Assessment of Graphene Oxide/PLA Composites as Green Dielectrics

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Abstract. Polylactic acid (PLA) is a biodegradable and biocompatible polymer potentially applicable in biomedical terrain. While substantial progress is demonstrated in studying the biodegradability of PLA, there is a lack of scientific data regarding its dielectric properties in literature, for its holistic development as a complex green dielectric material. Considering the exceptional electrical and antimicrobial properties of graphene oxide (GO), PLA/GO composites were prepared using the injection molding technique. To overcome the shortcomings, the dielectric constant and ac conductivity of GO, neat PLA and PLA/GO composites were investigated at room temperature at 26\degree C with variations in frequency from 1Hz to 1MHz. Interestingly, it was shown that GO possessed a giant dielectric constant in the order of $10^5$ at 1Hz, and consequently, the dielectric properties of neat PLA dramatically increased. The measured values are fitted using the modified Debye’s expression and the fitting parameters evaluated.

1. Introduction

PLA is a biodegradable polymer manufactured from renewable agricultural resources and is used in various applications. PLA-based materials are pervasive in biomedical terrain due to their biocompatible, hydrolytic degradation, and biologically inert nature that can be engineered chemically. PLA degrades by hydrolysis and oxidation. Water molecules break the ester bonds present in the backbone of PLA chains and the free radicals generated by phagocytes in the body during wound healing, depolymerizes PLA eliminating the need for additional surgeries to remove the devices. These materials can be explored for being used as bone fixation screws, bioresorbable sutures, stent coating, etc [1,2]. The need for green biodegradable electronic devices is instrumental in solving the problem of disposal of waste of synthetic electronic devices. The PLA can satiate the need for a biodegradable substrate while designing green electronic devices and can be replaced by inorganic semiconductors like Si, Ge. PLA can further be availed as a capacitive sensor in FETs. However, the present study explores GO possessing exceptional properties as fillers to enhance the $\varepsilon_r$ values of PLA. Knowing the values, the composite materials can also serve the purpose of connecting various components in an electronic device.

2. Material and methods

2.1. Material

PLA of grade 4042D was purchased from Nature Works, USA. Graphite powder, Potassium permanganate (KMnO\textsubscript{4}), Conc. sulphuric acid (H\textsubscript{2}SO\textsubscript{4}), Hydrogen Peroxide (H\textsubscript{2}O\textsubscript{2})
2.2 Synthesis of GO

GO was synthesized adapting Hummer’s method. 25 ml conc. H$_2$SO$_4$ was added to 1g of graphite powder. H$_2$SO$_4$ triggers exfoliating graphite layers leading to intercalations, followed by the slow addition of 3g of KMnO$_4$ as an oxidant. The conc. H$_2$SO$_4$ reacts with oxidant KMnO$_4$ to form a stark oxidant Manganese heptoxide (Mn$_2$O$_7$), an active species in the oxidation of graphite. Due to intercalation after reaction with H$_2$SO$_4$, the strong oxidant has access to the space between graphite layers, creating various functional groups such as hydroxyl (-OH), epoxide (-O-), and carboxyl (-COOH). With the addition of 100 ml distilled water after stirring for 4 h, water reacts with the already present oxidant Mn$_2$O$_7$ to obtain HMnO$_4$ and MnO$_2$. HMnO$_4$ terminates the reaction followed by effervescence. Finally, 5ml of H$_2$O$_2$ is added to the solution which reacts with MnO$_2$, reducing it to manganese ions. These manganese ions and other ions are subsequently removed during ultrasonication for 1h.

2.3 Composite processing and fabrication

The PLA and GO powder were mixed mechanically with a micro compounding molding equipment at 170°C for 10 minutes. The molten composite samples were transferred after extrusion through a pre-heated cylinder to the mini injection molder in a bid to obtain the desired samples for analyzing multifarious properties. GO powder was mixed with 3% polyvinyl alcohol, finely grounded, and pressed with a 3.5-ton load to obtain the GO pellets.

2.4 Samples for characterization

Composite samples were prepared with a PLA matrix and different wt proportions of GO. The neat PLA matrix is B0. G1, G2, and G3 are composites of PLA with 1%, 2%, and 4% wt proportion of GO respectively. Samples were cut in 10mm × 10mm × 2mm rectangular pellets for characterization like XRD, FTIR study, and dielectric measurements using an LCR meter (IM 3536 HIOKE).

2.5 Degradation in the bacterial environment

5g of nutrient broth was dissolved in 200 ml of distilled water and uniformly poured in 4 conical flasks for 4 samples (B0, G1, G2, and G3). It was autoclaved for 45 minutes and kept in laminar airflow under UV for 20 minutes. Then 20μL of bacterial strain (Bacillus subtilis) was added to each flask and kept in an incubator at 30°C for 24 h. Samples were then put in the flask for 15 days followed by weighing for evaluation.

3 Results and discussion

![Graph](https://via.placeholder.com/150)

**FIGURE 1.** XRD of GO, PLA, GO/PLA

The XRD pattern of GO in Fig.1 renders a unique peek at a 2θ value of 9.178° corresponding to (001) reflection plane having interplanar spacing (d) 9.62784Å. The observed interplanar spacing in GO (9.62784 Å) is more than the standard interplanar spacing of graphite powder (3.54 Å). The increased interplanar spacing is due to the presence of different functional groups such as hydroxyl, epoxy, and carboxyl groups during the oxidation of graphite. XRD of
neat PLA is characterized by the broad peak around 15.74⁰ identifying the plane 200 having a full width at half maximum 9.66⁰. The broadened peak suggested amorphous nature and deformation in the orthorhombic structure of PLA. However, in PLA/GO composite, a broad peak appears around 14.56⁰ and FWHM changed to 8.98⁰ indicating molecular interaction between matrix and filler [7].

FIGURE 2. FTIR spectra of GO, PLA, GO/PLA

The FTIR bands at 1638.96 cm⁻¹ and 1089.94 cm⁻¹ present in GO as shown in Fig. 2 denotes –C=O stretching vibrations of the carboxylic acid and carbonyl group respectively formed due to oxidation of graphite [5]. The different peak assignments like C=O stretching, C-H bending, C-O-C stretching of neat PLA and PLA/GO composites are given in Fig. 2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sample (neat PLA)</th>
<th>GO (PLA/1%GO)</th>
<th>G1 (PLA/2%GO)</th>
<th>G2 (PLA/4%GO)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>ε_r</strong></td>
<td><strong>At 1 Hz</strong></td>
<td><strong>At 50 Hz</strong></td>
<td><strong>At 100 Hz</strong></td>
<td><strong>At 1 kHz</strong></td>
</tr>
<tr>
<td>B0 (neat PLA)</td>
<td>72±1.97</td>
<td>68±2.42</td>
<td>61±2.95</td>
<td>35±1.88</td>
</tr>
<tr>
<td>GO</td>
<td>4.92 X 10⁵</td>
<td>1.03 X 10⁵</td>
<td>6.99 X 10³</td>
<td>9.15 X 10²</td>
</tr>
<tr>
<td>G1 (PLA/1%GO)</td>
<td>487±4.89</td>
<td>469±5.15</td>
<td>437±5.09</td>
<td>438±4.49</td>
</tr>
<tr>
<td>G2 (PLA/2%GO)</td>
<td>478±5.93</td>
<td>459±4.72</td>
<td>420±5.29</td>
<td>419±4.96</td>
</tr>
<tr>
<td>G3 (PLA/4%GO)</td>
<td>473±5.36</td>
<td>453±4.88</td>
<td>423±5.91</td>
<td>419±5.75</td>
</tr>
</tbody>
</table>

Note: The values represent an average of 10 replicates

Table 1 betokens that at 1 Hz, the ε_r of GO is 4.92 X 10⁵. Such giant permittivity in GO is attributed to the presence of polar groups, interfacial polarization of delocalized electrons at grain boundaries, Dirac fermions, and surface plasmon resonance[5]. When the GO was used as fillers in PLA, the ε_r PLA increased from 72 at 1 Hz to a maximum of 487 in the sample G1 and decreased with an increase in GO loading for samples G2 and G3. The variation of ε_r frequency adheres to Debye’s relaxation.
The measured values are fitted using the modified Debye’s expression and from the fitted curve, values of static dielectric constant ($\varepsilon_s$), optical dielectric constant ($\varepsilon_\infty$), mean relaxation time ($\tau$) and deviation from Debyes theory ($\alpha$) were obtained. Table 2 denotes the values of fitting parameters.

**FIGURE 3.** (a) The dielectric dispersion spectrum of pristine PLA (b) Weightloss of composites in the bacterial environment

**TABLE 2.** Values of static dielectric constant, optical dielectric constant, relaxation time and deviation factor of neat PLA, GO, PLA/GO from fitting curves

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\varepsilon_s$</th>
<th>$\varepsilon_\infty$</th>
<th>$\tau$</th>
<th>$\alpha$</th>
<th>f in Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>B0</td>
<td>52.68863±0.28437</td>
<td>19.31334±0.28129</td>
<td>0.25851±6.7476E-4</td>
<td>-0.509±0.00558</td>
<td>3.8683</td>
</tr>
<tr>
<td>GO</td>
<td>477354.53781±5102.16056</td>
<td>-9240.544±1559.41429</td>
<td>2.70352±0.0496</td>
<td>0.03772±0.00967</td>
<td>0.36988</td>
</tr>
<tr>
<td>G1</td>
<td>469.97754±3.05867</td>
<td>438.1442±1.44329</td>
<td>1.10628±0.12305</td>
<td>-0.17161±0.094</td>
<td>0.9039</td>
</tr>
<tr>
<td>G2</td>
<td>446.41651±7.21301</td>
<td>413.34722±11.44461</td>
<td>1.2341±1.18755</td>
<td>0.38249±0.31198</td>
<td>0.81030</td>
</tr>
<tr>
<td>G3</td>
<td>476.94987±6.83738</td>
<td>417.25425±4.84227</td>
<td>0.94934±0.15478</td>
<td>-0.02906±0.13314</td>
<td>1.05336</td>
</tr>
</tbody>
</table>

Note: The values represent an average of 10 replicate

Fig.3 (b) depicts that post 30 days, the neat PLA degrades by 20% of its original weight when exposed to Bacillus subtilis, conceding the fact that the bacteria attack the PLA chains and splits them apart into monomers. Nonetheless, the loss of weight and rate of degradation decreases when GO fillers are incorporated into PLA. This signifies the antibacterial competence of the composite materials. With the increase in filler load, the weight loss further decreases denoting the bacterial resistant activity of GO.

**4. Conclusions**

The wide margin of $\varepsilon_r$ the value of GO i.e $5 \times 10^5$ at 1Hz to 75 at 1MHz, combined with its resistance to bacterial strain presents many opportunities in replacing traditional ceramic materials in industrial and medicinal applications.
like fabrication of superconductors, photovoltaic energy conversion in solar cells, coating for meninges, muscular connectors, etc. The PLA/GO composites having $\varepsilon_r$ in the spectrum 450-500 can replace Barium Strontium Titanates like materials in the fabrication of high dielectric constant capacitors, capacitive sensors, PTC resistors, transducers.

References