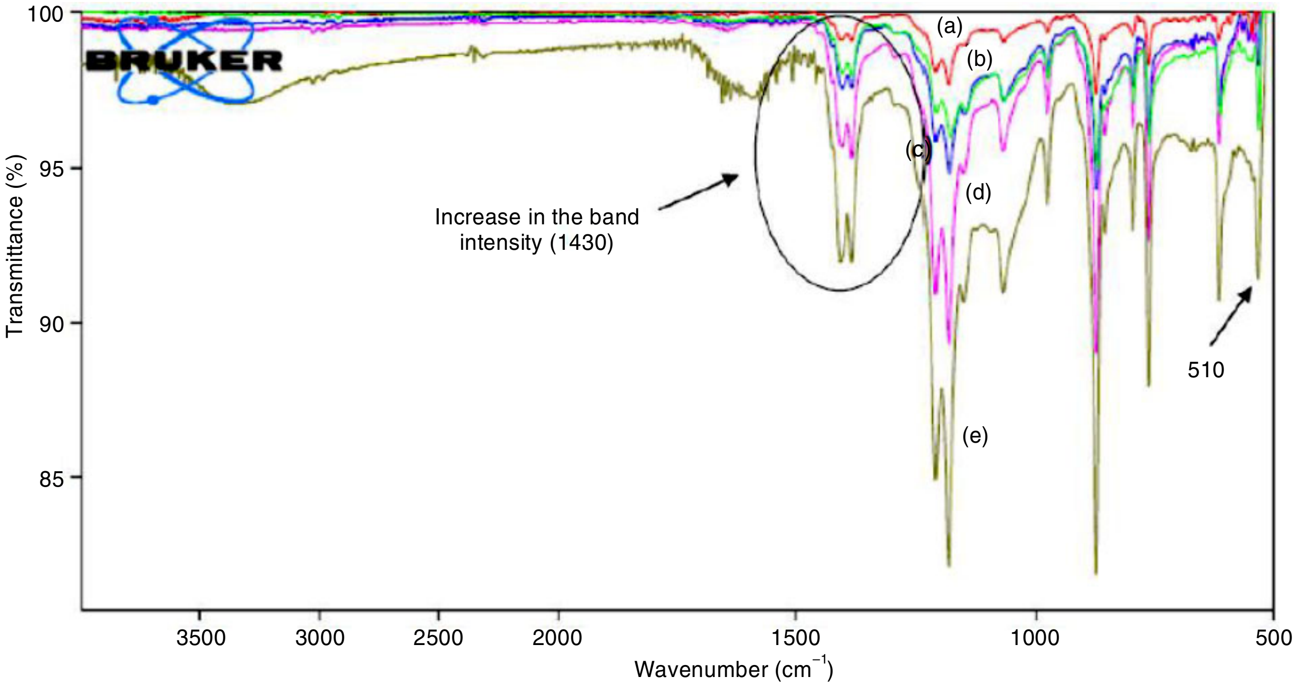

Fig. 2. FTIR spectra of PNC films consisting of (a) 0.0, (b) 0.1, (c) 0.3, (d) 0.5, (e) and 1.0 wt% Cu$_2$O NPs

that Cu$_2$O nanoparticles are present in the PNC film and embedded in PVDF polymer.

Zhao *et al*. [19] have reported Cu$_2$O stretching band near 632 cm^{-1} in PVDF-Cu$_2$O-GO PNC film. In their spectrum, a band at 736 cm^{-1} suggested that PVDF contains only α-phase. In presence of Cu$_2$O nanoparticles, bands appear at 840 and 510 cm^{-1} in PNC films. They also suggested that band at 510 cm^{-1} result from β-phase (PVDF) in the PNC film in presence of Cu$_2$O nanoparticles. The other band observed near 840 cm^{-1} was ascribed to formation of both β and γ-phase [3]. In general, β-phase of PVDF is of importance owing to its ferroelectric nature. Present results also showed that nanoparticles helped in converting electro inactive phase (α) to electroactive phase (β) of PVDF. Abdalla *et al*. [3] have reported the formation of both β and γ-phase in the PNC film in presence of bismuth vanadate nanoparticles.

XRD analysis: The XRD patterns of neat PVDF shows that PVDF is crystalline in nature in DMF and consist of only α-phase (Fig. 3). The peak at 18.5º from (202) plane suggest formation of only α-phase and no peak from nanoparticles. A sample consisting of Cu$_2$O nanoparticles, peaks from β-phase of PVDF and peak from nanoparticles were observed. The peak at 20.8º is from (200) plane of β-phase [3]. The diffraction peaks which were observed at 36.45º and 42.35º can be indexed to the (111) and (200) planes of face centered cubic (fcc) Cu$_2$O-crystal, respectively [3,6,7,16]. Presence diffraction peaks of both electroactive PVDF phase and Cu$_2$O suggested that nanoparticles are responsible for converting the α to β-phase of PVDF. Development of electroactive PVDF phase in PNC is required in enhancing the dielectric properties of PNC film.

Thermal analysis: Fig. 4 shows the variation of weight loss (%) against temperature for neat PVDF and two PNC films.

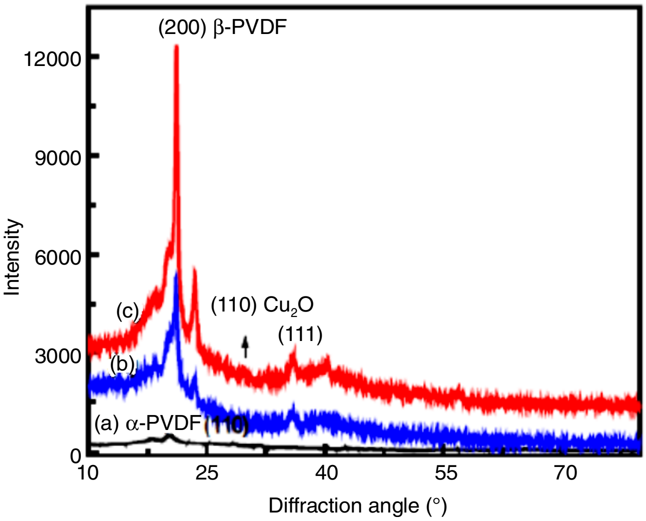

Fig. 3. XRD pattern of (a) PVDF; (b) PVDF-Cu$_2$O film with 0.1 wt % Cu$_2$O and (c) PVDF-Cu$_2$O film with 0.5 wt % Cu$_2$O nanoparticles

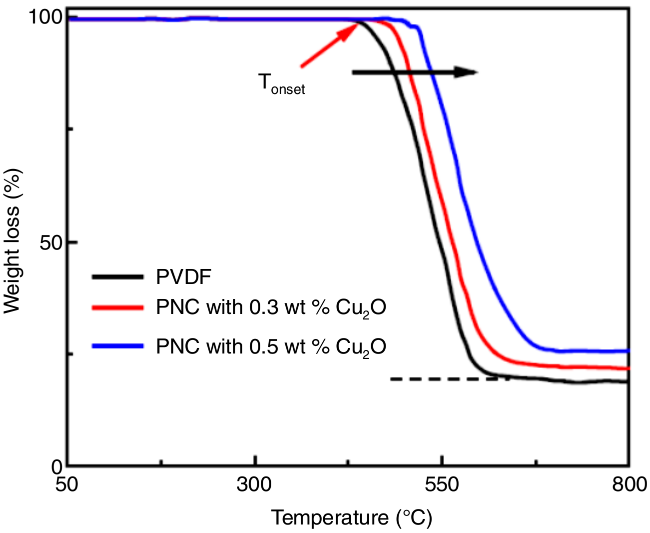

Fig. 4. Thermo-gravimetric analysis of neat PVDF and PVDF with Cu$_2$O nanoparticles

For PVDF, it is observed that PVDF starts decompose (Tonset) at 450 ºC and it continue upto 600 ºC. For PNC films, the decomposition temperature has increased. The Tonset has increased from 450 ºC in neat PVDF to 490 ºC in a PNC film containing 1 wt. % Cu$_2$O nanoparticles with 3 wt. % PVDF. It revealed that due to formation of interconnected network structure between Cu$_2$O nanoparticles and PVDF polymer (as shown in SEM images), the nanocomposite has gain strength and because of this, thermal stability has increased in PNC films. Also it is found from FTIR and XRD studies that the formation of highly polar β-PVDF phase in the PNC film helped in enhancing the packing of nanoparticles in PVDF matrix and henceforth increased the thermal stability [4].

Campos *et al*. [20] have also reported that due to incorporation of CaCO$_3$ particles into PVDF matrix, thermal stability of PNC film has increased drastically. It is found that nearly 79 % weight loss for the neat PVDF in the temperature range 440 to 550 ºC. The rate of weight loss has decreased to 75 % for PNC film containing 1 wt. % Cu$_2$O nanoparticles with 3 wt. % PVDF. Al-Hazmi *et al*. [4] have reported that nearly 80 % weight loss for neat PVDF in the temperature range 436 to 510 ºC. In presence of 5 wt. % Cu$_2$O, the rate of weight loss has decreased to 60 %. They also reported that the improvement of thermal stability in PNC films is due to the incorporation of the Cu$_2$O nanoparticles in the PVDF. The packing of polar crystalline β-phase in the nano-composites with respect to the non-polar β-phase of virgin PVDF is responsible for enhancing thermal degradation temperature. The electroactive properties of the PVDF depend on polar crystalline phase.

SEM analysis: The morphology, size distribution and its size details of Cu$_2$O nanoparticles were studied using SEM images. Fig. 5 depicts the SEM images of PNC films containing Cu$_2$O-nanoparticles (a) 0.1 and (B) 1.0 wt. % nanoparticles with PVDF. Fig. 5a showed that the particles were interconnected by PVDF polymer and relatively more pores are seen. Particles are almost spherical in shape and their average diameter lies between 100-200 nm. The size distribution is almost uniform. The diameter has increased to 250 nm in a sample containing 1.0 wt. % Cu$_2$O nanoparticles (Fig. 5b). The particles were found to be interconnected *via* polymer chain and fewer pores are observed. Formation of relatively less number of pores in this sample suggests that large numbers of nanoparticles in this sample hinder the pore formation in the PNC films.

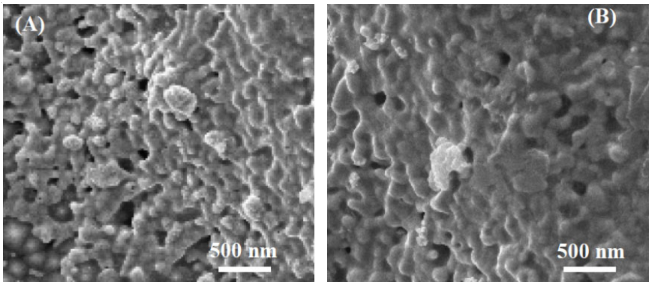

Fig. 5. SEM image of PVDF-Cu$_2$O films containing (A) 0.1 and (B) 1.0 wt % Cu$_2$O nanoparticles

Dielectric properties: Fig. 6a shows the plot of dielectric constant against frequency for undoped and Cu$_2$O doped PVDF PNCs at room temperature. It is clearly seen from the plot that a remarkable enhancement in dielectric constant of Cu$_2$O/ PVDF PNCs was achieved as compared to virgin PVDF. The neat PVDF showed dielectric constant value of 8 at frequency 100 Hz, while that of 1 wt. % Cu$_2$O doped PVDF PNC film has dielectric constant value around 175 at the same frequency. This notable enhancement is due to the formation of a network of micro-capacitors in PVDF matrix because of the incorporated Cu$_2$O nanoparticles, which resulted in Maxwelle Wagnere Sillars (MWS) polarization effect [4,17,20-22]. The MWS effect causes a trapping of free charges along the interface between the PVDF and Cu$_2$O nanoparticles [4]. Thereby, a significant enhancement of dielectric constant was achieved. It is also understood that Cu$_2$O nanoparticles modulate the phase of PVDF from non-polar α-phase to polar β-phase. The β-phase of PVDF plays a vital role in the improvement of dielectric constant in the PNCs as compared to neat PVDF. Further increase of incorporated Cu$_2$O nanoparticles into the PVDF matrix causes an aggregation of these nanoparticles and consequently leads

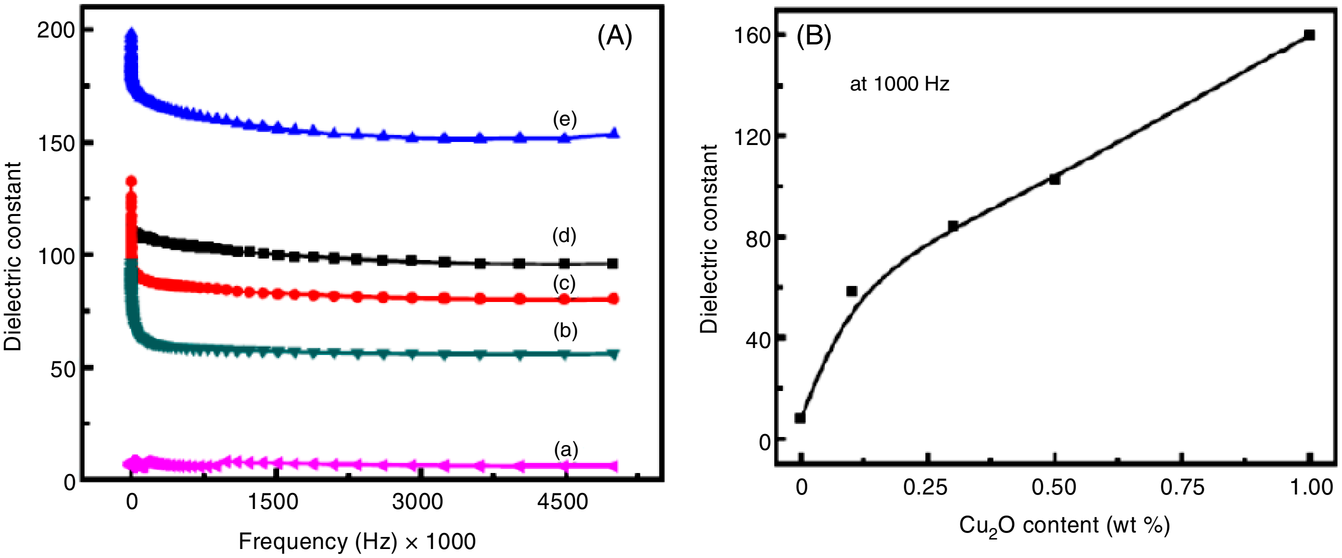

Fig. 6. (A) Variation of dielectric constant against frequency of PNC films consisting of (a) 0.0 (neat PVDF), (b) 0.1, (c) 0.3, (d) 0.5, (e) and 1.0 wt% Cu_2O nanoparticles at RT and (B) Variation of dielectric constant against nanoparticle-contents at 1000 Hz

to the increase of leakage current. Fig. 6b illustrates the variations of dielectric constant as a function of different concentrations of Cu_2O nanoparticles within the PVDF matrix at room temperature. It is noticed that dielectric constant varies non-linearly with nanoparticles content with a percolation threshold. The maximum value of dielectric constant (175 at 100 Hz) was found for the PNC with 1 wt. % Cu_2O nanoparticles.

Conclusion

Cuprous oxide (Cu_2O)/polyvinylidene difluoride (PVDF) polymer nanocomposite (PNC) films were developed and characterized using UV-visible, FTIR, XRD, thermal and dielectric plots. Present results showed that Cu_2O nanoparticles are interconnected *via* PVDF polymer which is confirmed by FTIR studies. The XRD and FTIR spectra also revealed that Cu_2O nanoparticles are responsible for phase transformation in the polymer. Inclusion of nanoparticles in the polymer results in drastic enhancement in the dielectric constant as compared to neat PVDF.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. K. Kruusamäe, A. Punning, A. Aabloo and K. Asaka, *Actuators*, **4**, 17 (2015); https://doi.org/10.3390/act4010017.
2. J. Yu, X. Huang, C. Wu and P. Jiang, *IEEE Trans. Dielectr. Elect. Insul.*, **18**, 478 (2011); https://doi.org/10.1109/TDEI.2011.5739452.
3. S. Abdalla, A. Obaid and F.M. Al-Marzouki, *Results Phys.*, **6**, 617 (2016); https://doi.org/10.1016/j.rinp.2016.09.003.
4. F.S. Al-Hazmi, D.M. de Leeuw, A.A. Al-Ghamdi and F.S. Shokr, *Curr. Appl. Phys.*, **17**, 1181 (2017); https://doi.org/10.1016/j.cap.2017.05.011.
5. W.E. Mahmoud, *J. Crystal Growth*, **312**, 3075 (2010); https://doi.org/10.1016/j.jcrysgro.2010.07.040.
6. M. Behera and G. Giri, *Mater. Sci. Poland*, **32**, 702 (2014); https://doi.org/10.2478/s13536-014-0255-4.
7. M. Behera and G. Giri, *Int. J. Ind. Chem.*, **7**, 157 (2016); https://doi.org/10.1007/s40090-016-0075-y.
8. Y. Abboud, T. Saffaj, A. Chagraoui, A. El-Bouari, K. Brouzi, O. Tanane and B. Ihssane, *Appl. Nanosci.*, **4**, 571 (2014); https://doi.org/10.1007/s13204-013-0233-x.
9. S. Sahoo, S. Husale, B. Colwill, T.M. Lu, S. Nayak and P.M. Ajayan, *ACS Nano*, **3**, 3935 (2009); https://doi.org/10.1021/nn900915m.
10. C.H. Kuo and M.H. Huang, *J. Phys. Chem. C*, **112**, 18355 (2008); https://doi.org/10.1021/jp8060027.
11. C.H. Cao and L. Xiao, *Adv. Mater. Res.*, **1015**, 623 (2014); https://doi.org/10.4028/www.scientific.net/AMR.1015.623.
12. A.R. Hajipour, F. Mohammadsaleh and M.R. Sabzalian, *J. Phys. Chem. Solids*, **83**, 96 (2015); https://doi.org/10.1016/j.jpcs.2015.03.010.
13. V. Bhavanasi, V. Kumar, K. Parida, J. Wang and P.S. Lee, *ACS Appl. Mater. Interf.*, **8**, 521 (2015); https://doi.org/10.1021/acsami.5b09502.
14. S. Kumar, V.S. Manikandan, A.K. Palai, S. Mohanty and S.K. Nayak, *Solid State Ion.*, **332**, 10 (2019); https://doi.org/10.1016/j.ssi.2019.01.006.
15. C. Zhao, J. Lv, X. Xu, G. Zhang, Y. Yang and F. Yang, *J. Colloid Interface Sci.*, **505**, 341 (2017); https://doi.org/10.1016/j.jcis.2017.05.074.
16. K. Sabira, P. Saheeda, M.C. Divyasree and S. Jayalekshmi, *Opt. Laser Technol.*, **97**, 77 (2017); https://doi.org/10.1016/j.optlastec.2017.06.008.
17. P.I. Devi and K. Ramachandran, *J. Exp. Nanosci.*, **6**, 281 (2011); https://doi.org/10.1080/17458080.2010.497947.
18. A.S. ELmezayyen, F.M. Reicha, I.M. El-Sherbiny, J. Zheng and C. Xu *Eur. Polym. J.*, **90**, 195 (2017); https://doi.org/10.1016/j.eurpolymj.2017.02.036.
19. C. Zhao, X. Xu, J. Chen and F. Yang, *J. Environ. Chem. Eng.*, **1**, 349 (2013); https://doi.org/10.1016/j.jece.2013.05.014.
20. J.S.D.C. Campos, A.A. Ribeiro and C.X. Cardoso, *Mater. Sci. Eng.: B*, **136**, 123 (2007); https://doi.org/10.1016/j.mseb.2006.09.017.
21. Y.C. Li, S.C. Tjong and R.K.Y. Li, *eXPRESS Polym. Lett.*, **5**, 526 (2011); https://doi.org/10.3144/expresspolymlett.2011.51.
22. I.H. Kim, D.H. Baik and Y.G. Jeong, *Macromol. Res.*, **20**, 920 (2012); https://doi.org/10.1007/s13233-012-0064-8.