

Article

Enhancing the Structural, Optical, Thermal, and Electrical Properties of PVA Filled with Mixed Nanoparticles (TiO₂/Cu)

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Abstract: In this work, new samples of PVA-TiO₂/Cu nanocomposites were prepared via the casting method. The prepared samples were examined using different analytical methods. An XRD analysis showed the semi-crystalline nature of the PVA polymer, as well as showing a decrease in the degree of the crystallinity of the PVA structure as a result of the addition of the mixed nanoparticles. TEM images indicate the spherical shape of the Cu NPs, with a size ranging from 2 to 22 nm, and the rectangular shape of the TiO₂ NPs, with a size ranging from 5 to 25 nm. It was evident via FTIR measurements that there were interactions between the functional groups of the PVA and the TiO₂/Cu NPs. The optical properties of the PVA nanocomposites were improved with an increase in the content of the TiO₂/Cu nanoparticles, as shown via a UV/Vis analysis. DSC curves showed an improvement in the thermal stability of the PVA-TiO₂/Cu nanocomposites after the embedding of the TiO₂/Cu nanoparticles. It was evident using impedance spectroscopy that the AC conductivity was improved by adding the TiO₂ and Cu nanoparticles to the polymeric matrix. The maximum AC conductivity was found at 1.60 wt.% of TiO₂/Cu nanoparticles in the PVA polymer, and this was 13.80×10^{-6} S/cm at room temperature. Relaxation occurred as a result of the charge carrier hopping between the localized state and the correlated barriers hopping model, describing the dominant mechanism, as presented in an electrical modulus analysis. These results indicate that the PVA-TiO₂/Cu nanocomposite samples can be used in energy storage capacitor applications and in the alternative separator-rechargeable lithium-ion battery industry.

Keywords: TiO₂/Cu nanoparticles; PVA; SEM; DSC; AC conductivity; dielectric parameters



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1. Introduction

Recent years have seen a rise in the use of nanocomposite materials in scientific research, with the promotion of physical properties and changes in energy storage technologies as essential components for practical applications. The current applications of nanocomposites include high-energy batteries, fuel cells, microwave absorbers, optoelectronics, gas sensors, and UV filters [1,2]. Many microelectronic devices require flexible, lightweight, dielectric/conductive polymer materials. By adding a few nanofillers, electrical conduction networks can be successfully formed in insulating polymers, leading to better optical and thermal properties [2–4]. Conductivity increases dramatically when conducting nanofillers, such as metallic nanoparticles and carbon nanotubes, are added to the polymeric matrix over a percolation threshold. Percolation occurs due to the growth of three-dimensional conductive channels in the polymer materials [1,3]. As with polymeric nanocomposites, they must be constantly studied in order to improve their electrical conductivity at low filler concentrations. Polyvinyl alcohol (PVA) is one of the most frequently

used host polymer materials because of its unique features, which include its perfect foil shape, excellent biocompatibility, optical transparency, high flexibility, and provision of H bonds to create complexes via the trapping of ions and NPs [3,5]. PVA is a polar polymer with OH bonded to methane carbons via a carbon chain backbone. PVA has strong dielectric features, a good charge storage capacity, and doping-dependent optical and electrical properties [3,6]. Due to its good optical features and ability to create oxygen barriers, it is considered an ideal candidate for use in multilayer coatings of solar cell applications [7]. Copper nanoparticles (Cu NPs) have recently gained more attention and have been extensively researched due to their tunable optical, electrical, magnetic, and catalytic capabilities. Cu NPs have improved nonlinear optical features, which gives them wide applications in optical devices and nonlinear optical applications. As a result of its excellent conductivity, low cost, and good biocompatibility, copper will become increasingly more significant as a necessary component in future nanodevices [8,9]. Titanium dioxide nanoparticles (TiO₂ NPs) have also drawn a lot of attention in recent years due to their outstanding biocompatibility, optical properties, corrosion resistance, and extraordinary electrochemical and catalytic abilities. TiO₂ properties are heavily influenced by non-structural characteristics, such as shape, crystal sizes and phases, aspect percentage, and distribution density [10,11]. TiO₂ NPs have been found to be excellent candidates as Li-ion hosts due to them being good capacity fillers with a low cost and harmless properties [11]. Conductive nanofillers are routinely added to the electrodes of lithium-ion batteries in order to construct a conductive percolation network [10]. As a result, many scientists are concerned with studying the chemical and physical properties of PVA nanocomposites doped with copper or TiO₂. Ali et al. [12] studied the radiation-induced synthesis of Cu/PVA nanocomposites and their catalytic activity. Nasar et al. [13] prepared Cu-PVA nanocomposites at different nanocompositions. An impedance analyzer displayed that the Cu NPs increased AC conductivity when increasing their concentration. It was suggested that Cu-PVA nanocomposites can be used in charge storage applications. Abdallah et al. [14] studied PEO/CMC/Cu NP nanocomposites, and they observed improvements in the dielectric and magnetic properties of filled samples, making these nanocomposites important materials for use in energy storage and nanoelectronic smart devices. El-Desoky et al. [15] studied the synthesis and the structural and electrical features of PVA/TiO₂ nanocomposites made using the sol–gel method in various TiO₂ phases. Ferdowsi and Mokhtari [16] prepared PVA/CdS and PVA/TiO₂ nanocomposites via the electro-spinning method as n-type semiconductors, and they observed that a sample with a ratio of 50:50 of PVA/CdS and PVA/TiO₂ is the best for use as a layer in solar cells due to its favorable optical energy gap (~2.53 and 3.31 eV).

In recent research, the casting method has been used to produce flexible, very light, polymeric samples with better electrical characteristics for use in electronics. TiO₂ and Cu nanoparticles are used as conductive nanofillers in this work, with PVA used as the host polymeric matrix. A comprehensive investigation of this system's structural and optical characteristics is discussed using a number of techniques and procedures.

2. Experimental Section

2.1. Materials

The following materials were used:

PVA was supplied from Mallinckrodt USA (molecular weight (M.W.) of 20,000 g/mol), and Cu NPs were supplied from Sigma/Aldrich (Missouri, MO, USA.). Titanium (IV) tetraisopropoxide [Ti(O-CH(CH₃)₂)₄] was purchased from Merck (Darmstadt, Germany). Nitric acid and NaOH were purchased from El-Nasr Co. Egypt (Cairo, Egypt). Double-distilled deionized water (DDW) was used as a solvent.

2.2. Preparation of TiO₂ NPs

The TiO₂ NPs were prepared using the following steps:

First, the sol–gel method was used to prepare the TiO₂ NPs by diluting titanium (IV) tetraisopropoxide in order to determine the amount of glacial acetic acid. Then, an

additional amount of DDW was added in order to obtain a clear glutinous solution with continuous stirring for 6 h. Next, we kept the solutions in the dark for 24 h so that the nucleation operation could be completed. Then, the solution was dried for 14 h at 130 °C in order to obtain the TiO₂ crystal. Finally, the solution was grinded and calcined for 4 h at 600 °C in order to obtain the TiO₂ NPs.

2.3. Preparation of PVA-TiO₂/Cu Nanocomposite Electrolytes

Nanocomposite samples were prepared using the casting method. PVA was dissolved by stirring in DDW for 8 h at 50 °C to obtain a clear solution. Then, the determined concentrations, 0.00, 0.20, 0.40, 0.80, and 1.60 wt.%, of the TiO₂ NPs and Cu NPs (50/50 wt.%) were embedded into the PVA solutions with continuous stirring for 3 h at 50 °C. Finally, the nanocomposite solutions were transferred to Petri dishes at 50 °C for 48 h in order to remove the solvent traces.

2.4. Characterization Analysis Instruments

The XRD patterns of the PVA-TiO₂/Cu nanocomposites were examined using a PANalytical XPert PRO/XRD diffractometer with CuK α radiation ($\lambda = 1.540 \text{ \AA}$). A TEM of model JEOL-JEM-1011 was used to calculate the size and shape of the TiO₂ NPs and Cu NPs. FTIR of the PVA-TiO₂/Cu in the wavenumber range of 400–4000 cm^{−1} was obtained using a JASCO/Nicolet/iS10 (Easton, MD, USA) spectroscope. The UV/Vis data of the nanocomposite films were examined using a JASCO/630 (Tokyo, Japan) spectrophotometer in the wavelength range of 200–900 nm. SEM images of the nanocomposite samples were examined via a scanning electron microscope (JEOL/JSM-5500) with 20 kV at a magnification of 5000 times. The thermal features of the polymeric samples from room temperature to 500 °C were tested via a Netzsch DSC 200 analyzer (Bayern-Germany). The AC electrical examinations of the PVA nanocomposites were carried out utilizing a programmable automatic Hioki 3531Z-Hitester with the Novocontrol Turnkey Concept 40 System between 0.1 Hz and 20 MHz at an oscillation voltage of 1.0 V in nitrogen gas at ambient temperature. The polymeric samples were fixed between two electrodes in the sample holder and placed in a cryostat.

3. Results and Discussion

3.1. XRD Analysis

The XRD spectra of the PVA filled with the TiO₂ and Cu nanoparticles are shown in Figure 1. The XRD spectra of the TiO₂ NPs shows the distinct peaks at $2\theta = 25.4^\circ, 36.1^\circ, 46.9^\circ, 53.9^\circ, 55.0^\circ$, and 62.3° , corresponding to the planes {101}, {004}, {200}, {105}, {211}, and {204}, respectively (JCPDS Card number 21-1276) [7]. These peaks confirm that the TiO₂ NPs have an anatase structure. In contrast, the pattern of the Cu NPs reveals diffraction peaks at $2\theta = 43.2^\circ, 50.4^\circ$, and 73.9° , corresponding to the planes {111}, {200}, and {220}, respectively (JCPDS Card number 04-0836) [12].

The crystallite sizes (D) of the Cu NPs and TiO₂ NPs were measured using Scherrer's relation [17]:

$$D = k\lambda/B\cos\theta \quad (1)$$

where k is a constant ($k = 0.94$), λ represents the XRD wavelengths, B is the line width at the half-maximum of the peak intensity, and θ is the diffraction angle.

The average crystallite size of the TiO₂ nanoparticles was 17 nm, while that of the Cu nanoparticles was 15 nm.

Figure 2 displays the XRD for the filled and unfilled PVA with different concentrations of the mixed nanoparticles (TiO₂ NPs and Cu NPs). PVA exhibits a prominent broad peak at $2\theta \approx 19.4^\circ$, which is assigned to the semicrystalline nature of the PVA matrix [18]. After filling, the crystallinity of the nanoparticles increases at the expense of the PVA polymer, as can be observed in the patterns of the doped nanocomposites. The interplay between the polymer and the fillers, which reduces the intermolecular interactions between the polymer chains and lowers the degree of crystalline growth, is the cause of the decrease in

the PVA peak after increasing the Cu and TiO₂ nanofiller content. Moreover, the positions of the hybrid nanoparticle peaks do not change with an increase in the nanoparticle content within the polymeric matrix, which confirms the complexation between the PVA polymer and the TiO₂ and Cu nanoparticles within the amorphous structures. Moreover, the XRD scans do not show obvious changes in the lattice constant of the nanoparticles, but the crystallite size varies slightly after adding the nanofiller to the polymeric matrix [15,19]. This enhancement of the amorphous structures of the nanocomposites samples confirms the compatibility and usefulness of Cu NPs and TiO₂ NPs as fillers in PVA, and it may lead to higher charge carrier mobility and AC conductivity [19]. The crystallinity ratio (Xr ratio) may be calculated via the Hermans–Weidinger method [20]:

$$\text{Xr \%} = \frac{(\text{Area under crystalline peaks})}{(\text{The total area under all peaks})} \times 100 \quad (2)$$

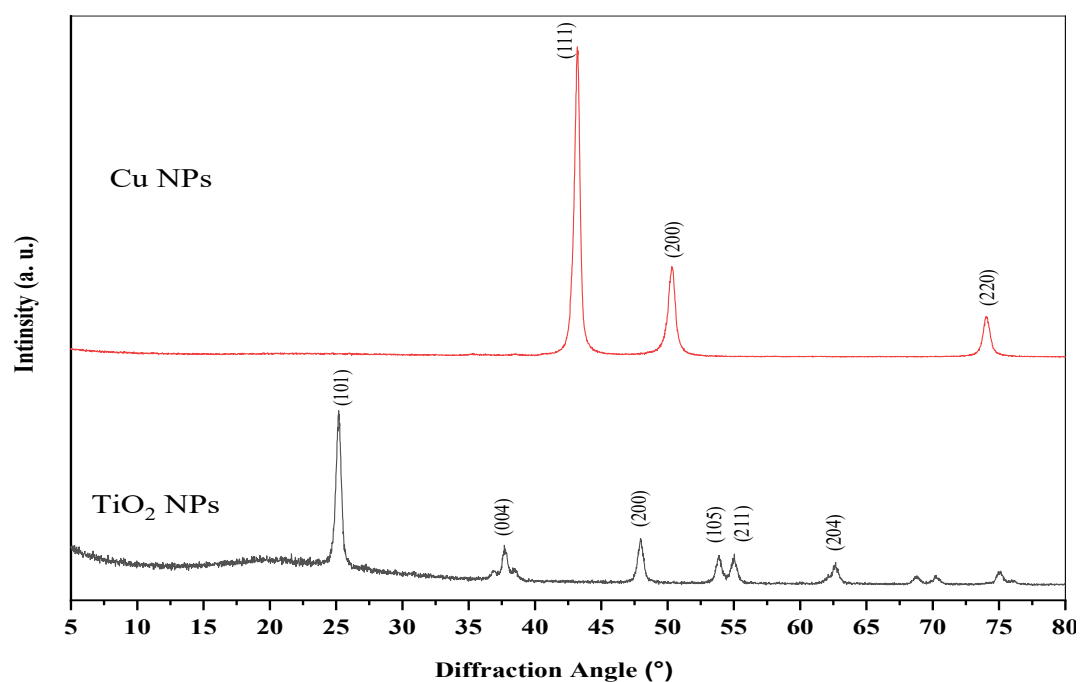


Figure 1. XRD spectra of pure titanium dioxide nanoparticles (TiO₂ NPs) and pure copper nanoparticles (Cu NPs) and their corresponding (hkl) planes.

In Table 1, it can be seen that the proportion of Xr is decreased (a decrease in the intensity of the main peaks of the PVA), which indicates that the addition of the Cu NPs and TiO₂ NPs increases the amorphous structure of the nanocomposite samples; this is due to the production of more defects in the PVA structure, and the crystalline phases of the PVA matrix are broken due to polymer–nanoparticle interactions [16]. The presence of the characteristic peaks of the hybrid nanoparticles qualitatively reveals that the doped nanoparticles occur homogeneously within the PVA structure [15,16].

Table 1. The crystallinity degree of the polymeric samples and crystallite sizes of TiO₂ and Cu NPs.

Samples	Sample Crystallinity (%)	Crystal Size of TiO ₂ (Corresponding to the Peak at 25.4°)	Crystal Size of Cu (Corresponding to the Peak at 43.2°)
Pure PVA	27.41	-	-
PVA/0.20% of (TiO ₂ /Cu)	21.16	-	24.14
PVA/0.40% of (TiO ₂ /Cu)	17.51	36.90	22.65
PVA/0.80% of (TiO ₂ /Cu)	10.08	18.78	19.24
PVA/1.60% of (TiO ₂ /Cu)	5.44	19.79	19.23

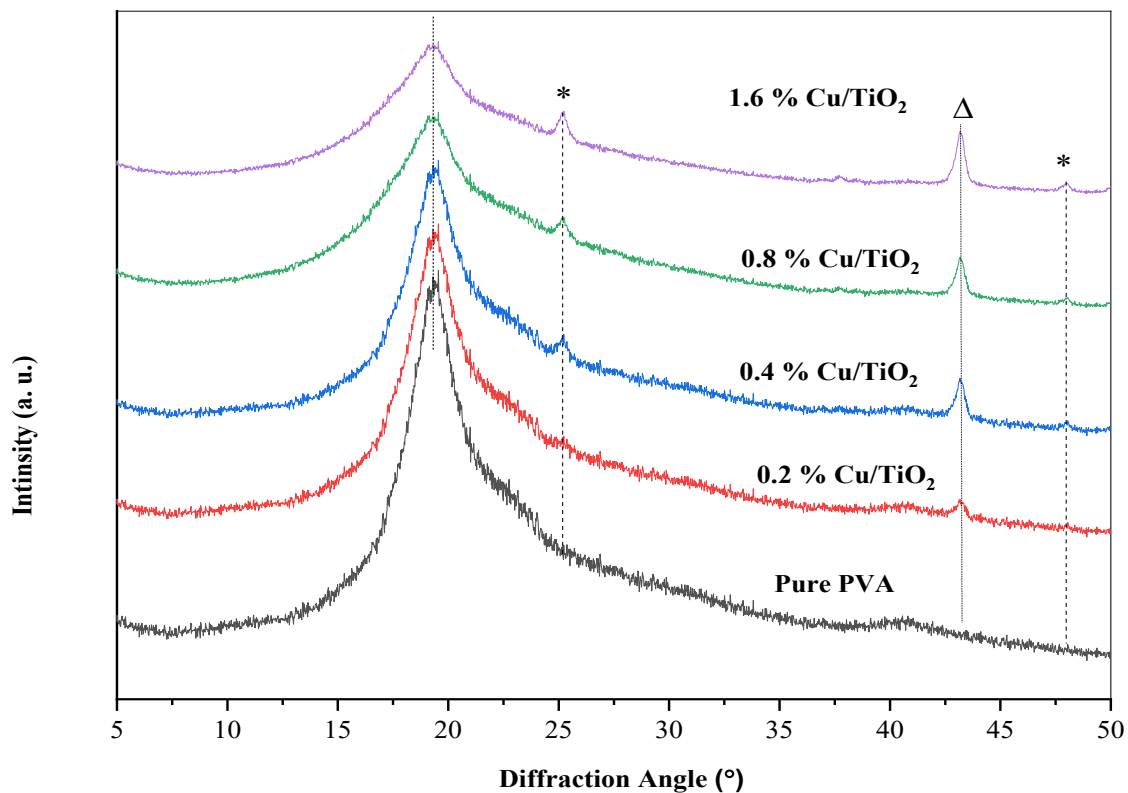
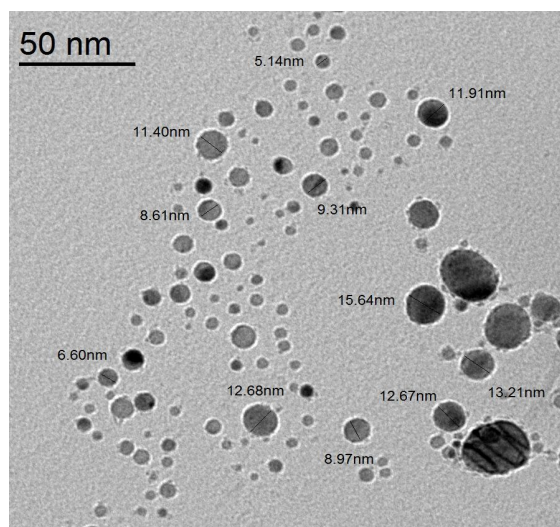


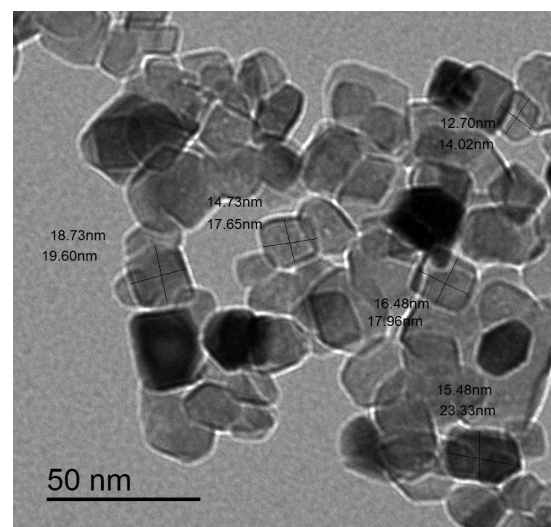
Figure 2. XRD patterns of pure PVA and PVA doped with different concentrations of the hybrid nanoparticles (TiO_2 NPs and Cu NPs). The phases of the TiO_2 NPs and Cu NPs are indicated by * and Δ , respectively.

3.2. TEM Micrographs

Transmission electron microscopy (TEM) was used to determine the size and shape of the produced nanoparticles. Figure 3a depicts the TEM image and the corresponding histogram of the Cu NPs, revealing that the nanoparticles are generally spherical, randomly dispersed, and have diameters ranging from 2 to 22 nm [14], whereas Figure 3b depicts the TEM image and the corresponding histogram of the TiO_2 NPs, which have a rectangular shape with lengths ranging from 5 to 25 nm [21,22].



(a)



(b)

Figure 3. Cont.

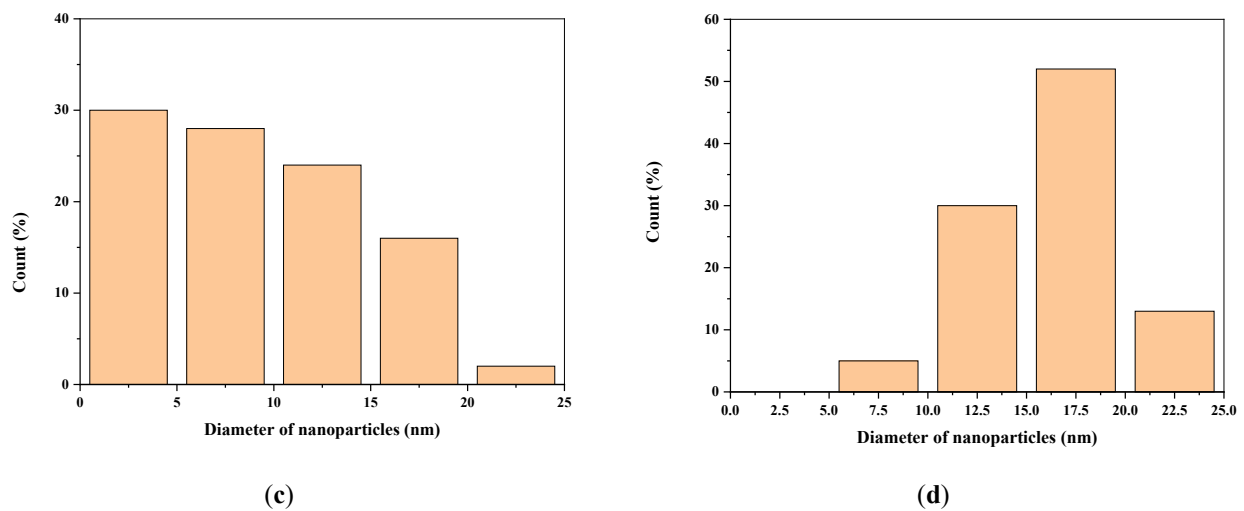


Figure 3. TEM images of (a) Cu nanoparticles and (b) TiO₂ nanoparticles and the corresponding histograms of diameter distribution of (c) Cu nanoparticles and (d) TiO₂ nanoparticles.

3.3. Fourier Transform Infrared (FTIR)

Figure 4 shows the FTIR spectra of the unfilled and filled PVA with different concentrations of the Cu NPs and TiO₂ NPs. The spectra of the PVA nanocomposites indicate the typical bending and tensile vibration peaks of the functional groups observed in the produced samples. The peak positions of the FTIR spectra and their assignments to the PVA-TiO₂/Cu NPs samples are recorded in Table 2. For the pure PVA, the bandwidth at around 3475 cm^{−1} is attributed to the stretching vibrations of PVA's OH [6,18]. The bands at 2942 cm^{−1} and 2908 cm^{−1} are ascribed to CH₂ asymmetric and symmetric stretching vibrations, respectively [23,24]. The absorption peaks at 1658, 1563, and 1428 cm^{−1} are assigned to C=C stretching, CH bending, and CH₂ symmetrical bending, respectively. The band at 1094 cm^{−1} is due to the C–O stretching of the carbonyl groups existing in the PVA backbone. The band at 852 cm^{−1} corresponds to the C–C stretching vibration. The band at 665 cm^{−1} corresponds to the wagging mode of the (OH) group, whereas the band at 918 cm^{−1} corresponds to CH₂ rocking, and the band at 1331 cm^{−1} relates to (CH₂OH) bending [6,24].

Table 2. Peak positions of the FTIR spectra and their assignments for PVA polymer.

Wavelength (cm ^{−1})	Band Assignments	Ref.
3475	O-H Stretching	[6,15]
2942	CH ₂ Asymmetric Stretching	[20,21]
2908	CH ₂ Symmetric Stretching	[20,21]
1658	C=C Stretching	[15,20,21]
1563	O-H & C-H Bending	[24]
1428	CH ₂ Symmetric Bending	[20]
1376	CH ₂ Wagging	[20,21]
1331	(CH+OH) Bending	[6,20]
1240	C-H Wagging	[24]
1138	C-C Stretching	[21]
1094	C-O Stretching	[20,24]
918	CH ₂ Rocking	[20,24]
852	C-C Stretching	[20,24]
665	O-H Wagging	[6,24]
478	C-O Bending	[20,24]
421	C-O Wagging	[24]

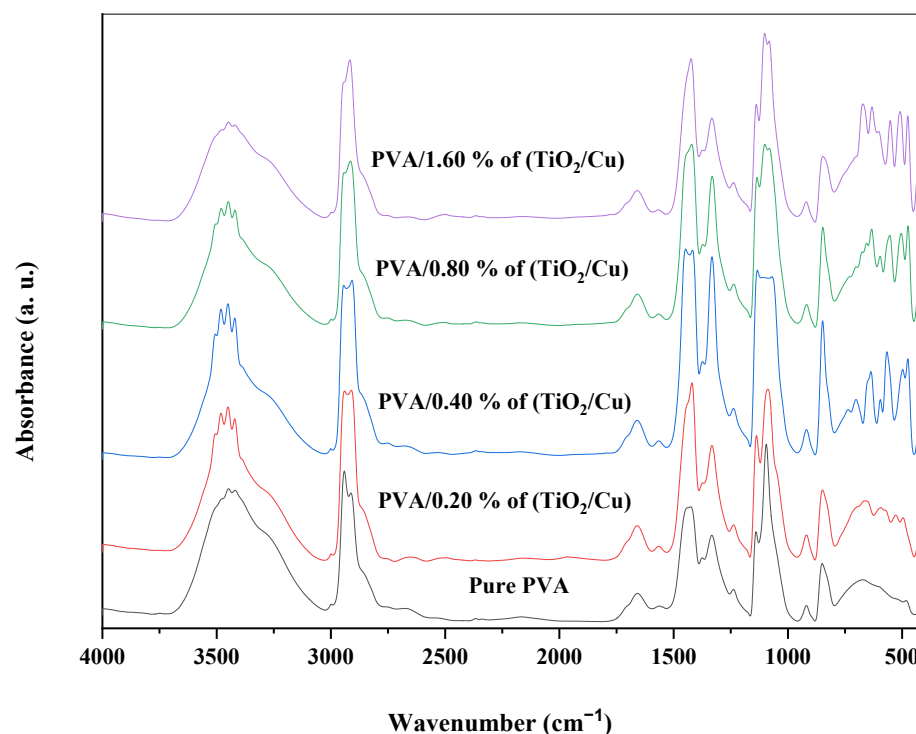


Figure 4. FTIR spectra of pure PVA polymer doped with different concentrations of TiO_2/Cu nanoparticles.

The spectra of the PVA filled with different contents of the Cu NP and TiO_2 NP films show properties that are the same as those of the pure PVA, but the intensities of the peaks are different. The intensity of the absorption peak at 3475 cm^{-1} corresponding to the OH-stretching vibration range is reduced compared to that of the pure PVA. This also demonstrates the possibility of a coordination reaction of the OH group of the PVA with the Cu NPs and/or TiO_2 NPs [12]. Moreover, the several new peaks appearing at 500 to 700 cm^{-1} are assigned to the characteristic vibrations of the Ti-O-Ti lattice in the TiO_2 NPs [25,26]. These results confirm that there are interactions between the structures of the TiO_2/Cu NPs and the PVA in the investigated nanocomposites. As can be seen in the FTIR spectra, the TiO_2/Cu NPs filled in the PVA appear to play a role in the physical limitations of the polymeric chain, resulting in some changes in the degree of crystallinity, molecular packing, and this polymer.

3.4. UV/Visible Absorbance

Figure 5 presents the UV/visible spectra of the prepared polymeric samples. The PVA spectra display an edge in the UV region at 207 nm , which may be caused by the $n \rightarrow \pi^*$ transition. After filling, the UV/visible spectra show four absorption peaks at the wavelengths of 246 , 299 , 397 , and 516 nm (due to the TiO_2 nanoparticles). The bands with shorter wavelengths (246 and 299) are assigned to the ligand-centered charge transfer (LCCT) transitions of the double bond ($\pi - \pi^*$), while the longer wavelength bands (397 and 516 nm) can be assigned to the metallic/ligand charge transfer (MLCT) transitions ($4d - \pi^*$) [27,28]. The presence and shift of such peaks might be assigned to the polymeric matrices' interactions/complexation behavior with the integrated Cu NPs and TiO_2 NPs, which affect the expected optical band gap. Tauc's famous Equation [29], which depicts the spectra dependence of the absorption coefficient near the edge, can be used to determine the optical gaps (E_g s) as follows:

$$\alpha = \frac{B(h\nu - E_g)^r}{h\nu} \quad (3)$$

where $h\nu$ is the photon energy, and B is the probability constant for the transition of the electrons. For the allowed indirect or direct transitions, the power r assigned to the transition behavior is approximately equal to $1/2$ or 2 , respectively.

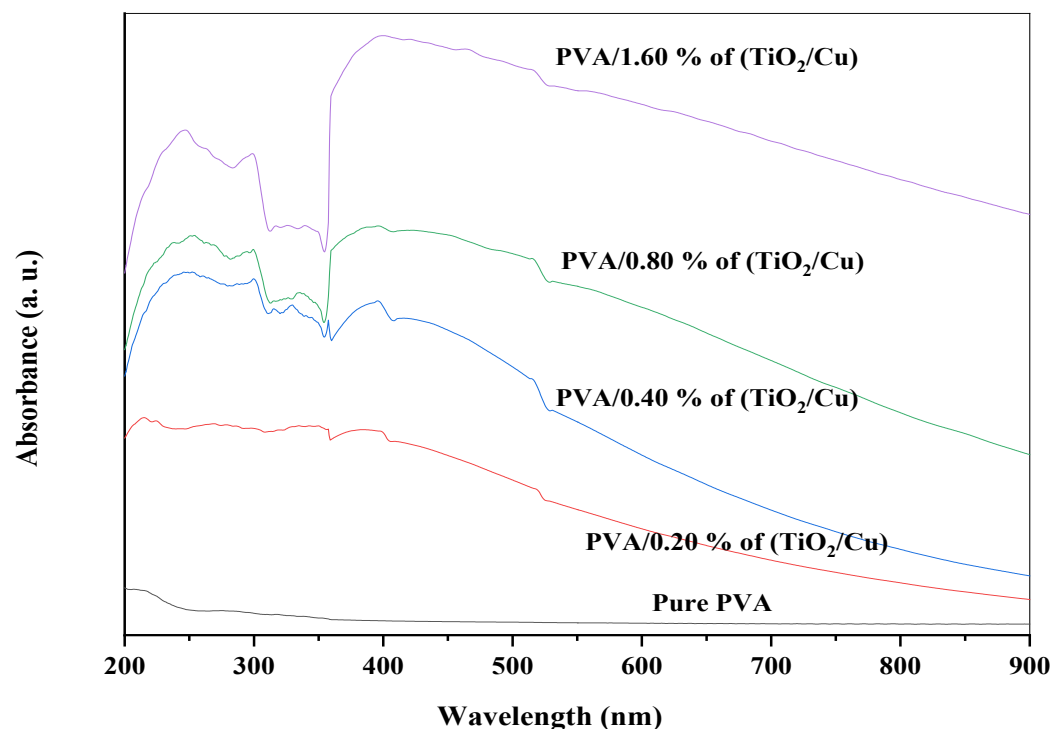


Figure 5. UV/vis spectra of PVA doped with different concentrations of TiO_2/Cu nanoparticles.

Figures 6 and 7 provide plots of $h\nu$ vs. $(\alpha h\nu)^2$ and $(\alpha h\nu)^{1/2}$ for the produced films. The optical energy gap values are reported in Table 3. When the PVA is doped with the Cu NPs and TiO_2 NPs, E_g decreases, which is assigned to the ability of the Cu NPs and TiO_2 NPs to modify electronic structures by forming various polaronic and impurity concentrations that increase with the density of localized states [29]. It has also been proven that the density of localized states is proportional to the concentration of such impurities and, thus, to the concentrations of Cu NPs and TiO_2 NPs. Increasing the content of Cu NPs and TiO_2 NPs can lead to a widening of the mobility gap between the different color centers. This overlap may be proof that E_g reduces as the Cu NP and TiO_2 NP ratio in the PVA increases. As shown in the Figure, the presence of the TiO_2/Cu NPs within the PVA polymer causes the jumping of the electrons in the valence band to the conduction band with the generation of more structural impurities and localized states in the forbidden band, thus decreasing the optical energy values of these doped films [21,30]. These results are in agreement with the XRD and electrical conductivity data. These enhancements of the optical energy values of the doped films indicate their suitability for electrochemical and opto-electronic applications.

Table 3. The indirect and direct optical energy gap values for PVA-Cu/ TiO_2 NP nanocomposites.

Samples	E_{gi} (inirect) (eV)	E_{gd} (direct) (eV)
Pure PVA	4.50	5.35
PVA/0.20% of (TiO_2/Cu)	2.82	4.17
PVA/0.40% of (TiO_2/Cu)	2.18	3.34
PVA/0.80% of (TiO_2/Cu)	2.04	3.24
PVA/1.60% of (TiO_2/Cu)	1.71	3.12

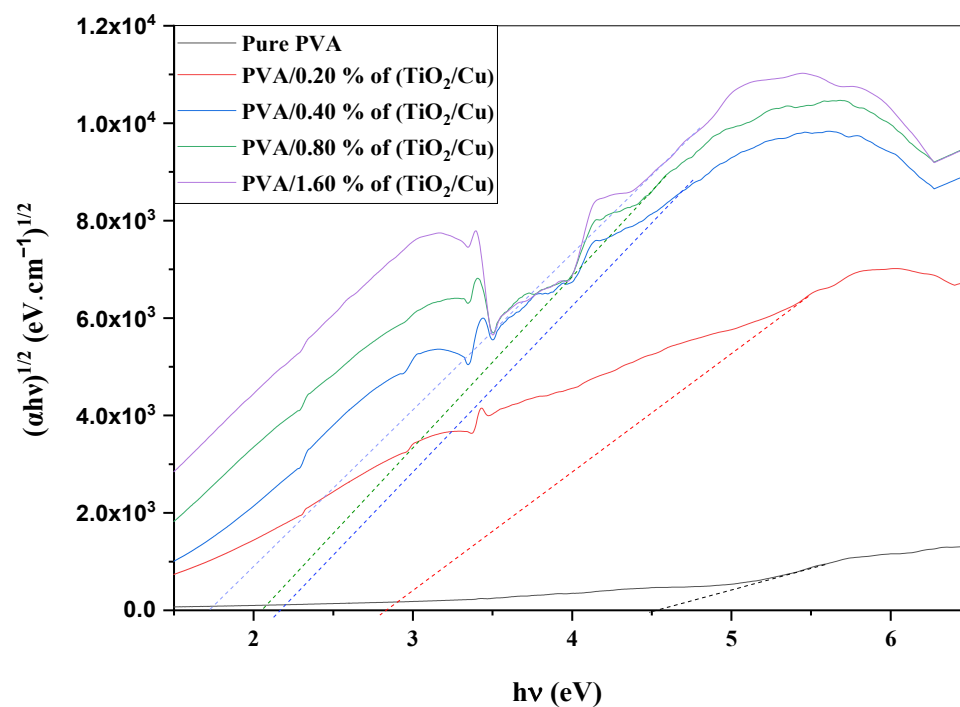


Figure 6. Plot of $(\alpha h\nu)^{1/2}$ versus $h\nu$ of PVA filled with various concentrations of TiO_2/Cu nanoparticles.

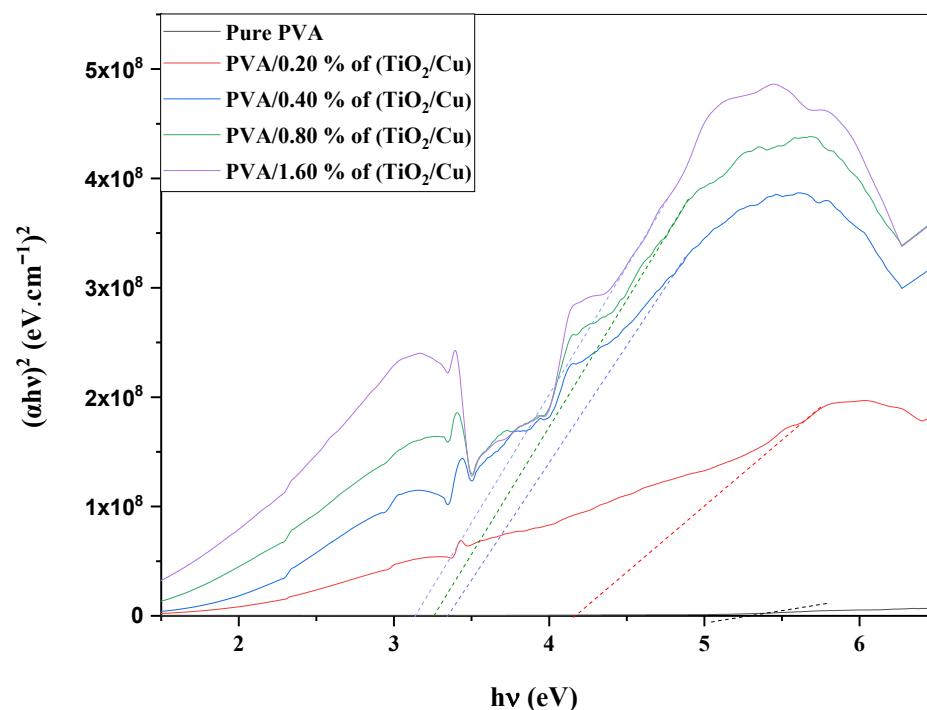


Figure 7. Plot of $(\alpha h\nu)^2$ versus $h\nu$ of PVA filled with various concentrations of TiO_2/Cu nanoparticles.

3.5. Morphology and Dispersibility of PVA-Cu/TiO₂ Nanocomposites

In order to investigate the micro-/nano-filler distributions within the nanocomposite samples, SEM images were obtained. The SEM images of the pure sample and the nanocomposite samples are shown in Figure 8. In Figure 8b,c, it can be observed that the Cu/TiO_2 nanoparticles are homogeneously dispersed in the polymeric samples. It is interesting to note that, during the preparation of the PVA-Cu/TiO₂ nanocomposite samples, morphological changes of PVA were observed [31]. The SEM micrographs of

the doped samples exhibit white granules and randomly dispersed groups of granules on the samples' surfaces. Moreover, in these images, it can be observed that Cu and TiO₂ are well-distributed on the samples' surfaces [32,33]. Furthermore, it is indicated that the modified Cu/TiO₂ nanofillers have excellent adhesion and strong interfacial bonding to the polymeric matrix. At higher concentrations of the Cu/TiO₂ nanoparticles, as shown in Figure 8d,e, the aggregation of granules can be observed on the samples' surfaces due to the complexation between the filler NPs and the polymer [14]. These morphological changes in the PVA indicate nanofiller–polymer interactions, showing that the nanocomposite components of the polymeric samples are compatible [34,35].

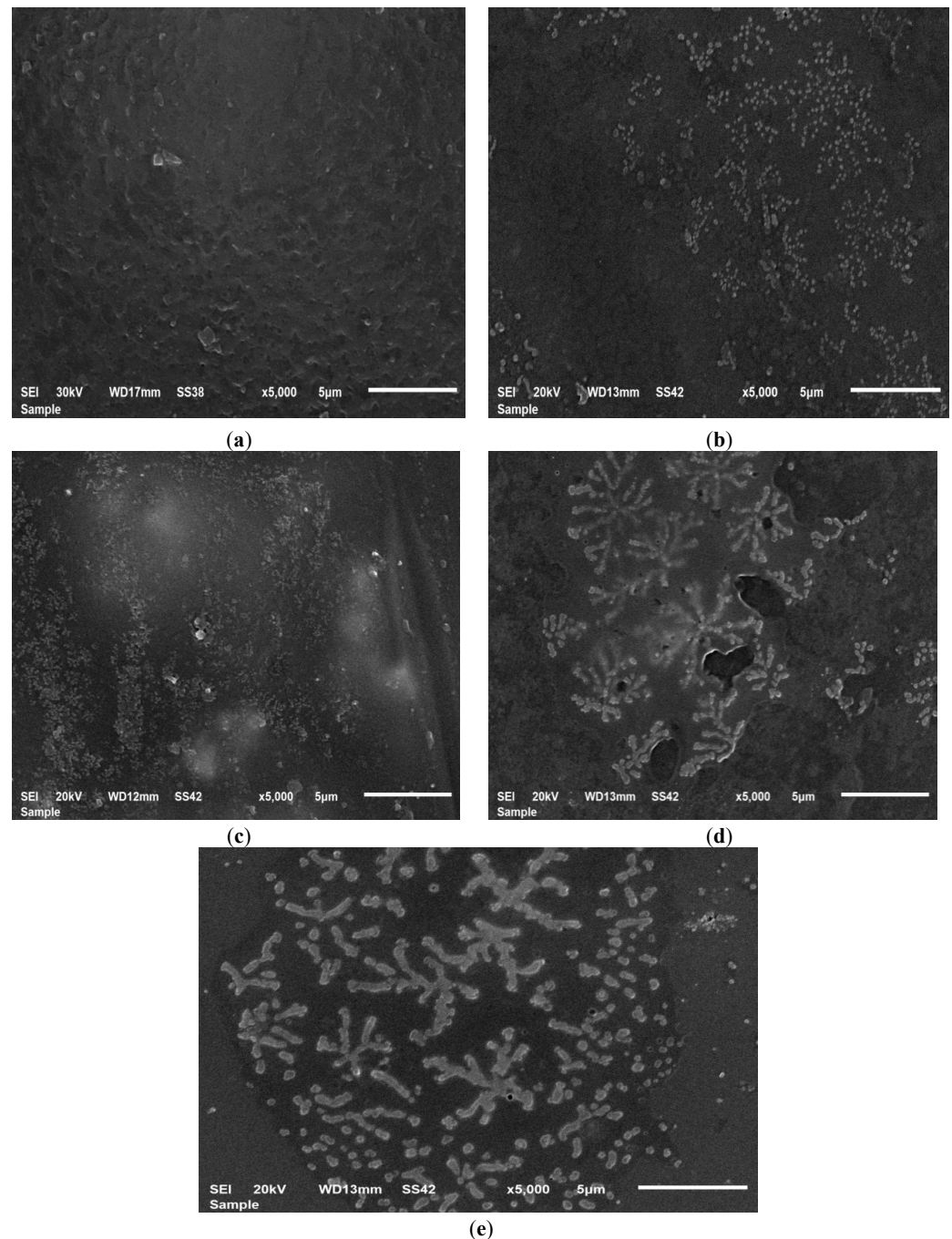


Figure 8. SEM images of the surfaces of (a) pure PVA and its complexes doped with different concentrations of TiO₂/Cu nanoparticles, that is, (b) 0.20, (c) 0.40, (d) 0.80, and (e) 1.60 (wt.%), at magnification of 5000 times.

3.6. DSC Analysis

The thermal features of the present electrolyte nanocomposites were calculated by using a DSC instrument to determine the thermal transitions [35,36]. The DSC spectra of the PVA-Cu/TiO₂ nanocomposite samples are shown in Figure 9. The thermogram of the pure PVA exhibits an endothermic peak near 83.85 °C, which was attributed to the glass transition temperature (T_g). The melting point temperature (T_m) and the decomposition temperature (T_d) of the pure PVA polymer show peaks at 227.08 and 300.49 °C, respectively. These three thermal transitions of all the polymeric samples are listed in Table 4. Based on these curves, the increase in the T_g values of the doped films indicates an increase in the stiffness of the polymer chains, and the average molecular weight of the PVA structure increased in the disorder region [37,38]. Moreover, these redshifts of the T_g and T_d positions to a higher temperature of the PVA-TiO₂/Cu NPs films indicate that the embedded TiO₂/Cu NPs caused the enhancement of the thermal stability of the PVA samples, reflecting the establishment of strong intermolecular interactions between the TiO₂/Cu NPs and the structure of the PVA, as displayed in the FTIR spectra. The lower T_m of the polymeric sample filled with 1.60 wt.% TiO₂/Cu NPs is associated with the lower surface free energy of spherulites [3,4]. The T_d position shifted to a higher temperature, indicating the presence of intermolecular interactions between the PVA matrix and the hybrid nanoparticles. The presence of these interactions was confirmed via the results of the XRD and FTIR analyses [4]. In addition, this thermal enhancement was due to the good dispersion of the TiO₂/Cu NPs and the increased degree of the amorphous ratio; this indicates that the increased resistance of the PVA to thermal oxidation was due to the cross-linking with the TiO₂/Cu NPs, which requires additional thermal energy for thermal transitions [37,39]. Thus, the DSC curves suggest that TiO₂/Cu NP-loaded PVA polymer has an overall enhanced thermal stability.

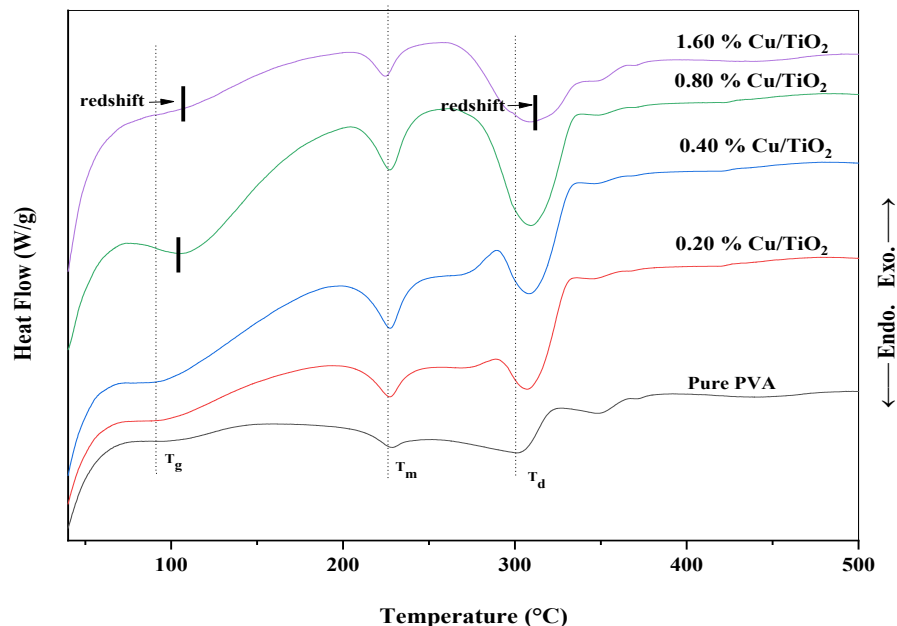


Figure 9. DSC curves of PVA filled with various contents of TiO₂/Cu NPs.

Table 4. T_g , T_m , and T_d for PVA doped with different concentrations of Cu/TiO₂ nanoparticles.

Polymeric Samples	T_g (°C)	T_m (°C)	T_d (°C)
Pure PVA	83.85	227.08	300.49
PVA/0.20 wt.% NPs	88.91	227.76	306.32
PVA/0.40 wt.% NPs	92.59	227.76	307.77
PVA/0.80 wt.% NPs	105.70	227.08	309.91
PVA/1.60 wt.% NPs	108.61	225.62	311.37

3.7. AC Conductivity

Figure 10 shows the variation in the AC conductivity as a function of frequency at room temperature (RT) for all the PVA-TiO₂/Cu NPs samples. The AC conductivity change can be used to examine the process of polymer/nanocomposite relaxations. An important frequency difference in the AC conductivity of the pure PVA and the nanocomposite samples was found with the external electrical field and the TiO₂/Cu NPs concentrations at RT. The lower frequencies were observed via the impedance of space charges at the electrode and electrolyte interfaces of the electrolytes. The calculation of the AC conductivity of the polymeric films was carried out by identifying the bulk resistance values with the thickness (d) and area (A) of the film, using the following equation [40]:

$$\sigma_{ac} = 1/\rho \quad (4)$$

where ρ is the electrical resistivity. As ions can remain for a relatively long time at low frequencies, there is more charge accumulation at the electrode/electrolyte interface. This delays the movement of the ions and, thus, lowers the conductivity. At higher frequencies, the AC conductivity is scattered, and this scattering is linked to the faster back-hopping of ions and can be demonstrated in terms of the bulk relaxation phenomenon [41]. The ionic conductivity becomes higher when the frequencies are at the higher frequencies of the PVA nanocomposite, and becomes corresponding to the increased mobility of Ti and Cu ions. It is possible that the improvement in the ionic conductivity when increasing the concentrations of TiO₂ and Cu is due to the NPs that interact with anions/cations [42,43]. The sizes of the nanoparticles are smaller than the particles of the host PVA, which enables them to penetrate the PVA matrices and catalyze the plasticizer ions in order to react with the chain molecules of the PVA, thus reducing the cohesive strength between the polymeric chains, which increases flexible segmental movements. Thus, the cohesion strength between the PVA chains is reduced, which causes a chain cutting movement beside the Cu⁺ conducting pathway on the surfaces of the nanofillers [6,44].

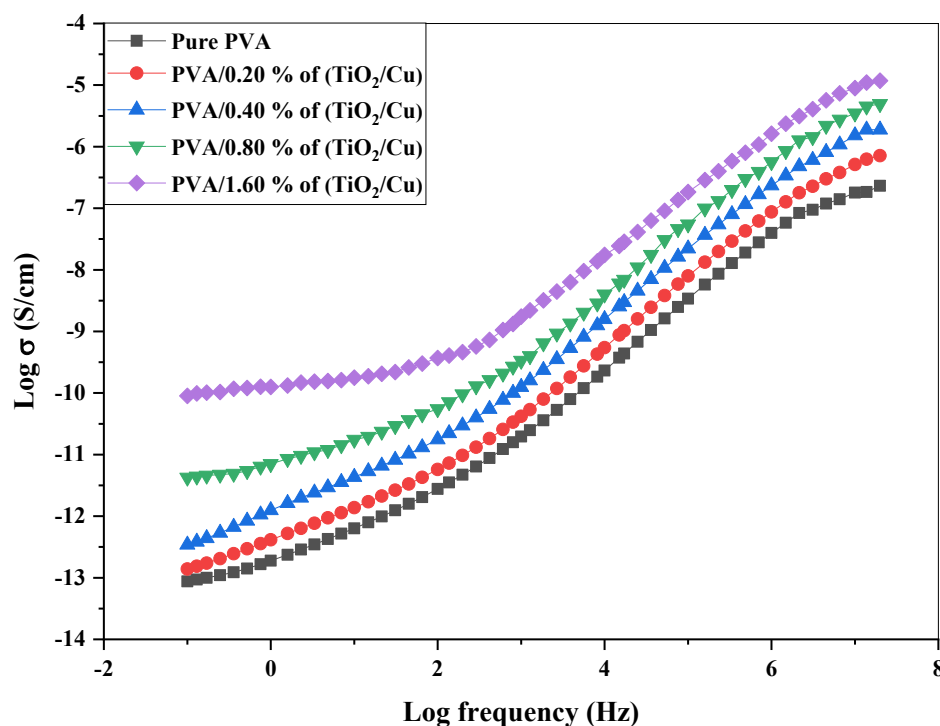


Figure 10. Frequency-dependent AC conductivity (σ) of PVA doped with various concentrations of TiO₂/Cu nanoparticles at RT.

3.8. Electric Modulus Examination

The modulus analysis mechanism has been proven to be an efficient method for revealing the conductivity relaxation in a polymer matrix. The features of bulk relaxation can be described via complex modulus (M^*) parts (real (M') and imaginary (M'')), which can be calculated using the following equations [45]:

$$M' = \epsilon' / (\epsilon'^2 + \epsilon''^2) \quad (5)$$

$$M'' = \epsilon'' / (\epsilon'^2 + \epsilon''^2) \quad (6)$$

where ϵ' is the storage energy, and ϵ'' is the energy loss.

The M' and M'' spectra of all the nanocomposite films at RT are displayed in Figures 11 and 12. In general, a long tail can be observed for all samples at low frequencies; this occurs with a rapid increase in M' , which follows at a high frequency, supporting the existence of a growing effect of electrode polarization with higher capacitance values at lower frequencies, as shown in Figure 11. However, the inhibition of the effect of the electrode polarization is obvious due to the higher values of the modulus and the existence of relaxation bands at higher frequencies [43,46].

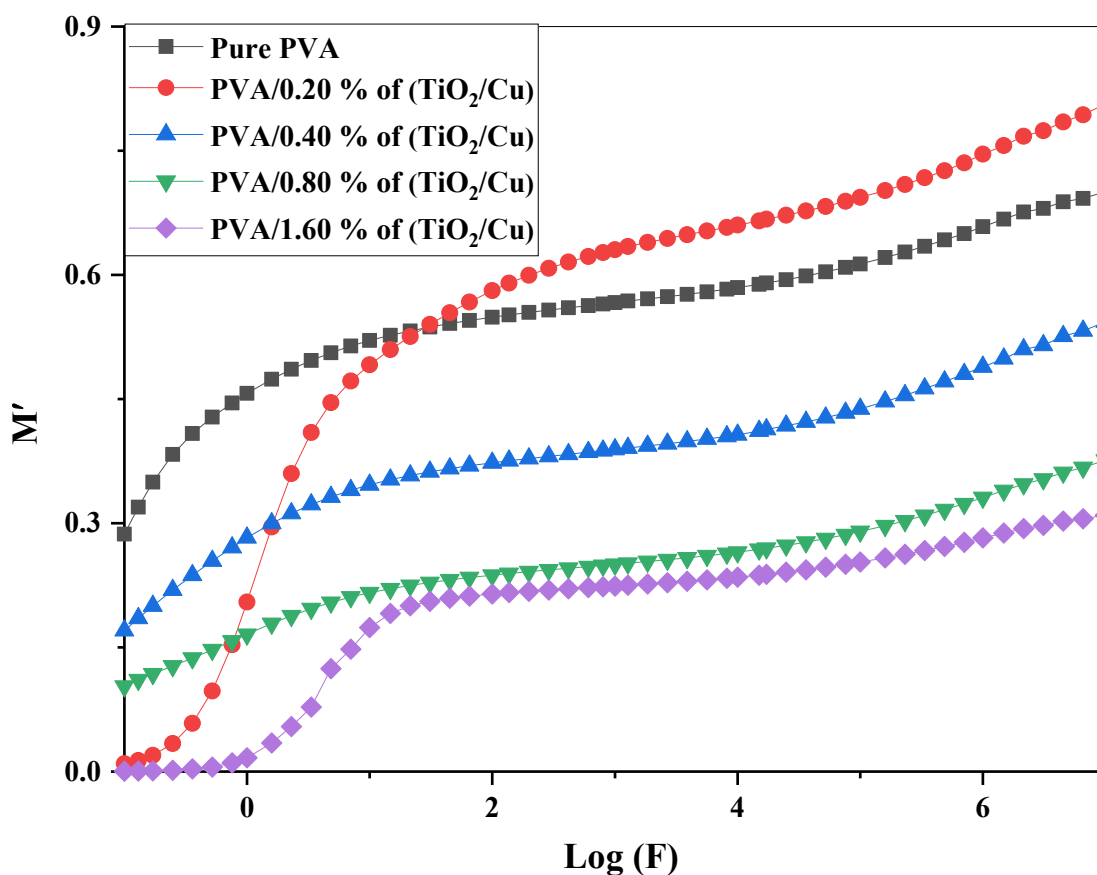


Figure 11. Frequency-dependent M' of PVA matrix doped with different concentrations of TiO_2/Cu nanoparticles at RT.

Moreover, as can be seen in the figure, the pure PVA has the highest M' of intensity, while the nanocomposite with the highest concentration of the TiO_2/Cu nanoparticles has the lowest; subsequently, the AC conductivity is the maximum when compared to that of the other nanocomposite samples. The M'' (the imaginary part of the electrical modulus) data indicate that, at higher frequencies, the maximum bands gradually decrease with an increase in the nanofiller (the TiO_2/Cu nanoparticles) concentration, as shown in Figure 12.

In M'' , a clear shift from the peak to the higher frequencies is observed when the concentration of nanofillers is increased. The relaxation frequency determines the frequency associated with each band, by which the relaxation time of the main conductivity can be calculated using the following equation: ($\tau_\omega = 1/2\pi f_{\max}$), where τ_ω is the time required to move ions from one site to another through the conduction operation [14,46]. A decrease in the relaxation time can be indicated when a variation in the peak frequency appears, as it shifts to higher frequencies when the nanofiller concentration is increased. This is due to the increased mobility and movements of the carrier segments [47]. The chain flexibility of the polymeric matrix is enhanced due to the addition of the TiO_2/Cu nanoparticles, which causes a decrease in the crystallinity ratio of the polymeric matrix. Reducing the relaxation time while increasing the chain segmental motion of the PVA is a well-documented fact, as it makes the transfer operation easier [48,49]. That is, the relaxation time remains lower with a higher ionic fluency that reflects increased AC conductivity due to the increased segmental motion of the nanocomposites [50,51].

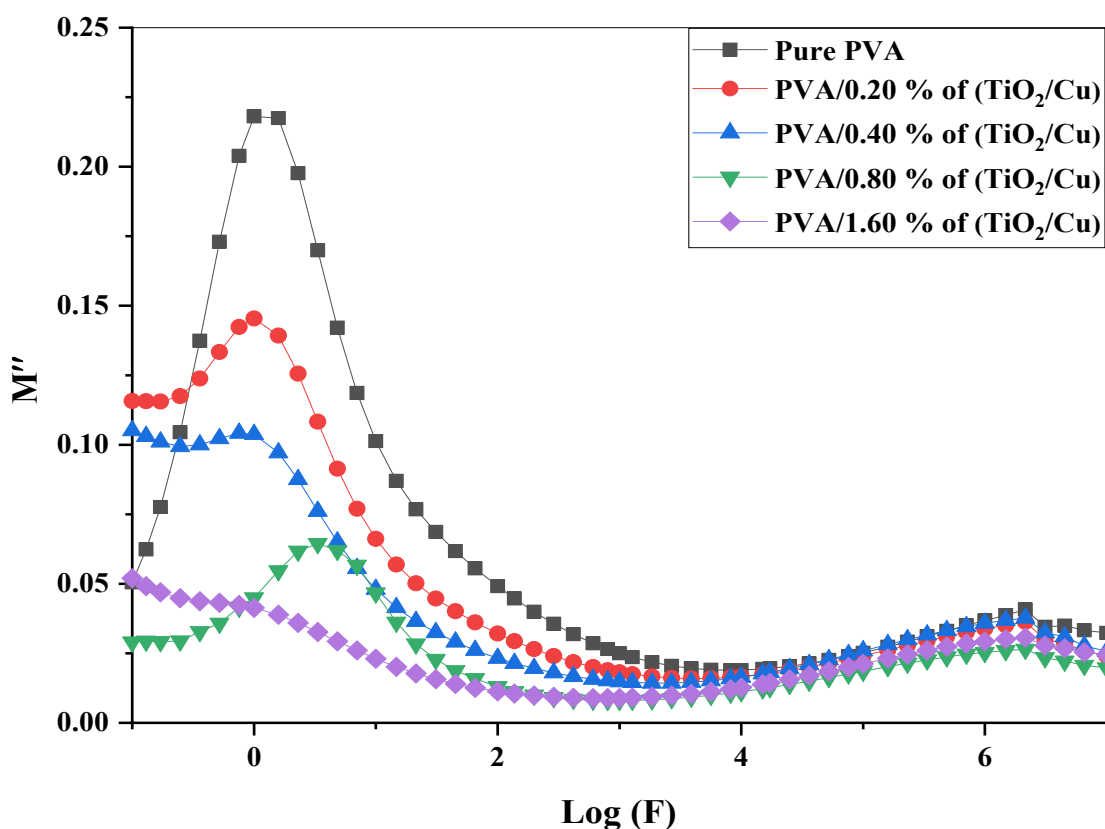


Figure 12. Frequency-dependent M'' of PVA matrix doped with different concentrations of TiO_2/Cu nanoparticles at RT.

4. Conclusions

The solution casting method was used to prepare PVA samples filled with TiO_2/Cu NPs. The nanoparticle sizes of the TiO_2 and Cu were about 5–25 and 2–22 nm, respectively, as shown in the TEM images. The degree of amorphosity of the PVA- TiO_2/Cu nanocomposites increased as the concentration of the hybrid NPs was increased, as found using an XRD analysis. The FTIR analysis showed excellent complexation between the PVA and the TiO_2/Cu NPs. The optical features, such as decreased optical energy gaps, were greatly improved with the increase in the concentration of the TiO_2/Cu NPs. The SEM micrographs of the doped films display white granules on the surfaces of the films, indicating the appearance of a homogeneous growth mechanism. The DSC curves show that the thermal stability of the PVA- TiO_2/Cu films increased remarkably with an increase in the concentration of the TiO_2/Cu NPs in the PVA polymer. An improvement in AC

conductivity was observed with an increase in the TiO₂/Cu NP concentration. This improvement was due to the increase in the mobility and charge carriers' concentrations in the doped samples. The relaxation peaks in M'' clearly indicate conductivity relaxation. The obtained structural, optical, electrical, and dielectric features of these PVA-TiO₂/Cu NP samples indicate that they can be used in many industries, such as energy storage, lithium-ion battery, and organic electronic industries.

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