Chapter 4

Fibre Surface Treatments

Abstract
Banana fibre has been modified with silane treatment, acetylation, cyanoethylation, latex treatment and mercerization to improve the interfacial bonding with phenol formaldehyde (PF) resin. Scanning electron microscopy was used to study the morphology of the banana fibre after the treatments. The tensile properties of the modified fibre were compared with the untreated fibre and found that the tensile strength and modulus of the fibre were decreased by all the treatments except cyanoethylation. Tensile, flexural and impact performance of phenol formaldehyde composites reinforced with various treated fibres were analyzed and compared with that of untreated fibre composite. The tensile and flexural properties of the fibre-reinforced composites were found to be increased by all the modifications except latex coating. Incorporation of heat treated, vinyl silane treated and acetylated fibre reinforced PF composites were found to have higher impact strength than that of untreated fibre/composites. The tensile fractographs of the composites were studied by scanning electron microscopy to analyze the fibre/matrix interaction, fibre pull out and fracture mechanism of the composites.

Results of this chapter have been accepted for publication in Composite Interfaces.
Intimate molecular contact at the fibre/matrix interface is necessary to obtain strong fibre/matrix interaction. Without intimate molecular contact, the interfacial adhesion will be weak, and the applied stress that can be transmitted from one phase to the other through the interface will accordingly be very low.

Poor adhesion of the hydrophilic fibres to the hydrophobic polymer matrices, their poor ageing and weathering resistance and high moisture absorption make the surface modifications of the fibres very important [1-6]. Ray et al. [7] studied the mechanical properties of vinyl ester matrix composites reinforced with alkali treated jute fibres and found that the modulus and tenacity of the fibre were increased by the treatment with alkali. They also found that the fibre pull out (debonding) was predominant for 2 hour alkali treated fibres, while for 8 hours alkali treated fibres it was fibre fracture and the combined mode of fracture occurred in between. The effects of chemical modification of coir and oil palm fibres by acetylation, silane treatment and titanate coupling agent on mechanical properties of the polyester composites was analyzed by Hill Khalil [8]. The interfacial strength, (ISS) between fibre and matrix (polyester or styrene) was found to be increased by acetylation. A slight increase in tensile strength, tensile modulus and impact strength of composites reinforced with modified fibre was also noted due to combination of a change in mechanical properties of the modified fibres and increased hydrophobicity of the surface allowing improved wetting of the fibre by the resin.

Calado et al. [9] used chemical treatment in order to change the polarity of the cellulose, thus improving the affinity between the polyester resin and the fibre. They subjected the fibres to a two-step treatment (first
sodium sulphate solution and then acetic anhydride (acetic acid mixture) to promote better adhesion to the polyester resin matrix. The chemical treatment improved the fibre/matrix interaction, as revealed by the brittle behavior of composites reinforced with treated fibre.

Thwe and Liao [10] evaluated the tensile behavior of modified bamboo/glass reinforced hybrid composites and found that the chemical modifications of fibres affect the tensile strength and modulus of the resultant composites. They found alkali treatment as the most effective method for achieving the highest tensile modulus in bamboo/glass fibre reinforced polypropylene hybrid composites. Khalil et al. [11] studied the effect of acetylation on the interfacial shear strength between plant fibres and various matrices. They found that chemical modification of the fibre creates more trans active surface molecules that would readily form bond with matrix. Sreekala et al. [12] studied the effect of different surface treatments on mechanical properties of oil palm fibre reinforced phenol formaldehyde composites. They found that due to hydrophilicities of PF resin and oil palm fibre they are highly compatible and the incorporation of the treated fibres in PF matrix decreases the tensile strength of the composites due to decreased chemical interaction between fibre and matrix. But the incorporation of the modified fibres resulted in composites having excellent impact resistance. The mechanical properties of silane treated and mercerized banana fibre reinforced polyester composites were analyzed by Pothen et al. [13]. Earlier studies from our laboratory show that there is good interaction between banana fibre and phenol formaldehyde resin than that in glass fibre and PF resin. [14]. However careful examination of the literature shows that no systematic work has so far been carried out to study the effect of chemical modification of banana fibre on the
properties of resultant banana fibre reinforced phenol formaldehyde composites.

This chapter discusses the modifications of banana fibres by various treatments viz. mercerization, silane couplings, acetylation, cyanoethylation, heat treatment and latex treatment to enhance the bonding with matrix. The physical changes induced by these treatments are analyzed by scanning electron microscopy. The changes in tensile properties of the fibre after treatments are systematically followed. The effect of these modifications on tensile, flexural and impact properties of the fibre-reinforced composites has been carefully evaluated. The interfacial properties and fracture mechanism in the modified and unmodified fibre reinforced composites have been analyzed by SEM.

4.1. Physical changes: SEM observations

The scanning electron micrographs of the untreated banana fibre surface and the fibre surface after treatments are given in Figure 4.1(a-g). From the SEM photographs it is clear that the morphology of the treated fibre surface is different from that of the untreated fibre. The untreated fibre surface is found to be smooth. However on alkali treatment the wax and cuticle in the fibre surface is removed by the interaction with alkali and the surface is becoming rougher.
Fibre surface treatments

**Figure 4.1.** (a-c). Scanning electron micrographs of (a) untreated (b) mercerized and (c) acetylated banana fibre.
d. Heat treatment showing tendency for disintegration

e- Latex treated and hydrophobic surface

f- Amino silane treatment and fibrillated surface

*Figure 4.1. (d-f). Scanning electron micrographs of (d) heat treated (e) latex treated and (f) amino silane treated*
Fibre surface treatments

The fibrillation is also found to occur as the binding waxy materials are removed from the surface of the fibre. Some micropores are also appearing in the treated fibres. The acetylated fibre is found to be more fibrillated and is becoming rougher than that of untreated banana fibre. The heat-treated fibre surface shows slight disintegration of the fibre along with fibrillation. This may be due to the removal of less stable noncellulosic constituents in the fibre. The latex treated fibre is found to have a thin coating of latex. This makes its surface hydrophobic and smooth. The aminosilane and vinyl silane treated fibres do not show any considerable change in microstructure, though there is fibrillation and presence of pores as in the case of alkali treated fibre. The presence of macrospores, rough fibre surface and fibrillation make it easy for the resin to penetrate into the fibre and thus a strong fibre/matrix bonding can be achieved. So the chemically modified fibre will be useful for the development of high performance composite materials. The effect of different chemical treatments on the diameter of banana fibre is given in Figure 4. 2.
It is clear from the figure that all the surface treatments except latex treatment decrease the fibre diameter and the effect is most prominent for acetylated, mercerized and silane treated fibres. The heat treatment does not change the diameter considerably.

4.2. Effect of treatments on tensile properties of banana fibre

The stress-strain curves of the untreated and modified fibres are given in Figure 4.3. Each fibre is composed of microfibrils held together by noncellulosic materials like lignin pectin etc. As the stress gradually increases some of these fibrils may break, the remaining fibrils will have to bear the total stress and will result in catastrophic failure. This is clear from the slope of the stress-strain curves. Upon chemical treatment, the cohesive interactions between the cellulose chains are destroyed due to the weakening of hydrogen bonding interactions. Brittleness of the fibre is substantially reduced by the treatments.
The tensile strength, modulus and elongation at break values of the modified fibres are given in Table 4.1. The tensile strength of the fibre is found to be decreased by all treatments except cyanoethylation. The heat treatment does not affect the tensile strength considerably although there is a slight decrease compared to the untreated fibre. Acetylation, treatments with silanes, and latex decrease the tensile strength and modulus of the fibre. The decrease in tensile properties of the fibre can be explained on the basis of morphological changes obtained from SEM. By most of the treatments, the fibrillation occurs and alkali soluble portion of the fibre dissolves. This will facilitate easier fibre fracture. Cyanoethylation increases the strength of banana fibre. Rout et al. [15] also obtained an increase in tensile strength for cyanoethylated coir fibres as a result of the increase in crystallinity for the ordering of cyanoethyl group. The elongation at break is found to be
maximum for latex treated fibres. This is in agreement with our expectations as there is a coating of high elongation natural rubber latex in the fibre surface.

**Table 4.1. Tensile properties of untreated and modified banana fibre**

<table>
<thead>
<tr>
<th>Fibre</th>
<th>Tensile strength (MPa)</th>
<th>Young's Modulus (GPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>578 ± 1.2</td>
<td>22.5 ± 0.41</td>
<td>2 ± 0.2</td>
</tr>
<tr>
<td>Latex treated</td>
<td>398 ± 9</td>
<td>4.64 ± 0.09</td>
<td>7 ± 0.5</td>
</tr>
<tr>
<td>Mercerised</td>
<td>425 ± 7.9</td>
<td>18 ± 0.23</td>
<td>3 ± 0.19</td>
</tr>
<tr>
<td>Amino silane treated</td>
<td>360 ± 9.2</td>
<td>5.21 ± 0.07</td>
<td>5 ± 0.4</td>
</tr>
<tr>
<td>Cyanoethylated</td>
<td>605 ± 12</td>
<td>25.4 ± 0.39</td>
<td>3 ± 0.18</td>
</tr>
<tr>
<td>Heat treated</td>
<td>530 ± 15</td>
<td>17.1 ± 0.15</td>
<td>4 ± 0.25</td>
</tr>
<tr>
<td>Vinyl silane treated</td>
<td>225 ± 11</td>
<td>5.5 ± 0.06</td>
<td>3 ± 0.11</td>
</tr>
<tr>
<td>Acetylated</td>
<td>422 ± 9.5</td>
<td>4.7 ± 0.04</td>
<td>6 ± 0.53</td>
</tr>
</tbody>
</table>

**4.3. Mechanical properties of composites**

**4.3.1. Tensile properties**

Tensile stress-strain curves of untreated and chemically treated banana fibre reinforced phenol formaldehyde composites are given in Figure 4. 4.
Figure 4.4. Tensile stress-strain curves of untreated and treated banana fibre reinforced composites

All the composites except the latex treated fibre reinforced composites are found to have higher stress value at any particular strain. The latex treated one, due to the presence of a rubber coating on the surface shows flexible nature. Almost all the composites show ductile behavior. The effect of chemical treatments on tensile strength, Young’s modulus and elongation at break values of the banana fibre reinforced PF composites are given in Figures 4.5, 4.6 and 4.7.
Tensile strength of the composites is found to have increased upon all the modifications except the latex treatment where the tensile strength is decreased. This decrease in tensile strength and modulus of the latex treated composite is due to the presence of rubbery layer on the fibre surface as shown in SEM photographs (Figure 4.1.e). Here the interface becomes very weak. Our earlier studies [14] have shown that there exists very good chemical interaction between the banana fibre and phenol formaldehyde resin as both are hydrophilic. The hydroxyl groups in cellulose and lignin can form hydrogen bonding interaction with hydroxyl groups of methylol or phenolic hydroxyl groups of phenol formaldehyde and upon curing these groups undergo condensation reaction as shown in Figure 3.3. However the presence of rubbery layer in the fibre makes it hydrophobic and decreases or even prevents the fibre/matrix adhesion. So the interface becomes weak and the composite fails easily.
Figure 4.6. The effect of different chemical treatments on the Young's modulus of banana fibre reinforced PF composites

Figure 4.7. The effect of different chemical treatments on the elongation at break (%) values of banana fibre reinforced PF composites
Alkali treated fibre reinforced PF composites show increase in tensile strength and modulus. Alkali treatment and heat treatment do not change the chemical structure of the fibre. Only physical changes take place here and the reason for the improvement in properties is also associated with these physical changes. Alkali treatment cleans fibre surface and develops microporocity with many pits and holes on the fibre [16]. Ray et al. [7] found that due to poor wetting of untreated jute fibres debonding of the fibre from vinyl ester matrix occurs with extensive pull out. When they treated the fibre with alkali for four hours much less fibre pull having shorter pull out lengths were observed and when treated for 8 hours the interfacial bonding was highly improved resulting in shear fracture of the composites. In the case of mercerized banana fibre also increase in tensile properties is observed. The SEM photographs reveals porous nature of the mercerized fibre. So the PF resin can penetrate into these pores obtained by the removal of hemicellulose and lignin. So the resin can penetrate into the fibre surface pores as well as the pores inside the microfibrillar bundles of the fibre so that the composite failure cannot occur by simple interfacial failure. i.e. a matrix layer can be seen inside the fibre and the composite fracture is very difficult.

In the case of heat-treated composites the interface is not affected. There is an increase in crystallinity of the fibre [17], which improves the composite properties. Similarly the decomposition of less stable components and volatile components occurs by the heating. So heat treatment also improves the tensile properties of composites though not as effective as other treatments.

Silane treatments, both amino and vinyl silane increase the tensile strength and modulus of composites. The tensile strength is found to be
higher for vinyl silane treated composite while the modulus is higher for amino silane treated one. In order to explain the mechanism of action, silanes can be represented by YR-Si(OR₂)₃, where R is an aliphatic linkage that serves to attach the functional organic groups to silicon. OR₂ is a hydrolysable alkoxy group. Traces of moisture in the fibre hydrolyse the silanes to form silanols.

\[ \text{YR}_1\text{Si(OR)}_{2}\text{Si(OH)}_{3} \]

The hydrolyzed silanol forms strong covalent bonds or H-bonds with OH group of cellulose. The individual coupling agent molecules attached to cellulose forms a continuous link. The long hydrophobic polymer chain of polymerized silane can adhere to the matrix mainly because of Van der Waals type attractive force. As a result, silane-coupling agents form a bridge at the interface. Thus the activated surface of cellulose can be represented schematically in Scheme 4.1.

In aminosilane the Y unit is -NH₂ group, which can react with -OH groups of other molecules of silanes or cellulose or OH groups of PF matrix. In vinyl (2-ethoxy methoxy) silane the Y group is the vinyl group. It is reported that the hydrophilic amino groups if present in silane coupling agent, can react with resin matrix and make a strong interface. If the amino group is not reactive it will be responsible for the poor water resistance of the fibre/matrix bond [17].
Acetylated fibre also shows enhancement in properties when compared to untreated fibre even more than mercerized fibre reinforced composites. In this case as the acetylation was carried out in presence of only glacial acetic acid, the extent of acetylation is very low. However improvement in properties is noted. Similar results were reported by Rong et al. [18] in acetylated jute fibre reinforced epoxy composites. They showed that the improvement in interfacial bonding is the results of the H-bonds between acetyl groups of the acetylated fibre and hydroxyl or amine groups in epoxy resin and mechanical interlocking between epoxy and the caved fibre surface due to the alkali pretreatment. Similarly in PF system also there are chances of H-bonding interaction between acetyl groups of acetylated banana fibre and OH groups of PF resin as schematically represented in Scheme 4.2. Hence an improvement in tensile strength and modulus is observed.
The elongation at break values of the untreated and treated composites are found to be almost the same. The minimum elongation is obtained for aminosilane treated composites.

![Scheme 4.2. Schematic model showing the H-bonding interaction at acetylated banana fibre reinforced phenol formaldehyde composite interface](image)

The scanning electron micrographs of untreated and treated banana fibre reinforced phenol formaldehyde composites are given in Figure 4.8. It is clear from the figure that the penetration of the resin into the fibre is improved by mercerization, acetylation and silane treatment. The latex treated fibre composite is found to have a weakly bound interface and a careful examination of the fibre shows that minimum fibre fracture has occurred in the pulled out fibre even at a lesser extent than untreated fibre.
Figure 4.8 (a-g). Scanning electron micrographs of the tensile fracture surfaces of untreated and treated banana fibre reinforced phenol formaldehyde composites
4.3.2. Flexural properties

Flexural strength is the ability of the material to withstand bending forces applied perpendicular to its longitudinal axis of the sample. The stresses induced due to the flexural load are combination of compressive and tensile stresses. For polymeric materials that break easily under flexural load, the specimen is deflected until rupture occurs in outer fibres. The flexural stress-strain curves of untreated and treated banana fibre/PF composites are given in Figure 4.9. In the case of latex treated fibre reinforced composites, the flexural strength abruptly decreases to a very small value at the break point. Silane treated and acetylated fibre composites are found to have brittle failure, indicating a high fibre/matrix interaction.

![Figure 4.9. Flexural stress-strain curves of untreated and treated banana fibre/PF composites](image)

In all other composites initiation of crack, its gradual propagation and finally the failure of the composite are clear from the varying slopes at different portions of
stress-strain curve. The flexural strength and modulus of banana fibre/PF composites are given in Table 4.2.

Table 4.2. Flexural properties of treated fibre composites

<table>
<thead>
<tr>
<th>Fibre</th>
<th>Flexural strength (MPa)</th>
<th>Flexural modulus (GPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>17±2</td>
<td>0.377±0.009</td>
<td>9±0.8</td>
</tr>
<tr>
<td>Latex treated</td>
<td>25±2.5</td>
<td>0.901±0.008</td>
<td>4±0.2</td>
</tr>
<tr>
<td>Mercerized</td>
<td>37±2</td>
<td>1.504±0.012</td>
<td>3±0.8</td>
</tr>
<tr>
<td>Amino silane treated</td>
<td>45±3.7</td>
<td>4.184±0.014.8</td>
<td>1±0.012</td>
</tr>
<tr>
<td>Cyanoethylated</td>
<td>23±3.1</td>
<td>1.509±0.009</td>
<td>2±0.02</td>
</tr>
<tr>
<td>Heat treated</td>
<td>33±4.5</td>
<td>1.284±0.011</td>
<td>4±0.14</td>
</tr>
<tr>
<td>Vinyl silane treated</td>
<td>29±1.9</td>
<td>2.722±0.017</td>
<td>2±0.13</td>
</tr>
<tr>
<td>Acetylated</td>
<td>32±3.3</td>
<td>6.064±0.012</td>
<td>1±0.06</td>
</tr>
</tbody>
</table>

In the case of composites, the flexural properties are controlled by the resistance to interlaminar failure. Therefore, high flexural strength and modulus of treated fibre reinforced composite is due to better interfacial adhesion in the composite. Boynard et al. [19] observed a slight increase in flexural properties for alkali treated sponge gourd fibre reinforced polyester matrix composites which is attributed to improved mechanical interlocking by the removal of outer surface of the fibers with the exposition of the inner fibrillar structure and consequent increase of the fibre surface area. The flexural strength is found to have 160% increase by aminosilane treatment of the fibre and 117% increase by mercerization. Acetylation and heat treatment also increases the flexural strength of the composites. The improved flexural properties of the treated fibre composites can be
explained due to the physical and chemical changes in the fibre surface induced by the treatments, which enhance the adhesion between the fibre and matrix as in the case of tensile properties. The elongation is found to be very low in acetylated, silane treated and mercerized composites.

4.3.3. Impact properties

The impact strength of a composite is influenced by many factors including the toughness properties of the reinforcement, the nature of interfacial region and frictional work involved in pulling the fibre from matrix. The nature of the interface region is of extreme importance in determining the toughness of the composite. The variation of impact strength with different chemical treatments is given in Table 4.3.

*Table 4.3. Impact strength of the treated and untreated composite*

<table>
<thead>
<tr>
<th>Composite</th>
<th>Impact strength (kJ/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>12±1.5</td>
</tr>
<tr>
<td>Latex treated</td>
<td>10±1</td>
</tr>
<tr>
<td>Mercerized</td>
<td>7±0.8</td>
</tr>
<tr>
<td>Amino silane treated</td>
<td>3±0.5</td>
</tr>
<tr>
<td>Cyanoethylated</td>
<td>8±0.6</td>
</tr>
<tr>
<td>Heat treated</td>
<td>16±2</td>
</tr>
<tr>
<td>Vinyl silane treated</td>
<td>12±0.9</td>
</tr>
<tr>
<td>Acetylated</td>
<td>14±0.6</td>
</tr>
</tbody>
</table>

From the table it is clear that impact strength of mercerized, aminosilane treated, and cyanoethylated banana fibre reinforced composites are lower than that of untreated fibre composites. Ray et al. [7] observed that in composites having weak interfacial bonding the crack propagated along the fibre/matrix interface causing debonding which leads to significant increase in the
energy absorbing capacity of the composites as a result of the large new surfaces produced and frictional work resulting from differential displacement between matrix and fibre increasing the impact fatigue resistance of the composites.

Cook and Gordon [20] have reported that weak fibre/matrix interface will result in tough composites that is itself formed from two brittle phases. The opening up of a new surface at the interface will result in absorption of energy, crack diversion and so forth. The fibre/ matrix adhesion to a great extent determines the strength of the composites. A weak interface will not facilitate efficient stress transfer and the resultant composite will also be weak. But the toughness of the composite will be high. So composites having strong interface will have low toughness value compared to that of one having weaker interface. The low impact strength of mercerized and amino silane treated composite is assumed to be due to the strong interface as evidenced from SEM photographs (Figure 4.8). Composite thus results in decrease in toughness and hence the impact strength. In the case of cyanoethylated and latex treated fibre/ composites the impact strength is found to be the minimum like the tensile strength. The very low value of the impact strength of cyanoethylated composite is assumed to be due to the decrease in toughness of the composite. In latex treated fibre naturally we expect higher impact strength as the toughness of the fibre is increased by the latex coating as evident from the area under the stress-strain curve of the fibre.

Vinyl silane treated, acetylated and heat treated composites show better impact strength. Hill and Abdul Khalil also got an improvement in impact strength for acetylated oil palm fibre reinforced polyester [21]. In acetylated fibre, the improved impact strength is assumed to be due to the improved toughness of the fibre. Similar results have been reported earlier [22].
References

9  V Calado, DW Barreto, JRM d’Almeida. *Polymers and Polymer Comp.,* **2** (2003) 31
13 LA Pothen, J George S Thomas. *Comp Interfaces*, **9** (2002) 335


