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Properties of sisal–CNSL composites

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Cashew nut shell liquid (CNSL) is a natural monomer blend that has been condensation poylmerized with formaldehyde in the presence of an alkaline catalyst to produce a thermosetting resin. Plain woven mats of mercerized sisal fibre have been impregnated with CNSL-formaldehyde resin to produce plain and corrugated laminated composites that have a mean tensile strength of 24.5 MPa and Young's modulus of 8.8 GPa. Bending tests have demonstrated that the corrugated composites have adequate strength for roofing applications. Dynamic mechanical thermal analysis has been used to assess the effect of simulated sunlight on composites as a function of time. After long irradiation times it has been deduced that the resin component of the composite undergoes further cross-linking whilst the reinforcing cellulosic sisal fibres suffer some degradation.

1. Introduction

1.1 Objectives

Many plant fibres have been successfully used as reinforcement for polyester and epoxy resins for the production of low-cost composite materials [1]. Whilst the science and technology of fibre-reinforced composites is well established in developed countries, the high cost of synthetic fibres and resins has made it difficult for this technology to be transferred to less affluent nations. Ideally, attractively cheap and commercially useful composite materials are sought which exploit the strength and stiffness of natural cellulosic fibres as reinforcements for natural resin or ceramic matrices.

Table I illustrates the properties and cost of some synthetic and plant fibres. The cost of sisal fibres per unit weight is about 10% of the cost of glass fibre, although the specific modulus of sisal fibre is about half that of glass fibre. The main objective of this work was to assess the mechanical properties of a composite system comprising sisal fibre in the form of plain woven mats and a natural resin, based on polymerized cashew nut shell liquid (CNSL). Mechanical tests have been carried out with a view to using the composite system as a roofing material in tropical countries where intense sunlight is expected to modify mechanical properties.

1.2. Structure and properties of sisal fibre

Sisal fibre is a hard fibre extracted from the leaves of the sisal plant (*Agave sisalana*). The plant, though native to tropical and sub-tropical North and South America, is now widely grown in tropical countries of Africa, the West Indies and the Far East. A sisal plant produces about 200–250 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 [2]. The sisal leaf contains three types of fibre [3]: 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 as shown in Fig. 1. They are seen in the cross-section as a wide crescent. The structure of the ribbon fibres gives them considerable mechanical strength. They are the longest fibres and unlike mechanical fibres they can be readily split longitudinally. Xylem fibres form part of the composite fibre bundles at the median line of fibres. They have an irregular shape and occur opposite the ribbon fibres, being separated from them by the vascular bundles. They are composed of thin-walled cells and are therefore easily broken up and lost during the extraction process.

A sisal fibre bundle, Fig. 2, 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. 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.

Table II illustrates the properties of some vegetable fibres [4] in relation to their composition and structure. It has been shown [5] that the tensile properties of sisal fibre are not uniform along the length of the fibre. The root or lower part has low tensile strength and modulus and high fracture strain. The fibre becomes stronger and stiffer at midspan and the tip has moderate strength and stiffness. The tensile properties

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TABLE I Representative properties of some synthetic and cellulosic fibres

Fibre	Density ($kg\,m^{-3}$)	Moisture content (%)	Tensile strength (MPa)	Tensile modulus (GPa)	Maximum strain (%)	Cost ($US kg^{-1}$)	Specific strength ($MPa\,m^3\,kg^{-1}$)	Specific modulus ($GPa\,m^3\,kg^{-1}$)	Modulus/cost ($GPa\,kg\,\$^{-1}$)
Carbon	1880	–	2400	400	–	200	1.277	213	2.00
S. steel	7850	–	1200	200	8	30	0.153	25.5	6.67
Glass	2540	–	1700	70	4.8	3.25	0.669	27.6	21.54
Sisal	1450	11	641	15	6.8	0.36	0.442	10.3	41.67
Jute	1450	12	530	13	2.0	0.30	0.366	9.0	43.33
Coir	1150	12	175	5	30	0.25	0.152	4.4	20.00

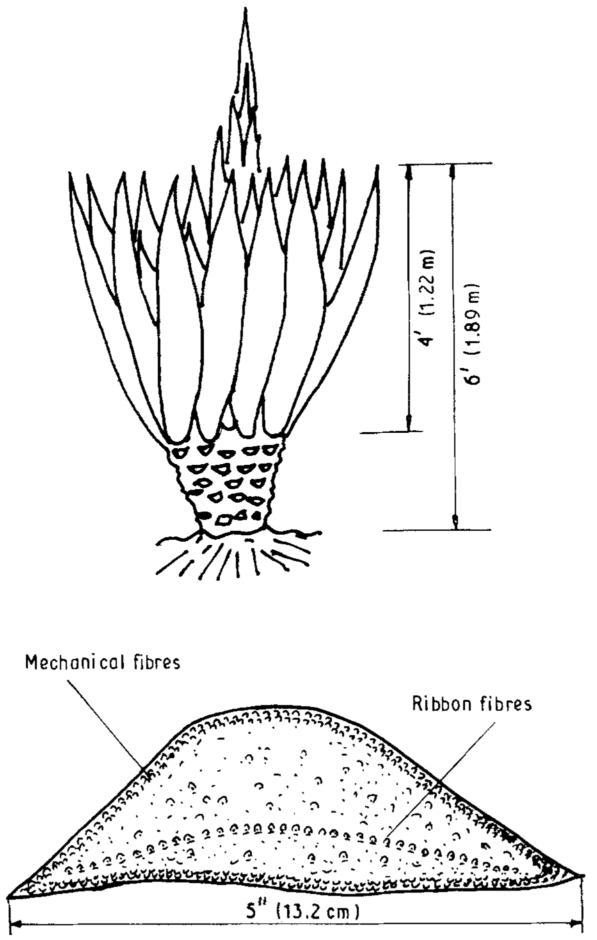

Figure 1 A sisal plant and the cross-section of a sisal leaf (*Agave sisalana*).

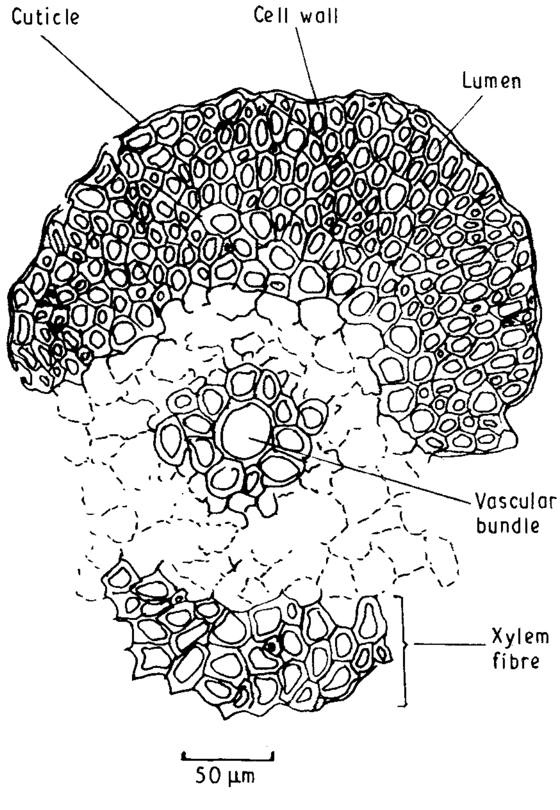

Figure 2 A sketch of a phloem (ribbon) fibre bundle in cross-section. The position of the vascular bundle and the xylem fibre in the pulpy leaf matrix are also shown.

TABLE II Properties of some vegetable fibres [4]

Fibre	Width or diameter (μm)	Density ($kg\,m^{-3}$)	Micro fibrillar angle (deg)	Cellulose/ lignin (%)	Moisture content (%)	Tensile strength (MPa)	Young's modulus (GPa)	Maximum strain (%)
Jute	25–120	1450	7–9	63/12	12	533	2.5–13.0	1–2
Coir	100–450	1150	30–49	37/43	11	153	4–6	15–40
Banana	80–250	1350	11	64/5	11	641	7.7–20.8	1.8–3.5
Sisal	50–200	1450	18–22	72/10	11	604	9.4–15.8	3–7
Pineapple leaf	20–80	1440	14–80	85/7	Hygroscopic	1020	34–82	0.8–1.6
Palmyra	70–1300	1092	30	–	—	158	3.3–7.0	3.2–11.2

are dependent on the strain rate, suggesting a strong viscoelastic behaviour. For tests conducted at a cross-head speed of $5\,mm\,min^{-1}$, the tensile strength increased from 463 to 840 MPa, the Young's modulus from 5.3 to 29.1 GPa and the elongation at fracture decreased from 16.8% to 3.9% from the root end to the centre of the fibre.

1.3. Cashew nut shell liquid

Cashew nut shell liquid (CNSL) is a blend of naturally occurring phenol-based monomers extracted from the spongy, honeycomb structure of the cashew nut shell, from the cashew tree, *Anacardium occidentale L.* The cashew tree is widely grown in tropical areas of South America, East Africa, India and the Far East. It has the potential to be developed as a substitute matrix material for the more expensive synthetic polymers. The principal chemical constituent of natural CNSL is anacardic acid. The other constituents are monophenol, cardol, 2-methyl cardol and cardonal. The chemical structures of these constituents are shown in Fig. 3. During extraction processes involving heat, the anacardic acid is decarboxylated into cardanol and the latter becomes the major constituent in technical CNSL. Table III illustrates the compositions of natural and technical CNSL.

Apart from monophenol, the other constituents have a characteristic pentadecyl side chain on the phenol ring. In some monomers, these aliphatic chains have been found to be unsaturated [7, 8]. Murthy *et al.* [9] were able to separate cardanol monomers from technical CNSL according to their degree of unsaturation and found the average unsaturation to be 1.7 and the average molecular weight to be about 300.

The polymerization of CNSL is made possible by the presence of the unsaturated side chain and the bifunctional groups on the ortho and para positions of the phenol ring. Addition polymerization is possible at the side chain unsaturation with the aid of free radical or ionic initiators. Acidic catalysts such as sulphuric acid, hydrochloric acid and diethyl sulphate have been reported [6, 10] to be capable of inducing polymerization through the formation of a carbonium ion on the unsaturated side chains. The phenol monomers in CNSL can be condensation polymerized with active H^+-containing compounds such as aldehydes at the ortho or para positions of the phenol ring.

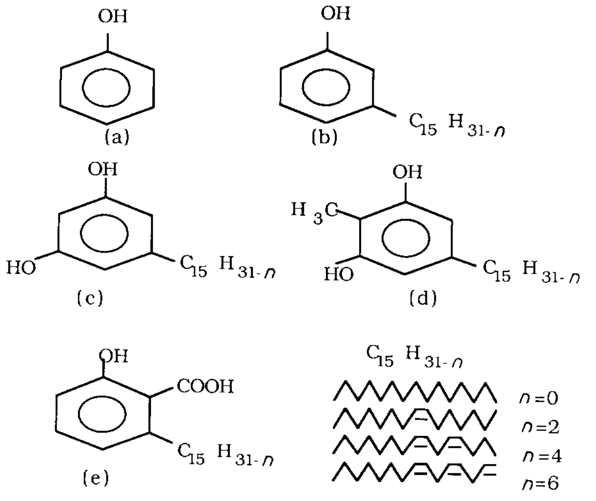

Figure 3 The chemical structures of constituents in natural CNSL. (a) Monophenol, (b) cardanol, (c) cardol, (d) 2-methyl cardol and (e) anacardic acid.

Under alkaline conditions, the reaction of the phenols with formaldehyde occurs in two steps. The first leads to the formation of hydroxymethyl compounds. Further condensation of the hydroxymethyl compounds with other phenol-based monomers produces a polymer chain linked by methyl bridges as shown in Fig. 4. Alternatively, the hydroxymethyl compounds formed after the initial step can be further condensation polymerized among themselves by heat [11]. Heating to temperatures between 160 and 300 °C in the presence of catalysts is known to enhance three-dimensional cross-linking of the polymer network, resulting in a hard, infusible and insoluble thermosetting polymer [6, 10]. It has been established [12] that the condensation reaction between cardanol and formaldehyde is independent of the degree of unsaturation of the side chain.

2. Experimental procedure

2.1. Materials preparation

Plain woven mats of high-grade sisal fibre were supplied by Tanzania Bag Corporation, Moshi, Tanzania. The mats have about eight yarns per inch (~ 3 per cm) and an average area density of $0.06\,g\,cm^{-2}$. The fibres were mercerized by soaking in a 0.5 N sodium hydroxide solution for 48 h. They were then dried and conditioned at 65% RH at 20 °C.

TABLE III The composition of natural and technical CNSL [6]

Component	Natural CNSL (%)	Technical CNSL (%)	Molecular weight
Cardanol	1.20	62.86	298
Cardol	11.31	11.25	314
2-methyl cardol	2.04	2.08	328
Anacardic acid	64.93	≤ 1.0	342
Monophenol	20.30	23.80	94

TABLE IV Composition of polymerization samples in parts by weight

Sample	CNSL	H_2CO	H_2SO_4	IPA	NaOH
A1	100	–	10	–	–
A2	100	–	8	2	–
A3	100	32	0.8	0.2	–
B1	100	32	–	–	1
B2	100	39	–	–	1
B3	100	42	–	–	1
B4	100	40	–	–	10
B5	100	48	–	–	2.5

CNSL was supplied by BP Chemicals, South Wales. A formaldehyde solution (37%–40% in water) was used. The CNSL was mixed with formaldehyde in the presence of an alkaline catalyst in various formulations and then cured to produce resol-type resins.

2.2. Resin characterization

The aim of this experimental work was to establish the polymerization and curing procedure suitable for CNSL-based composite materials. Although there are some hints from the literature as to which reagents can be used to polymerize CNSL, the formulations and procedures for curing are not available.

2.2.1. Polymerization of CNSL

The following reagents were used: cashew nut shell liquid (CNSL); concentrated sulphuric acid (H_2SO_4); 6 N sodium hydroxide solution (NaOH); iso-propyl alcohol (IPA, $CH_3CHOH–CH_3$, 2-propanol) and formaldehyde solution (37%–40%) (H_2CO).

Samples of resin were cast in small cylindrical polyethylene cups with dimensions of 30 mm diameter by 25 mm deep. The composition of the samples is presented in Table IV. Owing to evolution of gaseous products during polymerization, all preliminary mixing was carried out in a fume extraction chamber. Samples with designation A were polymerized using an acid catalyst and for those with designation B an alkaline catalyst was used.

For Sample A1, the acid was slowly added to the CNSL whilst the mixture was stirred continuously. The sample was left in the fume extraction chamber to gel at room temperature.

For Samples A2 and A3, four parts by weight of sulphuric acid were first diluted with one part of iso-propyl alcohol. The desired amount of the catalyst was then slowly added to the CNSL while stirring and left to gel at room temperature in the fume extraction chamber. For Sample A3, the formaldehyde was first added to CNSL before adding the acid catalyst. In addition to gelling at room temperature it was further cured at 60 °C for 3 days and then overnight at 100 °C.

For Samples B1, B2, B3, B4 and B5, the formaldehyde was first added to the CNSL and stirred to a homogeneous solution before adding the catalyst (NaOH). The samples were allowed to gel at room temperature overnight, post-cured at 60 °C for 3 h and then overnight at 100 °C.

2.2.2. Thermal gravimetric analysis

Thermal gravimetric analysis was used to ascertain the temperature at which the CNSL/formaldehyde resin begins to break down. This was essential to avoid causing damage to more sensitive equipment such as the differential scanning calorimeter (DSC) or the dynamic mechanical thermal analyser (DMTA) which were used for subsequent analysis. The resin constitution tested was a modified B4 resin, (see Section 3.1.1), specifically chosen for making composites with plain woven sisal mats.

The analysis was performed using a TG-750 Stanton Redcroft apparatus. Three samples weighing 35.9, 36.8 and 35.5 mg were used. The sample holder was cleaned ultrasonically in a 5% nital solution, rinsed in distilled water and acetone and then dried. The sample was then loaded, the cooling water and air supply were regulated and the apparatus was turned on. Temperature versus weight curves were obtained.

2.2.3. Differential scanning calorimetry (DSC)

A Du Pont 910 differential scanning calorimeter and a 9900 computer/thermal analyser were employed to establish the glass transition temperature of the CNSL/formaldehyde resin used for making composites.

2.3. Moulding of composites

Bi-directional composites were produced from plain woven sisal fabric mats and CNSL/formaldehyde resin. The sisal fabric was mercerized in a 0.5 N solution of NaOH by soaking for 48 h. It was then dried and conditioned and cut into 16 cm × 16 cm square mats.

The moulding procedure began by soaking the mats with the resin, which was best accomplished by spreading the resin using a hand roller until the mat was evenly wetted. Four layers of fibre mats were used, as this gave a reasonable composite thickness for mechanical tests as well as a moderate fibre volume fraction. The four layers of wetted mats were enclosed in a melinex film between two steel sheets with dimensions 18 cm × 18 cm and then placed in a hydraulic press to produce plain composite laminates.

Corrugated CNSL–sisal composites were moulded using a simple mould by compression moulding. The

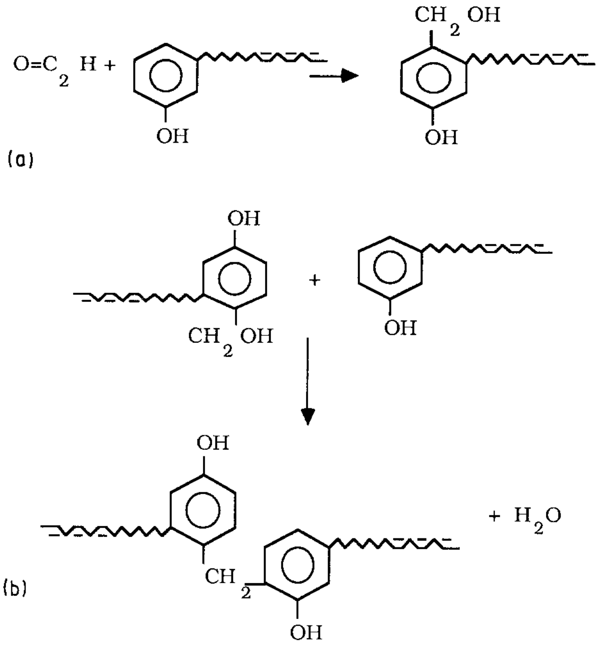

Figure 4 Condensation polymerization of cardanol with formaldehyde, (a) formation of hydroxymethyl compounds and (b) condensation of the hydroxymethyl compounds with other cardanol monomers.

mould was made of a matched pair of cast iron blocks with edge dimensions of 200 mm × 200 mm, each of which had one corrugated face. The press platens were heated to 150 °C before inserting the mould which was then pressed to 15 ton, and held for about 5 min. The specimen was removed and then coated with resin to ensure that no fibres were left unwetted. This practice was necessary because uneven distribution of resin during moulding left some areas unwetted. The resulting composite was about 2.5 mm thick, and had a fibre weight fraction of 88%. The composite was then left to gel at 60 °C overnight and post-cured at 100 °C for about 24 h.

2.4. Mechanical properties testing

2.4.1. Tensile tests

Tensile tests were performed on the plain composites made from the mercerized plain woven sisal mats and the CNSL/formaldehyde resin system. Dog-bone-shaped specimens were produced using a routing tool. A gauge length of 45 mm was marked in white for use with a Wallace optical extensometer system attached to a model 1195 Instron.

Before testing, the specimens were conditioned at 65% RH, and 20 °C for 1 week. Tests were conducted using a uniform cross-head speed of 1 mm min^{-1}. The tensile strength and the modulus were calculated from the load–deflection curves obtained from the Instron's chart recorder.

2.4.2. Crush bending tests

The corrugated sheet was cut longitudinally along the corrugation, into a single corrugation, one period wide, and then sliced into thin pieces to produce specimens of the geometry shown in Fig. 5. Specimens were conditioned by keeping them at 65% RH, 20 °C for 1 week. The specimens were then placed into an assembly for bend testing as shown in Fig. 6. This assembly ensured that there was no displacement of the edges of the specimen during testing.

The specimen assembly was mounted on an Instron 1122 machine ready for testing. A compressive load was gradually applied at the top of the corrugation, thereby imposing bending stresses on the specimen. The maximum load, $P_{\max}$, at which failure of the specimen occurs was noted. The bending strength of the specimen, $\sigma_{\max}$, was calculated using the equation

$$\sigma_{\max} = 0.1672\, P_{\max} L/bt^2 \qquad (1)$$

where L is the period of the corrugation, b is the specimen width and t is the thickness [5].

Tests were conducted for both sisal–epoxy, sisal–polyester and sisal–CNSL corrugated composites and for each composite system at least ten specimens were tested.

2.4.3. Dynamic mechanical thermal analysis (DMTA) and accelerated weathering

The main aim of the DMTA work was to investigate how the properties of the composite are affected by

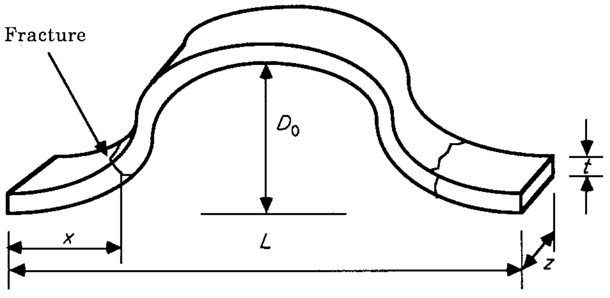

Figure 5 Specimen for crush bending tests on corrugated composites.

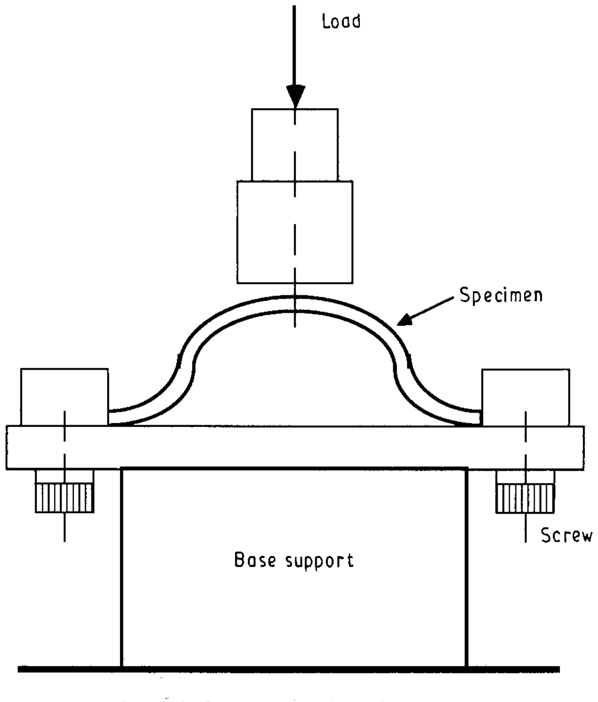

Figure 6 Bend test rig for corrugated specimen.

sunlight. It was a means of evaluating the effect of long-term outdoor exposure. The ultraviolet radiation in sunlight can cause degradation of both the cellulosic fibres and the polymeric matrix. Such structural changes in the chemistry of these materials may be reflected in the dynamic mechanical properties.

The Suntest is an accelerated testing machine which simulates a radiation distribution that is similar to sunlight using a xenon burner. The apparatus produces light intensity of about 150 klux with a radiation intensity of 1000 $W m^{-2}$ in the wavelength range between 300 and 830 nm. The specimen chamber usually heated up to between 40 and 50 °C. The amount of radiant energy falling on a surface per unit area per unit time is known as irradiance. The mean extra-terrestrial irradiance normal to solar beams just outside the earth's atmosphere is 1.35 $kW m^{-2}$. However, as the solar spectrum passes through the atmosphere it is substantially modified and a considerable amount of energy is lost by scattering and absorption even on clear days. The amount of energy reaching the earth's surface is dependent upon the actual path length and the atmospheric contents of the path. The mean irradiance in tropical/equatorial areas is about 200 $W m^2$. Hence with the Suntest equipment, 1 day's exposure is equivalent to 5 days of normal sunlight exposure in the tropics.

Plain CNSL–sisal composites were cut into small rectangular pieces of about 30 mm × 50 mm, which were then placed in the Suntest cabinet. Only one side of the specimen was exposed. The specimens were exposed for periods of 1, 4 and 8 weeks, equivalent to exposing for five times as long outdoors in the tropics.

The DMTA test facility consists of a mechanical spectrometer head, the DMTA, and a computer system. The mechanical spectrometer head has a demountable temperature enclosure, an electromagnetic drive assembly, a displacement transducer and demountable clamping devices. The DMTA imposes a sinusoidal stress on a sample in bending, shear or tensile modes and determines the sample modulus and tan δ as a function of temperature and/or frequency. The test specimens were rectangular with dimensions of 30 mm × 10 mm × 2.6 mm.

In this work a bending attachment in the form of a dual cantilever sample arrangement was used. The sample was clamped rigidly at both ends and its central point vibrated sinusoidally by the drive clamp. Tests specimen were scanned through the temperature range 25–200 °C at a single frequency of 1 Hz.

3. Results and discussion

3.1. Characterization of CNSL resin

3.1.1. Polymerization of CNSL

The polymerization characteristics of polymers listed in Table IV were examined. Sample A1 polymerized with an excessive exotherm and was almost solid within 2 h at room temperature. However, the gelling proceeded non-homogeneously such that when a droplet of acid fell into the resin, gelling occurred rapidly around it and even with stirring these gelly clusters could not be dispersed. Nevertheless, the solidified resin did not show any visible inhomogeneities.

Sample A2 gelled quickly with an exotherm, as for sample A1, and was almost fully gelled at room temperature after 2 h. Unlike sample A1, this sample gelled more uniformly and the fully cured sample was harder.

Sample A3 did not undergo any significant gelling even after leaving it overnight at room temperature. The sample was further cured at 60 °C, and after 3 days there was some slight gelling. The sample had acquired a sticky, gelly-like form. On further curing at 100 °C overnight it transformed into a rubber-like solid, still not as solid as Samples A1 and A2. The solid was porous, possibly due to condensation reaction products as well as liberation of gases following the breakdown of formaldehyde at high temperatures.

Samples B1, B2 and B3 gelled slowly at room temperature and could still be poured after 24 h. On heating to 60 °C, they quickly gelled and were fully gelled within 1 h. After post-curing at 100 °C, they had transformed into solid, but fragile materials. There was some slight bubbling at the top surface due to gaseous condensation products.

Sample B4 gelled in the same way as Samples B1, B2 and B3. However, it showed slightly more bubbling and porosity. Sample B5 gelled quickly and was fully gelled within a few hours at room temperature. Post-curing at 60 °C overnight almost fully gelled the sample. However, the sample showed excessive bubbling and porosity at the top surface.

The use of an acid catalyst that has been diluted with IPA results in a tough rigid matrix material, such as A2, that is homogeneous. However, the strong acid environment was found to be unsuitable for reinforcement of CNSL by sisal or any other cellulosic fibres as the fibres were attacked and decomposed by the acid. It is anticipated that the resin could also attack steel moulds.

The CNSL–formaldehyde combination with an alkaline catalyst is more promising although the matrix material is generally brittle. The condensation reaction of CNSL and formaldehyde requires at least a 1:1 molar ratio of these two constituents together with a small amount of an alkaline catalyst. The average molecular weight of CNSL can be estimated from the equation

$$M_{av} = \Sigma M_i W_i \qquad (2)$$

where M_i and W_i are the molecular weight and weight fraction of the constituents in CNSL, respectively.

From Table III, the average molecular weight of technical CNSL is seen to be about 251.8. The molecular weight of formaldehyde is 30. For a 37% solution, the equivalent molar weight is about 81.1. Hence a 1:1 stoichiometric composition of CNSL and formaldehyde would have the weight ratio 251.8:81.1 or 100:32.5.

In practice it is not possible to attain complete polymerization, where all the formaldehyde available is used up. Water vapour is a by-product of the condensation reaction, as shown in Fig. 4. In addition, some of the excess formaldehyde may decompose under heat to produce water vapour and carbon dioxide

$$CH_2O + O_2 = CO_2 + H_2O \qquad (3)$$

This leads to bubbling and porosity in the cast resin, hence its mechanical properties are poor. The evolution of gases during condensation can be suppressed by moulding at very high pressures. By reducing slightly the amount of catalyst to 0.5 parts by weight of resin instead of 10 parts by weight in Sample B4, a resin with a reasonably long pot life was produced, denoted B6. The molar ratio of CNSL to formaldehyde is about 1.25 (> 1) and the resulting resin is a resol type and can be readily cross-linked when cured at high temperatures.

The composition of resin B6 in parts by weight is: CNSL 100, formaldehyde 40, NaOH 0.5. The resin was gelled at room temperature for 24 h, post-cured for 3 h at 60 °C and then overnight at 100 °C. The fomulation B6 was used as the matrix component of sisal–CNSL composites which were tested in tension and crush bending. It is unfortunate that acid-cured resins are better casting resins, far stronger and tougher than those produced by condensation reactions involving formaldehyde. However, problems associated with fibre dissolution necessitate the use of the CNSL–formaldehyde alkaline catalyst system.

3.1.2. Thermal gravimetric analysis

Data from the TGA chart recorder for resin B6 have been analysed and plotted in Fig. 7. The percentage weight loss is plotted against temperature. The weight of the heated resin remains constant until close to 230 °C. Subsequent weight loss signifies the decomposition of the resin. It is, therefore, possible to perform differential scanning calorimetry up to 200 °C without risking any damage to the DSC from specimen volatilization.

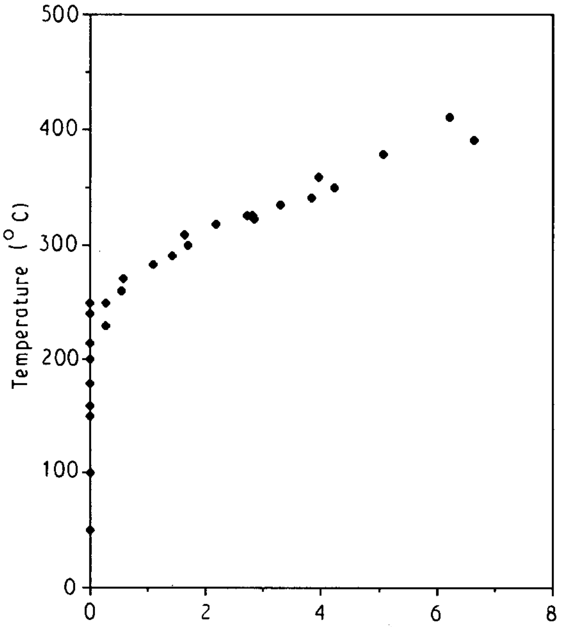

Figure 7 TGA curve for CNSL/formaldehyde resin.

3.1.3. Differential scanning calorimetry

The DSC curve for the CNSL/formaldehyde sample B6 is shown in Fig. 8. The mean glass transition temperature is 70.95 °C and the resin is not fully cross-linked. The condensation reaction of CNSL components with formaldehyde using an alkaline catalyst does not involve the aliphatic side chains. The presence of the side chains makes the polymer network more flexible. The degree of cross-linking could be improved by further curing at a higher temperature, varying the CNSL/formaldehyde ratio or increasing the amount of catalyst.

The application of heat has a tendency to promote further condensation and possibly formation of free radical ions on the points of unsaturation on the side chains, causing further cross-linking in the CNSL–formaldehyde network. The programme for processing the composite which involves moulding at an elevated temperature (150 °C), followed by prolonged cure at 100 °C, ensures that the resin in the composite is more cross-linked, giving the required brittle and elastic matrix material.

Increasing the proportions of the formaldehyde and catalyst in the resin mixture may compromise the resin's pot life and limit its capability to be used for moulding over a longer period after preparation. The resin composition B6 selected for these experiments had a reasonably long pot life (at least 12 h before gelling was noted). The use of a larger proportion of formaldehyde in the resin mixture also increases the overall cost of the resin.

3.2. Tensile testing of sisal–CNSL composites

The load–elongation curves obtained on the Instron chart recorder have been converted into stress–strain curves. A typical stress versus strain curve for a sisal–CNSL composite is shown in Fig. 9. The curve indicates that the composite is initially linear elastic in behaviour, implying that the resin system is highly cross-linked.

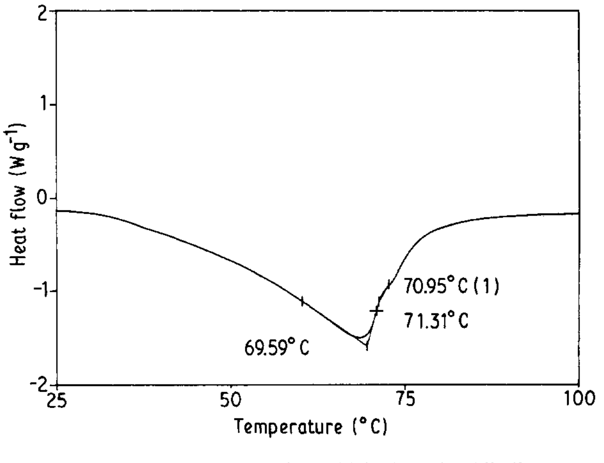

Figure 8 DSC curve for CNSL/formaldehyde resin. Alkaline catalyst. T_g at 10 °C min^{-1}.

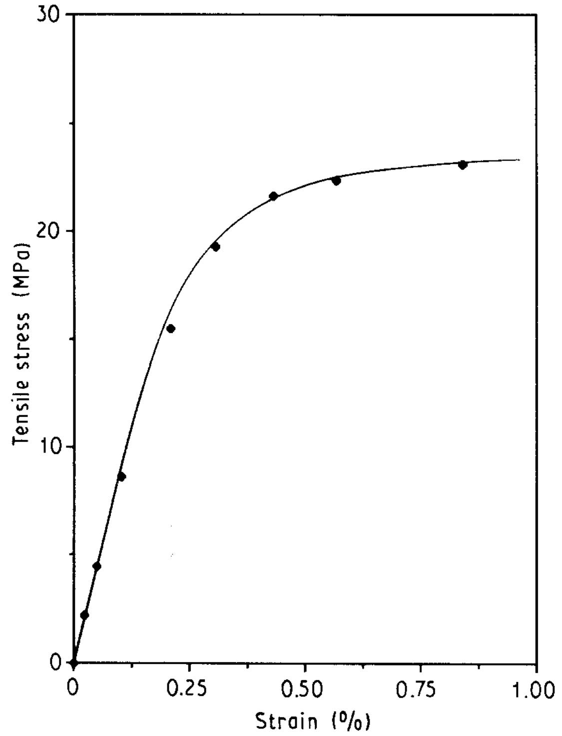

Figure 9 A typical stress–strain curve for a sisal–CNSL composite.

It was noted that the tested specimen did not fracture completely. Instead, failure was interlaminar and the laminae tended to separate out without gross tensile fracture of the reinforcing fibres. The samples had a mean tensile strength of 24.50 MPa with a standard deviation of 1.22 MPa. The mean Young's modulus was 8.81 GPa with standard deviation of 2.05 GPa.

The tensile strength of the sisal–CNSL is not very high when compared to most conventional composite systems. This is possibly due to poor interlaminar bonding which leads to interlaminar failure. It is evident from the absence of any tensile fracture of the reinforcing fibres, that the fibre strength is not utilized to its limit. Nevertheless, the composite system exhibits a respectable Young's modulus related to the high fibre content of the composite system (88% by weight).

3.3. Crush bending test

The results of crush bending tests on corrugated specimens of CNSL–sisal are compared with those for polyester–sisal and epoxy–sisal in Table V. The mean crush bending stress of corrugated sisal–CNSL composites was found to be 13.9 MPa with a standard deviation of 3.20 MPa. Failure of most specimens occurred at a distance 18.8 mm from the end supports where there is slight resin depletion due to the pressing geometry.

The CNSL–sisal results are considerably inferior to those for polyester and epoxy matrix specimens. The synthetic resins are lower in porosity and higher in volume fraction of resin, so the sisal fibres are better wetted out. A mathematical model [5] can be used to calculate the strength required of a corrugated panel for general roofing applications. It has been established that a bending stress of 0.88 MPa in the plane normal to the direction of the corrugations is required to carry a weight of 100 kg applied in the middle of such a panel with a loading span of 1.5 m. The bending strength of sisal–CNSL (13.9 MPa) is therefore more than adequately high to support the weight of a person walking on a corrugated roof.

The crush bend test on corrugated samples does not make an ideal assessment of the suitability of sisal–CNSL as a roofing material. For commercial validation a full-size panel would have to be produced and tested according to standards such as BS 4154 and BS 4203.

3.4. Dynamic mechanical thermal analysis

DMTA spectra from a sisal–CNSL composite are shown in Fig. 10. The dynamic storage modulus and loss tangent are plotted versus temperature. There is no well-defined glass transition in the temperature range observed and the sisal–CNSL composite is highly cross-linked. There are, however, two characteristic peaks on the damping curve which occur at about 55° and 150 °C.

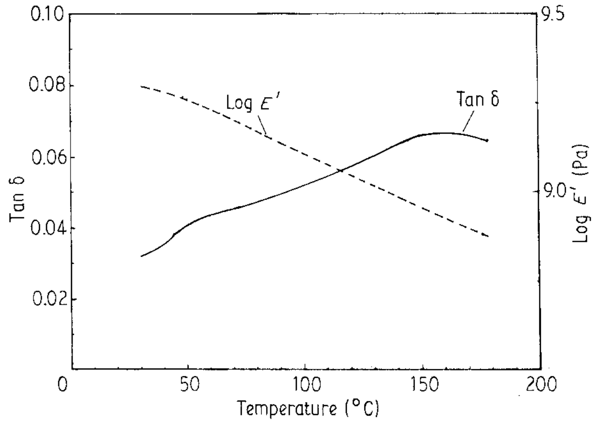

Figure 10 Storage modulus and loss tangent plotted versus temperature for a sisal–CNSL composite.

TABLE V Results of bending (crush) tests on corrugated specimens

Composite system	Length L (mm)	Depth D_0 (mm)	Width z (mm)	Thickness t (mm)	Mean crush stress (MPa)	Standard deviation (MPa)	Position of failure, x (mm)
Polyester–sisal	71	38	20	4.0	61.2	16.9	18.0
Epoxy–sisal	71	38	20	3.3	88.2	14.8	19.7
CNSL–sisal	71	38	20	2.3	13.9	3.2	18.8

The effect of sunlight on sisal–CNSL composites has been assessed by DMTA. Specimens were exposed in the Suntest equipment for 168, 672 and 1350 h, respectively. The storage modulus, loss modulus and loss tangent of exposed specimens are compared with those for unexposed specimens in Figs 11–13 respectively. It can be seen that significant changes in the dynamic mechanical properties of the composite occur as a result of exposure to simulated sunlight. The storage modulus increases with increasing exposure time whilst the damping decreases.

The two peaks observed in Fig. 10 become more distinct with longer exposure time. The double peaks are an indication of thermal transitions occurring within the constituents of the composite. These must relate either to the resin matrix or the cellulosic fibres. The low-temperature peak occurs at a temperature that is close to the glass transition temperature of the

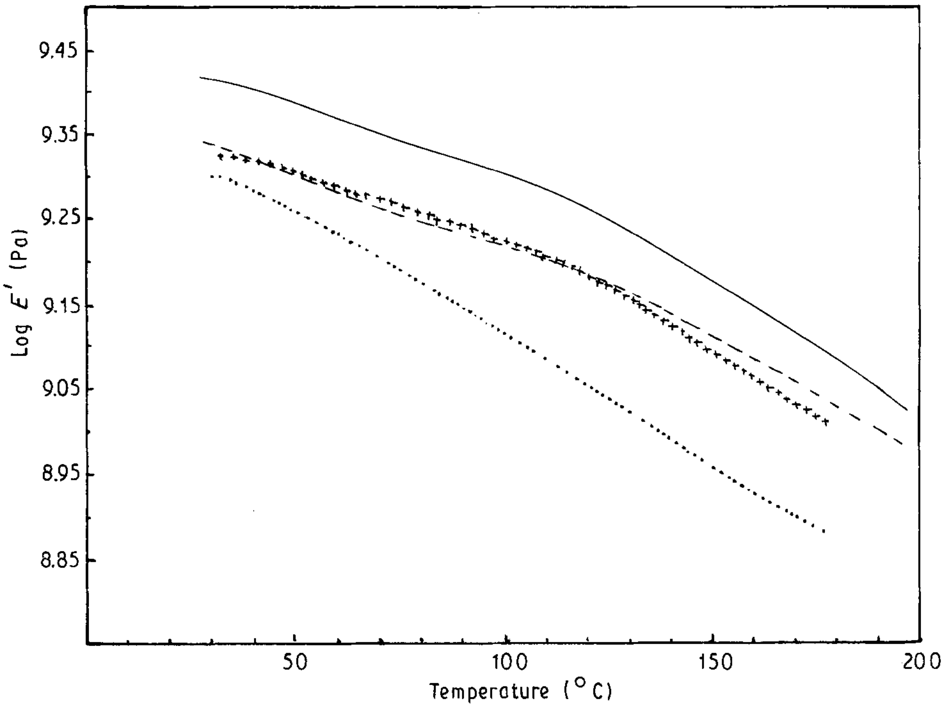

Figure 11 Effect of sunlight on storage modulus, for (–) 1350 h, (+) 672 h, (– – –) 168 h, (· · ·) 0 h.

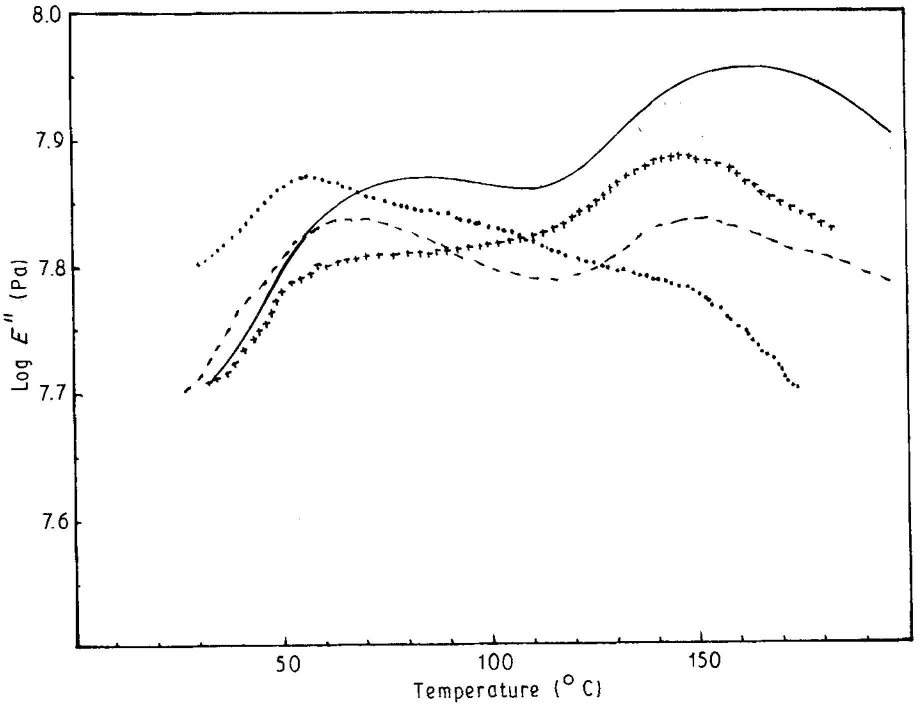

Figure 12 Effect of sunlight on loss modulus, for (–) 1350 h, (+) 672 h, (– – –) 168 h, (· · ·) 0 h.

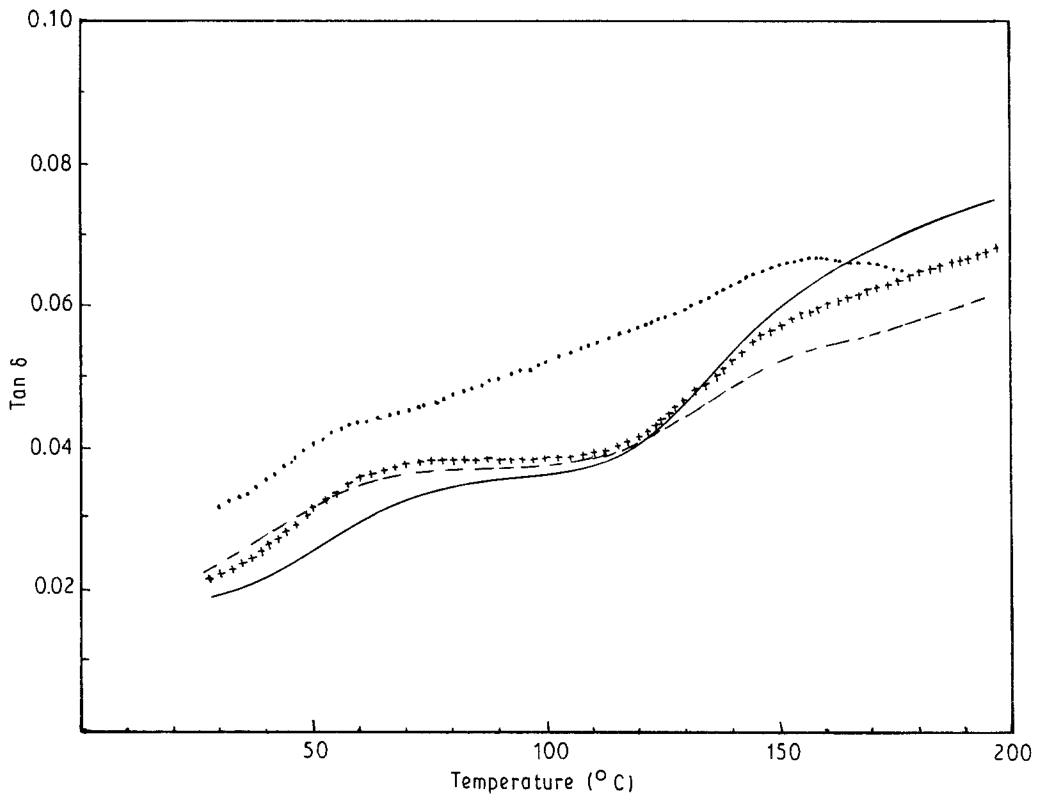

Figure 13 Effect of sunlight on damping for (–) 1350 h, (+) 672 h, (---) 168 h, (···) 0 h.

CNSL–formaldehyde resin evaluated by DSC in Fig. 9. The resin volume fraction of the composite is very low and the transitions in the resin are probably suppressed by the presence of the more predominant fibres.

If the low-temperature peak is attributed to transitions in the resin matrix then the higher temperature peak is likely to be due to transitions within the cellulosic fibres. At all temperatures scanned, the storage modulus, Fig. 11, generally increases with duration of exposure. This increase in stiffness will be a result of improvements in the degree of cross-linking of the polymer network. It is likely that this was a consequence of prolonged exposure of the polymer matrix in the Suntest chamber which reaches a temperature of approximately 45 °C.

Loss modulus spectra, Fig. 12, provide additional information. At low temperatures the loss modulus is observed to decrease with increasing exposure time consistent with the increase in the storage modulus. However, at higher temperatures, this trend is reversed, and the loss modulus is observed to increase with increasing sunlight exposure time. The loss modulus spectra and similarly the damping spectra, Fig. 13, exhibit two peaks at low and high temperatures. The high-temperature peak is more sensitive to changes in sunlight exposure time and its magnitude is higher for longer times of exposure. It has been suggested earlier that the high-temperature peak corresponds to transitions taking place within the cellulosic fibres. This suggests that sunlight degrades the cellulose causing the fibres to behave more compliantly.

The presence of short wavelength ultraviolet radiation in the sunlight spectrum is the main cause for degradation of the cellulose polymer network. It should be noted that this phenomenon is only observed at elevated temperatures and the stiffness of the composite is not affected at near ambient temperatures.

4. Conclusions

1. Cashew nut shell liquid (CNSL) monomer blend can be cured with an acid catalyst such as sulphuric acid in the presence of isopropyl alcohol (IPA) to produce a useful thermoplastic for general engineering applications. However, natural cellulosic fibre reinforcement dissolves in an acid catalyst cured CNSL resin matrix and acid catalysis is therefore impractical for composites applications.

2. CNSL can be condensation polymerized with formaldehyde in the presence of a sodium hydroxide catalyst to produce a resol-type polymer that can be used to bind sisal fibres to produce a cheap and useful composite. The resin is thermally stable up to 230 °C and is further cross-linked when exposed to simulated sunlight.

3. Thermal gravimetric analysis has demonstrated that CNSL resin cured with an alkaline catalyst is thermally stable to temperatures greater than 200 °C.

4. The glass transition temperature of the CNSL cured with an alkaline catalyst has been determined by differential calorimetry and has a value of 70.95 °C. The degree of cross-linking of the resin depends on its thermal history.

5. Composite sheets have been produced from plain woven sisal mats impregnated with CNSL resin. The

samples had a mean tensile strength of 24.50 MPa and a mean Young's modulus of 8.81 GPa.

6. The crush bending stress of corrugated sisal–CNSL panels is 13.9 MPa. This is adequate to allow these low-cost panels to be used for roofing applications.

7. Dynamic mechanical thermal analysis reveals that exposure to intense artificial sunlight increases the degree of cross-linking of the matrix phase of sisal–CNSL composites with time. At high temperatures sunlight degrades the cellulosic reinforcement. Near ambient temperature little degradation occurs.

8. Sisal–CNSL composites show potential for roofing applications in tropical countries such as Tanzania where the natural constituents are freely available. Further work is required to refine the composition and curing schedule for the CNSL resin system cured with an alkaline catalyst. Practical aspects of hot-pressing composite panels need investigation to reduce porosity and to decrease the fibre volume fraction so that stress transfer between fibres is improved. The dimensional stability and strength of panels in humid and wet environments require further evaluation.

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