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Effect of fibre length and chemical modifications on the tensile properties of intimately mixed short sisal/glass hybrid fibre reinforced low density polyethylene composites

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Abstract: Hybrid composites prepared by the incorporation of two or more different types of fibres into a single polymer matrix deserve much attention. This method of hybridisation of composites offers a profitable procedure for the fabrication of products while the resulting materials are noted for their high specific strength, modulus and thermal stability. The influence of the relative composition of short sisal/glass fibres, their length and distribution on the tensile properties of short sisal/glass intimately mixed polyethylene composites (SGRP) was examined. Different compositions of sisal and glass such as 70/30, 50/50 and 30/70 have been prepared with varying fibre lengths in the range of 1–10 mm. Emphasis has also been given to the variation of fibre–matrix adhesion with several fibre chemical modifications. Chemical surface modifications such as alkali, acetic anhydride, stearic acid, permanganate, maleic anhydride, silane and peroxides given to the fibres and matrix were found to be successful in improving the interfacial adhesion and compatibility between the fibre and matrix. The nature and extent of chemical modifications were analysed by infrared spectroscopy while improvement in fibre–matrix adhesion was checked by studying the fractography of composite samples using a scanning electron microscope. Assessment of water retention values has been found to be a successful tool to characterize the surface of the stearic acid modified fibres. It was found that the extent of improvement in tensile properties of SGRP varied with respect to the nature of chemical modifications between fibre and matrix. Improved mechanical anchoring and physical and chemical bonding between fibre and polyethylene matrix are supposed to be the reasons for superior tensile strength and Young's modulus in treated composites. Several secondary reasons such as high degree of fibre dispersion and reduced hydrophilicity in chemically modified fibres also are believed to play a role. Among the various chemical modifications, the best tensile strength and modulus was exhibited by the SGRP with benzoyl peroxide treated fibres. This is attributed to the peroxide-initiated grafting of polyethylene on to the fibres.

Keywords: sisal/glass hybrid; intimately mixed; fibre length; chemical modification

INTRODUCTION

In recent years, polymeric composites containing more than one type of fibrous reinforcement have gained great interest. This is because they yield excellent properties compared with those containing single reinforcements.[1–6] Hybrid composites possess many important characteristics such as high strength, high toughness, light weight, etc, making them ideal for engineering applications. At the same time, the cost can be substantially reduced by careful selection of reinforcements. The different types of hybrid composites and their properties have been reported in the literature[7,8] in detail. Pejis *et al*[7] investigated the influence of composition and adhesion level

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of polyethylene fibres on the mechanical properties of polyethylene/carbon hybrids with chromic acid treated polyethylene fibres. The system showed an improved impact performance that varied linearly with composition of carbon and polyethylene fibres. Improvement in adhesion level of the polyethylene fibre resulted in lower impact energies. Marom *et al*[8] investigated the hybrid effects in carbon/carbon and glass/carbon hybrid composites based on epoxy resin matrix. They found that the hybrid composite containing carbon and glass fibres exhibited a better hybrid effect than those having carbon/carbon fibres. This was attributed to the difference in the nature of the fibre–matrix interface and the mechanical strength of the respective fibres incorporated in the composite.

Investigation on lignocellulosic natural fibre reinforced polymer composites revealed that their properties can be more effectively utilized in their hybrid composites.[9–16] Moreover, the use of synthetic fibres such as carbon, kevlar, glass, etc, is very expensive compared with natural fibres. Natural fibre reinforced hybrid composites are much more economical to produce than the synthetic fibre reinforced hybrid composites. Mohan *et al*[13] reported that jute fibre could provide a reasonable core material in jute/glass hybrid laminate. They also proved that glass skins not only enhanced the mechanical properties but also protected the jute core from weathering. Pavithran and co-workers[9,10,16] carried out detailed investigation on sisal/glass and coir/glass hybrid fibre reinforced polyester resin hybrid composites giving emphasis to the effects of hybrid design on properties such as tensile and impact strength and work of fracture. They found that hybridisation of sisal or coir with glass fibre could enhance the overall mechanical properties while improving the weathering characteristics of sisal or coir fibre. However, lack of good interfacial adhesion and poor resistance to moisture absorption made the use of natural fibre reinforced hybrid composites less attractive. This problem can be partly solved by modifying the natural fibre surface with suitable chemical modifiers. It is well known that interfaces play a major role in deciding the physical and mechanical properties of the composites. In other words, the mechanical properties and environmental stability of the fibre reinforced polymer composites depend on the effectiveness of the interaction between fibre and matrix interface. Chemical, mechanical (interlocking or anchoring) and physical (acid/base type) interactions between fibre and matrix influence interfacial strength. The chemical reagents, which are normally used to give surface treatments to fibres in order to improve their compatibility with the matrix, are called coupling agents. It has been reported[17] that coupling agents perform different functions during their interaction with fibre and matrix. Many studies have reported on the fibre–matrix compatibility in hybrid as well as non-hybrid composites. Varma and co-workers[18–22] studied the effects of different coupling agents on the mechanical properties of jute and coir fibre reinforced nylon matrix. They used inverse chromatographic methods to evaluate the acid/base interactions at the interfaces of the matrix and reinforcing fibres. They also observed that mechanical interlocking (entanglement) made a major contribution to the composite mechanical strength. Wetting of polymer matrix on the surface of the fibre depends on the surface energy of the fibre. Hoecker and Karger-Kocsis[23] reported the effect of surface energetics of carbon fibres on the mechanical performance of carbon fibre reinforced epoxy composite. Many researchers[24,25] analysed the effect of polypropylene-maleic anhydride (MAH-PP) modification of cellulosic fibre using graft polymerisation techniques. The hybridisation effect of surface-treated mica and wood flour in polystyrene matrix on the mechanical properties was studied in detail by Maldas and Kokta.[14] They found that the treated wood/mica hybrid fibre reinforced polystyrene composites exhibited better properties than the untreated one. In another study they also analysed the compatibility of wood fibre (untreated and treated) with glass fibre in polystyrene matrix.[26] 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, pineapple and oil palm fibres, when they are used as reinforcements in natural rubber, polyethylene and phenol formaldehyde resin matrices.[27–31] All these studies reveal that chemical modification plays a major role in improving the overall performance of the composites.

We have already investigated the mechanical and thermal behaviour of intimately mixed and laminates of untreated short sisal/glass hybrid fibre reinforced low density polyethylene (LDPE) composites by giving emphasis to the orientation and composition of the fibres.[32–34] It was found that the composites containing longitudinally oriented fibres exhibit better mechanical properties than those with randomly oriented fibres. It is also an established fact that intimately mixed hybrid composites perform better than sandwich types in tensile properties. However, the flexural property of the latter are superior to intimately mixed hybrid composites. Hybrid effects were calculated using the additive rule of hybrid mixtures. The sandwich type and intimately mixed hybrid composites exhibited a negative and positive hybrid effect respectively in their tensile properties. However, an opposite situation was observed in the case of flexural behaviour.

In the present study, an effort was made to evaluate the tensile properties of intimately mixed short sisal/glass hybrid fibre reinforced LDPE as a function of fibre length and various surface chemical modifications on the fibre as well as the matrix. The effect of simultaneous changes in the length of both fibres (1–10 mm) was analysed. Sisal fibre is leaf fibre of high cellulosic content obtained from the plant *Agave sislana* and its hydrophilicity is very much greater than that of glass fibre (E-glass). Therefore the

compatibility of sisal fibre with inherently hydrophobic polyethylene can be expected to be lower than that of glass fibre with polyethylene. In order to enhance the compatibility between fibres and polymer, especially between sisal and polyethylene, it is essential to pretreat or modify the sisal and glass fibres, so that the interfacial adhesion can be increased. Treatments with reagents such as alkali, acetic anhydride, 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.

EXPERIMENTAL

Materials

LDPE granules obtained from M/S Indian Petrochemicals Corporation Ltd, Baroda, India was used. The long glass fibre roving and chopped glass fibres (6 mm) were supplied by Ceat Ltd, Hyderabad, India. Sisal fibre was obtained from local sources. The main physical characteristics and mechanical properties of these materials are listed in Tables 1 and 2.

Silane A 174 [$CH_2{=}C(CH_3){-}COO(CH_2)_3Si(OCH_3)_3$] was supplied by Union Carbide Co, Montreal, Canada. DCP and benzoyl peroxide (BPO) were obtained from BDH Chemicals, Poole, UK. Other reagents such as stearic acid, acetic acid, acetic anhydride, sodium hydroxide, potassium permanganate, maleic anhydride, etc, used in the study were of reagent grade.

The sisal fibre was washed with water and dried in an air oven at 60 °C for 5 h, before being chopped into the desired length for the fibre treatment and composite preparation. The details of different treatments are given below.

Table 1. Physical characteristics and mechanical properties of LDPE

Property	Value
Melt flow index g (10 min)$^{-1}$	40.0
Density (g cm^{-3})	0.918
Vicat softening point (°C)	85.0
Crystalline point (°C)	104
Tensile strength (MPa)	8.5
Modulus of elasticity (MPa)	130
Elongation at break (%)	110

Table 2. Physical characteristics and mechanical properties of sisal fibre and glass fibre

Fibre	Density (g cm^{-3})	Tensile strength (GPa)	Young's Modulus (GPa)	Elongation at break (%)	Diameter (μm)
Sisal	1.441	0.4–0.7	9–20	5–14	100–300
Glass	2.54	1.7–3.5	65–72	3	5–25

Fibre treatments

Sodium hydroxide treatment

The chopped sisal fibres were dipped in a solution of NaOH (2, 5, 10 and 12 %) with constant stirring for 30 min. Fibres were then taken out, repeatedly washed with distilled water and finally with water containing a little acid (dil. HCl). Then they were dried in an air oven at 50 °C for 6 h.

Acetylation (using acetic anhydride)

10 g sisal was kept soaked in glacial acetic acid for 1 h at room temperature. The acid was then decanted and soaking was continued in acetic anhydride (50 ml) containing two drops of concentrated sulphuric acid for 10 min. The fibre was separated using a buchner funnel, washed with water and dried in an air oven at 50 °C for 24 h.

Permanganate ($KMnO_4$) treatment

The alkali-treated sisal fibres were dipped in acetone solution of $KMnO_4$ having different concentrations (0.02, 0.04, 0.06, 0.1, 0.15, 0.2 %) for 2 min. Fibres were then separated and dried in an air oven under the same conditions mentioned above.

Stearic acid treatment

A solution of stearic acid in ethyl alcohol having different concentrations (1, 2, 3, 4, 5, 6, and 7 % by weight of fibre) was added dropwise into the sisal fibres with continuous stirring. The fibres were then dried in an air oven at 95 °C for 1 h.

Peroxide treatment

BPO (0.2–1.8 % by weight of polymer) and DCP (0.2–1.6 % by weight of polymer) treatments were done by a solution mixing technique using toluene as the solvent. Respective peroxides were added into a molten mass of polyethylene at the time of mixing with the fibres.

Silane treatment of sisal fibre

10 g of oven-dried and alkali-treated sisal fibre was mixed with silane (5 % by weight of fibre), carbon tetrachloride and (DCP) (2.5 % by weight of the fibre). The mixture was heated under reflux with continuous stirring for 2 h. The fibre was filtered and dried in an air oven for 2 h.

Silane treatment of glass fibre

A solution of silane coupling agent was prepared in 0.1 M acetic acid (concentration of silane was 0.5 weight %). The chopped glass fibres were dipped into this solution and then dried at 100 °C for 20 min. The fibres were subsequently rinsed with sufficient quantity of methanol to remove physisorbed silane from the glass surface. The fibres were then dried in an air oven at 50 °C for 2 h.

Maleic anhydride modification–preparation of maleic modified polyethylene (MAPE)
MAPE was prepared by the melt mixing of LDPE (100 g) with maleic anhydride (5 g) and BPO (0.3 g). The melt mixing was carried out in a Brabender Plasticorder at 125 °C and 60 rpm.

MAPE treatment
Different percentages of MAPE (1, 2, 4, 6, 8, 10, 12 and 14 % by weight of LDPE) were added to the melt of polyethylene during its solution mixing with fibres.

Preparation of composite sheets
Intimately mixed sisal/glass polyethylene blends were prepared by a solution mixing technique. The fibres were mixed with a slurry of LDPE using toluene as the solvent at 125 °C. In order to avoid agglomeration of fibres during mixing, glass fibres were added first to the slurry, followed by sisal fibres. The solvent was removed from the mix by evaporation. The dry mix was then extruded through a ram type hand extruder at a temperature of 125 ± 3 °C. The extrudates had diameters of 4 mm and were collected and aligned in a rectangular mould. They were then compression moulded at a pressure of about 70 MPa at a temperature of 125 ± 3 °C. The composite sheets so obtained were removed from the mould after cooling the mould below 50 °C. Rectangular slabs having size 120 × 26.5 × 2.5 mm were cut from the above composites for tensile testing. The terms SRP, GRP, SGRP used in this study correspond to sisal reinforced polyethylene, glass reinforced polyethylene and intimately mixed sisal/glass reinforced polyethylene composites respectively.

Tensile testing
Tensile testing of the hybrid composites was carried out on Zwick 1465 Universal Testing Machine (UTM) at a crosshead speed of 50 mm min^{-1} and a gauge length of 50 mm. A standard UTM tensile test programme was used to evaluate tensile properties such as ultimate tensile strength, Young's modulus and elongation at break. At least six specimens were tested for each composite and mean values were reported.

Infrared spectroscopy analysis
A Schimadzu IR-490 spectrophotometer was used to analyse the changes in the chemical structure of fibres with various types of treatments. Powdered fibre palletised with potassium bromide was used for recording the spectra.

Scanning electron microscopy (SEM) studies
Tensile fractography of composites was carried out using SEM (JEOL JSM 35 model). Fibre breakage analysis was carried out using an ordinary travelling microscope.

RESULTS AND DISCUSSION
Fibre length distribution
The fibre length distribution curves of sisal (6 mm) and glass (6 mm) in SGRP composite are shown in Fig 1. The lengths of the fibres were averaged on 100 representative items. It is seen that the fibre breakage during processing of the composite is more in the case of glass fibre due to its brittle nature than that of sisal fibre. In the case of sisal fibres different fibre lengths along with 6 mm are observed before mixing, which is due to the hand cutting of these fibres while 6 mm chopped glass fibres are obtained by machine cutting of the glass fibre roving.

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

$$L_c = \frac{\sigma_f r}{2\tau} \quad (1)$$

where σ_f is the fracture strength of the fibre, r is the radius, τ is the shear strength and L_c is the critical length of the fibre.

In the case of a short fibre reinforced composite, there exists a critical aspect ratio for the fibre at which the mechanical properties of the composite are maximized. But there are some conditions for a fibre to exhibit a critical aspect ratio in the composite. They are: (i) the shape of the fibre should be cylindrical; (ii) all fibres should be perfectly aligned in the load direction (longitudinal orientation); and (iii) 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 is meaningless.

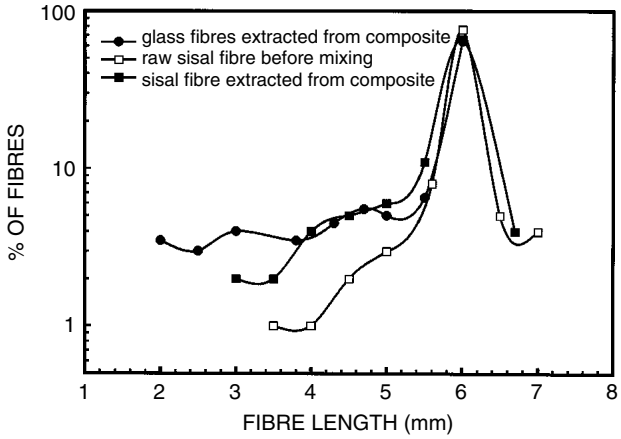


Figure 1. Fibre length distribution curve of sisal and glass fibre from SGRP (sisal/glass composition is 50/50) composites.

In order to study the effect of fibre length on the tensile properties of SGRP composites seven fibre lengths in the range of 1–10 mm were selected. SGRP composites with 50/50 composition of sisal and glass having an average fibre length of 1, 2, 3, 4, 6, 8 and 10 mm were prepared. Sets of SRP and GRP containing various fibre lengths were also prepared. The variation of tensile strength in longitudinal direction of SRP (20 % sisal), GRP (20 % glass) and SGRP (50/50 composition of SRP and GRP) as a function of different fibre lengths is shown in Fig 2. It has been observed that, in the case of SRP, tensile strength increases with increasing fibre length and reaches a maximum at 6–8 mm fibre length. For further increase in fibre length the tensile strength decreases. As the length of sisal fibre increases, the chance of its curling increases. The curly nature of fibres prevents the proper alignment of fibres in the (longitudinal direction) 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, block 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 enhancement in tensile strength for GRP is found to be around 2–3 mm fibre length. Beyond 3 mm, the tensile strength remains almost unchanged due to the severe breakage of glass fibres having higher length. As glass fibres are more brittle than sisal fibres, they are more susceptible to failure or breakage during normal processing operations such as mixing, extrusion and moulding. Therefore in GRP it is obvious that an optimum fibre length of less than 3 mm is required for getting maximum improvement in tensile properties. However, in the case of SGRP the decrease of 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 Fig 2 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 seen that the most probable length of sisal and glass fibres for obtaining maximum tensile properties in SGRP is 6 mm.

Effect of composition of fibres on tensile properties

The tensile properties of intimately mixed SRP (20 %), SGRP and GRP (20 %) at 6 mm fibre length are shown in Table 3. It is seen that as the volume fractions of glass increases, tensile properties except elongation at break increase. The increase in tensile strength of SGRP hybrid composites is due to the higher tensile strength of glass fibre than sisal fibre (Table 2) and also to the higher degree of dispersion of the sisal in the presence of glass fibres.[32,33] It is also noted that since glass fibres have a smaller diameter, they can pack well in the interstitial spaces between irregularly spaced sisal fibres, leading to a close-packed composite structure.

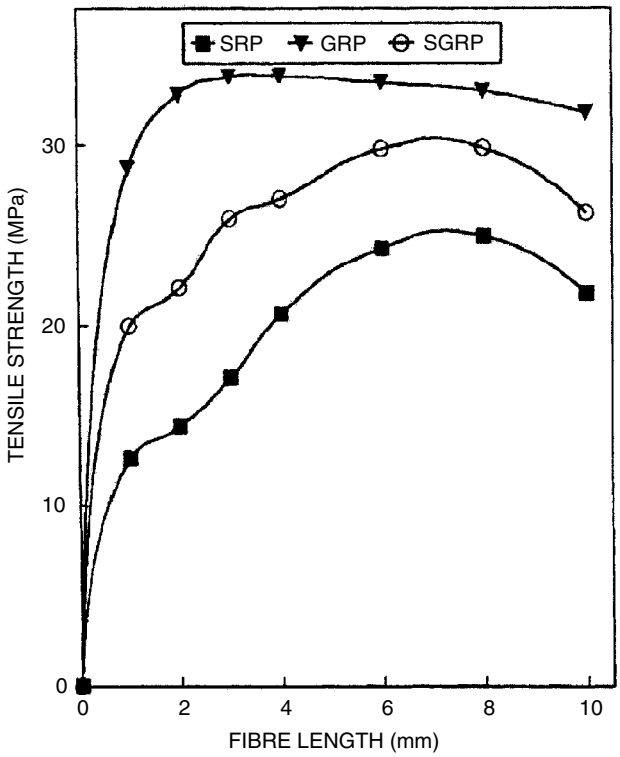


Figure 2. Influence of fibre length on tensile strength of composites (20 % sisal in SRP, 20 % glass in GRP and 50/50 sisal/glass composition in SGRP).

Table 3. Tensile properties of SRP, SGRP and GRP composites with 6 mm fibre length

Composite	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)
SRP (20 %)	24.23	714.285	6
SGRP (sisal/glass-70/30)	27.86	800.33	5
SGRP (sisal/glass-50/50)	29.75	1000.13	5
SGRP (sisal/glass-30/70)	31.23	1136.36	4
GRP (20 %)	33.98	1459.33	3

Effect of chemical modifications on tensile properties

Effect of sodium hydroxide treatment

The variation in tensile properties of SGRP as a function of sodium hydroxide concentration is shown in Fig 3. It is observed that there is an enhancement in tensile strength and Young's modulus with increasing concentration of sodium hydroxide. The maximum tensile strength and modulus can be observed at 5 % NaOH. This may be due to the increase in surface roughness of the sisal fibre as a result of leaching out of alkali-soluble such as components lignin, wax and fatty acids. On further increase of concentration up to 12 % there is a reduction in tensile properties, due to the extensive leaching out of lignin, which forms the backbone of sisal fibre. Hence 5 % NaOH is taken as the optimum concentration in this study.

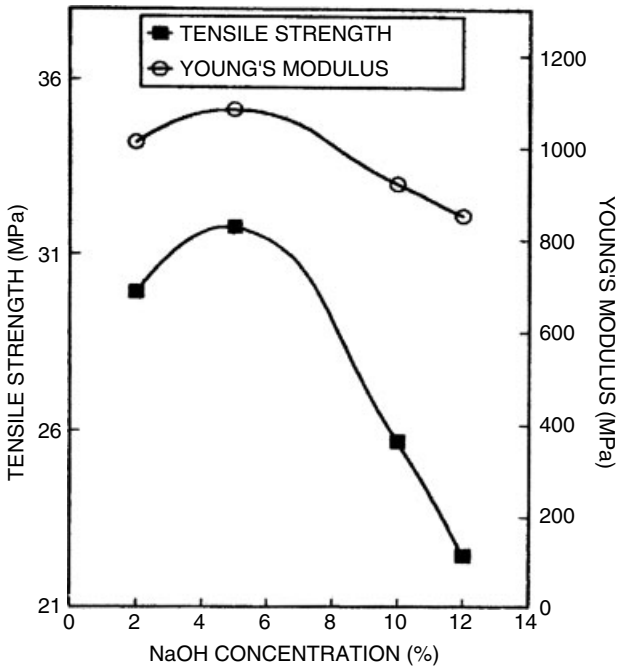
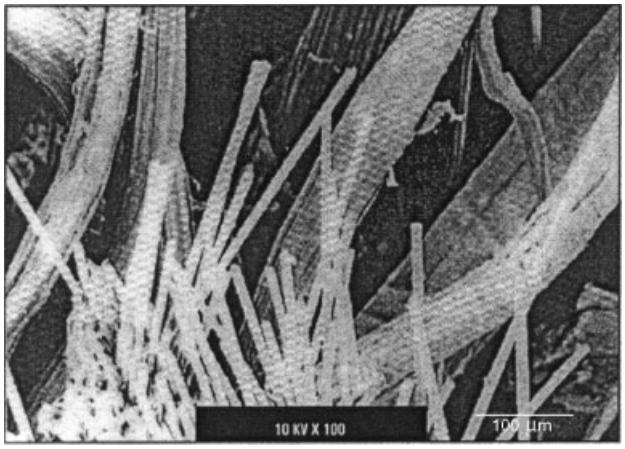


Figure 3. Effect of NaOH concentration on tensile properties of SGRP composites (sisal/glass composition is 50/50 and fibre length is 6 mm).

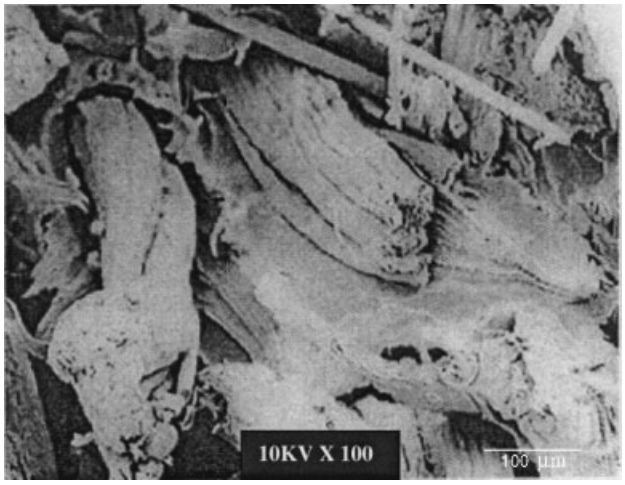
Table 4. Tensile properties of alkali treated SGRP composites; values in parentheses give the properties of untreated composites

Composite	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)
SGRP (sisal/glass-70/30)	31.26	831.27	5
	(27.86)	(800.33)	(5)
SGRP (sisal/glass-50/50)	31.83	1081.091	4
	(29.92)	(1000.131)	(5)
SGRP (sisal/glass-30/70)	31.45	1139.53	3
	(31.23)	(1136.36)	(4)

The tensile properties of 5 % NaOH treated SGRP at different relative compositions of sisal and glass are presented in Table 4. It is a general observation that alkali treatment improves the tensile properties of a composite, which is attributed to the increased mechanical interlocking between alkali treated sisal fibres and polyethylene matrix. The scanning electron micrographs of fracture surfaces of untreated and alkali treated hybrid composites are shown in Fig 4 it is seen that agglomerates of glass fibres are formed in untreated composites. The dispersion of fibres is more uniform in alkali treated composites. Normally, agglomerates of fibres formed from a polydispersed ungraded system, such as those formed between glass and sisal, are expected to carry a largest proportion of load. So the tensile properties are expected to be better for such system. However, the agglomerates formed between glass fibre alone will behave differently and therefore the agglomeration badly affects the uniform dispersion of fibres in the matrix. The enhancement in dispersion of fibre as a result of treatment is another contributing factor to the increase in tensile



(a)



(b)

Figure 4. SEM photographs of tensile fracture surfaces of (a) untreated and (b) alkali treated SGRP composites (sisal/glass composition is 50/50 and fibre length is 6 mm).

strength. Table 4 also reveals that when the system is alkali treated, changes in relative composition of fibres in SGRP have no significant effect on tensile strength or elongation at break. However, the Young's modulus was found to improve as the glass fibre content increased.

Effect of acetylation of sisal fibres

The influence of acetylation of sisal fibres on the tensile properties of SGRP is shown in Table 5. It is obvious that the tensile properties of SGRP composites with acetylated sisal are higher than those of the untreated composites. By the incorporation of acetylated sisal fibres, the strength of the SGRP at 70/30 composition 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 improvement in tensile properties of treated hybrid fibre composites is attributed to the presence of —CH_3 groups in acetylated sisal fibre, which paves the way for its better interaction with polyethylene. The methyl groups in acetylated sisal fibre are less polar than the —OH groups in untreated

Table 5. Tensile properties of acetylated SGRP composites; values in parentheses give the properties of untreated composites

Composite	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)
SGRP (sisal/glass-70/30)	32.23	919.53	5
	(27.86)	(800.33)	(5)
SGRP (sisal/glass-50/50)	32.86	1110.091	4
	(29.92)	(1000.131)	(5)
SGRP (sisal/glass-30/70)	31.51	1140.33	3
	(31.23)	(1136.36)	(4)

sisal fibre, and treated fibre will thus 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 (Fig 5). It is seen that the intensity of the —OH peak is reduced after acetylation as a result of esterification of the hydroxyl groups. The absorption band formed near 1740 cm^{-1} for acetylated sisal fibre indicates the strong carbonyl stretching frequency corresponding to the carbonyl group present in the ester group. So it is clear that, even though there is no direct chemical bond binding acetylated sisal fibre and polyethylene, it is the increased hydrophobicity of sisal after treatment that is responsible for the improvement in tensile properties.

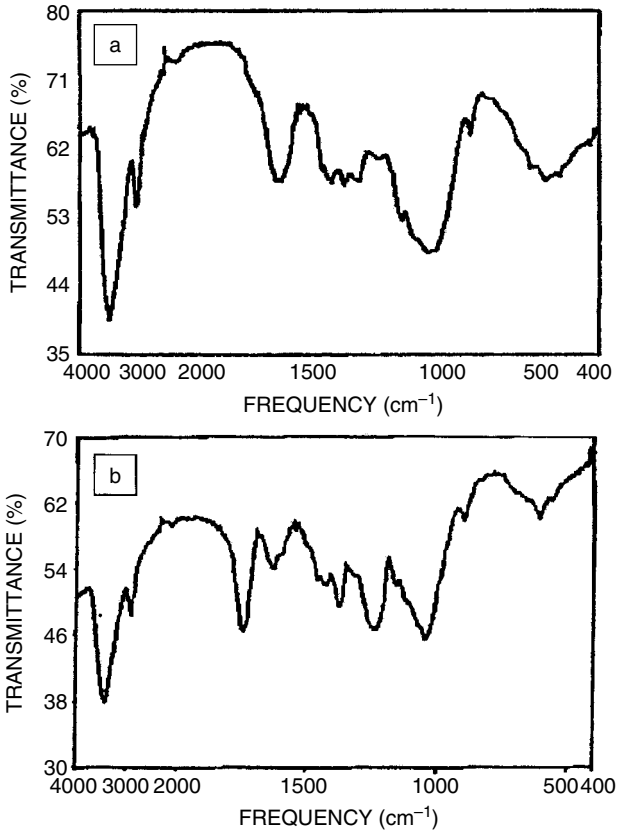
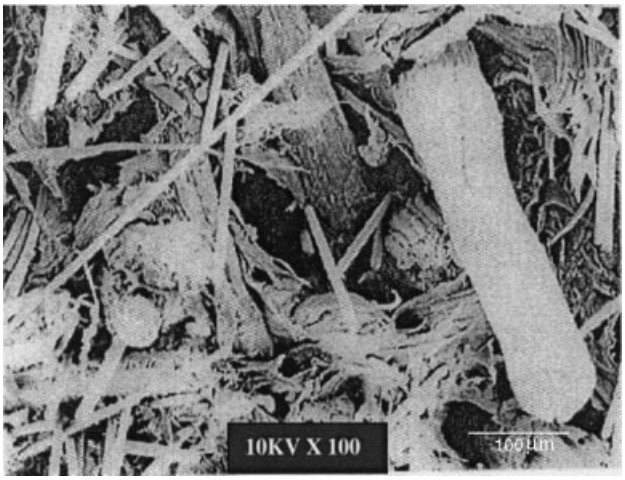
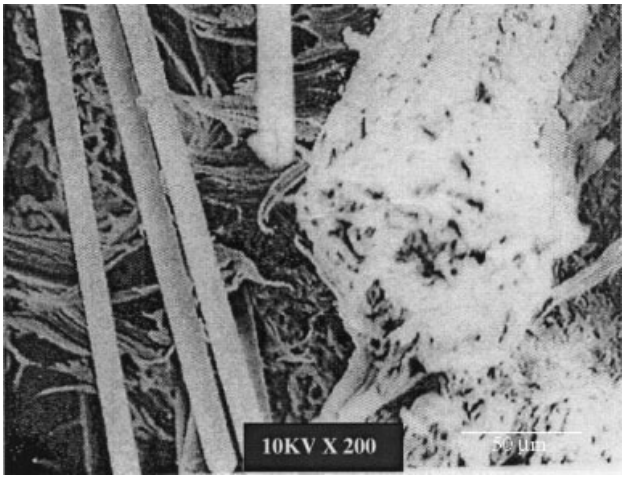


Figure 5. IR spectra of (a) untreated and (b) acetylated sisal fibre.



(a)



(b)

Figure 6. SEM photographs of tensile fracture surfaces of acetic anhydride treated SGRP composites (sisal/glass composition is 50/50 and fibre length is 6 mm) at two magnifications.

Scanning electron micrographs of fracture surface of acetylated SGRP at 50/50 composition are shown in Fig 6. Figure 6b shows the presence of polyethylene particles on the tip and surface of the acetylated sisal fibre. This indicates the better interaction between acetylated sisal and polyethylene.

Effect of stearic acid treatment

Figure 7 shows the effect of varying concentrations of stearic acid used in the treatment of sisal fibre on the tensile properties of SGRP with 50/50 composition of SRP and GRP. It is evident from the figure that there is an enhancement in tensile strength and modulus with increasing stearic acid concentration, with the maximum tensile strength at 4 % 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 has a worsening effect on the dispersion of fibres. The surface of stearic acid treated sisal fibres was characterized by measuring the water retention value (WRV) using the following method. A small quantity of untreated and treated sisal fibres (approximately 1 g) was placed in a test tube

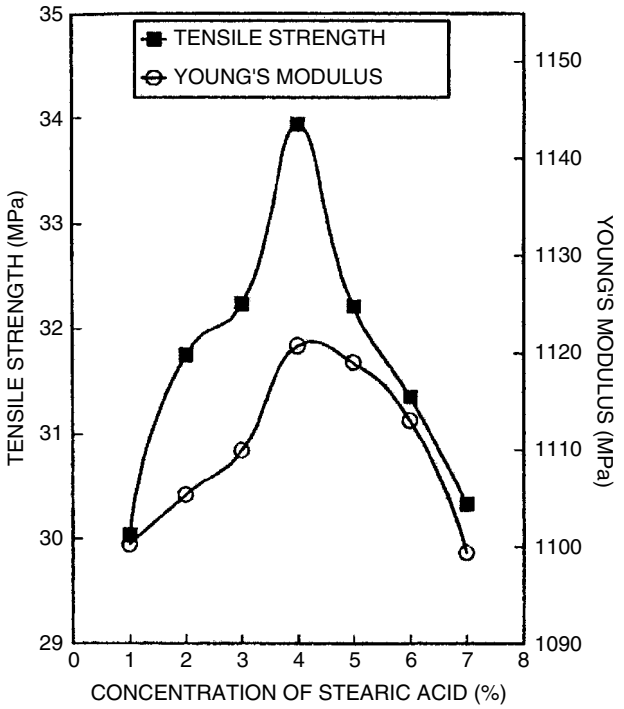


Figure 7. Effect of stearic acid concentration on tensile properties of SGRP composites (sisal/glass composition is 50/50 and fibre length is 6 mm).

with 6 ml water and shaken thoroughly for 15 min. The weight of wet fibres was measured (W_1). These fibres were kept in an air oven at 90 °C for 15 h to obtain the weight of dry fibres (W_2). Then

$$\mathrm{WRV} = W_1 - W_2/W_2 \qquad (2)$$

From Table 6 it is clear that the WRVs 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. 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. Table 7 shows the tensile property values of untreated and 4 % stearic acid treated SGRP hybrid composites. It shows that tensile strength and modulus values of treated

Table 6. Water retention values of stearic acid treated sisal fibres at different concentrations of stearic acid

Concentration of stearic acid (wt%)	Weight of wet fibres, W_1 (g)	Weight of dry fibres, W_2 (g)	WRV, $W_1 - W_2/W_2$
0	5.0372	1.2373	3.0711
1	4.5511	1.2215	2.7258
2	4.3431	1.2193	2.5619
3	4.3201	1.2150	2.5556
4	4.2711	1.2103	2.5289
5	4.1981	1.2097	2.4703
6	4.0799	1.2093	2.3737

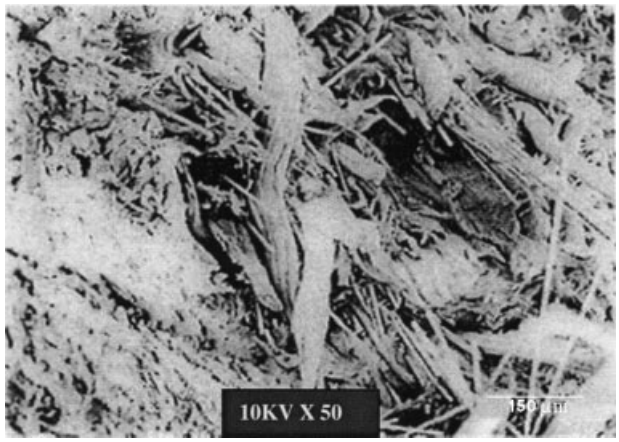
Table 7. Tensile properties of 4 wt% stearic acid treated SGRP composites; values in parentheses give the properties of untreated composites

Composite	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)
SGRP (sisal/glass-70/30)	32.79	1000.78	5
	(27.86)	(800.33)	(5)
SGRP (sisal/glass-50/50)	33.93	1120.78	4
	(29.92)	(1000.131)	(5)
SGRP (sisal/glass-30/70)	31.93	1141.64	4
	(31.23)	(1136.36)	(4)

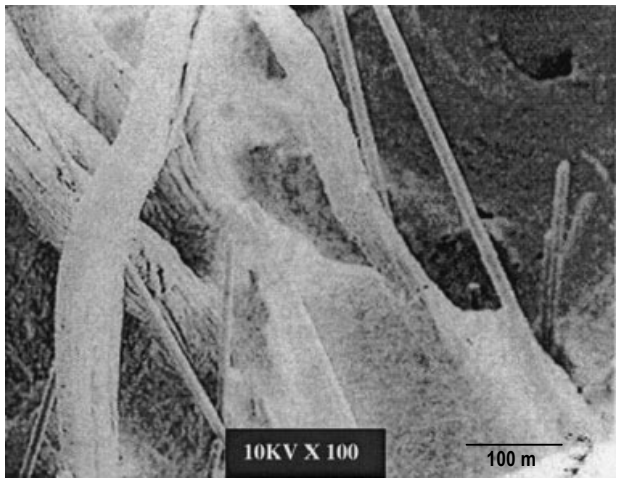
50/50 SGRP are higher than those of 70/30 and 30/70 composites. The scanning electron micrographs of stearic acid treated SGRP with 50/50 composition are shown in Fig 8. It is observed that good fibre dispersion is obtained in stearic acid treated composites.

Effect of permanganate ($KMnO_4$) treatment

Figure 9 shows the effect of permanganate concentration on the tensile properties of 50/50 SGRP



(a)



(b)

Figure 8. SEM photographs of tensile fracture surfaces of stearic acid treated SGRP composites (sisal/glass composition is 50/50 and fibre length is 6 mm) at two magnifications.

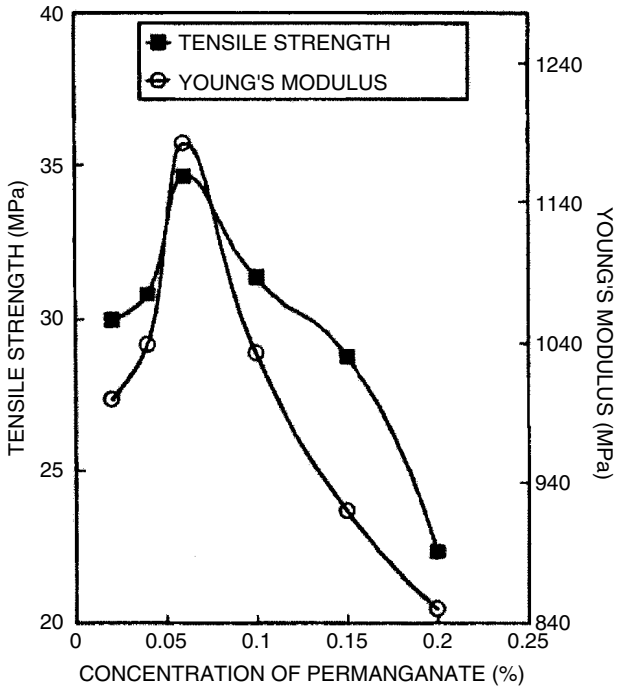


Figure 9. Effect of $KMnO_4$ concentration on tensile properties of SGRP composites (sisal/glass composition is 50/50 and fibre length is 6 mm).

composites. It is evident from the figure that permanganate treatment of sisal fibre improves tensile properties of SGRP, 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. The improvement in 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 as follows. The highly reactive MnO_4^- ion is responsible for initiating the graft reaction.

It is also clear from Fig 9 that the increase and decrease in properties observed as a result of concentration of permanganate is even more severe for Young's modulus than for tensile strength. Table 8 describes the tensile properties of untreated and permanganate (0.06 %) treated SGRP composites. It indicates that permanganate treatment improves the tensile strength and modulus of SGRP with 70/30 sisal/glass composition by the greatest amount (18 and 35 % respectively). The extent of increase decreases from 70/30 to 30/70. The scanning electron micrographs of tensile fracture surfaces of permanganate treated SGRP are shown in Fig 10. From the figures it has been observed that the dispersion of sisal and glass fibre is more uniform after treatment. This confirms the improvement in tensile properties of permanganate treated SGRP. It is also observable from Fig 10 that broken end of treated sisal fibre is split due to strong interaction between sisal and polyethylene matrix.

Table 8. Tensile properties of permanganate (0.06 wt%) treated SGRP composites; values in parentheses give the properties of untreated composites

Composite	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)
SGRP (sisal/glass-70/30)	32.97	1081.82	5
	(27.86)	(800.33)	(5)
SGRP (sisal/glass-50/50)	34.63	1182.24	4
	(29.92)	(1000.131)	(5)
SGRP (sisal/glass-30/70)	32.92	1152.56	3
	(31.23)	(1136.36)	(4)

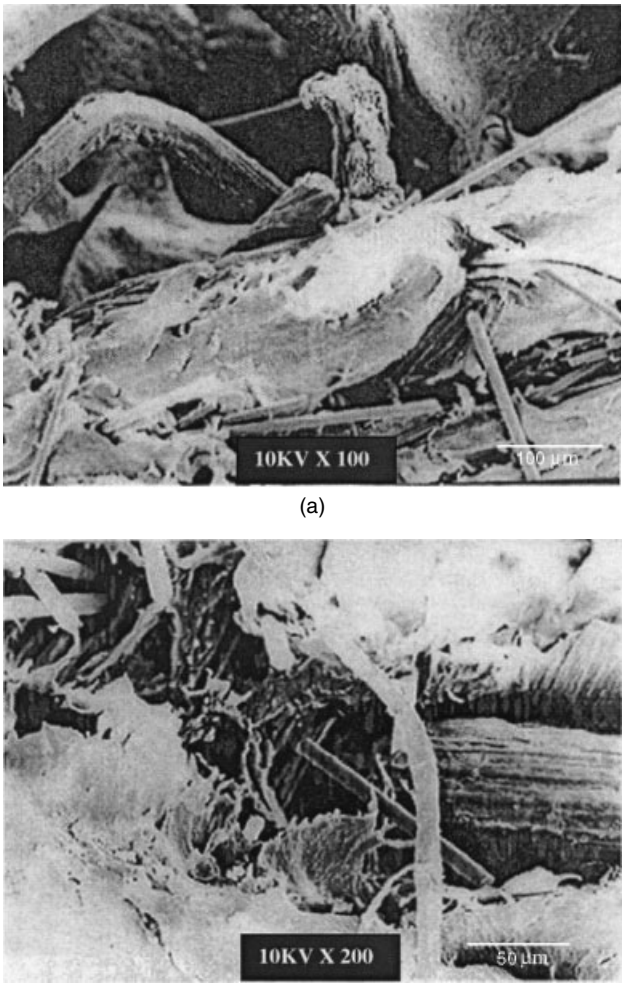


Figure 10. SEM photographs of tensile fracture surfaces of $KMnO_4$ treated SGRP composites (sisal/glass composition is 50/50 and fibre length is 6 mm) at two magnifications.

Effect of maleic anhydride modifications (MAPE)

Figure 11 shows the effect of MAPE concentration on the tensile properties of SGRP 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 is observed. The initial increase in tensile properties is due to the dipolar interactions between anhydride groups of MAPE and cellulosic —OH groups. Also, a

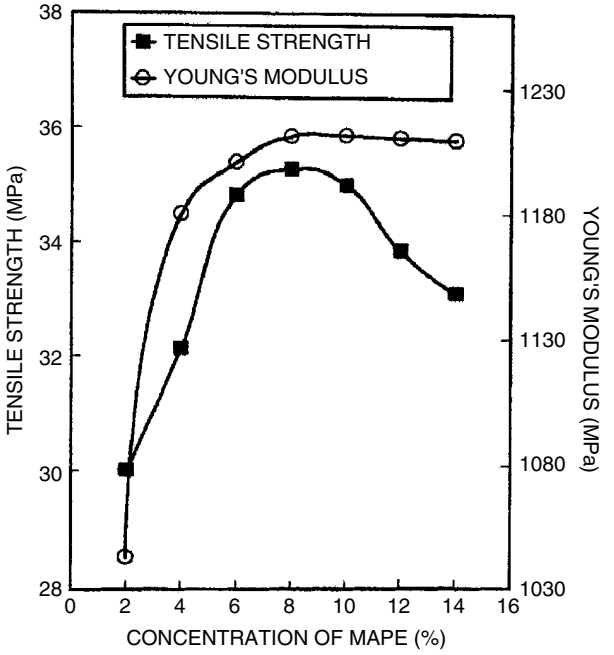


Figure 11. Effect of MAPE concentration on tensile properties of SGRP composites (sisal/glass composition is 50/50 and fibre length is 6 mm).

similar interaction may occur between the anhydride groups of MAPE and —OH groups present on the glass fibre surface. Infrared spectra of unmodified and maleic modified polyethylene are shown in Fig 12. Spectra were recorded 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.

Table 9 shows tensile properties of unmodified and maleic modified SGRP. 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 SGRP. As sisal content decreases, the degree of enhancement in tensile strength of SGRP also decreases. The scanning electron micrographs of fracture surfaces of maleic modified SGRP are shown in Fig 13. Polyethylene traces sticking to the surface of fibres especially on glass fibre indicates strong adhesion between MAPE and sisal and glass fibre.

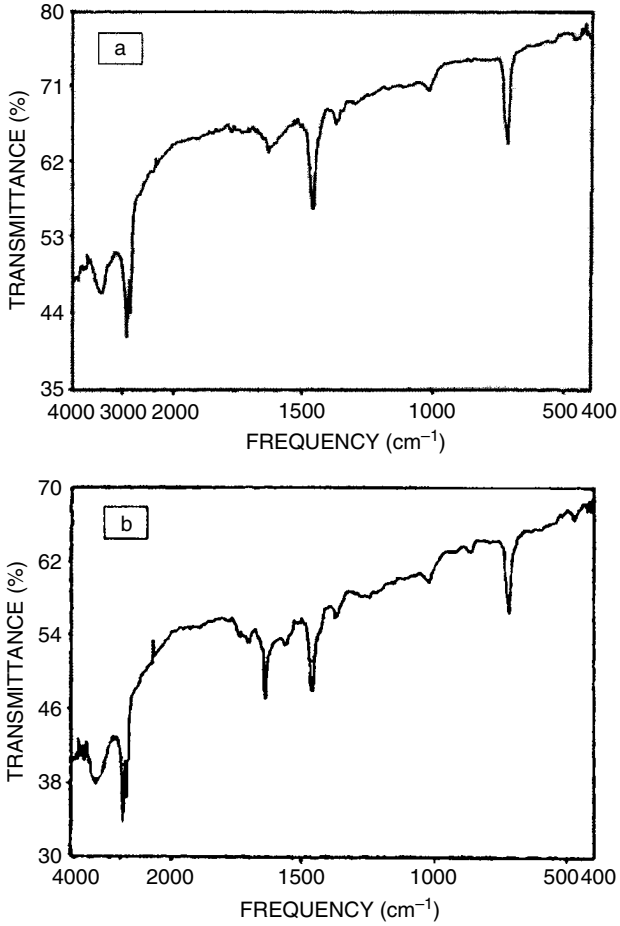


Figure 12. IR spectrum of (a) unmodified and (b) maleic anhydride modified polyethylene.

Effect of silane treatment

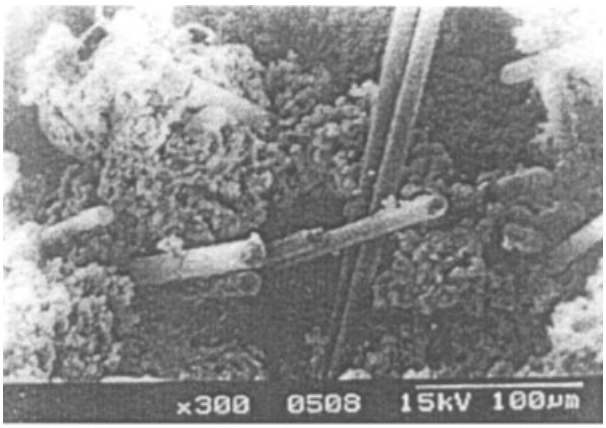
The effect of silane treatment on tensile properties of SGRP with 70/30, 50/50 and 30/70 compositions of SRP and GRP are shown in Table 10. In the case of 50/50 composition the enhancement in tensile strength and modulus due to modification are by 24 and 45 %, respectively. The vinyl group present in the silane undergoes polymerisation in the presence of DCP and forms a long hydrophobic polymeric chain on the fibre surface which interacts with the polyethylene matrix through van der Waals type of bonding. Thus silanes form a bridge at the interface of sisal and polyethylene matrix, and act like a compatibiliser, which binds two incompatible polymers.

Table 9. Tensile properties of MAPE treated SGRP composites; values in parentheses give the properties of untreated composites

Composite	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)
SGRP (sisal/glass-70/30)	34.97	1139.32	5
	(27.86)	(800.33)	(5)
SGRP (sisal/glass-50/50)	36.23	1228.28	4
	(29.92)	(1000.131)	(5)
SGRP (sisal/glass-30/70)	35.35	1209.51	3
	(31.23)	(1136.36)	(4)

Table 10. Tensile properties of silane treated SGRP composites; values in parentheses give the properties of untreated composites

Composite	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)
SGRP (sisal/glass-70/30)	34.34	1185	4
	(27.86)	(800.33)	(5)
SGRP (sisal/glass-50/50)	37.035	1458.35	4
	(29.92)	(1000.131)	(5)
SGRP (sisal/glass-30/70)	38.98	1606.77	3
	(31.23)	(1136.36)	(4)



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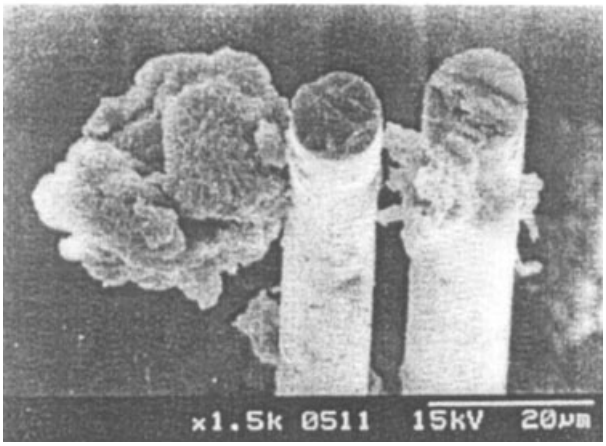


(b)

Figure 13. SEM photographs of tensile fracture surfaces of MAPE modified SGRP composites (sisal/glass composition is 50/50 and fibre length is 6 mm) at two magnifications.

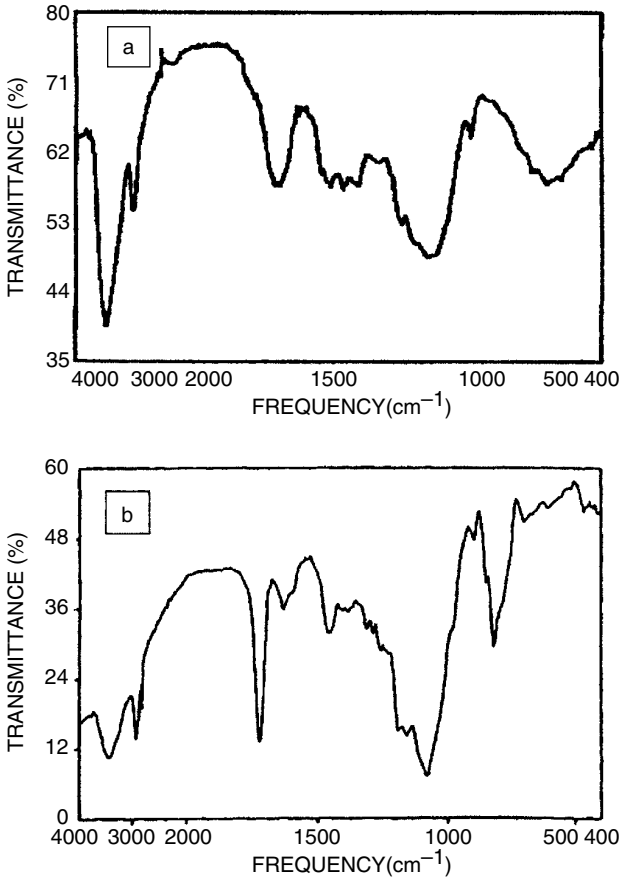


Figure 14. IR spectrum of (a) untreated and (b) silane treated sisal fibre.

Infrared spectra of untreated and treated sisal fibre are shown in Fig 14. The —OH peak intensity is reduced after silane treatment which indicates the reaction between cellulosic —OH group and silane. The 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. The same type of silane-induced interaction is also possible between glass fibre and polyethylene matrix.

Scanning electron micrographs of tensile fracture surfaces of silane treated SGRP are given in Fig 15. Both sisal and glass fibre pullout are less at the fracture surface, which confirms the fact that there exists good adhesion between treated fibres (sisal and glass) with polyethylene matrix. Figure 15 also reveals that silane treatment is more or less equally effective for both the fibres to improve their adhesion with polyethylene matrix.

Effect of peroxide (DCP and BPO) treatment

Figure 16 shows the effect of variation in peroxide concentration (DCP and BPO) on the tensile strength of SGRP, with 50/50 composition SRP and GRP. It indicates that SGRP exhibits maximum tensile strength at 1 % concentration of DCP and at 0.8 % concentration of BPO. However, further addition of peroxides to the system reduced the tensile strength. It is due to the cross-linking of LDPE, which increases the viscosity of the system considerably. This leads to a reduction in dispersion of fibres. The effects of DCP (1 %) and BPO (0.8 %) on the tensile strength are shown in Table 11. Comparison of the two treatments revealed that tensile strength and Young's modulus of BPO treated composites are superior to DCP treated composites. BPO has a higher decomposition rate and the decomposition takes place at a temperature of 80 °C. But the decomposition rate of DCP is low and its decomposition starts at approximately 140 °C. Since the fibre mixing was carried out at a temperature of 125 °C, the rate of peroxide radical formation from DCP is low at this temperature.

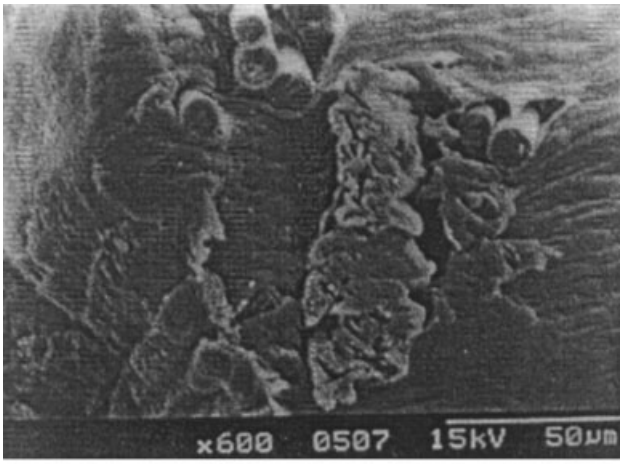
The increase in tensile properties of peroxide treated composites is attributed to the enhanced adhesion at the polymer fibre interface due to the peroxide-initiated free radical reaction between LDPE matrix and fibres. The expected mechanism of the peroxide induced grafting is shown below.

$$\text{PO-OP} \longrightarrow 2\text{PO}\bullet$$

$$\text{PO}\bullet + \text{PE-H} \longrightarrow \text{POH} + \text{PE}\bullet$$

Table 11. Tensile properties of peroxide treated SGRP composites; values in parentheses give the properties of untreated composites

	DCP treatment			BPO treatment		
Composite	Tensile Strength (MPa)	Young's modulus (MPa)	Elongation at break (%)	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)
SGRP (sisal/glass-70/30)	35.03	1303.7	4.7	35.77	1401.75	5
	(27.86)	(800.33)	(5)	(27.86)	(800.33)	(5)
SGRP (sisal/glass-50/50)	38.84	1583.28	3.9	39.08	1626	4
	(29.92)	(1000.13)	(5)	(29.92)	(1000.13)	(5)
SGRP (sisal/glass-30/70)	40.73	1726.98	2.2	41.92	1776.18	2
	(31.23)	(1136.36)	(4)	(31.23)	(1136.36)	(4)



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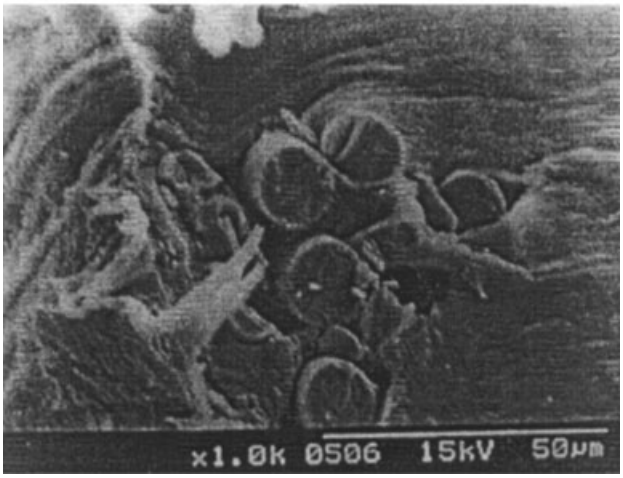


(b)

Figure 15. SEM photographs of tensile fracture surfaces of silane treated SGRP composites (sisal/glass composition is 50/50 and fibre length is 6 mm) at two magnifications.

$$\mathrm{PO}\bullet + \text{glass-H} \longrightarrow \mathrm{POH} + \text{glass}\bullet$$

$$\mathrm{PO}\bullet + \text{sisal (cellulose-H)} \longrightarrow \mathrm{POH} + \text{cellulose}$$

$$\mathrm{PE}\bullet + \text{cellulose}\bullet + \text{glass}\bullet \longrightarrow \text{Cellulose-PE-glass}$$

$$\mathrm{PE}\bullet + \mathrm{PE}\bullet \longrightarrow \text{PE-PE}$$

Figures 17 and 18 are the scanning electron micrographs of the tensile fracture surfaces of DCP and BPO treated hybrid composites. Figure 17 clearly shows that polyethylene penetrated into the sisal fibre as a result of DCP-induced grafting. It can also be observed that sisal fibre suffers extensive delamination or 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 α clear indication of the strong adhesion between glass fibres and polyethylene matrix. It is also seen that due to the brittle nature of glass fibres they do not undergo extensive delamination like sisal fibres. The delamination of sisal fibres confirms the fact that DCP treatment is more effective for the sisal–polyethylene than that of glass–polyethylene bonding. Figure 18 clearly shows traces of polyethylene sticking to the surface of glass fibre, which indicates the presence of good bonding between glass fibre and polyethylene in BPO treated composite. The figure also shows that the fibre pullout is less in the case of sisal compared with glass fibre, which again strongly emphasizes

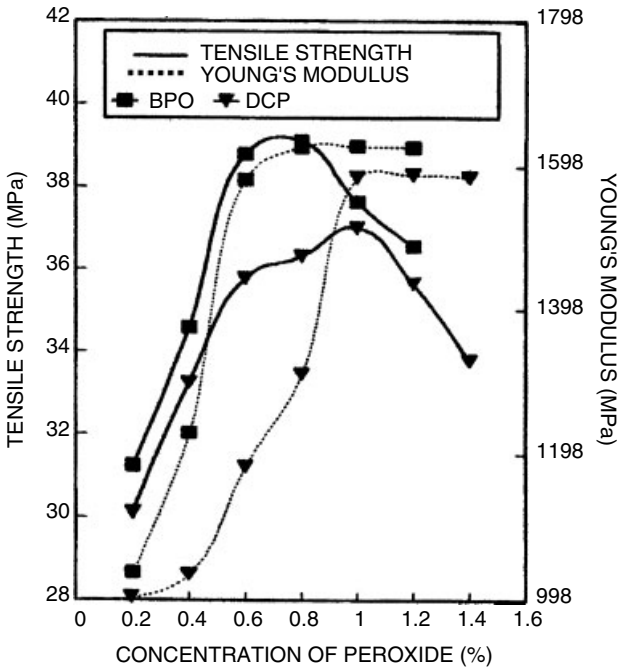
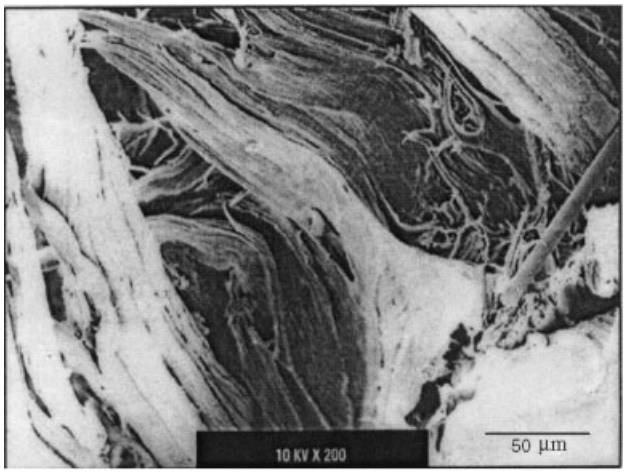


Figure 16. Effect of variation of peroxide concentration on tensile properties of SGRP composites (sisal/glass composition is 50/50 and fibre length is 6 mm).



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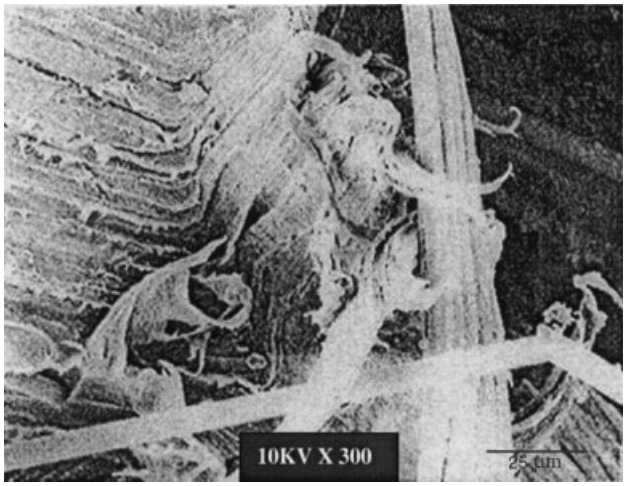
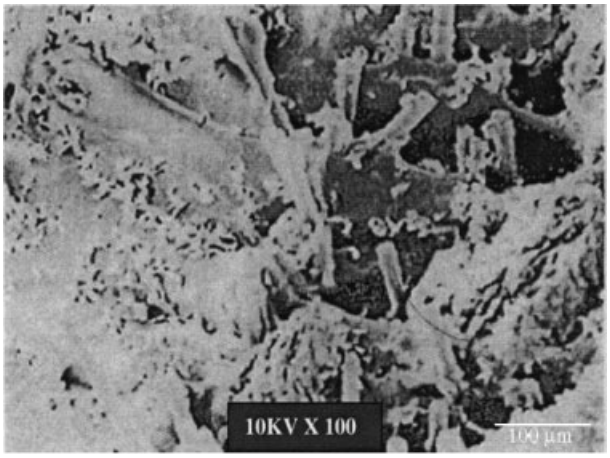
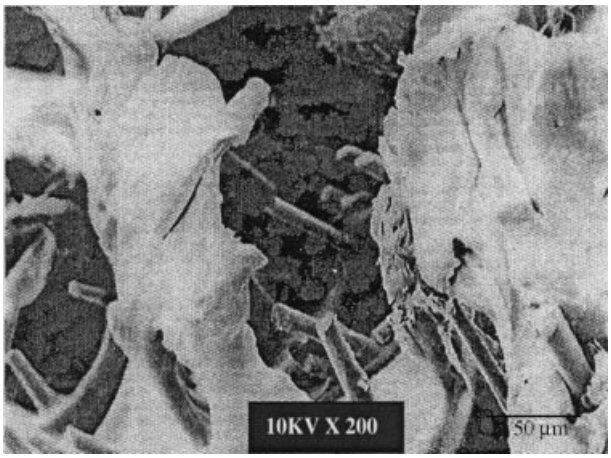


(b)

Figure 17. SEM photographs of tensile fracture surfaces of DCP treated SGRP composites (sisal/glass composition is 50/50 and fibre length is 6 mm) at two magnifications.



(a)



(b)

Figure 18. SEM photographs of tensile fracture surfaces of BPO treated SGRP composites (sisal/glass composition is 50/50 and fibre length is 6 mm) at two magnifications.

the fact that BPO treatment is more effective for sisal–polyethylene bonding.

Comparative efficiency of different treatments

The effects of the different types of treatments (alkali, acetic anhydride, stearic acid, $KMnO_4$, maleic anhydride, silane, DCP, BPO) on tensile properties can be compared (Fig 19 and 20). 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 increases slowly and then either decreases or levels off. It is evident from these figures that BPO, DCP and silane treated composites have the best tensile properties. The efficiency of the different treatments varies in the following order alkali < acetylation < stearic acid < $KMnO_4$ < MAPE < silane-A < DCP < BPO. Cost/performance ratio analysis shows that acetylation is more efficient than other treatments used in this study.

CONCLUSIONS

Hybrid composites of sisal/glass reinforced polyethylene (SGRP) composites were developed by varying the composition and length of the fibres. Variation in relative composition of fibres in SGRP produced notable changes in the tensile properties of the SGRP composites. The properties were increased with increase in volume fraction of glass fibres. Variation in fibre length and distribution made considerable differences to the strength and modulus of SGRP. As fibre length was increased the tensile strength and Young's modulus were increased and the increase was up to a fibre length in the range 6–8 mm (optimum range). The properties above and below the optimum fibre length showed comparatively low values. Also, it was noticed that, in the presence of glass fibre, dispersion of sisal in polyethylene was improved. This in turn leads to improvement in tensile properties.

Chemical modifications with reagents such as alkali, acetic anhydride, stearic acid, $KMnO_4$, maleic anhydride, silane and peroxides (dicumyl and benzoyl peroxide) improved the tensile properties of SGRP. These chemical modifications resulted in enhanced

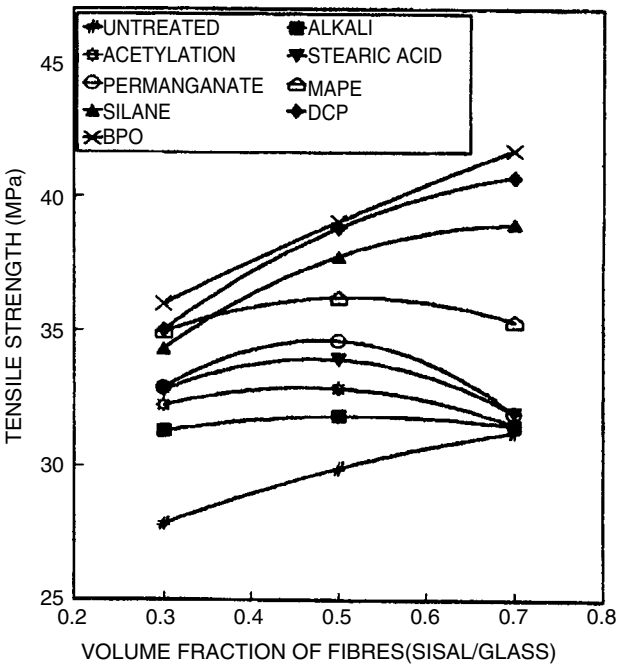


Figure 19. Effect of chemical modifications on tensile strength *versus* volume fraction of fibres in SGRP (volume fraction of fibres is calculated based only on the fibre content).

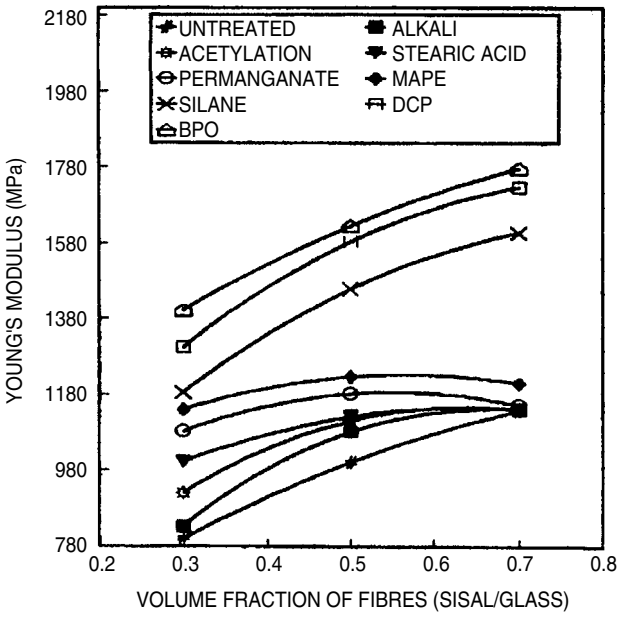


Figure 20. Effect of chemical modifications on Young's modulus *versus* volume fraction of fibres in SGRP (volume fraction of fibres is calculated based only on the fibre content).

fibre dispersion in the composite, reduced hydrophilicity of sisal fibre, and improved fibre–matrix compatibility through mechanical anchoring, physical and chemical bonding. The enhancement in tensile properties of alkali treated SGRP was associated with increased mechanical anchoring between sisal fibre and polyethylene matrix. Chemical modification with acetic anhydride, stearic acid, $KMnO_4$, maleic anhydride and silane-A enhanced the interfacial compatibility between fibre (especially sisal) and polyethylene matrix through physical bonding. Stearic acid modification on sisal fibre reduced its hydrophilicity and this enhanced its compatibility with polyethylene matrix. The improvement in tensile strength and modulus of peroxide treated SGRP composites was attributed to the peroxide-induced grafting (chemical bonding) of polyethylene on to fibres.

Scanning electron microscopy (SEM) and infrared (IR) spectroscopy were used to characterize the different chemical modifications. SEM photomicrographs of fractured surfaces of SGRP showed that interfacial adhesion between fibre and matrix was considerably higher in modified than in unmodified hybrid composites. Water retention values (WRVs) were used to characterize the stearic acid modified sisal fibres. It was observed that WRVs decreased as the concentration of stearic acid increased.

The effect of various chemical modifications on the tensile strength and modulus of SGRP varied as follows

$$\text{NaOH} < \text{acetic anhydride} < \text{stearic acid} < KMnO_4 < \text{maleic anhydride} < \text{silane-A} < \text{DCP} < \text{BPO}$$

Acetylation was found to be the most efficient treatment according to cost/performance ratio analysis. Finally, it is important to mention that chemically modified hybrid composites can be used for many applications. Studies are in progress in this direction.

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