Dielectric Properties of Polyvinyl Alcohol/ Polyacrylamide Blend Film Filled with Carbon Nanospheres

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Abstract

Carbon nanosphere / Polyvinyl alcohol/Polyacrylamide (CNS/PVA/PAM) nanocomposite films prepared via a solution casting method were studied for their structural and dielectric properties. Scanning Electron Microscopy (SEM) images of the CNS/PVA/PAM blends reveal the formation of circular islands of CNS and uniform blending with PVA/PAM matrix. XRD pattern shows a higher value with increase in blending ratio of PVA with CNS. The interaction of the dispersed and preformed CNS particles with the PVA/PAM chain was confirmed by the corresponding vibrational signaturing of PVA/PAM through FTIR. The dielectric constant increased from $[K = 134, 2K\text{ Hz}, 305\text{ Kelvin}]$ to $[K = 438, 2KHz, 333\text{ Kelvin}]$ and the composite films exhibited a high increase in the energy storage efficiency upto 75% (at 2KHz) in the case of 4%CNS /PVA/PAM 50:50 sample.

1. Introduction

The development of high dielectric (k) materials has generated enormous interest due to wide range of applications for rechargeable batteries, capacitors and other electrochemical devices [1]. Present research is focused on preparation and fabrication of nanostructured dopants such as nanoparticles, nanofibers, nanotubes, nanorods, and nanowires etc., for the improvement of dielectric, chemical and physical properties of polymer composites for various applications [2–3]. But due to low conductivity at room temperature, the use of such materials is limited and hence finding a suitable low cost material with a high dielectric constant (k) is crucial. Polystyrene, Polymethyl methacrylate, Polyvinylpyrrolidone, Polyvinyl alcohol, Polyacrylamide have been used as gate dielectric materials but the poor electrical strengths of these polymers lead to gate leakage current and poor device stability. Carbon-based materials have recently drawn more attention as fillers since these materials are known to enhance the mechanical and thermal properties of polymers [4]. Several reports in literature have focussed on using graphene oxide (GO) and graphene sheets, graphite nano-platelets and carbon nanospheres (CNS) as dopants for poly olefins, poly(acrylates), epoxy, elastomers and cellulose, chitosan, polyamide and poly(methyl methacrylate) etc[5].

Polyvinyl alcohol (PVA) is a transparent polymeric material consisting carbon chain as backbone and hydroxyl (OH) groups [6]. PVA shows good dielectric strength, fast charge transfer at electrode-composite interface in separator, supports for electrical and optical properties [7]. Polyacryl amide (PAM) is a hydrophilic polymer which is highly water-absorbent and forms a soft gel when hydrated and hence has gained a great extent of utility in wide range of industrial applications such as manufacturing of soft contact lenses, potable water treatment industry etc [8–9]. PAM hydrogel is low cost, non-toxicity, biological inertness, has good stability over mechanical and morphological properties [10–11]. Carbon nanospheres (CNS) are attractive material for nanocomposites due to control over their morphology and properties which makes it an appealing material for adsorption, catalysis, and hydrogen storage or electronics material applications.

To enhance the dielectric properties of polymer nanocomposites, methods like blending plasticization, copolymerization and addition of salts are adopted[12]. Polymer blending technique has found a wide range of commercial applications in past couple of decades due to its ease-of-synthesis, cost-effectiveness and versatility[13]. Especially in recent decades, blending of polymers with carbon nanomaterials have grabbed attention due to their electrical conductivity, low cost and chemical stability[14].

One of the most used elemental nanomaterials is nanosilver, which is used to dope polymer composites and shows ill effects on humans [15]. Similarly, TiO_2 -based blend composites focus on few practical challenges like low conductivity, uniform dispersion in aqueous suspension [16]. But Carbon nanoparticles show good mechanical, electrical conductivity, heat conductivity properties. Carbon nanomaterials have an advantage of being stable, nontoxic and environmentally friendly over other elemental nanomaterials. Different kinds of carbon nanoparticles in the form of nanotubes, nano flakes, nano rods, nano spheres have been synthesized till date and have been demonstrated to possess excellent blending properties compared to other nanomaterials. Amongst this carbon Nano spheres show potential application in optoelectronics, energy storage, sensors and encapsulating electrodes[17–19].

Numerous reports pertaining to the studies of carbon nanoparticles based blends have been published in past two decades. Ashwini Swaminathan et. al have investigated preparation and characterization of PVA/PAM/ NH_4SCN polymer film by ultrasound-assisted solution casting method for application in electric double layer capacitor[20]. Jin-Min Luo et al., studied on Hollow carbon nanospheres: syntheses and applications for post lithium-ion batteries [21]. Nitrogen doped hollow carbon nanospheres study by Hua Lin et al., showed a chemical approach toward preparing nitrogen-doped hollow carbon nanospheres [22].

In this work, we report the effect of CNS on PVA and PAM polymer nanocomposite on their structural and dielectric properties as well as the effect of temperature on them. The structural, thermal and morphological properties of CNS doped polymer nanocomposites has been studied using FT-IR and SEM techniques.

2. Experimental Methods

2.1 Materials and methods

CNS was synthesized by pyrolyzing camphor in the atmosphere at normal thermodynamic conditions [8]. A solution was prepared by taking PVA (S.D. fine-chem. Limited, Mumbai, India) and PAM (Sigma-Aldrich, USA) in 10ml of acetone separately and stirring for 24 hours. Both these solutions were then mixed and 4 weight % of CNS (Sigma-Aldrich, USA) was added to this mixture and stirred rigorously for 24 hours at 50°C . Different samples with different ratios of PVA and PAM and 4% CNS were prepared i.e., CNS: PVA: PAM; 4: 25:75, 4:50:50 and 4: 75:25 weight %. The resulting mixture was poured and dried for 48h in Petri

dishes and peeled-off from the petri dishes. The thicknesses of the prepared films found in the range of 150–250 μm .

2.2 Characterization

The surface morphology of the nanocomposites were studied using Scanning electron microscope (SEM) (JEOL 6390LA, USA). The XRD scan was executed in 2θ angle mode ranging from 5° – 50° with scanning speed of $1^\circ/\text{min}$ and step size of 0.01° using Bruker D8 Advance X-ray diffractometer with Ni-filtered of wavelength $1.5406 \text{ \AA}$. FTIR spectra were obtained using a Perkin Elmer spectrometer in KBr medium at room temperature in the absorption mode with a resolution of 4 cm^{-1} . The dielectric properties were obtained from HIOKI-IM3570 high precession impedance analyser with the frequency ranging from 4 Hz to 5 MHz and temperature range in between 303–343 K.

3. Results And Discussion

Figure 2 shows the FTIR spectra of pure CNS and composites (PVA/PAM/CNS) blend with different wt %. Pure PVA shows a band at 3447 cm^{-1} which corresponds to O–H stretching vibration of hydroxyl groups and transmittances observed at 2929 cm^{-1} is assigned to C–H asymmetric stretching, 2863 cm^{-1} observed band is assigned to C–H symmetric stretching, 1754 cm^{-1} is assigned to C = O stretching and band at 1089 cm^{-1} is assigned to C–O stretching group present on the PVA back bone and for composites. Bands appearing at 3302 cm^{-1} and 3105 cm^{-1} are stretching vibrations of $-\text{CONH}_2$ group which are involved in both inter and intra molecular interaction of hydrogen bonds in PAM coupled with –OH group of PVA at 3145 cm^{-1} and 3305 cm^{-1} . When PVA is added into PAM polymer matrix, 3000 cm^{-1} to 3600 cm^{-1} assigned to –OH stretching region and 1565 cm^{-1} assigned to bending vibration of hydroxyl group at 2925 cm^{-1} and 2759 cm^{-1} appear which are due to asymmetric and symmetric stretching vibrations of methylene group ($-\text{CH}_2$). The band appearing around 936 cm^{-1} corresponds to C–O stretching of acetyl group. Peaks 1433 cm^{-1} , 1360 cm^{-1} , 1254 cm^{-1} , 1119 cm^{-1} and 1042 cm^{-1} correspond to O–H and C–H bending, $-\text{CH}_2$ out of plane bending, $-\text{CH}_2$ bending, C–O–C asymmetric and symmetric stretching, respectively. Once CNS is added to form the PVA/PAM/CNS blend, two additional bands at 1350 cm^{-1} and 1580 cm^{-1} appear which correspond to D and G bands of CNS, respectively.

XRD pattern of PVA (Fig. 3) shows a peak at $2\theta = 18.82^\circ$ which corresponds to (10 – 1) plane with an additional peak at 25.8° corresponding to (101) plane. In PVA/PAM/CNS composite material the PVA peak shifts towards smaller 2θ value from 18.82° to 18.68° as the ratio of PVA to PAM content increases from 25–75% in the composite material indicating a tensile strain on the material. Increase in the crystallinity and intense peak is observed with increase in PVA content is seen. Two additional peaks appear at 30.07° corresponding to (111) plane and 41.09° corresponding to (202) plane are related to PVA.

The SEM images of polymer nanocomposites of PVA/PAM with CNS shows smooth surface with no holes detected, reflecting miscibility and homogeneous blend. Figure.4 (a) corresponds to pure CNS which

consists of uniformly agglomerated carbon nanospheres with spherically shaped particle with sizes ranging between 120 nm to 160 nm. Figure 4(b) and 4(c) show smooth and homogeneous surface of pure PVA and PAM polymer, respectively. Figure 4(d) shows the morphology of PVA/ PAM blend containing homogeneous surface with strap like structures. Figure 4(e) shows PVA/PAM-CNS blend composite confirming uniform distribution of CNS in the PVA/PAM matrix.

Figure 5 shows the study of dielectric constant as well as dielectric loss of PVA/PAM/CNS nanocomposites at room temperature and at different temperature. At lower frequencies high values are exhibited which indicates that the four polarizations are active whereas at higher frequencies, high periodic field reversal results in the inertia of the dipolar moments thereby reducing the values. At higher frequencies, the polarization cannot follow the changing electric field which causes a drop in the dielectric constant. For pure PVA and 4% CNS/PVA: PAM; 50:50 composite increase in the dielectric constant is observed. With increase in temperature, the intermolecular forces between the polymer chains are broken due to the orientation polarization with the periodic electric field thus higher relative permittivity. The orientation polarization has relaxation time of 10^{-11} sec. Therefore, if dipole orientation cannot keep up with the alternating field as the frequency increases, it would lead to decrease in the dielectric constant leading to dielectric dispersion.

At low frequency region, high dielectric constant is observed due to freely moving dipoles present in the polymer nanocomposites. Similarly, dielectric loss increases with the increase of PVA content which is due to the increase in polar group and this increase in dielectric constant and dielectric loss with PVA up to 75 wt% is attributed to the motion of free charge carriers of polymer composites and follows Maxwell–Wagner–Sillars (MWS) processes.

Figure 7 explains the frequency dependent dielectric loss of Pure PVA and PVA/PAM/CNS at room temperature, 323K, 333K and 343K respectively. These curves possess a similar trace as the plot of dielectric constant and change in steps are observed at the same frequency region. The phenomenon can be identified as interfacial polarization where the high values are presented at low frequency region. As the temperature increases the dielectric loss decreases this due to Maxwell-Warner –Sillar effect. At lower frequencies, dielectric loss is large because dipoles move freely within the polymer composites.

The dielectric studies show that dielectric constant decreases with high frequency at 323K, 333K and 343K temperatures. With increase in the frequency decrease in dielectric constant is observed which is due to incorporation of CNS causing the increase in the interfacial polarization. Above the threshold of 1 MHz frequency, the dielectric constant almost remains constant and with rise in temperature dielectric loss of polymer composites increases and also increase in temperature the relaxation peak was shifted towards higher frequency side. As the temperature is increased, the polar group will be freer to orient allowing it to keep up with the changing electric field in dielectric loss.

5. Conclusion

Polymer blends of PVA, PAM and CNS have been studied for their structural and dielectric properties. FTIR studies reveal the increase in the bond strength between PVA and PAM and blending with CNS. XRD pattern shows the presence of tensile strain on the matrix and an increase in the crystallinity with the increasing PVA percentage in the composition of the blend. The dielectric constant for PVA/PAM/CNS increased 3.25 times than that of pure PVA at 60°C.

Declarations

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References

1. Leif E.Asp,Emile S.Greenhalgh,Multifunctionality of Polymer Composites, **619–661**(2015).
2. X. Dan Yang, Y. Kong, Y. Ni, S. Xu, G. Huang, Shang, HaoXueWenliGuo, and L. Zhang, ACS Omega, 3, 14087 – 14096 (2018)
3. ChweeTeckLim panelKenry, Prog. Polym. Sci. **70**, 1–17 (2017)
4. ShujianCheng XiaoxiaoGuo, **WeiweiCai, YufengZhang, Xue-aoZhang**, Materials & Design,209, (2021)
5. M. Zahid, S. Ali, S. Saleem, M. Salman, Majid Khan **137**, 41 (2020)
6. M.A. Muhammad Aslam, Z.A. Kalyar, Raza, Polymer Engineering And Science **58, 12**, 2119–2132 (2018), ,)
7. N.K. RakhiNangia, A.S. Shukla, Preparation, Materials Science and Engineering **225**, 012044 (2017)

8. OguzOkay SeldaDurmaz, Polym. Bull. **46**(5), 409–418 (2001)
9. S.JaismNadher Layth, Daman RadhyAlkarawiHayder Jamel, Eurasian Journal of Analytical Chemistry,13(1b), (2018)
10. A.H. Shahid Bashir, M.A. Rajpar, N.A. Mujtaba, S. Alghamdi, K. Wageh, Ramesh, and S. Ramesh, *Polymers* **12**(11), 2702 (2020)
11. N. Hadrup, H.R. Lam. RegulToxicolPharmacol, 68:1–7 (2014)
12. R.F. Jagadish Naik, Bhajantri, 28, 906–919 (2018)
13. R. Song, M. Murphy, C. Li, Kang Ting,Chia Soo, and Zhong Zheng. Drug Des DevelTher **12**, 3117–3145 (2018)
14. W. Chen, Hu Weimin, D. Li, S. Chen, Z. Dai, Journal Science and Engineering of Composite Materials **25**(6), 1059–1073 (2018)
15. Q.-L. Yan et al., Nanoscale **8.9**, 4799–4851 (2016)
16. G.Z.L. Haoran Dong, C. Tang, F.C. Zhang, X. He, Y. He, Water Res. **79**(1), 128–146 (2015)
17. SerdarYildirim HazalGergeroglu, M. FarukEbeogluligil, SN Applied Sciences **2**, 603 (2020)
18. G. Zheng, S.W. Lee, Z. Liang, H.-W. Lee, K.Y.H. Yao, H. Wang, W. Li, Steven Chu & Yi Cui **9**, 618–623, (2014)
19. O. Neumann et al., ACS Nano Letters **7**, 42–49 (2013)
20. R. AshwiniSwaminathan, M. Ravi, G. Sasikumar, MahadevaiahDasaiah, Hirankumar, SakunthalaAyyasamy, Ionics, 26:4113–4128 (2020)
21. J.-M. Luo, Y.-G. Sun, Si-JieGuo Yan-Song Xu Bao-Bao Chang Chun-Tai Liu, An-Min Cao and Li-Jun Wan. Materials Chemistry Frontiers **4**, 2283 (2020)
22. H. Lin, W. Ye, Y. Liu, M. Liu, C. Song, HaoZhang,Rongwen Lu and ShufenZhang,Journals of MaterialsChemistry A, **8**, 1221–1228 (2020)

Figures

Figure 1

Synthesis of composite

Figure 2

FT-IR spectra of pure PVA and CNS doped PVA – PAM composites

Figure 3

XRD pattern of Pure PVA and CNS doped PVA/PAM Composite samples.

Figure 4

SEM images of a) CNS , b) pure PVA, c) pure PAM , d) blend of PVA with PAM and e) Blend of PVA/PAM with CNS

Figure 5

Variation of dielectric constant for different concentration of PVA/PAM/CNS at room temperature

Figure 6

Dielectric constant of blend PVA/PAM/CNS at different temperature.

Figure 7

dielectric loss of blend PVA/PAM/CNS at different temperature