The tunable permittivity of multi-walled carbon nanotubes/silver nanoparticles reinforced polyvinyl alcohol (PVA) nanocomposites at low frequency

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Abstract

This paper is about tailoring high permittivity of multi-walled carbon nanotubes/silver nanoparticles (MWNT-AgNP) filled polyvinyl alcohol (PVA) nanocomposites at low frequency. PVA/MWNT-AgNP nanocomposites were synthesized via solution-casting technique at low MWNT content with different loading of AgNP. The nanocomposites showed a significant increment in ac conductivity, $\sigma_{ac}$, and dielectric permittivity, $\varepsilon'$, by two orders of magnitude as compared to pure PVA. The maximum $\varepsilon'$ value was achieved about 600 at 1.0 wt% of AgNP due to the increased charge carriers density and high interfacial polarization within the nanocomposites. The relaxation frequency was shifted towards a higher value with the increased of AgNP content while the relaxation time was decreased by 40%. Field emission scanning electron microscopy (FESEM) images showed the enhanced distribution of MWNT in the presence of AgNP to provide conductive pathways in the matrix. This was confirmed by energy-dispersive x-ray (EDX) analysis and ultraviolet-visible (UV–vis) spectroscopy. As a result, PVA/MWNT-AgNP nanocomposites have great potential for electrical applications such as cable accessories, high charge-storage capacitor and electromagnetic interference shielding materials.

1. Introduction

Since the discovery of carbon nanotubes (CNT) by Iijima in 1991 has gained the worldwide attention for its derivatives materials [1]. CNT can be classified into single-walled nanotubes (SWNT) and multi-walled nanotubes (MWNT). Distinct from other carbon materials such as graphite or diamond, CNT is a one-dimensional (1D) structure with high aspect ratio due to large length and small diameter (less than 100 nm). This type of structure allows the mobility of electrical carriers along one controllable direction [2]. The mixture of CNT and insulating polymers could offer nanocomposites with an excellent electrical conductivity, easy processability, lightweight, low density, corrosion resistance and enhanced mechanical properties [3, 4]. The excellent performance of CNT can be achieved through uniform dispersion of the nanotubes to provide a conductive network in the matrices. However, poor processability of polymer nanocomposites constructed at large amount of CNT become a major problem due to high aggregation of CNT caused by van der Waals forces, which hinder the electrical flow of CNT [5].

Silver nanoparticles (AgNP) are amongst noble metal that exhibit unique electrical, optical, magnetic and catalytic properties that differ from their bulk counterparts due to nanosize, large surface area and quantum confinement effects [6, 7]. Distinct from bulk metals, AgNP can become insulator due to the discrete spacing between energy levels known as Kubo gap [8]. The electrical conductivity of AgNP would be comparable to the bulk metal when the thermal energy is beyond this gap. There are also few studies of AgNP in lowering dielectric loss of polymer nanocomposites triggered by Coulomb Blockade effect of single nanoparticles [9, 10]. Recently,
the effective used of metallic nanoparticles for absorption of electromagnetic wave at the metal–dielectric interface was reported at very high frequency [11, 12].

In recent years, there is emerging of advanced polymer nanocomposites by combining CNT and metal nanoparticles for the creation of greater functional hybrid materials. The combination of AgNP and CNT can further enhance their unique properties than the CNT and nanoparticles itself. Decoration of AgNP onto CNT from its reduced Ag salts are promoted due to the structure and high reactivity of CNT surface for the nanoparticles growth [13]. The excellent conductivity of both fillers in polymer nanocomposites have been extensively reported for potential use in electronic devices [14], biomedical application [15], electromagnetic shielding [11] and advanced nanocomposites [16, 17].

To date, not much work has been done on the dielectric permittivity (\(\varepsilon'\)) polymer nanocomposites incorporated by CNT–AgNP. The motivation towards high dielectric performance is beneficial for applications such as high electric energy storage [18] and electromagnetic wave absorption [12]. Traditional dielectric materials developed from inorganic materials such as mica and silicon dioxide exhibit tremendous dielectric, thermal and magnetic properties. However, they are brittle and require large energy consumption during the production [19]. Therefore, there is a need for high permittivity polymer nanocomposites composed of two or more constituents that offer low temperature processing and materials flexibility with good adhesive properties. Several studies on the dielectric properties of CNT/polymer nanocomposites has revealed a parallel trend of the dielectric permittivity and loss due to their high surface area to volume ratio [20, 21] Zhen et al reported on low frequency dependence of dielectric permittivity for polymer nanocomposites with CNT less than 5 wt% [22]. Polyvinyl alcohol (PVA) is an excellent host matrix for encapsulating metal nanoparticles and also suitable due to its biocompatibility, easy processability and good film properties. It is amongst promising polar polymer that can be applied as a dielectric medium [23]. The addition of AgNP with CNT is great importance because it can increase conductivity and introduce high permittivity PVA nanocomposites due to strong interfacial polarization created in a three-phase system. Such high permittivity is yielded upon the formation of conductive pathways because when AgNP comes into contact with nanotubes inducing more charge carriers (electrons and holes). Therefore, dielectric properties of the polymer nanocomposites can be designed with desired properties by optimizing the fillers content.

The present work aims to attain high dielectric permittivity of multi-walled carbon nanotubes-silver nanoparticles (MWNT-AgNP) reinforced PVA nanocomposites by tailoring various loading of AgNP at low MWNT content. The MWNT-AgNP were primarily synthesized via chemical method with different volume of silver nitrate (AgNO\(_3\)) as a precursor in the MWNT solution. Then, PVA nanocomposites were fabricated using the synthesized MWNT-AgNP by solution-casting technique. This paper discussed electrical conductivity and dielectric properties at low frequency range (100 Hz–1 MHz), as well as the analysis on surface morphology and UV–vis spectroscopy of the nanocomposites.

2. Experimental

2.1. Materials
Polyvinyl alcohol (PVA) powder (M\(_w\) = 31 000–50 000 g mol\(^{-1}\), 98%–99% hydrolyzed) was obtained from Aldrich, multi-walled carbon nanotubes (MWNT) with purity of >90% having a diameter of 4–20 nm and length of 10–30 \(\mu\)m were purchased from Nanoshel.co.uk. Hydrogen peroxide (H\(_2\)O\(_2\), 30%) and nitric acid (HNO\(_3\), 65%) supplied by R & M Chemicals were used for mild functionalization of the MWNT. Silver Nitrate (AgNO\(_3\), 0.1 mol L\(^{-1}\)) and N,N-dimethylformamide (DMF, 73.1 g mol\(^{-1}\)) supplied by R & M Chemicals were chosen as Ag precursor and the reducing agent, respectively. Sodium dodecyl sulphate (SDS) obtained from R&M Marketing Essex was selected as surfactants to ensure good dispersion of the MWNT and nanoparticles.

2.2. Synthesis of MWNT-AgNP
MWNT-AgNP were synthesized through chemical technique by reducing silver ions (Ag\(^+\)) from the silver salt (AgNO\(_3\)) in the presence of acid treated MWNT as described based on our previous work [24]. Initially, 420 mg of acid treated MWNT and 160 mg of SDS were added into 140 ml of DMF, and then sonicated in an ultrasonic bath for 30 min. The mixed solution was prepared in four beakers and heated to 80 \(^\circ\)C, followed by adding a different volume of aqueous AgNO\(_3\) (0.1 mol L\(^{-1}\)) into the solutions at a flow rate of 60 ml min\(^{-1}\) (table 1). The hot solution was stirred continuously for 1 h and left to cool overnight at room temperature. Then, the precipitated MWNT-AgNP were filtered and washed with ethanol, water and acetone for several times. Finally, the products were dried in a vacuum oven at 60 \(^\circ\)C for 24 h.
2.3. Preparation of PVA nanocomposites

PVA/MWNT-AgNP nanocomposites were prepared by solution mixing technique. Initially, 1 g of the synthesized MWNT-AgNP powder and 160 mg of SDS were dispersed in 100 ml of distilled water followed by ultrasonication in a water bath for 30 min. Next, 5 g of PVA was added into the mixed solution and slowly heated to 85 °C with continuous stirring at 750 rpm using overhead stirrer. The hot solution was held for 1 h to ensure a homogenous solution throughout the heating process. Then, the viscous solution was immediately cast to glass Petri dishes of 10 cm in diameter and left to dry at ambient room temperature. Subsequently, the prepared composite films were peeled off from the Petri dishes and stored in a vacuum desiccator before characterizations. The average film thickness was measured approximately 0.3 mm. These steps were repeated for fabricating the nanocomposites with different content of AgNP (0.1, 0.3, 1.0 and 1.8 wt%), which measured by using inductive coupled plasma-optical emission spectrometer (ICP-OES). PVA/MWNT nanocomposite was also fabricated in the similar steps.

2.4. Impedance spectroscopy measurements

The electrical and dielectric measurements were performed using a low frequency impedance analyzer, HIOKI LCR HiTester (3532-5), in a frequency range from 100 Hz to 1 MHz. The nanocomposite films were placed between two metal disk electrodes of 25 mm diameter and the electrical measurements were taken out at 25 ± 1 °C. The frequency dependence of dielectric properties and ac conductivity of the nanocomposites can be calculated from real, $Z'$ and imaginary, $Z''$ components of the complex impedance $Z$ as shown in the following relations [25]:

\[
Z' = Z \cos \varphi \quad (1)
\]
\[
Z'' = Z \sin \varphi \quad (2)
\]

where $\varphi$ is the phase angle. The value of dielectric permittivity $\varepsilon'$ and the dielectric loss $\varepsilon''$ of the composite film were obtained from the following equation:

\[
\varepsilon' = \frac{Z''}{2\pi fC_0Z^2} \quad (3)
\]
\[
\varepsilon'' = \frac{Z'}{2\pi fC_0Z^2} \quad (4)
\]

where $f$ is the measuring frequency, $C_0$ is the capacitance of the two electrode plates without sample and calculated by $C_0 = \varepsilon_r A/d$, where $A$ is the film area, $d$ is the thickness, $\varepsilon_r$ is the permittivity of the free space = $8.854 \times 10^{-12}$. The ac conductivity ($\sigma_{ac}$) of the thin film samples at a frequency were obtained from the following equation:

\[
\sigma_{ac} = 2\pi f\varepsilon_r\varepsilon'' \quad (5)
\]

Dielectric modulus is used to analyze the relaxation phenomenon due to space charge polarization by using the dielectric formula. The dielectric modulus in complex form is given by:

\[
M^* = \frac{1}{\varepsilon^*} = M' + iM'' \quad (6)
\]

where $M'$ and $M''$ are the real and imaginary part of the dielectric modulus. Calculation of the dielectric modulus is given by the following formula:

\[
M' = \frac{\varepsilon'}{(\varepsilon'^2 + \varepsilon''^2)} \quad (7)
\]
\[
M'' = \frac{\varepsilon''}{(\varepsilon'^2 + \varepsilon''^2)} \quad (8)
\]

| Table 1. The experimental composition of the prepared PVA/MWNT-AgNP nanocomposites. |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Samples                        | PVA (mg)        | MWNT (mg)       | SDS (mg)        | AgNO₃ (ml)      | DMF (ml)        |
| PVA/MWNT                       | 5000            | 420             | 160             | —               | —               |
| PVA/MWNT-Ag 0.1 wt%            | 5000            | 420             | 160             | 16              | 140             |
| PVA/MWNT-Ag 0.3 wt%            | 5000            | 420             | 160             | 60              | 140             |
| PVA/MWNT-Ag 1.0 wt%            | 5000            | 420             | 160             | 140             | 140             |
| PVA/MWNT-Ag 1.8 wt%            | 5000            | 420             | 160             | 327             | 140             |
2.5. Materials characterization

Surface morphologies of the nanocomposites were carried out by Field Emission Scanning Electron Microscopy (FESEM), while the elements present in the samples were characterized by energy dispersive x-ray (EDX) using an FEI QUANTA 450 FEG equipped with a thermally assisted field emission gun operated at 5–15 keV. The size and structures of MWNT-AgNP were examined using transmission electron microscope, (TEM, brand JEOL-JEM 2100-F). The samples were initially sonicated in deionized water, then dropped onto a copper grid and dried at room temperature for three days before testing.

Ultraviolet-visible (UV–vis) characterization was recorded with a spectrophotometer (Carry Win UV 50) by using a 1 cm quartz cuvette. The absorption spectra were scanned in the range of 200–800 nm. The samples were ultrasonicated in deionized water for 20 min to ensure a good dispersion of the samples prior to the UV–vis measurements.

3. Results and discussion

3.1. Electrical and dielectric spectroscopy analysis

Figure 1 shows a non-linear increasing trend of electrical conductivity against MWNT-AgNP loading in PVA nanocomposites measured at the frequency of 100 Hz. The electrical conductivity exhibits a significant increment when it undergoes an insulator to conductor transition close to a critical fillers loading known as percolation threshold. The maximum conductivity of the nanocomposites was increased by two orders of magnitude with respect to pure PVA. It shows the pronounced effect of adding AgNP at low MWNT content to increase electrical conductivity of pure PVA. The percolation theory describes well-known power laws for electrical conductivity, $\sigma$ and permittivity, $\varepsilon$ of nanocomposites with fillers content as shown in the following relations [20, 21]:

$$\sigma \propto (f - f_c)^t \quad \text{for } f > f_c \quad (9a)$$

$$\sigma \propto (f_c - f)^q \quad \text{for } f < f_c \quad (9b)$$

$$\varepsilon \propto (f - f_c)^{-t} \quad \text{for } f < f_c \quad (10)$$

where $f$ is the content of conductive fillers, $f_c$ is the percolation threshold, $t$ is the critical exponent of conducting region and $q$ is the dielectric exponent of insulating region.

Based on figure 1, the estimated values of $f_c$ and $t$ can be obtained by fitting the data in equation (9a) using least square fit. An inset shows the best linear fit to the log-log plots of the conductivity power laws, which gives $f_c = 0.15$ wt% and $t = 1.70 \pm 0.10$. The attained value of the critical exponent, $t$ is in good agreement with the universal value ($t \approx 1.6–2.0$) [20], which denotes morphology of the percolating MWNT-AgNP network.

Figure 2 shows that ac conductivity, $\sigma_{ac}$ of the nanocomposites with different loading of AgNP are invariant at a lower frequency and gradually increases with increasing the frequency. It can be seen that the $\sigma_{ac}$ plateau response of PVA was shifted towards higher frequency as the AgNP content increased in the nanocomposites. The $\sigma_{ac}$ value persists until a higher frequency because the electrons can easily move through infinite clusters of conductive networks within the nanocomposites. The electrical conduction occurred through numerous conductive pathways when the nanotubes and AgNP are in contact with each other, which allows the efficient mechanism of electron hopping in localized states [26]. However, there are limited percolating pathways below
the threshold value when there is inappropriate amount of Ag nanoparticles could occupy the interstitial positions within the matrix system that attached together with MWNT in random pathways. In addition, a lower electrical conduction was attributed to fewer direct contact between both fillers to provide continuous conductive pathways. This circumstance limits the charge transfer process between the fillers and PVA chains, which retains the insulating property of the polymer \[27\].

Figure 3(a) shows similar power-law dependencies for dielectric permittivity, \( \varepsilon' \) with respect to the MWNT-AgNP content in PVA nanocomposites. It indicates that the addition of AgNP was not only improved the conductivity but also induced polarization in the nanocomposites, which lead to an increase in the dielectric permittivity. The increased conductivity was associated with a large increment of dielectric permittivity near the percolation threshold due to the divergence of both insulating and conducting sides. The \( \varepsilon' \) values of the nanocomposites were substantially increased above the percolation threshold at the maximum value of 600,
which is about 60 times higher than pure PVA. For comparison, this increment is also nearly 20 times higher than PVA/MWNT. However, the $\varepsilon'$ values are decreased at 1.8 wt% with a further loading of AgNP. The occurrence of dielectric permittivity was initiated from MWNT $\pi$-orbital that provides a large field for moving electrons to be easily polarized [27]. In addition, the incorporation of AgNP could reduce the ohmic contact resistance between the nanotubes and increased the charge carriers (electrons or holes) concentration by injection or ejection of electrons in the valence or conduction bands [11]. Thereby, MWNT-AgNP have induced more polar groups into the polymer chains to be more conductive with high dielectric permittivity.

Figure 3(b) shows the dependence of dielectric permittivity on frequency of the PVA/MWNT-AgNP nanocomposites with different AgNP content. High $\varepsilon'$ values are observed at low frequency due to the large dipoles within the nanocomposites to orient themselves in the direction of an applied field [28]. The $\varepsilon'$ values
then gradually decreased with increasing frequency due to the relaxation process of the oriented polarization. Primarily, the \( \varepsilon' \) value of PVA exhibits a weak frequency dependence since the polarization depends on the freedom of chain movement attributed to hydroxyl groups as eternal dipoles in the polymer chain [23]. Meanwhile, PVA/MWNT nanocomposite only shows a slight increment in the \( \varepsilon' \) value with increasing frequency when compared to the pure PVA. This is in good agreement with the work done by Zhen et al [22], who claimed the weak frequency dependence of polymer nanocomposites filled by MWNT less than 5 wt%. Though, the incorporation of MWNT-AgNP significantly increased the \( \varepsilon' \) values of the nanocomposites with high frequency dependence from \( 10^2 \) to \( 10^6 \) Hz. There was a drastic change above the percolation threshold with increasing slope of the \( \varepsilon' \) curves when AgNP content increased from 0.3 to 1.0 wt%. The increased of dielectric permittivity with increasing AgNP was due to the piling of charges at the extended interfaces. This was ascribed to the strong interfacial polarization between matrix and MWNT-AgNP because of their differences in conductivity and polarizability. The dielectric relaxation takes place with increasing the frequency since the percolating network become closer to each other and then dominated by the matrix when many of the MWNT-AgNP were blocked by PVA layers. In addition, PVA is a polar polymer where the dipoles entrapped the electrons and caused interfacial polarization with the arrangement of large dipoles on the metal particles [29]. The dielectric behavior of nanocomposites also depends on several factors such as electrode effect, orientation, atomic and electronic polarization [30].

Figure 4 shows the dielectric loss, \( \varepsilon'' \) of the nanocomposites exhibited decreasing trend with the increase in applied frequency. The dielectric loss is due to the energy loss associated with charges motion and dipoles alignment. When the induced charges are unable to follow the periodic reversal of electric field, which is extremely fast at high frequency and could trigger to the decrease in \( \varepsilon'' \) values with a decline of the charges accumulation [31]. The features display large dielectric loss of the nanocomposites with increasing AgNP content up to 1.0 wt%, which is inversely proportional to the frequency and gradually decreased towards a higher frequency. This resulted in greater \( \varepsilon'' \) values compared to the pure PVA and PVA/MWNT nanocomposites. A significant increase in the \( \varepsilon'' \) values is associated with the enhanced electrical conductivity of the nanocomposites. However, the \( \varepsilon'' \) values were declined with a further loading of AgNP at 1.8 wt% due to less mobility of the charge carriers and lack segmental motion of the polymer. There is slight dielectric loss below the percolation threshold attributed to Coulomb blockade effect comes from single electron of isolated nanoparticles distributed in a definite space within the nanocomposites. This caused many tunnelling knots that prevent mobility of the electrons/charge carriers in a certain electric field [22].

A complex dielectric modulus, \( M'' \) (equations (6)–(8)) is used to predict dielectric relaxation when electric displacement remains constant due to space charge polarization [32, 33]. Figures 5(a), (b) illustrate the frequency dependence of the real (\( M' \)) and imaginary part (\( M'' \)) of the nanocomposites. The \( M' \) values initially were almost approaching zero at a lower frequency due to electrode polarization, and getting increased towards higher frequency [34, 35]. Meanwhile, \( M'' \) shows an asymmetric spectra that represent relaxation frequency of the nanocomposites. The \( M'' \) spectra elucidate mobility of the charge carriers with increasing the frequency. The charge carriers travelling over long distances at low frequency and upon reaching the maximum \( M'' \), their mobility is executed to localized motion over short distances. The peaks of \( M'' \) defines relaxation time, \( \tau \) of the orientated dipoles (\( \tau = 1/\omega_p \)), where the angular frequency is given by \( \omega_p = 2\pi f[31] \). It can be seen that the relaxation frequency of the nanocomposites shifted towards higher frequency and the relaxation time also reduced with the increased of AgNP. It denotes high mobility of the charge carriers to transfer from one site to
neighbouring sites in a shorter time due to the enhanced conduction process by percolating MWNT-AgNP within the nanocomposites. However, the nanocomposites incorporated with very low AgNP content exhibited a longer relaxation time. This is because the nanoparticles at below percolation threshold require high charging energy and inhibits the electrons from transferring through isolated metal islands (9).

3.2. Morphology analysis

Figure 6 shows transmission electron microscopy (TEM) of the synthesized MWNT-AgNP prior to the mixing with PVA matrix. The TEM image reveals the actual size and structure of MWNT with diameters of 10–30 nm. Whereas the present of AgNP can be spotted as the dark fine particles with average size of 5–10 nm. Some of the AgNP were deposited onto the nanotube surfaces, while others were isolated probably due to homogeneous
nucleation of the AgNP during the synthesis process. Whereas, the addition of SDS as surfactant helped to support heterogeneous nucleation of AgNP onto the MWNT surface [13].

Figures 7(a)–(d) display microstructural variations in FESEM micrographs of the PVA/MWNT-AgNP nanocomposites while in figure 7(e) shows the energy dispersive x-ray (EDX) analysis that confirms the presence of carbon, silver and oxygen. It demonstrates the predominance of MWNT with a little measure of AgNP embedded in the PVA matrix. It can be seen that the whole structure of MWNT embedded in the matrix are much curved and distributed with a high irregular interface, while AgNP were identified as the bright spherical spots that randomly deposited onto the MWNT networks. The observed diameters of MWNT within the PVA matrix are greater than the actual diameter captured from TEM image due to polymer wrapping along the nanotube surfaces. The MWNT networks served as the conducting bridges that facilitate the current flow, while AgNP increased the concentration of mobile charge carriers within the nanocomposites.

The micrograph in figure 7(a) shows poor dispersion of MWNT-AgNP within the nanocomposites where some large pores exist between the fillers and the matrix. The lack of fillers distribution caused a weak interfacial interaction at low loading of 0.1 wt% AgNP, which resulted in low dielectric permittivity. There is an improvement in the dispersion of MWNT-AgNP with the increased AgNP loading above percolation threshold of the nanocomposites (figures 7(b), (c)). It seems that the presence of AgNP attached to the MWNT surface have reduced van der Waals forces and prevented agglomeration amongst the nanotubes. This is in good agreement with a study showed by Xin and Li [36]. The significant increment in the conductivity and dielectric permittivity of the nanocomposites are ascribed to high physical interactions between polymer chains and the conductive networks of MWNT-AgNP. As the AgNP content increases, there would be a charge transfer complexes (CTC) occurs within amorphous regions of the PVA by reducing the potential barrier of two localized states to allow the transfer of charge carriers [27, 30, 37]. However, as the content of AgNP increased further up to 1.8 wt%, inducing large pores and metal clouds exist between the MWNT networks and the matrix (figure 7(d)). The uneven fillers distribution are formed when the nanoparticles were segregated in some parts of the polymer chains and increased entanglement of the MWNT bundles. This circumstance deteriorates
flexibility of the nanocomposites and retards mobility of the charge carriers, which lead to undesirable electrical conductivity and dielectric properties.

It is notable that the size range of AgNP increases with increasing AgNP content in the individual micrographs in which the average size was found to be 17 nm, 22 nm, 36 nm and 55 nm, respectively as shown in figure 8. An increment in the AgNP size was elucidated by the formation Ag cluster due to steric effect of metallic nanoparticles [38]. The aggregation behaviour of Ag clusters was also influenced by the large molecular chains of PVA that create complex steric configurations within the nanocomposites [39].

3.3. UV–vis analysis

Figure 9 presents the optical properties of pure PVA and PVA/MWNT-AgNP nanocomposites at different content of AgNP. PVA shows a shapeless absorption profile due to its transparent characteristics in the visible region (figure 9(a)). On the other hand, PVA/MWNT nanocomposite (figure 9(b)) displays a broad peak in the uv region at 254 nm, mainly attributed to the absorption of black colournanotubes arise from the π−π* transitions of the aromatic C=C bonds of MWNT [40]. Meanwhile, the spectra for PVA/MWNT-AgNP nanocomposites show more pronounced peaks intensity with asymmetrical shape in the range of 250–800 nm (figures 9(c)–(f)). The absorption peak at 254 nm is shifted to 262 nm with the increased content of AgNP in the nanocomposites. The redshift towards a longer wavelength indicates the absorption properties of MWNT are influenced by surface plasmon resonance (SPR) of AgNP embedded within the nanocomposites. The absorption spectra show a weak shoulder appeared nearly at 350 nm because of multiple AgNP transitions with increasing its particles size [41]. However, there is no SPR band of AgNP at 420 nm due to no electronic interaction at ground state since the charge transfer from AgNP to the MWNT has decreased the electron density of the metal core [42]. This is in good agreement with the work done by Zhang et al [43]. The width of absorption peaks become narrow with the increased content of AgNP especially at 1.0 wt% of AgNP. This indicates a preferential scattering of larger crystallites due to the interconnection of Ag nanoclusters during deposition process within the matrix. Additionally, the absorption could be influenced by the dielectric effective constant of surrounding medium [44]. The absorption spectra demonstrate a positive correlation with FESEM observation in which the redshift is ascribed to the increase in AgNP size and the charge transfer process [45, 46].

4. Conclusion

PVA/MWNT-AgNP nanocomposites were successfully fabricated by solution-casting technique. The MWNT-AgNP was primarily synthesized via chemical reduction method at different content of AgNP prior to the mixing with PVA. It was found that adding AgNP with low MWNT content not just improved electrical conductivity, but also induced high permittivity due to the increased charge carrier density and strong interfacial polarizations between both fillers and the matrix. The results demonstrated that the electrical and dielectric behaviour of the nanocomposites are greatly influenced by the amount and distribution of MWNT-AgNP as the conductive fillers in accordance with percolation theory. The ε′ value of the nanocomposites was achieved as high as 600 at 1.0 wt% of AgNP, which is about 60 times higher than pure PVA. Dielectric modulus signifies that relaxation peaks of the nanocomposites shifted towards higher frequency and the relaxation time decreased with increasing the AgNP content. Morphology analysis by FESEM revealed a better distribution of the percolating MWNT in the presence of AgNP due to the reduction of van der Waals forces among the nanotubes. UV–vis absorption profile correlated the FESEM observation, wherein the redshift of absorption peak at 262 nm was due to the increase in Ag particles size and the charge transfer from AgNP to the MWNT. However, incorporation of high AgNP content up to 1.8 wt% deteriorated dielectric properties of the nanocomposites because of the adverse effect on MWNT-AgNP distributions, which retards mobility of the charge carriers and flexibility of the polymer. In this regards, still many aspects to be improved in future due to the synergetic effect of MWNT-AgNP in triggering high permittivity of PVA nanocomposites for various electrical applications at low and high frequency range.

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Additional information

The authors declare that they do not have any conflict of interest.
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