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Published in:
Polymer Testing

Link to article, DOI:
[10.1016/j.polymertesting.2020.106650](https://doi.org/10.1016/j.polymertesting.2020.106650)

Publication date:
2020

Document Version
Publisher's PDF, also known as Version of record

[Link back to DTU Orbit](#)

Citation (APA):
Taj, M., Manohara, S. R., Hanagodimath, S. M., & Gerward, L. (2020). Novel conducting poly(3,4-ethylenedioxythiophene) – Graphene nanocomposites with gigantic dielectric properties and narrow optical energy band gap. *Polymer Testing*, 90, [106650]. <https://doi.org/10.1016/j.polymertesting.2020.106650>

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Material Properties

Novel conducting poly(3,4-ethylenedioxythiophene) – Graphene nanocomposites with gigantic dielectric properties and narrow optical energy band gap

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ARTICLE INFO

Keywords:

Nanocomposites
Polymer-matrix composites (PMCs)
Electrical properties
poly(3,4-ethylenedioxythiophene)
Energy storage
Graphene nanoplatelets

ABSTRACT

Novel nanocomposites, consisting of conducting poly(3,4-ethylenedioxythiophene) [PEDOT] and graphene nanoplatelets [GNPs], were successfully synthesized by in-situ chemical-oxidative polymerization of 3,4-ethylenedioxythiophene [EDOT] using ammonium peroxydisulfate as an oxidizing agent. The formation of PEDOT and its incorporation onto the surface of GNPs were confirmed by scanning electron microscopy, Fourier-transform infrared-spectroscopy, and X-ray diffraction. The optical energy band gap, E_g^{opt} , was determined by UV-Vis spectroscopy. Dielectric constant and loss as well as AC electrical conductivity, σ_{AC} , were determined in the frequency range from 10 Hz to 8 MHz. The PEDOT-GNP nanocomposites were found to have extremely large dielectric constant, ϵ' , significantly high σ_{AC} , and narrow E_g^{opt} values. In particular, PEDOT-GNP nanocomposite with 10 wt% GNP has a gigantic dielectric constant of the order of 9×10^5 at 1 kHz and a narrow optical energy band gap of 1.26 eV. The ϵ' values (10^8 to 10^5 in the frequency range from 10 Hz to 5 MHz) of PEDOT-10 wt% GNP are the highest among those reported in the literature for carbon based polymer nanocomposites. The massive quantity of micro-capacitors formed in the nanocomposites, prior to the creation of conductive networks, leads to the gigantic dielectric properties. The ϵ' and σ_{AC} values of PEDOT-10 wt% GNP nanocomposite were about 90 and 400 times larger than those of pure PEDOT. Our method should be particularly promising in the development of new materials for high energy storage applications.

1. Introduction

The intrinsically-conducting-polymers (ICPs) possessing a π -conjugated system have sparked considerable activity in the scientific community due to their wide variety of promising applications such as strain sensors, organic solar cells, anticorrosive coatings, electrochromic windows [1–4], batteries [5], supercapacitors [6], electromagnetic interference shielding [7], etc. The polyaniline, polypyrrole, polythiophenes, and their derivatives are the most common ICPs of scientific interest. Among these, the polyaniline family has been used for various multidisciplinary applications due to easy processing, low cost and environmental stability. However, the benzidine moieties present in their backbone might yield toxic products upon degradation. Polypyrrole is a promising polymer but is infusible and insoluble. Poly(3,

4-ethylenedioxythiophene) [PEDOT] developed in the 1980s in Germany, has excellent environmental and thermal stability, high optical transparency, high conductivity, and a narrow band gap. The 3 and 4 positions of the thiophene ring in EDOT monomer is protected by ethylenedioxy moiety, minimizing the probability of a side chain reaction during the polymerization. This results in a large conjugation length. Accordingly, PEDOT has many applications, such as antistatic coatings, organic light emitting diode (OLED), etc. [8–10].

Nanocomposites of ICPs have received great scientific interest due to their multifunctional properties. Combining the effect of each constituent can result in a polymer nanocomposites with improved properties because of the possible synergetic effects [11,12]. Modifications of ICPs using functional nanofillers of various shape, size and nature result in remarkable chemical and physical properties. Various types of PEDOT

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Fig. 1. FTIR spectra of pristine PEDOT and PEDOT-GNP nanocomposites.

Fig. 2. XRD pattern of pristine PEDOT and PEDOT-GNP nanocomposites.

composites using metals, organic materials, metal oxides, etc., have been tried to enrich the properties of PEDOT [13,14]. Nowadays, carbon nanofillers, such as graphene nanoplatelets [GNPs] and carbon nanotubes, are considered as promising fillers due to the strong interactions between the conjugated polymer and carbon nanomaterials. The flat surface of graphene is a better nucleating surface than the curved surfaces of carbon nanotubes [15–17]. The wonder material of our century, graphene, has attracted intensive attention as a novel nanofiller due to its remarkable thermal and electrical conductivity, good mechanical strength, low mass density, and large surface area [18–21].

There is an increasing need for materials having a high dielectric constant, ϵ' , due to their importance in electronics and electrical industry. However, a single composition material cannot meet this requirement. The blending of dissimilar materials is expected to provide composite having higher ϵ' values, especially polymer-matrix composites (PMCs). Therefore, in the present paper, a simple, effective, and environmental friendly route for the synthesis of PEDOT-GNP nanocomposites via chemical oxidative polymerization process has been

reported. These nanocomposites have been studied with the intent of developing nanocomposites having unique optical and dielectric properties by integrating the merits of constituents, i.e. PEDOT and GNPs. However, to our best knowledge, PEDOT-GNP nanocomposites with such properties have not been reported so far. The present investigations will provide a new idea for the design of a completely new class of dielectric materials well suited for applications in e.g. high-energy storage. In the present work, a systematic study on the effect of addition of GNPs into PEDOT is attempted for understanding the structural formation, and changes in optical, dielectric, and electrical properties of PEDOT-GNP nanocomposites. The dielectric properties, such as loss tangent, dielectric constant and dielectric loss, and electrical properties, such as AC and DC electrical conductivity, were measured to check the feasibility of PEDOT-GNP nanocomposites for energy storage applications.

2. Material and methods

2.1. Chemicals

3,4-ethylenedioxythiophene [EDOT] (97%) and ammonium peroxydisulfate [APS] (98%) were purchased from Alfa Aesar, USA. Graphene nanoplatelets [GNPs] (average thickness: 6–8 nm, surface area: 120–150 m²/g, particle size: 25 μ m) were obtained from Sigma-Aldrich, USA. De-ionized water having a resistivity of 18.2 M Ω -cm was used. All the chemicals were used as received without any further purification.

2.2. Synthesis of PEDOT-GNP nanocomposites

PEDOT-GNP nanocomposites were prepared by in-situ chemical oxidative polymerization of 3,4-ethylene-dioxy-thiophene in the presence of a suitable quantity of GNPs. An aqueous dispersion of EDOT was prepared from 1.33 ml of EDOT in 100 ml of de-ionized water under constant stirring. A known quantity of GNPs was added to this solution at various weight percentages (1, 2.5, 5, 10, and 15 wt %) and the solution was dispersed under constant stirring for 1 h. APS was added as an oxidizing agent to the above solution in 1:2 mol [EDOT:APS] ratios with respect to EDOT. The polymerization was allowed to carry on for 20 h under vigorous stirring. The nitrogen gas was bubbled continuously during polymerization to prevent the over-oxidation of PEDOT, which might decrease the electrical conductivity. The resulting dark-blue sample was washed with profuse quantity of an ethanol-deionized water mixture and dried at 60 °C for 24 h. The powder sample, thus obtained, was compressed to form 13 mm diameter pellets using a hydraulic press. The thickness of the pellets, as measured by a digital Vernier, was about 0.70 mm. Pristine PEDOT was synthesized by following a similar procedure in the absence of GNPs.

2.3. Instrumental techniques

The surface morphologies of PEDOT and its GNP nanocomposites were characterized by a JEOL JCM-6000 Plus scanning electron microscope [SEM]. X-ray diffraction [XRD] was performed using a PANalytical XPERT-3 diffractometer in the angular range 10 – 60° (2 θ) with Cu-K α radiation (λ = 1.5406 Å, accelerating voltage 40 kV). Fourier transform infrared [FTIR] spectroscopy data of pristine PEDOT and PEDOT-GNP nanocomposites were recorded by a Bruker Alpha FTIR spectrometer in the 400–4000 cm^{−1} wave number range. UV–Vis spectrophotometer (Shimadzu 1800) was used for recording the UV–Vis spectra in the 200–900 nm wavelength range. The frequency dependent dielectric properties (tangent loss, dielectric loss, and dielectric constant), and AC electrical conductivity were studied in the frequency range from 10 Hz to 8 MHz by a high-precision HIOKI-IM3536 LCR-meter and HIOKI-L2000 four-terminal probe [22]. All studies were carried out at room temperature.

Fig. 3. SEM images showing surface morphology of pristine PEDOT and PEDOT-GNP nanocomposites. Scale mark 10 μm . (a) PEDOT, (b) PEDOT-1 wt% GNP, (c) PEDOT-2.5 wt% GNP, (d) PEDOT-5 wt% GNP, (e) PEDOT-10 wt% GNP, (f) PEDOT-15 wt% GNP.

3. Results and discussion

3.1. Fourier transform infrared spectroscopy

FTIR spectra of pristine PEDOT and PEDOT-GNP nanocomposites are shown in Fig. 1. A distinguished IR band at about 890 cm^{-1} , which generally appears in the FTIR spectra of EDOT [ESI, Fig. S1], is due to C–H bending. However, it has disappeared in PEDOT [ESI, Fig. S1] and PEDOT-GNP nanocomposites, indicating successful formation of PEDOT chains through 2,2'-coupling. In case of PEDOT [ESI, Fig. S1], the observed vibrational-bands at about 1354 and 1516 cm^{-1} are attributed to C–C and C=C stretching of the quinoidal structure of thiophene ring and ring stretching of thiophene ring, respectively. The bands at 1054 , 1092 , and 1202 cm^{-1} could be assigned to C–O–C bond stretching in the ethylenedioxy group. In addition, the characteristic absorption bands at around 687 , 840 , and 978 cm^{-1} are due to C–S bond stretching vibration of thiophene ring [1,23,24].

The FTIR spectra of PEDOT-GNP nanocomposites also show similar characteristic peaks as those of pristine PEDOT, indicating that PEDOT

and its nanocomposite have a similar chemical structure. However, some of the characteristic peaks of the PEDOT are slightly shifted upon adding GNPs to pure PEDOT. Such shifting is due to strong cooperative interaction between GNPs and PEDOT, resulting in enhanced properties of synthesized nanocomposites at a molecular level. Moreover, the aromatic structures of PEDOT will interact strongly with the basal plane of graphite by π -stacking [25–27]. In addition, the transmission intensity for PEDOT-GNPs nanocomposites is lower than that of pure PEDOT due to the dominating phase of the PEDOT matrix.

3.2. X-ray diffraction analysis

The structure of PEDOT-GNP nanocomposites were examined by XRD measurements. Fig. 2 is a plot of XRD spectra of PEDOT and its nanocomposites having various GNPs wt% loadings. A broad diffraction peak at 25.4° ($d = 3.5\text{ \AA}$) in the XRD pattern of PEDOT [ESI, Fig. S2] is related to the interchain planar ring-stacking distance in polymer and is in good agreement with literature data [28]. The diffraction peaks observed at 26.3° (due to pure GNPs, ESI, Fig. S2) [29] and 25.4° (due to

Fig. 4. UV-Vis absorption spectra of pristine PEDOT and PEDOT-GNP nanocomposites.

pure PEDOT) in the XRD spectra of PEDOT-GNP nanocomposites are indicating successful formation of nanocomposites. It can also be observed from Fig. 2 that the characteristic peak of PEDOT becomes weaker and the peak of GNP become more apparent with increasing concentration of GNPs. A sharp intense peak is observed at 26.3° only for PEDOT-GNP nanocomposites having 10 and 15 wt% GNP. The peak sharpening can be related to periodic mono-distribution among polymer backbone chains, indicating that molecules of PEDOT are arranged more orderly in PEDOT-GNP nanocomposites. These results show that the crystallinity is enhanced in these nanocomposites and the ordered arrangement of molecules facilitates carrier transport, leading to the enhanced electrical conductivity in PEDOT-GNP nanocomposites [30, 31].

3.3. Scanning electron microscopy analysis

The SEM micrographs of GNPs, pristine PEDOT and PEDOT-GNP nanocomposites are presented in Fig. S3 (ESI) and Fig. 3(a–f), respectively. Fig. 3(a) displays roughly irregular spherical-like particles of PEDOT. The curved sheet-like structure of GNPs covered with irregular spherical-like particles of PEDOT are observed for PEDOT-GNP nanocomposites [Fig. 3(d–f)]. Such coverage results in increasing thickness of GNPs and decreasing van der Waals force between the GNPs, leading to a reduced agglomeration of GNPs in the PEDOT-GNP nanocomposites. Moreover, for polymer nanocomposites synthesized by in-situ polymerization, there will be a possibility of an EDOT arrangement on the surface of the GNPs due to a physically powerful π - π conjugation before the polymerization proceeds [31].

3.4. Optical properties

Fig. 4 shows UV-Visible absorption spectra for pure PEDOT and PEDOT-GNP nanocomposites. The low absorption in the visible region and an absorption peak at 860 nm with tail broadening into the near infrared region are observed for pure PEDOT [ESI, Fig. S4]. The broad absorption band observed in the near infrared region is due to the existence of bipolaron and polaron energy levels, suggesting a high level of doping in polymer. These results are in good conformity with those reported in literature [32,33].

Fig. 5 depicts the graph of $(ah\nu)^2$ versus photon energy for pristine PEDOT and its GNP nanocomposites. Extrapolation of the linear part to

zero absorption gives the optical energy band gap, E_g^{opt} (directly allowed) [22,34,35] of 1.51 eV for pure PEDOT. It was found that, E_g^{opt} generally decreases with increase in GNP loading in the polymer matrix [Table 1]. The smallest band gap (= 1.26 eV) was obtained for PEDOT-GNP with 10 wt% GNP. At 15 wt% GNP the band gap has slightly increased to 1.32 eV, possibly due to agglomeration of GNPs in the nanocomposite. According to Mott and Devis [35], the width of the mobility edge depends on the degree of defects and disorders present in the non-crystalline structure. In the forbidden gap, localized states are produced because of the presence of such defects. Therefore, the number of localized states increases with increase in concentration of GNPs in the PEDOT matrix, having a direct impact on the optical band gap of PEDOT [35,36].

3.5. Electrical transport properties

In polymer nanocomposites, the electrical transport may occur by tunneling of electrons between closely spaced conductive nanofillers or by direct contact between conductive elements [37]. Fig. 6 displays the dependence of AC electrical conductivity, σ_{AC} , on frequency for pristine PEDOT and its GNP nanocomposites. At lower concentrations, i.e. up to 5 wt% of GNP, σ_{AC} of nanocomposites is almost constant at lower frequencies and increases with increasing frequency at higher frequencies [ESI, Fig. S5]. This behaviour can be ascribed to the fact that, at lower concentrations, the conductive nanofillers, i.e. GNPs, may not be in contact with each other and conduction takes place only by tunneling mechanism. At higher concentrations of 10 and 15 wt% GNP, σ_{AC} of nanocomposites is almost frequency independent at lower frequencies and decreases with increasing frequency at higher frequencies [ESI, Fig. S6]. The σ_{AC} values of PEDOT-10 wt% GNP nanocomposite are 400 times more than that of pure PEDOT.

The inset graph in Fig. 6 demonstrates that σ_{AC} increases with increasing GNP concentration, possibly because of the creation of conductive networks due to the overlapping PEDOT coated GNPs. Among all nanocomposites, PEDOT-GNP with 10 wt% GNPs has larger conductivity (~ 14 S/cm) than pristine PEDOT ($\sim 3 \times 10^{-2}$ S/cm) in the entire frequency range. PEDOT-GNP-15 wt% nanocomposite has lower σ_{AC} values compared to that with 10 wt% GNP. This can be credited to increased viscosity of GNPs in the nanocomposite which hinders the charge carrier mobility.

In general, the frequency dependent σ_{AC} of a disordered system obeys power law:

$$\sigma_{AC} = \sigma_{DC} + A \omega^s \quad (1)$$

where σ_{DC} is the DC electrical conductivity, A is a constant and s is the power index of angular frequency, ω ($= 2\pi f$), which can take values between 0 and 1. The plateau region in the frequencies up to 1 MHz corresponds to σ_{DC} induced by the free charge carriers present in the samples. After a particular frequency known as the cross over frequency, the trapped charges gets stimulated and experience short range motion, leading to the increasing AC electrical conductivity [38,39].

The variation of DC electrical conductivity, σ_{DC} , as a function of GNP content in weight percentage is shown in Fig. 7. It is found that σ_{DC} increases from 2.9×10^{-2} S/cm (pure PEDOT) to 14.2 S/cm (PEDOT-10 wt% GNP nanocomposite). After 5 wt% GNP loading, a drastic increase in the σ_{DC} values is observed. Hence, 5 wt% GNP loading serves as the percolation threshold. The σ_{DC} plot shows two main states, one from 0 to 5 wt% GNP loading and other from 5 to 10 wt% GNP loading. The observed results can be explained by percolation hypothesis. According to this theory, a full conductive pathway will be formed throughout the polymer matrix, at a critical concentration of conducting filler, for the movement of charge carriers leading to an enhancement in σ_{DC} . The decrease in the value of σ_{DC} above 10 wt% of GNP content can be ascribed to the trapping of charge carriers. The obtained percolation threshold can also be related to the uniform dispersion and high specific

Fig. 5. $(\alpha h\nu)^2$ versus photon energy for pristine PEDOT and PEDOT-GNP nanocomposites.

Table 1

The directly allowed optical energy band gap, E_g^{opt} , for pristine PEDOT and PEDOT-GNP nanocomposites.

Sample name	E_g^{opt} (eV)
Pure PEDOT	1.51
PEDOT-1.0 wt% GNP	1.46
PEDOT-2.5 wt% GNP	1.32
PEDOT-5.0 wt% GNP	1.30
PEDOT-10 wt% GNP	1.26
PEDOT-15 wt% GNP	1.32

surface area of GNP [40,41].

3.6. Dielectric properties

The dielectric properties of pristine PEDOT and PEDOT-GNP nanocomposites have been studied in the frequency range of 10 Hz to 8 MHz. Dielectric studies helps to evaluate the electrical charge storing ability of a material [42,43]. Fig. 8(a) and (b) show the dependence of the dielectric constant, ϵ' , and dielectric loss, ϵ'' , on frequency, respectively. The ϵ' and ϵ'' values of PEDOT and its nanocomposites decrease with increasing frequency, at low frequencies, and remain nearly constant for the frequencies above 10^4 Hz. All samples show extremely larger values of ϵ' and ϵ'' at low frequencies, i.e. at frequencies less than 1 kHz. The PEDOT-10 wt% GNP nanocomposite shows the largest ϵ' and ϵ'' values in the whole frequency range (ϵ' : 10^8 to 10^5 and ϵ'' : 10^{12} to 10^6 in the

Fig. 6. The variation of AC conductivity, σ_{AC} , as a function of frequency for pristine PEDOT and PEDOT-GNP nanocomposites at room temperature. (A) pristine PEDOT, (B) PEDOT-1 wt% GNP, (C) PEDOT-2.5 wt% GNP, (D) PEDOT-5 wt% GNP, (E) PEDOT-10 wt% GNP, (F) PEDOT-15 wt% GNP. Inset graph (on left-hand side): σ_{AC} as a function of GNP content in wt% at 1 kHz.

Fig. 7. The variation of DC conductivity, σ_{DC} , of PEDOT-GNP nanocomposites as a function of GNP content in wt%.

frequency range from 10 Hz to 8 MHz) compared to other samples. These are the highest reported values of ϵ' in the literature for carbon based polymer nanocomposites. The ϵ' values of PEDOT-10 wt% GNP nanocomposite are 90 times more than those of pure PEDOT. The ϵ' and ϵ'' values as functions of GNPs content in wt % at 1 kHz are shown in the inset graphs of Fig. 8(a) and (b). PEDOT-10 wt% GNP nanocomposite has a gigantic dielectric constant of the order of 9×10^5 at 1 kHz.

The frequency dependence of ϵ' of PEDOT and its GNP nanocomposites can be described by dielectric relaxation [22]. At lower frequencies, the dipoles will have adequate time to align themselves in the field direction and hence, ϵ' is large. The interfacial polarization is prominent at lower frequencies. At upper frequencies, the dipoles are unable to reorient themselves fast enough and hence, ϵ' is small (Maxwell-Wagner-Sillars polarization effect) [44–46]. The electronic polarization is dominating at low frequencies.

The dependence of the loss tangent, $\tan\delta$, on frequency for pristine PEDOT and its GNP nanocomposites is shown in Fig. 9. Generally, dielectric loss results from interfacial, dipolar, conduction, and distortional loss in a dielectric material [47,48].

At low frequencies, the internal friction between the dipoles is large since the dipoles have ample time to align themselves in the field direction and hence, ϵ'' and $\tan\delta$ are large. At high frequencies, the dipoles have less time to align themselves in the field direction, resulting in lower values of ϵ'' and $\tan\delta$. The frequencies of the observed peaks in $\tan\delta$ spectra depend on the GNP concentration. These peaks are due to matching the applied frequency with the most feasible relaxation time of the hopping electrons [49]. The low ϵ'' and $\tan\delta$ values observed above 10^5 Hz, indicates that these nanocomposites are lossless materials at high frequencies.

The gigantic dielectric properties can be related to the creation of microcapacitors in the polymer nanocomposites [50]. According to the microcapacitor model, adjacent conducting fillers in the polymer matrix act as the electrodes and the polymer between them serves as dielectric, forming microcapacitor. These microcapacitors will help for the significant increase in dielectric properties. In case of PEDOT-GNP nanocomposites, the GNPs coated with PEDOT form enormous number of microcapacitors, each having capacitance, and hence, the dielectric properties increase dramatically. Our result shows that, PEDOT-10 wt% GNP nanocomposite has a much better dielectric performance than any other carbon-based polymer nanocomposite reported so far.

4. Conclusions

In the present work, the novel conducting PEDOT-GNP nanocomposites having extremely large dielectric constant, ϵ' , significantly high conductivity, σ_{AC} , and narrow band gap, E_g^{opt} , have been prepared by a simple, eco-friendly and effective route. The PEDOT-10 wt% GNP nanocomposite has a gigantic dielectric constant of the order of 9×10^5 at 1 kHz and a lowest optical energy band gap of 1.26 eV. The ϵ' values of PEDOT-10 wt% GNP nanocomposite (10^8 to 10^5 in the frequency range from 10 Hz to 5 MHz) are the highest among those reported in the literature for carbon based polymer nanocomposites. The enormous quantity of microcapacitors created in the nanocomposites, before the establishment of conductive networks, leads to these gigantic dielectric properties. ϵ' and σ_{AC} values are about 90 and 400 times larger, respectively, in PEDOT-10 wt% GNP nanocomposite than in pure PEDOT.

The synthesized PEDOT-GNP nanocomposites have gigantic ϵ' and ϵ'' values. But, the polymer nanocomposites having large ϵ' and small ϵ'' values are required for high energy storage with minimum energy loss. However, such polymer nanocomposites have not yet been achieved. If this challenge can be addressed properly, PEDOT-GNP nanocomposites may provide very large energy storage capacity analogous with electrochemical capacitors. In view of this prospect, further investigations on PEDOT-GNP nanocomposites for energy storage applications will be intended. Also, the present study will be extended to other carbon nanofillers in a near future.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Mohsina Taj: Methodology, Investigation, Formal analysis, Writing - original draft. **S.R. Manohara:** Supervision, Conceptualization, Investigation, Formal analysis, Writing - review & editing, Funding acquisition. **S.M. Hanagodimath:** Investigation, Formal analysis, Writing - review & editing. **L. Gerward:** Investigation, Formal analysis,

Fig. 8. The frequency dependence of (a) dielectric constant, ϵ' , and (b) dielectric loss, ϵ'' , for pristine PEDOT and PEDOT-GNP nanocomposites at room temperature. (A) pristine PEDOT, (B) PEDOT-1 wt% GNP, (C) PEDOT-2.5 wt% GNP, (D) PEDOT-5 wt% GNP, (E) PEDOT-10 wt% GNP, (F) PEDOT-15 wt% GNP. Inset graphs: ϵ' and ϵ'' as a function of GNP content in wt% at 1 kHz.

Fig. 9. The variation of loss tangent, $\tan\delta$, as a function of frequency for pristine PEDOT and PEDOT-GNP nanocomposites at room temperature. (A) pristine PEDOT, (B) PEDOT-1 wt% GNP, (C) PEDOT-2.5 wt% GNP, (D) PEDOT-5 wt% GNP, (E) PEDOT-10 wt% GNP, (F) PEDOT-15 wt% GNP. Inset graph (on right-hand side): $\tan\delta$ as a function of GNP content in wt% at 1 kHz.

Writing - review & editing.

Acknowledgements

S.R. Manohara wish to thank the Vision Group on Science and Technology (VGST), Department of Information Technology, Biotechnology and Science & Technology, Government of Karnataka, for providing financial support under project no. KSTePS/VGST/03/CISEE/2015–2016/GRD-470. All authors acknowledge helpful assistance with FTIR, SEM and UV–Vis measurement, respectively, by Drs. V. Udaykumar, Asis Sarkar and Nirankar Mishra of the Departments of Chemistry and Center of Applied Research and Nano-Technology at this institute. Mohsina Taj gratefully acknowledges a fellowship from the Directorate of Minorities, Government of Karnataka (GOKDOM).

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.polymertesting.2020.106650>.

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