CHAPTER 4

Influence of Fibre Surface Modifications on the Mechanical Performance of Oil Palm Fibre Reinforced Phenol Formaldehyde Composites

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Abstract

OPEFB fibres have been used as reinforcement in phenol formaldehyde resin. In order to improve the interfacial properties, the fibres for reinforcement were subjected to different chemical modifications such as mercerisation, acrylonitrile grafting, acrylation, latex coating, permanganate treatment, acetylation, and peroxide treatment. The effect of fibre coating on the interface properties has also been investigated. The incorporation of the modified fibres in PF resulted in composites having excellent impact resistance. Fibre coating enhanced the impact strength of untreated composite by a factor of four. Tensile and flexural performances of the composites were also investigated. Finally, in order to have an insight into the failure behaviour, the tensile and impact fracture surfaces of the composites were analysed using scanning electron microscope.
Mechanical performance of a fibrous composite is mainly determined by the fibre properties. Extent of interfacial interaction between the fibre and matrix determines the stress transfer ability of a fibrous composite. Possibility of forming mechanical and chemical bonding at the interface is mainly dependent on the surface morphology and chemical composition of the fibres, polarity of the matrix or presence of reactive probes in the matrix resin etc. Hydrophilicity of the fibre and resin is an important factor determining the extent of fibre-matrix adhesion. Therefore, microscopic analysis of fibre surface topology and fracture surface morphology deserves utmost importance in fibrous composites.

Natural fibres are amenable to modifications as they bear hydroxyl groups from cellulose and lignin. The hydroxyl groups may be involved in the hydrogen bonding within the cellulose molecules thereby reducing the activity towards the matrix. Chemical modifications may activate these groups or can introduce new moieties that can effectively interlock with the matrix. Surface characteristics such as wetting, adhesion, surface tension, porosity etc. can be improved upon modifications. Chemical bleaching of the fibres may lead to major changes in fibre surface roughness. The irregularities of the fibre surface play an important role in the mechanical interlocking at the interface. Parameters such as van der Waals force, dipole-dipole interactions, hydrogen bonds etc. determine the extent of physical bonding.Enhancement in the physical and chemical adhesion can be understood from the schematic model (Fig. 4.1). The model represents increase in adhesion of the resin onto the fibres due to the physical and chemical changes occurred on the fibre upon chemical treatments. Physical changes may include removal of the waxy cuticle layer, changes in the surface roughness, physical appearance of the fibre and density. This may lead to changes in the adhesive strength of the fibre onto the matrix. As a result, the interface properties of the composite will be improved. Chemical bond formation at the interface is possible by some treatments that lead to a higher compatibilized system. Extensive studies on the important modification methods for vegetable fibres and their effect on the mechanical performance of the natural fibre composites were reported.¹⁻¹²
Figure 4.1 Schematic model showing fibre modifications

Corona discharge treatment on cellulosic fibre and hydrophobic matrix was found to be effective in improving compatibilization between hydrophilic fibre and hydrophobic matrix.\textsuperscript{13} King and co-workers introduced electrochemical polymeric coatings for improving fibre-matrix adhesion in liquid crystalline polymer composites.\textsuperscript{14} Plasma treatment is another important method to achieve better interfacial bonding between fibre and matrix.\textsuperscript{15, 16} Modification effects by plasma treatment depend on the nature, flux and energy distribution of the incident species. Improved fibre-matrix interactions upon chemical modifications of natural fibres such as pineapple leaf fibre, sisal, banana etc. have already been reported by Thomas et al.\textsuperscript{17-20} Chemical modifications such as introduction of coupling agents, peroxide treatment, alkali and permanganate treatments make the pineapple leaf fibre more compatible with the hydrophobic polyethylene matrix thereby improving
the mechanical performance of the composites.\textsuperscript{17} Benzoxylation of the sisal fibre was found to enhance the tensile properties of the sisal reinforced polystyrene composites.\textsuperscript{18} Tensile properties of sisal fibre reinforced LDPE composites were enhanced upon chemical treatment.\textsuperscript{19} Silane treatment onto the banana fibre improves interfacial adhesion with polyester matrix, which increases the mechanical strength of the composite.\textsuperscript{20}

In this chapter the role of fibre surface modifications on the static mechanical properties of the composites is presented. Fibres were subjected to acetylation and mercerisation. Effects of benzoyl peroxide, permanganate treatment and $\gamma$ radiation of the fibre on the mechanical performance were tested. Coupling agents such as toluene diisocyanate and triethoxy vinyl silane were tried on the fibre surface in order to improve the interface properties. Acrylation reaction and acrylonitrile grafting were also performed on the fibre surface. In order to reduce the surface cracking and to improve impact strength, latex modification of the fibres were tried. The physical and chemical modifications occurred to OPEFB fibres on various treatments were discussed in Chapter 3. Mechanical properties of the oil palm fibre reinforced phenol-formaldehyde composites were investigated. The oil palm fibre is strongly polar due to hydroxyl groups and C-O-C links in its structure. This renders it more compatible with polar polymers. The phenol formaldehyde resole type resin is highly polar owing to its phenolic hydroxyl groups and methylol groups. Since both the fibre and the matrix are hydrophilic they are highly compatible. Chemical modifications may decrease the hydrophilicity of the fibre thereby reducing the interfacial adhesion. The influence of modifications such as mercerisation, peroxide treatment, permanganate treatment, acrylonitrile grafting on the mechanical properties of the composites has been studied in detail. The most characteristic property of the thermoset composites, the impact performance is highlighted in this study. More specifically, the influence of hydrophobic-hydrophilic balance on the impact properties has been analysed in detail. Finally the tensile and impact fractography of the modified and unmodified composites were analysed using scanning electron micrographs.
4.1 EFFECT OF FIBRE SURFACE MODIFICATIONS ON THE MECHANICAL PERFORMANCE OF THE COMPOSITES

4.1.1 Tensile Properties

Figure 4.2 gives tensile stress-strain behaviour of the parent and treated composites having 40wt.% fibre loading. Treatments such as mercerisation, permanganate and peroxide treatment on resin lead to brittle failure of the composites. The γ irradiated, acrylonitrile grafted as well as untreated composites show behaviour in between brittle and ductile failure. Isocyanate, silane, acrylated, latex coated and peroxide treated fibre composites can withstand the tensile stress to higher strain level. Necking followed by catastrophic failure is observed in untreated, mercerised, permanganate treated, acrylonitrile treated, γ irradiated and peroxide treated composites. Comparatively lower elongation is observed in these composites. Isocyanate treated, silane treated, acrylated, acetylated and latex coated composites show yielding and high extensibility. Latex modified composite exhibits maximum elongation and shows a rubbery nature.

![Tensile stress-strain behaviour of the parent and treated oil palm fibre/PF composites having 40 wt.% fibre loading](image)

**Figure 4.2** Tensile stress-strain behaviour of the parent and treated oil palm fibre/PF composites having 40 wt.% fibre loading.
Mechanical performance of unmodified oil palm fibre reinforced PF composites as a function of fibre length and fibre loading were analysed and are reported elsewhere.\textsuperscript{21} Tensile strength values of the composite show a marginal increase on permanganate treatment. The values are given in Table 3.4 (refer Chapter 3). Permanganate treatment of fibre leads to composites having better tensile properties. However on fibre modifications by other chemical agents, the tensile strength is found to be decreased. Natural fibre reinforced plastic composites often show enhancement in tensile properties upon different modifications owing to the increased fibre-matrix adhesion.\textsuperscript{22 - 24, 17 & 19} Treatments like mercerisation, peroxide, $\gamma$ irradiation and permanganate treatment do not make any major changes to the hydrophilicity of the lignocellulosic fibre. The interfacial bond remains intact even after these modifications. Generally, the interaction of cellulose fibre with PF resin is excellent due to the hydrophilic nature of cellulose and PF resin. This is shown schematically in Figure 4.3. Hydrophilicity of the fibre arises from the cellulosic hydroxyl groups and lignin hydroxyl groups, which are the major components of the fibre. These can easily form hydrogen bonds with the methylool and phenolic hydroxyl groups of the resole in the prepreg stage. On curing at 100$^\circ$C, these groups can undergo condensation reaction leading to a three-dimensional network between the fibre and matrix. However upon acetylation, silane treatment, isocyanate treatment, acylation, acrylonitrile grafting and on latex modification the hydrophilic fibre $-\text{OH}$ groups are replaced by hydrophobic moieties. This decreases the strength of the chemical interlocking at the hydrophilic centres of the phenol formaldehyde resin. Thus, effective stress transfer does not take place at the interface leading to easy debonding of the fibres under tension.

Tensile modulus of the composites at 2\% elongation (Table 4.1) shows slight enhancement upon mercerisation and permanganate treatment. The composite properties are mainly dependent on the interfacial strength. The interfacial strength in fact depends on the fibre and matrix properties. Modifications of the fibre play an important role on the interface properties. Increased adhesion upon mercerisation and permanganate treatment leads to better interfacial strength which
enhances the modulus of the composite. However, all other treatments show a decrease in tensile modulus due to the increased hydrophobicity of the fibre.

Elongation at break of the composites shows considerable change upon different modifications. Maximum elongation is observed for latex coated samples. The higher extensibility is attributed to the better stress transfer ability of the fibre due to the improvement in flexibility imparted as a result of latex coating. The variations in the elongation at break on different modifications are attributed to the changes in the chemical structure and bondability of the fibre.

Scanning electron micrographs of the tensile fracture of the untreated and treated composites reveal the failure mechanisms. Figure 4.4 shows the tensile fracture of untreated composite. Fibre breakage is the main failure criteria observed. Alkali treated composite shows better fibre matrix adhesion (Fig. 4.5).
Table 4.1  Tensile and Flexural Properties of Untreated and Treated Oil Palm Fibre Reinforced PF Composites

<table>
<thead>
<tr>
<th>Oil palm fibre/ PF composite</th>
<th>Tensile strength (MPa)</th>
<th>Tensile modulus at 2% elongation (MPa)</th>
<th>Elongation at break (%)</th>
<th>Flexural strength (MPa)</th>
<th>Flexural Strain at break (%)</th>
<th>Flexural modulus at 1% strain (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>37</td>
<td>1150</td>
<td>4</td>
<td>49</td>
<td>6</td>
<td>3050</td>
</tr>
<tr>
<td>Mercerised</td>
<td>35</td>
<td>1300</td>
<td>3</td>
<td>75</td>
<td>6</td>
<td>2950</td>
</tr>
<tr>
<td>Acetylated</td>
<td>19</td>
<td>800</td>
<td>6</td>
<td>36</td>
<td>7</td>
<td>1900</td>
</tr>
<tr>
<td>Peroxide on fibre</td>
<td>35</td>
<td>1125</td>
<td>3</td>
<td>71</td>
<td>3</td>
<td>3950</td>
</tr>
<tr>
<td>KMnO4</td>
<td>40</td>
<td>1200</td>
<td>4</td>
<td>55</td>
<td>3</td>
<td>3750</td>
</tr>
<tr>
<td>γ irradiated</td>
<td>21</td>
<td>825</td>
<td>3</td>
<td>30</td>
<td>2</td>
<td>2200</td>
</tr>
<tr>
<td>Isocyanate</td>
<td>20</td>
<td>700</td>
<td>8</td>
<td>32</td>
<td>9</td>
<td>1800</td>
</tr>
<tr>
<td>Silane</td>
<td>15</td>
<td>700</td>
<td>8</td>
<td>23</td>
<td>8</td>
<td>1200</td>
</tr>
<tr>
<td>Acrylated</td>
<td>18</td>
<td>600</td>
<td>9</td>
<td>29</td>
<td>8</td>
<td>1800</td>
</tr>
<tr>
<td>Acrylonitrile</td>
<td>26</td>
<td>800</td>
<td>4</td>
<td>52</td>
<td>5</td>
<td>2500</td>
</tr>
<tr>
<td>Peroxide on resin</td>
<td>37</td>
<td>1050</td>
<td>5</td>
<td>54</td>
<td>7</td>
<td>3050</td>
</tr>
<tr>
<td>Latex coated</td>
<td>13</td>
<td>550</td>
<td>9</td>
<td>16</td>
<td>8</td>
<td>700</td>
</tr>
</tbody>
</table>

Figure 4.4  SEM of tensile fracture of untreated oil palm fibre/PF composite (x50)

Figure 4.5  SEM of tensile fracture of alkali treated oil palm fibre/PF composite (x100)
Fibre-matrix debonding is clear from the fracture surface of acetylated composite (Fig. 4.6). Matrix cracking and fibre breakage were observed in peroxide treated fibre composite (Fig. 4.7). Permanganate treatment leads to very good fibre-matrix adhesion, as is evident from the highly fibrillated structure of the fibre (Fig. 4.8). Fracture surface of the silane treated composite shows crowded fibres and several broken ends (Fig. 4.9). This indicates decreased fibre-matrix interfacial adhesion. Fibre-matrix debonding is the main failure process observed in peroxide treated composites (Fig. 4.10). Fibrillation is observed here also.

**Figure 4.6** SEM of tensile fracture of acetylated oil palm fibre/PF composite (x98)  
**Figure 4.7** SEM of tensile fracture of peroxide treated oil palm fibre/PF composite (x46)

**Figure 4.8** SEM of tensile fracture of KMnO4 oil palm fibre/PF composite (x200)  
**Figure 4.9** SEM of tensile fracture of silane treated oil palm fibre/PF composite (x34)
4.1.2 Flexural Properties

The deformation behaviour of the untreated and treated composites having 40wt.% fibre loading under flexural stress is seen from Figure 4.11. In the case of $\gamma$ irradiated fibrous composites, the flexural stress abruptly decreases to a very small value at the break point. In all other treated composites, crack initiation and its gradual propagation is observed. The increasing deflection brings on matrix rupture progressively, resulting in fracture and pulling out of fibres, leading to a more or less regular decrease of strength. There is considerable energy absorption after partial failure of the sample. The regular decrease in the strength after partial rupture denotes composite’s sensitivity towards fibre distribution. The behaviour is similar to that obtained on application of tensile stress. Permanganate treated, peroxide treated, acrylonitrile grafted and $\gamma$ irradiated composites show necking effect. All others show yielding and high strain values. Composite’s ability to withstand the applied flexural stress can be manifested by the strain values (Table 4.1). Higher strain values indicate the increased elastic nature of the composite.

Resistance to the compressive failure of the composites is manifested in flexural tests. The flexural properties of the composites are given in Table 4.1.
Mercerisation and peroxide treatment on the fibre increase the flexural strength of the composites. Permanganate treatment and acrylonitrile grafting give moderate stiffness to the composite. Peroxide treatment on resin also enhances the stiffness. The variation in these properties can be explained on the basis of the changes in chemical interactions at fibre-matrix interface on various treatments as explained under tensile properties.

Flexural modulus at 1% strain is given in Table 4.1. Improvement in flexural modulus is observed upon peroxide and permanganate treatments. Flexural modulus is a measure of strength and stiffness of the composite. Decrease in the values upon other modifications is attributed to the weaker interfacial bond formed.

### 4.1.3 Impact Properties

The main disadvantages of the thermoset mouldings are high shrinkage during curing, high brittle behaviour and surface cracking. Phenol formaldehyde
mouldings exhibit all these drawbacks. Incorporation of the oil palm fibres in phenol formaldehyde almost eliminates these drawbacks. Impact performance of the resin largely improved upon fibrous reinforcement. In order to use as a structural material, the phenolic composite should have good resistance to impact. Figure 4.12 shows the izod impact strength of the unmodified and modified composites having 40 wt.% fibre loading. Much promising results are obtained on modifications. Latex coating, acetylation, silane and TDIC treatment leads to impact resistant composites. Increased hydrophobicity of the fibres upon these treatments leads to weak interfacial linkage thereby facilitating the debonding process on stressed condition. This leads to the fibre pull out.

![Izod Impact Strength Graph](image)

**Figure 4.12** Unnotched izod impact strength of the untreated and treated oil palm fibre fibre/PF composites having 40wt.% fibre loading

Detailed studies have already been reported on the impact resistance of short fibre reinforced polymer composites. Fibres may have a significant effect on the impact resistance probably through the principle of stress transfer. When an impact
load is applied perpendicular to the fibres, good fibre-matrix adhesion is required for even moderate impact strength. When it acts parallel to the reinforcing fibres the better impact strength are obtained if the adhesion is relatively poor and the fibres are short, so that maximum energy can be dissipated by mechanical friction during the pullout process and by debonding of the fibres.\textsuperscript{28} The strength of the matrix, the weakest part of the material should be related to the failure process. The total energy dissipated in the composite before final failure occurs is a measure of its impact resistance. The total energy absorbed by the composite is the sum of the energy consumed during plastic deformation and the energy needed for creating new surfaces. Major microfailure mechanisms operating during impact loading of the composite include initiation and propagation of matrix cracking, fibre-matrix debonding, fibre breakage and fibre pullout. The involvement of fibres in failure process is related to their interaction with the crack formation in the matrix and their stress transferring capability. The range of impact resistance provided by the fibres depend on several factors such as fibre rigidity, interfacial stress resistance, fibre aspect ratio etc.

Impact fracture morphology and failure mechanisms are clear from the respective scanning electron micrographs of impact fracture surface of untreated and treated composites. The failure process with respect to fibres is a combination of fibre pullout and fibre breakage and is evident from the respective scanning electron micrographs. Brittle fracture of the phenol formaldehyde matrix and fibre can be understood from the scanning electron micrograph of the untreated composite (Fig. 4.13). Alkali treated composite shows severe fibre breakage (Fig. 4.14). Fibre pullout occurs as a result of the impact failure in acetylated composites (Fig. 4.15). Impact strength shows lower value for permanganate treated composite. This may be due to enhanced fibre-matrix interlocking (Fig. 4.16). The silane treatment leads to easy debonding at the interface. The introduction of silane onto the fibre was found to make it more hydrophobic resulting in a decreased fibre-matrix interaction than in untreated composites.
This will lead to easy debonding of the fibres. Extra energy is needed to do the work of debonding which enhances the impact strength. Crack propagation is easier in this composite (Fig. 4.17). Liu and Kagawa investigated the basic problems involved in debonding and frictional sliding in fibre reinforced brittle matrix composites.²⁹
Figure 4.17  SEM of impact fracture of silane treated oil palm fibre/PF composite (x100)

REFERENCES