

Chemical Modification of Lignocellulosic Fibers I. Functionality Changes and Graftcopolymerization of Acrylonitrile onto Pineapple Leaf Fibers; Their Characterization and Behavior

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SYNOPSIS

This paper is an attempt to examine the commercial significance of an agro-waste “pineapple leaf fiber” (PALF). The quality enhancement of PALF has been tried through chemical modifications. Functionality changes in the above fiber have been done through mercerization, cyanoethylation, oxidation, and graftcopolymerization with acrylonitrile, using ceric ion as an initiator at varying concentrations of monomer, initiator, and mineral acid at a number of temperatures for various time intervals. The modified fibers have been characterized by FTIR spectroscopy and viscosity measurements. The extent of moisture regain, acid-alkali solubility, tensile modulus, dye-uptake ability, and thermal stability of the resulting materials have been tested and compared with the parent fiber. The significance of such chemical modification in the context of better textile performance and reinforcing behavior of the product in FRP has been discussed. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The present-day research in the field of polymer science and technology has been focussed in developing plastics, papers, adhesives, textile fibers, composites, blends, and many other industrial products from renewable resources, mostly the abundantly available agro-waste and lignocellulosic materials. This is expected to minimize the use of expensive synthetic polymers and fibers of petrochemical and mineral origin. Partial success in the use of polymers/fibers, blends, and simple and hybrid composites, etc., comprising these materials in the textile industry, construction industry, and other industrial sectors, have been achieved.¹⁻⁵⁴

However, this area of research is still at its infancy, especially in India. We are currently researching how to derive polymers, resins, and fibers from renewable resources and use them either as

such and/or through suitable chemical modifications for their better textile use, and develop reinforced plastics for suitable applications in industrial sectors. This communication is an aspect of our research program in this field of investigation.

EXPERIMENTAL

Materials and Methods

Purification of monomer, commercial nitrogen, and water was done by conventional methods.²¹ A 0.1 *M* solution of initiator “Ce(IV)” was prepared by dissolving 5.4823 g of ceric ammonium nitrate in 100 mL of 1 (*M*) nitric acid and the concentration of the stock solution was determined by cerimetry using ferroin as indicator. The pineapple leaf fibers were purified by soxhlet extraction with 1 : 1 benzene: ethanol mixture for 24 h, followed by washing with ethanol, water and ethanol, and then air dried. All other chemicals like NaOH, NaIO₄, acetic acid, methanol, chloroform, carbon tetrachloride, etc. were of A.R. grade.

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Table I Variation of Percent Grafting with Time

Time in Minutes	Percent Grafting
15	7.9
30	9.4
60	14.3
120	14.7
180	14.68
240	14.21

PALF = 0.5 g, [AN] = 0.745M, [Ce(IV)] = $0.5 \times 10^{-2}M$, $[H^+] = 0.05M$, Temp. = 35°C.

Methods of Chemical Modification

1. Mercerization of PALF: pineapple leaf fibers were immersed in sodium hydroxide solution of varying concentration from 1–10%, for various time intervals at 30°C. The fibers were then thoroughly washed with 0.1(N)
2. Cyanoethylation of PALF: cyanoethylation of NaOH-treated PALF was done as per the following method: 1–2 g of alkali-treated fiber was taken in a 250 mL conical flask fitted with standard joint (B24/19) and to that 20 mL of purified acrylonitrile (AN) was added and refluxed at 60°C for various time intervals between $\frac{1}{2}$ –6 h. The fibers were then washed with dilute acetic acid 2–3 times, followed by acetone and distilled water repeatedly, and air dried. Cyanoethylation of PALF was also carried out by direct treatment of the parent fiber with 20 mL AN in 20 mL acetone using a pyridine catalyst.
3. Preparation of oxypineapple leaf fiber: purified pineapple leaf fibers were oxidized with N/10 periodic acid at 35°C for 1–10 h. The oxidized fibers were then washed thoroughly

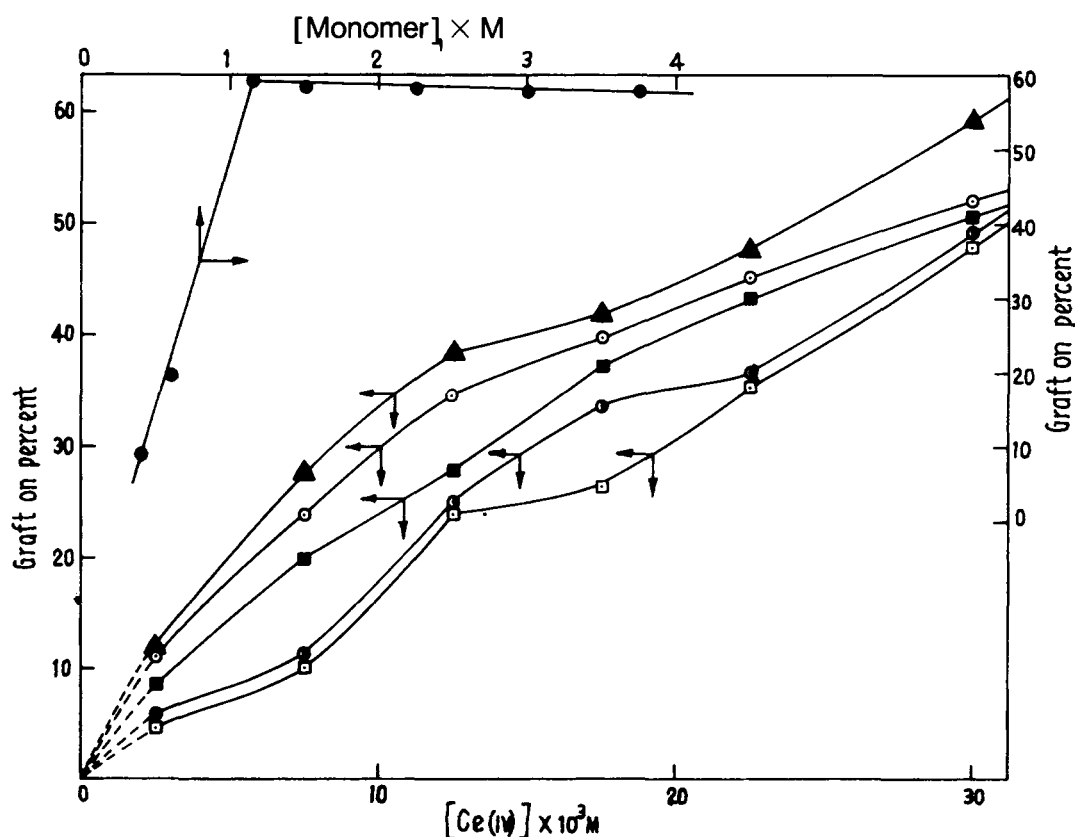


Figure 1 (a) Variation of percent grafting with monomer concentration: Fiber = 0.5 g, [Ce(IV)] = 0.02M, $[H^+] = 0.35M$, Temp. = 25°C, Time = 2 h, Plot = (●). (b) Variation of percent grafting with initiator concentration of various temperatures: Fiber = 0.5 g, [AN] = 0.754M, $[H^+] = 0.3M$, Time = 2 h. Plot (○) 20°C, (▲) 25°C, (●) 30°C, (○) 35°C, (□) 40°C.

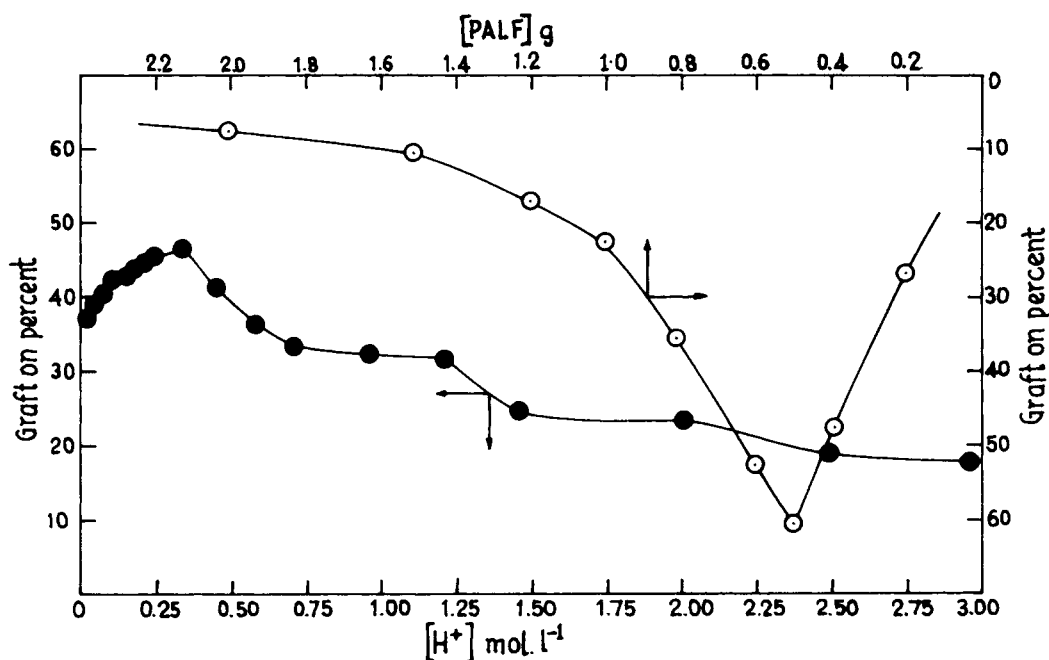


Figure 2 (a) Variation of percent grafting with acid concentration: Fiber = 0.5 gm, $[ce(IV)] = 0.02M$, $[AN] = 0.754M$, Temp. = $25^{\circ}C$, Time = 2 h, Plot (●). (b) Variation of percent grafting with weight of PALF: $[AN] = 1.131M$, $[ce(IV)] = 0.02M$, $[H^+] = 0.35M$, Temp. = $25^{\circ}C$, Time = 2 h, Plot (○).

with dil- Na_2CO_3 , followed by dilute acetic acid and deionized water.

- Method of grafting: graft copolymerization of acrylonitrile onto parent, cyanoethylated, and oxy PALF (0.2–1.0 g) was carried out separately in reaction vessels carrying inlet and outlet systems for deaeration. The fibers immersed in the required amount of monomer and aqueous nitric acid was deaerated by passing oxygen-free nitrogen for 1 h and sealed air tight. The reaction vessels were then kept in a constant shaking thermostat

maintained at the experimental temperature until the system attained thermal equilibrium. The required amount of ceric solution was then injected through the rubber capping, and grafting was carried out for the desired time, after which the reaction was arrested by adding an excess of ferrous ammonium sulphate solution. Homopolymers were extracted by repeated reflux with dimethyl formamide until the extract did not yield any precipitate with ethanol. The graft copolymers were then dried at $45^{\circ}C$ to constant

Table II Variation of Percent Grafting with Organic Solvents

Solvent Composition	Percent of Grafting			
	Acetic Acid	Methanol	Chloroform	Carbon Tetrachloride
5 : 95	45.62	45.52	43.14	51.52
10 : 90	44.2	43.94	35.2	46.9
20 : 80	43.12	42.8	32.0	42.8
30 : 70	38.22	38.0	27.8	40.8
40 : 60	32.28	30.32	24.0	26.4
50 : 50	19.54	24.85	6.6	23.8

PALF = 0.5 g, $[AN] = 1.13M$, $[Ce(IV)] = 2.0 \times 10^{-2}M$, $[H^+] = 0.35M$, Temp. $25^{\circ}C$, time = 2 h control graft % = 60.1.

Table III Variation of Percent Grafting with Time of Cyanoethylation

Time of Cyanoethylation in Hours	2% NaOH-Treated PALF	10% NaOH-Treated PALF	Direct CE Fiber in Pyridine
	Percent of Grafting	Percent of Grafting	Percent of Grafting
0	62.8	74.0	60.1
$\frac{1}{2}$	65.8	76.0	70.6
1	71.6	79.0	73.5
2	74.8	80.4	76.9
3	80.0	84.52	78.3
4	82.6	86.68	81.2
6	Loss of strength was observed	Loss of strength was observed	82.2

CEPALF = 0.5 g, [AN] = 1.13M, [Ce(IV)] = 0.02M, [H⁺] = 0.35M, Temp. = 25°C, Time = 2 h, control = 60.1%.

weight. The percent grafting was calculated. The oxy-PALF suffered loss of strength on grafting.

RESULTS AND DISCUSSIONS

Parent PALF

Acrylonitrile was graft copolymerized onto PALF under the conditions; PALF = 0.5 g, [AN] = 0.754M, [Ce(IV)] = $0.5 \times 10^{-2}M$ and [H⁺] = 0.05M at 35°C for various time intervals. The results of such studies are presented in Table I.

Effect of Monomer Concentration (m/p Ratio)

Acrylonitrile was grafted onto PALF at a number of concentrations (0.189M–3.77M) [m/p ratio (0.3024–6.032)] under PALF = 0.5 g, [Ce(IV)]

= 0.02M, [H⁺] = 0.35M, Temp. = 25°C time = 2 h. The percent grafting increased steadily up to a monomer concentration of 1.13M (m/p ratio of 1.8096) and then was almost constant (Fig. 1). The grafts were brittle beyond AN concentration of 1.13M.

Effect of Ceric Ion Concentration and Reaction Temperature

Graftcopolymerization was carried changing ceric ion concentration ($0.25 \times 10^{-2}M - 3.0 \times 10^{-2}M$) at a number of temperatures (20–50°C) with PALF = 0.5 g, [AN] = 0.754M, [H⁺] = 0.3M, time = 2 h. It is observed that the percent grafting increases with increase of ceric ion concentration (Fig. 1). It is further observed that the grafted samples at and beyond [Ce(IV)] = $2.25 \times 10^{-2}M$ were brittle. Therefore, further grafting was studied at [Ce(IV)] = $2.0 \times 10^{-2}M$.

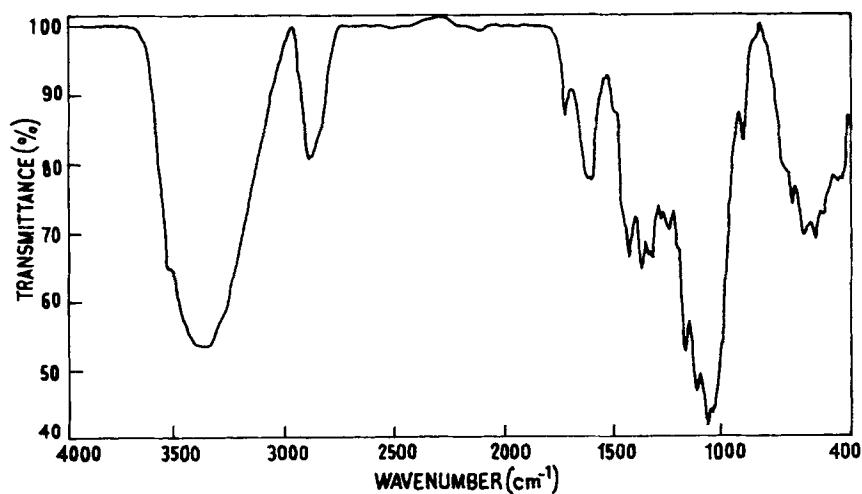


Figure 3 FTIR spectra of parent PALF.

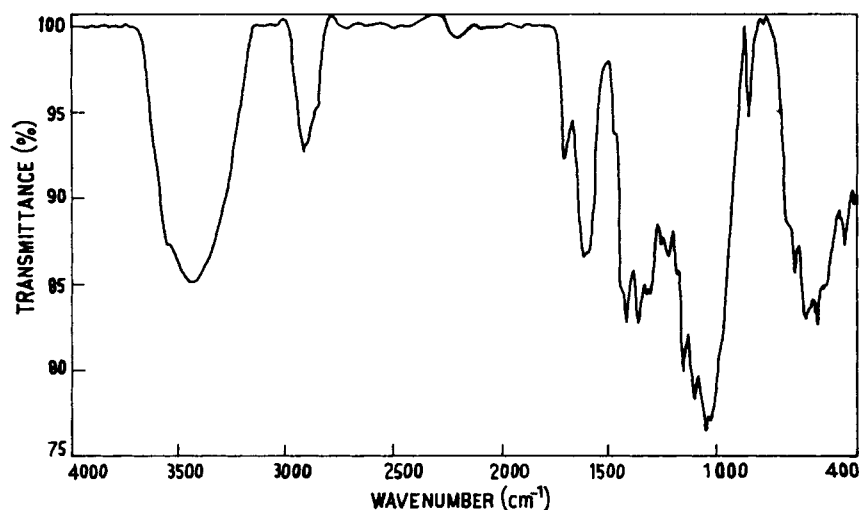


Figure 4 FTIR spectra of CEPALF.

Increase of temperature increases percent grafting up to 25°C and then decreases (Fig. 1). The decrease in percent grafting beyond 25°C is attributed to homopolymerization predominating over grafting. Ceric ion is itself capable of initiating homopolymerization of vinyl monomers.^{55,56} Premature termination of growing grafted chains by ceric ion is temperature sensitive.^{56,57}

Effect of Acid

Percent grafting increases from 37.6–46.6% with increase in nitric acid concentration (0.02–0.35 *M*) at PALF = 0.5 g, [Ce(IV)] = 2.0×10^{-2} *M*, [AN] = 0.754 *M*, temp. = 25°C, time = 2 h, beyond which it decreases (Fig. 2). The increase of percent grafting by increasing H^+ ion concentration is attributed to the increase in oxidation potential of ceric ion,⁵⁸

and this leads to ease redox-disproportion of PALF, resulting in a quantitative yield of free radical sites on the backbone of the latter to which monomer addition takes place.

Effect of PALF

Under the condition [AN] = 1.13 *M*, [Ce(IV)] = 2.0×10^{-2} *M*, [H^+] = 0.35 *M*, time = 2 h, temp. = 25°C, percent grafting increases (60.1%) with the weight percentage of PALF upto 0.5 g, beyond which it decreases (Fig. 2).

Effect of Organic Solvents

The grafting reaction has been studied at varying compositions (5 : 95–50 : 50) of organic solvents

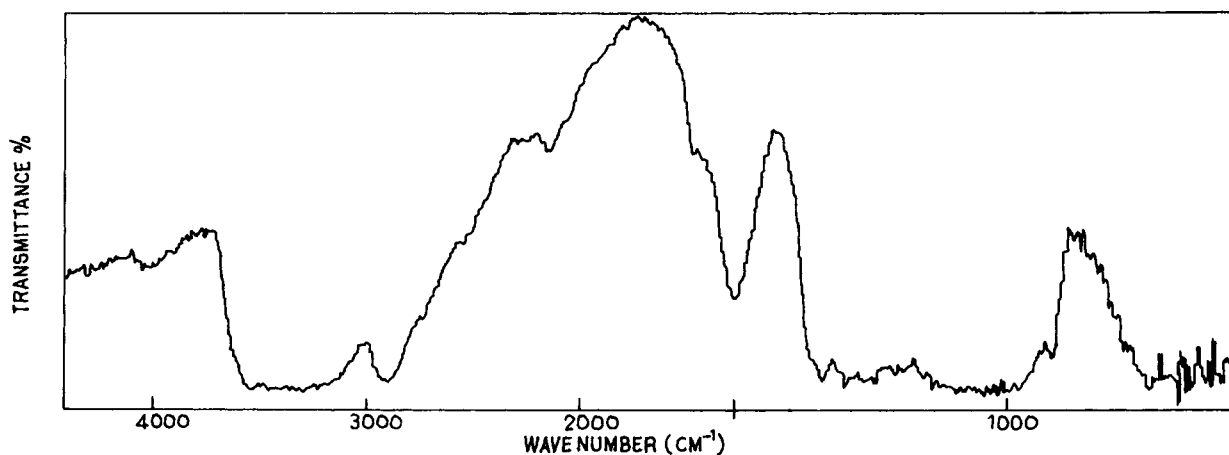


Figure 5 FTIR spectra of oxy-PALF.

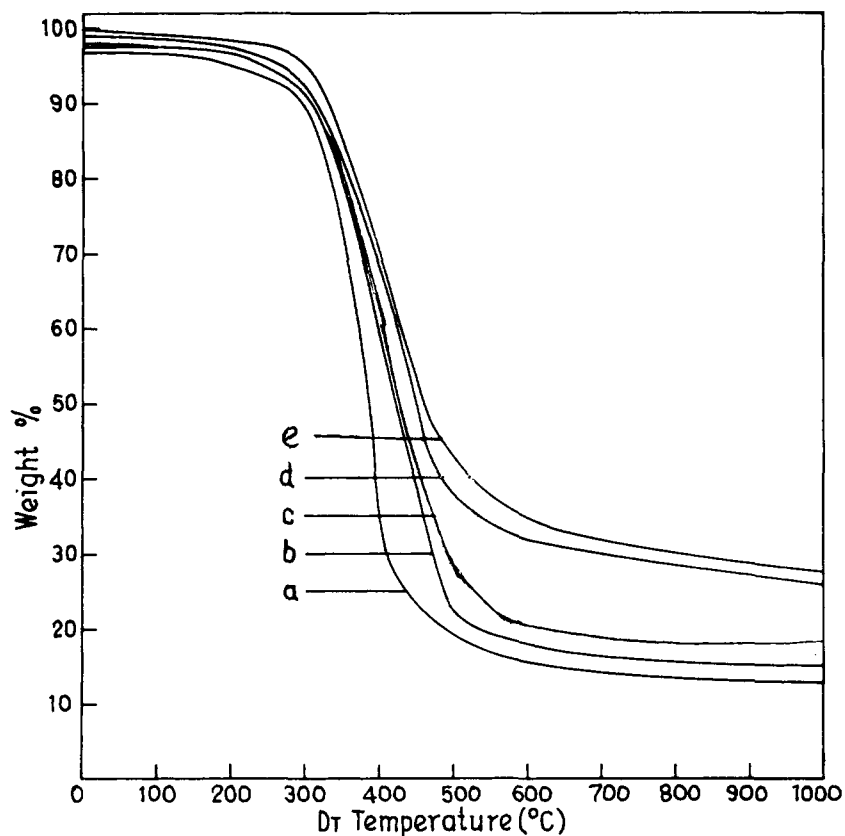


Figure 6 Primary thermograms of PALF and PALF-g-PAN copolymers. (a) Parent PALF (b) 7.9% graft on (c) 14.7% graft on (d) 47.9% graft on (e) 59.6% graft on.

such as acetic acid, methanol, chloroform, and carbon tetra chloride under the condition; PALF = 0.5 g, [AN] = 1.13M, [Ce(IV)] = 0.02M, [H⁺] = 0.35M at 25°C for 2 h. Percent grafting decrease is progressive with respect to the control for all solvents with increase in their proportion (Table II).

Effect of the Nature of Substrate Polymer on Percent Grafting

1. Alkali-treated fiber—PALF treated with 2% NaOH for 1 h and grafted under the condition; PALF-ONa = 0.5 g, [AN] = 1.13M,

Table IV Variation of Moisture Regain of PALF-g-PAN, PALF-CE, and CEPALF-g-PAN Samples with Various Percent Grafting

Percent Grafting	PALF-g-PAN		CE-PALF		CEPALF-g-PAN	
	Percent Moisture Regain in g/100 g of the Fiber	Time of Cyanoethylation in Hours	Percent Moisture Regain in g/100 g of the Fiber	Time of Cyanoethylation	Percent Grafting with Time of Cyanoethylation	Percent of Moisture Regain in g/100 g of the Fiber
0	28.306	0	29.5	(0 hr)	74.0	23.75
7.9	22.66	½	19.2	(½ hr)	76.0	14.40
14.3	21.55	1	18.88	(1 hr)	79.2	12.14
47.9	19.26	2	18.58	(2 hr)	80.4	9.47
59.6	14.32	3	17.04	(3 hr)	84.52	7.49
		4	15.04	(4 hr)	86.68	5.09
		6	8.64	(6 hr)	—	4.86

[Ce(IV)] = 0.02M, [H⁺] = 0.35M at 25°C for 2 h led to 62.8% grafting, while 10% NaOH-treated fiber under identical reaction conditions yielded 74.0% grafting. Further PALF treated with 10% NaOH for 2 h and grafted under the conditions as above, results in 85.8% grafting.

2. Cyanoethylated fiber—with cyanoethylated fibers grafted separately under the condition; CEPALF = 0.5 g, [AN] = 1.13M, [Ce(IV)] = 0.02M, [H⁺] = 0.35M at 25°C for 2 h, percent grafting increases with increase of the time of cyanoethylation (Table III). CEPALF is, thus, a better substrate than PALF and PALF-ONa for grafting of acrylonitrile.
3. Grafting onto oxy-PALF—acrylonitrile-grafted Oxy-PALF when refluxed with DMF for homopolymer extraction underwent disintegration. Such grafts were, therefore, found to be unimportant from commercial point of view.

CHARACTERIZATION AND PROPERTIES OF THE CHEMICALLY MODIFIED FIBER

Characterizations

FTIR

The parent and chemically modified fibers were characterised by FTIR spectra. The FTIR absorption pattern of parent PALF (Fig. 3) shows bands at 3395 cm⁻¹ due to OH— stretching, 2916 cm⁻¹ due to C—H stretching, 1735 cm⁻¹ due to C=O stretching at hemicellulose; 1606 cm⁻¹ due to C=C stretching of the aromatic ring in lignin components, 1428 cm⁻¹ due to —CH₂— bending, 1372 cm⁻¹ due to C—H bending, 1318 cm⁻¹ due to O—H bending, 1246 cm⁻¹ due to C—O stretching, 1059 cm⁻¹ due to C—O/C—C stretching and 897 cm⁻¹ arising from β-glucosidic linkage.

FTIR—spectra (Fig. 4) of CE-PALF shows very weak broad band in the region 3150–3605 cm⁻¹ due to a significant decrease in the concentration of O—H groups arising from cyanoethylation. Absorption at 2917 cm⁻¹ due to C—H stretching, 1735 cm⁻¹ due to C=O stretching in hemicellulose, 1631 cm⁻¹ for C=C stretching affected due to phenolic —OH cyanoethylation, 1430 cm⁻¹ due to CH₂— bending is observed. The OH— bending absorption at 1318 cm⁻¹ in PALF has almost disappeared due to cyanoethylation. Band at ~ 1247 cm⁻¹ is due to C—O stretching. Differential absorption nature at

1435 cm⁻¹ is due to β-cyanoethyl group, and at 2240 cm⁻¹ is due to aliphatic nitrile (—C≡N) group.

HIO₄ oxidized PALF fibers exhibited (Fig. 5) very weak broad band in the region 3140–3610 cm⁻¹, but no band characteristics of O—H stretching was identified. Band at 2915–2965 cm⁻¹ is due to C—H stretching and 1606–1620 cm⁻¹ is due to C=C aromatic stretching in lignin component. Very weak broad bands in the region 1205–1445 cm⁻¹ includes —CH₂— bending, C—H bending, C—O stretching, C—O/C—C' stretching. Very weak band at 1740 cm⁻¹ due to C=O stretching in hemicellulose is found. Band at 1640 cm⁻¹ is due to hydrogen bonded —CHO groups with neighboring chains. Very weak peak at 889 cm⁻¹ is ascribed to a small unit of the β-glucosidic ring that survived during oxidation.

These FTIR absorption data agree well with the chemical modifications imparted onto the fibers. The importance of such chemical modifications have been discussed in the testing of various properties of the modified materials.

Viscosity

Viscosity measurement of the grafted PAN chains obtained after decomposition of the backbone fiber of PALF-g-PAN and CEPALF-g-PAN samples, was made in dimethyl formamide at 30°C using a Ubbelohde-suspended level dilution viscometer with the help of Mark-Howaink relationship $[\eta] = KM_v^\alpha$. Molecular weight of PAN was of the order of 10⁵.

Properties

Moisture Regain

About 0.1 g of each of the PALF, CEPALF, PALF-g-PAN, CEPALF, and CEPALF-g-PAN were placed separately in previously weighted bottles. The bot-

Table V Effect of AN Grafting on the Extent of Acid-Alkali Solubility of PALF

Samples	Percent Grafting	Percent Acid Solubility	Percent Alkali Solubility
PALF	0	62.1	50.9
PALF-g-PAN	7.9	60.8	49.8
PALF-g-PAN	14.3	58.6	46.1
PALF-g-PAN	47.9	42.2	32.0
PALF-g-PAN	59.6	31.9	20.8

Table VI Dye Uptake Ability of PALF, PALF-g-PAN, CE-PALF, and CEPALF-g-PAN Samples

Percent Grafting	PALF-g-PAN			CE-PALF			CEPALF-g-PAN				
	Absorbance (O.D)	Concentration of Dye after Dyeing	Dye Uptake in g/kg Fiber	Time of Cyanoethylation	Absorbance (O.D)	Concentration of Dye after Dyeing	Dye Uptake in g/kg Fiber	Percent Grafting with Time of Cyanoethylation	Absorbance (O.D)	Concentration of Dye after Dyeing	Dye Uptake in g/kg Fiber
0	0.286	87.9×10^{-4}	0.451	0 h (PALF-ONa)	0.216	6.72×10^{-4}	0.669	($\frac{1}{2}$ h)	0.184	5.72×10^{-4}	0.768
19.8	0.216	6.72×10^{-4}	0.669	$\frac{1}{2}$ h	0.198	6.16×10^{-4}	0.725	(1 h)	0.176	5.47×10^{-4}	0.793
47.9	0.194	6.1×10^{-4}	0.731	1 h	0.168	5.22×10^{-4}	0.818	(2 h)	0.165	5.13×10^{-4}	0.828
59.6	0.166	5.16×10^{-4}	0.824	2 h	0.161	5.01×10^{-4}	0.840	(3 h)	0.142	4.42×10^{-4}	0.899
				3 h	0.156	4.85×10^{-4}	0.855	(4 h)	0.135	4.2×10^{-4}	0.921
				4 h	0.142	4.41×10^{-4}	0.899				
				6 h	0.136	4.23×10^{-4}	0.917				

Initial concentration of the dye solution = 13.41×10^{-4} .

tles were kept in an oven and heated at 60°C until a constant weight was obtained. The oven-dry samples were then kept in an artificial humidity chamber for a week. The bottles were weighed at intervals until constant weights were obtained.

% Moisture regain

$$= \frac{\text{Equilibrium wt. of fiber} - \text{ovendry wt.}}{\text{Ovendry Weight}} \times 100$$

The data in Table IV on the extent of moisture regain clearly indicate that both cyanoethylation and cyanoethylation followed by grafting bring about a significant reduction in the moisture regain (enhanced hydrophobicity) of PALF. These modified fibers may, therefore, serve as ideal reinforcement for fabrication of low-cost FRP with matrix resins.

Percentage of Acid-Alkali Solubility

The behavior of the parent PALF and PALF-g-PAN samples towards HCl and NaOH was determined by the percentage of acid-alkali solubility. For this, the samples were separately immersed in 0.1(N) HCl and 0.1(N) NaOH for various time intervals at 65°C using the sample liquor ratio 1 : 100. The treatment showed a decreased in acid and alkali solubility with an increase in percentage of grafting (Table V). However, extent of cyanoethylation almost did not have any effect on acid and alkali solubility.

Dye Uptake

The dye (1 g) (acid green) was dissolved in 100 mL of hot water with constant stirring until a clean solution was obtained. The dye solution (10 cc) was taken in a beaker and to that, 4 cc of 1% ammonium sulphate solution was added. The material to liquor ratio was adjusted to 1 : 40 by adding the required amount of water. Then the pH of the dyesolution was maintained between 5–5.5 by adding dil-acetic acid dropwise. The samples were prewetted and dipped into the dye solution. The beaker was then kept over a hot plate and the temperature was raised to 80°C by 5°C/min. Then from 80–100°C, the temperature was raised slowly by 1°/min. The dyeing was carried out at 100°C for 45 min until all the color is exhausted into the fiber. The concentration of dye solution and that remaining after dyeing were determined by the spectrophotometer by using the formulae:

$$C = \frac{\text{O.D.}}{a \times \lambda}$$

Table VII (A) Tensile Properties of PALF-g-PAN Samples with Various Percent Grafting

Samples	Percent Grafting	Elongation at Break (B.L. %)	Tenacity at Break g/Denier	Tensile Modulus at Break g/Denier
PALF	0	0.88	1.07	121.6
PALF-g-PAN	7.9	0.89	1.09	122.47
PALF-g-PAN	14.3	0.91	1.14	125.27
PALF-g-PAN	47.9	0.98	1.35	137.6
PALF-g-PAN	59.6	1.02	1.48	145.1

where O.D. = optical density, a = constant (0.4343°K), and $\lambda = 740$ nm.

The resulting dye uptake ability of the fibers were determined from the difference between the initial and remaining concentration of the dye solution and presented in the Table VI.

The above data clearly shows that the dye uptake ability of pineapple leaf fibers is progressive with the time of cyanoethylation and is higher than the PALF-g-PAN. Further, with dye uptake of CEPALF-g-PAN (% grafting = 76.0 – 86.85) is slightly higher than CEPALF. It is, therefore, suggested that dye uptake ability of PALF can be enhanced through simple chemical modification such as cyanoethylation rather than going to a cumbersome grafting process.

Mechanical Properties of PALF and Chemically Modified PALF

The elongation at break, tenacity at break, and the tensile modulus at break of PALF, PALF-g-PAN, and CEPALF-g-PAN fibers were tested using dutron tensile tester brand 20 kgf using the method of Haque et al.⁶

The tensile data reveal a moderate increase in the tensile modulus of PALF when grafted with AN;

on the other hand, CEPALF-g-PAN samples have higher percent grafting, but the increase in tensile modulus is not much.

Thermal Analysis (TGA)

Figure 6 shows the primary thermograms of parent PALF and PALF-g-PAN samples of 7.9, 14.3, 47.9, and 59.6 percent grafting. From the primary thermograms the decomposition temperature T_D has been calculated (Table VIII).

The results in Table VIII indicate that the thermal stability of PALF is influenced by grafting with acrylonitrile. All the graft copolymers have a higher degree of thermal stability with respect to parent PALF. The enhancement of thermal stability of PALF-g-PAN samples has been attributed to thermal cyclization of grafted PAN-chains to ladder structure that protects the backbone fibers from thermal decomposition. This is similar to that observed by Verma et al.⁵⁹ Application of Freeman carroll equation^{60,61}

$$\Delta \log \frac{dw}{dt} = n \Delta \log w - \frac{E}{2.303R} \Delta \frac{1}{T}$$

and the plots of $\Delta dw/dt$ vs. $\Delta \log w$ at constant $\Delta(1/T)$ yields linear plots from which the value of

Table VII (B) Tensile Properties of CE-PALF-g-PAN Samples with Various Percent Grafting

Samples	Percent Grafting with Time of Cyanoethylation	Elongation at Break (B.L. %)	Tenacity at Break g/Denier	Tensile Modulus at Break g/Denier
PALF	0 (0 h)	0.88	1.07	121.6
CEPALF-g-PAN	76.0 ($\frac{1}{2}$ h)	0.89	1.1	123.45
CEPALF-g-PAN	79.2 (1 h)	0.9	1.14	126.66
CEPALF-g-PAN	80.4 (2 h)	0.95	1.22	128.42
CEPALF-g-PAN	84.52 (3 h)	0.95	1.24	130.52
CEPALF-g-PAN	86.68 (4 h)	0.98	1.30	132.65

Table VIII

PALF-g-PAN	Percent of Wt. Loss Decomposition Temperature in °C (T_D)							
	100	200	300	400	500	600	700	800
Base fiber	3.34	5.0	9.17	69.17	80.84	87.27	90.0	92.72
7.9%	2.73	3.64	6.36	36.68	80.82	84.17	85.84	86.7
14.3%	2.5	3.34	5.0	35.67	80.0	82.5	84.17	85.0
47.9%	1.25	2.5	3.34	33.0	62.5	66.67	68.33	70.84
59.6%	0.84	1.67	3.17	30.0	62.5	66.67	68.33	70.0

the order of reaction (n) has been calculated to be unity. From the intercept of the plots the activation energy (E) involved in the pyrolysis has been computed to be 13.87 kcal mol⁻¹, 13.4 kcal mol⁻¹, 14.93 kcal mol⁻¹, 15.37 kcal mol⁻¹, and 15.86 kcal mol⁻¹ for PALF-g-PAN samples of grafting percent 0, 7.96, 14.7, 47.9, and 59.6, respectively.

REFERENCES

1. *Textile fibers*, H. R. Maursberger, Ed., John Wiley and Sons, New York, 1947.
2. *Textile Fibers and Their Uses*. Sixth Edition, J. B. Lippincott Company, Philadelphia, 1958.
3. A. D. Little, *Engineering Properties of Fibers*; Cambridge, MA (1966).
4. P. C. Mehta and I. M. Trevedi, *Cell. Chem. Technol.*, **7**, 401 (1973).
5. M. M. Haque, M. Habibuddowla, A. J. Mahmood, and A. J. Milan, *J. Polym. Sci. Polym. Chem. Ed.*, **18**, 1447-1458 (1980).
6. M. M. Haque and M. Habibuddowla, *J. Sci. Ind. Res.*, **15**(1-4), 64-70 (1980).
7. G. Wu and Y. Hu, *Fangzhi Xuebau*, **10**(10), 435-439 (1980).
8. M. Habibuddowla, *Graft Copolymerization of Lignocellulosic Fibers*, D. N. S. Hon, Ed., A. C. S. Symposium series. Vol. 182, 1982, pp. 73-82.
9. A. S. Dutta, B. K. Sarkar, and A. K. Mukhopadhyaya, *J. Appl. Polym. Sci.*, **27**(III), 4525-4527 (1982).
10. A. Hebeish, A. Higzy, and N. Y. Abozeid, *Angew Makromol. Chem.*, **121**, 69-87 (1984).
11. R. K. Samal, P. K. Sahoo, and H. S. Samantray, *J. Macromol. Sci. Rev. Macromol. Chem.*, **26**(1), 81-141 (1986).
12. R. K. Samal, R. N. Samal, and H. S. Samantray, *Polym. J.*, **18**(6), 471-478 (1986).
13. A. Hebeish, J. A. Bayazeed, and A. Hirazy, *Acta Polym.*, **39**(9), 494-499 (1988).
14. W. Gongsheng, W. Zingju, Z. J. Farcheng, and Y. Chengzneng, *Fang Zin Xuebau*, **9**(1), 17-18 (1988).
15. D. S. Verma and S. Murali, *Ind. J. Text. Res.*, **14**, 9-13 (1989).
16. P. Ghose, S. Biswas, and C. Datta, *J. Mater. Sci.*, **24**(1), 205-212 (1989).
17. R. K. Samal, H. S. Samantray, and R. N. Samaj, *J. Polym. Mater.*, **16**, 223-229 (1989).
18. R. K. Samal and H. S. Samantray, *J. Appl. Polym. Sci.*, **37**, 3085-3096 (1989).
19. R. K. Samal, R. N. Samal, S. Dash, and H. S. Samantray, *Ind. J. Text. Res.*, **14**(9), 187-190 (1989).
20. W. Gongsheng, L. Xanjian, W. Xanjian, W. Xingju, and J. Dauue, *Zirum Keuue Xuebau*, **1**, 107-111 (1989).
21. R. K. Samal, S. Dash, and A. K. Sahu, *J. Appl. Polym. Sci.*, **41**, 195-203 (1990).
22. R. K. Samal, S. Dash, R. N. Samal, and A. K. Sahu, *Ind. J. Fiber Text. Res.*, **15**, 104-107 (1990).
23. R. K. Samal, A. K. Sahu, M. Pani, S. Dash, and R. N. Samal, *Polym. Sci. Contemporary Themes*. Vol. 1, S. Sivram, Ed., Tata McGraw-Hill Pub. Co. Ltd., New Delhi, India, 1991, pp. 372-376.
24. *Proceedings of Workshop on Polymer Composites as substitutes for conventional Building materials*; 3rd October, 1988, New Delhi, India.
25. K. K. Shawla, E. E. A. Aragao, R. C. C. Monterio, F. C. Fernandez, and M. M. Moraes; in *Advance in Composite Materials*, Vol. 1, Pergamen Press, Oxford, 1980, pp. 114-124.
26. K. K. Chawla and A. C. Bastos, in *Proceedings 3rd. Int. Conf. on mechanical behaviour of composites*, Vol. 3, 1979, pp. 191-196.
27. P. Kumar, *Ind. J. Technol.*, **24**, 29-32 (1986).
28. P. Narain and S. S. Bhatnagar, *J. Sci. Ind. Res.*, **3**, 396-399 (1945).
29. A. R. Philip, *Eng. Mater. Des.*, **8**, 475-479 (1965).
30. S. V. Prasad, C. Pavithran, and P. K. Rohatgi, *J. Mater. Sci.*, **19**, 1443-1454 (1983).
31. P. J. Roe and M. P. Ansell, *J. Mater. Sci.*, **20**, 4015-4020 (1985).
32. H. Belmares, A. Barrera, E. Castillo, E. Verheugen, and M. Monjaves, *Ind. Eng. Chem. Prod. Res. Dev.*, **20**, 555-561 (1981).
33. M. N. Amin, A. M. Bhuiyan, and A. J. Mian; *J. Text. Inst.*, **81**, 167 (1990).

34. R. B. Chavan, S. Sanyal, R. K. Gupta, and A. K. Jain, *Ind. J. Text. Res.*, **12**, March, 17-20 (1987).
35. S. S. Bhatnagar, G. A. R. Khan, and L. C. Verman, *Indian Pat.*, **28**, 281 and **28**, 427 (1926).
36. M. Powrie and J. Speakman, *J. Text. Inst.*, 34T77 (1943).
37. A. R. Mukherjee, Ph.D. thesis, University of Heeds, 1948.
38. A. R. Phillip, *Rein Plast.*, **8**, 306 (1964).
39. British Standard 476: Part-7 *Fire Tests on Building Materials and Structures, Part-7; Surface Spread of Flame on Materials*, 1971.
40. S. J. Monte and G. Surgerman, SPI—33rd Annual Technical Conference; Reinforced plastics/composites Institute, Washington, DC, Section 2-C, 1978, 1.
41. A. N. Shah and S. C. Lakkad, *Fiber Sci. Technol.*, **15**, 43-44 (1981).
42. K. K. Chawla and J. R. M. D'Almeifia, *Progress in Science and Engineering of Composites* T. Hayashi, K. Kawala, and S. Ume Kawa Eds., ICCM-IV, Tokyo, 1982.
43. S. J. Monto and G. Sugerman, *Polym. Plast. Technol. Eng.*, **13**, 115 (1979).
44. I. K. Varma, V. Choudhary, M. S. Choudhary, B. S. Rao, A. Tripathy, and T. C. Goeo, *J. Appl. Polym. Sci.*, **30**, 1491 (1985).
45. I. K. Verma, B. S. Rao, M. S. Choudhary, V. Choudhary, and D. S. Varma, *Angew. Makromol. Chem.*, **130**, 191 (1985).
46. N. C. Sorn, A. Bagchi, and A. K. Mukherjee, *Ind. J. Text. Res.*, **12**, 78 (1987).
47. I. K. Varma and R. Bhatnagar, in *Proceedings of the Sixth National Symposium on Thermal Analysis*; E. B. Mirza and A. C. Momin, Eds., 1987, pp. VI22-VI26.
48. I. K. Varma, S. R. Amantha Krishna, and S. Krishnamoorthy, *Tex. Res. J.*, **58**, 486-494 (1988).
49. I. K. Varma, S. R. Anantha Krishna, and S. Krishnamoorthy, *Tex. Res. J.*, **58**, 537-543 (1988).
50. I. K. Varma, S. R. Ananthakrishnan, and S. Krishnamoorthy, *Composites*, **20**(4), 383-388, July (1989).
51. D. S. Varma and S. Murali, *Ind. J. Text. Res.*, **14**(1), 9-13 (1989).
52. N. C. Som and A. K. Mukherjee, *I. J. Text. Res.*, **14**(2), 80-85 (1989).
53. M. N. Amin, A. M. Bhuiyan, and A. J. Mian, *J. Text. Inst.*, **81**, 167 (1990).
54. N. C. Som and A. K. Mukherjee, *Int. J. Fiber Test. Res.*, **16**(2), 146-153 (1991).
55. M. Santappa and V. S. Ananthanarayanan, *J. App. Polym. Sci.*, **9**, 2437 (1967).
56. H. Namita and S. Machida, *Makromol. Chem.*, **97**, 209 (1966).
57. E. H. C. Edgecombe and R. G. W. Norrish, *Nature*, **197**, 282 (1963).
58. *Oxidation in Organic Chemistry*, K. B. Wiberg, Ed., Part-A, Academic Press, New York, 1965, pp. 244-246.
59. D. S. Verma and S. Rabisankar, *Angrew. Makromol. Chem.*, **28**, 191 (1973).
60. B. Carroll and E. S. Freeman, *J. Phys. Chem.*, **62**, 394 (1958).
61. E. S. Freeman and D. S. Anderson, *J. Polym. Sci.*, **54**, 253 (1961).

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