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Effect of chemical treatment on the tensile properties of short sisal fibre-reinforced polyethylene composites

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The effect of chemical treatment on the tensile properties of sisal fibre-reinforced LDPE (low density polyethylene) composites was investigated. Treatments using chemicals such as sodium hydroxide, isocyanate, permanganate and peroxide were carried out to improve the bonding at the fibre–polymer interface. The treatments enhanced the tensile properties of the composites considerably, but to varying degrees. The SEM (scanning electron microscopy) photomicrographs of fracture surfaces of the treated composites clearly indicated the extent of fibre–matrix interface adhesion. It has been demonstrated that the CTDIC (cardanol derivative of toluene diisocyanate) treatment reduced the hydrophilic nature of the sisal fibre and thereby enhanced the tensile properties of the sisal–LDPE composites. The SEM photomicrographs of the fracture surfaces have also shown that PE was highly bonded to the sisal fibre in CTDIC treated composites. The observed enhancement in tensile properties with the addition of small amounts of peroxides was attributed to the peroxide induced grafting of PE on to sisal fibre surfaces, as evident from the SEM photomicrographs of the fracture surfaces. It has been found that a low concentration of permanganate in the sisal–LDPE system during mixing considerably enhanced the mechanical properties. Among the various treatments, peroxide treatment of fibre imparted maximum interfacial interactions. Copyright © 1996 Elsevier Science Ltd.

(Keywords: sisal fibre; polyethylene; composites)

INTRODUCTION

In recent years, thermoplastic materials are being increasingly used for various applications[1]. Because of their increasing use combined with the high demand, the cost of the thermoplastics has increased rapidly over the past decade. This situation made it necessary to use low cost fillers as a means of reducing the cost of the end product. However, the widely used inorganic fillers, such as glass fibre and mica are very expensive compared to natural fibres[2]. Natural fibre-reinforced thermoplastic composites are more economic to produce than the original thermoplastics and, as a result, it may be possible to meet any future shortage of thermoplastics[3]. Moreover, the use of natural fibre in thermoplastic composites is highly beneficial, because the strength and toughness of the plastics can be improved. However, lack of good interfacial adhesion and poor resistance to moisture absorption made the use of natural fibre reinforced composites less attractive[4]. This problem can be overcome by treating these fibres with suitable chemicals.

Interfaces play an important role in the physical and mechanical properties of composites[5]. Reinforcement of fibres are normally given surface treatments to improve their compatibility with the matrix. Cellulosic fibres are also reported to be generally incompatible with hydrocarbon polymers due to the hydrophilic nature of the former; therefore, several treatments have been reported to improve the fibre–matrix interfacial bonding. Bisanda and Ansell[4] and Prasad *et al.*[6] have studied the effect of alkali treatment on the physical and mechanical properties of sisal–epoxy and coir–polyester composites, respectively. Varma and co-workers[7–11] have studied the effect of various coupling agents on the mechanical properties of jute and coir fibre-reinforced thermoset composites. The fibre–matrix interfacial bond strength is expected to be very poor in composites of cellulosic fibre, which is hydrophilic in nature, and polyethylene (PE) which is hydrophobic. Several treatments have been developed for the above system to improve the interface bonding[12–14]. Kokta and co-workers[12,13,15–17] have reported that coupling agents like silanes and isocyanates improve the mechanical properties and dimensional stability of cellulosic fibre–PE composites.

Peroxide induced adhesion in cellulose fibre-reinforced thermoplastic composites has attracted the attention of

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various workers due to the easy processability and improvement in mechanical properties[18–28]. Sapieha *et al.*[19] have reported that the addition of a small amount of benzoyl peroxide or dicumyl peroxide into cellulose fibre–LDPE (low density PE) systems during processing improves their tensile properties significantly. Potassium permanganate ($KMnO_4$) has been reported by Tripathy *et al.*[29] and Moharana *et al.*[30] to be a powerful initiator for grafting of methyl methacrylate on to jute fibres.

Very recently, in this laboratory we have successfully incorporated sisal fibre into elastomers and thermoplastics. Sisal is a high cellulose content leaf fibre obtained from the plant Agave-veracruz. It is abundantly available in the southern part of India, especially in Kerala and Tamil Nadu. Since it is a drought resistant plant, it can be cultivated in barren or dry lands. Due to the very good physical and mechanical properties of these fibres (*Table 1*), large scale production and cultivation will produce great changes in the natural fibre industry. Cost effective polymer products can be fabricated from the composites of sisal fibre with thermoplastic and thermosetting polymers. Processing characteristics, mechanical properties and rheological behaviour of the resulting composites have been reported by our research group[31–35]. In this paper, attempts have been made to study the effects of various chemical treatments such as sodium hydroxide, CTDIC (Cardanol derivative of toluene diisocyanate), peroxide and permanganate on the tensile properties of sisal–LDPE composites as a function of volume fraction, fibre length and fibre orientation.

EXPERIMENTAL

Materials

Sisal (Agave-veracruz) fibre was obtained from local sources. The physical and mechanical properties of sisal fibre are given in *Table 1*. The fibre was washed thoroughly with water and dried in an air oven at 80°C for 4–6 h, before being chopped into the desired length for fibre treatment and composite preparation. LDPE (Indothene 16MA400), was supplied by Indian Petrochemicals Corp., Baroda, India. The physical and mechanical properties of LDPE are given in *Table 2*.

Cardanol, the principal component of cashew nut shell liquid (CNSL) obtained from *Anacardium occidentale* L, is a plant-source raw material abundant in tropical countries like India (southern part) and Vietnam. Cardanol was supplied by Satya Chemicals, Madras. Toluene-2,4-diisocyanate (TDI) was obtained from Fluka, Switzerland. Dicumyl peroxide (DCP) (Varox DCP-R) was supplied by R. T. Vanderbilt Co., Norwalk, USA. Benzoyl peroxide (BP) was obtained from BDH Chemicals, Poole, UK. Potassium permanganate ($KMnO_4$) and sodium hydroxide (NaOH) used in the present study were of chemically pure grade. Dibutyl tin dilaurate was obtained from Scientific and Industrial Supplies Corp., Bombay.

Fibre treatment

Alkali treatment. The chopped fibres were taken in a stainless steel vessel. A 10% solution of NaOH was added into the vessel and stirred well. This was kept for 1 h with subsequent stirring. The fibres were then washed thoroughly with water to remove the excess of NaOH sticking to the fibres. Final washings were carried out with distilled water containing a little acid. The fibres were then air dried.

Preparation of urethane derivative of cardanol. The synthesis of a urethane derivative of cardanol was carried out using a 1/1 molar ratio of cardanol and TDI containing a free isocyanate group. Cardanol (a principal component of CNSL (30 g, 0.1 mol)) was taken in a pressure equalizing funnel and diluted with CCl_4 (50 ml) and 1 ml of dibutyl tin dilaurate as catalyst. TDI (17.4 g, 0.1 mol) was contained in a round bottomed flask of capacity 500 ml. The cardanol solution was added dropwise into TDI under constant stirring until the addition of cardanol was complete. The stirring was continued for one more hour for the completion of the reaction. The product formed contained one free isocyanate group for further reaction (*Figure 1*). The product obtained was used as such for further reaction.

Treatment of sisal fibre with isocyanate. The alkali-treated dried fibres were placed in a round bottomed flask and soaked with an appropriate volume of CCl_4 and a little (1 ml) dibutyl tin dilaurate catalyst. The round bottomed flask was fitted with a pressure equalizing funnel containing the urethane derivative. The urethane derivative was added into the flask dropwise with sufficient stirring. After the complete addition of

Table 1 Properties of sisal fibre

Fibre diameter (μm)	Lignin content (%)	Cellulose content (%)	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation at break (%)
100–300	4–5	85–88	400–700	9–20	5–14

Table 2 Physical and mechanical properties of low density polyethylene (LDPE; Indothene 16 MA 400)

Melt flow (g per 10 min)	Density (g ml^{-1})	Tensile strength at break (MPa)	Elongation at break (%)	Modulus of elasticity (MPa)	Vicat softening point (°C)	Crystalline point (°C)
40	0.916	9	200	140	85	104

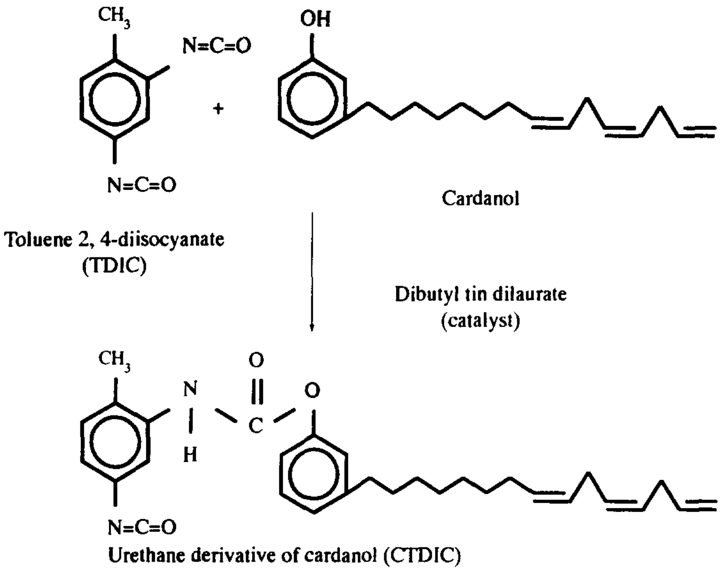


Figure 1 The reaction pathway for the preparation of urethane derivative of cardanol

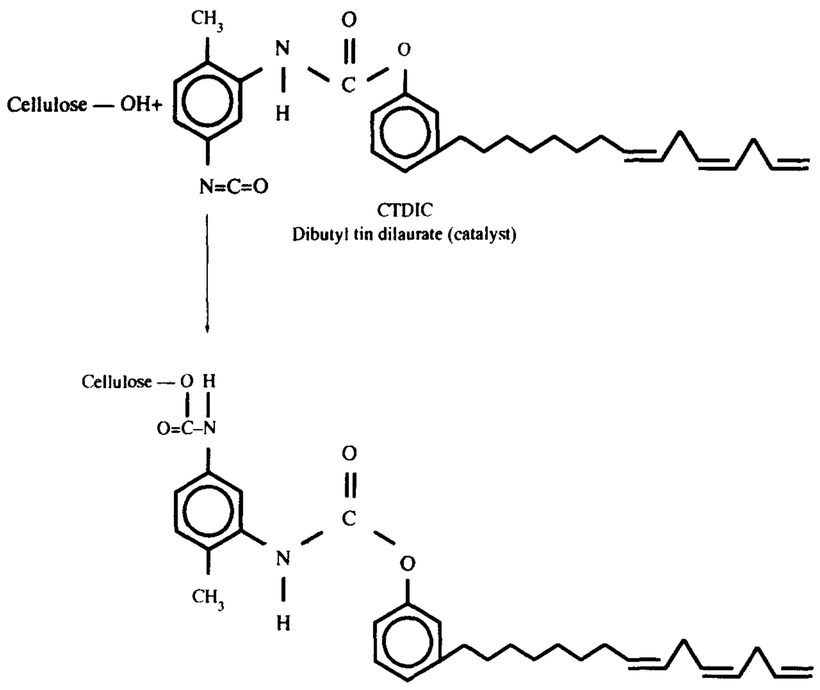


Figure 2 A possible reaction between the free isocyanate groups in CTDIC and cellulosic sisal fibre

urethane, the reaction was allowed to continue for one more hour (*Figure 2*). The urethane treated fibres were purified by refluxing with acetone for 8 h in a Soxhlet apparatus followed by repeated washing with distilled water. Finally, the fibres were oven dried at 80°C.

Dicumyl peroxide treatment. The alkali treated fibres (30 g) were soaked with 1 l of a 6% solution of DCP in acetone for 30 min. The solution was decanted and the fibres were air dried.

Benzoyl peroxide treatment. A similar procedure adopted as in the case of DCP was used here.

Permanganate treatment. The alkali treated fibres (30 g) were soaked with 1 l of $KMnO_4$ solution in acetone having different concentrations (0.005–0.205%) for 1 min. This was then decanted and the fibres were dried in air.

Preparation of LDPE–sisal composites

The LDPE–sisal composites were prepared by a solution mixing technique followed by extrusion as reported by Joseph *et al.*[32]. In the solution mixing method, the fibre was added to a viscous slurry of PE in toluene which was prepared by adding toluene to a melt of the polymer. The mixing was carried out manually in a stainless steel beaker using a stainless steel stirrer for a period of 10 min. The temperature of mixing was maintained at 110°C. The mix was then transferred into a flat tray as lumps and kept in a vacuum oven at 70°C for 2 h to remove the solvent. Composites containing 10, 20 and 30 wt% of fibre were prepared using fibres of length in the range 2–10 mm.

Preparation of composite sheets

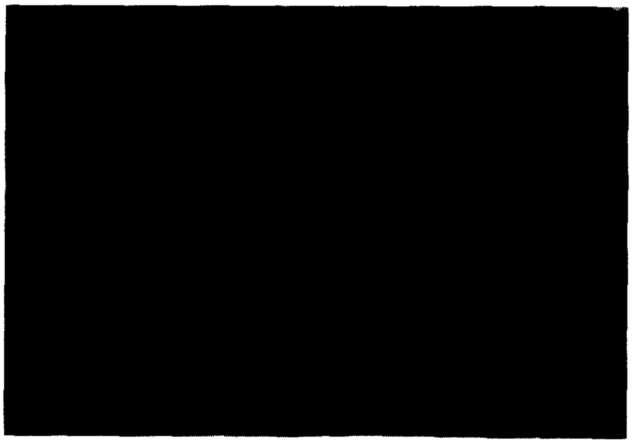
Sisal–LDPE randomly oriented fibre composites. Sisal–PE composites prepared by solution mixing were used for making the randomly oriented fibre composites. Composite specimens of dimensions 120 mm × 12.5 mm × 3 mm were prepared by injection moulding of the blends at 115 ± 5°C using a hand operated ram type injection moulding machine.

Sisal–LDPE oriented fibre composites. The specimens of oriented fibre composites were prepared from the blends obtained by the solution mixing method. A combination of injection and compression moulding techniques was used for making the composite sheets. The blend was first extruded into 4 mm thick cylindrical rods using a hand injection moulding machine. Rectangular specimens of size measuring 120 mm × 12.5 mm × 3 mm were prepared by closely aligning the cylindrical extrudates (120 mm long and 4 mm thick) in a leaky mould and then compression moulding, employing a pressure of about 4 MPa and a temperature of 115 ± 5°C. The mould was cooled below 50°C before removing the composite specimens from the mould. The orientation of the random and unidirectional composites were analysed by optical microscopy. *Figures 3a* and *b* and *4a* and *b* show the surfaces of the random and oriented composites. The figures indicate that the processing operation control the orientation. In the case of random composites we could not find any major difference in the orientations of the skin and the core. The orientation of the treated composites was also analysed by microscopy. It was found that orientation was unaffected by treatment.

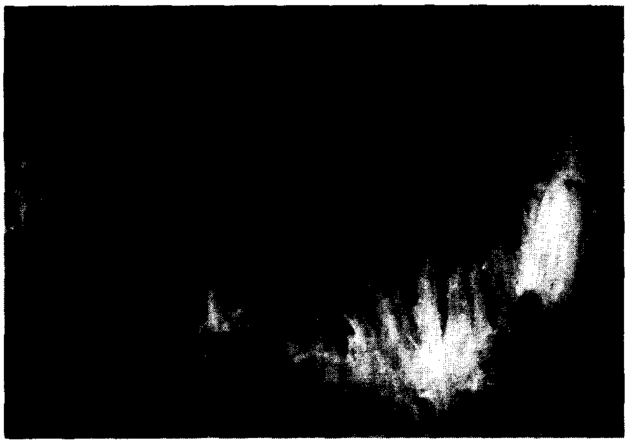
a

b

Figure 3 Optical micrograph of (a) the surfaces of randomly oriented composites and (b) the fracture surfaces of randomly oriented composites



a



b

Figure 4 Optical micrograph of (a) the surfaces of unidirectionally oriented composites and (b) the fracture surfaces of undirectionally oriented composites

Mechanical testing of composites

Tensile testing of rectangular specimens of size 120 mm × 12.5 mm × 3 mm was carried out using an Instron Universal testing machine model 1190 at a cross-head speed of 200 mm min^{-1} and a gauge length of 50 mm. The tensile modulus and elongation at break of the composites were calculated from the load–displacement curve. At least five specimens were tested for each set of samples and the mean values were reported.

Fracture surface morphology

The surfaces of the tensile fractured specimens were examined using a Jeol 35 C model scanning electron microscope (SEM).

Table 3 Variation of tensile properties of alkali treated sisal fibre–LDPE composites with fibre content (fibre length 5.8 mm; the values given in parentheses are the properties of untreated composites)

Fibre content (wt %)	Tensile strength (MPa)				Modulus (MPa)				Elongation at break (%)			
	Unidirectional	SD	Random	SD	Unidirectional	SD	Random	SD	Unidirectional	SD	Random	SD
0	9.2	0.1212	9.2	0.1818	140	0.1010	140	0.1818	200	0.1010	200	0.1010
10	17.67	0.21	13.28	0.2616	1700	0.2010	482	0.2116	5	0.1115	28	0.1335
	(15.61)	(0.2212)	(10.8)	(0.4310)	(1429)	(0.1985)	(324)	(0.3616)	(4)	(0.1010)	(27)	(0.1218)
20	24.24	0.1735	16.5	0.2818	2326	0.1985	926	0.1818	4	0.1330	12	0.1414
	(21.66)	(0.1885)	(12.5)	(0.3815)	(2088)	(0.2098)	(453)	(0.2515)	(3)	(0.1200)	(10)	(0.1313)
30	34.27	0.1865	18.8	0.4218	3328	0.1775	1140	0.1818	1	0.1135	10	0.1515
	(31.12)	(0.1515)	(14.7)	(0.4620)	(3086)	(0.1909)	(781)	(0.2705)	(2)	(0.1225)	(7)	(0.1465)

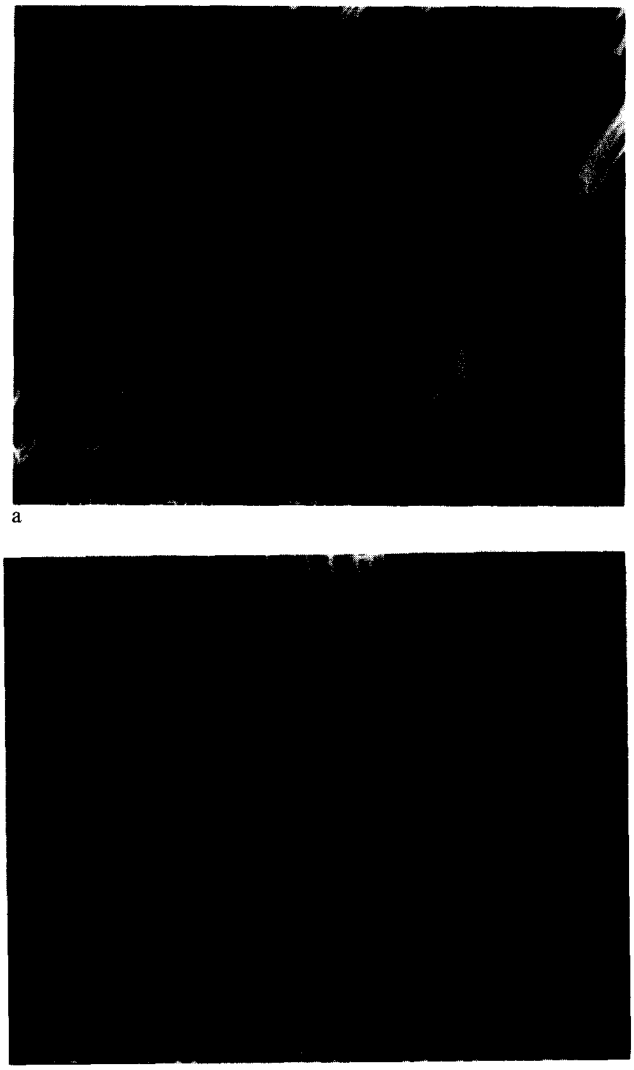
SD = standard deviation

RESULTS AND DISCUSSION

Effect of alkali treatment

Tensile properties of longitudinally and randomly oriented (alkali treated and untreated) sisal–LDPE composites with different fibre loading are presented in *Table 3*. From these tables it is clear that in both cases (randomly oriented and unidirectionally oriented composites), tensile strength and modulus increase with fibre loading. However, it is seen that the alkali treated composites showed superior tensile properties than untreated composites. This is due to the fact that alkali treatment improves the fibre surface adhesive characteristics by removing natural and artificial impurities, thereby producing a rough surface topography[4]. *Figures 5a* and *b* are the SEM photomicrographs of the surface of untreated and alkali treated sisal fibre, respectively. The treated fibre has a rough surface topography. In addition, alkali treatment leads to fibre fibrillation, i.e. breaking down of the composite fibre bundle into smaller fibres. This increases the effective surface area available for contact with the matrix[4]. In other words, alkali treatment reduces fibre diameter and thereby increases the aspect ratio. Therefore, the development of a rough surface topography and enhancement in aspect ratio offer better fibre–matrix interface adhesion and an increase in mechanical properties. *Figure 6* is the fracture surface morphology of the alkali treated sisal–LDPE composites. The better fibre–matrix adhesion can be readily seen from the figure. The existence of PE particles adhered on the fibre surface can be observed in alkali treated fibre composites. However, the untreated fibre surface is smooth (*Figure 7*) without any PE particles.

Table 4 shows the tensile properties of longitudinally and randomly oriented sisal–LDPE composites (both untreated and alkali treated) with different fibre lengths. It is interesting to note that alkali treated sisal–LDPE composites showed superior tensile properties than untreated composites at all fibre lengths. The strength and modulus of the composites show an enhancement in their values by increasing the average fibre length from 2.1 to 5.8 mm followed by a decrease in properties when a fibre length of 9.2 mm is employed. Observation of the composite specimens has shown that long fibres tend to bend or curl during moulding. This causes reduction in the effective length of the fibre below the optimum length in a particular direction, which results in a decrease of properties. The results indicate that there exists an optimum fibre length between 5.8 and 9 mm at which a maximum improvement in the properties of the composites can be achieved.


a

b

Figure 5 SEM photomicrograph of (a) the surface of untreated sisal fibre and (b) the surface of alkali treated sisal fibre

Effect of isocyanate treatment

It has already been reported that poly[methylene poly(phenyl isocyanate)] (PMPPIC) treated cellulose fibre–polymer composites exhibit superior mechanical properties and dimensional stability [13,36,37]. The functional group –N=C–O in PMPPIC is highly reactive to

Table 4 Variation of tensile properties of alkali treated sisal fibre–LDPE composites with fibre length (fibre content 30%; the values given in parentheses are the properties of untreated composites

Fibre length (mn)	Tensile strength (MPa)				Modulus (MPa)				Elongation at break (%)			
	Unidirectional	SD	Random	SD	Unidirectional	SD	Random	SD	Unidirectional	SD	Random	SD
0	9.2	0.1212	9.2	0.1212	140	0.1818	140	0.1818	200	0.1010	200	0.1010
2.1	21.57	0.1345	13.52	0.1318	1812	0.2835	526	0.1415	4	0.1125	14	0.1675
	(20.5)	(0.1212)	(11.38)	(0.1765)	(1687)	(0.3010)	(283)	(0.1215)	(4)	(0.1020)	(12)	(0.2010)
5.8	34.27	0.1865	18.8	0.4218	3328	0.1775	1140	0.1818	1	0.1135	10	0.1515
	(31.12)	(0.1515)	(12.5)	(0.4600)	(3086)	(0.1919)	(453)	(0.2715)	(2)	(0.1225)	(7)	(0.1465)
9.2	28.17	0.2015	–		2212	0.3112	–		4	0.1225	–	
	(25.9)	(0.1535)			(1716)	(0.3242)			(4)	(0.1135)		

SD = standard deviation

Figure 6 SEM photomicrograph of the tensile fracture surface of the alkali treated sisal fibre–LDPE composites showing PE penetrated into the fibre

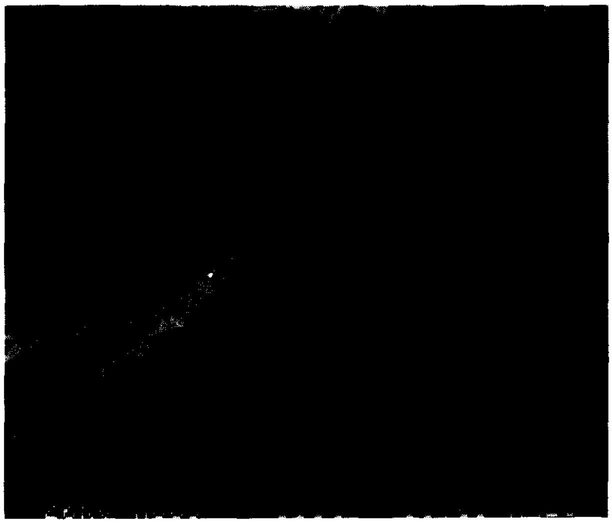
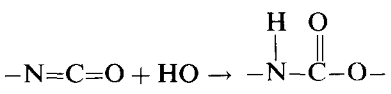


Figure 7 SEM photomicrograph of the tensile fracture surface of the untreated sisal fibre composites showing poor interaction between PE and fibre

the –OH groups of cellulose and lignin[36]. This leads to the development of a urethane linkage as shown below:



$$-N{=}C{=}O + HO \rightarrow -\overset{\displaystyle H}{\overset{|}{N}}-\overset{\displaystyle O}{\overset{\|}{C}}-O- \qquad (1)$$

Cardanol, the principal component of CNSL from *Anacardium occidentale*, is a plant-source raw material abundant in tropical countries like India (southern part) and Vietnam[37,38]. This liquid prepolymer contains a mixture of phenols possessing long saturated and unsaturated hydrocarbon chains at the *meta*-position[37]. The reaction path way for the preparation of urethane derivative of cardanol is given in *Figure 1*. The details of the preparation of the urethane derivative of cardanol was given in the Experimental section. The i.r. spectrum of the compound CTDIC exhibited the characteristic urethane peaks at 3350 cm^{-1} for –NH and 1720 cm^{-1} for –C=O stretching vibrations. The introduction of the cardanol moiety was indicated by the presence of a –C=C peak at 1620 cm^{-1}, –CH aromatic at 3020 cm^{-1} and –C–H aliphatic at 2980 cm^{-1}. The i.r. spectrum of the CTDIC also showed peaks at 1440 and 1590 cm^{-1} due to the –C=C aromatic ring stretching.

The cellulose hydroxyl groups in the fibre are relatively unreactive, since they form strong hydrogen bonds. Alkali treatment may destroy the hydrogen bonding in cellulosic hydroxyl groups, thereby making them more reactive[4,39]. The possible reaction between the free isocyanate groups in CTDIC and cellulose is illustrated in *Figure 2*. The linking of isocyanate with the fibre was by the formation of a chain of covalent chemical bonds.

Table 5 shows the tensile properties of CTDIC treated, alkali treated and untreated sisal–PE composites having 30% fibre loading. The fibre length used was 5.8 mm. In both cases (longitudinal and random) CTDIC treated fibre composites show superior tensile strength and modulus than alkali treated and untreated composites. As mentioned earlier, one of the major drawbacks associated with cellulosic fibres as reinforcement in polyolefin matrices is the divergent behaviour in polarities of both the phases, i.e. the hydrophilic nature of cellulose and the hydrophobic nature of polyolefins. By treating the cellulose fibre surface with CTDIC, the hydrophilic nature can be reduced. The long chain structure of CTDIC linked to the cellulosic fibre makes the fibre hydrophobic, compatible and highly dispersible in the PE matrix. This will result in a strong interfacial bond between the fibre and the PE matrix. This can be further understood from *Figures 8a* and *b*, which show that PE is highly bonded to the fibre surface. This facilitates effective stress transfer between the fibre and PE matrix. A possible hypothetical chemical structure of cellulose

Table 5 Variation of tensile properties of longitudinally oriented LDPE–sisal composites with fibre treatments (fibre length 5.8 mm; fibre content 30%; the values given in parentheses are the values of randomly oriented composites)

Composites	Tensile strength (MPa)	SD	Modulus (MPa)	SD	Elongation at break (%)	SD
Untreated	31.12	0.1515	3086	0.1919	2	0.1225
	(14.7)	(0.4620)	(781)	(0.2715)	(7)	(0.1465)
Alkali	34.27	0.1865	3328	0.1775	1	0.1135
treated	(18.8)	(0.4218)	(1140)	(0.1818)	(10)	(0.1515)
Isocyanate	41.5	0.1939	4066	0.1798	4	0.1212
treated	(19.5)	(0.2115)	(1230)	(0.1818)	(10)	(0.1020)

SD = standard deviation

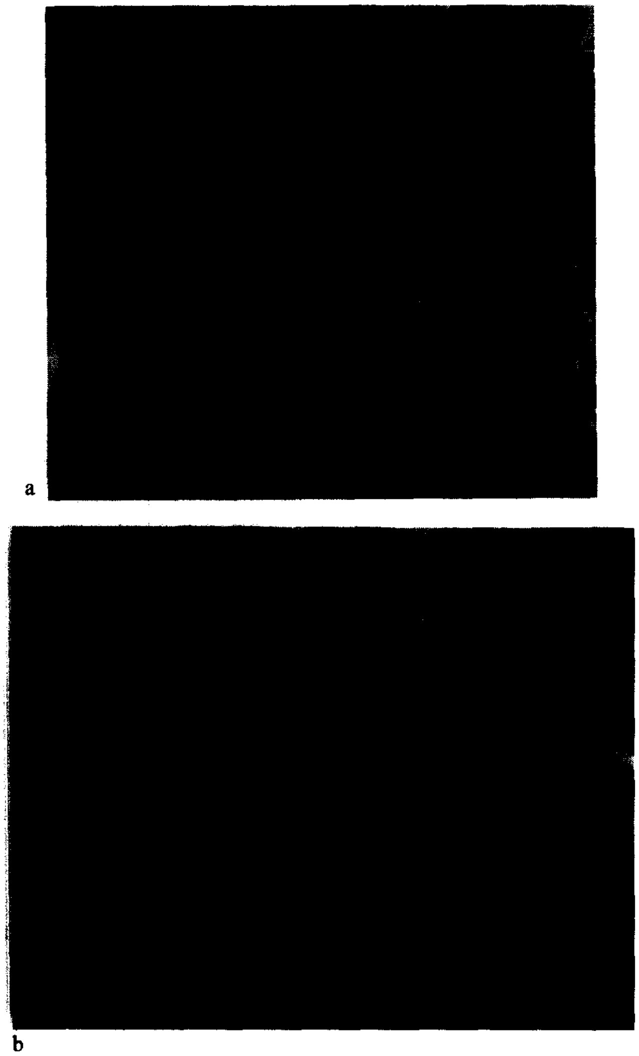


Figure 8 SEM photomicrograph of (a) tensile fracture surface of isocyanate (CTDIC) treated sisal–LDPE composites and (b) the magnified view of isocyanate (CTDIC) treated sisal fibre–LDPE composite showing PE grafted to fibre surface

fibre–CTDIC–PE in the interfacial area is given in *Figure 9*.

Effect of peroxide treatment

The effect of peroxide DCP and BP concentration on the tensile strength of sisal–LDPE composite (both unidirectional and random) at 30% fibre loading is shown in *Figure 10*. It is obvious from *Figure 10* that the tensile strength values of the composites increase with increase in concentration of peroxide up to a certain level (4% for DCP and 6% for BP) and then remains constant. This concentration may be defined here as critical peroxide concentration at which the tensile strength reaches maximum for a given fibre content[19]. The existence of a critical concentration of peroxide suggests that the grafting reactions terminate when the fibres are covered with grafted PE. Excess of peroxide causes some crosslinking of the PE and this has only a minor effect on the overall mechanical properties of the composites. It is clear from the above figure that DCP is more effective than BP at all levels of peroxide addition. This may be due to the difference in the relative rates of peroxide decomposition. It is reported that DCP has a lower decomposition rate than BP[19] and ensures better dispersion in the polymer matrix. Therefore, this is more efficiently utilized for the grafting reaction between LDPE and cellulose, which is discussed later.

Table 6 shows the tensile properties of peroxide treated randomly and unidirectionally oriented sisal–LDPE composites, respectively, at 30% fibre loading. It is interesting to note that peroxide treatment improves the tensile properties significantly. For example, the tensile strength of DCP treated randomly oriented fibre composites is 21.8 MPa. This is approximately 50% more than the tensile strength of the untreated composites (14.7 MPa). BP treated composites also show a similar increase in tensile properties. The modulus values of the treated composites also show a similar trend. The increase in the tensile properties offered by the peroxide treated composites is due to the peroxide initiated free radical reaction between the LDPE matrix and cellulose fibres as shown below:

$$\mathrm{RO{-}OR} \rightarrow 2\mathrm{RO}^{\cdot}$$

$$\mathrm{RO}^{\cdot} + \mathrm{PE{-}H} \rightarrow \mathrm{ROH} + \mathrm{PE}^{\cdot}$$

$$\mathrm{RO}^{\cdot} + \text{Cellulose-H} \rightarrow \mathrm{ROH} + \text{Cellulose}^{\cdot}$$

$$\mathrm{PE}^{\cdot} + \text{Cellulose}^{\cdot} \rightarrow \text{PE–Cellulose}$$

Figures 11 and *12* are the SEM photomicrographs of the tensile fracture surfaces of DCP and BP treated sisal fibre–LDPE composites, respectively. The above figures clearly indicate that PE is grafted on to the cellulose surface. A similar type of peroxide induced PE grafting on to cellulose fibre was reported by Sapieha *et al.*[19]. The treated fibres adhere well to the polymer matrix and undergo breaking and delamination during tensile failure, whereas untreated fibres are easily pulled out from the matrix during tensile failure. From the fracture surfaces of DCP treated and BP treated composites, it can be understood that the interfacial bonding is stronger in the DCP system.

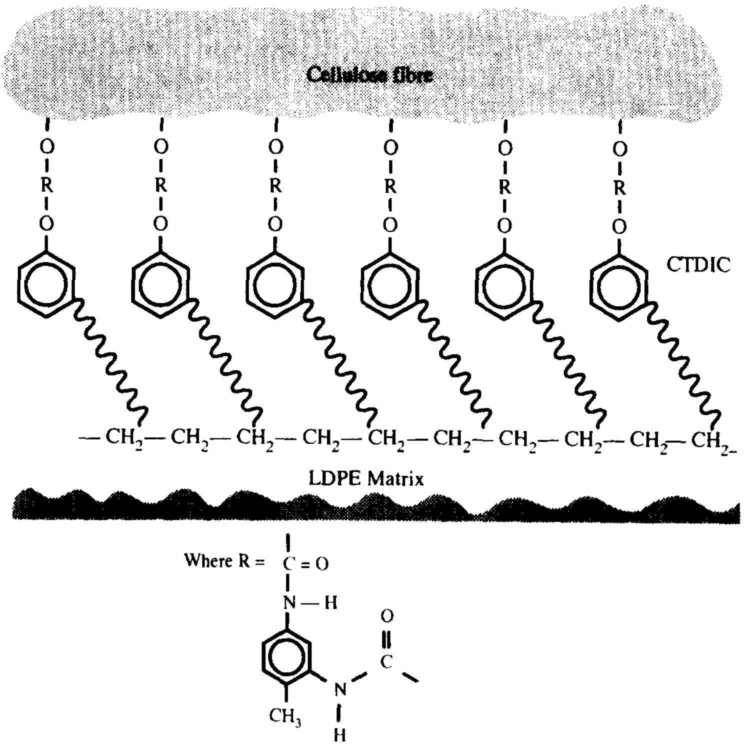


Figure 9 A possible hypothetical chemical structure of sisal fibre–CTDIC–PE in the interfacial area

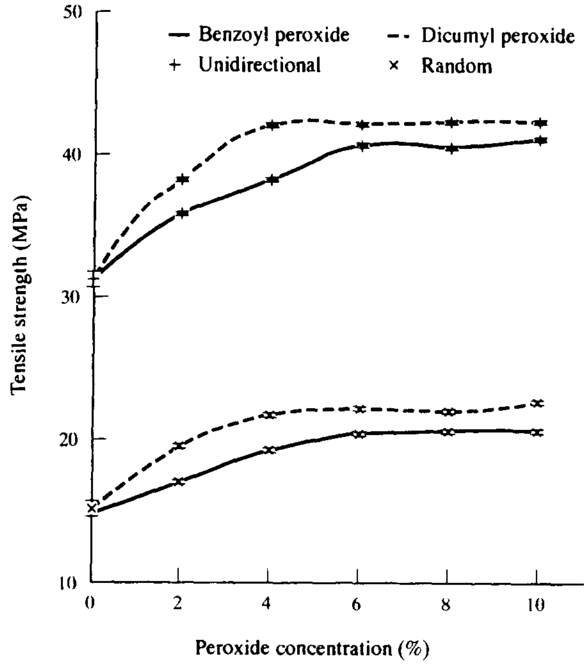


Figure 10 Effect of peroxide concentration on the tensile strength of sisal–LDPE composite at 30% fibre loading

Effect of permanganate treatment

Figure 13 shows the effect of permanganate concentration on the tensile strength of randomly and unidirectionally oriented sisal–LDPE composites at 30% fibre loading. It is seen that tensile strength reaches a maximum at a permanganate concentration of 0.055% and then decreases sharply with further increase in concentration. This may be due to the degradation of cellulosic fibres at higher permanganate concentration. So the permanganate concentration is a critical factor in determining the tensile properties of permanganate treated sisal–LDPE composites.

Figure 11 SEM photomicrograph of the dicumyl perodixe treated sisal fibre–LDPE composite showing PE grafted to fibre surface

Table 7 shows the tensile properties of permanganate treated (0.055%) sisal–LDPE composites. It is interesting to note that the tensile properties of permanganate treated composites showed a significant improvement as compared to untreated composites. The increase in tensile properties of permanganate treated composites is due to the permanganate induced grafting of polyethylene on to sisal fibres. The highly reactive Mn^{3+} ions are responsible for initiating graft copolymerization[30] as shown below:

$$\text{Cellulose–H} + \text{Mn(III)} \rightarrow \text{Cellulose–H–Mn(III) complex}$$

$$\text{Cellulose–H–Mn(III)} \rightarrow \text{Cellulose}^{\cdot} + H^{+} + \text{Mn(III)}$$

The SEM photomicrographs of the tensile failure surfaces of the permanganate treated composites indicate the grafting of PE on to cellulose fibre (*Figure 14*).

Table 6 Variation of tensile properties of sisal–LDPE composites with peroxide treatments (fibre content 30%; fibre length 5.8 mm)

	Tensile strength (MPa)				Modulus (MPa)				Elongation at break (%)			
Composites	Unidirectional	SD	Random	SD	Unidirectional	SD	Random	SD	Unidirectional	SD	Random	SD
Untreated	31.12	0.1575	14.7	0.4620	3086	0.1919	781	0.2715	1	0.1212	7	0.1465
BP treated	40.90	0.1435	20.6	0.1819	4018	0.1675	1326	0.3414	3	0.3264	9	0.1010
DCP treated	41.80	0.1635	21.8	0.7010	4156	0.1675	1448	0.1818	4	0.2010	10	0.1212

SD = standard deviation

Table 7 Tensile properties of untreated and $KMnO_4$ treated sisal–LDPE composites (fibre content 30%; fibre length 5.8 mm)

	Tensile strength (MPa)				Modulus (MPa)				Elongation at break (%)			
Composites	Unidirectional	SD	Random	SD	Unidirectional	SD	Random	SD	Unidirectional	SD	Random	SD
Untreated	31.2	0.1575	14.7	0.4620	3086	0.1919	781	0.2715	2	0.1212	7	0.1465
$KMnO_4$ treated	38.80	0.1825	19.8	0.3414	3816	0.1515	1264	0.2865	3	0.1363	8	0.2130

SD = standard deviation

Figure 12 SEM photomicrograph of the benzyoyl peroxide treated sisal fibre–LDPE composite showing PE grafted to the fibre surface

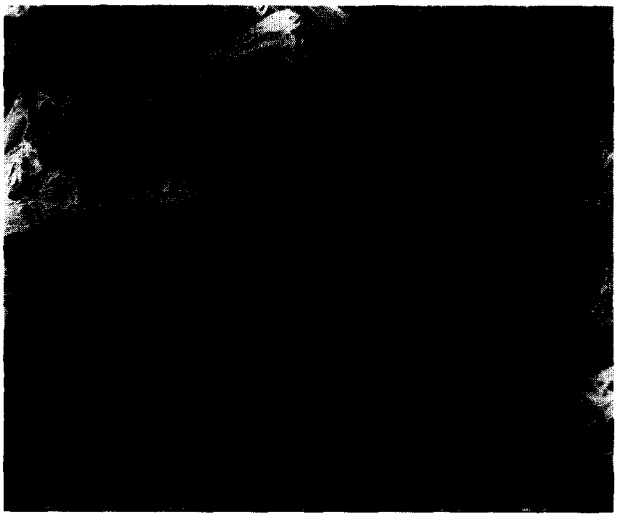


Figure 14 SEM photomicrograph of tensile fracture surface of the permanganate treated sisal–LDPE composites

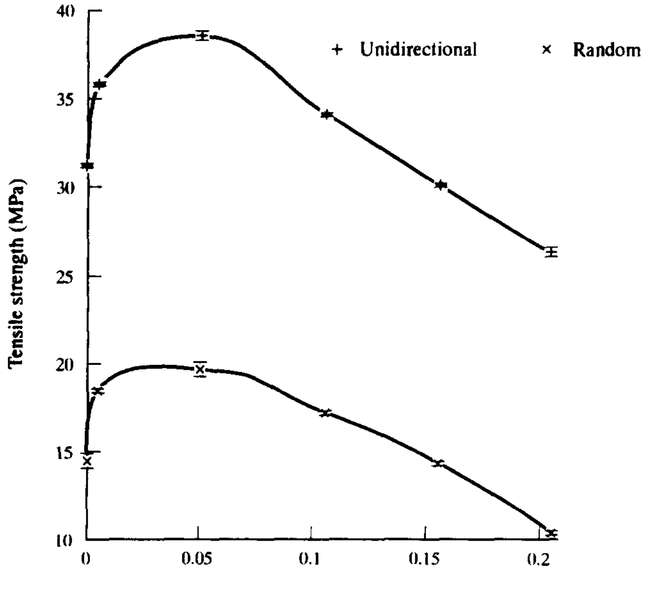


Figure 13 Effect of permanganate concentration on the tensile strength of sisal–LDPE composite at 30% fibre loading

Efficiency of different treatments

Finally, the effects of the different types of treatments [alkali, CTDIC, $KMnO_4$ (0.055%), DCP (10%) and BP (10%)] on the tensile modulus and tensile strength of the unidirectionally oriented composites (at 30% fibre loading) have been compared in *Figures 15* and *16*, respectively. From the above figures it is interesting to note that dicumyl peroxide treated and CTDIC treated composites show superior tensile properties than other chemically treated sisal fibre composites. The property increase upon various treatments varies in the order DCP > CTDIC > BP > $KMnO_4$ > alkali.

However, simple alkali treatment is more economical, though the treatment by DCP or permanganate is not very expensive because the amount required is very small. Similarly, CTDIC treatment is also not very expensive, due to the easy availability of the inexpensive natural prepolymer cardanol, obtained from CNSL resin. In India, especially in Kerala, cardanol is a very cheap material. Again, for the preparation of CTDIC, the TDI required is only a very small quantity. However, it is important to mention that CTDIC treated composites showed better retention in tensile properties after ageing than any other treatments[41].

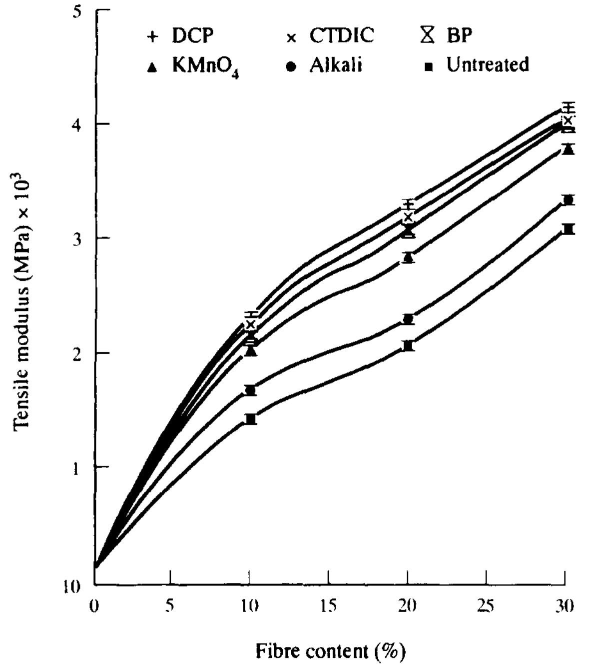


Figure 15 Effect of different types of chemical treatment on the tensile modulus of unidirectionally oriented sisal–LDPE composite at 30% fibre loading

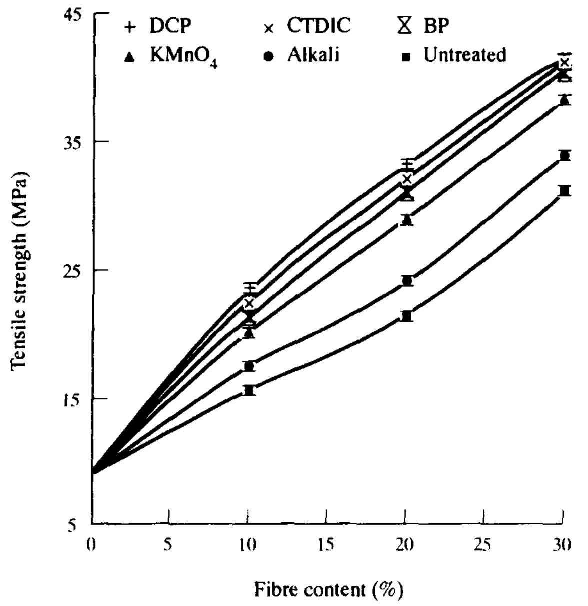


Figure 16 Effect of different types of chemical treatment on the tensile strength of unidirectionally oriented sisal–LDPE composite at 30% fibre loading

Figure 17 Photograph of the surfaces of longitudinally oriented sisal–LDPE composites

Figure 18 Photograph of the surfaces of randomly oriented sisal–LDPE composites

Surface finish of sisal–PE composites

The surface finish of the composites has been analysed to check if they exhibit wood like appearance. *Figures 17* and *18* show the photographs of the surfaces of the longitudinal and random composites. It is interesting to note that they exhibit wood like surface characteristics. The texture of the oriented composite is similar to Indian teak wood. Therefore, these composites have potential application as a substitute for wood.

CONCLUSIONS

The effects of different fibre treatments such as alkali, isocyanate, permanganate and peroxide on the tensile properties of sisal–LDPE composites were investigated as a function of fibre loading, fibre length and orientation. Alkali treated fibre composites showed better tensile properties than untreated composites due to their rough surface topography and increased aspect ratio. It has been seen that CTDIC treated composites exhibit superior mechanical properties. This may be due to the fact that the long chain structure of CTDIC linked to the cellulosic fibres makes the fibre hydrophobic, compatible and highly dispersible in the PE matrix. The SEM photomicrographs also support the strong fibre–matrix adhesion in sisal–LDPE composites. Peroxide treated composites showed an enhancement in tensile properties due to the peroxide induced grafting. Permanganate treated composites also showed a similar trend due to the permanganate induced grafting. Among the various types of treatments, CTDIC and DCP treatments showed the maximum properties. Finally, it is worth mentioning that these composites have wood like appearance and can be used as a substitute for wood.

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