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THERMAL BEHAVIOUR OF COIR FIBRES

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ABSTRACT

Thermal characterisation of naturally occurring coir fibres (*Cocos nucifera*) and modified bristle coir fibres was carried out with dynamic thermogravimetry. Thermogravimetric curves of three varieties of coir fibres (i.e. bristle, mattress and decorticated) were similar, thus indicating no difference in the chemical constituents of these varieties. Treatment of bristle coir fibres with 10% NaOH affected the thermal stability and a higher char yield was obtained. Treatment with acid (10% HCl or acetic acid) had no influence on the thermal behaviour of bristle coir fibres. Surface modification of coir fibres, by treatment with isopropyl triisostearoyl titanate, tolylene diisocyanate and unsaturated polyester resin, resulted in a reduction in weight loss below 150°C (due to absorbed moisture), which indicates that such treatment makes the fibre surface hydrophobic. No decrease in moisture absorption was observed in fibres treated with dichloromethyl vinyl silane or sebacoyl chloride.

Structural changes in coir fibres heated isothermally in an air oven at 150, 200 and 250°C for 1 h each were followed by FTIR. The major changes which took place could be explained in terms of oxidation, dehydration and depolymerisation of cellulosic components in the fibre. Elemental analysis of various fibre samples showed a reduction in H/C ratio of fibres heated to 250°C.

INTRODUCTION

The thermal degradation of natural fibres, like cotton cellulose and jute, has received considerable attention in the past [1,2]. The thermal behaviour of coir, which is also a naturally occurring fibre and is available in three varieties (bristle, mattress and decorticated), has received little attention. Coir is a multicomponent fibre whose chemical constituents are cellulose (36–43%), lignin (41–45%), hemicellulose (0.15–0.25%) and pectins (3–4%), together with some water-soluble materials. The thermal degradation of coir fibres is expected to be complicated due to the presence of the varied constituents.

The effects of crystallinity, orientation and cross-linking on the pyrolytic behaviour of cellulosic fibres have been described in considerable detail [3–6]. The thermal breakdown of cellulose proceeds essentially through two types of reaction. At lower temperatures (between 120 and 250°C), a

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gradual degradation, which includes depolymerisation, hydrolysis, oxidation, dehydration and decarboxylation, takes place. At higher temperatures, rapid volatilisation occurs, accompanied by the formation of levoglucosan and a charred product. Decomposition leads to loss of fibre strength and a marked reduction in $\overline{DP}$ (degree of polymerisation). Initial molecular weight loss is severe and occurs via the rupture of chains at the crystalline–amorphous interface [7]. The effect of additives (e.g. NaCl, $NaHSO_4$, etc.) and the effect of chemical treatments (e.g. alkali, acid, etc.) on the degradation of cellulose has also been reported [1].

The thermal behaviour of other constituents of coir fibres, i.e. lignin, hemicellulose and pectins, has not been investigated systematically. It would therefore be of interest to study the thermal behaviour of coir fibres. Dynamic thermogravimetry was used for thermal characterisation of bristle, mattress and decorticated coir fibres; these results are reported in this paper.

The bristle coir fibres were also modified by treatment with acid, alkali, dichloromethyl vinyl silane (DMVS), isopropyl triisostearoyl titanate (TTS), tolylene diisocyanate (TDI) and unsaturated polyester (USP) resin. The thermal behaviour of these modified fibres was also evaluated. The effect of such treatments of coir fibres on their mechanical properties, X-ray crystallinity and regaining of moisture has already been reported [8–11].

EXPERIMENTAL

Materials

Three varieties of coir fibres (bristle, mattress and decorticated) were obtained from Central Coir Research Institute, Coir Board, Alleppey, Kerala. Sodium hydroxide (Merck) and isopropyl triisostearoyl titanate (TTS) (Kenrich Petrochemical Inc.) were used as received. Tolylene diisocyanate (TDI), benzene, dimethyl sulphoxide and pyridine were of BDH grade and were purified by distillation before use.

Treatment of bristle coir fibres

Bristle coir fibres were washed with distilled water to remove the salt which is always present in the fibres due to the retting process in saline waters. These fibres have been designated as desalted.

The treatment of coir fibres with aqueous acid or base solutions (10% HCl, 10% acetic acid and 10% NaOH) was carried out at 30°C for 4 h. Fibres were then washed thoroughly with distilled water to ensure the complete removal of acid/base and dried under vacuum at 60°C for 18–24 h.

Bristle coir fibres were treated with benzene solutions of dichloromethyl vinyl silane (DMVS) (0.50%, 15 min, 78°C), sebacoyl chloride (SC) (0.5%, 15 min, 30 °C) and isopropyl triisostearoyl titanate (TTS) (1.5%, 30 min, 78 °C). Details of these treatments are described elsewhere [8–10].

The reaction of tolylene diisocyanate (TDI) was carried out with alkali-treated bristle coir fibres in dimethyl sulphoxide. For this, 4 g alkali-treated bristle coir fibres were heated at 90 °C for 2.5 h in DMSO containing 2 g TDI and 0.06 g pyridine (catalyst). Fibres were then filtered, washed with dioxane to remove unreacted diisocyanate and DMSO, and dried at 60 °C for 18 h followed by drying over phosphorus pentoxide in a desiccator at room temperature.

Coir fibres were also treated with solutions of unsaturated polyester (USP) resin in methylethyl ketone. Resin solutions containing 10, 25 and 50% USP resulted in a weight increase of 1.0, 8.0 and 25% of coir fibres, respectively [11].

THERMAL CHARACTERISATION OF COIR FIBRES

The thermal properties of untreated and chemically treated fibres were studied by thermogravimetry (TG) using a DuPont 1090 thermal analyser equipped with a 951 TGA module. A heating rate of 10 °C min^{-1}, and a sample weight of 10 ± 2 mg were used, and experiments were done in a nitrogen atmosphere at a flow rate of 60 $\text{cm}^3\ \text{min}^{-1}$. The thermogravimetric trace was characterised by determining:

(i) Weight loss in the region 40–150 °C. This weight loss has been attributed to the moisture content of the fibres.
(ii) Temperature of maximum rate of weight loss, T_{max}, which is obtained from a plot of the rate of weight loss versus temperature. If degradation occurred in two steps, then $T_{\text{max}-1}$ and $T_{\text{max}-2}$ could be obtained from the differential thermogravimetric (DTG) curve.
(iii) Weight loss in the first step of degradation, Y, was obtained from the weight remaining at the end of this step. The final temperature for the first step was ascertained from the DTG curve as the valley point between $T_{\text{max}-1}$ and $T_{\text{max}-2}$.
(iv) Temperature of completion of degradation (T_{f}).
(v) Percentage residual weights at $T_{\text{max}-1}$ and $T_{\text{max}-2}$.
(vi) Percentage char yield at 450 °C.

Coir fibres were also subjected to isothermal heat treatment in an air oven at 150, 200 and 250 °C for 1 h each. Samples were than cooled to room temperature in a desiccator over P_2O_5.

FTIR spectra of various thermally treated coir fibre samples in the form of KBr pellets were recorded using a Nicolet MX5-FTIR spectrophotometer. For this purpose fibres were finely powdered and thoroughly mixed with KBr before making the pellet.

A Perkin-Elmer 240C elemental analyser was used to determine the carbon, hydrogen and nitrogen contents of various fibre samples. For this purpose fibres were dried at 60°C for 18 h in a vacuum oven.

RESULTS AND DISCUSSION

Thermal characterisation

Bristle, mattress and decorticated coir fibres

Approximately 3–5% weight loss was observed between 40 and 150°C, which is due to absorbed water (Table 1). The weight loss in this region was similar in bristle and decorticated fibres (~ 5%) while it was lower in mattress and desalted coir fibres (~ 3%).

The thermogravimetric (TG) traces of coir fibres showed a two-step weight loss in the temperature range 289–400°C (Fig. 1). The rate of weight loss was lower in the first step. $T_{\mathrm{max}-1}$ and $T_{\mathrm{max}-2}$ were observed at 291 ± 2 and 341 ± 4°C, respectively. The final decomposition temperature (T_f), obtained by extrapolation, was at ~ 360°C in all fibre samples. The first decomposition step may be due to the dehydration of various constituents of the coir fibres, while the second step may be attributed to the elimination of levoglucosan from cellulosic components along with the breakdown of lignin.

The residual weight at $T_{\mathrm{max}-2}$ and char yield at 450°C were similar in bristle, mattress and decorticated fibres, but a lower char yield was observed in desalted coir fibres. In untreated bristle, salt also contributed to the residual weight at 450°C; thus a higher char residue was obtained (~ 33%).

TABLE 1

Results of thermogravimetric analysis of various coir fibres

Property evaluated	Untreated bristle coir fibres	Desalted bristle coir fibres	Untreated mattress coir fibres	Untreated decorticated coir fibres
$T_{\mathrm{max}-1}$ (°C)	292	293	–	295
$T_{\mathrm{max}-2}$ (°C)	339	367	339	346
T_f (°C)	358	390	360	310
Residual weight at $T_{\mathrm{max}-1}$ (%)	77	84	–	85
Residual weight at $T_{\mathrm{max}-2}$ (%)	52	44	54	52
Weight loss up to 150°C (%)	5.5	3.0	5.0	5.0
Weight loss Y (%)	27	27	26	22
Char yield at 450°C (%)	33.5	25	34	30

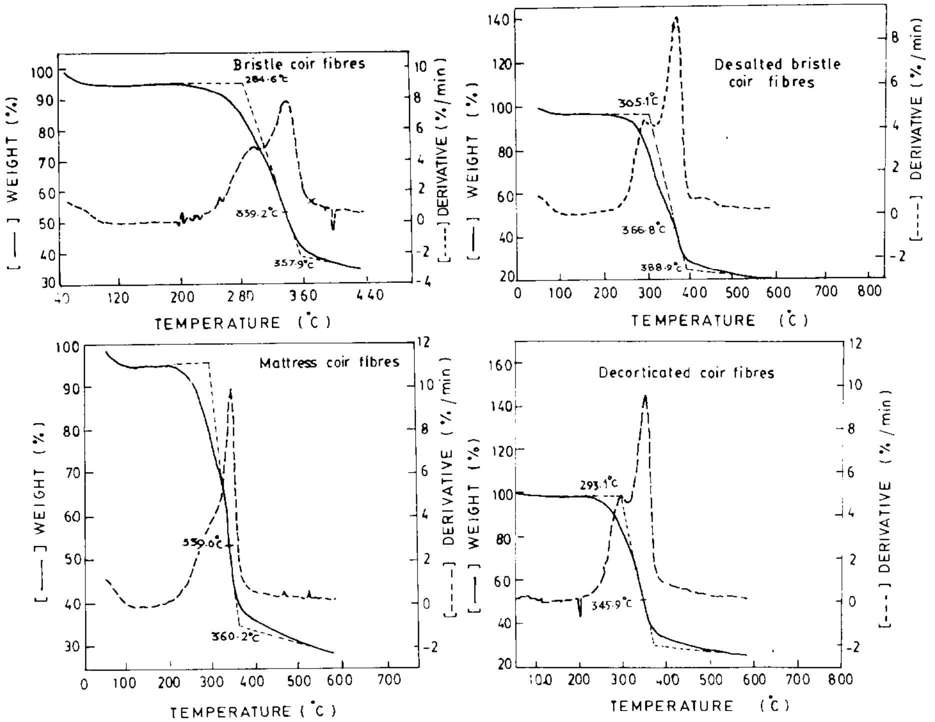


Fig. 1. Thermogravimetric traces of coir fibres in nitrogen atmosphere (heating rate, 10°C $\min^{-1}$).

These results indicate that the three varieties of coir fibres have a similar distribution of constituents and cannot be distinguished from one another by thermal techniques.

Bristle coir fibres treated with alkali and acid

The treatment of coir fibres with 10% alkali resulted in a considerable increase in $T_{\max-2}$. It is likely that the initial decomposition in coir fibres is initiated by the cementing material. On alkali treatment there is a partial loss of such cementing material via the rupture of ester linkages between polyuronic acid and lignin [8]. The observed increase in $T_{\max-2}$ could, therefore, be accounted for by the presence of high molecular weight components in the cementing material.

The overall char yield of alkali-treated coir fibres was more than that of desalted coir fibres (Table 2). A reduction in volatile levoglucosan formation on alkali-catalysed degradation of cellulose has been reported in the literature [12].

Treatment of bristle coir fibres with 10% HCl or acetic acid did not affect the thermal characteristics of the fibres (Table 2).

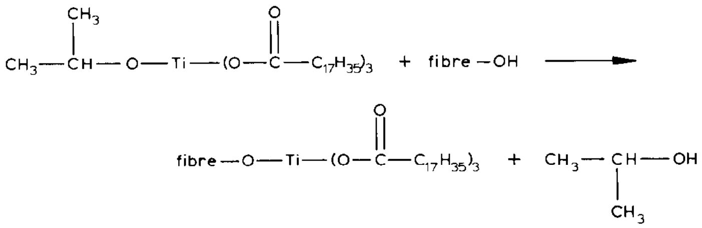
TABLE 2

Results of thermogravimetric analysis of chemically treated bristle coir fibres

Property evaluated	Alkali-treated	Hydrochloric acid-treated	Acetic acid-treated
$T_{\max-1}$ (°C)	–	300	295
$T_{\max-2}$ (°C)	366	368	339
T_f (°C)	385	392	–
Residual weight at $T_{\max-1}$ (%)	85	85	78
Residual weight at $T_{\max-2}$ (%)	50	48	50
Weight loss up to 150°C (%)	4	5	5
Weight loss Y (%)	23	25	29
Char yield at 450°C (%)	30	27	23

Chemically treated bristle coir fibres

Isopropyl triisostearoyl titanate is expected to react with the hydroxyl groups in the coir fibres leading to the formation of hydrophobic surfaces:



$$CH_3{-}\underset{\displaystyle CH_3}{\overset{}{C}}H{-}O{-}Ti{-}(O{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}C_{17}H_{35})_3 + \text{fibre}{-}OH \longrightarrow \text{fibre}{-}O{-}Ti{-}(O{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}C_{17}H_{35})_3 + CH_3{-}\underset{\displaystyle CH_3}{C}H{-}OH$$

This is expected to reduce the moisture content of the fibres.

Treatment of coir fibres with TTS in benzene solution reduced the moisture content, as indicated by the weight loss in the range 40–150°C (Table 3). The moisture content, however, was unaffected on treatment of

TABLE 3

Results of thermogravimetric analysis of bristle coir fibres treated with various reagents

Property evaluated	TTS	DMVS	SC	TDI
$T_{\max-1}$ (°C)	295	285	285	–
$T_{\max-2}$ (°C)	352	348	354	343
T_f (°C)	376	369	378	384
Residual weight at $T_{\max-1}$ (%)	82	85	84	–
Residual weight at $T_{\max-2}$ (%)	49	53	52	59
Weight loss up to 150°C (%)	2	5	4	3
Weight loss Y (%)	28	23	22	–
Char yield at 450°C (%)	28.5	32	32	35.0

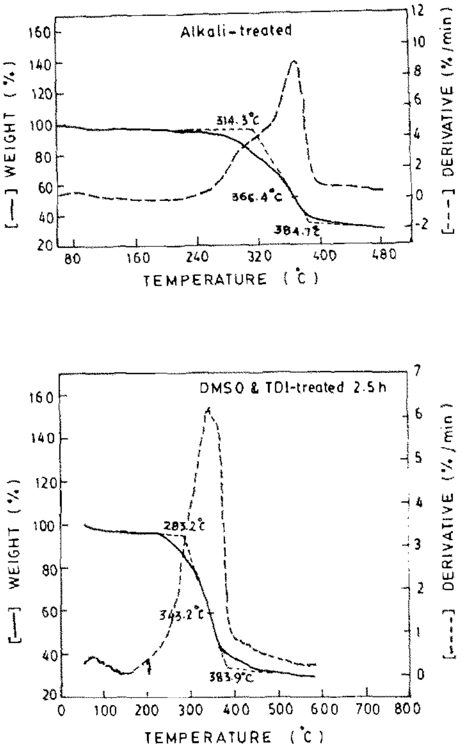


Fig. 2. Thermogravimetric traces of bristle coir fibres treated with 10% NaOH and TDI in DMSO, in nitrogen atmosphere (heating rate, 10° C min^{-1}).

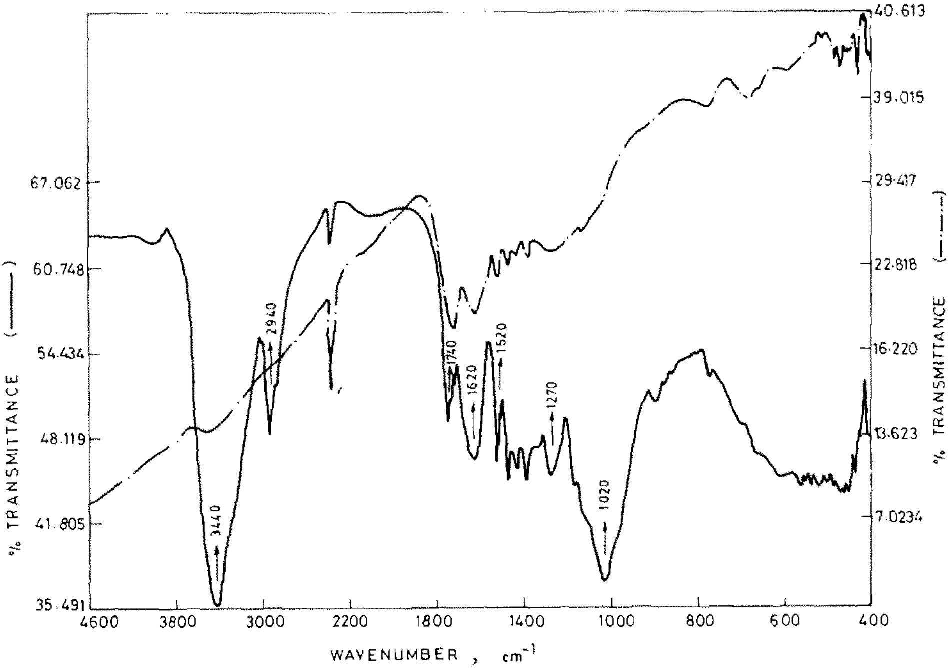


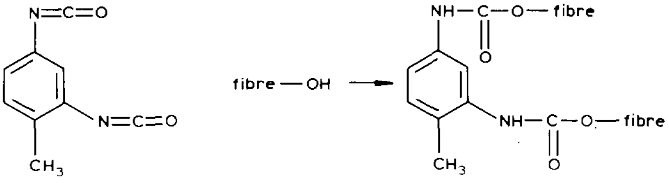
Fig. 3. FTIR spectra of untreated bristle coir fibres (———) and fibres heated to 250° C for 1 h (—·—·—).

coir fibres with SC and DMVS. The residual weight at $T_{\max-1}$ was similar to that of desalted coir fibres.

A slight increase in $T_{\max-2}$ was observed on chemical treatment with TTS, DMVS and SC, but the char yield at 450°C and residual weights at $T_{\max-1}$ and $T_{\max-2}$ were similar in all these samples.

The chemical treatments are expected to modify the surface characteristics of the coir fibres without affecting the bulk characteristics. Hence, a change in surface-dominated properties of thermal behaviour (i.e. moisture regain) was expected. Char yield is dependent on the nature of chemical constituents comprising the bulk of these fibres.

Alkali treatment of bristle coir fibres may yield some low molecular weight products, which may be extracted by polar organic solvents (like DMSO). Swelling of the fibrils in the fibres by DMSO would facilitate the penetration of TDI, which would react with the cellulose component of the fibre as follows:



TDI

Hence alkali-treated coir fibres were extracted with DMSO and a DMSO solution of TDI for 2.5 h and subjected to thermal analysis after drying. In both the treated fibres, degradation proceeded in a single step and almost identical thermal behaviour was observed. The overall char yield of treated coir fibres was higher than that of alkali-treated fibres (Fig. 2).

TABLE 4

Results of thermogravimetric analysis of USP resin and resin-treated bristle coir fibres

Property evaluated	10% resin-treated	25% resin-treated	50% resin-treated	USP resin
$T_{\max-1}$ (°C)	296	293.6	297.7	321.5
$T_{\max-2}$ (°C)	350	349	348	389
T_f (°C)	368	371	370	411
Residual weight at $T_{\max-1}$ (%)	73	80	80	–
Residual weight at $T_{\max-2}$ (%)	53	46	49	30
Weight loss up to 150°C (%)	4	4	3	–
Weight loss Y (%)	19	33	30	–
Char yield at 450°C (%)	33.0	27.5	27.5	5.0

Resin-treated bristle coir fibres

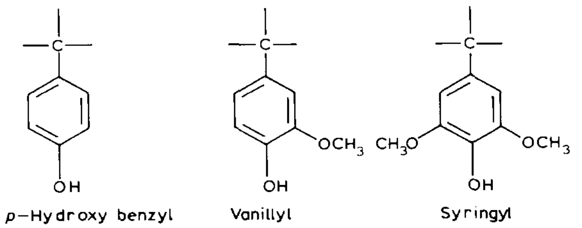
The thermal behaviour of USP resin was first evaluated by TG. USP resin was stable up to 200°C and started losing weight above this temperature. The initial decomposition was observed at 329.5°C and T_{max} at 389°C. Almost complete weight loss was observed at 410°C.

The T_{max-2} of coir fibres is lower than the T_{max} of USP resin. On treatment of coir fibres with USP resin an increase in thermal stability was observed (Table 4). An increase was observed in T_{max-2} for fibres in which 1% of the resin had been incorporated. However, no further change was observed on increasing the resin content of coir fibres from 1 to 25%. Compared to untreated bristle coir fibres all the USP resin-treated fibre samples showed a lower weight loss up to 150°C. A reduction in char yield with increasing percentage of resin incorporated was also observed. This may be because the resin only has a 5% char yield compared to 33% for coir fibres.

ISOTHERMAL DEGRADATION OF COIR FIBRES

Heating coir fibres for 1 h at 150°C in an air oven did not result in any significant change in appearance and the original colour of the fibres (i.e. light brown for bristle, desalted bristle, TTS-treated bristle and mattress; dark brown for alkali- and TDI-treated fibres) was retained. Fibres heated to 200°C showed a darkening in colour and at 250°C all the fibre samples became almost black in colour.

FTIR spectra of coir fibres heated to 150, 200 and 250°C were analysed to ascertain the structural changes occurring in the fibres. Oxidation of the constituents of coir fibres (i.e. cellulose, lignin, etc.) is expected to lead to the formation of carbonyl groups (ν(C=O), 1740 ± 15 cm^{-1}). Dehydration of coir fibres may lead to a reduction in hydroxyl content. Some idea of the oxidative degradation can be obtained by comparing the intensities of absorption bands in the ratio 1740 cm^{-1} (νC=O)/2940 cm^{-1} (νC–H). A slight increase in this ratio was observed for fibres heated to 150°C. This indicates that besides loss of water, oxidation probably occurred at the primary alcoholic group (C_6) in the glucose repeat-unit of cellulose. Lignin, having the following monomeric unit:



may be unaffected at this temperature (Fig. 3).

Changes in the intensity of peaks were much more significant for fibres heated to 200°C, thereby indicating that intra-ring dehydration occurred with the oxidation of secondary alcoholic groups into ketone groups. The decreased intensity of the peak at 2940 cm^{-1} indicates that there was a decrease in the number of CH_2 groups which could have been due to oxidation or the formation of volatile degradation products such as low molecular weight hydrocarbons.

For fibres heated to 250°C, distinct changes were observed in the finger-print region, i.e. 1400–1000 cm^{-1}. The absorption peak at 1020 cm^{-1} was considerably reduced in intensity, and in untreated bristle coir fibres, it disappeared completely. The absorption peak at 1160 cm^{-1} (characteristic of anti-symmetrical C–O–C stretching) reduced in intensity. Such a change has been attributed to depolymerisation of cellulose in jute fibres [2]. The medium intensity peak at 1270 cm^{-1} was also reduced while the weak absorption band at 1320 cm^{-1} disappeared completely. In addition to these changes, a considerable reduction in intensity of the absorption band at 3440 cm^{-1} (characteristic of the stretching vibrations of the hydrogen-bonded hydroxyl groups) was also observed.

The FTIR studies thus revealed that the major changes in coir fibres heated to 250°C are oxidation, dehydration and slight depolymerisation of the cellulosic component.

The elemental composition of bristle coir fibres, after heating at various

TABLE 5

Effect of thermal treatment of coir fibres on elemental composition

Thermal treatment (°C)	Carbon (%)	Hydrogen (%)	H/C ratio	Empirical formula
Bristle coir fibres				
Nil	47.56	5.28	1.33	$C_{1.34}H_{1.79}O$
150	48.08	5.34	1.33	$C_{1.37}H_{1.83}O$
200	49.36	5.51	1.34	$C_{1.46}H_{1.96}O$
250	58.82	3.17	0.64	$C_{2.06}H_{1.33}O$
Desalted bristle coir fibres				
Nil	45.69	5.12	1.33	$C_{1.24}H_{1.66}O$
150	50.66	5.71	1.35	$C_{1.54}H_{2.09}O$
200	51.85	5.75	1.32	$C_{1.63}H_{2.16}O$
250	58.26	3.98	0.81	$C_{2.05}H_{1.68}O$
Mattress coir fibres				
Nil	46.17	5.19	1.34	$C_{1.26}H_{1.70}O$
150	46.67	5.24	1.34	$C_{1.29}H_{1.74}O$
200	49.76	5.43	1.30	$C_{1.48}H_{1.93}O$
250	55.66	3.63	0.78	$C_{1.82}H_{1.42}O$

TABLE 6

Elemental composition of chemically treated bristle coir fibres after thermal treatment

Thermal treatment (°C)	Carbon (%)	Hydrogen (%)	H/C ratio	Empirical formula
NaOH-treated				
Nil	45.72	5.51	1.44	$C_{1.27}H_{1.83}O$
150	47.37	5.53	1.40	$C_{1.34}H_{1.88}O$
200	48.50	5.58	1.38	$C_{1.40}H_{1.94}O$
250	52.34	4.81	1.10	$C_{1.63}H_{1.80}O$
TDI-treated				
Nil	44.32	5.04	1.37	$C_{1.16}H_{1.59}O$
150	48.81	5.75	1.41	$C_{1.43}H_{2.02}O$
200	50.32	5.78	1.37	$C_{1.53}H_{2.10}O$
250	55.99	4.71	1.01	$C_{1.90}H_{1.92}O$
TTS-treated				
Nil	45.59	5.16	1.34	$C_{1.23}H_{1.66}O$
150	49.68	5.60	1.35	$C_{1.48}H_{2.0}O$
200	50.17	5.59	1.33	$C_{1.51}H_{2.02}O$
250	52.96	4.46	1.00	$C_{1.66}H_{1.67}O$

temperatures for 1 h, is given in Tables 5 and 6. It is obvious from these results that the H/C ratio decreased on isothermal heating of fibres and this reduction was largest at 250°C. An almost identical decrease in H/C ratio was observed in bristle, desalted bristle, mattress and TTS-treated bristle coir fibres up to 200°C (Table 5). Only at 250°C was a slight difference in the H/C ratio of various fibre samples noticed.

A higher H/C ratio was observed for coir fibres treated with NaOH and TDI (Table 6). In these fibre samples, some of the cementing material had been lost during treatment. This is perhaps responsible for the observed increase in H/C ratio in these fibres.

The degradation of coir fibres is much more complex than that of cellulose [13] because of the presence of the lignin component. Coir fibre is stable below 150°C and only absorbed moisture is lost from the fibres. Beyond this temperature the possible oxidation of the glucose unit in cellulose takes place. At 250°C it also undergoes dehydration and slight depolymerisation. Dehydration probably occurs randomly along the chains of the glucose units in the amorphous regions, leading to elimination of water and a considerable drop in $\overline{\mathrm{DP}}$. Dehydration is accompanied by the formation of conjugated carbonyl and ethylenic groups but the appearance of the latter in the IR spectrum is masked by the existing peaks. In addition to these changes, breakdown of weak sites, like the linkage between polyuronides and lignin, also takes place.

Isothermal heating of fibres at 150°C is accompanied by the loss of absorbed water. As a consequence, the H/C ratio remains unaltered but the empirical formula is changed in almost all fibre samples. At higher temperatures (i.e. 200 or 250 °C), isothermal heating resulted in a decrease in H/O or H/C ratio and an increase in C/O ratio. These observations cannot be explained solely on the basis of dehydration or oxidation of cellulosic units but indicate aromatisation of the various constituents of coir fibre.

CONCLUSIONS

On the basis of these studies the following conclusions can be drawn.

(a) Various varieties of coir fibres (i.e. bristle, mattress and decorticated) used in the present work have a similar distribution of chemical constituents, which is reflected in their similar thermal behaviour.

(b) Treatment of coir fibres with alkali leads to a modification in their thermal stability. A higher char yield was obtained in these fibres at 450 °C.

(c) Isothermal studies with alkali-treated fibres revealed a lower carbon/oxygen ratio at 200 or 250 °C than that in the bristle or desalted bristle coir fibres; thereby indicating a lesser extent of dehydration and a higher extent of oxidation in these residues.

(d) Treatment with TTS or TDI of coir fibres resulted in a decrease in moisture absorption by the fibres. However, such treatment did not alter the thermal characteristics of these fibres.

REFERENCES

1 F.J. Kiljer, in N.M. Bikales and L. Segal (Eds.), High Polymers, Vol. V, Part V, Interscience, New York, 1971, p. 1015.
2 M.K. Sridhar, G. Basavarajappa, S.G. Kasturi and N. Balasubramanium, Indian J. Text. Res., 7 (1982) 87.
3 M. Jaffé, in E.A. Turi (Ed.), Thermal Characterisation of Polymeric Materials, Academic Press, New York, 1981, p. 750.
4 A. Basch and M. Lewin, J. Polym. Sci., Polym. Chem. Ed., 11 (1973) 3071.
5 A. Basch and M. Lewin, J. Polym. Sci., Polym. Chem. Ed., 12 (1974) 2053.
6 H. Rodrig, A. Basch and M. Lewin, J. Polym. Sci., Polym. Chem. Ed., 13 (1975) 1921.
7 A. Broido, A.C. Javier-Son, A.C. Quano and E.M. Barrall, J. Appl. Polym. Sci., 17 (1973) 3627.
8 D.S. Varma, M. Varma and I.K. Varma, Text. Res. J., 54 (1984) 827.
9 D.S. Varma, M. Varma and I.K. Varma, J. Reinf. Plast. Compos., 4 (1985) 419.
10 D.S. Varma, M. Varma and I.K. Varma, J. Polym. Mater., submitted.
11 D.S. Varma, M. Varma and I.K. Varma, Ind. Eng. Chem., Prod. Res. Dev., in press.
12 T.P. Nevell, in T.P. Nevell and S. Haig Zeronian (Eds.), Cellulose Chemistry and its Applications, Ellis Horwood, Chichester, 1985, p. 231.
13 O. Hinojosa, J.C. Arthur and T. Mares, Text. Res. J., 43 (1973) 609.