CHAPTER 4

ORGANOMODIFIED HYDROXYAPATITE REINFORCED POLYSULFONE NANOCOMPOSITES

4.1 INTRODUCTION

The bone is the second most frequently transplanted human tissue and its demand is growing in medical market for the reconstruction of bone defects (Tran et al 2009). The worldwide number of orthopedic surgical operations performed is growing steadily due to the combination of longer average human life span and more active lifestyle. In the USA alone, 152,000 hip replacements and 299,000 knee replacement operations were undertaken and 59,000 revisions of hip and knee replacements were carried out in 2010, so that over $5 billion is currently being spent annually on orthopedic related conditions. Currently used methods of broken and defective bone treatment apply metal orthopedic implants, unfortunately showing many deficiencies, metals are stiffer than natural bones and after serving the purpose they have to be removed from body during second surgery. It remains a great challenge to design an ideal bone graft that emulates nature’s own structure (Murugan and Ramakrishna 2005).

Bioactive polymer/hydroxyapatite nanocomposites are currently being intensively investigated as materials for promotion of bone tissue regeneration and reconstruction (Liu and Webster 2007). The advantages of polymeric biomaterials, compared to metallic or ceramic materials, are the ease of manufacturing components having various and complex shapes,
reasonable cost and their ability to possess a wide range of physical and mechanical properties. Additionally, hydroxyapatite (HA) is one of the most attractive materials for bone implants because of its composition and biological similarity to natural tissues. It can be obtained in a nanostructured form, which facilitates its fine dispersion in the polymer matrix as well as producing advantageous interactions with bioactive polymer and tissue. Also nanosize of hydroxyapatite offer more surface areas to influence the interactions. Such materials show very good osteointegration, stimulate osteoblast adhesion, enhance deposition of calcium phosphate forming apatite layer on the surface of the implant (Damien and Revell 2004).

This chapter combines orthopedics and nanotechnology to prepare PSf nanocomposite bone implant with integrated bioactivity and physico-chemical properties for bone tissue engineering. The favorable properties of PSf like high strength, biological inertness, unique long life under sterilization procedures and resistance to most common hospital chemicals enable it to use in biomedical field (Konieczna et al 2004). The confirmed biocompatibility of PSf allows it to be combined with hydroxyapatite to obtain a bionanocomposite. PSf nanocomposites with variable amounts of stearic acid modified nanohydroxyapatite (n-SHA) were prepared by solution casting method and their mechanical, hydrophobic, thermal and biocompatible properties were investigated. Nanohydroxyapatite (n-HA) prepared by the chemical precipitation method were organically modified with stearic acid and characterized using different techniques, such as ATR-FTIR, XRD and TEM. Further, these particles were incorporated into polysulfone by solution casting method. The microstructure of the PSf nanocomposites was studied by ATR-FTIR spectroscopy and AFM. Various mechanical properties like Young’s modulus, tensile strength, and elongation at break were characterized by standard methods. The effect of addition of nanofiller on the hydrophobic and thermal properties of polysulfone was
examined. The bioactivity of the nanocomposites was evaluated by monitoring the concomitant formation of apatite on the material surface after soaking them in simulated body fluid (SBF). Moreover, the protein adsorption on the nanocomposite surface, which plays a prominent role in attachment and spreading of osteoblast cells, were studied quantitatively by adsorption experiments and qualitatively by AFM imaging. To evaluate high performance industrial applications of the prepared nanocomposites, apart from the mechanical and thermal analysis, aging studies of PSf nanocomposite films were also conducted using different solvents and the results were compared with those of neat PSf films.

4.2 CHARACTERISATION OF HYDROXYAPATITE NANOPARTICLES

4.2.1 ATR-FTIR Analysis Nanoparticles

Figure 4.1 presents FTIR spectra of nanohydroxyapatite and stearic acid modified nanohydroxyapatite. The characteristic bands in the spectra of n-HA at 3571 and 630 cm\(^{-1}\) arising from the stretching and vibration of OH group respectively. The band at 1457 cm\(^{-1}\) is ascribed to CO\(_3^{2-}\) group \((v_3)\) present in n-HA, which is an indicator of carbonate in the hydroxyapatite structure. The bands at 1100, 900, 610 and 500 cm\(^{-1}\) are due to vibration of PO\(_4^{3-}\) in crystalline calcium phosphate phase (Elliot et al. 1985). In the case of n-SHA, the new absorption bands at 2954, 2848, 1471 and 1430 cm\(^{-1}\) are due to vibration of PO\(_4^{3-}\) in crystalline calcium phosphate phase (Elliot et al. 1985). In the case of n-SHA, the new absorption bands at 2954, 2848, 1471 and 1430 cm\(^{-1}\) are due to CH\(_3\) and CH\(_2\) groups results from stearic acid. This confirms the presence of stearic acid on the surface of HA fillers. The band at 1548 cm\(^{-1}\) is ascribed to asymmetric stretching vibration of COOCa from the interaction between COOH and Ca\(^{2+}\), and the one at 879 cm\(^{-1}\) assigned to HPO\(_4^{2-}\) group coming from reaction of PO\(_4^{3-}\) with H\(^+\) from COOH group (Li et al. 2004).
4.2.2   XRD Analysis of Nanoparticles

The XRD patterns of n-HA and n-SHA are shown in the Figure 4.2. The sharp XRD peaks at 27.3°, 28.63°, 31.96°, 33.23°, 34.30°, 40.22°, 44.23°, 46.70°, and 52.72° indicate the well crystalline phase of HA (Cao et al 2010). The pure crystalline phase of HA is confirmed by the absence of other forms such as Ca(OH)$_2$, CaO, β-tricalcium phosphate and α-tricalcium phosphate in the XRD patterns. The insignificant decrease in the intensity of n-SHA is attributed to the decrease in crystallinity by the organomodification of n-HA using stearic acid.
4.2.3 TEM Analysis of Nanoparticles

The TEM images of the n-HA and n-SHA dispersed in alcoholic medium are shown in Figure 4.3. It shows that the HA nanoparticles have rod like structure with about 50-70 nm in length and 20-30 nm in width. The dispersion of HA nanoparticles after modification is obviously better than that before modification. Hence, improved compatibility is expected between n-SHA filler and PSf matrix. The dispersion of n-HA nanoparticles after modification is obviously better than that before modification. Hence, improved compatibility is expected between n-SHA filler and PSf matrix.
4.3 PREPARATION OF POLYSULFONE/n-SHA NANOCOMPOSITES

A homogeneous solution of polysulfone was prepared by dissolving appropriate amount of polymer in DMF followed by stirring for 10 h at 50°C. Then, stearic acid modified nanohydroxyapatite (n-SHA) 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 n-SHA. Thin films of thickness 0.2 ± 0.02 mm were prepared by solution casting method using TLC applicator. The samples were air-dried under flowing air for 24 h to allow the solvent to evaporate and subsequently vacuum-dried at 40°C for 48 h to remove any trapped solvent in the film. The PSf/n-SHA composites were designated as PHA0, PHA1, PHA3, and PHA5 respectively according to the weight percentage of nanoparticle loading.

Figure 4.3 TEM images of the n-HA and n-SHA
4.4 RESULTS AND DISCUSSION

4.4.1 Morphological Analysis

4.4.1.1 ATR-FTIR analysis of nanocomposites

The chemical interaction between the PSf and the nanoparticles in PSf nanocomposites were characterized using ATR-FTIR spectroscopy. The representative FTIR spectra of the PSf and PSf/n-SHA nanocomposites at different filler concentrations are shown in Figure 4.4.

![Figure 4.4 ATR-FTIR spectra of (a) PHA0 (b) PHA1 (c) PHA3 and (d) PHA5](image)

The peaks at 1160, 1240, 1325, 3100 and 2900 cm\(^{-1}\) are the characteristic vibration bands of PSf. In the PSf nanocomposites the characteristic peaks of n-SHA such as 1448, 1549, 2924, 2854 and 3572 cm\(^{-1}\) are retained. The peaks at 963, 1034, 1090 and 2077 cm\(^{-1}\) for PO\(_4^{3-}\) of n-SHA
were moved to 972, 1039, 1100 and 2085 cm\(^{-1}\) in the nanocomposite, respectively. The displacement of these peaks of n-SHA and PSf indicate the molecular interactions between nanofiller and PSf in the nanocomposites. At lower concentration of the n-SHA, intensity of the corresponding peaks is lower, and with increasing n-SHA concentration, the intensity of the peaks increases. These results reflect that there is relatively strong interaction between polymer and the nanoparticles and will greatly affect the interfacial behavior and mechanical properties of the nanocomposites.

4.4.1.2 AFM images of the nanocomposites

AFM was used to study the surface morphology as well as the nanofiller dispersion in the PSf matrix which distinguishes filler aggregates and single filler particles in the polymer matrix. In Figure 4.5 (a-d), the phase images of the nanocomposites with filler concentration 0, 1, 3 and 5 wt% are given. Figure 4.5 (a) shows the phase image of the neat matrix. As seen in the figure the neat PSf surface is smooth and homogeneous. In the images of filled nanocomposites, discrete particles embedded in the PSf matrix are seen. The nanocomposites with 1 wt% and 3 wt% loading clearly show more individualized and uniform distribution of filler without any remarkable agglomeration. When the filler content reached 5 wt%, many aggregates on a micrometer scale were observed on the surface of the nanocomposites. This difference is important in determining the properties of the resultant nanocomposites including mechanical, thermal, and barrier properties (Hwang et al 2004).
Figure 4.5 AFM images of PSf nanocomposites: (a) PHA0 (b) PHA1 (c) PHA3 and (d) PHA5

The surface roughness of bone implant has a significant influence on the adhesion and proliferation of osteoblasts (Nelea et al 2004). The changes in the surface topography of nanocomposites could be determined quantitatively in terms of surface parameters, such as the average roughness, $R_a$ and the root mean square (RMS) roughness, $R_q$. The $R_q$ and $R_a$ values of composites are given in Table 4.1.
Table 4.1 Roughness parameters of PSf/n-SHA nanocomposites

<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>PSHA0</td>
<td>3.02</td>
<td>2.22</td>
<td>0.80</td>
</tr>
<tr>
<td>PSHA1</td>
<td>4.99</td>
<td>3.56</td>
<td>1.43</td>
</tr>
<tr>
<td>PSHA3</td>
<td>5.72</td>
<td>4.14</td>
<td>1.58</td>
</tr>
<tr>
<td>PSHA5</td>
<td>9.09</td>
<td>6.61</td>
<td>2.48</td>
</tr>
</tbody>
</table>

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 all the nanocomposites show higher ($R_q$ - $R_a$) values compared to that of neat polymer, which confirms the presence of filler particles on the surface. It was found that roughness parameters increase with increase of filler loading and show maximum value at 5 wt%. When the amount of fillers is augmented to a certain extent, the high viscosity of casting solution and lot directional-aligned filler grains existing on the surface result in a rapid increase of surface roughness (Taurozzi et al 2010). Since natural bone has a nano rough surface consisting of nanosized hydroxyapatite and collagen molecules, producing nano rough surfaces on these implants is more favorable for early osteoblast adhesion and growth on nanocomposite surface, which improves orthopedic implant efficacy (Sato and Webster 2004). Therefore the use of the substrate with higher roughness provides coatings with better adhesion on the substrate, suitable for biomedical applications.

4.4.2 Contact Angle Studies

Contact angle measurements were carried out with water to determine the influence of n-SHA incorporation on the hydrophobicity of PSf.
The contact angle of neat PSf was 85°. With the addition of 1, 3 and 5 wt% nanofiller, the values of contact angles were increased to 86.5°, 88° and 89.7° respectively, which indicate that the presence of n-SHA in the PSf matrix improves the hydrophobicity of the nanocomposite surfaces. Figure 4.6 shows the representative pictures of contact angle measurements with water as the liquid. The increase in hydrophobicity is mainly attributed to the difference in both the chemical properties of PSf surface and its surface morphology. In order to have a homogeneous dispersion in hydrophobic polymeric host, n-HA surface was modified with stearic acid, which lowers the hydrophilicity of filler surface and impart hydrophobic characteristics to the surface of n-HA (Lai et al 2007). According to the Gibbs adsorption isotherm, the difference in the surface energy of components of multi-component system could result in a relative enrichment at the air interface by the lower surface energy material. A lowered equilibrium surface energy, that results from the placement of the lower surface energy component at the surface, is achieved at the cost of maintaining a gradient between the surface and bulk composition (Lewin 2003). In the PSf/n-SHA nanocomposite system, lower surface energy makes n-SHA components migrate to the surface due to the difference in the surface energy of the components. The correlation between AFM surface analysis and water contact angle measurements indicated that the increase in surface roughness increases the hydrophobicity by increasing the surface area (Khayet et al 2003). These results indicate that the addition of n-SHA can increase the hydrophobic nature of the PSf and the contact angles can be changed significantly through changing the concentration of the additive.

Surface properties play a critical role in the cell-implant interaction either directly by the controlling adsorption of proteins present in the cell culture medium or by guiding cell spreading with suitable topography (Bartolo et al 2001). Various surface parameters such as surface free energy,
work of adhesion, interfacial free energy, spreading coefficient and Girifalco-
Good's interaction parameter of the nanocomposites were analyzed from the
contact angle values and are presented in Table 4.2. As the filler loading
increases, total solid surface free energy, $\gamma_{sv}$, decreases which means that the
wetting of liquids is lower, when compared to the neat PSf. The polar forces
acting on the surface of the nanocomposites decreased compared to the neat
polymer and thus the total solid surface free energy decreased. In the case of
interfacial free energy, $\gamma_{sf}$, shows an opposite trend to that of surface free
energy, which increases with increase in n-SHA concentration. The work of
adhesion, $W_A$, which is the work required to separate the solid and liquid
shows a decreasing trend similar to that of surface free energy. When the filler
content increases, the work of adhesion value for the water as probe liquid decreases and showed minimum value for PSHA5.

Table 4.2 Surface free energy, Interfacial free energy, Work of adhesion, Spreading coefficient and Girifalco-Good’s interaction parameter values of PSf/n-SHA nanocomposites

<table>
<thead>
<tr>
<th>Samples</th>
<th>Contact angle (°)</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 ($\phi$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSHA0</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>PSHA1</td>
<td>86.5</td>
<td>30.56 (0.53)</td>
<td>28.57</td>
<td>5.44</td>
<td>-68.35</td>
<td>0.80</td>
</tr>
<tr>
<td>PSHA3</td>
<td>88.0</td>
<td>29.75 (0.91)</td>
<td>32.75</td>
<td>3.54</td>
<td>-70.25</td>
<td>0.75</td>
</tr>
<tr>
<td>PSHA5</td>
<td>89.7</td>
<td>28.16 (0.72)</td>
<td>37.32</td>
<td>1.38</td>
<td>-72.41</td>
<td>0.70</td>
</tr>
</tbody>
</table>

*Numbers in the parenthesis are standard deviation

The spreading coefficient of the liquid, Sc, with respect to the filler loading was calculated using equation (2.7). If the value is positive, the implication is that the liquid spontaneously wet and spread on a solid surface and if it is negative the lack of wetting and spreading can be ascertained. The obtained values indicate that as the filler content increases, the spreading coefficient become more negative which shows an increase in hydrophobicity.

The interaction parameter between the polymer and the liquids was calculated using the Girifalco-Good’s equation. Highest value of interaction parameter was observed in the case of neat PSf. The decrease in the value of Girifalco-Good’s interaction parameter by the addition of n-SHA indicates that the incorporation of n-SHA to PSf matrix reduce the interaction of water with the polymer nanocomposite surface.
4.4.3 Mechanical Properties

The mechanical properties of the PSf nanocomposites with varying filler content were characterized by tensile tests, and thus tensile strength, elongation at break and Young’s modulus were calculated. From Figure 4.7, it can be seen that mechanical properties like tensile strength and elongation at break of nanocomposites show a tendency to increase and then decrease with increasing n-SHA content. The highest value of tensile strength and elongation at break were obtained for the nanocomposite with 3 wt% of filler loading. A 30 % increase in tensile strength and a 72 % improvement of elongation at break were achieved by the addition of 3 wt% nanofiller.

![Figure 4.7 Tensile strength and elongation at break of PSf/n-SHA nanocomposites](image)

The significant improvement in tensile strength and elongation at break is due to the uniform dispersion of n-SHA and the improved interfacial adhesion between n-SHA and PSf matrix, which results in the effective transfer of
applied stress to the n-SHA from the PSf matrix (Luyt et al 2009; Liu and Webster 2010). The potential explanation for the decrease in the tensile strength after optimum filler content (3 wt%) is mainly due to the agglomeration of n-SHA particles, which was evidenced from the morphological analyses. In the nanocomposite with 5 wt% filler loading, discontinuity in the form of debonding exists because of non-adherence of n-SHA to the PSf. This results in the ineffective stress transfer at the PSf/n-SHA particles interface (Thomas et al 2009).

Tensile modulus, expressing the stiffness of the material, is a bulk property that depends primarily on the geometry, particle size distribution and concentration of the filler. Tensile modulus showed noticeable improvement with addition of nanofiller to PSf matrix. From the Figure 4.8, it is observed that, for the addition of 5 wt% of n-SHA, around 45% increase in modulus occurred. It is well known that the modulus increases for a polymer when any mineral filler is incorporated into it.

![Figure 4.8 Tensile modulus of PSf/n-SHA nanocomposites](image)
This is reasonable because the rigid inorganic fillers have higher stiffness values than that of the organic polymer (Fu et al 2008; Abraham et al 2009). The ability of nanocomposites to tailor the mechanical strength by varying the filler content makes it a suitable candidate material for more effective orthopedic applications from a mechanical perspective.

4.4.4 Thermal Properties

4.4.4.1 Thermogravimetric analysis

The thermal stability of polymers and nanocomposite is an important property for designing the material for a particular use in a specific field (Leszczynska and Pielichowski 2008). In order to determine the thermal stability of PSf nanocomposites with different nanofiller 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 4.9.

The two step TGA curves of PSf nanocomposites are similar to those of neat PSf, indicating that the thermal decomposition of PSf nanocomposites must mostly stem from the PSf. The incorporation of n-SHA into PSf matrix insignificantly increased the thermal decomposition temperatures and the char yields of PSf nanocomposites. The presence of n-SHA could lead to the stabilization of PSf matrix, resulting in the increase of the thermal stability of PSf nanocomposites. The successful incorporation of the n-SHA nanoparticles in the PSf matrix enhances the thermal stability of nanocomposites 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 (Zou et al 2008). The similar trend was reported for nanocomposites in which stearic acid modified calcium carbonate nanoparticles were used as nanofillers in the polymer matrix (Wen et al 2007). Based on these studies, it is clear that thermal
degradation is not a concern during sterilization prior to the clinical use of PSf nanocomposite biomaterials. Also, the improved thermal stability of PSf nanocomposites is relevant to the potential use of these materials in demanding engineering applications.

Figure 4.9 Thermogravimetric curves of PSf/n-SHA nanocomposites

4.4.5 Biocompatibility Studies

4.4.5.1 Simulated body fluid test

The evaluation of apatite formation in SBF is a useful model to confirm the in vivo bioactivity of nanocomposites before implantation, thus saving both animals and experimental time. The bone-bonding ability of the PSf/n-SHA nanocomposites was evaluated by examining the apatite forming ability on its surface in a simulated body fluid (SBF) with ion concentrations nearly equal to those of human blood plasma. AFM images of nanocomposites after soaking in SBF for 7 days are presented in Figure 4.10.
This allows the comparison of nanocomposite surfaces with varying filler concentration before and after soaking in SBF. The white deposits on the surfaces confirm the formation of apatite layer. In the case of unfilled samples, some scattered and discrete deposits were seen on the surface. In the case of PSf nanocomposites, the deposition increased with the increasing filler content. When the filler content reached 5 wt%, these deposits cover the entire nanocomposite surface and large aggregated deposits were found at different areas of the nanocomposite surface, which is not in the case of samples with lower filler content. This suggests that the large deposits might have been formed by a secondary nucleation mechanism onto nanosized calcium phosphate entities initially formed. The nucleation of apatite should be easier on a surface of the same nature (apatite) compared to the nucleation on a chemically different surface. Even the surface roughness has no pronounced effect on the initial heterogeneous nucleation of apatite, rough topography of 5 wt% nanocomposites is beneficial for the further growth and mechanical attachment of apatite coating on the implant surface (Barrere et al 2004).

The mechanism for nucleation and growth of apatite on the implant surface was proposed by Hench et al (Hench et al 2007). The exchange of hydrogen $\text{H}_3\text{O}^+$ from the SBF solution with Ca in the nano hydroxyapatite fillers on the nanocomposite surface gives rise to the formation of Si-OH groups and leaves behind a silica-rich leached layer. The formation of apatite is closely related to the amount of Si-OH groups present on the surface of bioactive materials, since Si-OH groups are proposed to provide specific favorable sites for the apatite nucleation. The high surface area of the nanofillers on the implant surface facilitates the exchange of $\text{Ca}^{2+}$ in hydroxyapatite with $\text{H}_3\text{O}^+$ from the SBF solution and leads to higher density of Si-OH groups on the surface, which results in the higher apatite nucleation rate with increasing filler content.
Once the apatite nuclei are formed, they grow spontaneously by the transport of Ca$^{2+}$, HPO$_4^{2-}$, OH$^-$, and CO$_3^{2-}$ species from the SBF solution to the nuclei and the fast deposition of apatite. From this it is well evidenced that n-SHA incorporation not only acts as reinforcing filler, but also influences the bioactive character to the nanocomposites (Rodrigo et al 2007).
4.4.5.2 Protein adsorption studies

The proteins adsorbed on a biomaterial surface after implantation largely govern the biocompatibility and host response of the implant biomaterial. Protein adsorption in a PSf nanocomposite surface starts with a monolayer formation by the interaction between the nanocomposite surface and proteins and subsequent layers are formed by the disulfide linkages between the monolayer proteins in the surface and proteins in the bulk solutions. The structure of the monolayer formed on the surface has profound effect on the interaction of cells with the implant and is largely governed by the chemistry and morphology of the polymer surface (Palacio et al 2010). In order to evaluate implant’s potential towards cell adhesion applications, it is important to understand how the nanostructure of the PSf nanocomposite implant will influence the initial protein adsorption. As shown in Figure 4.11, the protein adhesion capacity of nanocomposites increased with increase in the filler content.

![Figure 4.11 Dependency of filler content on the protein adsorption of PSf nanocomposites](image)

Figure 4.11 Dependency of filler content on the protein adsorption of PSf nanocomposites
The improved protein adhesion capacity of nanocomposites is due to the increased surface area and nanoscale surface characteristics of n-SHA which provides more available sites for protein adsorption. The hydrophobic interaction between the protein and implant surface is maximum in nanocomposites, when compared to that of neat PSf because of the presence of hydrophobic n-SHA which maximizes the interfacial free energy. As the concentration of n-SHA increases, more n-SHA fillers could be exposed on the PSf nanocomposite surfaces to lower the surface energy of the system, which results in the improved protein adsorption capacity (Han et al 2003; Pellenc et al 2008). The non-polar surfaces facilitates conformational reorientations leading a strong inter protein and protein surface interactions.

Topographical AFM images of PSf nanocomposites after protein adsorption are depicted in Figure 4.12. The presence of BSA molecules on implant surface is confirmed from the spherical features seen on the surface of the nanocomposites. The thickness of the layer denotes the amount of adsorbed BSA and the comparison between the images showed that the extent of adsorption increases with nanofiller content. The positive correlation between extent of protein adsorption and the hydrophobicity of nanocomposite surface suggests that the hydrophobic interaction is a major driving force for adsorption (Yoon et al 1999). Scheme 4.13 represents the illustration of the mechanism of the spreading process of a protein cluster in time on the hydrophobic and the hydrophilic surfaces. Proteins tend to adsorb more extensively and less reversibly at hydrophobic surfaces than at hydrophilic surfaces. With increasing degree of hydrophobicity of the surface, the ease of exchange of adsorbed protein molecules with the bulk aqueous phase is generally reduced. This difference can be attributed to a greater degree of unfolding at hydrophobic surfaces following instantaneous protein adsorption, which leads to the development of strong interfacial hydrophobic
Figure 4.12  AFM images of PSf nanocomposites after protein adsorption
(a) PSHA0 (b) PSHA1 (c) PSHA3 and (d) PSHA5

Scheme 4.1  Schematic illustration of the mechanism of the spreading process of a protein cluster on the hydrophobic and the hydrophilic surface
interactions and associated displacement of vicinal water molecules from the unfavorable environment of the surface. This explains the experimental finding that the affinity of proteins to nanocomposite surfaces increases with increasing nanofiller content (Tilton et al 1991).

Further, increased protein adsorption on PSf nanocomposites with increase in percentage filler content is also related to its high surface roughness. The increase in surface roughness favors the transport of protein preferentially to the valleys on the nanocomposite surface (Hao and Lawrence 2004). The results from these experiments serve as a guide to tune protein adsorption behavior of polymer nanocomposite surface as a function of filler composition and to understand the role of nanomorphology in cell polymer nanocomposite interactions (Rabe et al 2011).

4.4.6 Aging Studies

The solvent adsorption for the neat polysulfone and nanocomposite samples were examined and the percentage change in the weight and tensile strength of neat PSf and PSf/n-SHA nanocomposites after immersing in ethanol, potassium hydroxide solution and engine oil for 7 days at room temperature were studied.

From the Figure 4.13, it is clearly observed that the permeability values decreased substantially up on nanofiller addition. In PSf nanocomposites, the n-SHA fillers incorporated in the polymer matrix take up the free volume within the polymer matrix and create a tortuous path for the permeating molecules. Hence the solvent passing through the nanocomposites has to go through a more constrained path due to the occupation of voids by the fillers (Thomas et al 2009; Tomlal et al 2009). Thus, the permeability of the solvents showed a decrease in low filler loading. The maximum improvement in barrier properties at 3 wt% filler additions is owing to the
good dispersion of n-SHA and strong interaction between PSf and n-SHA in nanocomposites as evidenced from AFM analysis.

Figure 4.13 Change in weight of PSf/n-SHA nanocomposites after immersing in solvents

On the other hand, if the filler is incompatible with the polymer matrix, voids tend to occur at the interface, which tends to increase the free volume of the system and thereby increases the permeability through it (Thomas et al 2011). This is the reason for the increased permeation rate of solvents above 3 wt% filler loading.

As shown in Figure 4.14, the retention ability of the tensile strength of PSf nanocomposites increases with respect to the filler content and showed a maximum at 3 wt%. The addition of n-SHA to PSf prevents the direct penetration of solvents to the matrix which results in retention of mechanical property compared to that of neat polymer. As the filler content increases
above 3 wt%, the retention ability shows a decreasing trend due to the aggregation of n-SHA leading to a decrease of aspect ratio of nanoparticles as evidenced from the morphological analysis.

Figure 4.14 Change in tensile strength of PSf/n-SHA nanocomposites after immersing in solvents

4.5 CONCLUSION

The PSf nanocomposites with variable amounts of stearic acid modified nano hydroxyapatite were prepared using solution casting method and their mechanical, thermal, hydrophobic, aging and biocompatible properties were investigated. ATR-FTIR analysis of nanocomposites indicated the strong interaction results between the PSf and nanofiller. AFM measurements showed the presence of filler particles on the surface of nanocomposites which caused the increase in \( (R_q - R_a) \) values compared to that of neat polymer. The mechanical properties of the nanocomposites like tensile strength and elongation at break showed improvements at lower filler
content and decreased with higher filler loading. Young’s modulus showed
increasing trend with respect to the filler loading. The hydrophobic properties
of the nanocomposites were enhanced by the incorporation of n-SHA. The
incorporation of nanoparticles in the PSf matrix improved the thermal
stability by acting as physical barriers against the thermal decomposition of
PSf nanocomposites. The nanocomposites induced a dense and continuous
layer of apatite, after soaking them in simulated body fluid for 7 days. The
increased surface area and nanoscale surface characteristics of n-SHA provide
more available sites for protein adsorption on the nanocomposite surface with
increasing filler content. All these results indicate that the PSf
nanocomposites fulfill the basic requirements of a bone implant and have the
potential to be applied in bone tissue replacement and regeneration
applications.