CHAPTER 5

ORGANOMODIFIED GRAPHENE REINFORCED POLYSULFONE NANOCOMPOSITES

5.1 INTRODUCTION

Recently, the use of graphene as reinforcement for polymer has attracted both academic and industrial interest because it can produce a dramatic improvement in properties of polymer nanocomposites at extremely small level of loading. It was also reported that the improvement in mechanical, thermal, gas barrier, electrical and flame retardant properties of graphene based polymer nanocomposites are much better in comparison to that of clay or other carbon filler reinforced polymer nanocomposites. The properties and the abundance of graphene based fillers have exceptional potential to revolutionize the use of nanocomposites and enable their use in widespread applications (Kim et al 2010). Although clay nanocomposites have started to appear in large quantities in consumer products, functionalized graphene provides an exciting opportunity as a new nanofiller, because it offers properties that are equal to or better than those of CNTs but with the scale and practicability of clay (Tang et al 2011). Different organic polymers have been used to fabricate graphene filled polymer nanocomposites due to its potential to result in materials and devices with extraordinary properties. Studies are piling up to develop engineering data and design guide-lines for graphene based polymer nanocomposites.
The improvement in physicochemical properties of the nanocomposites depends on the distribution of graphene layers in the polymer matrix as well as interfacial bonding between the graphene layers and polymer matrix. Full utilization of graphene nanoplatelets in polymer nanocomposite applications inevitably depends on their abilities to achieve full exfoliation and complete dispersion in the polymer matrix. Because of their high specific surface area and tendency to form irreversible agglomerates pristine graphene is not compatible with organic polymers. The surface modification of graphene is an essential step for obtaining a molecular level dispersion of individual graphene in a polymer matrix (Niyogi et al 2011).

This chapter studies the fabrication of chemically functionalized graphene reinforced PSf nanocomposites using a solution casting method. Graphene (GN) nanoplatelets were organically modified with ODA and characterized using different techniques, such as ATR-FTIR, XRD and TEM. As the property enhancements correlate strongly with nanocomposite microstructure, effective characterization of morphology is important to establishing structure-property relationships of these materials. So the dispersion of graphene nanoplatelets within the polymer matrix was investigated using ATR-FTIR, XRD, AFM and TEM. The effects of addition of this organofiller on the hydrophobic, mechanical, thermal and dielectric properties of PSf were examined. The aging studies of PSf nanocomposite films were done using different solvents and the results were compared with those of unfilled PSf films. Attempts have been made to correlate the changes in physico-chemical properties of the nanocomposites with its morphology and filler-matrix interactions.
5.2 CHARACTERISATION OF GRAPHENE NANOPLATELETS

5.2.1 ATR-FTIR Analysis of Nanoplatelets

The chemical changes occurring upon treatment of graphene with octadecylamine were investigated by FTIR spectroscopy. Figure 5.1 shows the FTIR patterns of GN and ODA modified graphene (OGN). For graphene, the peak at 3413 cm$^{-1}$ was attributed to -OH stretching vibrations of adsorbed water molecules, and the peak at 1626 cm$^{-1}$ can be attributed to -OH bending vibrations. The presence of carboxyl and epoxy functional groups was detected at around 1735 cm$^{-1}$ and 1225 cm$^{-1}$, 1053 cm$^{-1}$, respectively. These main characteristics peaks indicated that GN had been synthesized successfully (Liu et al 2010). In OGN, the peak at about 3400 cm$^{-1}$ was associated with –NH stretching vibration. The C=C stretching vibration of ODA at 1493 and 1577 cm$^{-1}$ were also found. The characteristics asymmetric stretching vibration of C-H bonds of the alkyl groups at 2854 and 2925 cm$^{-1}$ in addition to those seen in FTIR spectra of GN (Pramoda et al 2010).

Figure 5.1 FTIR patterns of GN and OGN
5.2.2 TEM Analysis of Nanoplatelets

TEM images of unmodified and ODA modified graphene nanoplatelets are shown in Figure 5.2. Graphene nanoplatelets resemble rippled silk waves with some wrinkles and folding on the surface and edge. They are transparent and very stable nature under the electron beam. TEM images showed that most parts of the nanoplatelets are homogeneous and quite smooth.

![TEM images of graphene nanoplatelets: (a) Unmodified (b) ODA modified.](image)

Figure 5.2 TEM images of graphene nanoplatelets: (a) Unmodified (b) ODA modified.

5.3 PREPARATION OF POLYSULFONE/ORGANOMODIFIED GRAPHENE NANOCOMPOSITES

PSf used in this study was pre-dried in a vacuum oven at 120°C for at least 12 h. An appropriate amount of polysulfone is added to DMF followed by stirring for 10 h at 50°C. Then, OGN was mixed with PSf solution and stirred at 50°C for 24 h with varying filler amounts as 0, 0.5, 1 and 2 wt%. The solution was sonicated for 30 minutes to avoid agglomeration of graphene. Thin films of thickness $0.2 \pm 0.02$ mm were prepared by solution casting method using TLC applicator and dried in a vacuum oven for the complete removal of solvent. The PSf/OGN nanocomposites were designated as PG0, PG0.5, PG1, and PG2 respectively according to the weight percentage of OGN loading.
5.4 RESULTS AND DISCUSSION

5.4.1 Morphological Analysis

5.4.1.1 ATR-FTIR analysis of nanocomposites

ATR FTIR analysis of PSf/graphene nanocomposites was carried out to verify the presence of fingerprint functional groups that should be present from the successful coupling of the polymer with graphene. The representative FTIR spectra of the PSf and PSf/OGN nanocomposites at various filler concentrations are shown in Figure 5.3. For the neat PSf film, the characteristics vibration bands occurred at 1160, 1240, 1325, and 3000 cm\(^{-1}\). After the formation of PSf/OGN nanocomposites, the characteristics peaks of PSf shifted slightly to lower wave-numbers. This indicates the molecular interactions have taken place between the PSf and OGN. Furthermore, in the polymer nanocomposites the characteristic peaks of OGN are retained.

![Figure 5.3 ATR-FTIR spectra of (a) PG0 (b) PG0.5 (c) PG1 and (d) PG2](image-url)
5.4.1.2 X-ray diffraction analysis of nanocomposites

XRD provides an insight into the dispersion and orientation of graphene nanoplatelets in PSf nanocomposites. Figure 5.4 shows the XRD patterns of OGN and PSf/OGN nanocomposites with 0.5, 1, and 2 wt% filler loading.

![Figure 5.4 XRD patterns of PSf/OGN nanocomposites](image)

OGN exhibits a refraction peak at $2\theta = 26.98^\circ$ (i.e., $d = 0.33$ nm). The neat PSf sample exhibits several broad reflection peaks with the most intense peak at $2\theta = 18.1^\circ$ (i.e., $d = 0.48$ nm). The PSf nanocomposites at 0.5 wt% and 1 wt% OGN loading show the diffraction peak of PSf only. In the case of PG0.5 and PG1, characteristic diffraction peak associated with the OGN is not observed. These results clearly demonstrated that the regular and periodic structure of graphene is disappeared in PG0.5 and PG1 due to the exfoliation of OGN in the PSf matrix. The PG2 nanocomposite shows a
characteristic peak of OGN at 26.8° with larger $d$-spacing ($d=0.39$ nm). The peak indicates that the platelets are not exfoliated. The existence of peak is due to the fact that, even though the layer spacing increases, there is an attractive force between the nanoplatelets to stack them in an ordered structure which was detected by wide angle X-ray scattering. The increase in the interlamellar spacing is due to the intercalation of PSf chains on surface and in between graphene nanoplatelets, which disrupts the van der Waals interactions between the platelets. Since the tactoids are internally disordered or not well aligned to one another, the intensity of peak is low (Chang et al 2008).

### 5.4.1.3 AFM images of the nanocomposites

AFM images of surfaces of the neat PSf and nanocomposite films over a scan area of $5\mu m \times 5\mu m$ are displayed in Figure 5.5. It was found that the surface morphologies of PSf/OGN nanocomposites were different from that of neat PSf film. Besides a more or less dark background, bright areas are visible, which represent graphene nanoplatelets distributed in the PSf matrix. The images of nanocomposites with 0.5 wt% and 1 wt% graphene loading clearly show uniform distribution of filler without any remarkable agglomeration. The uniform distribution and homogeneity of graphene filler inside the polymer could be attributed to the chemical functionalization of graphene. In the nanocomposites, the edge-to-edge nearest neighbor length correlation distance decreases with increasing graphene content. When the graphene content reached 2 wt%, the nanoplatelets tend to aggregate in the PSf matrix forming large flake like structures with dimensions ranging from few nanometers to hundreds of nanometers. The aggregation appeared in the PG2 nanocomposites can be attributed to the less effective interaction between the PSf matrix and OGN nanoplatelets. AFM results showed that the graphene nanoplatelets were uniformly dispersed at lower filler loading, but
aggregations were formed when the graphene concentration was high. The surface parameters, such as the average roughness, $R_a$ and the root mean square (RMS) roughness, $R_q$ (Table 5.1), were higher than those of neat PSf.

![AFM images of PSf/OGN nanocomposite films: (a) PG0 (b) PG0.5 (c) PG1 and (d) PG2](image)

**Figure 5.5** AFM images of PSf/OGN nanocomposite films: (a) PG0 (b) PG0.5 (c) PG1 and (d) PG2

<table>
<thead>
<tr>
<th>Nanocomposites</th>
<th>RMS ($R_q$) (nm)</th>
<th>$R_a$ (nm)</th>
<th>$R_q - R_a$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PG0</td>
<td>3.02</td>
<td>2.22</td>
<td>0.80</td>
</tr>
<tr>
<td>PG0.5</td>
<td>7.34</td>
<td>4.85</td>
<td>2.49</td>
</tr>
<tr>
<td>PG1</td>
<td>9.67</td>
<td>5.77</td>
<td>3.90</td>
</tr>
<tr>
<td>PG2</td>
<td>12.49</td>
<td>7.86</td>
<td>4.63</td>
</tr>
</tbody>
</table>

Table 5.1 Roughness parameters of PSf/OGN nanocomposites
5.4.1.4 TEM images of the nanocomposites

TEM images of PSf nanocomposites with 1 and 2 wt% OGN loading are shown in Figure 5.6 (a and b) respectively, to provide a quantitative evaluation of platelet distribution in the PSf. In Figure 5.6 (a), one platelet oriented perpendicular to the sample surface is visible over the entire imaging area. This reveals the uniform dispersions of graphene throughout the PSf matrix with exfoliated structure. The functionalization of graphene weakens the interactions between the graphene nanoplatelets and facilitates good compatibility between graphene and PSf to achieve nanoscale dispersion. In Figure 5.6 b, dark portions indicate many graphene layers in a particular region of nanocomposite. In PG2, the PSf chains adsorb on the surface of the nanoplatelets or intercalate between the graphene sheets result in an intercalated structure (Zhang and Qiu 2011).

Figure 5.6 Representative TEM micrographs showing the dispersion of the OGN in the PSf nanocomposites: (a) 1 wt% graphene loading and (b) 2 wt% graphene loading

5.4.2 Contact Angle Measurements

The wetting behavior of the nanocomposite surface is very important in fundamental research and practical applications. The
hydrophobicity of the PSf/OGN nanocomposite films was determined from the contact angle measurements and the results have been confirmed by determining the surface energy parameters. The contact angle of neat PSf was 85° which is in accordance with the higher hydrophobicity of neat PSf. The contact angle of PG0.5, PG1, and PG2 nanocomposite films were 89.1°, 92.8° and 95.2° respectively. The increase in water contact angle ascertains the increase in the hydrophobic nature of the nanocomposite surfaces with increase in filler loading.

The hydrophobicity of nanocomposite surface was determined by two factors: the surface composition and the microstructure. The morphology of the nanocomposite surface influences the hydrophobicity, since the water wettability strongly depends on the surface roughness of the films. AFM studies showed the evolution of microstructural features responsible for surface roughness, which is attributed to the undulating features, originated from film fabrication processes and exposed inclusions in the PSf nanocomposites (Murugaraj 2010). The difference in the composition on the nanocomposite surface also contributes to the hydrophobic behavior of the nanocomposite surface. The incorporation of hydrophobic OGN platelets in PSf matrix increases the hydrophobicity of the nanocomposite surface by thermodynamically controlled enrichment of the surface by nanoplatelets.

The information about the surface tensions of PSf nanocomposite was calculated using Young equation. From the single contact angle measurement, surface free energies, $\gamma_{sv}$ and corresponding surface parameters such as work of adhesion, interfacial free energy, spreading coefficient and Girifalco-Good’s interaction parameter were calculated and results are presented in Table 5.2. The calculated surface parameters of the nanocomposite films were used to obtain a quantitative determination of the magnitude of their hydrophobicity.
Table 5.2  Surface free energy, Interfacial free energy, Work of adhesion, Spreading coefficient and Girifalco-Good’s interaction parameter values of PSf/OGN nanocomposites

<table>
<thead>
<tr>
<th>Samples</th>
<th>Contact angle (θ)</th>
<th>Surface free energy ($\gamma_s$) mJ/m²</th>
<th>Interfacial free energy ($\gamma_{sl}$) mJ/m²</th>
<th>Work of adhesion ($W_A$) mJ/m²</th>
<th>Spreading coefficient (Sc) mJ/m²</th>
<th>Girifalco-Good’s interaction parameter(φ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PG0</td>
<td>85.0</td>
<td>31.81 (0.45)</td>
<td>25.09</td>
<td>7.34</td>
<td>-66.45</td>
<td>0.84</td>
</tr>
<tr>
<td>PG0.5</td>
<td>89.1</td>
<td>29.10 (0.50)</td>
<td>31.88</td>
<td>2.14</td>
<td>-71.65</td>
<td>0.76</td>
</tr>
<tr>
<td>PG1</td>
<td>92.8</td>
<td>27.75 (0.34)</td>
<td>38.85</td>
<td>-2.55</td>
<td>-76.35</td>
<td>0.69</td>
</tr>
<tr>
<td>PG2</td>
<td>95.2</td>
<td>25.96 (0.44)</td>
<td>44.30</td>
<td>-5.59</td>
<td>-79.39</td>
<td>0.64</td>
</tr>
</tbody>
</table>

*Numbers in the parenthesis are standard deviation

5.4.3  Mechanical Properties

The homogeneity of nanocomposites and the stronger interfacial interaction between nanofillers and the polymer matrix have a significant effect on the mechanical properties. Upon the graphene loading, the mechanical behavior of the nanocomposites apparently exhibits an enhancing trend. From the Table 5.3, the tensile strength of the nanocomposite containing 1 wt% graphene was 7.75 MPa, while that of the neat PSf sample was 4.72 MPa; i.e., the tensile strength was increased by 65%. The highest value of tensile strength obtained for the nanocomposite with 1 wt% graphene loading is due to the nanoscale dimension of the OGN phase and the nearly perfect orientation and fine dispersion of the nanoplatelets in the PSf matrix. The degree of structural organization of the graphene platelets in the nanocomposite maximizes the number of PSf-OGN interactions and constrains the polymer-chain motion, which resulted in a highly efficient load transfer between the PSf matrix and the stiff OGN nanoplatelets. The elongation at break of the composites also showed the same trend by the incorporation of OGN nanoplatelets. The elongation at break showed an increase of 91% for the nanocomposite with 1 wt%.
Table 5.3 Mechanical properties of the neat PSf and PSf/OGN nanocomposites

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tensile strength (MPa)</th>
<th>Young’s modulus (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PG0</td>
<td>4.72 (0.2)*</td>
<td>147(0.3)</td>
<td>33(0.8)</td>
</tr>
<tr>
<td>PG0.5</td>
<td>6.98 (0.1)</td>
<td>199(0.2)</td>
<td>51(1.2)</td>
</tr>
<tr>
<td>PG1</td>
<td>7.75 (0.1)</td>
<td>218(0.1)</td>
<td>63(0.7)</td>
</tr>
<tr>
<td>PG2</td>
<td>5.96(0.1)</td>
<td>239(0.4)</td>
<td>37(0.8)</td>
</tr>
</tbody>
</table>

*Numbers in the parenthesis are standard deviation

Further increase of graphene content, decreases the tensile strength from 7.75 to 5.96 MPa. The potential explanation for the decrease in the tensile strength after optimum OGN content (1 wt%) is the change in morphology from exfoliated to intercalated as evidenced from AFM and TEM analysis. At 2 wt% filler loading, graphene nanoplatelets restack together due to the existence of van der Waals force of the nanoplatelets. The slippage of piled graphene nanoplatelets during the tensile testing have less effective enhancement on the mechanical properties of the nanocomposite. This can be explained from the schematic models in Figure 5.7. It is assumed that there are three types of arrangements for the nanoplatelets in the PSf matrix upon increasing nanofillers: (1) they are individually dispersed in the matrix at intervals, (2) the edges of the sheets just join together side by side and (3) the graphene platelets are stacking together by layers. Among these, the second one (2) is the ideal condition, exhibiting the ultimate contribution to the mechanical behaviors with the greatest efficiency. With the increase of graphene loading, the arrangement would be changed to (3). When the amount of filler concentration reaches a critical content, the distance between two platelets is so small that they stack together easily due to the van der Waals force. There exists a critical point of the mechanical properties upon the nanoplatelet content, i.e., a loading of 1 wt%, and this phenomenon is
called as mechanical percolation. Lower than this content, the exfoliated graphene nanoplatelets can be well-dispersed in the polymer matrix, and the increase of loading has a significant improvement on the mechanical properties, while further loading may cause the nanoplatelets stacking together, weakening the efficiency of the mechanical improvement.

Figure 5.7 Schematic models of various dispersion types of graphene nanosheets in PSf matrix: (1) Graphene nanoplatelets are individually dispersed in the matrix at intervals (2) The edges of graphene nanoplatelets just join together side by side and (3) Graphene nanoplatelets are restacking together by layers

The modulus of all PSf/OGN nanocomposite films was significantly higher than that of neat PSf film. It is observed that modulus value increases monotonically with graphene content and showed the maximum value for 2 wt% graphene addition. Although the amounts of graphene in all PSf nanocomposite films were not very high, the enhancement of modulus by graphene addition is clearly observed. The addition of 0.5 wt% graphene into the PSf matrix causes the increase of modulus by 38%. The improvement of mechanical properties of polymer/graphene nanocomposites suggested the use of these materials in transport applications, where the
combination of high strength and light weight provides environmental advantages for enhanced fuel-efficiency vehicles.

5.4.4 Thermal Properties

5.4.4.1 Thermogravimetric analysis

The thermal stability of PSf/OGN nanocomposites plays an important role in determining their working temperature limits and operational conditions prior to their use in industrial applications (Wang et al 2009). The thermal performance of the PSf/OGN nanocomposites was determined from TGA analysis and the results are illustrated in Figure 5.8. The TGA patterns indicate that the PSf and nanocomposites exhibit two step decomposition mechanisms. But in the case of nanocomposites the second degradation step was completely disappeared and the degradation follows a single step mechanism, which indicated the improved thermal stability of PSf nanocomposites. The disappearance of second degradation step is due to the physical cross linking between the OGN nanoplatelets and PSf, which in turn increased the heat of oscillation and pyrolysis temperature of PSf chain (Yu et al 2011).

The thermal degradation characteristics of the nanocomposites presented in Table 5.4 confirmed the improved thermal stability of nanocomposites compared to that of neat PSf. The degradation temperature of nanocomposites are shifted to higher temperatures and showed maximum values at 1 wt% filler loading due to the homogeneous dispersion and the large aspect ratio of OGN nanoplatelets. The successful incorporation of the OGN nanoplatelets in the PSf matrix enhances the thermal stability by acting as an insulator and mass transport barrier to the volatile products generated during decomposition, as well as by assisting in the formation of char after thermal decomposition.
Figure 5.8 Thermogravimetric curves of PSf/OGN nanocomposites

The strong interaction of nano dispersed OGN nanoplatelets with PSf chains induces a steric effect in macro-chains of nanocomposite that restricts the thermal motions of PSf chain (Zhang et al 2010). However, OGN loading beyond 1 wt% in PSf matrix showed a decreasing trend in their thermal decomposition temperature. These findings were attributed to the fact that, at low filler contents homogeneous exfoliation and random dispersion of nanoplatelets is achieved on a nanometer level, whereas the higher filler loading destabilizes the matrix, because of the aggregation of graphene nanoplatelets (Kashiwagi et al 2009). Thus the results of thermal analysis show that thermal resistance of exfoliated nanocomposite was superior to intercalated one.
Table 5.4  \[T_{\text{onset}}, T_{\text{max}}, \text{and percentage weight loss at } 300^\circ\text{C}, 600^\circ\text{C and } 800^\circ\text{C}\] of PSf/OGN nanocomposites

<table>
<thead>
<tr>
<th>Nanocomposites</th>
<th>(T_{\text{onset}}) (°C)</th>
<th>(T_{\text{max}}) (°C)</th>
<th>Percentage weight loss at</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>300°C</td>
</tr>
<tr>
<td>PG0</td>
<td>496</td>
<td>516</td>
<td>3.19</td>
</tr>
<tr>
<td>PG0.5</td>
<td>513</td>
<td>535</td>
<td>2.13</td>
</tr>
<tr>
<td>PG1</td>
<td>514</td>
<td>533</td>
<td>1.5</td>
</tr>
<tr>
<td>PG2</td>
<td>507</td>
<td>555</td>
<td>2.2</td>
</tr>
</tbody>
</table>

5.3.4.2  Differential Scanning Calorimetry

DSC analysis was carried out to investigate the influence of OGN nanoplatelets dispersion on the glass transition temperatures (\(T_g\)) of the PSf. DSC curves of neat PSf and PSf/OGN nanocomposites with different filler concentration are shown in Figure 5.9. When the filler content was about 0.5 wt\%, the PSf/OGN nanocomposites exhibited an increase in \(T_g\) compared to the neat PSf. At 1 wt\% filler loading, \(T_g\) of the nanocomposites showed a sharp increase to 206°C, which was about 13°C more than that of neat PSf. The variation of \(T_g\) with respect to the filler concentration indicates that glass transition temperature of the PSf increases upon the incorporation of OGN nanoplatelets. This increase in \(T_g\) is attributed to the confinement of intercalated polymer within the nanoplatelets that prevents the segmental motions of the polymer chains and further decreases the free volume (Faun et al 2008). The anchored polymer chains in the PSf nanocomposites could reduce free volume, where the segment relaxation was much slower than that in the neat PSf. This restricted relaxation behavior for the polymer nanocomposites depends primarily on the extent of exfoliation of the OGN nanoplatelets and the interaction strength between the nanoplatelets and PSf matrix. This maximum increment of \(T_g\) at 1 wt\% filler content is due to the
optimum exfoliation compared to the intercalated structure at 2 wt% filler loading as evidenced by the morphological analysis (Qiao and Brinson 2009). A slight decrease in the value of $T_g$ at 2 wt% filler loading is due to the occurrence of unexfoliated aggregates which reduce the intermolecular interaction between PSf and OGN nanoplatelet as evidenced from morphological analysis (Matraszek et al 2008). The increase in the glass transition temperature of PSf matrix by the incorporation OGN nanoplatelets assured the application of these nanocomposites in high temperature environment.

![Figure 5.9 DSC curves of PSf/OGN nanocomposites](image)

**Figure 5.9 DSC curves of PSf/OGN nanocomposites**

### 5.5.5 Dielectric Analysis

The dependence of dielectric properties of the PSf nanocomposite films on the content of graphene was studied at room temperature. Figure 5.10 shows the dielectric constants of the PSf/graphene nanocomposite films with
varying graphene contents of 0, 0.5, 1 and 2 wt% in the frequency range from 1 kHz to 1 MHz. The dielectric constants of all nanocomposites are higher than that of neat PSf and the value increases with increasing concentration of graphene. This is attributed to the high electrical conductivity and current-carrying capacity of graphene which enhances the dipole-dipole interactions. The relative high dielectric constants of the PSf/OGN nanocomposites are desirable in many practical electronic applications (He et al 2008).

![Graph showing dielectric constant vs. frequency](image)

**Figure 5.10** Effect of frequency on the dielectric constant of PSf nanocomposite films: (a) PG0 (b) PG0.5 (c) PG1 and (d) PG2

### 5.5.6 Aging Studies

The aging studies of the PSf/OGN nanocomposites were carried out and the results are shown in the Figures 5.11 and 5.12. As can be seen, solvent permeation of all PSf nanocomposite samples were found to be lower than those of neat PSf because of the incorporation of graphene nanoplatelets
into the PSf matrix, which led to a longer tortuosity of the diffusion pathway of solvent molecules. With respect to the filler content, the solvent permeation decreases initially and reaches a minimum at 1 wt%. This decrease at 1 wt% filler addition is owing to the good dispersion of OGN nanoplatelets and strong interaction between PSf and OGN nanoplatelets in nanocomposites (Picard et al 2007).

Figure 5.11 Change in weight of PSf/OGN nanocomposites after immersing in solvents

As the filler content increases above 1 wt%, the solvent permeation shows an increasing trend due to the aggregation of graphene leading to a decrease of aspect ratio of nanoplatelets as evidenced from the morphological analysis. Beyond 1 wt% filler loading, agglomerates may cause the formation of large scale holes or free volumes in the PSf matrix which can act as low resistance pathways for solvent transport within the nanocomposite.
The reduction in the tensile strength after aging indicates the low retention ability of the neat polymer, as shown in Figure 5.12. The incorporation of OGN nanoplatelets to PSf has increased the retention ability of the nanocomposites by preventing the direct penetration of solvents to the matrix. With the increase in weight percent of graphene, the absolute value of the changing rate of the tensile strength decreased and reached its minimum at 1 wt%. At 1 wt% graphene loading, the retention ability of nanocomposites showed an increase of 0.1 %, 0.05 % and 0.02 % for ethanol, KOH and engine oil, respectively. When the filler content reached 2 wt%, the agglomeration of graphene nanoplatelets at higher filler loading reduces the retention ability of nanocomposite due to the formation of microcracks.
5.6 CONCLUSION

In this study, organomodified graphene nanoplatelets reinforced PSf nanocomposites were prepared with varying percentage of filler loading using solution casting method. The morphology of the nanocomposites was analyzed by ATR-FTIR, XRD, AFM and TEM techniques. The contact angle measurements showed that hydrophobicity of nanocomposite increased with increasing graphene content due to the enrichment of nanofillers on nanocomposite surface and increasing surface roughness, as evidenced from AFM analysis. The PSf/OGN nanocomposite films exhibited a significant improvement on the mechanical properties due to the high specific surface area, enhanced nanofiller-matrix adhesion/interlocking arising from their wrinkled (rough) surface, as well as the two-dimensional (planar) geometry of graphene platelets. As a representative example, a 65 % increase of tensile strength were achieved by adding 1 wt% graphene nanoplatelets, indicating the efficient load transfer between the graphene and PSf matrix. Upon the loading of the nanoplatelets, it is assumed that there might be an optimal point of the extent of improvements for tensile strength and elongation at break. The modulus of the nanocomposite with 2 wt% graphene loading is 63 % greater than that of neat PSf sample. The thermal properties improved significantly in comparison with pure PSf. The $T_g$ of the nanocomposites showed an increase at about 13ºC at 1 wt% filler loading due to the confinement of polymer within the graphene nanoplatelets that prevents the segmental motions of the PSf chains. The dielectric constant of the PSf nanocomposites increased linearly with graphene concentration and showed relatively high dielectric constant when the graphene content was 2 wt%. In summary, graphene based PSf nanocomposites are remarkable materials that combine the mechanical, thermal, hydrophobic, aging and dielectric properties, and processing advantages of thermoplastics. The multifunctional property enhancements coupled with their potential low cost showed that the prepared PSf/OGN nanocomposites are promising candidate for high performance applications.