Chapter 5

EFFECT OF FIBRE LENGTH AND CHEMICAL MODIFICATIONS ON THE TENSILE PROPERTIES OF INTIMATELY MIXED SHORT SISAL/GLASS HYBRID FIBRE REINFORCED LOW DENSITY POLYETHYLENE COMPOSITES

Part of the results presented in this chapter has been communicated to Composites Science and Technology (1999)
5.1. Introduction

Polymeric composites containing more than one type of fibrous reinforcements have gained greatest interest recently because they yield hybrid composites with excellent performance\textsuperscript{1-3} such as high strength, high toughness, light weight, with cost reduction. The different types of hybrid composites and their properties have been reported in the literature\textsuperscript{4-5} in detail. Miwa and Horiba\textsuperscript{4} found that the tensile strength of epoxy resin carbon/glass hybrid composites increased with increase in fibre length, and it remained almost unchanged after the fibre length reached a certain value. Peijs et al.\textsuperscript{5} investigated on the mechanical properties of polyethylene/carbon hybrids with chromic acid treated polyethylene fibres. The system showed an impact performance that varied linearly with composition of carbon and polyethylene fibres. Marom et al.\textsuperscript{6} pointed out that the epoxy hybrid composites containing carbon and glass fibres exhibited maximum hybrid effect than those having carbon/carbon fibres. This was attributed to the difference in the nature of fibre-matrix interface and the mechanical strength of the respective fibres incorporated in the composite.

Natural fibre reinforced hybrid composites are much more economic to produce than the synthetic fibre reinforced hybrid composites. Mohan and Kishore\textsuperscript{7} proved that glass skins, not only enhanced the mechanical properties of jute glass hybrid laminate but also protected the jute core from weathering. Pavithran and co-workers\textsuperscript{8,9} carried out detailed investigation on sisal/glass, coir/glass hybrid fibre reinforced polyester resin hybrid composites giving emphasis to the changes in hybrid design on the properties such as tensile and impact strengths and work of fracture. They found that hybridisation of sisal or coir with glass fibre could enhance the overall mechanical properties meanwhile improving the weathering
characteristics of sisal or coir fibre. The problem of weak interfacial adhesion and poor resistance to moisture absorption of natural fibre reinforced hybrid composites can be partly solved by modifying natural fibre surface with suitable chemical modifiers. The chemical reagents, which are normally used to give surface treatments to fibres in order to improve their compatibility with matrix, are called coupling agents. Varma and co-workers\textsuperscript{10,11} studied the effects of different coupling agents on the mechanical properties of jute and coir fibre reinforced thermoset composites. Ulkem and Schreiber\textsuperscript{12} used inverse chromatographic method to evaluate the acid/base interactions at interfaces of matrix and reinforcing fibres. They observed that mechanical interlocking (entanglement) was making a major contribution to the composite mechanical strength. Hoecker and Kocsis\textsuperscript{13} reported the effect of surface energies of carbon fibres on the mechanical performance of carbon fibre reinforced epoxy composite. Felin\textsuperscript{14} and Gatenholm\textsuperscript{15} analysed the effect of polypropylene-maleic anhydride (MAH-PP) modification on cellulosic fibre using graft polymerisation technique. Thomas and co-workers reported the effects of various treatments such as alkali, potassium permanganate (KMnO$_4$), dicumyl peroxide (DCP), silane, isocyanate, etc., on sisal, coir and pineapple, when they are used as reinforcements in natural rubber and polyethylene matrices.\textsuperscript{16,17}

In this chapter, present study, an effort was made to evaluate the tensile properties of intimately mixed short sisal/glass hybrid fibre reinforced low density polyethylene as a function of fibre length and various surface chemical modifications on the fibres as well as on the matrix. Treatments such as alkali, acetylation, stearic acid, permanganate (KMnO$_4$), silane, maleic anhydride and peroxides were tried in sisal/glass/LDPE hybrid composites so as to improve the overall performance in mechanical properties. The effect of simultaneous change in the length of both fibres (1-10 mm) was analysed.
5.2. Results and discussion

5.2.1 Fibre length distribution

Since the ultimate physical properties of composite materials are strongly dependent on fibre length, it is important to monitor the fibre length distribution and its changes during the processing operation. This will be helpful to identify the factors, which control fibre fracture under the shearing action of the mixing and extrusion device. Since the fibre phase in a composite material is polydispersed in length, it is necessary to characterise the system using two main length parameters widely used in the polymer field. Therefore the concept of a meaningful average fibre length is not suitable but two simple averages have been used. They are the number and weight average lengths, mathematically defined by the equations (5.1) and (5.2)

\[
\bar{L}_N = \frac{\sum N_i L_i}{\sum N_i}
\]  

(5.1)

\[
\bar{L}_W = \frac{\sum N_i L_i^2}{\sum N_i L_i}
\]  

(5.2)

where \(\bar{L}_N\) is the number average fibre length, \(\bar{L}_W\) is the weight average fibre length, \(N_i\) is the number of fibres having a particular length \(L_i\). The ratio of \(\bar{L}_W/\bar{L}_N\), called polydispersity index (PDI) is a measure of the fibre length distribution. As the fibre length distribution broadens, the value \(\bar{L}_W/\bar{L}_N\) is expected to increase. Table 5.1 represents the values of \(\bar{L}_N\), \(\bar{L}_W\), PDI and the change in PDI values of the fibres as a result of composite preparation. From Table 5.1 it can be noticed that both before and after composite preparation, \(\bar{L}_W\) is either same or slightly higher than \(\bar{L}_N\) values. This is an expected fact as can be seen from equations (5.1) and (5.2) itself. Moreover the difference between \(\bar{L}_W\) and \(\bar{L}_N\) is higher for the fibre system after composite preparation. These effects
came from the fact that when $L_N$ is sensitive to fibres with shorter lengths while $L_W$ is sensitive to those with higher lengths. However, for fibre system after composite preparation $L_W$ and $L_N$ are found to be lower than that before composite preparation. It is also important to mention that PDI value shows an increase for fibres after composite construction. This clearly indicates the extensive fibre breakage involved in the mixing, extrusion and moulding processes. Such a composite containing a polydispersed ungraded fibre system can be expected to be easily processable because smaller fibres can fill the interstitial sites between large fibres.

Table 5.1. Details of fibre breakage before and after processing the composite

<table>
<thead>
<tr>
<th>Designation</th>
<th>Fibres before processing</th>
<th>Fibres from composite</th>
<th>PDI difference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$L_N$ (mm)</td>
<td>$L_W$ (mm)</td>
<td>PDI</td>
</tr>
<tr>
<td>GRP (3 mm)</td>
<td>2.791</td>
<td>2.9144</td>
<td>1.0550</td>
</tr>
<tr>
<td>SRP (6 mm)</td>
<td>5.812</td>
<td>5.8690</td>
<td>1.0068</td>
</tr>
<tr>
<td>GRP (6 mm)</td>
<td>6.000</td>
<td>6.0000</td>
<td>1.0000</td>
</tr>
<tr>
<td>GSRP (sisal-6 mm)</td>
<td>5.924</td>
<td>5.9647</td>
<td>1.0068</td>
</tr>
<tr>
<td>GSRP (glass-6 mm)</td>
<td>6.000</td>
<td>6.0000</td>
<td>1.0000</td>
</tr>
</tbody>
</table>

Table 5.1 also shows that the maximum value of PDI of fibres from the composite is obtained for GRP composite while the minimum PDI is for SRP, both containing 6 mm fibres. This indicates that the extent of fibre breakage is more severe in glass fibre reinforced composites. Similarly Table 5.1 also reveals that the
percentage of glass fibre breakage is low in GSRP composites compared to that in GRP composites. This fact can be made clearer by taking difference in PDI values of fibres before and after composite preparation. The data also confirms the fact that the extent of glass fibre breakage is maximum in GRP containing 6 mm fibres and minimum in GRP containing 3 mm fibres. This fact emphasises that as the length of glass fibre increases, severe breakage results. Comparatively low PDI values of sisal in SRP and GSRP suggest the narrow fibre length distribution of sisal while higher values of PDI for glass fibres in GRP and GSRP indicate the broad fibre length distribution of glass fibres. The fibre length distribution curves of sisal (6 mm) and glass (6 mm) in GSRP composite are shown in Figures 5.1 and 5.2 respectively.

Figure 5.1. Fibre length distribution curves of sisal fibre from GSRP (50/50 composition of SRP/GRP) composites
Figure 5.2. Fibre length distribution curves of glass fibre from GSRP (50/50 composition of SRP/GRP) composites

It is observable from Figure 5.1 that the peak of the curves does not undergo much shift as a result of composite preparation but the curve as a whole shift to left side of the x-axis after mixing. A comparison of the Figures 5.1 and 5.2 reveals that the degree of shift from higher to a lower aspect ratio after composite preparation is higher for glass than sisal fibres. This is normally expected from the brittle nature of glass fibres. It is clear that sisal fibre also undergoes breakage as can be seen from the decrease in height of the peak in Figure 5.1. The monodispersed system of glass fibres before processing also is observable in Figure 5.2.

5.2.2 Tensile properties

5.2.2.1 Effect of fibre length

In short fibre reinforced polymer composites, the applied load is transmitted from matrix to the fibre through a shearing action at the fibre-matrix interface. Consequently tensile strength of these composites are greatly influenced by the
interfacial shear strength. This interfacial shear strength interturn depends on the critical fibre length or critical aspect ratio of the fibre, which is given by the equation below.

\[ l_c = \frac{\sigma_f r}{2\tau} \]  

(5.3)

where \( \sigma_f \) = Fracture strength of the fibre

\( r \) = Radius of the fibre

\( \tau \) = Shear strength of the fibre

\( l_c \) = Critical length of the fibre

In the case of a short fibre reinforced composite, there exists a critical aspect ratio for fibre at which the mechanical properties of the composite are maximised. But there are some conditions for a fibre to exhibit a critical aspect ratio in the composite. They are: (1) the shape of the fibre should be cylindrical in shape, (2) all fibres should be perfectly aligned in the load direction (longitudinal orientation), and (3) fibre to fibre contact should be absent in the composite. If these three conditions are not satisfied in the system under study the concept of critical aspect ratio turns meaningless. In order to study the effect of fibre length on the tensile properties of sisal/glass hybrid composites (GSRP), seven fibre lengths in the range of 1-10 mm were selected. GSRP composites with 50/50 composition of sisal and glass having an average fibre length, 1, 2, 3, 4, 6, 8 and 10 mm were prepared. Another set of SRP and GRP containing various fibre lengths also were prepared. The variation of tensile strength in longitudinal direction of SRP (20% sisal), GRP (20% glass) and GSRP (50/50 composition of SRP and GRP) as a function of different fibre lengths is shown in Figure 5.3. It has been observed that in the case of SRP, tensile strength increases with increase in fibre length and becoming maximum around 6-8 mm fibre length. For further increase in fibre length, the tensile strength decreases. As length of the sisal fibre increases, the chance of its curling also increases.
Fibre length (mm)

Figure 5.3. Influence of fibre length on tensile strength of SRP (20% sisal), GRP (20% glass) and GSRP (50/50 SRP/GRP) composites

The curly nature of fibres prevents the proper alignment of fibres (longitudinal direction) in the composites. This may be a possible reason for the reduction in tensile strength at higher fibre length. In addition to this, it has been observed that long sisal fibres owing to their curly nature, blocks the easy passage of extrudate at the die entrance of extruder. Therefore, long sisal fibres have many disadvantages as far as technological and processing aspects are concerned. The results of tensile behaviour of SRP at different fibre lengths shows that there exists an optimum fibre length between 6 to 8 mm, at which maximum tensile properties of the composite can be achieved. From Figure 5.3, the enhancement in tensile strength for GRP is found to be around 2-3 mm fibre length. Beyond 3 mm, it is seen that, the tensile strength is almost unchanged due to the severe breakage of glass fibres having higher length. Inherently glass fibres is too brittle in nature than sisal fibres, therefore glass fibres are more susceptible to failure or breakage during normal processing operations such as mixing, extrusion and moulding. The higher extent of glass fibre breakage compared to sisal and its direct dependence on the
length of the glass fibre is evidenced from the difference in $\bar{L}_W/\bar{L}_N$ values before and after composite processing shown in Table 5.1. Therefore in GRP, it is obvious that an optimum fibre length less than 3 mm is required for getting maximum improvement in tensile properties. However, in the case of GSRP (Figure 5.3) tensile strength increases as the length of the sisal and glass increases simultaneously, and the increase continues up to 6-8 mm range. The decrease in tensile strength after 8 mm length is due to the combined effects of curling of sisal fibre and severe breakage of glass fibres. The results from the Figure 5.3 clearly indicate that the tensile properties of intimately mixed sisal/glass hybrid composites are highly dependent on the length of sisal fibre. In this study, we have optimised the length of sisal and glass fibres for obtaining maximum tensile properties in GSRP as 6 mm. The tensile strength and Young's modulus, values of SRP, GRP, and GSRP at different fibre lengths are shown in Table 5.2.

Table 5.2. 
Tensile strength and Young's modulus values of composites with different fibre lengths

<table>
<thead>
<tr>
<th>Fibre length</th>
<th>Tensile strength (MPa)</th>
<th>Young's modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SRP (20%)</td>
<td>GRP (20%)</td>
</tr>
<tr>
<td>1</td>
<td>12.57</td>
<td>28.76</td>
</tr>
<tr>
<td>2</td>
<td>13.37</td>
<td>32.83</td>
</tr>
<tr>
<td>3</td>
<td>17.05</td>
<td>33.71</td>
</tr>
<tr>
<td>4</td>
<td>20.59</td>
<td>33.75</td>
</tr>
<tr>
<td>6</td>
<td>24.27</td>
<td>33.39</td>
</tr>
<tr>
<td>8</td>
<td>24.97</td>
<td>32.91</td>
</tr>
<tr>
<td>10</td>
<td>21.77</td>
<td>31.73</td>
</tr>
</tbody>
</table>
5.2.2.2 Effect of composition of fibres

The tensile properties of intimately mixed SRP (20%), GSRP [GSRP (1)-70/30 SRP/GRP, GSRP (2)-50/50 SRP/GRP, GSRP (3)-30/70 SRP/GRP], GRP (20%) at 6 mm fibre length are shown in Table 5.3. It is seen that as the volume fractions of glass increases tensile properties except elongation at break increases. The increase in tensile strength of GSRP hybrid composites is due to the higher tensile strength of glass fibre than sisal fibre and also due to the higher degree of dispersion of the sisal in presence of glass fibres. It is also noted that since glass fibres have comparatively less diameter, they can pack well in the interstitial spaces between irregularly spaced sisal fibres, leading to a close packed composite structure.

Table 5.3. Tensile property values of SRP, GRP and GSRP with 6 mm fibre length

<table>
<thead>
<tr>
<th>Designation</th>
<th>Tensile strength (MPa)</th>
<th>Young’s modulus (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SRP (20%)</td>
<td>24.23</td>
<td>714.285</td>
<td>6.1</td>
</tr>
<tr>
<td>GSRP (70/30)</td>
<td>27.86</td>
<td>800.33</td>
<td>5.3</td>
</tr>
<tr>
<td>GSRP (50/50)</td>
<td>29.75</td>
<td>1000.13</td>
<td>4.5</td>
</tr>
<tr>
<td>GSRP (30/70)</td>
<td>31.23</td>
<td>1136.36</td>
<td>3.7</td>
</tr>
<tr>
<td>GRP (20%)</td>
<td>33.98</td>
<td>1459.33</td>
<td>3</td>
</tr>
</tbody>
</table>

5.2.2.3 Effect of chemical modifications

Glass fibre is less reactive to modifying agents compared to sisal fibre because reactive groups are comparatively less in glass fibre. Hence chemical modifications are mainly concentrate on sisal fibre.
(a) **Effect of sodium hydroxide treatment (NaOH)**

The variation in tensile properties of GSRP as a function of sodium hydroxide concentration is shown in Figure 5.4. It is observed that there is an enhancement in tensile strength and Young's modulus on increasing the concentration of sodium hydroxide. The maximum tensile strength and modulus can be observed at 5% concentration of sodium hydroxide. On further increase of concentration up to 12%, there is a reduction in tensile properties. The reduction in tensile properties of GSRP with increase in the concentration of NaOH is due to the leaching out of lignin, which forms the backbone of sisal fibre. This can be confirmed by the increase in surface roughness of the treated fibres compared to untreated ones.

![Graph showing effect of NaOH concentration on tensile properties of GSRP](image)

*Figure 5.4. Effect of NaOH concentration on tensile properties of the GSRP (50/50 SRP/GRP) composites*
The scanning electron micrographs of untreated and alkali treated sisal fibre are shown in Figures 5.5a and 5.5b. As a result of alkali treatment, not only the thickness of the fibre is affected, but the surface of the fibre also becomes rough. The increase in surface roughness is due to the leaching out of alkali-soluble components like lignin, wax, fatty acids etc. Since 5% NaOH is taken as the optimum concentration. The tensile properties of 5% NaOH treated GSRP at different relative compositions of sisal and glass are presented in Table 5.4.

![SEM photographs of (a) untreated and (b) alkali treated sisal fibre.](image)

**Figure 5.5.** SEM photographs of (a) untreated and (b) alkali treated sisal fibre.

<table>
<thead>
<tr>
<th>Designation</th>
<th>Tensile strength (MPa)</th>
<th>Young’s modulus, (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GSRP (70/30)</td>
<td>31.26 (27.86)</td>
<td>831.27 (800.33)</td>
<td>5.1 (5.3)</td>
</tr>
<tr>
<td>GSRP (50/50)</td>
<td>31.83 (29.92)</td>
<td>1081.091 (1000.131)</td>
<td>4.3 (4.5)</td>
</tr>
<tr>
<td>GSRP (30/70)</td>
<td>31.45 (31.23)</td>
<td>1139.53 (1136.36)</td>
<td>3.4 (3.7)</td>
</tr>
</tbody>
</table>

Values in parenthesis correspond to the properties of untreated composites.
It is a general observation that alkali treatment improves the tensile properties of composite. The reason is attributed to the increased mechanical interlocking between alkali treated sisal fibres and polyethylene matrix. Considerable leaching out of soluble components on alkali treatment increases the effective surface area of the fibres by changing the shape of the fibres from less cylindrical to more ribbon like structure. The scanning electron micrographs of fracture surfaces of untreated and alkali treated hybrid composites are shown in Figures 5.6a and 5.6b. From the figure it is seen that agglomerates of glass fibres are formed in untreated composites. That is, dispersion of fibres is more uniform in alkali treated composites. Normally, agglomerates of fibres formed from a polydispersed ungraded system, such as that formed between glass and sisal are expected to vary a larger proportion of load. So the tensile properties are expected to be better for such a system. But the agglomerates formed between glass fibre alone will behave differently and therefore the agglomeration worsely affects the uniform dispersion of the fibres in the matrix. The enhancement in dispersion of fibres as a result of treatment is another contributing factor for the increase in tensile strength. Table 5.4 also reveals the fact that when the system is alkali treated, changes in relative composition of fibres in GSRP has no prominent effect in tensile strength and elongation at break. But the Young’s modulus is found to be improving as the glass fibre content increases.

Figure 5.6. SEM photographs of tensile fracture surfaces of (a) untreated and (b) alkali treated GSRP (50/50 SR/GRP) composites
(b) **Effect of acetylation of sisal fibres**

The influence of acetylation of sisal fibres on the tensile properties of GSRP is shown in Table 5.5. It is obvious that the tensile properties of GSRP composites with acetylated sisal are higher than that of untreated composites (values are in bracket). By the incorporation of acetylated sisal fibres, the strength of the GSRP at 70/30 composition is improved by 15%, that of 50/50 by 12% and that of 30/70 by 10%. This behaviour is due to the relative decrease in the concentration of acetylated sisal fibres from 70/30 to 30/70. The mechanism of the reaction between cellulosic -OH groups of sisal fibre and acetic anhydride is shown in Scheme 5.1.

<table>
<thead>
<tr>
<th>Designation</th>
<th>Tensile strength (MPa)</th>
<th>Young's modulus, (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GSRP (70/30)</td>
<td>32.23 (27.86)</td>
<td>919.53 (800.33)</td>
<td>5 (5)</td>
</tr>
<tr>
<td>GSRP (50/50)</td>
<td>32.86 (29.92)</td>
<td>1110.091 (1000.131)</td>
<td>4 (5)</td>
</tr>
<tr>
<td>GSRP (30/70)</td>
<td>31.51 (31.23)</td>
<td>1140.33 (1136.36)</td>
<td>3 (4)</td>
</tr>
</tbody>
</table>

Values in parenthesis correspond to the properties of untreated composites.

**Scheme 5.1. Mechanism of acetylation in sisal fibre**
The improvement in tensile properties of treated hybrid fibre composites is attributed to the presence of \(-\text{CH}_3\) groups in acetylated sisal fibre which paves the way for its better interaction with polyethylene. Methyl groups in acetylated sisal fibre being less polar compared to the \(-\text{OH}\) group in untreated sisal fibre, treated fibre will be much more compatible with an inherently non-polar matrix such as polyethylene. Moreover the decrease in the polarity of sisal fibre on acetylation manifests also as a reduction in its hydrophobicity. The change in chemical structure of the sisal fibre on acetylation was analysed using IR spectra (Figure 5.7). It is seen that intensity of \(-\text{OH}\) peak is reduced after acetylation as a result of esterification of the hydroxyl groups. Absorption band formed near 1740 cm\(^{-1}\) for acetylated sisal fibre indicates the strong carbonyl stretching frequency corresponding to the carbonyl linkage present in the ester group. Scanning electron micrographs of the surface of acetylated sisal fibre is shown in Figure 5.8.

**Figure 5.7.** IR spectrum of (a) untreated and (b) acetylated sisal fibre.
A hypothetical model of polyethylene-acetylated fibre interface is shown in Figure 5.9. So it is clear that, even though there is no direct chemical bonds binding acetylated sisal fibre and polyethylene, it is the increased hydrophobicity of sisal after treatment, which is responsible for the improvement in tensile properties.

Figure 5.9. Hypothetical chemical structure of acetylated GSRP composites in the interfacial area

The scanning electron micrographs of fracture surface of acetylated GSRP at 50/50 composition are shown in Figures 5.10a and 5.10b. Figure 5.10b shows the presence of polyethylene particles on the tip and surface of the acetylated sisal fibre. This indicates the better adhesion between acetylated sisal and polyethylene. Figure 5.10 also indicates that the dispersion of the sisal and glass fibres is very
much improved after the treatment. It is due to the formation of more viscous part in the system after incorporating the treated sisal fibres.

Figure 5.70. SEM photographs of tensile fracture surfaces of acetic anhydride treated GSRP (50/50 SRP/GRP) composites

(c) Effect of stearic acid treatment

Figure 5.11 shows the effect of varying concentration of stearic acid used in the treatment of sisal fibre, on the tensile properties of GSRP with 50/50 composition of SRP and GRP. It is evident from the figure that there is an enhancement in tensile strength and modulus on increasing the stearic acid concentration. From the figure it can be observed that maximum tensile strength is exhibited at 4% stearic acid concentration. The increase in tensile strength is due to the greater degree of dispersion of stearic acid treated sisal fibres, but above 4% concentration, stearic acid shows a worsening effect on the dispersion of fibres.

The surface of stearic acid treated sisal fibres was characterised by measuring the water retention value (WRV). Water retention value can be measured using the following method. A small quantity of untreated and treated sisal fibres (approx. 1 g) was taken in a test tube with 6 ml water and shaken thoroughly for 15 min. Thus the weight of wet fibres was measured ($W_1$). These
wet fibres were kept in an air oven at 90°C for 15 h to obtain the weight of dry fibres \((W_2)\). Then

\[
\text{Water Retention Value (WRV)} = \frac{W_1 - W_2}{W_2} \tag{5.4}
\]

From the Table 5.6 it is clear that the water retention values decrease steadily as the concentration of stearic acid increases. These results indicate that the surface of the fibre becomes more hydrophobic with increasing concentration of stearic acid used for the treatment. Stearic acid treatment increases the contact angle between the fibre surface and water and this factor decreases the wetting of fibre with water. Stearic acid imparts hydrophobic character to the sisal fibre which makes the sisal fibre more compatible with hydrophobic polyethylene.
Figure 5.12. **SEM photographs of tensile fracture surfaces of stearic acid treated GSRP (50/50) composites**

(d) **Effect of permanganate treatment (KMnO₄)**

Figure 5.13 shows the effect of permanganate concentration on the tensile properties of 50/50, GSRP composites. It is evident from the figure that permanganate treatment on sisal fibre improves tensile properties of GSRP, but the improvement is only up to 0.06 concentration of permanganate. Beyond 0.06% concentration, the properties show a drastic decrease. This is due to the degradation of sisal fibre during the treatment process.

Figure 5.13. **Effect of KMnO₄ concentration on tensile properties of GSRP (50/50) composites.**
Scanning electron micrograph of permanganate treated sisal fibre is shown in Figure 5.14. It is seen that permanganate treatment reduces the diameter of the sisal fibre considerably compared to untreated fibre shown in Figure 5.5a.

The improvement in the tensile properties as a result of treatment of sisal fibre can be explained in terms of the permanganate induced grafting of polyethylene on to sisal fibres. The mechanism of the reaction is shown Scheme 5.2.

The highly reactive MnO₄⁻ ion is responsible for initiating the graft reaction

$$KMnO_4 \rightarrow K^+ + MnO_4^-$$

$$\text{Cellulose-H} + MnO_4^- \rightarrow \text{Cellulose-H-O-Mn-O}^-$$

$$\text{Cellulose-H-O-Mn-O}^- \rightarrow \text{Cellulose}^+ + H-O-Mn-O^-$$

$$\text{Cellulose}^+ + PE \rightarrow \text{Cellulose-PE}$$

Scheme 5.2. Mechanism of the action of permanganate on sisal fibre

It is also clear from Figure 5.13 that the increase and decrease in properties observed as a result of concentration of permanganate is severe for Young’s modulus than for tensile strength. Table 5.8 describes the tensile properties of untreated (in brackets) and permanganate (0.06%) treated GSRP composites. It
indicates that permanganate treatment improves the tensile strength and modulus of GSRP with 70/30 sisal/glass composition by maximum extent (18 and 35% respectively). But the extent of increase decreases from 70/30 to 30/70. The scanning electron micrographs of tensile fracture surfaces of permanganate treated GSRP are shown in Figure 5.15. From the figure it has been observed that the dispersion of sisal and glass fibres is more uniform after treatment. This confirms the improvement in tensile properties of permanganate treated GSRP. It is also observable from the Figure 5.14 that broken end of treated sisal fibre is splitted due to strong interaction between sisal and polyethylene matrix.

Table 5.8. Tensile property values of permanganate (0.06 %) treated GSRP composites

<table>
<thead>
<tr>
<th>Designation</th>
<th>Tensile strength (MPa)</th>
<th>Young’s modulus (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GSRP (70/30)</td>
<td>32.97 (27.86)</td>
<td>1081.82 (800.33)</td>
<td>5 (5)</td>
</tr>
<tr>
<td>GSRP (50/50)</td>
<td>34.63 (29.92)</td>
<td>1182.24 (1000.131)</td>
<td>4 (5)</td>
</tr>
<tr>
<td>GSRP (30/70)</td>
<td>32.92 (31.23)</td>
<td>1152.56 (1136.36)</td>
<td>3 (4)</td>
</tr>
</tbody>
</table>

Values in parenthesis correspond to the properties of untreated composites.

Figure 5.15. SEM photographs of tensile fracture surfaces of KMnO₄ treated GSRP (50/50 SRP/GRP) composites.
(e) Effect of Maleic anhydride modifications (MAPE)

Figure 5.16 shows the effect of MAPE concentration on the tensile properties of GSRP with 50/50 composition of sisal and glass. It is seen that up to 8% concentration of MAPE, the tensile strength goes on increasing but above 8%, a decrease was observed. The initial increase in tensile properties is due to the dipolar interactions between anhydride groups of maleic modified polyethylene and cellulosic -OH groups. A similar interaction also may be formed between anhydride group of MAPE and -OH group present on the glass fibre surface. The mechanism of the reaction is shown in Scheme 5.3.

![Figure 5.16. Effect of MAPE concentration on tensile properties of GSRP (50/50 SRP/GRP) composites.](image)
Scheme 5.3. Mechanism of maleic anhydride modification on polyethylene

Infra-red spectra of unmodified and maleic modified polyethylene are shown in Figure 5.17. Spectra was recorded only after removing the unreacted maleic anhydride using acetone. A strong peak at 1640 cm\(^{-1}\) of MAPE indicates the stretching frequency of carbonyl groups of anhydride part present in the polymer. A hypothetical model of the interface between MAPE with cellulosic -OH of the sisal and -OH of the glass fibre is shown in Figure 5.18.

Table 5.9 shows the tensile properties of unmodified and maleic modified GSRP. It is clear that there is improvement in all the properties except elongation at break as a result of modification. It also shows that maximum improvement in properties except tensile strength was observed in the case of 70/30 composition of GSRP. As sisal content decreases, the degree of enhancement in tensile strength of GSRP also decreases.
Figure 5.17. IR spectrum of (a) unmodified and (b) maleic anhydride modified polyethylene

Figure 5.18. Hypothetical chemical structure of maleic anhydride modified interface between sisal or glass fibre and polyethylene matrix
Table 5.9. Tensile property values of MAPE treated GSRP composites

<table>
<thead>
<tr>
<th>Designation</th>
<th>Tensile strength (MPa)</th>
<th>Young’s modulus (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GSRP (70/30)</td>
<td>34.97 (27.86)</td>
<td>1139.32 (800.33)</td>
<td>5 (5)</td>
</tr>
<tr>
<td>GSRP (50/50)</td>
<td>36.23 (29.92)</td>
<td>1228.28 (1000.131)</td>
<td>4 (5)</td>
</tr>
<tr>
<td>GSRP (30/70)</td>
<td>35.35 (31.23)</td>
<td>1209.51 (1136.36)</td>
<td>3 (4)</td>
</tr>
</tbody>
</table>

Values in parenthesis correspond to the properties of untreated composites

The scanning electron micrograph of fracture surface of maleic modified GSRP is shown in Figure 5.19. Polyethylene traces sticking to the surface of fibres especially on glass fibre indicates strong adhesion between MAPE with sisal and glass fibre.

Figure 5.19. SEM photographs of tensile fracture surfaces of MAPE modified GSRP (50/50 SRP/GRP) composites

(f) Effect of silane treatment

The effect of silane treatment on tensile properties of GSRP with, 70/30/50/50 and 30/70 compositions of SRP and GRP are shown in Table 5.10.
In the case of 50/50 composition, the enhancement in tensile strength and modulus due to modification are by 24 and 45% respectively. In order to explain the mechanism of treatment action, a scheme has been provided as in Figures 5.20 and 5.22.

<table>
<thead>
<tr>
<th>Designation</th>
<th>Tensile strength (MPa)</th>
<th>Young’s modulus (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GSRP (70/30)</td>
<td>34.34 (27.86)</td>
<td>1185 (800.33)</td>
<td>4 (5)</td>
</tr>
<tr>
<td>GSRP (50/50)</td>
<td>37.035 (29.92)</td>
<td>1458.35 (1000.131)</td>
<td>4 (5)</td>
</tr>
<tr>
<td>GSRP (30/70)</td>
<td>38.98 (31.23)</td>
<td>1606.77 (1136.36)</td>
<td>3 (4)</td>
</tr>
</tbody>
</table>

Values in parenthesis correspond to the properties of untreated composites.

In these figures, silane is represented by a general formula YR-SiX₃ where Y is a functional group, R is an aliphatic linkage that serves to attach the functional organic group to silicon and X represents hydrolysable alkoxy groups bonded to silicon. For example, X is (-OCH₃) group in the silane [CH₂=C(CH₃)-COO(CH₂)₃Si(OCH₃)₃] used in this study. The mechanism of action of silane to sisal and glass are given below:

**Table 5.10. Tensile property values of silane treated GSRP composites**

**Figure 5.20. Hypothetical chemical structure of silane treated composites at the interfacial area of sisal fibre and polyethylene matrix**
Mechanism of action of silane to sisal fibre

The trace amount of bound moisture in the sisal fibre hydrolyse silanes to silanols

\[ \text{YR}_1 \text{SiX}_3 + \text{H}_2\text{O} \to \text{YR}_1\text{Si(OH)}_3 \quad \text{where} \quad \text{X} = \text{OR}_2 \]

The hydrolysed silanol first forms hydrogen bonds with-OH group of cellulose in the sisal fibre. The vinyl group present in the silane undergoes polymerisation in the presence of DCP and forms a long hydrophobic polymerised silane chain. This chain strongly interacts with the hydrophobic polyethylene matrix through van der Waals type of bonding. Thus silane forms a bridge at the interface of sisal and polyethylene matrix, and acts like a compatibiliser, which binds two incompatible polymers. A hypothetical model of the interface between the polyethylene matrix and sisal is shown the Figure 5.20.

Infrared spectra of untreated and silane treated sisal fibre is shown in Figure 5.21. It is seen that -OH peak intensity is reduced after silane treatment which indicates the reaction between cellulosic -OH group and silane. Peak at 1720 cm\(^{-1}\) of silane treated sisal indicates the carbonyl stretching frequency of ester group present in the silane. Silane treated sisal shows a peak at 820 cm\(^{-1}\) which confirms the presence of Si-O bond. The broad peak at 3400 cm\(^{-1}\) represents O-H stretching vibrations of the Si-OH group and cellulosic -OH group.

![IR spectrum of silane treated sisal fibre](image-url)
(ii) *Mechanism of action of silane to glass fibre*

Glass fibre consists of randomly distributed groups of oxides and the composition of these oxides are varied according to the grades of glass fibres. Glass fibre used in this study was E-glass and its composition is shown in Table 5.11. Some of the oxides such as SiO$_2$, Fe$_2$O$_3$, Al$_2$O$_3$, etc. are non-hygroscopic which absorb water only as hydroxyl group [E-OH, where E is Si, Fe, Al] and some other oxides are hygroscopic which absorbs molecular water. There are hydrogen bonds existing between these water molecules and -OH groups present in the glass fibre.

*Table 5.11. Different components and their content present in E-glass fibre*

<table>
<thead>
<tr>
<th>Name of the component</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>52.4</td>
</tr>
<tr>
<td>Al$_2$O$_3$, Fe$_2$O$_3$</td>
<td>14.4</td>
</tr>
<tr>
<td>CaO</td>
<td>17.2</td>
</tr>
<tr>
<td>MgO</td>
<td>4.6</td>
</tr>
<tr>
<td>Na$_2$O, K$_2$O</td>
<td>0.8</td>
</tr>
<tr>
<td>B$_2$O$_3$</td>
<td>10.6</td>
</tr>
</tbody>
</table>

The presence of -OH groups on the glass fibre has been reported in literature. The molecular water present in the glass fibre hydrolyse silanes to silanols (Figure 5.22a). These silanols form hydrogen bonding with -OH groups formed on the glass fibre surface (Figure 5.22b) as in the previous case. On drying the treated glass fibre, water is removed and a reversible reaction may be occurring between the silanol and the fibre surface. As a result of this condensation reaction,
a polysiloxane layer is formed on the glass fibre surface (Figure 5.22c). In other words, a chemisorbed layer of silane is formed on glass fibre surface while silane is physisorbed on polyethylene by van der Walls type of interactions (Figure 5.22d). The possibility of the above reaction mechanism has been already reported.\textsuperscript{19}

(a) \[ \text{YR—SiX}_3 + \text{H}_2\text{O} \rightarrow \text{YR—Si(OH)}_3 \]

(b) Glass fibre

(c) Glass fibre

(d) Glass fibre

Figure 5.22. The reaction mechanism silane treatment on glass fibre (a) hydrolysis of silane, (b) hydrogen bonding between hydrolysed silane and hydroxyl group on the glass surface, (c) formation of polysiloxane ring on the glass fibre surface, and (d) hypothetical chemical structure of glass/silane/polyethylene in the interfacial area.
Scanning electron micrographs of tensile fracture surfaces of silane treated GSRP is given in the Figure 5.23. It has been observed that both sisal and glass fibre pullout is less at the fracture surface, which confirms the fact that the presence of strong adhesion between silane treated sisal and glass fibre with polyethylene matrix. Figure 5.23 also reveals that silane treatment is more or less equally effective for both fibres to improve their adhesion with polyethylene matrix.

Figure 5.23. SEM photographs of tensile fracture surfaces of silane treated GSRP (50/50 SRP/GRP) composites

(g) Effect of peroxide [dicumyl (DCP) and benzoyl peroxide (BPO)] treatment

Figure 5.24 shows the effect of variation in peroxide concentration (DCP and BPO) on the tensile strength of GSRP, with 50/50 composition of SRP and GRP. It indicates that GSRP exhibits maximum tensile strength at 1% concentration of DCP and at 0.8% concentration of BPO. But further addition of peroxides to the system reduced the tensile strength. It is due to the crosslinking of LDPE, which increases the viscosity of the system considerably. This leads to a reduction in dispersion of fibres. The effect of DCP (1 %) and BPO (0.8 %) on the tensile properties of GSRP at three different composition of SRP and GRP are shown in Table 5.12. Comparison of the two treatments, revealed that tensile strength and Young’s modulus of BPO treated composites is superior to DCP treated composites. BPO has a higher decomposition rate and the decomposition takes place at a temperature of 80°C. But decomposition rate of DCP is low and its decomposition starts only at 140°C. Since the fibre mixing was carried out at a
temperature of 125°C, complete decomposition of DCP does not take place. The insufficient decomposition rate of DCP lowers its tensile properties.

Figure 5.24. Effect of variation of peroxide concentration on tensile properties of GSRP (50/50 SRP/GRP) composites

Table 5.12. Tensile property values of peroxide treated GSRP composites

<table>
<thead>
<tr>
<th>Designation</th>
<th>DCP treatment</th>
<th>BPO treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tensile strength (MPa)</td>
<td>Young’s modulus (MPa)</td>
</tr>
<tr>
<td>GSRP (70/30)</td>
<td>35.03 (27.86)</td>
<td>1303.7 (800.35)</td>
</tr>
<tr>
<td>GSRP (50/50)</td>
<td>38.84 (29.92)</td>
<td>1583.28 (1000.13)</td>
</tr>
<tr>
<td>GSRP (30/70)</td>
<td>40.73 (31.23)</td>
<td>1726.98 (1136.36)</td>
</tr>
</tbody>
</table>

Values in parenthesis correspond to the properties of untreated composites.
The increases in tensile properties of peroxide treated composites is attributed to the enhanced adhesion at the polymer fibre interface due to the peroxide initiated free radical reaction between LDPE matrix and fibres. The expected mechanism of the peroxide induced grafting is shown below.

\[
\begin{align*}
PO-OP & \rightarrow 2PO \cdot \\
PO \cdot + PE-H & \rightarrow POH + PE \cdot \\
PO \cdot + \text{glass-H} & \rightarrow POH + \text{glass} \cdot \\
PO \cdot + \text{sisal (cellulose-H)} & \rightarrow POH + \text{cellulose} \cdot \\
PE \cdot + \text{cellulose} \cdot + \text{glass} \cdot & \rightarrow \text{Cellulose-PE-glass} \\
PE \cdot + PE \cdot & \rightarrow \text{PE-PE}
\end{align*}
\]

Figures 5.25 and 5.26 are the scanning electron micrographs of the tensile fracture surfaces of DCP and BPO treated hybrid composites. The Figures 5.25a and 5.25b clearly show that polyethylene is penetrated into the sisal fibre as result of dicumyl peroxide induced grafting. It can also be observed that sisal suffers extensive delamination and splitting due to its strong adhesion with polyethylene matrix. The figures also reveal that the number of glass fibre pullouts is very much reduced after peroxide treatment, which is a clear indication of the strong adhesion between glass fibres and polyethylene matrix. It is also seen that due to the brittle nature of the glass fibres, they are not undergoing extensive delamination like sisal fibres. The delamination of sisal fibre confirms the fact that dicumyl peroxide treatment is more effective for the sisal-polyethylene than that of glass-polyethylene bonding. Figure 5.26 clearly shows that traces of polyethylene is sticking to the surface of glass fibre which indicates the presence of good bonding between glass fibre and polyethylene matrix in BPO treated composite. The figure also shows that fibre pullout is less in the case of sisal compared to glass fibre which again strongly emphasises that BPO treatment is more effective for sisal-polyethylene bonding.
(h) Comparative efficiency of different treatments

The effects of the different types of treatments (alkali, acetylation, stearic acid, KMnO4, maleic anhydride, silane, DCP, BPO) on tensile properties is compared in Figures 5.27 and 5.28. It is a general fact that every modification improves the tensile properties of the composites and as the volume fraction of glass in the system increases the tensile property slowly increases and then either drops or levels off. It is evident from these figures BPO, DCP and silane treated composites show better tensile properties. The efficiency of the different treatments varies in the following order alkali < acetylation < stearic acid < KMnO4 < MAPE < silane < DCP < BPO. The stress-strain curves of above untreated and treated
GSRP with 50/50 composition are depicted in Figure 5.29. It is seen that the yield stress is maximum for treated and minimum for untreated GSRP composites. It has also been seen that stiffness of the treated composites is higher than that of untreated composites.

Figure 5.27. Effect of chemical modifications on tensile strength of GSRP hybrid composites

Figure 5.28. Effect of chemical modifications on Young's modulus of GSRP hybrid composites
Figure 5.20. The effect of chemical modifications on stress-strain behaviour of GSRP (50/50) composites

5.3. References