Novel glass materials-based (PVA/PVP/Al₂O₃/SiO₂) hybrid composite hydrogel membranes for industrial applications: synthesis, characterization, and physical properties

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ABSTRACT

Metal oxides e.g., Al₂O₃ and SiO₂ loaded-hydrogel blended membranes composed of poly(vinyl alcohol)/poly(vinyl pyrrolidone) (PVA/PVP, PVA/PVP/Al₂O₃, PVA/PVP/SiO₂, PVA/PVP/Al₂O₃/SiO₂) were successfully prepared on precleared glass plates by dip coating method. Meanwhile, series of obtained crosslinked hydride composite hydrogel membranes were successfully prepared using solution-casting method. Samples have been characterized for use in microelectronic devices. Results of X-ray diffraction revealed that the structure of doped sample with nanoparticle has a polycrystalline structure (hexagonal and Orthorhombic), while FE-SEM micrographs show grains in nanoscale and homogenous in nature of membranes. Interestingly, optical measurements of composites blended membranes were recorded using UV/Vis spectrometer. The optical parameters such as refractive index and optical energy gap were estimated. Moreover, complex dielectric constants were calculated optically for all composites, the experimental data shows the additive of nanoparticles composites has a direct energy band gap. Where, Eₕ for PVA/PVP/SiO₂, PVA/PVP/Al₂O₃ and PVA/PVP/Al₂O₃/SiO₂ at 1.82, 2.55, and 1.95 eV, respectively. While the sample PVA/PVP has an indirect band gap Eₕ of value 2.24 eV. Finally, the frequency dependence of the transport properties was measured, where results showed improvement of dielectric behavior with metal oxides loading. The experimental data of composite blended membranes can be used in optoelectronics devices.
1 Introduction

In the last decade, polymer nanocomposite materials and blended hydrogel membranes have become one of the important research fields in the advanced materials science and engineering [1–6]. Preparation and characterization of nanocomposite materials in bulk, thin film and membranes have been investigated for several applications including; flexible nano-dielectric substrate, electrical insulator for electronic devices, transient electronic antennas, sensors, energy storage, electromagnetic pollution, interference shielding, energy conversion instruments, packaging for electronic devices and as a base for the manufacture of opto-electronic devices [5–14]. Polymer nanocomposites materials have potential impact in electronic device industry due to their physical properties of inorganic nanofillers and the host polymer matrix; since, the electrostatic interactions between functional groups of the polymer chain and the nanometallic. In addition to their interface has an important in the formation of opto-electronic transport and physical and chemical properties of the polymer nanocomposites [1, 3, 15]. The applications of polymer nanocomposites are depending on their physical properties, which in turns could be tailored by the selecting conditions of preparation including; inorganic nanofiller, its electronic nature of surface, filler in the composition, concentration of nanoparticles in polymer, and a suitable preparation method. Previously, researchers have prepared numerous polymer nanocomposites with different inorganic nanofillers, polymers and polymer blends and characterized them for their physiochemical properties for using as flexible nanodielectrics can be used as electrical insulation and/or substrates in electronic devices [16–23]. Among these polymers, both poly(vinyl alcohol) (PVA) and poly(-vinyl pyrrolidone) (PVP) are biocompatible, biodegradable, and Echo-friendly (non-hazard) synthetic polymers that have been widely used as biomaterials for medical applications. Moreover, PVA and PVP are easily soluble in water and can form transparent films in the visible light; particularly when the film is fabricated by the solution-casting method. Recently, PVA/PVP films have been used in the insulation of organo-electronic devices due to its low electrical resistivity [24–26]. PVA and PVP backbone are belonging to hydroxyl (–OH) and carbonyl (C=O) functional groups, respectively, which exhibit electrostatic interactions between the nanoparticles and nanofillers. Thus, this is the reason behind choosing them as binding and sealing factors in the fabricated of the modern composite smart materials [27–30]. Moreover, PVA and PVP were widely utilized in many applications e.g., for instance electronics, electrical, and biomedical engineering industry such as sensors, electronic devices and the energy storing [31–36].

Among common metal oxides nanoparticles, Al2O3 has been prepared for filling PVA/PVP matrices as PVA/Al2O3 films, both bulk and films investigated for several applications [37–43]. Recently, the physical properties of Al2O3 filled PVA/PVP blended films have been reported [44]. Our literature review confirms additive of Al2O3 with SiO2 nanoparticles filled PVA/PVP blend composite nanomaterials have not been investigated. The contribution here is to add SiO2 in combination with Al2O3 in the PVA/PVP matrix. Herein, Al2O3 and SiO2 were filled into PVA/PVP blended membranes due to their properties including wear resistance, electrical insulation, good thermal conductivity, high adsorption capacity, thermal stability, high strength and stiffness, better mechanical strength, non-toxic and cost effectiveness as inexpensive fillers [38–43].

In this paper, we demonstrate the successful growth of nano-metal oxides filled in blended hybrid hydrogel membranes based on PVA/PVP, PVA/PVP/Al2O3, PVA/PVP/SiO2, and PVA/PVP/Al2O3/SiO2. The uniform cast blended composite membranes were mainly fabricated of dope solution composed of PVA, PVP, Al2O3 and SiO2 using solution-casting technique. Solution-Casting method is cost-effective, eco-friendly, simple, easily processing method, can be applied at ambient conditions, and can be easily scaled up for industrial application for mass production. As previously reported [44, 45], for avoiding the aggregation of nanoparticles the polymeric solution/nanoparticles mixture can be stirred well, then sonicated for 15 min. X-ray and FE-SEM analyses were used to examine the membrane crystallography-structure and surface features, respectively. While optical study of blended composite membranes was studied using UV/Vis spectroscopy. The dielectric and mechanical behaviors of the membranes have been studied at room temperature.
2 Materials and methods

2.1 Materials

Polyvinyl pyrrolidone (PVP, Mwt. 40,000 g/mol) was purchased from Thermo-Fisher, Germany. Polyvinyl alcohol (PVA, Mwt. 72,000 g/mol; 86% hydrolyzed) was obtained from Loba Chemie, India. AlCl₃·6H₂O and SiO₂ were purchased from TEOS, (99.99%) Sigma-Aldrich, Germany. Glutaraldehyde, (50% in H₂O, with purity 90%) and glycerol (≥ 99.5%) were purchased from Merck, Germany. Distilled water was used during the membrane’s preparation.

2.2 Preparation of Al₂O₃ and SiO₂ nanoparticles

Nanoparticles of Al₂O₃ (γ-alumina) were synthesized using a precipitation method. Typically, 0.8 M AlCl₃·6H₂O was dissolved in 240 mL of deionized water, and 8 mL of Tween-80 was added to the last mixture. After 1 h, a 50% aqueous solution of formamide as the precipitation agent, was added drop by drop to the mixture with continuous ultrasonication to adjust the pH ~ 7 at 70 °C for 3 h. A gelatinous white precipitate was produced indicating the formation of Al(OH)₃. This precipitate was filtered and washed with ethanol and water several times. The solution was dried in furnace at 90 °C, the resulting white gel was calcined in a muffle furnace at 550 °C for 5 h in air at a heating rate of 5 °C min⁻¹, then Al₂O₃ nanoparticles formed from Al(OH)₃. Nanoparticles of Si₃O were produced using a precipitation method, where Si₃O was dissolved in deionized water. After 1 h, a 50% aqueous solution of formamide, as the precipitation agent, was added drop by drop to the mixture with continuous ultrasonication to adjust the pH ~ 7 using NaOH at 60 °C for 3 h. This precipitate was filtered and washed with methanol and water several times. After drying in a furnace at 90 °C, the resulting powder was calcined in a muffle furnace at 600 °C for 5 h in air at a heating rate of 5 °C min⁻¹, and then Si₃O nanoparticles were produced.

2.3 Preparation of PVA/PVP hybrid hydrogel membrane

The uniform cast film membranes were mainly fabricated of dope solution composed of PVA, PVP, Al₂O₃ and SiO₂ using solution-casting technique. Briefly, PVA/PVP hybrid hydrogel membrane was prepared by mixing equal volumes of both 10% (w/v) PVA and PVP with a volume ratio of (1:1) into 13 mL distilled water, where the mixture was stirred for two hours at room temperature. Subsequently, 10% (w/v) of each Al₂O₃ and SiO₂ nanoparticles were incorporated, individually into the polymeric mixture solution with continuous stirring at 50 °C for another 1 h, for obtaining PVA/PVP/Al₂O₃ and PVA/PVP/SiO₂ composite hydrogel membranes, respectively. Then, the composite solution was ultrasonicated for 15 min to remove any air bubbles. Consequently, the elasticity of different resultant membranes was enhanced by adding 2 mL of glycerol (as plasticizer) to each membrane, then stirring for 10 min till completely mixed. After that, 5% (w/v) of glutaraldehyde (as a crosslinker) was added to the polymer-filler composite hydrogel and stirred for 10 min at ambient temperature. Each dope solution was poured into a glass petri dish by the solution-casting method, and the cast film was kept in the vacuum oven at 60 °C for 24 h. All previous steps were done to blend both 5% (w/v) Al₂O₃ and 5% (w/v) SiO₂; simultaneously into the PVA/PVP mixture polymer solution. The series of obtained crosslinked hydride hydrogel membranes were successfully prepared as following (PVA/PVP (control), PVA/PVP/Al₂O₃, PVA/PVP/SiO₂, and PVA/PVP/Al₂O₃/SiO₂) composite hydrogel membranes.

2.4 Characterizations and measurements

XRD patterns of untreated PVA/PVP, PVA/PVP/Al₂O₃, PVA/PVP/SiO₂, PVA/PVP/Al₂O₃/SiO₂ were obtained on a (Bruker D8, Germany) advance diffractometer using CuKα radiation (λ = 1.540 Å), operating at 40 kV and 40 mA. Scans were performed with a detector step size of 0.02° s⁻¹ over an angular range of 2θ from 10 to 80 °C.

Morphological analysis of PVA/PVP, PVA/PVP/Al₂O₃, PVA/PVP/SiO₂ and PVA/PVP/Al₂O₃/SiO₂ samples (5 × 5 × 1 mm) were characterized by field emission scanning electron microscopy (FE-SEM, Nova Nano SEM 230, Czech). X-ray energy diffraction (EDS) spectroscopy was performed to investigate the chemical elements of nano-composites and the relative percentage of elements was calculated.

Optical spectra were measured by spectrophotometer (Jasco V-570, Spain) wavelength range...
(0.2–2.5 μm). Optical parameters of the membranes have been estimated. The dielectric properties were measured at room temperature using LCR meter precision (Agilent technologies 4284A) with active electrodes on surface area 12.0 cm². The experimental data measured as a function of frequency over the range (20 Hz–1 M Hz) at a potential electric field of 1-V.

The mechanical measurements of Vickers hardness, a micro-hardness tester (DHV-1000-CCD, Beijing, China) with a normal load at 0.5 kg (load holding time: 10 s) was used. Five indentations were developed on each sample and then the average hardness was calculated with an error of ±0.2 GPa. The compressive strength of each sample (10 × 10 × 2 mm) was tested using an electro-mechanical universal testing machine (CSS-44100, China), with an accuracy of ±1%.

3 Results and discussion

3.1 Chemical structure of composite membranes

XRD patterns of all investigated (PVA/PVP, PVA/PVP/SiO2, PVA/PVP/Al2O3 and PVA/PVP/Al2O3/SiO2) composite membranes are shown in Fig. 1. It was noticed that, all samples have a polycrystalline structure except only PVA/PVP sample which exhibit an amorphous structure, as shown in Fig. 1a. The experimental data of XRD pattern of pure PVA/PVP sample agrees with the data published elsewhere [47]. Sharp compacted patterns started at 2θ = 16.5° to 25°, are observed in case PVA/PVP membrane corresponding to maximum intensity which confirm PVA/PVP blended formation. These results indicate that, the blends become more semi-crystalline with the increase of concentration of PVA in PVP [46].

![X-Ray diffraction of hybrid hydrogel membrane](image)

Fig. 1  X-Ray diffraction of hybrid hydrogel membrane; a PVA/PVP, b PVA/PVP/Al2O3, c PVA/PVP/SiO2 and d PVA/PVP/Al2O3/SiO2 of the cross-section of membranes were prepared on precleared glass plates by dip coating method
Figure 1b presents XRD pattern of PVA/PVP/SiO\textsubscript{2} composite membranes, this data shows four peaks with adding SiO\textsubscript{2} nano filler, where one sharp peak at $2\theta = 20^\circ$, while other three peaks are detected at $2\theta = 16.5^\circ$, $2\theta = 26.3^\circ$, and $2\theta = 66.5^\circ$. These peaks confirm the semi-crystalline behavior of PVA/PVP/Si\textsubscript{2}. Notably, it is noticed that SiO\textsubscript{2} incorporation significantly enhances the crystallinity degree of PVA/PVP membrane. The presented data in Fig. 1c and d) show XRD patterns of PVA/PVP/Al\textsubscript{2}O\textsubscript{3} and PVA/PVP/Al\textsubscript{2}O\textsubscript{3}/SiO\textsubscript{2} composite membranes. It is clear from the graphs that, incorporation of nano fillers enhance the degree of crystallinity of composite membranes. All peaks of SiO\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3} appear with the small FWHM and higher intensities than the pure PVA/PVP membrane. Also, X-ray data of prepared composite membranes are tabulated in Table 1, where the structure parameter shows the different structures for all analyzed samples. The structural of PVA/PVP is amorphous, however, PVA/PVP/Al\textsubscript{2}O\textsubscript{3} is orthorhombic; while both PVA/PVP/SiO\textsubscript{2} and PVA/PVP/Al\textsubscript{2}O\textsubscript{3}/SiO\textsubscript{2} exhibit a hexagonal structure.

| Membranes composition | Crystal system | Space group-Sg number | $a$ (Å) | $b$ (Å) | $c$ (Å) | $V$ ($10^6$ pm$^3$) | $\alpha$ | $\beta$ | $\gamma$ |
|-----------------------|----------------|-----------------------|--------|--------|--------|-----------------|--------|--------|--------|
| PVA/PVP               | Orthorhombic   | Cmcm (63)             | 2.8668 | 12.2230| 3.6907 | 129.32         | 90     | 90     | 90     |
| PVA/PVP/Al\textsubscript{2}O\textsubscript{3} | Orthorhombic   | Cmcm (63)             | 2.8668 | 12.2230| 3.6907 | 129.32         | 90     | 90     | 90     |
| PVA/PVP/SiO\textsubscript{2}               | Hexagonal      | P3221 (154)           | 4.8992 | 4.8992 | 5.3832 | 111.9          | 90     | 90     | 120    |
| PVA/PVP/Al\textsubscript{2}O\textsubscript{3}/SiO\textsubscript{2} | Hexagonal      | P3121 (152)           | 4.8678 | 4.8678 | 5.3658 | 110.11         | 90     | 90     | 120    |

![Fig. 2 SEM image of hybrid hydrogel membrane.](image)

a) PVA/PVP, b) PVA/PVP/Al\textsubscript{2}O\textsubscript{3}, c) PVA/PVP/SiO\textsubscript{2} and d) PVA/PVP/Al\textsubscript{2}O\textsubscript{3}/SiO\textsubscript{2} of the cross-section of membranes were prepared on precleared glass plates by dip coating method.

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composite membranes are displayed in Fig. 2. As seen, all investigated membranes have uniform surface structure, however the greatest grain size and porous surface structure is observed with PVA/PVP membrane, compared to three composite membranes groups, which is agree with X-Ray results. SEM images of PVA/PVP, PVA/PVP/SiO₂, PVA/PVP/Al₂O₃ and PVA/PVP/Al₂O₃/SiO₂ samples were investigated with different magnifications as shown in Fig. 2.

Figure 2a presented SEM image of PVA/PVP pristine blended membrane which exhibited homogeneous with porous surface structure, which ensures high miscibility of PVA with PVP in the blend. Also, SEM micrograph of PVA/PVP membrane is found to be in good agreement with the previous reports of ratio of 1:1 wt% PVA and PVP blend polymers [7, 40]. It is clear as in Fig. 2a–d that, the incorporation of small additive of nano-size of SiO₂ and Al₂O₃ particles exhibit a considerable variation in the surface of the sample PVA/PVP mixture matrix membranes. In addition to, it can be clear that incorporation of Al₂O₃ nanoparticles are uniformly distributed into PVA/PVP interior structure. This indicates a suitable polymer with nanoparticle collaboration verifying great compatibility between the organic and inorganic components in PVA/PVP membranes. For further evidence, the surface morphology of composite membranes became more uniform, smooth, pores less and compacted surface structure after incorporation of nano fillers (i.e., Al₂O₃

![Dependence of wavelength of UV/Vis spectra of transmittance, absorbance, absorbance, and reflection of PVA/PVP, PVA/PVP/Al₂O₃, PVA/PVP/SiO₂ and PVA/PVP/Al₂O₃/SiO₂](image)

Fig. 3  Dependence of wavelength of UV/Vis spectra of a transmittance, b absorbance, c absorbance, and d reflection of PVA/PVP, PVA/PVP/Al₂O₃, PVA/PVP/SiO₂ and PVA/PVP/Al₂O₃/SiO₂
and/or SiO₂), compared to surface morphology of pristine PVA/PVP membranes.

### 3.2 Optical and dielectric results of composite membranes

#### 3.2.1 Optical measurements

Optical properties including transmittance, reflectance and absorbance dependence on wavelength of tested composite membranes are shown in Fig. 3a–d. As seen in Fig. 3a, PVA/PVP membrane had the highest transmittance value at low wavelength (300–350 nm), compared to other three composite membranes. This may be due to that the grain size of PVA/PVP sample is smaller than PVA/PVP/SiO₂, PVA/PVP/Al₂O₃ and PVA/PVP/Al₂O₃/SiO₂ composite membranes. While, Fig. 3b shows the optical absorption spectra for PVA/PVP, PVA/PVP/SiO₂ and PVA/PVP/Al₂O₃ membranes. Where, PVA/PVP/Al₂O₃/SiO₂ shows the highest absorption values due to the coupled incorporation of both nano fillers of SiO₂ and Al₂O₃ in the polymeric matrix (Fig. 3c).

Figure 3d presents the reflectance of PVA/PVP, PVA/PVP/SiO₂, PVA/PVP/Al₂O₃ and PVA/PVP/Al₂O₃/SiO₂ composite membranes as a function of wavelength. It is noticed that, PVA/PVP/PVA/PVP/SiO₂, PVA/PVP/Al₂O₃ and PVA/PVP/Al₂O₃/SiO₂ composite membranes had almost the same behavior of reflectance, however PVA/PVP/Al₂O₃ exhibit the highest reflectance due to the leakage current of Al₂O₃ nanoparticles; meanwhile PVA/PVP/Al₂O₃/SiO₂ membrane shows the smallest values of reflectance. While, Fig. 3c shows the absorbance spectra for PVA/PVP/Al₂O₃/SiO₂ sample, it was observed from Fig. 3c that, PVA/PVP/Al₂O₃/SiO₂ membrane had the highest value of absorbance than other samples. This could be attributed to, PVA/PVP/Al₂O₃/SiO₂ sample membrane consists of two layers of PVA/PVP, with Al₂O₃/SiO₂ nanoparticles which improve the absorption of the applied photon energy. Also, we have used the transmittance and reflection data to calculate the absorption coefficient (α) of these

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**Fig. 4** Dependence of a ($\alpha$hv)$^2$ and b ($\alpha$hv)$^{0.5}$ on photon energy (hv) for PVA/PVP, PVA/PVP/Al₂O₃, PVA/PVP/SiO₂ and PVA/PVP/Al₂O₃/SiO₂. The dependence of c refractive index (n) and d extinction coefficient on photon energy of PVA/PVP, PVA/PVP/Al₂O₃, PVA/PVP/SiO₂ and PVA/PVP/Al₂O₃/SiO₂.

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investigated membranes using the Eq. (1) as follow [38]:

\[ \alpha = \left( \frac{1}{d} \right) \ln \left[ \frac{(1 - R)^2}{T} \right], \tag{1} \]

where \(d\) is the film thickness, \(R\) and \(T\) are the reflectance and the transmittance for these films. The optical energy gap \(E_g\) is determined from the absorption spectra curves using the empirical equation [39]:

\[ \alpha = A(hv - E_g)^p, \tag{2} \]

where \(A\) is a constant, \(E_g\) is the energy band gap, \(v\) is the frequency of the incident light and \(h\) is Planck’s constant. The constant \(P\) takes different values depending on the kind of optical transition of these films. \(P = 0.5\) for direct allowed transition (direct energy gap) and for indirect allowed transition the value of \(P\) will equal 2.

The absorption coefficient \((\alpha hv)^2\) dependence on photon energy \((hv)\) of tested composite membranes is shown in Fig. 4. The optical energy gap \(E_g\) was estimated from the extrapolation of the linear part of the curves in Fig. 4 for all membranes samples. It was found that, PVA/PVP membrane samples had an indirect band gap \((E_g\) of value \((2.24\ eV)\), while all other composite membranes with filled nano fillers \(i.e.,\) (PVA/PVP/SiO\(_2\), PVA/PVP/Al\(_2\)O\(_3\) and PVA/ PVP/Al\(_2\)O\(_3)/SiO\(_2\)) have direct energy band gap. Where, \(E_g\) for (PVA/PVP/SiO\(_2\), PVA/PVP/Al\(_2\)O\(_3\) and PVA/PVP/Al\(_2\)O\(_3)/SiO\(_2\)) composite membranes had direct band gaps at \((1.82, 2.55,\ and\ 1.95\ eV)\), respectively.

Interestingly, PVA/PVP/Al\(_2\)O\(_3)/SiO\(_2\) composite membrane displays the smallest value of energy band gap at \(1.95\ eV\), due to the large amount of incorporated nanoparticles of SiO\(_2\) and Al\(_2\)O\(_3\) in PVA/PVP matrix, which make sublevel between valance and conduction bands near fermi level. This means that, the type of additive nanoparticles or nano fillers in the tested membranes shows interesting role in alteration of band gap energy of tested composite membranes.

Both extinction coefficient and refractive index \((n)\) of membranes were calculated using the known empirical equations (Eqs. 1 and 2) [40]. Figure 4 shows the refractive index as function of the photon energy of tested membranes. Nevertheless, tested composite membranes had the similar behavior of the refractive index \((n)\) with photon energy, the \((n)\) values decrease with energy increases for the tested composite membranes. Notably, the composites
membranes have a value of \( (n) \) decreases with incorporation of nanoparticles, due to the leakage current appeared with adding metal oxide (Al\(_2\)O\(_3\)) [41]. Moreover, the extinction coefficient is almost constant with increasing the photon energy at lower energy less than 2.2 eV. However, at higher energy the values increase with increasing the photon energy, due to increasing the reflection coefficient of composite membranes.

### 3.2.2 Optical conductivity calculations

The dielectric constant \( (\varepsilon') \) and dielectric tangent loss \( (\varepsilon'') \) of tested composite membranes were calculated using the known impractical equations (Eqs. 3 and 4) [47]:

\[
\varepsilon' = (n^2 + k^2)
\]

\[
\varepsilon'' = \left( (n^2 + k^2) \right)^2 - \left( (n^2 + k^2)^{0.5} \right)
\]

Figure 5a and b shows both dielectric constant \( (\varepsilon') \) and dielectric loss \( (\varepsilon'') \) dependence of the photon energy for tested composites membranes. The values of the dielectric constants \( (\varepsilon') \) and \( (\varepsilon'') \) have been increased significantly as the photon energy increased for composite membranes. The dielectric constant \( (\varepsilon') \) of the sample doped with Al\(_2\)O\(_3\) (PVA/PVP/Al\(_2\)O\(_3\)) shows the highest value compared with other samples (PVA/PVP, PVA/PVP/SiO\(_2\), and PVA/PVP/Al\(_2\)O\(_3\)/SiO\(_2\)). In addition to the dielectric loss \( (\varepsilon'') \) of the (PVA/PVP/Al\(_2\)O\(_3\)) composite is higher than all other samples. This can be supposed that the dielectric structure is composed of high conductive grains separated by poor conducting thin grain boundaries, seems like capacitor. At higher photon energy, a localized accumulation of charges exhibited due to the interfacial polarization [46].

Figure 5c and d show the optical conductivity \( (\sigma_1) \) and imaginary part of the optical conductivity \( (\sigma_2) \) as functions of the photon energy for these membranes. The optical conductivity was estimated using the following equations [48-50].

\[
\sigma_1 = \frac{\varepsilon'' \cdot c}{2\varepsilon'}
\]

\[
\sigma_2 = \frac{(1 - \varepsilon') \cdot c}{4\varepsilon'}
\]

The behaviors of both \( (\sigma_1) \) and \( (\sigma_2) \) for all composites membranes is the same with \( (hv) \), by meaning that, while the values of \( (\sigma_1) \) and \( (\sigma_2) \) increases with the applied photon energies for all composite membranes. In addition to, optical conductivity increases in tested samples with additive of nanoparticles incorporation like Al\(_2\)O\(_3\). It is known that the aluminum oxide nanoparticle is conductor, while SiO\(_2\) is amorphas insulator. So, the optical conductivity of PVA/PVP/Al\(_2\)O\(_3\) membrane has higher conductivity values than that samples of PVA/PVP/SiO\(_2\) membrane.

### 3.3 Dielectric properties of composite membranes

The dielectric properties of PVA/PVP, PVA/PVP/SiO\(_2\), PVA/PVP/Al\(_2\)O\(_3\) and PVA/PVP/Al\(_2\)O\(_3\)/SiO\(_2\) composite membranes were measured as function of frequencies at room temperature. In Fig. 6a; it is...
noticed that the dielectric constant decreases with increasing the frequency from 100 Hz to 1 MHz. This is the typical behavior of PVA/PVP membrane with decreasing value of the dielectric constant with increasing frequency. The dielectric constant-value of the PVA/PVP samples decreased from 50,000 at frequency 100 Hz to 35,000 at frequency 1 M Hz. While sample with nanoparticle of Al2O3, the $\varepsilon''$-value (60,000) is higher than PVA/PVP sample (50,000), even the Al2O3 is metal. One can see here the dielectric constant-value of the sample with SiO2 nanoparticle. As in Fig. 6 (a), the relation between dielectric constant and frequency is linear decreeing and this is the behavior of dielectric materials. Moreover, the fast decreases at high frequency (10 kHz to 1 M Hz) is due to the motion of the dipole moment. It is knowing that the dipole moment cannot flow the rotation of the applied electric field, and the dipoles stop rotation and/or slow down their motion the dielectric constant decreased at high frequency 4445.

Figure 6b presented frequency-dependence imaginary part of the complex dielectric constant [dielectric loss ($\varepsilon''$)]. It is noticed that the dielectric loss value is higher at low frequency region (100 Hz–10 kHz), while with increasing frequency (f > 10 kHz), in this region the dielectric loss become small value and constant at high frequency. Further there is no effect of the frequency on all samples. All samples have nearly constant dielectric loss values and nearly constant with changing frequency. The behavior of the dielectric loss seems to be similar to dielectric materials, where at low frequency the dielectric loss value (0.2), with increasing the frequency, the loss decreased to be 0.02. This is the behavior of the insulator materials. Moreover, at higher frequency region (100 Hz–10 kHz) the dielectric loss is constant up to frequency 1 M Hz.

Figure 7 shows the resistance of the nanocomposites samples (M $\Omega$) as function of the frequency at room temperature. The resistance decreased rapidly with increasing frequency. The decreasing resistance with frequency means the electric conductivity increased linearly with frequency. So, the charges of the nanoparticles can move easily under the effect of the frequency. We notice that the resistance of the PVA/PVP/Al2O3/SiO2 sample is changed from 100 to 5 M $\Omega$ at higher frequency (1 MHz), this means that the SiO2 dominated the charge of Al2O3.

### 3.4 Mechanical properties of composite membranes

Mechanical properties of PVA/PVP, PVA/PVP/SiO2 and PVA/PVP/Al2O3 composite membranes are shown in Table 2. It was found that, PVA/PVP/SiO2 membrane shows the highest values of both Young’s Modulus and stress and the lowest both strain and extension, compared to PVA/PVP and PVA/PVP/Al2O3. As one can be observed that, SiO2 nanoparticles incorporation improve significantly mechanical strength of PVA/PVP membrane to fabricate nanocomposite membranes for device application.

| Sample name | Max Force (N) | Max stress (N/mm$^2$) | Max strain (%) | Max. displacement (mm) | Young’s modulus (MPa) | Elastic modulus (N/MM$^2$) |
|-------------|--------------|----------------------|----------------|------------------------|----------------------|---------------------------|
| PVA/PVP     | 48           | 30                   | 635            | 85                     | 277                  | 2.21                      |
| PVA/PVP/Al2O3 | 55          | 38                   | 459            | 66                     | 422                  | 4.2                       |
| PVA/PVP/SiO2 | 65           | 47                   | 422            | 69                     | 543                  | 4.95                      |
This might be due to the presence of –OH groups in PVA/PVP and their hydrophilic nature which are compatible with PVA. Further, PVA/PVP/SiO₂ membrane shows good nanoparticle/matrix bonding and exhibits high tensile strength and Young’s modulus with Al₂O₃ and SiO₂ incorporation into PVA/PVP membranes.

4 Conclusions

Metal oxides composite PVA/PVP blended membranes (PVA/PVP, PVA/PVP/Al₂O₃, PVA/PVP/SiO₂, and PVA/PVP/Al₂O₃/SiO₂) were successfully prepared and characterized on precleared glass plates by dip coating method. The series of obtained crosslinked hydride hydrogel membranes were successfully prepared using solution-casting technique. The samples were characterized for their eco-friendly green technology-based optoelectronic device applications. X-ray analysis and SEM investigation revealed that the structure of composite membranes with both Al₂O₃ and SiO₂ had a polycrystalline structure, grains with nano-sized and uniform nature of membranes. Also, the results of optical properties such as, optical band gap, refractive index and absorption coefficient were determined. Moreover, the dielectric and mechanical results were calculated for all these membranes. The experimental data shows the additive of nanoparticles composites have a direct energy band gap. Where, \( E_g \) for PVA/PVP/SiO₂, PVA/PVP/Al₂O₃ and PVA/PVP/Al₂O₃/SiO₂ at 1.82, 2.55, and 1.95 eV, respectively. While the sample PVA/PVP has an indirect band gap \( E_g \) of value 2.24 eV. Finally, the frequency-dependence of AC transport properties was investigated, and the results showed enhanced dielectric properties. The experimental data of membranes could be used as high-k layer in membranes transistors and optoelectronic devices.

Author contributions

1-All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by [AIA], [SAS] and [EAK]. The first draft of the manuscript was written by [AIA] and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript. 2. The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request. 3-The authors declare that no funds, grants, or other support were received during the preparation of this manuscript.

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Data availability

This work described has not been published before; that it is not under consideration for publication anywhere else; that its publication has been approved by all co-authors, if any, as well as by the responsible authorities—tacitly or explicitly—at the institute where the work has been carried out. The publisher will not be held legally responsible should there be any claims for compensation.

Declarations

Conflict of interest The authors declare that they have no conflict of interest. The submitted work is original and is not have been published elsewhere in any form or language. Authors are welcomed to suggest or comment from reviewers.

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