Original Article

Preparation, structural analysis, morphological investigation and electrical properties of gold nanoparticles filled polyvinyl alcohol/carboxymethyl cellulose blend

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ABSTRACT

Polymer nanocomposite samples have been prepared through the solution casting method utilizing a polymer blend of polyvinyl alcohol and carboxymethyl cellulose (70/30 wt.%) as organic host matrix and different concentrations of biosynthesized gold nanoparticles (Au NPs) by the leaf extract of green mint (Mentha Spicata L.) as inorganic nanofiller. The structural, optical and morphological properties of these samples have been through FT-IR, XRD, UV/Vis. and SEM techniques. The FT-IR spectra confirm the blend components are miscible by the formation of Hydrogen bond interaction and show the polymer-nanoparticle interactions. The XRD analyses depict the semicrystalline structure of these samples and the crystallinity degree decrease with increase of Au NPs content within the PVA/CMC structure. The TEM micrograph of biosynthesized Au NPs indicates that shapes of these NPs are spherical NPs and triangular/hexagonal nanoplates with average size range 5–29 nm. The alternating electrical conductivity, electrical impedance, complex dielectric permittivity and electric modulus spectra of prepared samples have been investigated at 25 °C in the frequency range (0.1 Hz–20 MHz). Thus, the variations in values of conductivity, dielectric permittivity and relaxation times indicate the feasibility of these materials as flexible nanodielectric of frequency tunable permittivity for radio/audio frequency operating micro-electronic/conventional devices.

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1. Introduction

The blending process of some polar polymers has a significant interest in the modification/development of new polymeric material with significant properties that differ from the parent polymers [1–3]. This process is an effective method for the preparation of flexible polymeric matrix with a high degree of miscibility instead of new polymer synthesisation [4]. Among these polymers, the semicrystalline PVA and amorphous CMC are potentially non-toxic, hydrophilic and biodegradable [5,6]. Further, these polymers have the ability to form excellent flexible-type film through solution casting technique. Due to the high durability, good clarity, excellent electrical properties of thermally stable PVA, it has various applications like flexible water-soluble packing films, textile sizing, paper coating, polarizing sheets production and solid polymer electrolyte preparation [7–10]. On the other hand, the natural CMC polymer retains various desirable properties like low cost, water maintaining, suspension, emulsification and excellent film forming [11,12]. Thus, CMC is considered as a promising material for industrial and biotechnological applications such as paper making, textures, electrical elements, toilet products, printing and medicine [7,12]. The hydroxyl group (OH) within the chain backbone of PVA and CMC structures acts as a functional group for inter- and intra- hydrogen bonding. El-Sayed et al. [5] studied the optical, thermal and dielectric properties of CMC/PVA blends and concluded that these blends are miscible with each other and the composition (70/30 wt.% ) of PVA/CMC blend shows low absorption edge compared to other prepared samples. Also, they found that this composition exhibits higher dielectric constant. Saadiah et al. [6] investigated the structural, morphological and electrical conductivity of CMC/PVA blends. Further, they studied the interactions within the CMC/PVA through density functional theory (DFT) calculations. They depicted the formation of intermolecular forces of H-bonding within the CMC/PVA hybrid polymer between the –OH group of PVA and –COO− group of CMC.

Polymer nanocomposite materials comprise the significant properties of the inorganic nanofiller and also the flexible polymer matrix [13,14]. Thus, these hybrid materials introduce a multifunctional advanced polymeric material for enormous technological uses such as in the development of the next fabrication of optoelectronic devices, solar cells, energy storage devices and the nanodielectric applications [4,14–16]. The choice of Au NPs in the of the nanocomposite preparation is due to its high chemical/mechanical stabilities, electrical conductivity, outstanding plasmonic activity, catalytic properties and antimicrobial activities [1,3,17,18]. Morsi et al reported the improvement of thermal and optical properties of PVP/CMC polymer blend due to the in situ formation of Au NPs within this polymeric matrix [11]. Abdelrazik et al. [19] found the enhancement of optical and thermal properties of PEO/PVP matrix at low content of Au NPs. Further, several authors reported that the electrical and dielectric properties of various polymer nanocomposite films containing different concentrations of Au NPs were significantly improved [20–22].

Various methods have shown the Au NPs can be prepared by the physical and chemical ways [1,3,11,17,23], but because of the usage of toxic chemicals, it becomes a man-
pH = 6. This mixture was warmed for 10 min and its colour turned to reddish-brown. This colour changing depicted that the plant extract behaved as a bioreducing agent for the gold ions. The obtained Au NPs solution was centrifuged and the deposited powder was washed for three times.

2.3. Preparation of PVA/CMC/Au nanocomposite samples

The PVA (2.1 g/100 mL) and CMC (0.9 g/150 mL) powders were dissolved in DD at 80 °C, separately. To obtain the PVA/CMC solution (70/30 wt.%), these solutions of virgin polymers were mixed through magnetic stirrer for 6 h to have a homogeneous solution of PVA/CMC blend at the same previous temperature. The required quantities of Au NPs (0.02, 0.04, 0.08 and 0.16 Au NPs) were mixed with the previously prepared PVA/CMC solution for 15 min. Further, these nanocomposite solutions were immersed device in ultrasonic device for 10 min to improve the NPs dispersion and homogeneous solutions were obtained. Subsequently, these solutions were cast onto a poly propylene dishes and it were put in oven for 5 days at 40 °C. Finally, the materials had become a flexible-type freestanding polymer nanocomposite films with thickness (0.14–0.18 mm).

2.4. Characterization techniques

The complexation between PVA/CMC and Au NPs was investigated using Fourier transform infrared spectroscopy (Nicolet iS10, USA) in the wavenumber range (400–4000 cm⁻¹). The morphology of these nanocomposite films was investigated through scanning electron microscopy (SEM, JEOLJSM 6510LV). The X-ray diffraction (XRD) analysis of biosynthesized Au NPs and PVA/CMC/Au nanocomposite samples were measured using PANalytical X’pert Pro MPD diffractometer at a scan rate (0.05/°s) with Cu-Kα radiation (λ = 1.5406 Å) at voltage 30 kV. The size and shape prepared Au NPs were studied through transmission electron microscope (TEM, JEOL-JEM-1011, Japan). The electrical and dielectric parameters of pure PVA/CMC and the filled films (0.02 and 0.16 wt.% Au NPs) were measured by broad band dielectric spectroscopy (Novocontrol Turnkey Concept 40 System) in nitrogen atmosphere. The copper electrodes of diameter 2.5 cm were prepared through using vacuum coating unit. Further, these parameters were measured in the temperature variation from 25 to 100 °C for the nanocomposite film (0.02 wt.% of Au NPs) and the temperature value was adjusted by the QUATRO Cryosystem. The absorbance spectra of the prepared samples were measured using a spectrophotometer (V-570 UV/VIS/NIR, Jasco, Japan) in the wavelength range (190–1000 nm).

3. Results and discussion

3.1. FT-IR spectroscopy

The FT-IR spectroscopy has been assured using to detect the functional groups of virgin polymers and its interactions with the prepared Au NPs. Fig. 1 indicates the FT-IR absorption spectra of virgin polymers (PVA and CMC), pure PVA/CMC blend, and the nanocomposite samples. Further, the FT-IR peaks and its assignments for the virgin polymers are listed in Tables (1 and 2) [2,27–30].

Compared the FT-IR absorption spectra of virgin polymers (PVA and CMC) and the pure blend, there are a significant differences. The broadness of OH stretching vibration is increased and its position is shifted to 3454 cm⁻¹. The appearance of both the (O=O) group of PVA and the (COO⁻) group of CMC in the spectrum of blend, where the C=C group is appeared as a weak shoulder at 1710 cm⁻¹ and the absorbance of (COO⁻) of blend is small with more broadness as compared to that of CMC polymer, indicates that the blend components are miscible. Further, the functional groups in the wavenumber region 1520–800 cm⁻¹ are significantly affected because of the blending process as the broadness of these functional groups is increased. Further, the absorbance of the functional group of blend at 1376 cm⁻¹ is largely decreased as compared to that the pure PVA and the functional group of PVA at 1250 is appeared as a weak shoulder at 1240 cm⁻¹ in the PVA/CMC spectrum. The crystalline peak of the PVA structure at 1094 cm⁻¹ is negatively affected due to blending with CMC. This peak is the characteristic alcohol peak and becomes broader because of the interference of the vibrational mode of this peak and that of the CH—O—CH₃ group of CMC structure at 1062 cm⁻¹. All these observations depict the formation of intermolecular H-bonding within the hybrid polymer matrix (Scheme 1), where the PVA polymer a large tendency to hydrogen form bonding with other polymers containing highly electronegative groups such as CMC. It is worth mentioning that the presence of carbonyl functionalities within the PVA structure because of the residual acetate groups after the PVA preparation from the hydrolysis of polyvinyl acetate [23].

From Fig. 1b, the vibrational bands of PVA/CMC matrix are significantly affected due to the Au NPs addition. The broad-
Fig. 1 – FT-IR spectra of pure PVA, CMC, PVA/CMC blend and the filled samples with different concentration of Au NPs.

ness of OH band and intensity of CH$_2$ asymmetric stretching band are reduced. The absorbance of the functional bands in the wavenumber range 1800–800 cm$^{-1}$ decreases gradually with the increase of Au NPs content. The FT-IR spectra of the nanocomposite samples (0.08 and 0.16 wt.% Au NPs) are found entirely varied in comparison to that of the pure PVA/CMC blend and the nanocomposite films (0.02 and 0.04 wt.% Au NPs), where the vibrational bands at 1735, 1376 and 915 cm$^{-1}$ are absent. The band 915 cm$^{-1}$ refers to the syndiotactic structures of PVA matrix [9]. Furthermore, the absorbance of (COO$^-$) and (CH–O–CH$_2$) groups is reduced. Thus, these considerable variations in the absorbance of all absorption bands indicate that there is the formation of nanoparticle–polymer interactions, such as hydrogen bonding or van der Waals interaction, between the (OH)/(COO$^-$) groups of PVA/CMC and the Au NPs (Scheme 2). This leads to a decrease in the crystallinity degree of the nanocomposite films and the formation of charge transfer complexes, where the PVA/CMC matrix acts as an electron donor and the Au NPs serves as an electron acceptor. These interactions influence the
Table 1 – Assignments of the FT-IR characterization bands of the pure PVA and pure CMC.

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Wavenumber (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH stretching</td>
<td>3402</td>
</tr>
<tr>
<td>CH(_2) asymmetric stretching</td>
<td>2922</td>
</tr>
<tr>
<td>Carboxylate (COO(^{-})) stretching group</td>
<td>1597</td>
</tr>
<tr>
<td>CH(_2) scissoring</td>
<td>1416</td>
</tr>
<tr>
<td>OH bending</td>
<td>1322</td>
</tr>
<tr>
<td>CH(=)O–CH(_2) stretching</td>
<td>1062</td>
</tr>
<tr>
<td>–</td>
<td>25</td>
</tr>
<tr>
<td>–</td>
<td>50</td>
</tr>
</tbody>
</table>

Table 2 – The \(\sigma_{dc}\), \(\tau\) and \(\tau_m\) values for PVA/CMC blend, the nanocomposite samples (0.02 and 0.16 wt.%) and also for the nanocomposite sample (0.02 wt.%) at different temperatures.

<table>
<thead>
<tr>
<th>T (^\circ)C</th>
<th>(\sigma_{dc}) ((\Omega^{-1}) cm(^{-1}))</th>
<th>(n)</th>
<th>(\tau) (s)</th>
<th>(\tau_m) (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure blend</td>
<td>4.79 \times 10^{-12}</td>
<td>0.55</td>
<td>15.92 \times 10^{-3}</td>
<td>0.55 \times 10^{-3}</td>
</tr>
<tr>
<td>0.02</td>
<td>4.13 \times 10^{-12}</td>
<td>0.58</td>
<td>47.66 \times 10^{-3}</td>
<td>0.05 \times 10^{-4}</td>
</tr>
<tr>
<td>0.16</td>
<td>2.74 \times 10^{-12}</td>
<td>0.68</td>
<td>–</td>
<td>9.58 \times 10^{-3}</td>
</tr>
<tr>
<td>PVA/CMC-0.02 wt.% Au NPs</td>
<td>4.13 \times 10^{-12}</td>
<td>0.58</td>
<td>47.66 \times 10^{-3}</td>
<td>0.05 \times 10^{-4}</td>
</tr>
<tr>
<td>25</td>
<td>4.04 \times 10^{-9}</td>
<td>0.29</td>
<td>1.24 \times 10^{-3}</td>
<td>1.004 \times 10^{-6}</td>
</tr>
<tr>
<td>50</td>
<td>3.08 \times 10^{-8}</td>
<td>0.20</td>
<td>6.1 \times 10^{-4}</td>
<td>2.30 \times 10^{-7}</td>
</tr>
</tbody>
</table>

Scheme 2 – Mechanism of interactions between Au NPs and the monomers of PVA and CMC.

dynamics of entire chain structures of the nanocomposite samples.

3.2. SEM

Fig. 2 shows the SEM micrographs of pure PVA/CMC blend and the filled samples at magnification 2500 times. From Fig. 2a, the surface of blend is relatively rough, due to the semicrystalline nature of blend, without any phase separation as a result from the miscibility of PVA and CMC polymers. This micrograph corroborates the findings of Saadiah et al. [6]. From Fig. 2b–e, the Au NPs addition produces considerable modification in the surface morphology of blend. From Fig. 2b, the concentration of Au NPs (0.02 wt.%) has slightly smooth surface and the surface roughness reduces with continuous increasing the nanofiller content. Also, the Au NPs are distributed uniformly with no aggregation (Fig. 2b,c). From Fig. 2d, there is low degree of agglomeration for the Au NPs that largely increases in the form of bright spots (Fig. 2e). It can be concluded that the nanocomposite films (0.02 and 0.04 wt.% Au NPs) have relatively smooth surfaces with no aggregation of Au NPs and depicts the suitability to use them as insulator and substrate for the development of microelectronic devices. These morphological changes indicate nanoparticle-polymer interaction depicting good compatibility between the inorganic and organic constituents within the nanocomposite samples.

3.3. XRD

The XRD patterns have been performed for the PVA/CMC blend, filled samples and the biosynthesized Au NPs, as shown in Fig. 3, to show the changes within the structure of nanocomposite samples. From Fig. 3b, the XRD patterns of Au NPs are
in agreement with the results of its face-center cubic (FCC) structure [JCPDS file no. 04-0784] [11,17,31,32].

The semicrystalline PVA polymer exhibits broad diffraction peak at 19.50° that indicates to orthorhombic PVA (101) reflection plane [JCPDS file no. 41-1049] [8]. Similarly, Rajeh et al. [27] reported main diffraction peak of semicrystalline CMC polymer at 2θ = 21.50°. Thus, the diffraction peak at 19.70° in the XRD pattern of PVA/CMC blend indicates its semicrystalline nature because of the existence of PVA with content (70 wt.%) within the blend structure. It can be observed that the incorporation of NPs into the PVA/CMC matrix decreases the peak intensity and increases the main peak broadness. Also, there are no diffraction peaks attributed to the NPs phases, which indicates the dissolution of NPs within the polymeric matrix [19,20]. These observations depict that nanoparticle-polymer interactions break the PVA/CMC crystallites and the crystalline phases of the nanocomposite samples decreases. Further, electrostatic interaction of Au NPs with the PVA/CMC chains disturbs the crystalline phases of PVA/CMC within the filled samples. Thus, these PVA/CMC/Au nanocomposite samples are suitable for the solid polymer electrolyte preparation since the reduction of crystallinity degree is important for the improvement of electrical conductivity in solid ion dipolar complex.

3.4. TEM

The TEM micrographs of prepared NPs and the nanocomposite sample (0.16 wt.% Au NPs) are indicated in Fig. 4a,b. The shapes of biosynthesized Au NPs with average size range 5–29 nm are spherical nanoparticles and triangular/hexagonal nanoparticles (Fig. 4a). The presence of triangular/hexagonal shapes indicates the rapid adsorption of the functional groups of extract on the (111) facets of newly produced Au NPs [33]. From the TEM micrograph of the nanocomposite sample, the Au NPs with anisotropic structure of spherical, hexagonal triangular and truncated triangular are existed with average size range 5–38 nm (Fig. 3b). The strong adsorption of the functional groups of the PVA/CMC blend-coated Au NPs on the selected facets of Au nuclei make this surface become hindered in growth process as the others grow fast. Further, the growth rate is decreased along the adsorbed surface (111) that may result in the formation of anisotropic plate form of Au NPs [34]. The increase in the size range of the nanocomposite sample is because of the existence of Au NPs with high content which assists the ability of Au NPs to move and aggregate. From Fig. 4c, the ring shape of selected area electron diffraction pattern of the prepared NPs confirm their (FCC) crystalline nature [11,17].

3.5. Electrical properties

3.5.1. AC conductivity and impedance results

The spectra of real part \( \sigma' \) of the complex AC electrical conductivity of pure PVA/CMC and the filled films (0.02 and 0.16 wt.% Au NPs) at 25 °C are shown in Fig. 5a. The \( \sigma' \) values increase non-linearly with increase of frequency (f) and show DC plateau behavior over the audio frequency (AF) region (f <20 kHz) and as well over the radio frequency (RF) region (f >20 kHz), which are because of the semicrystalline nature of these samples. The behavior of \( \sigma' \) has been reported previously [15,28,35]. The \( \sigma' \) values of these films rapidly decrease with the decrease of f in due to the electrode polarization (EP) effect, where the accumulation of more and more charges exists at the electrode surfaces and interface of electrolyte. This results in a reduction in a number of mobile ions, and therefore, leads to the decrease of the ionic conductivity of the studied material. It is observed that in AF region, the \( \sigma' \) value of pure PVA/CMC blend is large as compared to the val-
makes the contribution of charge in electrical conductivity is less. Further, the incorporation of NPs produces charge transfer complexes (CTC) in which the movement of charges exists through coulomb forces and electric field [15]. Form this table, the n values are less than 1 indicating that the charge transportation within the polymeric matrix follows the hopping conduction mechanism [28]. These electrical conductivity results depict the suitability of the nanocomposite films for electrical insulation in the microelectronic devices as flexible polymeric nanodielectric and the development of next-fabrication flexible-type biodegradable green electronic.

The real part of impedance ($Z'$) of the investigated samples at 25 °C is shown in Fig. 5b. The $Z'$ values in the AF range are significantly influenced by Au NPs, while these values are smaller as compared to that of the PVA/CMC blend in the RF region (inset figure). In the AF region, the $Z'$ values of the investigated films are around G2 range that depicts their large electrical insulation of these dielectric materials at low f values, and subsequently, these samples may be utilized for the low power based microelectronic devices worked at AF range. From Fig. 5c, the reactive part of impedance ($Z''$) value of the nanocomposite samples is large as compared to the $Z'$ values implying the prevailing capacitive behavior of these dielectric films. Thus, these samples are favorable for the applications of capacitive devices.

At different temperatures, the $\sigma'$, $Z''$ and $Z''$ spectra of the PVA/CMC/0.16 wt.% sample are shown in Fig. 6. From Fig. 6a, there is a large improvement for the $\sigma'$ values with increasing the temperature (T) of the nanocomposite sample depicting its thermally activated electrical conduction behavior. Further, this implies that the increase of the free charge carrier’s number and their mobility increases. The temperature dependent $\sigma_{dc}$ values are investigated through power law fit to the AF region. At various T, the obtained values of n and $\sigma_{dc}$ are listed in Table 2, where the $\sigma_{dc}$ value improves with T depicting the thermally activated $\sigma_{dc}$ behaviour of the nanocomposite sample. Also, the values of n reduce implying that charge hopping conduction mechanism is thermally activated process within the studied nanocomposite sample. The T dependent $\sigma_{dc}$ value of PVA/CMC/0.16 wt.% sample is plotted in Fig. 6b, where the linear behavior of this plot depicts the Arrhenius dependence of $\sigma_{dc}$. The activation energy ($E_a$) of this nanocomposite sample is determined through the Arrhenius’s relation $\sigma = \sigma_0 \exp (-E_a/k_B T)$, respectively, as the $\sigma_0$ is the pre-exponential factor, T is the temperature and $k_B$ is the Boltzmann’s constant. The obtained value of $E_a$ is 0.51 eV which is significantly low. Thus, this suggests that the suitability of the nanocomposite samples in the solid electrolytes preparation as the potential barrier for the charge hopping is small. The temperature-dependent $Z'$ and $Z''$ spectra are shown in Fig. 6c,d. The values of $Z'$ and $Z''$ are largely decreased by when the temperature is increased. From these spectra, the prepared samples can be used as nanodielectrics in the electronic devices development such as antennas, capacitors and organic field effect transistors because the performance of such devices is greatly controlled by the electrical conductivities of these dielectric materials.

Fig. 3 – X-ray diffraction pattern for pure blend, blend with different concentration of Au NPs and the prepared Au NPs.

values of filled samples, while in RF region it exhibits a reverse trend. The $\sigma'$ values follow the Jonscher’s power law [36]:

$$\sigma' (\omega) = \sigma_{dc} + A\omega^n$$

(1)

The values of exponent factor (n) from power law fit and dc electrical conductivity ($\sigma_{dc}$) for the investigated samples are listed in Table 2. From this table, the $\sigma_{dc}$ values progressively reduce with the increase of Au NPs content within the PVA/CMC matrix. For a dielectric material, the $\sigma_{dc}$ value is controlled by the mobility of charge ($\mu_e$), charge density ($n_e$) and the mobile charge value as shown in the following relation:

$$\sigma_{dc} = \varepsilon n_e \mu_e$$

(2)

Thus, the reduction in $\sigma_{dc}$ values for the nanocomposite samples indicates that there is the decrease of the charge mobility because of the polymer-nanoparticle interactions. Therefore, the charge migration becomes slower and this
3.5.2. Dielectric spectra

The frequency-dependent \( \varepsilon' \) and \( \varepsilon'' \) spectra of the complex permittivity \( \varepsilon^* \) for the investigated samples are obtained from the following equations [28]:

\[
\varepsilon^* (\omega) = \varepsilon' - j\varepsilon''
\]

(3)

\[
\varepsilon' = \frac{1}{tC}\varepsilon_0 A
\]

(4)

\[
\varepsilon'' = \sigma /\omega\varepsilon_0
\]

(5)

\[
tan\delta = \varepsilon'' /\varepsilon'
\]

(6)

where, \( C \) is the measured capacitance, \( t \) is the film thickness, \( A \) the electrode cross-section area, \( \varepsilon_0 \) is the permittivity of free space and \( tan\delta \) is the dielectric loss tangent. Fig. 7a–c shows the \( \varepsilon' \), \( \varepsilon'' \) and \( tan\delta \) values of pure PVA/CMC and the filled films (0.02 and 0.16 wt.% of Au NPs) at 25 °C. These figures confirm the obtained electrical and impedance spectra. From these figures, the \( \varepsilon' \) values of nanocomposite sample (0.02 wt.% of Au NPs) are larger than that of the blend sample in the RF and AF regions. For the nanocomposite sample (0.16 wt.% of Au NPs), the \( \varepsilon' \) values are lower than that of the blend sample in the AF range and these values are higher in the RF range. Further, the \( \varepsilon'' \) values of the two nanocomposite samples are lower than that of pure blend. The \( \varepsilon' \) values are high at low \( f \) because of the interfacial polarization (IP) effect [9] as a result from the difference in the conductivity and permittivity values of the blend matrix and the Au NPs, where the dielectric polarizability increases because the charges accumulate at the interfaces of various conductivity constituents within the filled samples. Moreover, it is noted that the \( \varepsilon' \) and \( \varepsilon'' \) values of the investigated samples are almost frequency independent over the RF
blend sample. This is a rebuttal for the existence of electrostatic interactions between the dipolar segments of PVA/CMC chain and the surface of Au NPs that hinder the dipolar ordering of polar blend, resulting in reduction for the dielectric permittivity values of this nanocomposite sample. Further, this reduction can be attributed to the nanoconfinement effect [9] that mainly results in the increase of hindrance by the NPs to the dipolar group motion of the polymeric chains with the time varying electric field. Therefore, the dipolar polarization of this sample decreases. From the literature survey, the same dielectric permittivity results were as well reported [9,15,35].

Fig. 7c indicates that the tanδ spectra show in the middle f region relaxation peak that is assigned to the local chain dynamics of PVA/CMC. This peak is shifted to lower frequencies in the spectra of nanocomposite sample (0.02 wt.% Au NPs) and disappeared in the spectra of nanocomposite sample (0.16 wt.% Au NPs). The dielectric relaxation time τ is determined through the relation \( \tau = (2\pi f_p)^{-1} \), where the \( f_p \) is the tanδ peak frequency and the \( \tau \) values are listed in Table 2. The value of the nanocomposite sample as compared to that of the PVA/CMC sample confirms that the significant electrostatic interactions between the functional dipolar groups of PVA/CMC and the NPs results in more hindrance to the segmental motion of polymeric chains. These observations infer that there is good dispersion for the Au NPs within the PVA/CMC matrix that results in increase for the nanofiller/polymer interactions.

**Fig. 8a-c** depicts the dielectric spectra of \( \varepsilon' \), \( \varepsilon'' \) and tanδ for the nanocomposite sample (0.02 wt.% Au NPs) at different temperatures, which gradually improve with the increase of temperature. This improvement is large in the AF range as compared to that of the RF range of these spectra (inset figures). The dc electrical conductivity and IP effect contributions at low \( f \) are the basic cause for relatively large raise of the \( \varepsilon' \) values with increase of \( T \). The relaxation peak of tanδ spectra moves towards high \( f \) with increasing \( T \) that increases the free volume and assists the polar chain segments orientation of the PVA/CMC macromolecules [12,28]. The temperature dependent \( \tau \) values are listed in Table 2, which reduce with the increase of \( T \) that weakens the nanofiller-interactions and facilitates the polymer chain dynamics [12,35].

### 3.5.3. Electric modulus spectra

**Fig. 9a,b** shows the complex electric modulus \( M'(\omega) \) spectra of the investigated samples which are calculated by the following relation:

\[
M'(\omega) = 1/e * (\omega) = M' + jM'' = \varepsilon'(\varepsilon^2 + \varepsilon'^2) + j\varepsilon''(\varepsilon^2 + \varepsilon'^2)
\]

The electric modulus spectra are important since it indicate the bulk response of the dielectric sample and doesn’t depend on the effect of electrode polarization. The \( M' \) spectra increase non-linearly with increase of \( f \), while \( M'' \) spectra show relaxation peak in the AF range that is assigned to the PVA/CMC chain motion. The peak in high \( f \) is due to the re-orientation motion of polar groups of the PVA/CMC chains and this peak is disappeared in the spectra of two nanocomposite samples. The modulus relaxation time \( \tau_m \) value is calculated from the following relation: \( \tau_m = (2\pi f_m)^{-1} \), where \( f_m \) is the value indicating to the peak. The calculated \( \tau_m \) value is listed in Table 2.

![Graph](image)
The rise \( \tau_m \) value of the nanocomposite sample (0.16 wt.%) may be due to the formation of Au NPs aggregations and the low \( \tau_m \) value of the nanocomposite sample (0.02 wt.%) is due to the fine dispersion of NPs within the PVA/CMC structure. From Table 2, the \( \tau \) value is higher than the \( \tau_m \) value that is expected since most of the polymer nanocomposite samples show this pattern [15,35,37].

Fig. 9c indicates the Argand plots (M” versus M’) for the investigated samples. The Argand plot for the pristine sample is deviated from the semicircular arc, which indicates that the relaxation processes are non-Debye type (no single relaxation time) [27]. This can be due to the occurrence of different polarization mechanisms under the effect of external electric field, like ionic, electronic and dipolar polarization. Therefore, a various relaxation times exist. The Argand plots of the nanocomposite samples change to half semicircles that confirm the Debye type relaxation process of these filled samples. Further, the radii of these semicircles of these nanocomposite samples are largely decrease due to the increasing of ionic mobility resulting in the improvement of conductivity [38,39].

Fig. 10a,b shows the M’ and M” spectra of nanocomposite sample at different temperatures. The M’ values reduce as the temperature of nanocomposite increases with the increase of T, while the relaxation peak of M” spectra shows a progressive raise of its height with a shift towards high f region. The T dependent values of \( \tau_m \) are listed in Table 2 which indicates a reduction with the T increase. This reduction depicts the improvement of the polymeric matrix flexibility. Fig. 10c shows the Argand plots of the nanocomposite sample (0.02 wt.%) at different temperatures, where the plots depict the relaxation processes are Debye type and these plots move toward the origin with increasing T because of the increase of electrical conductivity.

3.6. UV/Vis. spectroscopy

Fig. 11 shows the UV/Vis. absorption spectra for the prepared Au NPs, pure PVA/CMC blend and the filled samples. The spectrum of Au NPs shows an absorption peak at 531 nm which is referred to the surface plasmon resonance peak (SPR) of Au NPs [3,17–19]. Also, this peak is responsible for the transfer colors from yellow for the bulk gold chloride to pinkish-red for the prepared NPs. Thus, this peak confirms the successful preparation of Au NPs by the mint extract.

The spectrum of virgin PVA/CMC blend shows absorbance peak at 195 nm that is assigned to the n–π* transition [28,40,41]. Further, this spectrum exhibits a sharp absorption edge that gradually red shifted with an increase in absorbance in the filled samples when the Au NPs concentration increases, where the color of films is changed from transparent to
Fig. 7 – Frequency dependent $\varepsilon'$, $\varepsilon''$ and $\tan\delta$ of pure blend and the nanocomposite samples (0.02 and 0.16 wt.%) at 25 °C.

Fig. 8 – Frequency dependent $\varepsilon'$, $\varepsilon''$ and $\tan\delta$ of the nanocomposite sample (0.02 wt.%) at different temperatures.

pinkish-red color. These observations depict the complexation of Au NPs with the functional groups of blend structures (PVA and CMC) and also confirm the variation in the optical energy band gap ($E_g$) of the nanocomposite samples with a change of added Au NPs contents. These filled samples also show relatively weak absorbance peak at about 537 nm and the intensity of this peak gradually increases with the continuous increase of Au NPs concentration within the PVA/CMC matrix. Also, the observed SPR peak is an evidence of the Au NPs existence within the PVA/CMC matrix. Fundamentally, the SPR is an oscillation of high-density free electrons occurring because of
the effect of light radiation \cite{19,22}. Thus, the improvement of SPR peak intensity for the filled samples is absolutely because of the increase of total surface area to volume ratio of the NPs, and this confirm the suitability of these flexible polymer nanocomposite samples as photosensors for many biomedical and optoelectronic applications. The red shift of SPR peak from 531 nm for the prepared NPs to 542 nm for the nanocomposite sample (0.16 wt.%) implies the increase of Au NPs size as confirmed by the TEM micrographs, due to its presence with high content.

3.6.1. Determination of $E_g$

The $E_g$ values of the Au/PVA/CMC nanocomposite samples near the fundamental absorption edge have been determined using the following equation \cite{28,42}:

$$\alpha \nu = B(\nu - E_g)$$

(8)
where, $\alpha$ is the absorption coefficient, $hv$ is the photon energy, $B$ is a constant and $m=1/2$ for indirect and 2 for direct allowed transitions. The $\alpha$ value has been obtained via the expression $\alpha = 2.303 \left( \frac{\text{Absorbance}}{L} \right)$, where $L$ is the sample thickness. Fig. 12a,b shows the $(\alpha h^2)$ and $(\alpha h)^{0.5}$ versus $h\nu$ plots of the PVA/CMC/Au nanocomposite films. The straight-line portions of these plots are extrapolated to zero absorbance to obtain the $E_g$ values for direct and indirect transitions that are reported in Table 3. The estimated $E_g$ value for pure PVA/CMC is consistent with the reported values in the literature [40]. Table 3 shows that the $E_g$ values of filled samples gradually reduce with the increase of Au NPs concentrations that may be explained in terms of the formation of charge transfer complexes (CTCs) between the functional groups of PVA/CMC and the atoms of Au NPs [19,41] as indicated in the FT-IR analysis. This reduction presumes to increase with the degree of disorder for the localized state’s generation in the material, where the incorporation of NPs may produce energy levels within the band gap of PVA/CMC matrix which results in narrowing the $E_g$ [20,22]. Thus, these nanocomposite samples are suitable materials for optoelectronic devices and electrochemical applications.

### 4. Conclusion

The polymer nanocomposite samples composed of PVA/CMC matrix with different concentrations of Au NPs as nanofiller had been prepared by the solution casting technique. The FT-IR results confirmed the formation of strong interactions between the $-\text{OH}--\text{COO}^-$ groups of PVA/CMC and the Au NPs. From the SEM micrographs, the dispersion of a small amount of Au NPs modified the rough surface morphology of the PVA/CMC blend to smooth for the nanocomposite samples and these NPs aggregates on the surface of nanocomposite samples with high content of Au NPs. These samples were semicrystalline and the incorporation of Au NPs reduced the degree of crystallinity as indicated in the XRD analysis. The TEM micrographs showed the size range increased from 5 to 29 nm for the prepared NPs to 5–38 nm for the nanocomposite sample (0.16 wt.% Au NPs). The $\sigma^{\prime}$ values obtained from $\sigma^{\prime}$ spectra in the low $\nu$ region of the nanocomposite samples were lower than that of the pristine sample. The Au NPs addition with high content decreased the dielectric permittivity due to the nanoscale confinement effect that leads to an increase for the hindrance of polymeric chain motion. The UV/Vis. spectra depicted the presence of Au NPs within the filled samples by the SPR peak of Au NPs and the reduction of $E_g$ values for the filled samples due to the formation of charge transfer complexes (CTCs) between the functional groups of PVA/CMC matrix and the atoms of Au NPs. From the structural properties and the dielectric spectra, these nanocomposite samples are suitable as insulator/substrate for AF operated electrical/electronics devices and as low dielectric permittivity nanodielectric for electronic devices of RF ranges.

**Fig. 11** – The UV/Vis. spectra of pure blend and the blend filled with different concentrations of Au NPs.

**Table 3** – Optical energy gap for pure PVA/CMC blend and the filled samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$E_g$ (eV)</th>
<th>indirect</th>
<th>direct</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure blend</td>
<td>5.14</td>
<td>5.76</td>
<td></td>
</tr>
<tr>
<td>0.02 wt.% Au NPs.</td>
<td>4.96</td>
<td>5.57</td>
<td></td>
</tr>
<tr>
<td>0.04 wt.% Au NPs.</td>
<td>4.85</td>
<td>5.44</td>
<td></td>
</tr>
<tr>
<td>0.08 wt.% Au NPs.</td>
<td>4.76</td>
<td>5.36</td>
<td></td>
</tr>
<tr>
<td>0.16 wt.% Au NPs.</td>
<td>4.10</td>
<td>4.82</td>
<td></td>
</tr>
</tbody>
</table>

**Fig. 12** – (a) $\alpha h^2$ and (b) $(\alpha h)^{0.5}$ versus $h\nu$ plots of pure PVA/CMC and the filled films.
**Conflict of interest**

The authors declare that they have no conflict of interest.

**REFERENCES**


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