CHAPTER 3

ORGANOFLUROHECTORITE CLAY REINFORCED POLYSULFONE NANOCOMPOSITES

3.1 INTRODUCTION

Polymer layered silicate nanocomposites are an important class of materials where layered silicates are dispersed in a polymer matrix to enhance the mechanical, thermal, rheological, optical, and electrical properties of the neat polymer (Ray and Easteal 2007). Though these bulk properties have been recognized as important features of polymer nanocomposites, surface properties are also of significant characteristic for the better practical utility. Now a days, the fabrication of hydrophobic polymer surfaces has been an interesting subject in both academic research and industrial applications (Shang et al 2005; Gu et al 2006). The improvement of hydrophobicity of PSf nanocomposites is applicable not only for resisting water and fog condensation, but also for preventing contamination. This has stimulated great interest in improving the hydrophobic nature of polysulfone by the incorporation of nanoparticles without affecting the bulk properties.

Molecular transport through polymer clay nanocomposites is also one of the relevant research areas due to the ability of nanoclay particles to control the diffusion and permeation of molecules through the polymer matrix. The enhancement in barrier properties of clay nanocomposites is mainly influenced by the type of clay particle, amount of filler, high aspect ratio of the clay platelets and its compatibility with the host matrix.
(Osman et al 2004). Although layered silicates are microns in lateral size, their thickness about 1 nm, retain the optical transparency of nanocomposites, which is not possible for conventional polymer composites (Choudalaski et al 2004). PSf is used for making transparent containers holding the potassium hydroxide electrolyte of Nickel-Cadmium battery and for automobile parts under the bonnet. The enhancement of material properties of polysulfone by the addition of clay is expected to offer significant weight reduction and increased life span of the battery and automobile parts.

It is known that surface active additives in polymer composites migrate to the surface and change the surface properties of the materials. Studies reported that fluorine is the most effective element for enhancing the hydrophobicity of the polymer surface (Hare et al 1954). FH clay is an environmentally friendly and readily available clay mineral with high-aspect ratio and high-surface area. But, one of the drawbacks of pristine FH clay is the incompatibility between hydrophilic clay and hydrophobic PSf, which often cause agglomeration of FH clay in PSf matrix. In the nanocomposites, if the interaction between polymer and filler is not favorable, the improvements in properties of nanocomposites will be much lower than what may be expected. Therefore, surface modification of FH clay is the most important step to achieve compatibility between clay and PSf in the polymer nanocomposite. The most popular modification for clays is to exchange the interlayer inorganic cations (e.g., Na⁺, Ca⁺) with organic ammonium cations. In the present study, octadecylamine has been used for the modification of pristine FH clay to make it hydrophobic and compatible with the PSf. The key aspect of surface modification of FH clay with ODA was to swell the interlayer space up to a certain extent and hence reduce the layer-layer attraction, which allow a favorable diffusion and accommodation of PSf into the interlayer space.
The present chapter investigates the development of PSf nanocomposites reinforced with octadecylamine modified fluorohectorite (OFH) clay using solution casting method. The dispersion of layered silicates within the polymer matrix was investigated using ATR-FTIR, XRD, AFM and TEM analysis. Contact angle of nanocomposite films was determined to study the effect of clay addition on hydrophobicity of nanocomposite surface. Further, the effects of addition of this organo filler on the mechanical, thermal, hydrophobic and dielectric property of polysulfone are also examined. The aging studies of PSf nanocomposite films were done using different solvents and the results were compared with those of neat PSf films. Attempts have been made to correlate the changes in physico-chemical properties of the nanocomposites with its morphology and filler-matrix interactions.

3.2 PREPARATION OF POLYSULFONE/OFH CLAY NANOCOMPOSITES

PSf used in this study was pre-dried in vacuum oven at 120°C for at least 12 h. An appropriate amount of polysulfone was added to DMF followed by stirring for 10 h at 50°C. Then, organoclay was mixed with PSf solution and stirred at 50°C for 24 h separately with varying filler amounts as 0, 1, 3 and 5 wt%. The solution was sonicated for 30 minutes to avoid agglomeration of clay. Thin films of thickness 0.2 ± 0.02 mm were prepared by solution casting method using TLC (Thin layer chromatography) applicator and dried in vacuum oven for the complete removal of solvent. The PSf nanocomposites consisting 0, 1, 3 and 5 wt% of organomodified fluorohectorite clay were designated as PS0, PS1, PS3, and PS5 respectively.
3.3 RESULTS AND DISCUSSION

3.3.1 Morphological Analysis

3.3.1.1 ATR-FTIR analysis

ATR-FTIR was used to examine the extent of interaction between clay and polymer. Figure 3.1 shows the FTIR patterns of FH clay, OFH clay, PSf and PSf/clay nanocomposites at different OFH clay concentrations. The common features in the FTIR spectra for fluorohectorite clay are the presence of characteristic bands at 3450, 1620, 1045, and 520 cm\(^{-1}\) due to –OH stretching of water, –OH deformation of water, Si–O stretching, and Al–O–Si deformation, respectively (Breu et al 2001; Yeh et al 2005). OFH shows the presence of new band at around 1472 cm\(^{-1}\) for CH\(_2\) scissoring.

![ATR-FTIR spectra](image)

Figure 3.1 ATR-FTIR spectra of (a) PS0 (b) PS1 (c) PS3 (d) PS5 (e) OFH clay and (f) FH clay
Furthermore, the intensity of −OH peaks has diminished due to the ion exchange reaction. This suggests that octadecylamine surfactant has been intercalated into the gallery of the FH clay. The characteristic vibration bands of PSf are at 1160 cm\(^{-1}\) (symmetric sulfone stretching), 1240 cm\(^{-1}\) (aromatic ether), 1325 cm\(^{-1}\) (asymmetric sulfone linkage), 3000−3100 cm\(^{-1}\) (aromatic CH\(_3\) stretching) and 2900−3000 cm\(^{-1}\) (aliphatic CH\(_3\) stretching) (Lim et al 1991; Chen and Evans 2004; Voicu et al 2009; Dizman et al 2010). The peaks observed for PSf nanocomposites remained the same as those of neat PSf. These results show that there were no major chemical and structural changes occurred in PSf nanocomposites, owing to the presence of OFH clay. Hence, characterization methods such as XRD and other microscopic methods will be useful to deduce a conclusion regarding the interaction between clay and the polymer.

### 3.3.1.2 X-ray diffraction analysis

XRD was used to determine the interlayer spacing of silicate layers in original layered silicates and in the intercalated nanocomposites. Figure 3.2 shows a series of X-ray diffraction patterns for FH clay, OFH clay and PSf/OFH clay nanocomposites with different compositions. It is clear that in organically modified clay the peak shifted from 7.2° to 4.3° by a decrease in intensity. The \(d\)-spacing of the clay increases from 1.22 nm to 2.05 nm on organo-modification due to the presence of octadecyl ammonium ion in the galleries of clay. (Kornmann et al 2005). This ascertains that the FH clay became organically modified. This increase in the layer to layer spacing of FH makes it appropriate for the intercalation of polymer molecules. In the case of X-ray diffraction patterns of 1 and 3 wt% nanocomposites, the peak around \(2\theta = 4.3^\circ\) associated with the layered structure of organophilic clay were not observed. This shows that regularly-layered silicates do not exist, and that the silicate layers are exfoliated. However, for 5 wt% nanocomposite,
a broader peak is observed on the lower angle side which is an indication of the fact that the OFH clay is partially exfoliated or intercalated at this particular filler loading. The shift in peak towards lower angles means that the interlayer distance of the OFH clay increased. The reason for the decrease in the intensity of peak is that the tactoids are internally disordered or not well aligned to one another. These changes in the microstructure of PSf/OFH clay nanocomposites with the addition of varying percent of OFH clay play a key role in determining their performance. That will be discussed in subsequent sections.

Figure 3.2  XRD patterns of PSf/OFH clay nanocomposites: (a) FH clay (b) OFH clay (c) PS1 (d) PS3 and (e) PS5
3.3.1.3  AFM images of the nanocomposites

AFM images provide detailed information of the surface morphology of the nanocomposite film and helpful to investigate the interfacial properties. In Figure 3.3 (a-d), the phase images of the nanocomposites with filler concentration 0, 1, 3 and 5 wt% are given. Figure 3.3 (a) shows the phase image of the neat PSf matrix. As can be seen in the figure the neat PSf surface is smooth and homogeneous. In the images of the filled nanocomposites (Figure 3.3 (b-d)), it can be seen that the nanoclay in the matrix appears as globules from the lower loading to higher loading. The number of platelets increases with respect to the loading and many aggregates on a micrometer scale were observed on the surface of 5 wt% nanocomposite.

Figure 3.3  AFM images of PSf nanocomposite films: (a) PS0 (b) PS1 (c) PS3 and (d) PS5
The changes in the surface topography could be determined quantitatively in terms of surface parameters, such as the average roughness, $R_a$ and the root mean square (RMS) roughness, $R_q$ (Maiti and Bhowmick 2006). The $R_q$ and $R_a$ values of nanocomposites are given in Table 3.1. In case of the neat PSf, $R_q$ value was found to be 3.02 nm and $R_a$ was 2.22 nm. Generally, $R_q$ and $R_a$ values will be almost equal, if there is no large deviation from the mean surface level. The difference between $R_q$ and $R_a$ value of 0.80 nm suggests that there is not much undulation for neat PSf matrix. It can be seen that nanocomposites show higher ($R_q - R_a$) values when compared to that of neat PSf matrix, which confirms the presence of filler particles on the surface. It was found that roughness parameters increase with increase of percentage of clay loading and show maximum value at 5 wt% loading (Thomas et al 2009).

<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>PS0</td>
<td>3.02</td>
<td>2.22</td>
<td>0.80</td>
</tr>
<tr>
<td>PS1</td>
<td>5.39</td>
<td>3.85</td>
<td>1.54</td>
</tr>
<tr>
<td>PS3</td>
<td>6.62</td>
<td>4.97</td>
<td>1.65</td>
</tr>
<tr>
<td>PS5</td>
<td>10.39</td>
<td>7.80</td>
<td>2.59</td>
</tr>
</tbody>
</table>

### 3.3.1.4 TEM images of the nanocomposites

TEM analysis allows a qualitative understanding of the internal structure of PSf/OFH clay nanocomposites and substantiates the results obtained from XRD. The TEM images of selected nanocomposites are given in Figure 3.4 (a and b). The lower filler loading showed exfoliated structures in which the layered structure of OFH clay has been destroyed and individual clay platelets were seen in the PSf matrix (Figure 3.4 (a)). However, the
higher filler loading like 5 wt% showed intercalated structure in which polymer chains were intercalated between the clay platelets (Figure 3.4(b)).

![Representative TEM frames showing the dispersion of the OFH clay in the PSf nanocomposites: (a) exfoliated structure of 3 wt% clay loading and (b) intercalated structure of 5 wt% clay loading](image)

**Figure 3.4** Representative TEM frames showing the dispersion of the OFH clay in the PSf nanocomposites: (a) exfoliated structure of 3 wt% clay loading and (b) intercalated structure of 5 wt% clay loading

### 3.3.2 Contact Angle Measurements

Contact angle measurements were carried out with water to determine the hydrophobicity and surface properties of PSf/OFH clay nanocomposites. The contact angle of neat PSf was 85° which is in accordance with the higher hydrophobicity of neat PSf. Figure 3.5 shows the representative pictures of the measurements with water as the liquid. With the addition of 1, 3 and 5 wt% clay content, the contact angles increased to 88.7°, 93.4° and 97.8° respectively, which indicate that the addition of OFH clay can be a useful way to improve hydrophobicity of the neat PSf. The increase in hydrophobicity is mainly attributed to the difference in both the chemical properties of polymer surface and its surface morphology. In order to have a
homogeneous dispersion in hydrophobic PSf matrix, the hydrophilicity of FH clay was decreased through ion-exchange reactions with octadecyl-ammonium cations, which in turn lower the hydrophilicity of the silicate surface (Ma et al 2007). In PSf/OFH clay nanocomposite system, the surface composition may differ from that in the bulk since the lower surface energy clay components migrate to the surface due to the difference in the surface energy of the components. The accumulation of the filler at the surface of the nanocomposite films can be explained as the result of overall unfavorable entropic and enthalpic interactions. As the filler loading increases, the extension of polysulfone molecules around this larger filler particle lowers the polymer molecule’s conformational freedom. With increasing filler content, this entropic penalty reaches a threshold value when the filler can no longer be accommodated by extended polymer chains. Under these conditions, the clay aggregate is expelled out of the casting mixture to the free surface for an entropic gain. Thus, the nanocomposite surfaces become more hydrophobic relative to the neat PSf due to the formation of film surface with lower equilibrium surface energy (Lewin 2003). Fluorine is the most effective element for lowering the surface free energy because it has a small atomic radius and the biggest electronegativity among all atoms. Hence it forms a stable covalent bond with carbon, resulting in a surface with low surface energy. Thus, the increase in hydrophobicity can also be explained by the presence of fluorine in the incorporated OFH clay in nanocomposite surface (Hare et al 1954).

The correlation between hydrophobicity and surface roughness of the polymer nanocomposites was investigated using AFM. The changes in morphology of the PSf nanocomposites can be quantified by root-mean-square roughness values ($R_{\text{rms}}$). The neat PSf film has an $R_{\text{rms}}$ value equal to 0.8 nm, while for nanocomposites with 1, 3 and 5 wt% clay loading, the $R_{\text{rms}}$ values are 1.65, 2.40 and 2.59 nm respectively. It was found that the increasing roughness on the polymer surface increases the contact angle (Liang et al 2006).
Figure 3.5 Representative figures of contact angle measurements of (a) PS0 (b) PS1 (c) PS3 and (d) PS5 with water as liquid

From the measured contact angle values, surface free energies, $\gamma_{sv}$ of the nanocomposite films were calculated using equations (2.3) and (2.4). Since, both the equations have given almost same $\gamma_{sv}$ values, various surface parameters such as work of adhesion, interfacial free energy, spreading coefficient and Girifalco-Good’s interaction parameter were calculated based on the values obtained from equation (2.4) and results are presented in Table 3.2. The calculated surface parameters of the nanocomposite films were used to obtain a quantitative determination of the magnitude of their hydrophobicity. The total surface free energy values, $\gamma_{sv}$, decreases with increase of percentage weight of filler loading. The $\gamma_{sv}$ value of neat PSf was 31.81 mJ/m$^2$ and it decreased to 24.16 mJ/m$^2$ by the incorporation of 5 wt% clay. In the case of interfacial free energy, $\gamma_{sf}$, shows an opposite trend to that of surface free energy, which increases with increase in clay concentration.
The $\gamma_{sl}$ values increase with respect to percentage clay content and show a maximum for 5 wt% filled system. Work of adhesion, $W_A$, calculated using the equation 2.6, shows a decreasing trend similar to that of surface free energy. The 5 wt% nanocomposite shows the lower value at $-8.88 \text{ mJ/m}^2$. The decreasing trend of $W_A$ shows that the hydrophobic behavior of PSf/OFH clay nanocomposites is increased with increasing percentage of organoclay content.

Table 3.2  Surface free energy, Interfacial free energy, Work of adhesion, Spreading coefficient and Girifalco-Good’s interaction parameter values of PSf/OFH clay nanocomposites

<table>
<thead>
<tr>
<th>Samples</th>
<th>Contact angle (°)</th>
<th>Surface free energy ($\gamma_S$) mJ/m$^2$</th>
<th>Interfacial free energy ($\gamma_{sl}$) mJ/m$^2$</th>
<th>Work of adhesion ($W_A$) mJ/m$^2$</th>
<th>Spreading coefficient ($Sc$) mJ/m$^2$</th>
<th>Girifalco-Good’s interaction parameter($\phi$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS0</td>
<td>85.0</td>
<td>31.81 (0.51)*</td>
<td>25.09</td>
<td>7.34</td>
<td>-66.45</td>
<td>0.84</td>
</tr>
<tr>
<td>PS1</td>
<td>88.7</td>
<td>29.56 (0.43)</td>
<td>31.37</td>
<td>2.65</td>
<td>-71.14</td>
<td>0.77</td>
</tr>
<tr>
<td>PS3</td>
<td>93.4</td>
<td>26.75 (0.59)</td>
<td>39.61</td>
<td>-3.31</td>
<td>-77.11</td>
<td>0.68</td>
</tr>
<tr>
<td>PS5</td>
<td>97.8</td>
<td>24.16 (0.60)</td>
<td>47.58</td>
<td>-8.88</td>
<td>-82.68</td>
<td>0.60</td>
</tr>
</tbody>
</table>

*Numbers in the parenthesis are standard deviation

The spreading coefficient of the liquid, $Sc$, is the work done in spreading one liquid over a unit area of surface and was calculated according to equation (2.7) (Padday 1959). For non-spreading system, $Sc$, possesses negative values and positive value of spreading coefficient implies the spontaneous wetting of liquid on the solid surface. The obtained values indicated that with the increase of percentage filler content, the spreading coefficient become more negative which shows an increase in hydrophobicity. A good understanding of the degree of interaction between the test liquid and PSf nanocomposite surface can be obtained from the Girifalco-Good’s interaction parameter (Girifalco and Good 1957). It is equal to unity if the
intermolecular forces acting across the interface are alike. For water as a test liquid, with increasing clay loading, this parameter shows a decreasing trend and is deviating from unity. This means that, compared to the neat polymer, the interaction between the liquid and polymer surface is low for nanocomposites. This result clearly demonstrates that incorporation of organomodified fluorohectorite clay is an effective method to improve the hydrophobicity of the polymer surface by changing its physico chemical surface characteristics.

3.3.3 Mechanical Properties

The mechanical properties of the organoclay reinforced PSf nanocomposites and the neat PSf matrices were evaluated by tensile studies. The neat polymer shows a tensile strength of around 4.7 MPa. From Figure 3.6, it can see that all the compositions showed a tensile strength higher than that of the neat PSf polymer. The tensile strength increases up to 3 wt% of organoclay loading and then decreases for the higher loading. The nanocomposites having 3 wt% nanofiller show maximum tensile strength of approximately 5.9 MPa. It is understood that at 3 wt% organoclay loading higher levels of interaction between filler and matrix facilitates stress transfer to the filler phase. When the flexible PSf matrix is reinforced with rigid layered silicates, the polymer, particularly that adjacent to the filler particles, become highly restrained mechanically. This enables a significant portion of an applied load to be carried by the filler which facilitates an improvement of the tensile strength. The excellent clay matrix interfacial adhesion and the large aspect ratio of layered silicate are responsible for this efficient stress transfer between clay and matrix (Tjong 2006). Also, the occurrence of strong interfacial interaction between the OFH clay and PSf matrix leads to some shear zones when the nanocomposites are under stress. Because of this strong interaction and development of shear zones, tensile strength of the
nanocomposites is increased at 3 wt%. However, in the case of increased filler loading both these parameters show a decreasing trend due to filler-filler interaction (Neilson 1966). The potential explanation for the decrease in the tensile strength after optimum clay content (3 wt%) is mainly due to the change in morphology from exfoliated to intercalated as described in XRD analysis. In the case of 5 wt% nanocomposite, discontinuity in the form of debonding exists because of poor adherence of layered silicate to the polymer and the stress transfer at the OFH clay/PSf interface becomes ineffective (Pramanik et al 2001). As shown in Figure 3.7, the elongation at break also showed maximum value at 3 wt% clay loadings. There are several more explanations responsible for this behavior such as (i) the clay may strengthen the PSf by reducing slippage during straining, (ii) the clay may act as physical

![Figure 3.6 Tensile properties of polysulfone nanocomposites](image)

Figure 3.6 Tensile properties of polysulfone nanocomposites
entanglements to reinforce tensile properties of the nanocomposites, and (iii) the clay may alter the strained microphase morphology of the PSf in such a way that results in improved tensile properties (Lee et al 2006). At high percentage of clay loadings, the nanoclay agglomerates may act as stress concentrators and reduce the elongation at break (Camila et al 2010).

![Elongation at break of polysulfone nanocomposites](image)

**Figure 3.7 Elongation at break of polysulfone nanocomposites**

Young’s modulus, expressing the stiffness of the material, shows noticeable improvement, with addition of OFH clay to PSf, as shown in Figure 3.6. A linear increase in the modulus can be seen with percentage of the organoclay loading. The neat polymer showed a tensile modulus value around 145 MPa while the corresponding value for nanocomposites with 5 wt % of clay is around 210 MPa, i.e., around 55 % increase is observed. It is well known that the modulus for a polymer increases when any mineral filler is
incorporated into it. This is reasonable because the rigid inorganic fillers have higher stiffness values than the organic polymer (Xiqiao 2001). So, it is obvious that the addition of layered silicate resulted in the tremendous increase of modulus due to the nanometric dispersion of the silicate layers giving efficient reinforcement leading to improved stiffness of the material. The high aspect ratio of the layered silicate also contributes to the improvement of stiffness of the PSf nanocomposites (Neilson 1966; Quang and Donald 2006). Further, the elastic deformation transfer occurring in the polymer/clay interfaces accounts for the increased stiffness (Rong et al 2001).

3.3.4 Thermal Properties

3.3.4.1 Thermogravimetric analysis

Thermal properties of PSf nanocomposites are important due to the fact that thermal degradation is one of the important criterions for designing these materials for high performance engineering applications (Riva et al 2002). Hence in order to determine the thermal stability of nanocomposites with different clay content (0, 1, 3, and 5 wt%), thermal behavior of the nanocomposites were analyzed using TGA and the resultant thermo grams are shown in Figure 3.8. The TGA patterns indicate that the PSf and nanocomposites exhibit two step decomposition mechanisms. The mechanism of the two step thermal decomposition of PSf was reported previously by Molnar et al. The onset of degradation for neat PSf starts at around 400°C and ends at around 568°C. The $T_{\text{max}}$ for this first degradation step is around 510°C. The weakest links in PSf are the carbon-sulfur bond between the aromatic ring and the sulfone group, and the carbon-carbon bond between the methyl group and the central carbon of the isopropylidene moiety. Therefore, the step corresponds to the release of products expected such as $\text{SO}_2$, benzene and phenol; toluene, styrene and xylene. The second stage of decomposition
Figure 3.8 Thermogravimetric curves of PSf/OFH clay nanocomposites

starts at around 568°C and $T_{\text{max}}$ for this step is around 657°C. This stage involves the loss of diphenyl ether, biphenyl, dibenzofuran, and their alkyl or alkoxy derivatives as degradation products (Molnar et al 2005).

The thermal degradation characteristics of the PSf nanocomposites are presented in Table 3.3. The onset temperatures as well as the $T_{\text{max}}$ values of the first and second degradation steps, for all nanocomposites are shifted to higher temperatures. This increase in degradation temperature denotes the improved thermal stability of nanocomposites compared to that of neat PSf and is attributed to the successful incorporation of the clay platelets in the polymer matrix (Tien et al 2002). The increase in the thermal stability of nanocomposites could be explained by the formation of char on the nanocomposite surface by the presence of impermeable OFH clay layers in
the PSf matrix (Zhu et al 2001). This char hinders the diffusion of volatile products from polymer bulk and reduce the rate of mass loss (Lu et al 2008). The changes in the dynamics of polymer molecules reduce the transport of reactive species in nanocomposites and cause changes in kinetics of chemical reactions proceeding during thermal decomposition of PSf (Zanetti et al 2001). Another factor contributing to the thermal improvement is the action of fluorohectorite as thermal insulating material, which reduces the heat transport in nanocomposite material by accumulating the thermal energy in it (Stretz et al 2005).

Table 3.3  \( T_{\text{onset}} \), \( T_{\text{max}} \) values and char yield of PSf/OFH clay nanocomposites

<table>
<thead>
<tr>
<th>Nanocomposites</th>
<th>( T_{\text{onset}} ) for first degradation (°C)</th>
<th>( T_{\text{max}} ) for first degradation (°C)</th>
<th>( T_{\text{max}} ) for second degradation (°C)</th>
<th>Char yield at 700°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS0</td>
<td>493</td>
<td>510</td>
<td>658</td>
<td>2.39</td>
</tr>
<tr>
<td>PS1</td>
<td>495</td>
<td>515</td>
<td>662</td>
<td>4.33</td>
</tr>
<tr>
<td>PS3</td>
<td>496</td>
<td>516</td>
<td>665</td>
<td>4.95</td>
</tr>
<tr>
<td>PS5</td>
<td>497</td>
<td>517</td>
<td>666</td>
<td>6.59</td>
</tr>
</tbody>
</table>

3.3.4.2 Differential scanning calorimetry

Differential scanning calorimetric (DSC) curves of neat PSf and PSf/OFH clay nanocomposites are given in Figure 3.9. The variation of \( T_g \) with respect to the clay concentration indicates that glass transition temperature of the PSf increases upon the incorporation of OFH clay. When the clay content was about 1 wt%, the PSf/OFH clay nanocomposites exhibited a marginal increase in \( T_g \) compared to that of neat PSf (3°C increase). At 3 wt% clay loading, \( T_g \) of the nanocomposites showed an increase to 189°C, which was about 6°C more than that of neat PSf. This
increase is attributed to the confinement of intercalated polymer within the silicate galleries that prevents the segmental motions of the PSf chains. These anchored polymer chains could form an interphase region, where the segment relaxation was slower than that in the bulk. The restricted relaxation behavior for the PSf nanocomposites in exfoliated structures depends primarily on the extent of exfoliation of the layered silicates and the interaction strength between silicates and PSf matrix. It is well depicted from the study that stabilization of morphology through interaction between the components increases the $T_g$ of PSf nanocomposites at 3 wt%. This maximum increment of $T_g$ at this clay content is due to the optimum exfoliation compared to the intercalated structure at 5 wt% clay loading as evidenced by the morphological analyses (Matraszek and Szczygie 2008).

![DSC curves of PSf/OFH clay nanocomposites](image)

**Figure 3.9** DSC curves of PSf/OFH clay nanocomposites
The slight decrease in the $T_g$ at 5 wt% clay loading is due to the aggregation of OFH clay which reduces the intermolecular interaction between PSf and OFH clay (Sreedhar et al 2006). The increase in the glass transition temperature of PSf matrix by the incorporation OFH clay assured the application of these nanocomposites in high temperature environment.

### 3.3.5 Dielectric Analysis

Figure 3.10 shows the dielectric constant of the PSf/OFH clay nanocomposite films with various clay contents of 0, 1, 3 and 5 wt% in the log of the frequency range from 1 kHz to 1 MHz at room temperature. A reduction in the values of dielectric constant was observed with the incorporation of organoclay into the PSf matrix and this reduction of dielectric constant is dependent on the clay concentration. When the OFH clay content was 5 wt%, the nanocomposites showed relatively lower dielectric constant, around 2.7, compared to that of neat PSf. It is well known that the dielectric constant of a material is related to the polarization. When an alternating current is applied to the sample, the polarization could be initiated. However, in the case of PSf nanocomposites, the nanoscopic confinement effects of the layered silicates within the polymer matrix terminated the regular long chains of the polymer and prevent the segmental motions of the polymer chains (Anastasiadis et al 2000). This restricted relaxation behavior for the polymer chains reduced the dielectric constant of nanocomposites compared to that of the neat PSf. Also, the polarization of the PSf nanocomposites is very difficult due to high stiffness of the material as the clay content increased (Zhang et al 2005). The dielectric loss (tan $\delta$) for 3 wt % clay content was found to be minimum compared with higher loadings. The loss factor was found to be more for samples with higher clay loadings due to the non uniform distribution of the clay particles and the formation of larger clay aggregates in the matrix (Runcy et al 2012).
3.3.6 Aging Studies

The PSf nanocomposites intended for use as electrolyte container of Nickel-Cadmium battery and as car under the bonnet components must maintain mechanical properties in the working fluid over their target life times. The percentage change in weight and tensile strength of neat PSf and PSf/OFH clay nanocomposites after immersing in ethanol, potassium hydroxide solution and engine oil at room temperature for 7 days were studied. Tensile tests are generally more applicable and preferred to assess mechanical property changes, since other mechanical properties are not appreciably varied by the reagents. Three test specimens were used for each material being tested and each reagent involved.
In the case of neat PSf, permeation is a two stage process in which the solvent molecules are first adsorbed and positioned in the free volume holes of the polymer that are created by the Brownian motion of the chains or by thermal perturbations. Diffusion occurs by the jumping of the adsorbed molecules to the neighboring holes (Choudalaski and Gotsis 2009). From the Figure 3.11, the permeation of solvents into the nanocomposite samples was found to be reduced due to the presence of OFH clay in the PSf matrix. The solvent permeation of nanocomposites decreased with respect to the filler content and reaches a minimum at 3 wt%. When diffusion takes place through a PSf nanocomposite containing uniformly dispersed clay platelets, the diffusing molecules have to travel additional path length around these flake like barriers.

![Figure 3.11 Change in weight of PSf/OFH clay nanocomposites after immersing in solvents](image-url)
The exfoliated morphology at 3 wt% is likely to be most effective in reducing diffusivity in which the flake like barriers are positioned parallel to the film surface and perpendicular to the direction of mass transport (Picard et al 2007). Thus, the diffusion is controlled by the microstructure of the nanocomposite and the interaction between PSf and OFH clay (Osman et al 2004).

As the clay percent loading increases above 3 wt%, the diffusivity shows an increasing trend. There are several possible reasons for this discrepancy. For high clay content, it is difficult to keep a high degree of platelet dispersion and avoid the presence of exfoliated structure. Hence, a natural aggregation of silicate layers occurs which leads to a decrease of aspect ratio of nanoclay (Gao et al 2008). This is well evidenced from the results obtained from XRD and TEM analysis, presented earlier. These agglomerates cause the formation of large scale holes or free volumes in the PSf matrix which act as low resistance pathways for solvent transport within the nanocomposite (Manninen et al 2005). The random or parallel arrangement of clay platelets to the diffusion direction is another reason for the increase of solvent diffusion beyond 3 wt% of organoclay loading (Nazarenko et al 2007). Figure 3.12 represents the (a) perpendicular (b) parallel and (c) random orientations of clay platelets to the diffusion direction in exfoliated and intercalated nanocomposites.

![Diagram showing different orientations of clay platelets](image)

**Figure 3.12** Schematic representation of (a) perpendicular (b) parallel and (c) random orientation of clay platelets to the diffusion direction in exfoliated and intercalated nanocomposites
DSC analysis indicates the link between glass transition temperature and the solvent resistance of nanocomposites. PS3 nanocomposite shows higher value of $T_g$ when compared to those of PS0, PS1 and PS5. At temperature below the glass transition temperature, the nanocomposites are in glassy state, with very little internal void space. The nanosized clay restricts the molecular dynamics of the polymer chains surrounding the clay and makes the nanocomposite hard and brittle. The retarded relaxation of PSf polymer chains due to the presence of OFH clay increases the $T_g$ value which in turn reduces the penetration of solvent molecules through the nanocomposites (Sorrentino et al 2006).

![Figure 3.13 Change in tensile strength of PSf/OFH clay nanocomposites after immersing in solvents](image)

**Figure 3.13** Change in tensile strength of PSf/OFH clay nanocomposites after immersing in solvents

As shown in Figure 3.13, the reduction in the tensile strength after aging indicates the low retention ability of the neat PSf. In the case of neat
PSf, as the polymer absorbs the solvent, the liquid behaves like a plasticizer and weakens the cohesive forces. Also, the chemical attack leads to the breaking of covalent bonds along the polymer chain and decrease its molecular weight. Due to these two actions, the long term contact of solvent with the PSf reduces its mechanical property (Veith et al 1991). The incorporation of OFH clay to PSf has increased the retention ability of the nanocomposites by preventing the direct penetration of solvents to the matrix. With the increase of clay content, the absolute value of the changing rate of the tensile strength decrease, reaching its minimum, 3 wt%, and then increase. The deterioration of tensile strength at higher clay loading can be explained by the formation of microcracks. Another contributing factor to the phenomenon is that, the more the clay content, the more brittle the nanocomposite matrix becomes, and thus, the more susceptible to cracking (Raveendran et al 2006).

3.4 CONCLUSION

The present chapter dealt with the development of PSf/OFH clay nanocomposites by solution casting method for high performance applications. The mechanical, hydrophobic, thermal, dielectric and aging properties of nanocomposites have been studied. Morphology of the nanocomposites was analyzed by ATR-FTIR, XRD, AFM and TEM. XRD results indicated the formation of exfoliated structure for 1 wt% and 3 wt% OFH clay incorporations. The surface properties, as assessed by contact angle measurements, showed significantly increased hydrophobicity of the nanocomposites relative to the neat PSf matrix. Correlation between AFM surface analysis and water contact angle measurement showed that as the surface roughness increases, water contact angle also increases. The improvement of hydrophobicity was confirmed by the negative value of spreading coefficient and decrease of Girifalco-Good’s interaction parameter.
The nanocomposites showed marked improvement in the tensile strength and elongation at break at lower filler loading (3 wt%) due to the strong interaction between nanoclay and polymer. The addition of OFH clay in the polymer matrix improved the thermal stability by acting as effective physical barriers against the thermal decomposition in PSf nanocomposites. An increase in glass transition temperature was established from differential scanning calorimetric measurements. The dielectric constant of nanocomposites decreased with the increase of the clay content and the films showed relatively low dielectric constant when the OFH clay content was 5 wt%. Solvent permeability of the composites decreased considerably due to the tortuous path created by the addition of nanofillers. A strong link between solvent resistant properties and glass transition temperature of the nanocomposites was evaluated from the studies. It is worth mentioning that the improved material properties and aging performance of these nanocomposites with the addition of organoclay in PSf matrix obviously offers immense potential in industrial and automobile applications.