

A novel polyvinyl alcohol/polyethylene glycol (PVA/PEG) polymeric blend doped with graphene oxide for energy storage devices

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ABSTRACT

A developed polyvinyl alcohol/polyethylene glycol (PVA/PEG) blend containing different concentrations of graphene oxide GO (PVA/PEG-GO) as dielectric materials for energy storage devices was studied. 80 wt% of PVA/ 20 wt% of PEG were doped with 0.5, 1.5, and 3 wt% of graphene oxide and prepared using the solution casting technique. The electrical properties, the dielectric constant (ϵ'), dielectric loss (ϵ''), and ac conductivity (σ_{ac}), in a wide range of frequencies, were extensively investigated. The GO strongly enhanced the dielectric constant (energy storage) of the produced PVA/PEG blend, while a little variation was observed in dielectric loss (energy loss). A higher frequency shift was observed in the loss tangent peak, reflecting an augmentation in the mobility speed of the ions, causing a longer relaxation time. In response to the electric field, the charge carriers' mobility has a short range. The addition of GO caused a reduction in the semicircle diameter of a Cole-Cole profile. The ac conductivity was found to obey the power law, and the ionic conduction dominates the conductivity in all the studied frequency ranges. The produced PVA/PEG-GO blends had significant energy storage characteristics, making them an excellent choice for dielectric materials in energy storage devices.

Keywords: Energy storage, Supercapacitor, Dielectric properties, Graphene oxide, PVA/PEG polymer.

1-Introduction

Being one of the cornerstones of technology development, the continuous demand for energy is constantly increasing (1-2). Because of the multiplicity of risks resulting from the use of fossil fuels in energy production, scientists have developed new ways to produce clean energy, such as wind, nuclear, and solar energy (3-6). However, clean energy production sources also face several obstacles, the most important of which is how to store the generated energy, which necessitates the need to search for methods and technologies to store energy effectively (7-8). Generally, energy storage devices, both chemically (such as batteries and electrochemical capacitors) and physically (such as dielectric capacitors), are the only two ways to store energy (9-10). Although batteries have a high energy density, the slow mobility of the charge carriers and the long charging-discharging duration are the big problems facing batteries as energy storage devices, and therefore they are usually used in long-term stable energy facilities (9-10). Electrochemical capacitors are characterized by suitable power and energy density, but their complex structure complicates the main obstacle in front of their storage for further energy (11-12). On the other hand, physical storage devices represented by dielectric capacitors are characterized by high energy density, simple structure, high safety, and very high charge-discharge rates. Hence, the use of dielectric capacitors has spread widely in various medical, industrial, and military devices; however, their lower energy storage is the main disadvantage in energy storage devices (13-14). Hence, the current studies were based on increasing the capacity of the dielectric capacitors by improving the dielectric energy materials. Dielectric storage materials used in capacitors vary, including polymeric, ceramic, and glass materials (15-16). Dielectric polymers were characterized by high electrical breakdown strength, flexibility, and suitable chemical stability; however, the low dielectric constant and poor resistance to high temperatures are the main obstacles that need improvement (17-18). Graphene is a two-dimensional material that has a large specific surface area, a high elastic modulus, and a Young's modulus. Additionally, graphene has good electrical and thermal conductivity and carrier mobility. These excellent properties have enabled graphene to achieve a high rate of development (19-20). Long Zhang et al. in 2019

prepared a perfluorooctanoic acid-doped polyaniline/graphene oxide/poly(vinylidene fluoride) (PFOA rPANI/rGO/PVDF) nanocomposite to enhance the dielectric properties. The authors found that the fabricated PFOA-rPANI/rGO/PVDF nanocomposites had a high dielectric constant while maintaining low dielectric loss. The highest dielectric constant of nanocomposites could reach 1754 at a low filler volume fraction of 0.5% (21). Simantini Majumda et al in 2022 inlaid CS/PMMA blended solid electrolytes with graphene oxide (GO) to enhance their specific capacitance. The authors succeed in obtaining an effective specific capacitance of $\sim 294 \text{ Fg}^{-1}$ with Ag-decorated MnCoFeO_4 nanoparticles anchored onto an rGO electrode (22).

Hence, based on the foregoing, a PVA/PEG blend (PVA/PE-GO1) was inlaid with 0.5, 1.5, and 3 wt% of graphene oxide (PVA/PE-GO2, PVA/PE-GO3, and PVA/PE-GO4,) to enhance their dielectric properties. The electrical properties, dielectric constant, loss tangent, and ac conductivity were extensively studied.

2. Experimental

80 wt% of PVA/ 20 wt% of PEG (PVA/PEG-GO1) blend were prepared by the solution casting technique. The PVA powder was dissolved in deionized water at 90°C for an hour with continuous stirring until complete miscibility. Meanwhile, PEG was dissolved in deionized water at room temperature. Both solutions were mixed and stirred for an additional hour, and then 1 gm of glycerine was added to the mixture with continuous stirring for an additional hour. A PVA/PEG-GO1 blend was loaded with different concentrations of graphene oxide (0.5, 1.5, and 3 wt%), were which labeled as PVA/PEG-GO2, PVA/PEG-GO3, and PVA/PEG-GO4. To prepare graphene oxide GO-loaded samples, GO was dispersed in 10 ml of deionized water using an ultrasonicator for 20 minutes before being added to the PVA/PEG-GO1 blend. Finally, the mixed solutions were poured onto glass Petri dishes and left to dry at room temperature for 48 hours. The samples were cut in disk form with a diameter of 1.0 cm and a thickness of 0.05 cm, which were sandwiched between two brass electrodes after being properly coated with silver paste on their faces to ensure good connections. The dielectric analysis was performed at room temperature with a constant applied voltage of 1 V using the LCR bridge (Instek LCR - 821 meter) covering the frequency range $5 - 50 \times 10^6$ Hz. Using relations 1, 2, and 3, the dielectric constant ϵ' (the real portion of the complex dielectric), dielectric loss ϵ'' (the imaginary part of the complex dielectric), and ac conductivity σ_{ac} of the samples were calculated (23-24).

$$\epsilon' = \frac{d}{\epsilon_0 A} C \quad (1)$$

$$\epsilon'' = \epsilon' \tan \delta \quad (2)$$

$$\sigma_{ac} = \omega \epsilon_0 \epsilon'' \quad (3)$$

where, C, d, A, ϵ_0 , and ω are the capacitance of the sample, the thickness of the sample, the cross-section area of each of the parallel surfaces of the sample, the permittivity of air, and the angular frequency respectively.

3. Results and Discussion

Figures 1a and b show the frequency dependence of both the dielectric constant ϵ' (energy storage) and dielectric loss ϵ'' (energy loss) of the produced PVA/PEG-GO1-4 blends. A reduction in both ϵ' and ϵ'' with the increase in the frequency for all the studied PVA/PEG-GO blends was observed. It is also observed that both ϵ' and ϵ'' have higher values at low frequencies compared to the higher ones. In the low frequency region, the higher ϵ' and ϵ'' arose due to the electrode and the interfacial effects (23-25). In the high frequency region, due to the accumulation of charges resulting from the non-diffusion of ions as a result of the periodic reversal speed of the electric field, the values of ϵ' and ϵ'' decreased. The observed augmentation in ϵ' and ϵ'' with GO loading for all the studied frequencies arose as a result of the easy orientation mechanism of dipoles in response to the applied electric field and dipoles initiated by GO particles, which results in higher polarization and consequently an accumulation of charge occurred leading to higher dielectric constant values (23-25), which is similar to the observation of Mohd Sadiq et al. in 2022 (28).

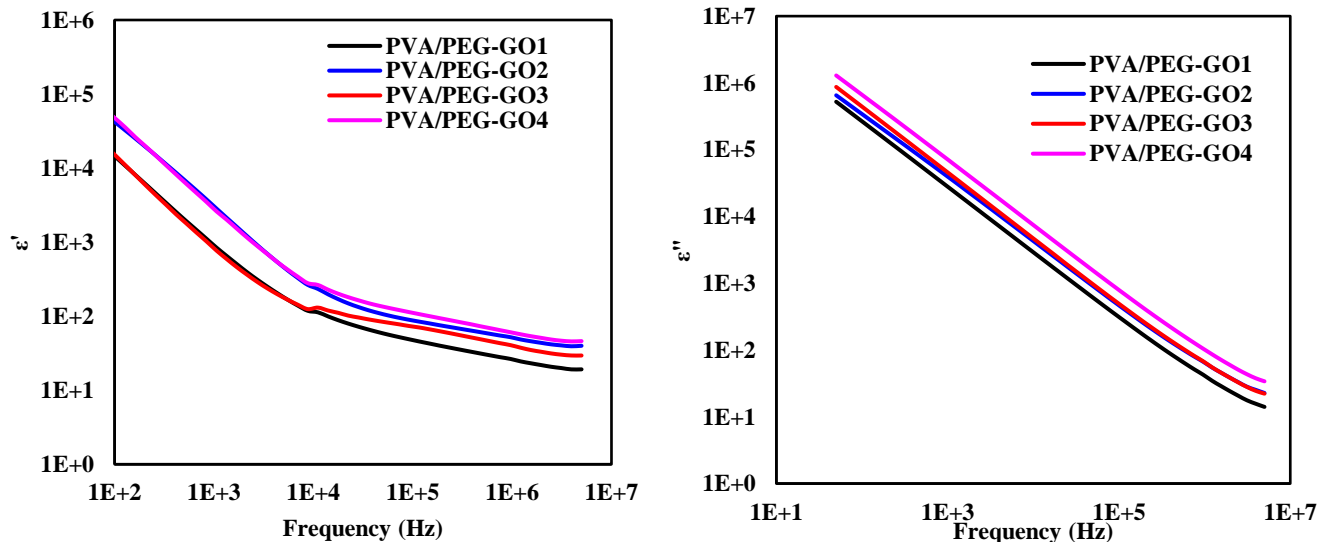


Figure 1: The frequency dependence of the dielectric a) constant and b) loss for all the studied PVA/PEG-GO blends

The dependence of loss tangent $\tan \delta$ (representing the ratio of the energy loss to the energy stored ϵ''/ϵ' in an applied AC field) on frequency for all the studied samples is shown in **Figure 2a**. It is clearly observed that the $\tan \delta$ sharply reduced with the frequency increase. As GO content increases, there is a shift in peak towards the higher frequency, which reflects the large relaxation time. The dependence of relaxation frequency ν_{max} and relaxation time τ on the GO contents is shown in **Figure 2b**. An augmentation ν_{max} and reduction in τ were observed up to 0.5 wt% of GO loading and thereafter slightly increased above 0.5 wt % loading of GO filler particles. As the GO content increases, the movement speed of the charge carriers increases, leading to an increase in the relaxation rate, causing a shift of the frequency peak maximum ν_{max} towards the higher frequency

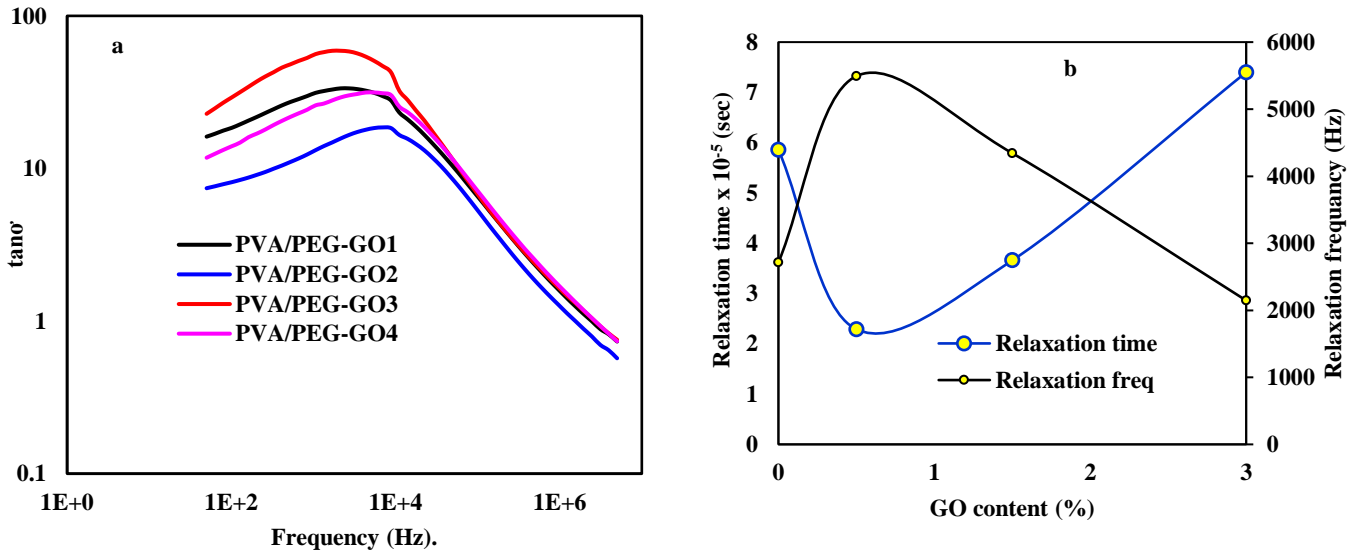


Figure 2: The variation of a) $\tan \delta$ with frequency for all the studied PVA/PEG-GO blends and b) relaxation frequency and time with GO concentration

The description of the dielectric properties of supercapacitor materials has been preferred by using the electric modulus formalization (E) based on the following relation (29).

$$E = \frac{1}{\epsilon} = E' + iE'' = \frac{\epsilon''}{\epsilon'^2 + \epsilon''^2} + i \frac{\epsilon'}{\epsilon'^2 + \epsilon''^2} \quad (4)$$

where, E' and E'' are real and imaginary parts of the complex electric modulus, respectively.

As can be seen from **Figures 3a** and **b** that both E' and E'' increased sharply as the frequency increased. The rapid increment in the E' and E'' with the frequency increase attributed to the short-

range mobility of charge carriers (29). A lack in restoring force of the flow charges is conducted in response to the electric field reflecting on the charge carriers' mobility range, causing its shortness (25, 30).

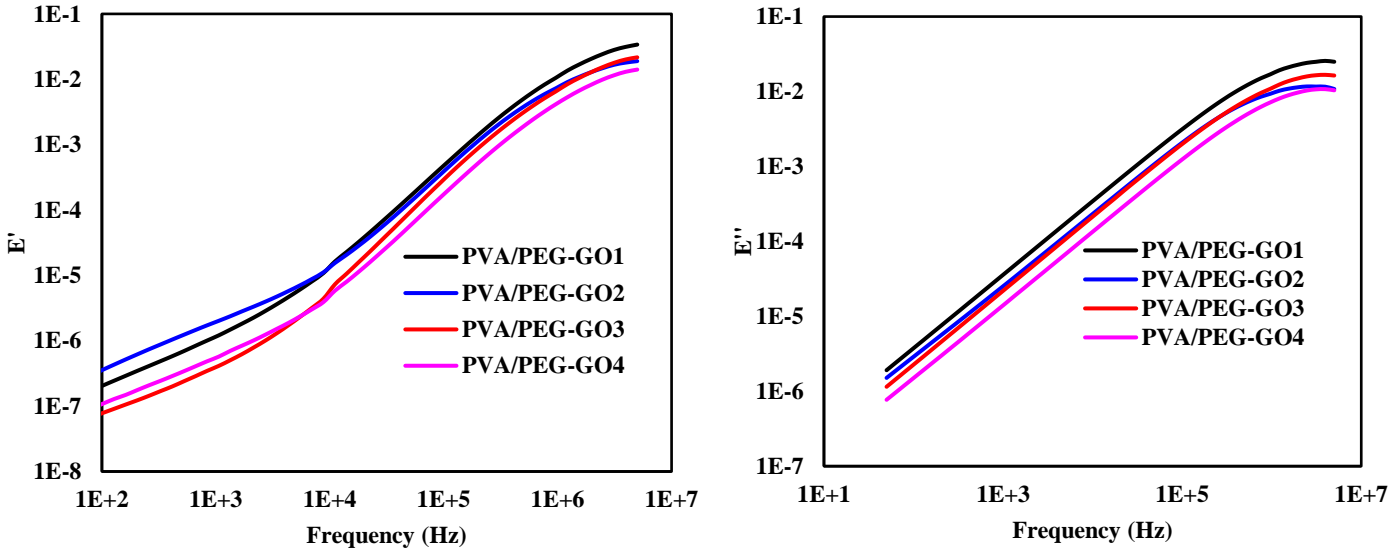


Figure 3: a) The real part E' and b) the imaginary part E'' of the electric modulus for all the studied PVA/PEG-GO blends

Figure 4 depicts the Nyquist or Cole-Cole plots of E'' versus E' for different contents of GO loading PVA/PEG. It was observed that the obtained behavior perfectly matches with the Debye behavior. The diameter of the semicircle decreases upon GO loading for the PVA/PEG samples.

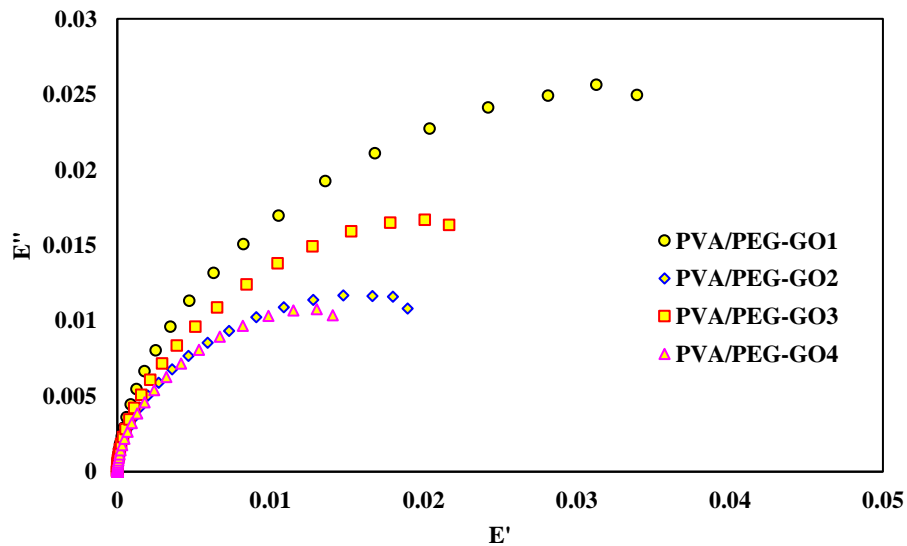


Figure 4: Cole-Cole plots of E'' versus E' for all the studied PVA/PEG-GO blends

The ac conductivity of the produced PVA/PEG-GO blends is shown in **Figure 5**. It was observed that the conductivity increased with the frequency and perfectly matched Jonscher's universal power law ($\sigma_{ac}(\omega) = \sigma_{dc} + A\omega^m$) (30). The values of frequency exponent m were varied between 0.17-0.46 for VA/PEG-GO1-4 blends. The observed augmentation of ac conductivity is attributed to the ionic mechanism. Moreover, the conductivity of the PVA/PEG-GO2-4 blends is greater than that of the VA/PEG-GO1 blend, which may be due to the increased mobility of the polymer chain and the charge carriers and hence the conductivity (24-25). Similar results were reported by Asmaa M.M. Ibrahim et al. and A. M. El Sayed et. al (28-29).

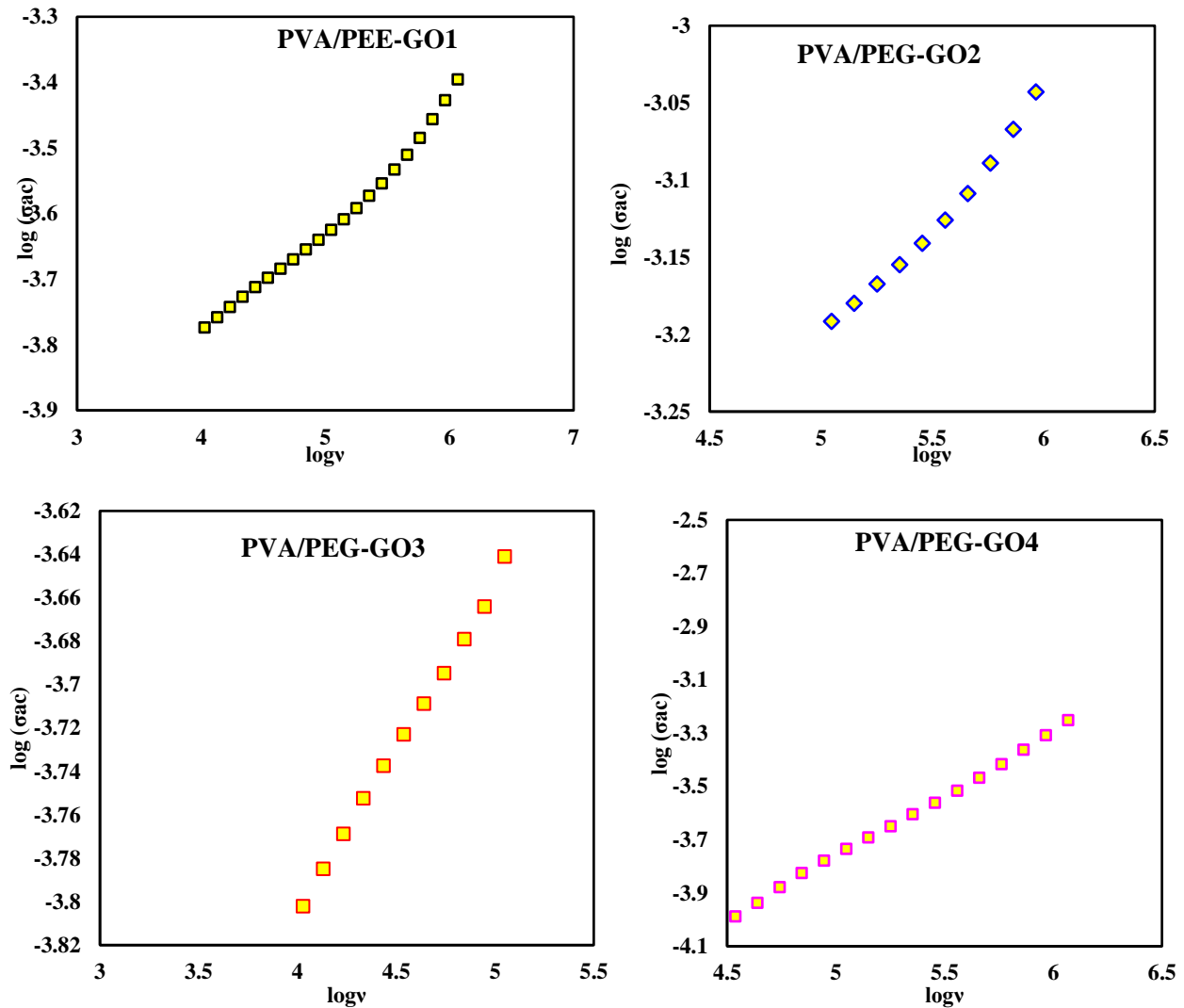


Figure 5: The variation of $\log(\sigma_{ac})$ with $\log(\nu)$ for all the studied PVA/PEG-GO blends

As shown in **Table 1**, the σ_{dc} was increased and the frequency exponent m was decreased with GO loading up to 0.5 wt%. while the polarizability strength A was decreased at 0.5 wt% of GO and re-

increased beyond 0.5 wt%. Generally, the variation of σ_{dc} and m depend mainly on the type of the prominent conduction mechanism. The reduction of m value refers to small polaron, which is in accordance with the hopping conduction in amorphous. On the other hand, mix PVA/PEG blend with GO forms a large number of conductive three-dimensional semiconducting networks, leading to hopping of the charge carrier from the conducting clusters to the neighbors (25, 27, 30). The fluctuation of the polarizability strength A arose as a result in the small/large polaron ratio (29-30).

Table 1: The deduced values of dc conductivity σ_{dc} , polarizability strength A , and frequency exponent m all samples at room temperature

Sample code	$\sigma_{dc} \times 10^{-5} (\Omega \cdot \text{cm})^{(-1)}$	$A (\Omega^{(-1)} \text{cm}^{(-1)}) \times 10^4$	m
PVA/PEG-GO1	140	3.1	0.17
PVA/PEG-GO2	180	0.7	0.153
PVA/PEG-GO3	240	2.5	0.151
PVA/PEG-GO4	300	125.8	0.46

Conclusion

A series of GO doped PVA/PEG polymeric blends (PVA/PEG-GO1-4) was produced to be used as dielectric materials in energy storage devices. The produced materials had high-energy storage values and relatively low energy loss. The considered PVA/PEG-GO blends had a large relaxation time, reflecting their high efficiency in energy storage. The ionic conductivity is dominant in the produced PVA/PEG-GO blends. Hence, the produced PVA/PEG-GO blends had appropriate specifications to be used as dielectric materials in energy storage devices.

• Conflict of Interest

The authors declare that there is no conflict of interest related to the article.

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