Enhancement investigations on dielectric and electrical properties of niobium pentoxide (Nb$_2$O$_5$) reinforced poly(vinylidene fluoride) (PVDF)- graphene oxide (GO) nanocomposite films

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**ABSTRACT**

An ultra high dielectric constant nanocomposites comprising of poly(vinylidene fluoride) (PVDF) as a polymer matrix and niobium pentoxide (Nb$_2$O$_5$)-reinforced graphene oxide (GO) have been successfully developed using solution casting technique. Scanning electron microscopy (SEM) demonstrates that the homogeneous dispersion of Nb$_2$O$_5$ and GO within the PVDF matrix was realized. The dielectric and electrical properties of the resulting PVDF-GO-Nb$_2$O$_5$ nanocomposites films as a function of frequency were studied. The dielectric constant of the nanocomposites system reached a value of about $\approx$140 at 100 Hz, with a relatively low dielectric loss factor ($\approx$ 1.4). The enhanced dielectric performance of the PVDF-GO-Nb$_2$O$_5$ nanocomposites was ascribed to the presence of Nb$_2$O$_5$ onto the GO, which exhibits strong interaction between GO and PVDF matrix through hydrogen bonding. Moreover, the experimental results fit well with percolation theory and near the percolation threshold ($f_c < 2 \text{ wt}\%$) with high dielectric constant was achieved for PVDF-GO-Nb$_2$O$_5$ nanocomposites. Furthermore, the AC electrical conductivity was also noticeably enhanced. Our strategy provides a facile method to prepare high dielectric constant and relatively low dielectric loss PVDF-GO-Nb$_2$O$_5$ nanocomposite films that might be suitable for energy storage applications.

**1. Introduction**

Polymeric nanocomposites containing selected inorganic fillers with elevated dielectric constant and low dielectric loss have brought about considerable attention in the field of energy storage devices [1], sensors [2], and flexible electronics, due to their inherent advantages of high break down strength, easy process ability, mechanical flexibility, and economical efficiency [3,4]. In order to meet the miniaturization and inexpensive requirements of energy storage devices, dielectric nanocomposites with relatively high dielectric constant, high break down strength, and low loss materials are strongly desired. Great efforts have been made to prepare flexible nanocomposite films using polymers and highly conductive fillers for justifying the candidature of dielectric and electrical behavior of material [4]. In recent few years, many research groups are trying to develop high dielectric constant polymer nanocomposites for embedded capacitor applications [5]. However, Graphene is a class of smart material with sp$^2$ hybridized monolayer carbon atoms arranged in two-dimensional honey comb lattice-like structure. Graphene is reported to have an extraordinary property, which includes high surface area, high electronic conductivity, young’s modulus, and thermal conductivity, respectively [6,7]. In order to improve the thermal, dielectric and electric performance of the polymer nanocomposites, graphene makes it suitable for use as inorganic filler-based materials. The bulk amount of graphene can be formed by the chemical reduction of graphene oxide (GO) by graphite as precursor [8]. Using this chemical technique, huge scale manufacture of graphene is expected to be the simplest and most useful technique as graphite is cheap and easily available. On the other hand, GO are two-dimensional carbon-based materials with different oxygen containing functional groups including hydroxyl, carbonyl, and epoxide [9]. The presence of these functional groups of GO is strongly hydrophilic in nature and also the individual sheets of GO is well dispersed in water. Moreover, it has been reported that the improvement of thermal stability, mechanical, and electrical properties of GO-reinforced polymers is due to their huge aspect ratio, high strength, and the strong attachment with polymer matrix [10].

Niobium pentoxide (Nb$_2$O$_5$), one of the most important transition metal oxides has immense interest due to their potential applications in gas sensors, catalysts, micro-electronics, and optoelectronic industries [11]. However, the Nb$_2$O$_5$ is an n-type semiconductor with a band gap of about 3.4 eV, low in comparison with...
other oxide [12]. This niobium pentoxide has several advantageous characteristics including surface area enables for easy modification by intercalation, superficial modification and formation of nanosheets or nanoscrolls [13–15]. Moreover, it is also used as promising doping agent for tailoring nanostructured composites materials for potential applicability in the various fields. Niobium pentoxide is biocompatible as well as it enhances bioactivity and corrosion resistance of the respective nanocomposites [16–18]. In this study, the niobium pentoxide-reinforced graphene-oxide-based polymer nanocomposites have achieved significant increase in dielectric constant with improved conductivity and suppressed loss. Besides, polymers are most normally used as dielectric materials with high mechanical flexibility, good process ability, low cost, and high dielectric strength [19]. Especially, the ferroelectric polymers such as poly(vinylidene fluoride) (PVDF) and its co-polymers poly(vinylidene fluoride co-hexa fluoropropylene) (PVDF-HFP), which is a semi-crystalline thermoplastic polymeric materials with extraordinary high piezo and pyro electric coefficient, better thermal stability, chemical resistance, high dielectric constant (≈10) and high breakdown strength [20–22].

In the present investigation, the flexible polymeric nanocomposite films with high dielectric constant and suppressed dielectric loss by using graphene oxide (GO), niobium pentoxide (Nb$_2$O$_5$) as the fillers and poly(vinylidene fluoride) (PVDF) as the matrix was prepared by solution casting techniques. A study concerning niobium pentoxide-reinforced graphene-oxide-based materials has not been previously reported in the literature so far. Keeping in mind, we have fabricated PVDF-GO-Nb$_2$O$_5$ nanocomposite films with enhanced dielectric and electrical properties. The current work is focused on preparation of nanocomposites which optimizes the dispersion level of GO and Nb$_2$O$_5$ particles within the polymeric matrix to get improved dielectric properties (dielectric constant and dielectric loss) and electrical performance (AC conductivity) of the nanocomposites than the neat polymer. Besides, the dielectric and electrical performance of the PVDF-GO-Nb$_2$O$_5$ nanocomposite films were analyzed by using impedance analyzer in a wide range of frequency from 100 Hz to 1 MHz at room temperature. We believed that this study may provide a perspective utility of Nb$_2$O$_5$ for the development of ultra high dielectric and electrical performance of the nanocomposites for energy storage applications.

2. Experimental detail

2.1. Chemicals and materials

Poly(vinylidene fluoride) (PVDF) powder ($M_n = 180,000$ g/mol) was purchased from Sigma-Aldrich, India, and used as polymeric matrix. Natural flake graphite was purchased from mK NANO, USA. Potassium permanganate (KMnO$_4$), sulfuric acid (H$_2$SO$_4$), sodium nitrate (NaNO$_3$), hydrogen peroxide (H$_2$O$_2$) (30 wt %), and hydrochloric acid (HCl) were purchased from Merck, India. The niobium pentoxide (Nb$_2$O$_5$) powder was supplied by Spectrochem. Pvt. Ltd., India. The N, N-dimethylformamide (DMF) was obtained from Himedia Laboratories Pvt. Ltd, India and used as solvent for the preparation of PVDF-GO-Nb$_2$O$_5$ nanocomposite films. All the chemicals were of analytical grade and used without further purification.

2.2. Synthesis of graphene oxide (GO)

Graphene oxide (GO) was synthesized according to some previously reported modified Hummer’s method [23,24]. In this synthesis method, graphite powder, NaNO$_3$, and KMnO$_4$ were added to a H$_2$SO$_4$ solution under continuous stirring for 1 h in a round-bottom flask. The reaction mixture was stirred and maintained temperature at 35°C for 1 h. Then, 90 ml of deionized water was added, while keeping the temperature at 98°C for 15 min and warm water was poured slowly followed by a drop wise addition of 30% H$_2$O$_2$ with continuous stirring for 2 h until the color of the solution changed to golden yellow. As a result, the reaction mixture was filtered and washed several times with distilled water, until the pH of the supernatant was reaches 7 using centrifugation at 8500 rpm for 45 min. The product was dried at 45°C in a vacuum oven until completely dried and finally to get the purified graphene oxide.

2.3. Preparation of PVDF-graphene oxide (GO)-Nb$_2$O$_5$ nanocomposites

The PVDF-GO-Nb$_2$O$_5$ nanocomposite films with different weigh percentage of Nb$_2$O$_5$ contents were prepared by solution casting technique. Firstly, poly(vinylidene fluoride) (PVDF) was dissolved in N, N-dimethylformamide (DMF) and stirred for 1 h to ensure homogeneity of the solution. Then, previously synthesized GO was dispersed into the mixture of DMF and PVDF under ultra-sonication bath for 30 min and further continuously stirred for 30 min at room temperature. Predetermined amounts of Nb$_2$O$_5$ particles were dispersed in DMF by using an ultrasonic bath for 30 min and then suspension was added into the PVDF solution. The resulting mixture was stirred vigorously for several hours to improve the dispersion of the Nb$_2$O$_5$, GO and simultaneously to remove the air bubbles to form a stable suspension. Subsequently, the resultant solution was casted into a piece of clean glass petri dish and dried in a vacuum oven at 80°C for 4 h to evaporate DMF solvent to produce the PVDF-GO-Nb$_2$O$_5$ nanocomposite films. All the resultant
2.4. Characterization techniques

The TEM measurement of graphene oxide (GO) was carried out in the transmission electron microscope (JEOL 2100) operating at 200 kV. SEM observations were performed to analyze the detailed microstructure of the Nb$_2$O$_5$ reinforced graphene oxide (GO) nanocomposite films by using a scanning electron microscopy (SEM, ZEISS EVO-18). The UV-Visible absorption spectrum of well dispersed GO were recorded on a Shimadzu UV-2450 UV-visible spectrophotometer. The Fourier-transform infrared (FTIR) spectrum of the graphene oxide was measured on a spectrometer (5700 FTIR, Nicolet) by using KBR pellet. The dielectric and electrical responses of the PVDF-GO-Nb$_2$O$_5$ nanocomposite films in the frequency range from 100 Hz to 1 MHz were measured using an impedance analyzer (HIOKI 3570 Impedance analyzer).

3. Results and discussion

The schematic illustration of the bonding interaction between GO, Nb$_2$O$_5$ and PVDF nanocomposites is shown in Scheme 2. The niobium pentoxide (Nb$_2$O$_5$)-reinforced GO and PVDF matrix exhibits improvement of dielectric and electrical performance of the nanocomposites. This may be due to the strong interfacial interaction between Nb$_2$O$_5$, GO and PVDF matrix. Moreover, there is a strong interaction between hydrogen ion of GO with O atoms of Nb$_2$O$_5$ and fluorine groups in the polymer chain through hydrogen bonding [25,26]. This hydrogen bonding helps GO dispersion in the PVDF matrix and also significantly improves the compatibility of the nanocomposites [25–28].

**Scheme 1.** Schematic illustration for preparation of PVDF-GO-Nb$_2$O$_5$ nanocomposite films.
Scheme 2. Schematic illustration of bonding interaction between PVDF, GO and Nb$_2$O$_5$ followed for the fabrication of PVDF-GO-Nb$_2$O$_5$ nanocomposite films.

0.5 wt% and 2.5 wt% of Nb$_2$O$_5$-reinforced GO-PVDF composite films (Figure 1(b,c)), GO plays a vital role in the nucleation and growth of Nb$_2$O$_5$ which is dispersed uniformly in the PVDF matrix without apparent agglomeration. In the presence of Nb$_2$O$_5$ and graphene oxide (GO), the polymer matrix acquire reinforcement and consequently plastic constraint may occur [36]. This leads to the formation of spherical structure of GO within which Nb$_2$O$_5$ particles get embedded and dispersed within the polymer matrix. This may be due to the improved interfacial interaction between Nb$_2$O$_5$-GO and the PVDF matrix through polar groups of Nb$_2$O$_5$ which promotes the effectiveness of filler particles [37]. In addition, the graphene oxide sheets are readily

Figure 1. (a) TEM images of graphene oxide (GO) and Figure 1(b,c) SEM micrographs of the PVDF-GO nanocomposites filled with (b) 0.5 wt% and (c) 2.5 wt% of Nb$_2$O$_5$ content.
dispersed into the polymer matrix, due to the existence of hydrophilic oxygen containing functional groups on their surface. Moreover, the incorporation of Nb_2O_5 and GO into PVDF matrix has led to increased interfacial area of attachment and also contribute to the improvement in dielectric constant of the PVDF-GO-Nb_2O_5 nanocomposites. The formation of these Nb_2O_5-reinforced GO sheets in a local area is helpful for the improvement of electrical conductivity and dielectric properties of the nanocomposites [37,38].

Figure 2(a) shows the UV-Visible absorption spectrum of graphene oxide. According to the absorption spectra, the spectrum of graphene oxide has a strong absorption peak at about 230 nm related to n-n* transition of the C-C aromatic bond and weak absorption (a small shoulder) at 300 nm due to n—n* transitions of C = O bond [39–41]. The FTIR spectrum of GO in Figure 2(b) shows a broad peak appeared at 3444 cm\(^{-1}\) is responsible for stretching mode of –OH bond, reveals the presence of hydroxyl groups in graphene oxide. It shows characteristic absorption peak at 1721 cm\(^{-1}\) and 1376 cm\(^{-1}\) corresponds to the C = O and -C-O stretching of carboxylic groups, aromatic –C=C (1639 cm\(^{-1}\)), epoxy – C-O (1241 cm\(^{-1}\)), and alkoxy -C-O (1069 cm\(^{-1}\)) indicating the existence of oxygen containing functional groups on the graphene oxide [41–45].

### 3.2. Dielectric and electrical properties of PVDF-GO nanocomposite films

Figure 3 represents the dielectric constant (\(\varepsilon_r\)) and AC electrical conductivity for neat PVDF and PVDF-GO nanocomposites comprising 10 wt% of GO contents as a function of frequency at room temperature. As shown in Figure 3(a,b), it is observed that both the value of dielectric constant and ac electrical conductivity is larger than that of the PVDF matrix, which can be attributed to the hopping conduction mechanism of GO in the PVDF matrix [46]. The value of the dielectric constant decreases with increase in frequency for PVDF-GO composite (Figure 3(a)), which is a general feature of polar dielectrics. The low dielectric constant at high-frequency region and high dielectric constant at low-frequency region is the typical characteristic of space charge relaxation effect. But in case of neat
PVDF, the dielectric constant becomes saturated at frequency region\( (10^3 \text{ to } 10^6 \text{ Hz}) \) due to dipolar polarization and interfacial polarization [47–50]. Moreover, at low-frequency region, slight increase in the dielectric constant is noticed, which may be due to the contribution of all the types of polarizations (electronic, atomic, dipolar, interfacial) [49–51]. Furthermore, with 10 wt% of GO, the dielectric constant is decreasing with increase in frequency may be ascribed to the failure of the interfacial polarization process to keep up with the changing step of the external applied electric field. Thus, at a high-frequency range, these properties of the composites are dominated by the relaxation process of PVDF matrix [49,50]. The AC conductivity (Figure 3(b)) increases with increase in frequency because the conduction may be due to increase in the hopping of charge carriers with increase in frequency [52,53]. However, the PVDF-GO composites the value of the AC electrical conductivity gradually increased with increase in frequency and higher than that of neat PVDF over the whole frequency range, which may be due to the better dispersion of conductive GO in the PVDF matrix resulting easy passage of the charge carriers through the material [54]. It is interesting to note that in case of neat PVDF the whole conductivity spectrum consists of two different regimes: (1) the frequency-independent plateau regime (2) frequency-dependent regime corresponding to AC conductivity. The plateau regime detected in the low-frequency region shifts toward high-frequency [55]. On increasing the frequency, the electrical conductivity transmutes from frequency-independent DC conductivity to frequency-dependent AC conductivity. The low-frequency plateau signifies the migration of charge carrier through defects by hopping like motion. On the other hand, at high frequencies the conduction may be due to hopping of electron and conductivity increases due to increase in the hopping frequency [52,53]. In addition, with the presence of conductive GO may improve the electrical conductivity of the PVDF composites, favorable for the enhancement of dielectric constant of the PVDF composites. Moreover, the dielectric constant of neat PVDF is \( \approx 6.0 \) at 100 Hz, but the dielectric constant for two phase PVDF-GO nanocomposite is \( \approx 35 \), which is moderately low, although nearly six times larger than that of the neat polymer matrix. Previously, it has been reported that a high weight percentage of filler loading (> 60 wt %) is essential to achieve high dielectric constant polymer-based nanocomposites [56], but it may also have some adverse effect on prepared nanocomposites in terms of the crystallinity and flexibility.

### 3.3. Dielectric properties of the PVDF-GO-Nb_2O_5 nanocomposites

To achieve excellent dielectric properties of the PVDF-GO-Nb_2O_5 nanocomposites, the effect of different weight percentage of Nb_2O_5 particles on the electrical performances was investigated. Figure 4 shows the dependence of dielectric constant of PVDF-GO-Nb_2O_5 nanocomposite films with different weight percentage of Nb_2O_5 contents in the room temperature frequency range (100 Hz to 1 MHz). As shown in Figure 4(a), it is observed that the dielectric constant value of the nanocomposites exhibit significant development with the increase of Nb_2O_5 content over the entire frequency range. For instance, the value of the dielectric constant increases from \( \approx 30 \) to 140 (100 Hz), when the filler content increased from 0.5 to 2.5 wt%, which is about 24 times larger than that of pristine PVDF film. However, the dielectric constant of neat PVDF and PVDF-GO-Nb_2O_5 nanocomposites decreases with increase in frequency. Also with gradual increase in the weight percentage of Nb_2O_5, the dielectric constant goes on increasing especially at low-frequency region. This reveals, by incorporating conductive filler (Nb_2O_5) into the polymer matrix results enhancement

![Figure 4](image-url)  
**Figure 4.** (a) Dielectric constant \( (\varepsilon_r) \) and (b) dielectric loss \( (\tan \delta) \) of the PVDF-GO-Nb_2O_5 nanocomposite films as a function of frequency.
of the dielectric constant, which is owing to the effect of interfacial or Maxwell–Wagner–Sillars (MWS) polarization [57–60]. The interfacial polarization is associated with the entrapment of free charges generated at the interface of Nb$_2$O$_5$, GO and the polymer matrix due to their unusual dielectric constant and conductivity of the nanocomposites. Moreover, with the increase in frequency, the interfacial polarization cannot follow the external electric field change, thus there is a sharp reduction of space charge polarization and slow down dielectric relaxation of the matrix of the nanocomposites. This also leads to the decrease in the dielectric constant at higher frequency region [60,61].

Figure 4(b) shows the dependence of dielectric loss of PVDF-GO-Nb$_2$O$_5$ nanocomposites as a function of frequency at room temperature. The dielectric loss relates to the measurement of the energy dissipation in a dielectric material through application of alternating electric field. As shown in Figure 4(b), it is observed that the entire nanocomposites show improved dielectric loss due to the incorporation of conductive Nb$_2$O$_5$-reinforced GO into PVDF matrix. In the low-frequency region, the polarization in the nanocomposite is less due to non alignment of dipoles in the direction of the electric field, which causes less dissipation of energy resulting decrease in the dielectric loss. On the other hand, when the frequency increases (>10$^5$ Hz), polarization is increased due to more dipole alignment in the direction of the applied electric field, which enhances the conductivity in the nanocomposite [62,63]. Consequently, more energy dissipation takes place causing increase in the dielectric loss values. The nanocomposite with 2.5 wt% of Nb$_2$O$_5$ exhibits the dielectric loss value (≈ 1.4) at a frequency of 100 Hz. Such loss is the inevitable consequence of the considerably improved conductivity of the nanocomposites and can be considered as main aspect of the percolative nanocomposites [64]. However, the GO are isolated by the Nb$_2$O$_5$ layers composed of GO and polymer matrix, which results in the formation of conductive networks and these conductive networks can give rise to leakage current in the nanocomposites. The higher weight percentage of filler loading may provide more conductive pathway and thus the dielectric loss values is increased [48].

The variation of the dielectric constant and dielectric loss with Nb$_2$O$_5$ loading at two particular frequencies from 10$^2$ Hz and 10$^3$ Hz is presented in Figure 5. It is observed from the Figure 5(a), the value of the dielectric constant increases with increase in frequency and also increases with increasing weight percentage of filler loadings. However, the Nb$_2$O$_5$-reinforced GO-PVDF nanocomposites reveal a superior dielectric constant than that of the neat PVDF and PVDF-GO nanocomposites. However, the nanocomposite shows higher dielectric constant in lower frequency regions may be due to the increase in the interfacial polarization [58–60]. For the weight percentage of Nb$_2$O$_5$ content lower than 2.5 wt%, the dielectric constant of the nanocomposites increases gradually and found to be 25, 45, 65, and 120, respectively, for 0.5 wt% to 1.5 wt% of filler loading. The improvement of dielectric constant (<10$^2$ Hz) may be due to the rise of frequency explained on the basis of the movement of polymer chain segments does not have sufficient time to catch up with the application of electric field. Furthermore, the tunneling resistance among the GO strongly sensitive to thermal fluctuation is reduced with increase of frequency [65]. As a result, the conductivity of the nanocomposites is improved; this favors the enhancement of the dielectric constant. The dielectric loss of the nanocomposites is another crucial parameter for dielectric application of the prepared PVDF-GO-Nb$_2$O$_5$ nanocomposites. As shown in Figure 5(b), the value of the dielectric loss (≈ 1.4 at 100 Hz) steadily increases with increase in the weight percentage of Nb$_2$O$_5$ contents; which may be the outcome of the conductive paths within the nanocomposite system. Meanwhile,

![Figure 5](image-url)  
Figure 5. Dielectric constant (a) and dielectric loss (b) of the PVDF-GO-Nb$_2$O$_5$ nanocomposites as a function of the various weight percentage of Nb$_2$O$_5$ contents at 10$^2$ Hz and 10$^3$ Hz.
these conductive paths may give rise to high electrical conductivity and increase in the current leakage therefore the value of the dielectric loss increased at higher filler loading [66].

Figure 6 shows the variation of dielectric constant ($\varepsilon_r$) of PVDF-GO-Nb$_2$O$_5$ nanocomposites as a function of different weight percentage of the Nb$_2$O$_5$ at 100 Hz and room temperature. The dielectric constant of the nanocomposites increases gradually with increase in the filler loading, but increases considerably when the Nb$_2$O$_5$ filler content comes closer to 1.5 wt%. At this stage, parallel micro-capacitors were hard, due to the presence of large distance between two neighboring sites of GO and Nb$_2$O$_5$. As weight percentage of Nb$_2$O$_5$ increases above 1.5 wt% and reached percolation threshold, the dielectric constant values increased noticeably. Interestingly, it is observed that the dielectric constant was enhanced from ≈140 to 144 when content of Nb$_2$O$_5$ increased from 1.5 wt% to 2.5 wt%, which suggests the incorporation of Nb$_2$O$_5$. Even at low concentration of Nb$_2$O$_5$ appreciably improved the dielectric constant of the resultant PVDF-GO-Nb$_2$O$_5$ nanocomposites. This progress of dielectric constant near the percolation threshold can be explained by the presence of microcapacitor networks [56,66]. So the vicinity of percolation threshold, a large number of conductive Nb$_2$O$_5$ networks were separated by thin dielectric layer composed of PVDF matrix and graphene oxide, consequence upon this result in the formation of small capacitors throughout the PVDF-GO-Nb$_2$O$_5$ nanocomposites. Thus, the PVDF-GO-Nb$_2$O$_5$ nanocomposite films near the percolation threshold can be considered as a large electrode area and high charge storage capability, which encourage the rapid increase of capacitance. Moreover, the nanocomposites with 2.5 wt% of Nb$_2$O$_5$ achieve a maximum dielectric constant value ≈140, which is nearly about 22 times higher than that of the pure PVDF. The variation of the dielectric constant ($\varepsilon_r$) near the percolation threshold is given by the power law [66,67],

$$\varepsilon = \varepsilon_m (f_c - f)^{s}$$

(1)

where $\varepsilon$ and $\varepsilon_m$ is the dielectric constant ($\varepsilon_r$) of the PVDF-GO-Nb$_2$O$_5$ nanocomposites and the neat PVDF matrix, respectively. f is the weight percentage of Nb$_2$O$_5$ contents of the nanocomposites, $f_c$ is the percolation threshold, and s is the critical exponent. Figure 6 shows that experimental data fit well to the log–log plots of the power law on linear scale using Equation (1) gives $f_c = 2.0$ wt% with the critical exponent of s = 0.997. In addition, the critical exponent nearly agrees well with that in the universal percolation theory (s ≈ 1). Besides, this result is not always observed in practical continuum system [68].

### 3.4. AC electrical conductivity study

Figure 7 shows the dependence of AC electrical conductivity ($\sigma_{ac}$) of the PVDF-GO-Nb$_2$O$_5$ nanocomposites with different weight percentage of Nb$_2$O$_5$ content as a function of frequency. For the nanocomposites with low weight percentage of Nb$_2$O$_5$ contents (≤ 1.5 wt %), the conductivity curves exhibit a frequency independence character in low-frequency range, which suggests an insulator to conductor transition owing to the presence of some conductive paths in the nanocomposites. However, the conductivity of all said nanocomposites increases linearly with increase in frequency for all loaded weight percentage of filler content and is larger than that of the neat PVDF. When

![Figure 6](image_url)  
Figure 6. Shows the best fit of the dielectric constant of the PVDF-GO-Nb$_2$O$_5$ nanocomposites with various weight percentages of Nb$_2$O$_5$ contents at 100 Hz to Equation (1).
fNb2O5 approaches fc, the percolation threshold and uphold the power laws \[ \sigma \propto \omega^\mu \] as f Nb2O5 \( \rightarrow \) fc \( \text{(2)} \)

In Equation (2), \( \omega \) is the angular frequency (equal to 2\( \pi \) \( \nu \)), \( \nu \) is the frequency and \( \mu \) is the corresponding critical exponent, always between 0 and 1. The experimental data of the PVDF-GO-Nb2O5 nanocomposites with \( \nu = 1.5 \text{ wt\%} \) (near fc) give \( \mu = 0.99 \) (See Figure 7(b)). Moreover, this result is slightly larger than that of the common value (\( \mu_{\text{uni}} = 0.70 \)) from the percolation theory [29].

4. Conclusions

In summary, the Nb2O5-reinforced GO-PVDF nanocomposite films were prepared successfully by using solution casting technique. The PVDF-GO-Nb2O5 nanocomposites were carefully analyzed by SEM analysis and experimental results showed homogeneous dispersion of the GO and Nb2O5 particles into the polymer matrix. The strong interfacial interactions were observed between Nb2O5, GO and PVDF matrix. The dielectric and electrical performance of the PVDF-GO-Nb2O5 nanocomposites were measured in a wide range of frequencies from \( 10^2 \) Hz to \( 10^6 \) Hz. The PVDF-GO-Nb2O5 nanocomposites exhibited considerable increment in the dielectric constant, which is associated with homogeneous dispersion of GO and Nb2O5 particles within the polymer matrix may be attributed to the interfacial or Maxwell–Wagner–Sillars (MWS) polarization effect [46,47]. At the filler content 2.5 wt\%, the value of dielectric constant reaches \( 140 \) and a minimized dielectric loss (1.4) was noticed at the frequency of 100 Hz. The dielectric constant of PVDF-GO-Nb2O5 nanocomposites was 24 times greater than pristine PVDF films on the other hand it is fou times greater than two-phase PVDF-GO nanocomposites.

Besides, the dielectric constant of PVDF-GO-Nb2O5 nanocomposite follows the percolation theory and showed percolation threshold of fc = 2 wt\%. These findings put forward the PVDF-GO-Nb2O5 nanocomposite films might be suitable candidates for the development of high-performance dielectric composite materials for energy storage applications.

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Disclosure statement

No potential conflict of interest was reported by the author(s).

References

[1] Lin B, Li ZT, Yang Y, et al. Enhanced dielectric permittivity in surface-modified graphene/PVDF composites prepared by an electrospinning-hot pressing method. Compos Sci Technol. 2019;172:58–65.
[2] Sankar S, Naik AA, Anilkumar T, et al. Characterization, conductivity studies, dielectric properties, and gas sensing performance of in situ polymerized polypyrrole/copper alumina nanocomposites. J Appl Polym Sci. 2020;137:49145.
[3] Yao M, Cheng Y, Zhou Z, et al. Recent progress on the fabrication and applications of flexible ferroelectric devices. Mater Chem C. 2020;8:14–27.
[4] Pan C, Kou K, Jia Q, et al. Improved thermal conductivity and dielectric properties of h BN/PTFE composites via surface treatment by silane coupling agent. Compos Part B Eng. 2017;111:83–90.
[5] Dikin DA, Stankovich S, Zimmey EJ, et al. Preparation and characterization of graphene oxide paper. Nature. 2007;448:457–460.
[6] Soldano C, Mahmood A, Dujardin E. Production, properties and potential of graphene. Carbon. 2010;48:2127–2150.

[7] Kuilla T, Bhadra S, Yao D, et al. Recent advances in graphene based polymer composites. Prog Polym Sci. 2010;35:1350–1375.

[8] Schedin F, Geim AK, Morozov SV, et al. Detection of individual gas molecules adsorbed on graphene. Nat Mater. 2007;6:652–655.

[9] Stankovich S, Dikin DA, Piner RD, et al. Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide. Carbon. 2007;45:1558–1565.

[10] Bourlinos AB, Gournis D, Petridis D, et al. Graphite oxide: chemical reduction to graphite and surface modification with primary aliphatic amines and amino acids. Langmuir. 2003;19:6050–6055.

[11] Kotresh S, Ravikiran YT, Vijaya Kumar SC, et al. Solution-based spin cast processed poly pyrrrole/nio bium pentoxide nanocomposite as room temperature liquefied petroleum gas sensor. Mater Manuf Process. 2016;31:1976–1982.

[12] Jamil M, Khan ZS, Ali A, et al. Studies on solution processed graphene-Nb_2O_5 nanocomposite based photoanode for dye-sensitized solar cells. J Alloys Compd. 2017;694:401–407.

[13] Sarahan MC, Carroll EC, Allen M, et al. K_Nb_2O_5-derived photocatalysts for hydrogen evolution from water: nanoscrolls versus nanosheets. J Solid State Chem. 2008;181:1678–1683.

[14] Ebina Y, Sasaki T, Watanabe M. Study on exfoliation of layered perovskite-type niobates. Solid State Ion. 2002;151:177–182.

[15] Nunes BN, Lopes OF, Patrocinio AOT, et al. Recent advances in niobium-based materials for photocatalytic solar fuel production. Catalysts. 2020;10:126.

[16] Li Y, Munir KS, Lin J, et al. Titanium-niobium pentoxide composites for biomedical applications. Bioact Mater. 2016;1:127–131.

[17] Mazur M, Kalisz M, Wojcieszak D, et al. Determination of structural, mechanical and corrosion properties of Nb_2O_5 and (Nb_2Cu_1-x)O thin films deposited on Ti_4Al V alloy substrates for dental implant applications. Mater Sci Eng C. 2015;47:211–221.

[18] Skroczczyk K, Antunes MM, Han X, et al. Niobium pentoxide nanomaterials with distorted structures as efficient acid catalysts. Commun Chem. 2019;2:129.

[19] Oliveira LCA, Oliveira HS, Mayrink G, et al. One-pot synthesis of CdS@Nb_2O_5 core–shell nanostructures with enhanced photocatalytic activity. Appl Catal B-Environ. 2014;152:403–412.

[20] Zeng X, Deng L, Yao Y, et al. Flexible dielectric papers based on biodegradable cellulose nanofibers and carbon nanotubes for dielectric energy storage J. Mater Chem C. 2016;4:6037–6044.

[21] Achaby ME, Arrakhiza FZ, Vaudreulla S, et al. Piezoelectric polymorph formation and properties enhancement in graphene oxide-PVDF nanocomposite films. Appl Surf Sci. 2012;258:7668–7677.

[22] Jiang ZY, Zheng GP, Han Z, et al. Enhanced ferroelectric and pyroelectric properties of poly(vinylidene fluoride) with addition of graphene oxides. J Appl Phys. 2014;115:204101.

[23] Marcano DC, Kosynkin DV, Berlin JM, et al. Improved synthesis of graphene oxide. ACS Nano. 2010;4:4806–4814.

[24] Moharana S, Mahaling RN, Silver (Ag)-graphene oxide (GO)-poly (vinylidene fluoride-co- hexafluoropropylene) (PVDF-HFP) nanostructured composites with high dielectric constant and low dielectric loss. Chem Phys Lett. 2017;680:31–36.

[25] Changa X, Wang Z, Quana S, et al. Exploring the synergetic effects of graphene oxide (GO) and polyvinylpyrroliodone (PVP) on poly(vinylidene fluoride) (PVDF) ultrafiltration membrane performance. Appl Surf Sci. 2014;316:537–548.

[26] Zhang X, Nguyen H, Daly M, et al. Nanoscale toughening of ultrathin graphene oxide-polymer composites: mechanochemical insights into hydrogen-bonding/ von der Waals interactions, polymer chain alignment, and steric parameters. Nanoscale. 2019;11:12305–12316.

[27] Shao L, Li J, Guang Y, et al. PVA/polyethyleneimine-functionalized graphene composites with optimized properties. Mater Design. 2016;99:235–242.

[28] Compton OC, Cranford SW, Putz KW, et al. Tuning the mechanical properties of graphene oxide paper and its associated polymer nanocomposites by controlling cooperative intersheet hydrogen bonding. ACS Nano. 2012;6:2008–2019.

[29] Mishra AK, Ramaprabhu S. Functionalized graphene sheets for arsenic removal and desalination of sea water. Desalination. 2011;282:39–45.

[30] Aziza M, Syuhada F, Halima A, et al. Preparation and characterization of graphene membrane electrode assembly. J Teknol. 2014;69:11–14.

[31] Li Y, Wang Q, Wang T, et al. Preparation and tribological properties of graphene oxide/nitride rubber nanocomposites. J Mater Sci. 2012;47:730–738.

[32] Bhawal P, Ganguly S, Chaki TK, et al. Synthesis and characterization of graphene oxide filled ethylene methyl acrylate hybrid nanocomposites. RSC Adv. 2016;6:20781–20790.

[33] Narksitpan S, Thongtem S. Synthesis and characterization of transparent graphene oxide nanosheets. Ferroelectr Lett Sect. 2014;41:94–99.

[34] Stobinski L, Lesiak B, Malolepszy A, et al. Graphene oxide and reduced graphene oxide studied by the XRD, TEM and electron spectroscopy methods. J Electron Spectros Relat Phenomena. 2014;195:145–154.

[35] Maity N, Mandal A, Nandi AK. Interface engineering of ionic liquid integrated graphene in poly(vinylidene fluoride) matrix yielding magnificent improvement in mechanical, electrical and dielectric properties. Polym. 2015;65:154–167.

[36] Haworth B, Raymond CL, Sutherland I. Polyethylene compounds containing mineral fillers modified by acid coatings. 2: factors influencing mechanical properties. Polym Eng Sci. 2001;41:1345–1364.

[37] Xu XL, Yang C, Yang J, et al. Excellent dielectric properties of poly(vinylidene fluoride) composites based on partially reduced graphene oxide. Compos Part B Eng. 2017;109:91–100.

[38] Li H, Chen Z, Liu L, et al. Poly(vinyl pyrrolidone)-coated graphene/poly(vinylidene fluoride) composite films with high dielectric permittivity and low loss. Compos Sci Technol. 2015;121:49–55.

[39] Sunderrajan S, Miranda LR, Pennathur G. Improved stability and catalytic activity of graphene oxide/chitosan hybrid beads loaded with porcine liver esterase. Prep Biochem Biotechnol. 2018;48:343–351.

[40] Khalili D. Graphene oxide: a promising carbocatalyst for the regioselective thiocyanation of aromatic amines, phenols, anisols and enolvable ketones by
hydrogen peroxide/KSCN in water. New J Chem. 2016;40:2547–2553.

[41] Chaiyakun RS, Witt-anun N, Nuntawong N, et al. Preparation and characterization of graphene oxide nanosheets. Procedia Eng. 2012;35:759–764.

[42] Ikhsan NI, Kumar PR, Pandikumar A, et al. Facile synthesis of graphene oxide–silver nanocomposite and its modified electrode for enhanced electrochemical detection of nitrite ions. Talanta. 2015;144:908–914.

[43] Lai Q, Zhu S, Luo X, et al. Study of ultraviolet-visible light absorbance of exfoliated graphite forms. AIP Adv. 2012;2:032146.

[44] Shah R, Kausar A, Muhammad B. Characterization and properties of poly(methyl methacrylate)/graphene, poly(methyl methacrylate)/graphene oxide and poly(methyl methacrylate)/p-Phenylendiamine-graphene oxide nanocomposites. Polym Plast Technol Eng. 2015;54:1334–1342.

[45] Sahoo G, Sarkar N, Swain SK. The effect of reduced graphene oxide intercalated hybrid organoclay on the dielectric properties of polyvinylidene fluoride nanocomposite films. Appl Clay Sci. 2018;162:69–82.

[46] Prasad K, Prasad A, Chandra KP, et al. Electrical conduction in 0–3 BaTiO3/PVDF composites. Integr Ferroelectr. 2010;117:55–67.

[47] Zhang XJ, Wang GS, Wei YZ, et al. Polymer-composite with high dielectric constant and enhanced absorption properties based on graphene–CuS nanocomposites and polyvinylidene fluoride. J Mater Chem A. 2013;1:12115–12122.

[48] Kuang X, Liu Z, Zhu H. Dielectric properties of Ag@C/ PVDF composites. J Appl Polym Sci. 2013;129:3411–3416.

[49] Zhou W, Wang Z, Dong L, et al. Dielectric properties and thermal conductivity of PVDF reinforced with three types of Zn particles. Compos Part A Appl Sci Manuf. 2015;79:183–191.

[50] He D, Wang Y, Song S, et al. Polymer-based nanocomposites employing Bi2S3@SiO2 nanorods for high dielectric performance: understanding the role of interface polarization in semiconductor-insulator core-shell nanostructure. Compos Sci Technol. 2017;151:25–33.

[51] Fu J, Hou Y, Zheng M, et al. Improving dielectric properties of PVDF composites by employing surface modified strong polarized BaTiO3 particles derived by Molten Salt Method. ACS Appl Mater Interfaces. 2015;7(44):24480–24491.

[52] Ata AMAE, Attia SM, Meaz TM. AC conductivity and dielectric behavior of CoAl2Fe2xO4. Solid State Sci. 2004;6(1):61–69.

[53] Melagiriyappa E, Jayanna HS, Chougule BK. Dielectric behavior and ac electrical conductivity study of Sm1+ substituted Mg–Zn ferrites. Mater Chem Phys. 2008;112:68–73.

[54] Kou Y, Zhou W, Li X, et al. Enhanced dielectric properties of PVDF nanocomposites with modified sandwich-like GO@PVP hybrids. Polym Plast Technol Mater. 2020;59(6):592–605.

[55] Deepti PL, Patri SK, Choudhary RNP, et al. Dielectric, impedance and modulus spectroscopy of Ta-based layered perovskite. Phase Transit. 2019;92:642–656.

[56] He FA, Lam KH, Fan JT, et al. Novel syndiotactic polystyrene/BaTiO3-graphite nanosheets three-phase composites with high dielectric permittivity. Polym Test. 2013;32:927–931.

[57] Tamura R, Lim E, Manaka T, et al. Analysis of pentacene field effect transistor as a Maxwell-Wagner effect element. J Appl Phys. 2006;100:114515.

[58] Li Y, Fan M, Wu K, et al. Polydopamine coating layer on graphene for suppressing loss tangent and enhancing dielectric constant of poly(vinylidene fluoride)/graphene composites. Compos Part A Appl Sci Manuf. 2015;73:85–92.

[59] Zhi X, Mao Y, Wen S, et al. γ-aminopropyl triethoxysilane functionalized graphene oxide for composites with high dielectric constant and low dielectric loss. Compos Part A Appl Sci Manuf. 2015;76:194–202.

[60] Liu L, Zhang Y, Lv F, et al. Polymide composites composed of covalently bonded BaTiO3@GO hybrids with high dielectric constant and low dielectric loss. RSC Adv. 2016;6:86817–86823.

[61] Dang ZM, Yuan JK, Zha JW, et al. Fundamentals, processes and applications of high-permittivity polymer–matrix composites. Prog Mater Sci. 2012;57:660–723.

[62] Xie B, Zhang H, Zhang Q, et al. Enhanced energy density of polymer nanocomposites at a low electric field through aligned BaTiO3 nanowires. J Mater Chem A. 2017;5:6070–6078.

[63] Paik H, Xhoo YY, Hong S, et al. Effect of Ag nanoparticle concentration on the electrical and ferroelectric properties of Ag/P(VDF-TrFE) composite films. Sci Rep. 2015;5:13209.

[64] Feng Y, Li WL, Wang JP, et al. Core–shell structured BaTiO3@carbon hybrid particles for polymer composites with enhanced dielectric performance. J Mater Chem A. 2015;3:20313–20321.

[65] Yousef N, Sun X, Lin X, et al. Highly aligned graphene/ polymer nanocomposites with excellent dielectric properties for high-performance electromagnetic interference shielding. Adv Mater. 2014;26:5480–5487.

[66] Yang Y, Sun H, Yin D, et al. High performance of poliyimide/CoCu3Ti2O7@Ag hybrid films with enhanced dielectric permittivity and low dielectric loss. J Mater Chem A. 2015;3:4916–4921.

[67] Shafee EE, Gamal ME, Isa M. Electrical properties of multi walled carbon nanotubes/ poly(vinylidene fluoride/trifluoroethylene) nanocomposites. J Polym Res. 2012;19:9805–9808.

[68] Ahmad K, Pan W, Shi SL. Electrical conductivity and dielectric properties of multiwalled carbon nanotube and alumina composites. Appl Phys Lett. 2006;89:133122.

[69] Huo X, Li W, Zhu J, et al. Composite based on Fe3O4 @BaTiO3 particles and polyvinylidene fluoride with excellent dielectric properties and high energy density. J Phys Chem C. 2015;119:25786–25791.