4. GRAPHENE OXIDE AND ZINC OXIDE REINFORCED HYDROXYPROPYL METHYLCCELLULOSE AND POLYVINYLALCOHOL BLEND NANOCOMPOSITES

4.1 INTRODUCTION

Transition metal oxide reinforced PNCs have attracted much attention due to their encouraging properties and numerous potential applications in various fields of research. The electrical properties of such nanocomposites depend on the volume fraction, the size of nanoparticles, preparation method and also polymer/filler interface [248]. Zinc oxide (ZnO) has attracted enormous scientific attention because of its multifunctional properties and tremendous application potential. ZnO is one of the most promising materials for electronics and optoelectronic devices such as transparent conductors, LEDs, organic photovoltaic cells, piezo and pyroelectric materials, thin film transistors and humidity and toxic gas sensors [249 - 252]. It is a potential semiconductor with a wide bandgap of ~3.37 eV. It can be synthesized into various nanostructures such as nanowires, nanotubes and nanoparticles of different shape and size. ZnO has several favourable properties which include good transparency, high electron mobility, good physical and chemical stability, photo-catalytic activity and strong photoluminescence at room temperature. It has also been used as a promising material for supercapacitor applications due to its low cost, abundant availability, eco-friendliness and electrochemical activity [253]. The combination of transition metal oxides such as ZnO with graphene-based materials such as GO to fabricate PNCs holds great promise as an effective way to enhance the capacitance value. The successful intercalation of these metal oxides into graphene sheets may prevent the agglomeration and stacking which can lead to the formation of high-performance novel composite materials [254]. In addition, the investigations based on ZnO/GO based PNCs are very limited. Hence, ZnO and GO are used as fillers in the present study.
Hydroxypropyl Methylcellulose (HPMC) belongs to the group of cellulose ethers. It is a water soluble, biocompatible and biodegradable polymer having a wide range of applications. HPMC is also soluble in polar organic solvents, making it possible to use both aqueous and non-aqueous solvents. HPMC has unique solubility properties with solubility in hot and cold organic solvents. HPMC forms flexible and transparent films from aqueous solution and forms a gel upon heating at temperatures in the range 75-90°C. HPMC is most commonly used in the food industry as a stabilizing agent, as a protective colloid, as a thickener and as an emulsifier. Polyvinyl alcohol (PVA) is another water-soluble polymer which has been studied extensively due to its excellent chemical stability, biodegradability, biocompatibility and eco-friendliness. Both HPMC and PVA are semi-crystalline polymers having an excellent film forming ability. In addition, both polymers are compatible with each other and forms miscible blends when blended together. Knowing this fact, we have chosen HPMC and PVA as the polymer matrix in the present study to get combined effect of both polymers on the final properties of nanocomposites. In addition, GO filled composites with biodegradable and biocompatible polymers and nano-fillers can combine the ductile properties of a polymer matrix and high strength of nano-fillers. This is mainly due to the presence of various oxygen-containing functional groups present in the structure of GO, which improves interfacial interaction between GO and the polar polymer matrix [255].

Hence, the main objective of the present study is to prepare new polymer/inorganic nanocomposites based on unique combination of two fillers such as GO and ZnO and also to widen the application window of GO/ZnO filled HPMC/PVA blend nanocomposites for energy storage applications. The dispersion of fillers into polymer matrix was examined using different analytical techniques. The detailed investigations of HPMC/PVA/GO/ZnO nanocomposites were carried out by studying their
structural, thermal, morphological, mechanical, optical and dielectric properties.

4.2 EXPERIMENTAL PROCEDURE

4.2.1 Synthesis of Graphene Oxide

GO was synthesized from natural graphite powder using modified Hummers method [169]. In a typical synthesis process, 3 g of graphite powder was added with 150 ml of concentrated H$_2$SO$_4$, to which 3 g of NaNO$_3$ was subsequently added and mixed well in a 1000 ml round bottom flask. The mixture was kept in an ice bath for 4 hours with stirring at temperature 5°C and 9 g of KMnO$_4$ was gradually added with constant stirring. To prevent the sudden increase in temperature and the explosion, the rate of addition of KMnO$_4$ was controlled carefully. The ice bath was then removed and the mixture temperature was maintained at 40°C. After stirring for 2 hours until it became a brown paste, 100 ml of distilled water was added for dilution followed by stirring at 98°C for about 1 hour until the color changed from brown to yellow. Subsequently, the mixture was diluted by adding 500 ml of deionized water. This was followed by addition of 30 ml of H$_2$O$_2$ (30 wt %) to the mixture to reduce residual KMnO$_4$. This solution was filtered, centrifuged and washed several times with distilled water to remove acidity. Finally, the product was vacuum dried at 60°C for 12 hours to obtain GO powder with the particle size of about 1-5 µm.

4.2.2 Preparation of HPMC/PVA/GO/ZnO Nanocomposite Films

HPMC/PVA/GO/ZnO nanocomposite films with different loadings of GO/ZnO hybrid fillers were prepared by colloidal processing technique. The loadings of ZnO nanoparticles was varied from 0 to 25 wt % and that of GO from 0.5 to 2.5 wt % as shown in Table 4.1.
Table 4.1: Feed compositions of HPMC/PVA/GO/ZnO nanocomposites

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>HPMC (wt %)</th>
<th>PVA (wt %)</th>
<th>GO (wt %)</th>
<th>ZnO (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50</td>
<td>50</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>44.5</td>
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<td>0.5</td>
<td>5</td>
</tr>
<tr>
<td>3</td>
<td>39</td>
<td>50</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>4</td>
<td>33.5</td>
<td>50</td>
<td>1.5</td>
<td>15</td>
</tr>
<tr>
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</tr>
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<td>6</td>
<td>22.5</td>
<td>50</td>
<td>2.5</td>
<td>25</td>
</tr>
</tbody>
</table>

The protocol for the synthesis of HPMC/PVA/GO/ZnO nanocomposite is given in Figure 4.1. First, PVA powder was completely dissolved in distilled water at 75°C for 3 hrs and kept aside until it is cooled down. On the other hand, HPMC powder was also dissolved separately in distilled water. Both PVA and HPMC solutions were mixed together and stirred for 4 hrs. The required quantity of ZnO nanoparticles and GO powder was dispersed separately in distilled water using an ultrasonication technique and subsequently added to the HPMC/PVA blend solution. The resulting HPMC/PVA/GO/ZnO dispersion was stirred overnight and further dried in a hot air oven at 60°C for 8 hrs by pouring on an optically flat glass petri dish. The dried HPMC/PVA/GO/ZnO nanocomposite films were peeled off from the glass petri dish and used for further study. The photographs of as prepared nanocomposite films are shown in Figure 4.2 (a-f).
Figure 4.1: Synthesis protocol of HPMC/PVA/GO/ZnO nanocomposites.
Figure 4.2: Photographs of HPMC/PVA/GO/ZnO nanocomposite films
(a) HPMC/PVA blend (b) 0.5 wt %GO+5 wt % ZnO
(c) 1.5 wt %GO+15 wt % ZnO (d) 2.5 wt %GO+25 wt % ZnO
(e, f) nanocomposite films are bent to demonstrate their flexibility.
4.3 RESULTS AND DISCUSSION

4.3.1 FTIR Analysis

FTIR spectroscopy is a very useful and convenient technique to study the interaction between two or more components of nanocomposites. In this study, FTIR analysis of HPMC/PVA/GO/ZnO nanocomposite films was carried out to analyze the functional groups, the nature of bonding and to understand the structural changes in the nanocomposites due to the incorporation of GO/ZnO hybrid fillers. Figure 4.3 (a-d) shows the FTIR spectra of PVA, HPMC, GO and ZnO powder.

![FTIR spectra of (a) PVA (b) HPMC (c) GO (d) ZnO.](image)

Figure 4.3 (a) represents the FTIR spectrum of neat PVA, which shows the peaks at 916 cm⁻¹ and 850 cm⁻¹, confirming the presence of skeletal vibrations of PVA [256]. The neat PVA film showed characteristic
broadband at 3340 cm\(^{-1}\) and 1088 cm\(^{-1}\) which are attributed to O-H stretching and C-O stretching vibrations respectively. The band at 2928 cm\(^{-1}\) corresponds to C-H asymmetric stretching vibration of the alkyl group and the band at 1733 cm\(^{-1}\) can be attributed to the C=O stretching vibration of the carbonyl group. The bands for unsaturated carbonyl groups and conjugated double bonds of PVA were observed at 1735 cm\(^{-1}\) and 1600 cm\(^{-1}\) respectively and the band at 1640 cm\(^{-1}\) is attributed to an acetyl C=O group of PVA. The corresponding bending and wagging vibrations of -CH\(_2\) groups were observed at 1438 and 1378 cm\(^{-1}\) respectively. In addition, the band at 1247 cm\(^{-1}\) can be assigned to C-H wagging vibrations [257]. Figure 4.3 (b) shows the FTIR spectrum of HPMC. The band at 3456 cm\(^{-1}\) is attributed to OH stretching vibrations. The band at 2908 cm\(^{-1}\) is due to symmetric stretching vibrations of methyl and hydroxypropyl group. The band at 2328 cm\(^{-1}\) is attributed to O-H stretching vibrations or intramolecular hydrogen bonding. The band at 1740 cm\(^{-1}\) is due to stretching vibrations of C=O groups present in HPMC. The bands at 1450 cm\(^{-1}\) and 1379 cm\(^{-1}\) are attributed to –CH\(_2\) scissoring and O-H bending vibrations respectively [258]. The broadband at 1049 cm\(^{-1}\) is attributed to C-C and C-O vibrations of cellulose.

The FTIR spectrum shown in Figure 4.3 (c) depicts characteristic peaks of GO. The band at 3441 cm\(^{-1}\) corresponds to the O-H stretching vibration and the band at 2920 cm\(^{-1}\) is assigned to C-H stretching. The band at 1635 cm\(^{-1}\) is attributed to C=C bond of an unoxidized sp\(^2\) group. The band at 1396 cm\(^{-1}\) can be attributed to C-O stretching vibrations of a carboxylic group and the band at 1116 cm\(^{-1}\) corresponds to C-O stretching vibrations of an alkoxy group of GO [259]. Thus, the FTIR spectrum of GO gives evidence of different functional groups (carbonyl, hydroxyl and epoxy) present in its structure. Figure 4.3 (d) shows FTIR spectrum of commercial ZnO nanoparticles. The FTIR spectrum of ZnO shows a characteristic peak at 430 cm\(^{-1}\) which is attributed to Zn-O-Zn stretching vibrations [260]. The FTIR
peaks at 1374 cm\(^{-1}\) and 2331 cm\(^{-1}\) were also observed in the spectrum of ZnO which are attributed to the stretching vibrations of C=C and C-H groups. Other small peaks at 1220 cm\(^{-1}\), 1546 cm\(^{-1}\) and 1735 cm\(^{-1}\) are attributed to the adsorbed carbonate moieties [261]. Figure 4.4 (a-f) shows FTIR spectra of HPMC/PVA (50/50) blend and HPMC/PVA/GO/ZnO nanocomposite films. Figure 4.4 (a) depicts FTIR spectrum of HPMC/PVA (50/50) blend film which shows all the characteristics peaks of both HPMC and PVA, indicating the miscibility and compatibility between both polymers. Similarly, FTIR spectra of nanocomposite films are depicted in Figure 4.4 (b-f) which shows characteristics peaks of all the components, indicating that the nanocomposites are successfully prepared.

![Figure 4.4: FTIR spectra of HPMC/PVA/GO/ZnO nanocomposites](image)

(a) HPMC/PVA blend (50/50) (b) 0.5 wt %GO+5 wt % ZnO (c) 1 wt %GO+10 wt % ZnO (d) 1.5 wt %GO+15 wt % ZnO (e) 2 wt %GO+20 wt % ZnO (f) 2.5 wt %GO+25 wt % ZnO.
4.3.2 Raman Analysis

Raman spectroscopy is a powerful technique to characterize the graphene or graphene-based materials as it can discriminate between graphite and graphene. Raman spectroscopy is strongly sensitive to the electronic structure of materials and it is very useful in determining the number of graphene layers [262]. The main features in the Raman spectroscopy of carbon-based materials such as graphene and GO are the presence of G and 2D band. G band is common in all forms of carbon materials and provides information about the in-plane vibrations of sp² bonded carbon atoms. D band results from a single phonon lattice vibrations and gives information about the presence of sp³ bonded carbon atoms [263]. The Raman spectra of graphite and GO powders are depicted in Figure 4.5.

![Raman Spectra of Graphite and GO powder.](image)

**Figure 4.5: Raman Spectra of Graphite and GO powder.**
The pristine graphite shows an intense G band at 1585 cm\(^{-1}\) which correspond to the first order scattering of the \(E_{2g}\) mode (\(E_{2g}\) phonons of sp\(^2\) bonded carbon atoms), the 2D band at 2674 cm\(^{-1}\), and a weak D band at 1326 cm\(^{-1}\) corresponding to structural defects and disorders inherent in the graphite (\(A_{1g}\) phonons of sp\(^3\) bonded carbon atoms) [264, 265]. The Raman spectrum of GO shows an intense D band at 1365 cm\(^{-1}\) and the G band at 1629 cm\(^{-1}\) with D/G intensity of 0.83. After chemical oxidation, the G band of GO (1629 cm\(^{-1}\)) is up shifted compared with that of pristine graphite (1585 cm\(^{-1}\)) which could be due to the presence of isolated double bonds that resonate at frequencies higher than that of G band of graphite [266]. Thus, harsh chemical oxidation has resulted in significant structural changes in the graphite lattice leading to the formation of various oxygen-containing functional groups at the basal plane and at the edges. The Raman spectra of HPMC/PVA/GO/ZnO nanocomposite films are depicted in Figure 4.6 (a-d). For nanocomposites with 0.5 wt % GO loadings, a weak D band was observed at 1360 cm\(^{-1}\) and the G band at 1627 cm\(^{-1}\). For nanocomposites with 1 wt % GO loadings, the D band was observed at 1345 cm\(^{-1}\) with an increased intensity and the G band was observed at 1598 cm\(^{-1}\). For nanocomposites with 1.5 wt % GO, the D band was observed at 1340 cm\(^{-1}\) and the G band was observed at 1592 cm\(^{-1}\). For 2.5 wt % GO loadings, the D and G band was observed at 1345 cm\(^{-1}\) and at 1601 cm\(^{-1}\) respectively. Thus, the existence of GO in the HPMC/PVA/GO/ZnO nanocomposites was confirmed by Raman spectroscopy.
4.3.3 X-ray Diffraction Analysis

XRD analysis is an effective method for determining the state of exfoliation of nano-fillers in the polymer matrix. Figure 4.7 (a-e) shows XRD patterns of PVA, HPMC, HPMC/PVA blend, graphite and GO powder. The XRD pattern of pristine PVA is given in Figure 4.7 (a) which shows a sharp diffraction peak at $\theta = 19.44^\circ$ attributing to (101) reflections. This indicates the semi-crystalline nature of PVA which is attributed to the presence of strong inter and intramolecular hydrogen bonding between different monomer units of PVA [267].
Figure 4.7: XRD spectra of (a) PVA (b) HPMC (c) HPMC/PVA blend (50/50) (d) Graphite (e) GO.

The XRD pattern of neat HPMC given in Figure 4.7 (b) shows a single broad peak at $2\theta = 20.03^\circ$ indicating that HPMC is an amorphous polymer [268] and the XRD pattern of HPMC/PVA blend given in Figure 4.7 (c) shows a broad peak at $2\theta = 19.93^\circ$. The XRD pattern of graphite powder is depicted in Figure 4.7 (d). Pristine graphite shows a sharp characteristic diffraction peak at $2\theta = 26.42^\circ$ with the d-spacing of 0.33 nm, corresponding to the hexagonal lattice of (002) plane [130]. The XRD pattern of graphite also shows two other small peaks at $2\theta = 44.12^\circ$ and $2\theta = 54.35^\circ$ attributed to the hexagonal lattice of (100) and (004) respectively. The XRD pattern of GO shows a single characteristic diffraction peak at $2\theta = 11.55^\circ$ with the d-spacing of 0.82 nm [269]. The increase in the d-spacing value is attributed to the intercalation of water molecules on the graphite layer leading to the formation of oxygen-containing functional groups [112]. This indicates that the
oxidation process has disrupted the highly ordered crystalline structure of natural graphite. Figure 4.8 (a-f) shows the XRD pattern of ZnO nanoparticles and HPMC/PVA/GO/ZnO nanocomposites.

Figure 4.8: XRD spectra of HPMC/PVA/GO/ZnO nanocomposites
(a) ZnO nanoparticles (b) 0.5 wt % GO + 5 wt % ZnO
(c) 1 wt % GO + 10 wt % ZnO (d) 1.5 wt % GO + 15 wt % ZnO
(e) 2 wt % GO + 20 wt % ZnO (f) 2.5 wt % GO + 25 wt % ZnO.

Figure 4.8 (a) shows XRD pattern of ZnO nanoparticles having several obvious diffraction peaks at 2θ = 31.7°, 34.3°, 36.3°, 47.4°, 56.5°, 62.8° and 67.9° which corresponds to (110), (002), (101), (102), (110), (103) and (112) lattice planes of ZnO (JCPDS80-0074). All the XRD peaks of ZnO were observed in the diffraction patterns of HPMC/PVA/GO/ZnO nanocomposites, but the characteristic diffraction peaks of GO disappears. This indicates that GO was completely exfoliated into single graphene sheet and homogeneously mixed in the polymer matrix resulting in the formation of exfoliated nanocomposites.
4.3.4 Thermogravimetric Analysis

The thermal stability of PNCs is an important property because these nanocomposites materials are often used as high-performance engineering plastics. Figure 4.9 (a-f) shows TGA thermograms of HPMC/PVA blend film and HPMC/PVA/GO/ZnO nanocomposites. It can be noted that HPMC/PVA blend film shows decomposition in three stages. The first decomposition stage for HPMC/PVA blend was started at the temperatures slightly below 100°C and went up to 150°C which is due to the presence of moisture in the sample. The second degradation stage observed in the temperature range 150°C-360°C can be attributed to the decomposition of polymer chains. The third stage was observed in the temperature range 360°C-500°C which is attributed to the decomposition of residual carbon. The HPMC/PVA/GO/ZnO nanocomposites also show three-stage decomposition and the degradation stages were shifted slightly towards higher temperature. The first stage of decomposition for nanocomposites was started at the temperature slightly below 100°C and went up to 250°C, which could be attributed to the pyrolysis or decomposition of labile oxygen-containing functional groups [270]. The second decomposition stage in the temperature range 250°C-360°C could be due to the splitting of polymer chains. The third decomposition stage is in the temperature range 360°C-500°C which could be due to decomposition of the polymer chain, resulting in a carbonaceous residue. In this temperature range, the HPMC/PVA/GO/ZnO nanocomposites showed less weight loss as compared to HPMC/PVA blend which could be due to the good dispersion of GO/ZnO hybrid fillers into HPMC/PVA matrix and the strong interaction between them. This indicates that the thermal stability of nanocomposites has improved as compared to HPMC/PVA blends.
Figure 4.9: TGA analysis of HPMC/PVA/GO/ZnO nanocomposites
(a) HPMC/PVA blend (50/50) (b) 0.5 wt % GO+5 wt % ZnO
(c) 1 wt % GO+10 wt % ZnO (d) 1.5 wt % GO+15 wt % ZnO
(e) 2 wt % GO+20 wt % ZnO (f) 2.5 wt % GO+25 wt % ZnO.

4.3.5 Morphological Studies

The quality of dispersion is most commonly characterized quantitatively using optical and electron microscopy techniques. To obtain an insight on the morphology and the microstructure of HPMC/PVA/GO/ZnO nanocomposites, POM was used in the present study. POM images of HPMC/PVA blend and HPMC/PVA/GO/ZnO nanocomposites are depicted in Figure 4.10 (a-f). From POM images, it can be observed that the surface of the nanocomposite film is smooth since the GO and ZnO were uniformly distributed within the polymer matrix. There is a good adhesion between the polymers and the fillers. However, some low degree of agglomeration was
observed when ZnO loading was increased as shown in Figure 4.10 (d-f). The degree of dispersion of GO and ZnO was further analyzed by SEM observations. Figure 4.11 (a-f) illustrates the SEM images of ZnO nanoparticles and HPMC/PVA/GO/ZnO nanocomposites. The SEM micrograph shown in Figure 4.11 (a) indicates that the ZnO nanoparticles have a relatively uniform particle size with the existence of some agglomerates. These agglomerates of nanoparticles are due to the high surface interaction between nanoparticles having high specific surface area and high surface energy. The SEM micrographs of HPMC/PVA/GO/ZnO nanocomposites with 0.5 wt % GO loading is given in Figure 4.11 (b) which shows scattered waves like morphology indicating that the ZnO nanoparticles are intercalated between GO sheets forming the novel microstructure. For higher GO loading as shown in Figure 4.11 (c-f), the surface of nanocomposites exhibits river-like structures indicating that GO was highly dispersed in the polymer matrix. Thus, the river-like structures developed by GO interconnected with ZnO nanoparticles may improve the capacitance value, leading to an enhanced dielectric property. Hence, SEM results demonstrate that the mixing method used in this work was effective to exfoliate and disperse GO into polymer matrix with no stacking.
Figure 4.10: POM images of HPMC/PVA/GO/ZnO nanocomposites
(a) HPMC/PVA blend (50/50) (b) 0.5 wt %GO+5 wt % ZnO
(c) 1 wt %GO+10 wt % ZnO (d) 1.5 wt %GO+15 wt % ZnO
(e) 2 wt %GO+20 wt % ZnO (f) 2.5 wt %GO+25 wt % ZnO.
Figure 4.11: SEM images of HPMC/PVA/GO/ZnO nanocomposites
(a) ZnO nanoparticles (b) 0.5 wt %GO+5 wt % ZnO
(c) 1 wt %GO+10 wt % ZnO (d) 1.5 wt %GO+15 wt % ZnO
(e) 2 wt %GO+20 wt % ZnO (f) 2.5 wt %GO+25 wt % ZnO.
4.3.6 Dielectric Properties

Figure 4.12 (a-f) shows the dielectric constant of HPMC/PVA blend and HPMC/PVA/GO/ZnO nanocomposites as a function of frequency in the range 50 Hz to 20 MHz and temperature in the range 40-150°C. It can be seen that the dielectric constant is high at a lower frequency as compared to that at a higher frequency and the effect is more pronounced at higher loading of GO/ZnO hybrid filler. Such frequency dependent behavior of dielectric constant is due to interfacial polarization, which can be identified by low-frequency dielectric measurements based on MWS method [270-272]. The maximum dielectric constant (4.11) for HPMC/PVA blend film was observed at 50 Hz and at 150°C as shown in Figure 4.12 (a). The dielectric constant of HPMC/PVA/GO/ZnO nanocomposites has increased with increase in the filler loadings. For 0.5 wt % GO and 5 wt % ZnO loading, the highest value of dielectric constant (36.26) was observed at 50 Hz and at 150°C as shown in Figure 4.12 (b). Thus, the dielectric constant has obviously increased from 4.11 for HPMC/PVA blend to 36.26 for 0.5 wt % GO and 5 wt % ZnO loading and then increases sharply to 103.51 at 50 Hz and at 150°C for the nanocomposites with 2.5 wt % GO and 25 wt % ZnO nanoparticle loading. Comparing with HPMC/PVA blends, a 25-fold increase in dielectric constant was observed for nanocomposites containing 2.5 wt % GO and 25 wt % ZnO loading. This suggests that different compositions of GO/ZnO hybrid fillers were homogeneously dispersed in the polymer matrix resulting in the formation of high k-dielectric composite materials.
Figure 4.12 (a): Dielectric constant of HPMC/PVA (50/50) blend.

Figure 4.12 (b): Dielectric constant of HPMC/PVA/GO/ZnO nanocomposite with 0.5 wt % GO+5 wt % ZnO.
Figure 4.12 (c): Dielectric constant of HPMC/PVA/GO/ZnO nanocomposite with 1 wt % GO+10 wt % ZnO.

Figure 4.12 (d): Dielectric constant of HPMC/PVA/GO/ZnO nanocomposite with 1.5 wt % GO+15 wt % ZnO.
Figure 4.12 (e): Dielectric constant of HPMC/PVA/GO/ZnO nanocomposite with 2 wt % GO+20 wt % ZnO.

Figure 4.12 (f): Dielectric constant of HPMC/PVA/GO/ZnO nanocomposite with 2.5 wt % GO+25 wt % ZnO.
The dielectric loss is one of the most important parameters of materials characterization and it is commonly used as a measure of the energy dissipation in dielectric materials. The dielectric loss of dielectric materials generally arises from conduction process, interfacial polarization, and molecular dipole movement [273]. Figure 4.13 (a-f) shows the dielectric loss (\( \tan \delta \)) of HPMC/PVA blend and HPMC/PVA/GO/ZnO nanocomposites as a function of frequency in the range 50 Hz to 20 MHz and temperature in the range 40-150°C. From Figure 4.13 (a-f), it can be seen that the values of dielectric loss are high at low frequencies and as the frequency increases, the dielectric loss also decreases. This is obvious because the excellent dispersion of GO/ZnO hybrid fillers into the polymer matrix can increase the interfacial area between them, which leads to stronger interfacial polarization in the low-frequency range [274]. The maximum value of the dielectric loss (0.75) for HPMC/PVA blend film was observed at 50 Hz and at 40°C as shown in Figure 4.13 (a). It was also observed that the dielectric loss of HPMC/PVA/GO/ZnO nanocomposites has increased with increase in the filler loadings. For 0.5 wt % GO and 5 wt % ZnO loading, the highest values value of the dielectric loss (1.39) was observed at 50 Hz and at 150°C as shown in Figure 4.13 (b). Thus, the dielectric loss has obviously increased from 0.75 for HPMC/PVA blend to 1.39 for 0.5 wt % GO and 5 wt % ZnO loading and then increases sharply to 3.14 at 50 Hz and at 150°C for the nanocomposites with 2.5 wt % GO and 25 wt % ZnO nanoparticle loading as shown in Table 4.2. For HPMC/PVA/GO/ZnO nanocomposites, the dielectric loss increases rapidly as compared to HPMC/PVA blend. The introduction of inorganic fillers into polymer matrix usually enhances the dielectric loss of the composites which is due to enhancement of charge carriers in the system induced by the nano fillers [275]. Thus, such materials having excellent dielectric properties find applications in electrical charge storage or energy storage devices such as embedded capacitors.

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Figure 4.13 (a): Dielectric loss of HPMC/PVA (50/50) blend.

Figure 4.13 (b): Dielectric loss of HPMC/PVA/GO/ZnO nanocomposite with 0.5 wt % GO+5 wt % ZnO.
Figure 4.13 (c): Dielectric loss of HPMC/PVA/GO/ZnO nanocomposite with 1 wt % GO+10 wt % ZnO.

Figure 4.13 (d): Dielectric loss of HPMC/PVA/GO/ZnO nanocomposite with 1.5 wt % GO+15 wt % ZnO.
Figure 4.13 (e): Dielectric loss of HPMC/PVA/GO/ZnO nanocomposite with 2 wt % GO+20 wt % ZnO.

Figure 4.13 (f): Dielectric loss of HPMC/PVA/GO/ZnO nanocomposite with 2.5 wt % GO+25 wt % ZnO.
Table 4.2: Maximum values of dielectric constant and dielectric loss obtained for HPMC/PVA/GO/ZnO nanocomposites

<table>
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<tr>
<th>GO loading (wt %)</th>
<th>ZnO loading (wt %)</th>
<th>Dielectric Constant (ε)</th>
<th>Dielectric Loss (Tan δ)</th>
</tr>
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<td>5</td>
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<td>2.5</td>
<td>25</td>
<td>103.51, 50 Hz, 150°C</td>
<td>3.14, 50 Hz, 150°C</td>
</tr>
</tbody>
</table>

4.4 CONCLUSION

In summary, GO was prepared by modified Hummers method. The formation of GO was confirmed by Raman, FTIR and XRD analysis. HPMC/PVA/GO/ZnO nanocomposites were prepared by colloidal blending method which is very cost effective and eco-friendly process. The nanocomposite films showed good flexibility. The FTIR and XRD analysis indicate that GO was completely exfoliated into individual GO sheets leading to the formation of exfoliated nanocomposites. The SEM results revealed the uniform distribution of GO and ZnO nanoparticles throughout the polymer matrix, indicating the strong interfacial interaction between polymers and the fillers. The enhancement in the mechanical properties of nanocomposites
can be ascribed to the homogeneous dispersion of GO sheets and ZnO nanoparticles in the polymer matrix and strong interfacial interaction between all the components. The HPMC/PVA/GO/ZnO nanocomposites showed high dielectric constant and low dielectric loss. The increase in dielectric constant of nanocomposites is due to increase in the interfacial polarization between GO/ZnO hybrid fillers and the polymer matrix. A high dielectric constant (103.51) at 50 Hz and at 150°C and low dielectric loss (3.14) at 50 Hz and at 150°C are obtained for nanocomposites with 2.5 wt % GO and 25 wt % ZnO nanoparticles loadings. Thus, these GO/ZnO based PNCs are the potential candidate for energy storage applications and the protocol presented in this work could be useful in developing various graphene-based materials for wide range of technological applications.