DEVELOPMENT OF SISAL FIBRE REINFORCED PLASTICS

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ABSTRACT

Plant fibres have proved suitable for reinforcement of thermoset and thermoplastic polymeric matrices. The fibres improve both the strength and toughness of polymeric resins such as epoxy, polyester and phenolic. There is a wide range of polymeric matrix materials on the market. These are however very expensive and are therefore uneconomic to use with plant fibres. On the other hand, there exists in tropical countries, a wide range of natural resins from plants some of which are already being exploited commercially. These include cashew nut shell liquid (CNSL) and tannin. In this paper, the structure and mechanical properties of sisal fibre are presented. An evaluation of their effectiveness as a reinforcement of epoxy resin is made with some emphasis on the effect of chemical modification of the fibre surface.

INTRODUCTION

Plant fibres provide strong, low cost, lightweight alternatives to manmade fibres. In addition, plant fibres have the advantages of having a very reactive surface chemistry and a high work of fracture. The fibres are recyclable or can be designed to be combustible to allow recovery of their energy content, unlike manmade fibres such as glass fibres. Other potential advantages over manmade fibres include reduced tool wear and safer handling and working conditions. In addition to these technical advantages, there are also the significant environmental advantages of using fibres which come from a continually renewable resource and which utilize atmospheric carbon dioxide rather than carbon from mined resources.

The most common current source of industrial plant fibres is wood. Wood fibres have the advantage of being uniform, readily available and well

known but the disadvantage of being short (mean fibre length 2.7 mm). However, this is not the only possible source of plant fibre. Tanzania has an abundant resource of sisal, coir, kapok, cotton, bamboo and straw. These fibres are readily available in large quantities and offer longer individual fibres (e.g. sisal fibre bundle, up to 1200 mm).

Sisal is a hard fibre extracted from the leaves of the sisal plant (Agave Sisalana). The agavaceae are a family of monocotyledons fibre producing plants. The genus agave is made up of about 300 species, nearly all of which are native to tropical and subtropical North and South America. By the beginning of this century, some of these species had been introduced to a large number of other tropical countries in Africa, the West Indies, and the Far East. This was largely due to expansion of demand for hard fibres in the industrialized countries of Western Europe, America and Japan.

The market value of sisal and its demand suffered worse damage following the introduction of synthetic fibres in the fibre markets. The synthetic fibres were now being deployed in applications that had been previously dominated by the natural vegetable fibres, and were relatively cheaper, until after the 1973 oil crisis.

Many plant fibre have been successfully used as reinforcement for polyester and epoxy resins for the production of low cost composite materials [1]. This alternative use of plant fibres comes at a time when new end uses of these fibres are being sought, to improve the economies and quality of life in the developing countries where they are produced ideally, attractively cheap and commercially useful composite materials are sought which exploit the strength and stiffness of natural cellulosic fibres as reinforcement to polymeric materials.

Plant fibres have the following advantages over manmade synthetic fibres and certain mineral fibres:

(i) They are cheap, and require less energy to produce
(ii) It is easy to dispose them after use because they are biodegradable.
(iii) They are very light, and result in composites with good specific properties.
(iv) Due to the polymeric nature of cellulose, they are compatible

with most polymeric plastics.

(v) They are non toxic, and do not cause cancer

(vi) They possess moderate strength and stiffness to merit use as reinforcement materials to plastics.

However, these fibres have certain limitations. These include high water and moisture absorption which causes swelling and results in dimensional instability. The fibres undergo biodegradation, hence they have a limited lifespan. It has also been reported [2] widely that they undergo degradation under the influence of ultraviolet radiation. It is also well established that the mechanical and physical properties of most plant fibres are variable, and non uniform, making difficult the prediction of the resulting properties of composites made thereof.

Table 1 illustrates the properties and cost of some synthetic and plant fibres. The cost of sisal fibre is about 10% that of glass fibre.

Table 1: Representative properties of some fibres [2]

Fibre	Density (kgm^{-3})	Tensile Strength (MPa)	Tensile Modulus (GPa)	Max Strain (%)	Cost (US$/kg)
Carbon	1880	2400	400	-	200
Stainless Steel	7850	1200	200	8	30
Glass	2540	1700	70	4.8	3.25
Sisal	1450	640	15	6.8	0.36
Jute	1450	530	13	2.0	0.30
Coir	1150	175	5	30	0.25

STRUCTURE AND PROPERTIES OF SISAL FIBRE

A sisal plant produces about 200 to 250 leaves before flowering, each of which contains 1000 - 1200 fibre bundles. The leaf is composed of 4% fibre, 0.75 cuticle, 8% dry matter and 87.25% water [3]. The sisal leaf contains of three types of fibres: Mechanical, ribbon and xylem fibres.The mechanical fibres are mostly found around the periphery of the leaf.

They have a more or less thickened horseshoe shape and seldom divide during extraction processes. They are the most predominant and their fineness dictates the grading and general commercial usefulness of sisal fibre. Ribbon fibres occur in association with the conducting tissues in the median line of the leaf. They are seen in the cross section as a wide crescent. The structure of the ribbon fibre given them considerable mechanical strength. They are also the longest fibres and unlike mechanical fibres, key are readily split longitudinally. Xylem fibres form part of the composite fibre bundles at the median line of fibre. They are composed of thin walled cells and are therefore easily broken up and lost during the extraction process.

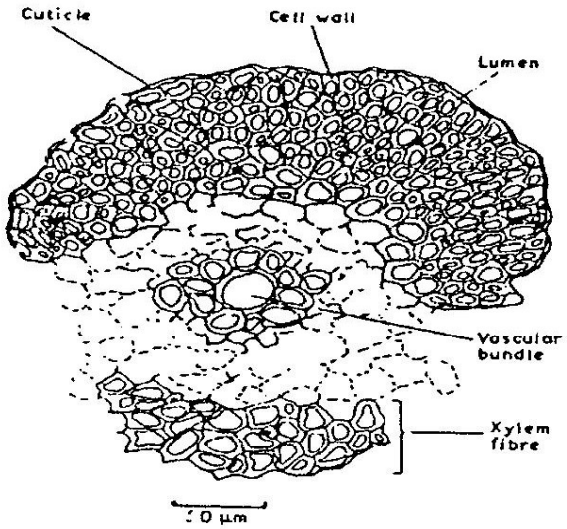

Fig. 1. The cross section of a phloem (ribbon) fibre bundle

Fig.1 illustrates the phloem (ribbon) fibre bundle in cross-section. The position of the vascular bundle and the xylem fibre in the pulpy leaf matrix are also shown. A typical sisal fibre bundle, consists of several hundred or so parallel tubular fibres, which are 4-12 µm across with cell wall thicknesses of 1-2 µm. The cell wall is a composite structure of lignocellulosic material reinforced by helical microfibrillar bands of cellulose. The helical nature of microfibrils is illustrated in Fig 2.

Generally, the strength and stiffness of plant fibres depends on the cellulose content and the spiral angle which the bands of microfibrils in the inner secondary cell wall make with the fibre axis.

Fig. 2. The microfibrillar cellulose bands revealed in a sisal fibre cell wall.

High values for the tensile strength and Young's modulus are always associated with a higher cellulose content and lower microfibrillar angle. On the other hand, high liquid contents and high microfibrillar angle lead to high strains to fracture. These trends are clearly evident in Table 2, showing the mechanical properties with respect to structure of various plant fibres.

Mclaughlin et al [5] postulated that the fibre bundle behaved like a composite material constituting of a strong crystalline phase of cellulose and a tough amorphous phase constituting the matrix. It was first assumed that the microfibrillar spiral angle θ of the inner secondary wall in a particular cell is constant. The second assumption was that the cells within a particular species are identical. It was first postulated that if E_c is the Young's modulus of the microfibril making an angle θ, its component in the axial direction E_a is:

$$E_a = E_c \, Cos^2 \theta \qquad (1)$$

They then applied the simple rule of mixtures to derive the Young's modulus of the fibre, E_f as:-

$$E_f = w_c \, E_c Cos^2 \theta + w_{nc} \, E_{nc} \qquad (2)$$

where E_c and E_{nc} are the Young's moduli values for the crystalline and non-crystalline regions, w_c and w_{nc} are their weight fractions respectively.

Table 2: Effect of structure and composition on the mechanical properties of some plant fibres [4].

Fibre	Cellulose Content (%)	Microfibrillar Angle (Degrees)	Initial Modulus (GPa)	Ultimate Tensile Strength (MPa)	Elongation Max (%)
Coir	43	30-49	4-6	106-175	17-47
Banana	65	10	7.7-20	54-754	10
Sisal	67	10-22	9.4-15.8	568-640	3-7
Pineapple	81	8-14	34.5-82.5	413-1627	0.8-1.6
Palmyra	40-52	29-32	4.4-6.1	180-215	7-15
Jute	63	7-9	2.5-13	533	1-2

If we assume the Young's moduli for the crystalline and non-crystalline phases to be 45 and 3 GPa respectively, then the predicted value of the Young modulus for the six fibres would be as shown in Table3 below.

Table 3: Predicted values of the Young's modulus using Mclaughlins model

Fibre	*Young' Modulus* (GPa)
Coir	13
Banana	29
Sisal	28.15
Pineapple	35.6
Palmyra	17.0
Jute	28.9.

The values for most of the fibres shown are higher than experimental values shown earlier in Table 2.

CHEMICAL MODIFICATION OF THE FIBRE SURFACE

The external surface of sisal fibre cell is covered by a layer of waxy lignin/ hemicellulosic materials with which the cell is bonded to its adjacent neighbours in the fibre bundle. When a sisal fibre bundle is polished, a loosely

attached scale-like substance, the cuticle, comes off exposing the shiny, smooth and waxy surface. The presence of the cuticle and the waxy surface inhibit the formation of chemical or mechanical bonds at the fibre-matrix surface. In most cases, they prohibit direct contact of the resin to the fibre surface. Additionally, wetting or spreading of the wet resin on the fibre surface is inadequate due to high surface smoothness.

The wetting and spreading phenomena of a liquid on a solid surface can be understood by considering the equilibrium conditions at the boundary of a liquid drop in contact with a solid surface as illustrated in Fig. 3.

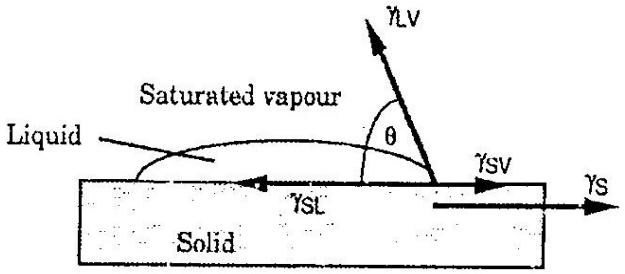

Fig.3. Schematic vector representation of vapour liquid-solid equilibrium on a planar surface.

The Young's equations is derived as :

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos\theta \qquad (3)$$

where γ_{SV} and γ_{LV} are the solid and liquid surface tensions in equilibrium with the saturated liquid vapour, γ_{SL} is the interfacial tension between the liquid and solid, and θ is the contact angle between the liquid and solid. The Dupre equation defines the work of adhesion W_a in terms of the Young's equation, as:

$$W_a = \gamma_S + \gamma_{LV} - \gamma_{SL} \qquad (4)$$

Combining equations (3) and (4) yields the Young-Dupre equation:

$$W_a = (\gamma_S - \gamma_{SV}) + \gamma_{LV}(1 + \cos\theta) \qquad (5)$$

The above relations are only valid for an ideal smooth surface plane. The surface topography in terms of roughness effectively determines the ac-

tual area of contact at the solid and liquid interfaces. The surface roughness is thus defined as:

$$r = \frac{\cos\theta_r}{\cos\theta} \tag{6}$$

where θ and θ_r are the contact angles for smooth and rough surfaces respectively. According to Wenzel[6], the surface roughness is simply the ratio of the true surface area to the apparent planar area. Substituting equation (6) into equations (3) and (4) gives the Wenzel equation:

$$(\gamma_{SL})_r = r\gamma_{SL}$$
$$(\gamma_S)_r = r\gamma_S$$
$$(W_a)_r = W_a + (r-1)(\gamma_S - \gamma_{SL}) \tag{7}$$

It is thus obvious from equation (7) that the work of adhesion can be increased only by increasing the surface roughness and the solids surface tension. The later is affected by chemical modification on the surface such as to create more trans-active surface molecules that would readily form chemical bonds with, or diffuse into the liquid.

The large amount of hydroxyl groups which occur throughout the structure of cellulose is largely responsible for the hydrophillic nature of most plant fibres, as water is easily attracted and held through hydrogen bonding. This in turn, reduces the interfacial strength between fibre surface and a polymer resin where chemical or mechanical bonding would be expected. The philosophy behind surface modifications is therefore to improve compatibility and bonding characteristics by creating compatible surface energies and formation of chemical as well as mechanical bonds. The desired surface modification is that which additionally alters the water or moisture uptake, enhances rot ad mildew resistance, thus resulting in imported mechanical and physical properties.

The bond strength can be improved through one or more of the following:-

(a) cleaning the surface by dissolving the fatty substances and the layer of cuticle. This additionally roughens the surface and increases the capillarity or surface tension of the fibre surface.
(b) reacting the fibre with reagents that could make it hydrophobic,

through the elimination of the hydroxyl groups on the cellulose chain while grafting a polymer group compatible with the resin matrix. These are referred to as interfacial agents.

Mercerization is one of the oldest techniques for cleaning textile fibres. The treatment consists of soaking of the fibre in a caustic soda solution, followed by rinsing in water before drying. The mercerization treatment improves the fibre surface's adhesive characteristics by removing natural and artificial impurities from the surface. X-ray examination of native and mercerized cotton fibre [7] has shown that mercerization changes the form of cellulose crystallites, increasing the amount of amorphous cellulose at the expense of crystalline cellulose. The surface tension, hence wettability of mercerized fibres is higher. This results in better bonding through a form of mechanical interlock between the matrix and the roughened fibre surface. Mercerization also results into fibre bundle fibrillation, that is, breaking down the composite fibre bundle into smaller fibres. Fibrillation in turn results in increased effective fibre surface area available for contact with the wet matrix. Interfacial complying agents are used on glass fibre in order to improve the interfacial bond with polymeric matrices in glass fibre reinforced composites. These form stable covalent bonds with both the mineral surface and the resin. Silane coupling agents are the most common. These have been found to work quite well on sisal and other cellulose based materials. All commercial silane coupling agents are of the general structure $X_3 S_i (CH_2)_n Y$, where n = 0-3, X is a hydrolysable group on silicon, and Y is an organofunctional group, selected for compatibility with a given resin. The hydrolysable groups are essential for generating intermediate silanols:

$$X_3Si(CH_2)Y + 3H_2O \text{ ---------- } (HO)_3Si(CH_2)_nY + 3HX$$

As a silanol or hydrolyzable silane approaches a surface that is covered with water, it competes with water for the surface because of its capacity to form strong hydrogen bonds. Then the silanol bonds itself into the positions of surface hydroxyls MOH, with the elimination of water.

$$RSi(OH)_3 + H_2O + MOH \text{ ---------- } RSi(OH)_2OM + 2H_2O$$

where $R = (CH_2)_nY$.

Isocyanates are another class of reagents that have been successfully used as wood fibre binders and have shown promise as reagents to improve moisture resistance[8]. Isocyanates are characterized by the - N=C=O group, capable of reacting with almost any active hydrogen. They react with cellulose hydroxyl groups H0-M to yield a urethane,

$$R-N=C=O + HO-M \longrightarrow R-\overset{H}{\underset{|}{N}}-\overset{O}{\underset{|}{C}}-OM$$

Urethane Carbamate

The 4-4' - diphenylmethane di-isocyanate (MDI) is now widely used in particleboard manufacture.

EXPERIMENT WORK

Chemical modification of Sisal fibres

High grade sisal fibres were supplied by the Tanzania sisal authority (TSA). The fibres were subjected to the following treatments:-

(i) Dewaxing: Fibres were soaked for 24 hrs in a solution of benzene and Methylated splint 1:1 in a sealed glass vessel. They were then rinsed in distilled water and then dried in an oven at 100 °C.

(ii) Mercerization: Dewaxed samples were mercerized by soaking them in a 1.0M solution of sodium hydroxide for about 72 hours, rinsed in distilled water and then dried as above.

(iii) Silane treatment: An organofunctional silane, A1100, was supplied by Union carbide (UK) Ltd. Some mercerized sisal fibres were treated in a 100% silane solution for one hour, while others were treated for 24 hours in a 5% solution of silane in methanol.

A 0.1M solution of ceric ammonium nitrate (CAN) was used as catalyst and all reactions were carried out at room temperature, 20 °oC and atmosphere pressure.

Evaluation of moisture resistance

Fibre samples in the original "as received", dewaxed, mercerized and silane (100%) treated conditions were used. Fibre sample of about 1g were obtained from each group of treated fibres. they were first dried in a vacuum chamber, than weighed using a sensitive electronic balance (± 0.0001 g), then exposed to moisture in a controlled humidity chamber at 65% RH, 20 °oC. Weight changes were monitored after short intervals of time.

Moulding of Composites

Unidirectional composites were produced from an epoxy resin system, Araldite LY 1927GB supplied by Ciba Geigy Plastics, using two compression moulds meant for rectangular section and round section unidirectional composites. The composites were allowed to get at room temperature for about 24 hours while under pressure. The composites were then extracted from the moulds and cured at 60 °C for 2 hours, at 80 °C for another 2 hours, and then at 100 °oC overnight as specified by the resin manufacturer. Unidirectional composes were manufactured using fibres in the 'as received', mercerized and silane treated conditions.

Mechanical Testing

Compression tests

The tests were carried out on dry and wet composites according to BS2782 Part 3: Method 345A: 1979. The specimens were in the form of right cylinders 12 mm diameter and 18 mm in height. An Instron 1122 machine was used and all tests were performed at a cross head speed of 1 mm/min. The wet composites head been soaked in distilled water for 5 days.

Flexural tests

Three-point loading bend tests were performed on wet and dry composites in accordance with ANSI/ASTM D 790-71 (1978) on an Instron 1122 machine. Test specimens, 125 mm long, 12.7 mm wide and about 5 mm thick were used at a loading span of 80 mm.

EXPERIMENTAL RESULTS AND DISCUSSION

The moisture gain as a percentage of sample dry weight has been plotted against time, for the samples tested in 4.2 as shown in Fig. 4. It is clearly seen that the silane treated fibres have the best moisture resistance, compared to dewaxed, mercerized and untreated fibres. The moisture absorption in the non-silane treated conditions appear to follow some parabolic rule, that is, the moisture increases initially at a fast rate which gradually decreases reaching zero at equilibrium. There is no mechanism to stop the absorption of moisture. However, when the fibres are treated in silane, initially the moisture content appears to drop, signifying that the fibres contained residual unreacted silane. Further exposure results into moisture stabilizing with almost no absorption of moisture even after 6,000 minutes of exposure. This phenomenal achievement is a result of the formation of a reactive surface in which OH groups have been replaced by the silanols as described earlier.

The silane treatment is employed on glass fibres to produce improved interfacial bonding in glass-polymer composites. It is supposed that the same treatment would improve chemical bonding in sisal -polymer composites.

The effect of fibre treatment on the compressive strength is shown in Fig. 5. A linear regression line has been fitted through the strength values for the silane treated data points and these correspond closely to the mercerized data. Untreated composites produce composites with significantly less strength than treated fibres but in each case, a consistent variation with fibre volume fraction is observed.

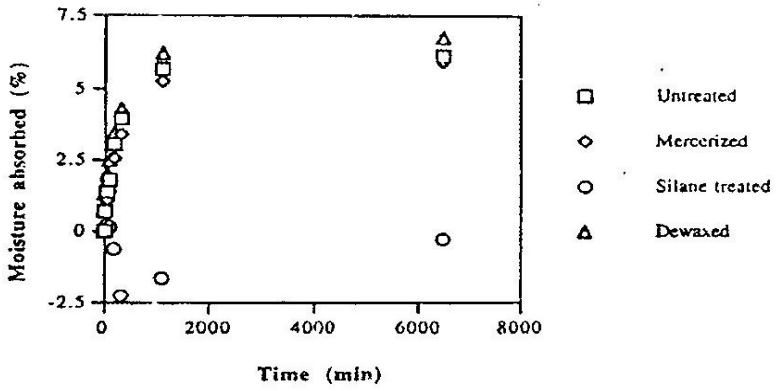

Fig. 4 Effect of chemical modification on the moisture absorption

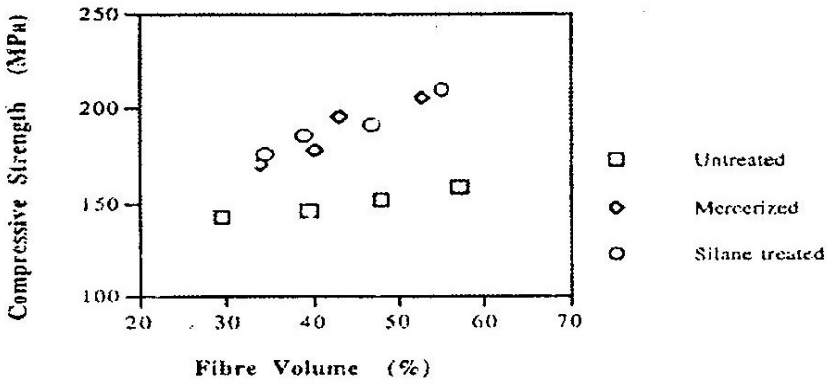

Fig. 5 The influence of chemical modification and fibre volume fraction on the compressive strength of sisal-epoxy composites

The compression test subjects the material being tested to severe shear stresses at the fibre-matrix interface, and is therefore a good indicator of the bonding strength. The material normally fails by kinking or buckling of the fibres, after shearing off from the matrix. Results in Fig. 5 therefore clearly show how bonding has improved after mercerization and silane treatment.

The flexural strength and flexural modulus of sisal-epoxy composites have been plotted against fibre volume fractions as shown in Fig 6 and Fig 7. These results show that fibre treatment has little effect on flexural properties. In a three point band test, a sample will experience tensile, compressive and shear loads and the failure mechanism, and hence strength, is likely to differ from that in an all compressive test. The flexural modulus remains

almost independent of the chemical modifications as shown in Fig. 7.

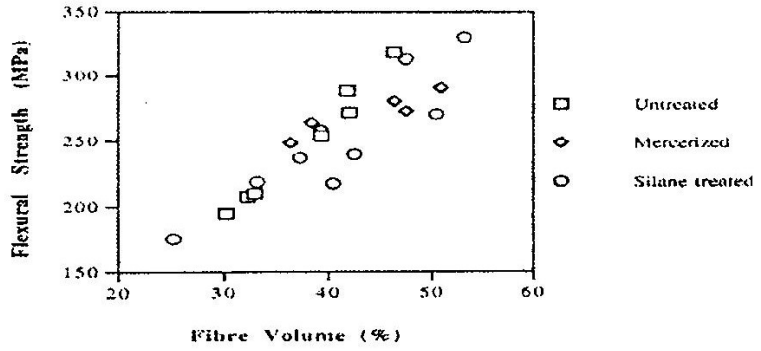

Fig. 6 The influence of chemical modification and fibre volume fraction on the flexural strength of sisal-epoxy composites

The three point bend test used did not provide critical shear stresses because the span/depth ratio used was high (16:1). That is why, the results obtained do not show any marked distinction between the untreated and treated fibre composites as all data points are randomly scattered within the same range and show nearly the same correlation. What is noted is the general trend of linear variation of the flexural strength with fibre volume fraction.

Similarly, there is no clear distinction between untreated and treated fibre composites as far as the flexural modulus is concerned, as clearly shown by Fig. 7. To be able to assess the bonding effectiveness for each test, a short span interlaminar shear stress test should have been used.

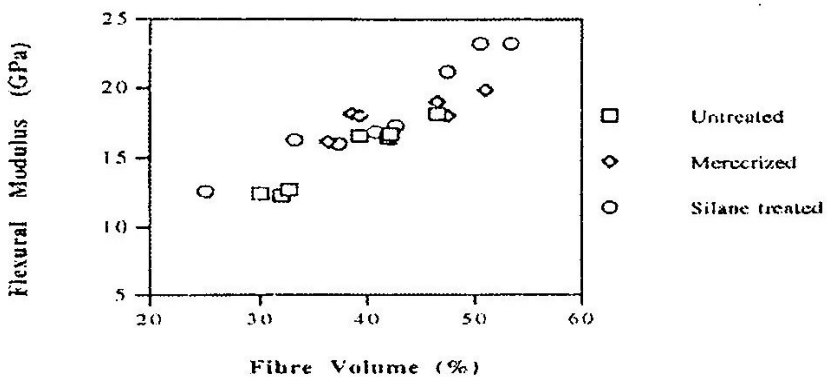

Fig. 7 The influence of chemical modification and fibre volume fraction on the flexural modulus of sisal-epoxy composites

The mean compressive strength, flexural strength and flexural modulus have been evaluated for composites containing 40% fibre volume, and these are shown in Table 4. These data show that sisal fibre generally improves the overall mechanical properties in composites. Both the strength and stiffness are :

Table 4: Mean Mechanical and Physical Properties of Sisal - Epoxy Composites of 40% fibre volume fraction

Material/ Treatment	Compressive Strength (MPa)	Flexural Strength (MPa)	Flexural Modulus GPa	Water absorbed (%) after 72 hrs soaking	Density
Epoxy resin (unreinforced)	120.0	95.0	3.1	-	1.17
Untreated dry composite	148.0	266.5	15.93	-	1.14
Mercerized dry composite	183.1	262.1	17.63	-	1.24
Silane dry composite	184.8	244.5	17.36	-	1.25
Untreated wet composite	62.53	221.7	9.15	15.6	-
Mercerized wet composite	75.83	200.7	10.12	9.0	-
Silane wet composite	98.53	237.2	12.33	5.0	-

Mercerization is observed to improve the mechanical properties of the composite. This is thought to be due to improved mechanical and chemical bonding following the removal of the waxy surface leaving behind a rougher surface that leads to improved wettability as predicted by the Wenzel's equation.

The flexural properties of wet silane treated sisal-epoxy composites are superior to those not treated in silane. It is observed that chemical modification of sisal fibres using the silane coupling agent gives significant improvements to the composite properties under wet conditions. Also, the compressive strength of wet composite is increased by a further 30%. As expected, the flexural properties (strength and modulus) increase linearly with fibre volume fraction almost in accordance to the rule of mixtures. These results affirm the useful advantage of fibre chemical modification in terms of resistance to moisture and water absorption and improved mechanical properties of the composite. Further work is however required to establish cheaper chemical modification reagents, because silanes are very expensive and would be uneconomic to use with sisal fibre.

POTENTIALS AREAS FOR FURTHER RESEARCH

In most tropical developing countries, there exists a wide variety of plant fibres which have not been exploited. These include pineapple leaf fibre, banana fibre, kapok or silk cotton and coir. There is need to explore methods to harness these fibres into modules suitable for polymer reinforcement. There are also other potential natural polymers from plants that are available, and which could be further developed to yield useful binding matrices for the plant fibres. Development of geotextiles from plant fibres for soil conservation in both urban and rural areas is another potential area for research. National and international research institutions need to make collaborative efforts in addressing to these potential areas of research, which, provide the developing countries with opportunity to reap direct economic benefits from their natural resources.

CONCLUSIONS

The following conclusions can be made from this work:

(i) Sisal fibres can be chemically modified using organo-functional silanes to produce composites with improved mechanical properties and resistance to moisture

(ii) The mechanical properties of unidirectional sisal - epoxy composites are directly proportional to the sisal fibre volume fraction.

From this paper, it can be generally concluded that sisal fibres and many other plant fibres can be employed as reinforcement to plastic materials to yield composite materials with useful engineering applications. The utilization of natural instead of synthetic polymers as matrix materials in such composites is however, the only possible way to transfer composite technology to tropical developing countries.

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