7. GRAPHENE OXIDE REINFORCED POLY (4-STYRENESULFONIC ACID) AND POLYVINYLALCOHOL BLEND COMPOSITES WITH ENHANCED DIELECTRIC PROPERTIES

7.1 INTRODUCTION

The synthesis of novel composite materials having high dielectric constant and low dielectric loss is highly desirable because of their widespread applications in embedded and multilayer capacitors, gate dielectrics for field effect transistors and energy storage devices [316, 317]. A fascinating way of enhancing the dielectric properties of polymers is by dispersing conducting fillers such as metal nanoparticles, carbon nanotubes, carbon fibers, etc. into polymer matrix [10, 58, 307, 318]. Several studies have demonstrated GO as an excellent filler for the fabrication of polymer composites with high dielectric constant and low dielectric loss for energy storage applications [270, 319]. Polyimide/GO composites were prepared by Wang et al. [320] via in-situ polymerization using NH$_2$ functionalized GO as filler and observed improvement in the mechanical and dielectric properties of composites. The composites of PVDF incorporated with PVA modified reduced graphene oxide (PVA-RGO) exhibited high values of dielectric constant and low values of dielectric loss than that of PVDF/RGO composites [212]. Thus, in order to harness the exceptional and extraordinary properties, it is essential to achieve uniform dispersion of GO in the polymer matrix.

PSSA is a polyelectrolyte. It has often been used as a dopant for the polymerization of conductive polymers. It has excellent film forming and coating capability. PSSA can be added to a polymer matrix having cation exchange properties providing higher capacity and diffusion of ionic species resulted from the large size of the polystyrene sulfonate (PSS$^-$) [321]. Linear
or cross-linked PSSA has been used in semi-interpenetrating polymer network (IPN). PSSA has been used as a proton exchange membrane material in polymer electrolyte fuel cells. On the other hand, PVA is a synthetic, non-toxic semi-crystalline polymer having high dielectric strength and high transparency. PVA also has good optical and mechanical properties and excellent thermal stability. It is usually selected as a cross-linker because of its film-forming ability, hydrophilic properties and the high density of reactive chemical functionalities. PSSA has often been blended with PVA to form semi-interpenetrating polymer network through in-situ synthesis [322] or through an impregnation process [323]. These strategies involve the use of intra and intermolecular hydrogen bonding resulting in a dense structure with the flexible film forming property and good chemical resistance.

In this chapter, the fabrication and characterization of novel polymer composites featuring PSSA and PVA as a matrix and GO as filler have been reported. To the best of our knowledge, there are no published reports on GO reinforced PSSA/PVA blend composites. Herein, the fabrication of PSSA/PVA/GO composites as a flexible high dielectric constant material is reported for the first time. These composites can be suitable for energy storage applications in advanced electronic devices.

7.2 EXPERIMENTAL PROCEDURE

7.2.1 Preparation of PSSA/PVA/GO Composite Films

Different compositions of PSSA/PVA/GO composite films with GO loadings varying from 0 - 3 wt % were prepared by the colloidal processing technique. The feed compositions used for the preparation of PSSA/PVA/GO composites are given in Table 7.1. The desired amount of PVA powder was first dissolved in distilled water at 60°C for 4 hours. GO powder was dispersed separately in water and sonicated for 1 hour. Subsequently, the aqueous dispersion of GO was added to the aqueous PVA solution and
stirred continuously for 4 hours followed by the addition of PSSA solution to PVA/GO dispersion. The resulting PSSA/PVA/GO dispersion was stirred vigorously for 8 hours, followed by casting onto a cleaned Teflon petri dish and drying at 60°C for 4 hours. The PSSA/PVA/GO composite films of thickness in the range of 80-100 μm were removed from the Teflon petri dish and used for further study. The protocol for the synthesis of PSSA/PVA/GO composites is given in Figure 7.1. The photographs of different compositions of PSSA/PVA/GO composite films are shown in Figure 7.2 (a-e), indicating the formation of a homogeneous dispersion of GO into PSSA/PVA blend matrix. It can be seen that the PSSA/PVA blend film is colourless and transparent. However, after the addition of GO the composite film exhibits brown colour and the transparency of PSSA/PVA/GO composite films decrease noticeably when the GO content was further increased up to 3 wt %. A high level of transparency indicates that PSSA/PVA/GO composite films have the excellent potential for display encapsulation. Thus, the transparency to the opacity of the composite film can be controlled simply by varying the GO content. The possible interaction between PSSA, PVA and GO is presented schematically in Figure 7.3.

Table 7.1: Feed compositions of PSSA/PVA/GO composites

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>PSSA (wt %)</th>
<th>PVA (wt %)</th>
<th>GO (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50</td>
<td>50</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>29.5</td>
<td>70</td>
<td>0.5</td>
</tr>
<tr>
<td>3</td>
<td>29</td>
<td>70</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>28.5</td>
<td>70</td>
<td>1.5</td>
</tr>
<tr>
<td>5</td>
<td>28</td>
<td>70</td>
<td>2</td>
</tr>
<tr>
<td>6</td>
<td>27.5</td>
<td>70</td>
<td>2.5</td>
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<tr>
<td>7</td>
<td>27</td>
<td>70</td>
<td>3</td>
</tr>
</tbody>
</table>
Figure 7.1: Protocol for the synthesis of PSSA/PVA/GO composites. The photographs of bottles shows the dispersion of GO with different loadings (a) 0.5 wt % GO (b) 1 wt % GO (c) 1.5 wt % GO (d) 2 wt % GO (e) 2.5 wt % GO (f) 3 wt % GO. The photographs of PSSA/PVA/GO composite films with different GO loadings (a) 0.5 wt % GO (b) 3 wt % GO (c) composite film is bent to demonstrate its flexibility.
Figure 7.2: Photographs of PSSA/PVA/GO composite films with different GO loading (a) PSSA/PVA (50/50) blend (b) 0.5 wt % GO (c) 1 wt % GO (d) 1.5 wt % GO (e) 3 wt % GO.
Figure 7.3: Schematic representation of the possible interaction between PSSA, PVA and GO.
7.3 RESULTS AND DISCUSSION

7.3.1 FTIR Analysis

The FTIR spectra of PSSA and PSSA/PVA blend are shown in Figure 7.4 (a, b). The FTIR spectrum of PSSA shows a broad peak at 3400 cm\(^{-1}\), attributed to the \(-\text{SO}_3\text{H}\) group of PSSA [324]. The presence of the band at 1035 cm\(^{-1}\) in FTIR spectrum of PSSA is attributed to symmetric stretching vibrations of \(-\text{SO}_3\) group [325]. The band identified at 1175 cm\(^{-1}\) is due to asymmetric stretching vibrations of S=O group [326]. The wagging vibration of C-H in 1, 4 substituted benzene ring of PSSA at 800 cm\(^{-1}\) was also observed [327].

![FTIR spectra of PSSA and PSSA/PVA blend](image)

Figure 7.4: FTIR spectra of (a) PSSA (b) PSSA/PVA (50/50) blend.
In the FTIR spectrum of PSSA/PVA blend; the intensity of peaks has reduced when compared to FTIR spectrum of pure PSSA. In addition, in comparison with the O-H peak of PSSA (3400 cm\(^{-1}\)), the O-H peak of PSSA/PVA blend is slightly shifted towards lower wavenumbers, indicating the formation of hydrogen bonding between –SO\(_3\)H group of PSSA and O-H group of PVA \([324]\). The FTIR spectra of PSSA/PVA/GO composite films with different compositions is depicted in Figure 7.5 (a-f) which shows characteristics FTIR peaks of each component present in the composite. Also, it can be seen that the strong FTIR bands in the range 3000-3500 cm\(^{-1}\) are slightly blue-shifted, indicating the establishment of intermolecular hydrogen bonding interactions between the oxygen containing functional groups of GO, O-H group of PVA and the –SO\(_3\)H group of PSSA.

![Figure 7.5: FTIR spectra of PSSA/PVA/GO composite films](image)

(a) 0.5 wt % GO (b) 1 wt % GO (c) 1.5 wt % GO (d) 2 wt % GO (e) 2.5 wt % (f) 3 wt % GO.
7.3.2 Raman Analysis

The Raman spectra of PSSA/PVA/GO composite films with different compositions are shown in Figure 7.6 (a-e). It can be seen that the PSSA/PVA/GO composite films show the Raman spectra which are very similar to that of GO with slight shifts in the D and G bands. Such shifts in Raman bands are attributed to the restoration of sp\textsuperscript{2} hybridized carbon. Thus, Raman spectroscopy results indicate that there are a good interfacial adhesion and stress transfer between the polymer chains and GO \cite{328}, suggesting hydrogen bonding interaction between the oxygen containing functional groups of GO, O-H group of PVA and the –SO\textsubscript{3}H group of PSSA.

![Raman spectra of PSSA/PVA/GO composite films](image)

**Figure 7.6:** Raman spectra of PSSA/PVA/GO composite films

(a) 0.5 wt % GO (b) 1 wt % GO (c) 1.5 wt % GO (d) 2 wt % GO (e) 3 wt % GO.
7.3.3 X-ray Diffraction Analysis

The XRD pattern of PSSA and PSSA/PVA blend is depicted in Figure 7.7 (a, b). The XRD pattern of pristine PSSA shows two broad humps at $2\theta = 30.19^\circ$ and $2\theta = 41.02^\circ$, confirming the amorphous nature of PSSA. The XRD pattern of PSSA/PVA blend shows a low-intensity peak at $2\theta = 19.25^\circ$ which belongs to PVA and two broad humps at $2\theta = 30.17^\circ$ and $2\theta = 41.06^\circ$ which belongs to PSSA. Also, the intensity of PVA peak is reduced in the blend which could be due to the interaction between $–\text{SO}_3\text{H}$ group of PSSA and the $–\text{OH}$ group of PVA. Thus, XRD pattern of PSSA/PVA blend indicates that both PSSA and PVA are miscible.

![XRD patterns of (a) PSSA (b) PSSA/PVA (50/50) blend.](image)

Figure 7.7: XRD patterns of (a) PSSA (b) PSSA/PVA (50/50) blend.
The XRD patterns of PSSA/PVA/GO composite films with different compositions is depicted in Figure 7.8 (a-f) which shows a single diffraction peak at $2\theta = 19.44^\circ$ which is attributed to the crystalline peak of neat PVA. The XRD peak of GO was not observed in PSSA/PVA/GO composites which imply that GO sheets were fully exfoliated into individual graphene sheets and dispersed in the polymer matrix at the molecular level.

![XRD spectra of PSSA/PVA/GO composite films](image)

**Figure 7.8:** XRD spectra of PSSA/PVA/GO composite films
(a) 0.5 wt % GO (b) 1 wt % GO (c) 1.5 wt % GO (d) 2 wt % GO (e) 2.5 wt % GO (f) 3 wt % GO.

### 7.3.4 UV-vis Spectroscopy

The dispersion stability of GO into polymer matrices is the key in exploring the aqueous synthesis routes for the fabrication of graphene-based polymer composites. In the present study, UV-vis spectroscopy was carried out to observe the Plasmon transitions in PSSA/PVA/GO colloids. Graphene
reinforced polymer colloids can exhibit interesting absorption patterns at the wavelengths around 230 nm, 260 nm, and 300 nm. These absorption patterns correspond to $\pi$, $\sigma$ and $\pi$ electron transition (with different bond energies) respectively. The UV-vis spectrum of PSSA in the inset of Figure 7.9 shows a sharp peak around 228 nm and a small shoulder around 262 nm which are attributed to the $\pi - \pi^*$ Plasmons of the benzenoid ring of PSSA. The UV-vis absorbance spectra of PSSA/PVA/GO colloids with different compositions is given in Figure 7.9 (a-f) which show two sharp peaks at 195 nm and at 225 nm in addition to a shoulder peak at 262 nm for all the samples which indicate the significant interaction between the functional groups of PSSA and PVA and oxygen containing functional groups of GO.

![Figure 7.9: UV-vis spectra of PSSA/PVA/GO composites (a) 0.5 wt% GO (b) 1 wt% GO (c) 1.5 wt% GO (d) 2 wt% GO (e) 2.5 wt % GO (f) 3 wt % GO (Inset: UV-vis spectrum of PSSA).](image)
7.3.5 Thermogravimetric Analysis

The TGA thermograms of PVA and PSSA/PVA blend are shown in Figure 7.10. It is apparent from the figure that PVA exhibits three-step degradation. The first step of degradation occurs in the temperature range 70°C-150°C, which could be due to the elimination of adsorbed water. The second degradation step occurs in the temperature range 150-400°C which could be attributed to the decomposition of the polymer structure. The final degradation step occurs in the temperature range 400-700°C, which is attributed to the decomposition of the residual carbon.

![TGA thermograms of PVA and PSSA/PVA (50/50) blend.](image)

Figure 7.10: TGA thermograms of PVA and PSSA/PVA (50/50) blend.

The TGA thermogram of PSSA/PVA blend shows two-step degradation. It is apparent that PSSA/PVA blend exhibits a very less weight loss in the first step of decomposition which occurs from room temperature to 300°C. The second decomposition step starts above 300°C and it can be
seen that the blend samples showed very less weight loss (about 20%) in the temperature range 300°C-700°C, which is very smaller amount when compared to neat PVA (about 50%). The higher decomposition temperature for PSSA/PVA blend indicates that PSSA/PVA blend has better thermal stability as compared to neat PVA which could be due to the strong interaction between –SO$_3$H group of PSSA and the –OH group of PVA. The TGA thermograms of different compositions of PSSA/PVA/GO composites are depicted in Figure 7.11 (a-e). The composites showed three step decomposition behavior. The first decomposition step occurs in the low-temperature range 50-150°C which is due to evaporation of moisture or adsorbed water [329]. The second decomposition step occurs in the temperature range 150-300°C which could be due to the splitting of polymer main chain. The third decomposition step occurs in the temperature range 300-500°C which could be attributed to the decomposition of the polymer backbone [329]. Thus, higher decomposition temperatures were observed for PSSA/PVA/GO composite films which could be due to the excellent dispersion of GO into the polymer matrix and the high aspect ratio of GO. The TGA results indicate that the mobility of the polymer segments and GO at the interfaces is suppressed by the strong hydrogen bonding interactions between them, resulting in the improved thermal stability of composites.
7.3.6 Morphological Studies

Figure 7.12 (a-f) represents optical microscopy images of different compositions of PSSA/PVA/GO composite films. At 50 µm scale resolution, a fairly good distribution of GO in the polymer matrix can be seen which could be due to strong hydrogen bonding interactions between PSSA, PVA and GO and good miscibility between them. Considering the presence of various hydrophilic groups on the surface of GO, one may expect the homogeneous dispersion of GO in hydrophilic polymer systems such as PSSA and PVA. In addition, GO readily exfoliates in water via hydrogen bonding interactions and forms well-dispersed aqueous colloids [270].
Scanning electron microscopy (SEM) was employed to gain further insight into the dispersion of GO in the polymer matrix. It is important to accomplish uniform dispersion of GO within the polymer matrix and good interfacial adhesion between GO and polymer matrix is highly desirable to enhance the performance of polymer/GO composites. The SEM micrographs of different compositions of PSSA/PVA/GO composites are depicted in Figure 7.13 (a-f). It can be seen that the PSSA/PVA/GO composites exhibit typical crumpled morphology which is mainly attributed to the high flexibility and high aspect ratio of GO. It is apparent that GO was fully exfoliated into individual graphene sheets and most of the graphene sheets are well dispersed in the polymer matrix without any re-stacking. This indicates that there is a good interfacial adhesion between GO and polymer matrix.
Figure 7.12: POM micrographs of PSSA/PVA/GO composite films
(a) 0.5 wt% GO (b) 1 wt% GO (c) 1.5 wt% GO (d) 2 wt% GO
(e) 2.5 wt% GO (f) 3 wt% GO.
Figure 7.13: SEM micrographs of PSSA/PVA/GO composites
(a) 0.5 wt% GO (b) 1 wt% GO (c) 1.5 wt% GO (d) 2 wt% GO
(e) 2.5 wt% GO (f) 3 wt% GO.
7.3.7 Dielectric Properties

Figure 7.14 (a-g) shows the dielectric constant plots of PSSA/PVA (50/50) blend and different compositions of PSSA/PVA/GO composites, measured in the frequency range 50 Hz to 20 MHz and temperature in the range 40-150°C. It is apparent from the figure that the dielectric constant value is high at the lower frequency and with further increase in frequency, the dielectric constant decreases. Such frequency dependent behavior of dielectric constant is due to the ceasing of different polarizations with the increase in the frequency [312]. The maximum value of dielectric constant for PSSA/PVA (50/50) blend was $\varepsilon = 82.67$ at 50 Hz and at 150°C. The dielectric constant has increased when GO was added to PSSA/PVA blend. For example; for composites with 0.5 wt % GO loadings the maximum value of dielectric constant was $\varepsilon = 118.79$ at 50 Hz and at 150°C and for composites with 3 wt % GO loading the maximum value of dielectric constant was $\varepsilon = 297.91$ at 50 Hz and at 150°C. Thus, more than 3.5 fold increase in the dielectric constant was observed for PSSA/PVA/GO composites with 3 wt % GO loading as compared to PSSA/PVA blend. Table 7.2 represents comparative values of dielectric constant and dielectric loss tangent observed for PSSA/PVA/GO composites. It can be seen that all the high values of dielectric constant for composites were observed at low frequencies which are attributed to the contribution from space charge polarizations [319, 330, 331]. Also, the flexibility of polymer chain has an influence on the dielectric constant of composites at low frequency. The magnitude of dielectric constant is greatly affected by the presence of dipoles in the polymer matrix which are highly mobile. Thus, the introduction of GO into the polymer matrix has improved the dielectric constant significantly.
Figure 7.14 (a): Dielectric constants of PSSA/PVA (50/50) blend as a function of frequency at various temperatures.

Figure 7.14 (b): Dielectric constants of PSSA/PVA/GO composites with 0.5 wt% GO loading as a function of frequency at various temperatures.
Figure 7.14 (c): Dielectric constants of PSSA/PVA/GO composites with 1 wt% GO loading as a function of frequency at various temperatures.

Figure 7.14 (d): Dielectric constants of PSSA/PVA/GO composites with 1.5 wt% GO loading as a function of frequency at various temperatures.
Figure 7.14 (e): Dielectric constants of PSSA/PVA/GO composites with 2 wt% GO loading as a function of frequency at various temperatures.

Figure 7.14 (f): Dielectric constants of PSSA/PVA/GO composites with 2.5 wt% GO loading as a function of frequency at various temperatures.
Figure 7.14 (g): Dielectric constants of PSSA/PVA/GO composites with 3 wt% GO loading as a function of frequency at various temperatures.

Table 7.2: Maximum values of dielectric constant and dielectric loss obtained for PSSA/PVA/GO composites

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>GO loading (wt %)</th>
<th>Dielectric constant ($\varepsilon$)</th>
<th>Dielectric loss (tan$\delta$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>82.67, 50 Hz, 150°C</td>
<td>1.56, 50 KHz, 140°C</td>
</tr>
<tr>
<td>2</td>
<td>0.5</td>
<td>118.79, 50 Hz, 150°C</td>
<td>1.69, 50 KHz, 140°C</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>150.05, 50 Hz, 150°C</td>
<td>1.73, 50 KHz, 140°C</td>
</tr>
<tr>
<td>4</td>
<td>1.5</td>
<td>163.31, 50 Hz, 150°C</td>
<td>1.79, 50 KHz, 140°C</td>
</tr>
<tr>
<td>5</td>
<td>2</td>
<td>191.38, 50 Hz, 150°C</td>
<td>2.17, 50 KHz, 140°C</td>
</tr>
<tr>
<td>6</td>
<td>2.5</td>
<td>262.40, 50 Hz, 150°C</td>
<td>2.42, 50 KHz, 140°C</td>
</tr>
<tr>
<td>7</td>
<td>3</td>
<td>297.91, 50 Hz, 150°C</td>
<td>2.64, 50 KHz, 140°C</td>
</tr>
</tbody>
</table>
Dielectric loss is another important dielectric property which is a measure of energy dissipation resulted from the movement of molecules when an external electric field is applied. Hence, the magnitude of the dielectric loss tangent can be used to evaluate the interfacial adhesion between the polymer matrix and the filler. Figure 7.15 (a-g) represents the dielectric loss tangent plots of PSSA/PVA (50/50) blend and different compositions of PSSA/PVA/GO composites. It is apparent from the figure that all the composites have similar dielectric loss behavior, i.e. low dielectric loss tangent values at low frequency. In addition, there exists a broad peak at 50 KHz for PSSA/PVA (50/50) blend and for all the composites samples, which is attributed to $\beta$ relaxation. The reason for such relaxation peak in the dielectric loss tangent plots is that the movement of polymer chains was maintained with the change of the external frequency leading to the dipolar loss. The maximum value of dielectric loss tangent for PSSA/PVA (50/50) blend was $\tan \delta = 1.56$ at 50 KHz and at 140°C. The dielectric loss tangent has increased when GO was added to PSSA/PVA blend. For composites with 0.5 wt % GO loading, the dielectric loss tangent value was $\tan \delta = 1.69$ at 50 KHz and at 140°C. For example; for composite with 3 wt % GO loading, the dielectric loss tangent value was $\tan \delta = 2.64$ at 50 KHz and at 140°C. However, the values of dielectric loss are low compared to dielectric constant values of composites, which is highly desirable for the applications of composites in advanced electronic devices such as embedded capacitors. Thus, the improvement in the dielectric properties of PSSA/PVA/GO composites with different compositions is attributed to the strong interfacial adhesion between the constituents of composites.
Figure 7.15 (a): Dielectric loss plots of PSSA/PVA blend (50/50) as a function of frequency at various temperatures.

Figure 7.15 (b): Dielectric loss plots of PSSA/PVA/GO composites with 0.5 wt% GO loading as a function of frequency at various temperatures.
Figure 7.15 (c): Dielectric loss plots of PSSA/PVA/GO composites with 1 wt% GO loading as a function of frequency at various temperatures.

Figure 7.15 (d): Dielectric loss plots of PSSA/PVA/GO composites with 1.5 wt% GO loading as a function of frequency at various temperatures.
Figure 7.15 (e): Dielectric loss plots of PSSA/PVA/GO composites with 2 wt% GO loading as a function of frequency at various temperatures.

Figure 7.15 (f): Dielectric loss plots of PSSA/PVA/GO composites with 2.5 wt% GO loading as a function of frequency at various temperatures.
Figure 7.15 (g): Dielectric loss plots of PSSA/PVA/GO composites with 3 wt% GO loading as a function of frequency at various temperatures.

7.4 CONCLUSION

In conclusion, GO was produced using a modified Hummers method and subsequently reinforced into PSSA/PVA blend matrix to obtain PSSA/PVA/GO composites using colloidal processing technique. GO sheets were homogeneously dispersed in the polymer matrix and stable dispersions were obtained owing to the presence of the highly hydrophilic oxygen-containing functional groups of GO. The excellent reinforcement of composites was achieved due to the strong interfacial interaction between PSSA, PVA and GO via hydrogen bonding which was confirmed by FTIR spectroscopy. The XRD results clearly indicate that GO was fully exfoliated into individual graphene sheets. The higher decomposition temperatures were observed for PSSA/PVA/GO composites as compared to PSSA/PVA blend indicating the improvement in the thermal stability of composites. The improved thermal stability of composites can be attributed to the excellent
dispersion of GO into the polymer matrix and the high aspect ratio of GO. The improved dielectric performance of PSSA/PVA/GO composites is attributed mainly to the homogeneous dispersion of GO in the polymer matrix and the strong interaction between PSSA, PVA, and GO. The PSSA/PVA/GO composites constitute a new type of graphene-based composites to be used as a high dielectric constant material in advanced energy storage devices.