CHAPTER 4
MODIFICATION OF PEANUT SHELL POWDER (PSP) AND ITS CHARACTERIZATION

4.1 Introduction .......................................................................................................................... 86
4.2 Results and Discussion ......................................................................................................... 88
4.3 Conclusions .......................................................................................................................... 99
References ................................................................................................................................... 100

Abstract: Peanut shell is one of the major agricultural waste materials and their use as reinforcement material in the fabrication of composites is very attractive. Major disadvantages of the use of PSP are its hydrophilic character. Hence surface modifications are necessary to develop composites with hydrophobic matrix. Surface modifications of PSP was done by coupling agent, triethoxy vinyl silane (TVS) and maleic anhydride (MA) and they were characterized by UV-Visible spectroscopy, FTIR, XRD, TG, SEM and TEM. The detailed analysis of UV and FTIR spectra reveals the exposure of cellulose to the surface and decrease in the concentration of hydrogen bonding. The removal of lignin, hemicellulose etc on modification was supported by the increase in crystallinity observed from XRD. This has been further confirmed by SEM and TG studies.

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4.1 INTRODUCTION

Natural filler reinforced composites developed from organic products show better performance compared to synthetic fillers and they are having the properties such as enhanced biodegradability, combustibility, light weight, non toxic nature decreased environmental pollution, low cost, and recyclability, etc. These added advantages makes the natural fibre composites among the high performance composites [1–5]. Composites of petroleum based matrix reinforced with natural fillers from waste material to develop cost effective products with diverse application is an alternative choice to reduce already depleting petroleum resources. The seed shells of various crops which are usually discarded as wastes, used as natural filler is one attractive and efficient solution for better reuse of the resources. Inspite of its several merits, these natural fillers have inherent drawbacks such as poor wettability, incompatibility with some polymeric matrices, high moisture absorption by the fibres and hence only poor adhesion with polyer matrix. These properties affect the interior strength of the composites. Major reason for the poor compatibility of these seed shells lies with the hydrophobic and non polar nature of matrix whereas the natural fibres and seed shells are hydrophilic and polar in nature. Another important drawback is the high moisture absorption of natural fibers leading to swelling and the presence of voids at the interface, which results in poor mechanical properties and reduces dimensional stability of composites [6–12]. Other restriction to the successful exploitation of natural fibers for durable composite application is the low microbial resistance and
susceptibility to degradation. These properties pose serious problems during shipping, storage and composite processing. Surface modification of fibre or seed shell is an attractive alternative to overcome this problem. Many researchers reported that the surface modification through alkali treatment and reaction with coupling agent increase the interfacial bonding with the matrix and this process improves the overall performance of the composites. Certain reagents may activate hydroxyl groups of the fillers or introduce new moieties that can effectively interlock with the matrix. Suggesting a definite theory for the mechanism of bonding by chemicals in composites is a complex problem. Generally, chemical coupling agents perform two functions. The first is the reaction of hydroxyl groups of cellulosic part of the filler and the second is the reaction of the derived group with functional groups of the matrix [12-20].

Joseph et al. studied the environmental durability of chemically modified banana fiber reinforced phenol formaldehyde (PF) composites. They observed that silane, sodium hydroxide and acetylation treatments improved the resistance of the banana/PF composites on outdoor exposure and soil burial [14]. Mohan et al[15] studied the chemical treatment of sisal fibres using alkali and clay. The analytical results revealed that the fibre-matrix compatibility, interface strength, adhesion, glass transition temperature and tensile properties of composites were improved through NaOH–clay treatment of fibre. Richa et al [16] studied the composites of phenol formaldehyde with silane treated and untreated oil palm fibre and they observed that the chemical treatment increased the thermal
stability and mechanical properties of the composites. Activation energy and crystallization kinetics of untreated and treated oil palm fibre reinforced phenol formaldehyde composites have also been studied. Rong et al [17] investigated the effect of fiber treatment on the mechanical properties of unidirectional sisal-reinforced epoxy composites. Treatments including alkalization, acetylation, cyanoethylation and the use of silane coupling agent were carried out to modify the fiber surface and its internal structure. Sareena et al [18] studied the effect of modification of PSP by sodium hydroxide on the mechanical properties of composites with NR. However, no serious studies were carried out to exploit the potential of surface modification of PSP, which is usually discarded as agricultural waste and the same for composite fabrication using SBR.

Therefore, the present chapter highlights the surface modification of PSP by chemical treatments using two important coupling agent triethoxyvinyl silane (TVS) and maleic anhydride (MA). After chemical modification, they were characterized using differential spectral and analytical techniques as, UV-visible spectroscopy, FTIR, XRD, TG, SEM, TEM and DLS.

4.2 RESULTS AND DISCUSSION

4.2.1 Chemical treatment of Peanut shell powder

The PSP powder was dried and pretreated with NaOH to get alkali treated PSP (APSP). Then the APSP was treated with triethoxyvinyl silane to develop silane treated PSP (SPSP) and washed and dried to form SPSP in two particle size.
The reaction occurring during alkaline treatment and silane modification can be shown as in scheme 4.1[19].

\[
\text{Fibre-OH} + \text{NaOH} \rightarrow \text{Fibre-ONa} + \text{NaOH} \quad \text{(Alkaline pretreatment to activate fibre hydroxyl groups for silane modification)}
\]

\[
\begin{align*}
\text{CH}_2=\text{CH-Si-OCH}_2\text{CH}_3 + \text{H}_2\text{O} & \rightarrow \text{CH}_2=\text{CH-Si-(O•H)}_2\text{CH}_3 \\
\text{O-CH}_2\text{CH}_3 & \quad \text{OH}
\end{align*}
\]

(Formation of silanol by hydrolysis of silane)

\[
\begin{align*}
\text{Fiber-OH} + \text{H}_2\text{C} &= \text{C} \rightarrow \text{Fiber-OSi-CH=CH}_2 \\
\text{OH} & \quad \text{OH} \\
\text{OH} & \quad \text{OH}
\end{align*}
\]

(Reaction of silanol with OH group of natural fibre)

**Scheme 4.1** Reaction during silane modification of filler

The APSP was then refluxed with maleic anhydride and acetone to get maleic anhydride PSP (MPSP). The treated fibres were washed thoroughly with water to remove residual chemicals and then dried [20]. The reaction occurring during maleic anhydride treatment can be shown as in scheme 4.2.
4.2.2 Characterisation of modified PSP

4.2.2.1 UV-Visible Spectroscopy

The UV spectra of PSP before and after treatments are shown in figure 4.1. The UV spectrum does not show any intense band. The broad band appeared at 280 nm may be due to the absorption by lignin present in the natural filler. The UV spectra of APSP and SPSP show weak bands at 236 nm can be due to the presence of carbonyl group in the cellulose. The feeble nature of the UV band at 236 nm after modification may be attributed to the functionalization taking place only at the exposed outer surface of the filler. Another weak bands at 227 nm in SPSP and 226 nm in MPSP can be ascribed to the vinyl group [21].
Chapter 4: Modification of PSP

Figure 4.1. UV absorption spectra of (A) UPSP, APSP and SPSP (B) UPSP, APSP and MPSP

4.2.2.2 FTIR spectroscopy

4.2.2.2.1 Characterisation of SPSP

FTIR spectra of UPSP, APSP and SPSP are presented in figures 4.2 A and B. The stretching frequency at 3393 cm\(^{-1}\) is characteristic for \(-\text{OH}\) group present in the cellulose of fibre. During modification most of the \(-\text{OH}\) groups are replaced as \(-\text{ONa}\) group in alkaline treatment and \(-\text{O-Si-R}\) in silane treatment. The intensity of \(-\text{OH}\) band is found to be decreases on modification due to decrease in concentration of hydrogen bonding in the fibers between the cellulosic hydroxyl groups [2]. The stretching frequency at 1740 cm\(^{-1}\) corresponds to carbonyl group present in the non-cellulose components like lignin in natural lignocellulose filler. The absence of this stretching frequency in figure 4.2B reveals that it is partially removed during modification. These observations are analogous to those reported earlier [18,22]. In the FTIR spectrum of SPSP figure 4.2B the characteristic stretching
frequencies are observed at 1607, 1169 and 1013 cm⁻¹. The frequencies at 1607 and 1013 cm⁻¹ are the characteristic absorptions resulting from the C=C of silane coupling agent. The frequency at 1169 cm⁻¹ is due to the presence of Si-OEt, which gives evidence for attachment of polysiloxane on the fibre surface and the condensation reaction between the silane coupling agent and the fibre [22].

![Figure 4.2(A)](image)

**Figure 4.2(A)** FTIR spectra of UPSP, APSP and SPSP (B) Spectrum of SPSP

### 4.2.2.2 Characterisation of MPSP

FTIR spectra of UPSP, APSP and MPSP are shown in **figure 4.3**. In general three spectra are similar but the frequency at 1735 cm⁻¹ disappears after mercerization and reappears after coupling with maleic anhydride. These observations are due to non celluloses including hemicellulose, fats, wax and pectin, which were partially removed after surface modification by alkali. Similar observations has also been made by other researchers [23,24]. The reappearance of small frequency peak at 1725 cm⁻¹ in **figure 4.3** after maleation of
Chapter 4: Modification of PSP

APSP by maleic anhydride attributed to the presence of the ester group. The lowering in the intensity of OH stretching frequency in the spectrum figure 4.3 provided further evidence for successful maleation [20]. Surface morphology (figure 4.4) also confirmed the removal of external impurities which appeared to be harder than untreated fibres.

![FTIR spectra of UPSP, APSP and MPSP](image)

**Figure 4.3** FTIR spectra of UPSP, APSP and MPSP

### 4.2.3 SEM analysis

Figures 4.4 A, B and C show the SEM images of PSP before and after chemical treatment with silane and maleic anhydride respectively. These photographs prove that the images of untreated surface are smoother than the treated one. This is due to the partial removal of impurities like hemicellulose, lignin and pectin as a result of mercerization. The rough surface of chemically treated PSP is responsible for both mechanical interlocking and binding reaction, thereby increasing the filler-matrix adhesion [25,26].
4.2.4 XRD analysis

Native cellulose, ie cellulose as it occurs in nature, the main component of all samples under study, can be found in the crystalline or amorphous form and can be observed by X-ray diffractogram. X-ray patterns of UPSP, APSP, SPSP and MPSP were exhibited in figure 4.5 Distinct peaks at 2θ =18 and 22° represents the cellulose crystallographic planes 110 and 002 respectively. These can be attributed to crystalline scattered and diffuse peaks associated with disordered regions, ie the highest peak intensity at 2θ =22° represent the crystalline material and peak at 2θ =18° corresponds to amorphous form. The peak at 2θ =22° is sharper for APSP, SPSP and MPSP than
Chapter 4: Modification of PSP

UPSP. The sharper diffraction pattern is an indication of higher crystallinity in the structure of the treated PSP. The percentage of crystallinity can be calculated using the equation 4.1 and listed in the table 4.1. Many researchers [27–29] investigated the effect of surface modification of fibres using chemical treatments from their XRD and observed an increase in the crystallinity index. Similar results were noted in the present study. The X ray diffractogram (figure 4.5) shows that the intensity at the I_{002} crystallographic peak is higher for APSP, SPSP and MPSP than UPSP. The increase in the crystallinity can be attributed to the removal of extractives and cementing amorphous components like lignin, hemicellulose and pectin and the calculated crystallinity index values confirm these observations.

Degree of crystallinity calculated using the equation 4.1

\[ DC = \frac{I_{200} - I_{am}}{I_{200}} \times 100 \] (4.1)
are presented in **table 4.1**. This is further supported by SEM and FTIR results. Similar explanations have already been offered by different authors [28,29]

**Table 4.1** Percentage crystallinity of different PSPs

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UPSP</td>
<td>13.9</td>
</tr>
<tr>
<td>APSP</td>
<td>42.01</td>
</tr>
<tr>
<td>SPSP</td>
<td>43.02</td>
</tr>
<tr>
<td>MPSP</td>
<td>40.39</td>
</tr>
</tbody>
</table>

### 4.2.5 TG and DTG analysis

**Figures 4.6A and B** displays respectively the thermogravimetric curves (TG) and the corresponding derivative curves (DTG) of UPSP, SPSP and MPSP. The primary weight loss in the temperature range 90-110 °C is due to the evaporation of surface water. The substantial weight loss of 70% in the temperature range around 200-500 °C is due to the decomposition of major chemical components of natural fibre, hemicelluloses, cellulose and lignin. Kabir [30] and Shibata et al [31] reported that, hemicelluloses are generally supposed to decompose first, followed by cellulose and lignin. UPSP decomposes in the wide range 215-420 °C, the SPSP decomposes in the range 233-362 °C and the MPSP decomposes in the range 248-368 °C The $T_{onset}$ for UPSP is 215 °C, which corresponds to 16% weight loss. But $T_{onset}$ for SPSP is 233 °C and MPSP is 248 °C which corresponds to 10% weight loss. This indicates that the
Chapter 4: Modification of PSP

chemical treatments influenced the partial removal of hemicelluloses, lignin, pectin and others. The figure 4.6B shows the DTG of unmodified and modified filler. The peak point in dM/dT, DTG$_{\text{max}}$ also proved that thermal stability of PSP increased on modification. From table 4.2 and figures 4.6A and B it is observed that the thermal stability of PSP increased by surface treatment using silane coupling agent and maleic anhydride which is fully supported by the XRD analysis data.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_{\text{onset}}$ (°C)</th>
<th>$T_{\text{final}}$ (°C)</th>
<th>$T_{50}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UPSP</td>
<td>215</td>
<td>420</td>
<td>297</td>
</tr>
<tr>
<td>SPSP</td>
<td>233</td>
<td>362</td>
<td>342</td>
</tr>
<tr>
<td>MPSP</td>
<td>248</td>
<td>368</td>
<td>343</td>
</tr>
</tbody>
</table>

$T_{\text{onset}}$-Onset degradation temperature, $T_{\text{final}}$-Temperature corresponds to maximum weight loss, $T_{50}$-Temperature corresponds to 50% weight loss.

![Figure 4.6](image_url) (A) TG curves of UPSP, SPSP and MPSP (B) DTG curves of UPSP, SPSP and MPSP
4.2.6 Particle size analysis of the filler

The particle size of filler was measured by Transmission Electron Microscopy (TEM) and Dynamic Light Scattering (DLS). From TEM (figure 4.7) only particles agglomerated to form large particle size in micron scale were observed. Similar observations were already by other researchers [32]. The PSP was sonicated using water suspended sample and analyzed by the DLS particle size analyzer. Figure 4.8 also shows the DLS data, which implies that UPSP and SPSP used for composites have particle size above 100 nm with an average particle size of 567 nm [33, 34].

Figure 4.7 TEM image of PSP

Figure 4.8 DLS data of PSP
4.3 CONCLUSIONS

Chemical treatment has been found to be efficient for improving its hydrophobic character to increase its compatibility with hydrophobic matrix SBR. Chemical treatment of pretreated PSP using alkali removes most of lignin, hemicellulose, wax, fatty substances and other impurities and exposes cellulose to filler surface. Coupling agent such as triethoxy vinyl silane and maleic anhydride were used for surface modification of the filler PSP. This was confirmed by UV-visible spectroscopy and FTIR spectroscopic methods. The chemical treatment of filler increased the crystallinity which was observed by XRD. The change in the morphology of PSP was confirmed by SEM, the surface becomes rough after modification in comparison with smooth and clear surface of untreated PSP. These were also observed through thermogravimetry and differential calorimetry. It was observed that thermal stability of chemically treated PSP was higher than that of untreated PSP. The removal of surface impurities on filler may be an advantage to filler for matrix adhesion as it facilitates both mechanical interlocking and the bonding reactions.
REFERENCES


Chapter 4: Modification of PSP


Chapter 4: Modification of PSP


