

# Effect of Chemical Modifications on FTIR Spectra. II. Physicochemical Behavior of Pineapple Leaf Fiber (PALF)

R. K. SAMAL, MUKUL C. RAY

Macromolecular Research Laboratory, Department of Chemistry, Ravenshaw College, Cuttack 753003, Orissa, India

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**ABSTRACT:** This article highlights chemical modifications like alkali treatment, dinitrophenylation, benzylation, and benzylation–acetylation carried out on an pineapple agrowaste leaf fiber (PALF). The parent and chemically modified PALF were characterized by FTIR spectra, pH measurement, and detection of nitrogen. The percent moisture regain (extent of hydrophobicity), mechanical strength, and chemical inertness of parent and chemically modified fibers were evaluated. The modified fibers showed significant hydrophobicity, improved mechanical strength, and moderate chemical resistance. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 2119–2125, 1997

**Key words:** chemical modification; FTIR spectra; physicochemical behavior; pineapple agrowaste leaf fiber

## INTRODUCTION

The use of agrowastes/lignocellulosic fibers as reinforcements for developing low cost light weight composites has been an emerging arena in the field of polymer science and technology. This is aimed at partial replacement of conventional and pollution causing fibers, such as glass, carbon, borosilicate, aramide, etc., in the composite industry, so that economical engineering can be provided to the plastic industry for multiple applications from sports items, low cost housings, and household items to composites. This has necessitated imparting significant hydrophobicity to these fibers for ideal bonding to the matrix resins to make fiber reinforced plastic (FRP) durable.<sup>1–7</sup> In our laboratory we employed simple routes with cheap chemicals<sup>8–12</sup> to meet commercial needs in natural fiber reinforced composites. These reinforced composites are expected to be more economical than those reported earlier using costly reagents and cumbersome routes. The present report sums up a few of our many attempts.

## EXPERIMENTAL

### Materials and Methods

Pineapple leaf fibers (PALFs) were purified by Soxhlet extraction with a 1 : 1 benzene–alcohol mixture for 72 h followed by washing with acetone and ethanol and air drying. Acetone, acetic acid, acetic anhydride, benzoyl chloride, 2,4-dinitrochlorobenzene ethanol pyridine, NaOH, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, HCl, NH<sub>4</sub>OH, and H<sub>2</sub>O<sub>2</sub> were of analytical grade.

### Methods of Chemical Modifications

#### *Alkali Treatment (PALF—ONa)*

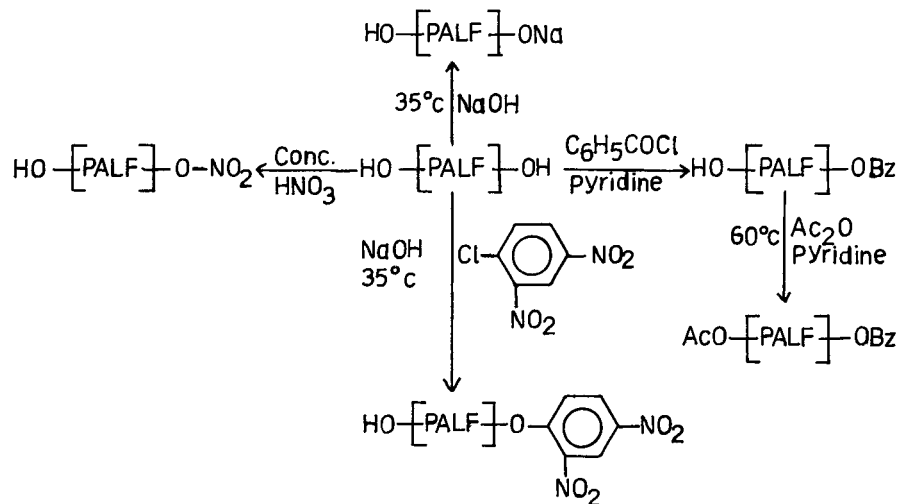
Pineapple leaf fibers were treated with NaOH solution of varying concentrations (2–10% w/v) for 1 h at 35°C with occasional shaking followed by washing with dilute acetic acid and distilled water for a week to leach out the absorbed alkali. The materials were then air dried.

#### *Nitration (PALF—O—NO<sub>2</sub>)*

One gram of PALF was treated with 40 mL of concentrated HNO<sub>3</sub> for a few seconds. The fibers

Correspondence to: R. K. Samal.

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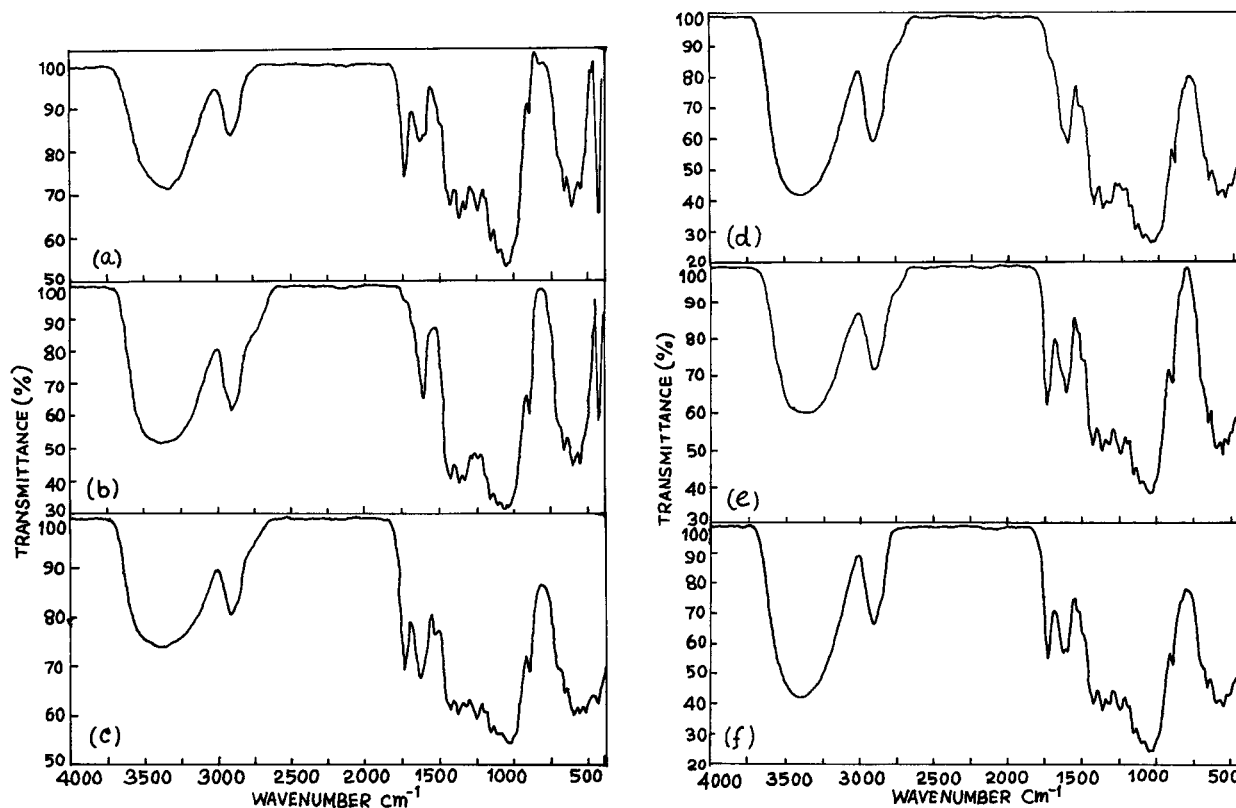
**Figure 1** Schematic model of chemical modifications on PALF.

were thoroughly washed with distilled water and air dried.

#### Dinitrophenylation (PALF—DNP)

One gram of PALF pre-wetted with 2% NaOH solution was placed in a 250-mL conical flask fit-

ted with a standard joint. To that 20-mL of a 5% solution of 2,4-dinitrochlorobenzene in acetone was added and refluxed at 60°C for various time intervals of 1–6 h. The dinitrophenylated fibers were washed with ethanol followed by distilled water and then air dried.



**Figure 2** FTIR spectra of PALF: (a) parent PALF, (b) PALF—ONa, (c) PALF—O—NO<sub>2</sub>, (d) PALF—DNP, (e) PALF—OBz, (f) PALF—OBz—OAc.

### Benzoylation (PALF—OBz)

One gram of PALF preswelled with acetone was treated with 20 mL of benzoyl chloride in the presence of 2 mL pyridine as catalyst in a 250-mL conical flask. The contents were shaken in an ice water bath for about 30 min. After the reaction ceased, the product was removed, squeezed, washed with  $\text{NH}_4\text{Cl}$  solution followed by dilute acetic acid and distilled water, and finally air dried.

### Benzoylation–Acetylation (PALF—OBz—OAc)

Benzoylated PALF was subjected to acetylation by refluxing 1 g of PALF—OBz with 20 mL of acetic anhydride in 1 mL pyridine as catalyst at  $60^\circ\text{C}$  for 1 h in a 250-mL conical flask. The acetylated fibers were well washed with acetone and ethanol. A schematic presentation of various chemical modifications of PALF are given in Figure 1.

### FTIR Spectroscopy

The FTIR spectra of the samples were recorded in KBr pellets in a Bruker IFS 66V FTIR spectrophotometer.

### pH Determination

The pH of the parent and modified fibers were recorded in deionized water using a Systronics-324 pH meter standardized with a buffer solution of pH 4 and 9.

### Nitrogen Detection

The nitrated and the dinitrophenylated fibers were subjected to nitrogen detection following Lassaigne's technique.<sup>13</sup>

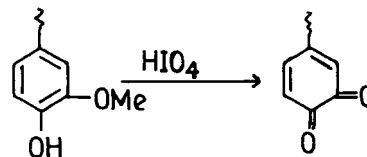
## RESULTS AND DISCUSSION

Upon dinitrophenylation the fibers appeared to be light yellow while nitration turned the fibers deep yellow. In other modifications no significant color changes appeared.

### FTIR Spectroscopy

Parent and modified PALF were analyzed to ascertain whether such modifications truly occurred in the fiber. The FTIR spectra of parent and modi-

fied PALF are shown in Figure 2. The exact position and probable assignments of the bands are given in Table I. In comparison to parent PALF, the PALF—ONa, PALF—O—NO<sub>2</sub>, PALF—DNP, PALF—OBz, and PALF—OBz—OAc showed a reduction in O—H stretching intensity and shifting of the peak from  $3349.9\text{ cm}^{-1}$  to  $3347.3$ ,  $3411.5$ ,  $3405.4$ ,  $3355.0$ , and  $3413.7\text{ cm}^{-1}$ , respectively, indicating participation of some free hydroxyl groups in these chemical reactions. The point of reaction was probably at the lignin—OH and C<sub>6</sub>—OH of the glucopyranose unit in the cellulose component. But perhaps it may not have involved C<sub>2</sub> and C<sub>3</sub> hydroxyl as Malpardi oxidation,<sup>14</sup> because HIO<sub>4</sub> was found to be positive with modified PALF. However, consumption of HIO<sub>4</sub> cannot be taken as final proof of the noninvolvement of the C<sub>2</sub>—C<sub>3</sub> glycolic linkage of the glucopyranose units in the cellulose component in the oxidation, because HIO<sub>4</sub> is a well-known oxidizer that causes facile oxidation of guaiacol (*o*-methoxyphenol) units to *o*-quinones.<sup>15,16</sup>



Thus, the coniferyl alcohol moiety in lignin that is structurally analogous to guaiacol is perhaps facilitating oxidation to a quinone structure. Therefore, it is difficult to be sure at this stage of the participation of C<sub>2</sub>— and C<sub>3</sub>—OH groups in the modification. A strong and sharp band at  $1737.4\text{ cm}^{-1}$  due to a C=O stretch of the hemicellulose components in the parent PALF disappeared in PALF—ONa. Alkali treatment of PALF destroys the C=O unit of the uronic acid residue in hemicellulose, perhaps arising from the intermolecular addition of the alcoholate ( $-\text{CH}_2-\text{O}^-\text{Na}^+$ ) and/or the phenolate ( $-\text{Ph}-\text{O}^-\text{Na}^+$ ) from cellulose and lignin components to the C=O group. The C=O stretching band at  $1737.2\text{ cm}^{-1}$  in PALF—OBz shifts to  $1736.7\text{ cm}^{-1}$  in PALF—OBz—OAc. This band in PALF—OBz—OAc is more intense, indicating a combined effect of the  $-\text{O}-\text{CO}-\text{Ph}$  and  $-\text{O}-\text{CO}-\text{CH}_3$  groups arising from benzoylation and acetylation, respectively. In dinitrophenylated fiber the C=O band again disappears. This is because dinitrophenylation has been carried out in the presence of NaOH. The band of medium intensity at  $1639.1\text{ cm}^{-1}$  in nitrated PALF may perhaps be attributed to the

**Table I FTIR Spectra of Parent and Chemically Modified PALF**

PALF	PALF—ONa	PALF—O—NO <sub>2</sub>	PALF—DNP	PALF—OBz	PALF—OBz—OAc	Possible Assignment
3349.9	3347.3	3411.5	3405.4	3355.0	3413.7	O—H str. vibration (str. vib.)
2903.8	2902.3	2916.2	2903.5	2915.8	2904.7	C—H str. vib.
1737.4	—	1753.2	—	1737.2	1736.7	C=O str. vib. of hemicellulose
1634.9	1637.6	1639.1 <sup>a</sup>	—	—	1631.5	Absorbed water
1608.3	1610.0	—	1605.4	1603.4	1604.6	Aromatic C=C str. vibration
—	—	1530.5	1528.7	—	—	Aromatic assym. C—NO <sub>2</sub> str. vib.
1429.4	1430.8	1431.0	1430.7	1429.4	1430.5	O—H in plane bending
1374.2	1372.1	1376.6	1373.0	1373.4	1374.6	C—H aliphatic bonding vib.
1321.1	1320.0	1324.6	1322.3	1325.4	1320.7	O—H bending and C—O str.
1163.3	1164.6	1163.2	1164.7	1163.5	1163.6	Assym. C—O—C ring str. vib.
1112.1	1116.6	1113.4	1112.6	1112.4	1113.8	Assym. in phase ring str. vib.
1058.6	1059.9	—	1059.6	1055.9	1059.5	C—O/C—C str. vib.
—	—	1024.5	—	—	—	
897.9	898.9	896.7	896.8	897.2	897.6	$\beta$ -glycosidic linkage
668.1	667.2	—	667.2	666.6	667.1	Out of plane bending vib. of intermolecular H-bonded O—H
613.0	607.5	606.3	611.2	—	609.0	
561.5	559.3	560.6	559.4	559.3	559.7	Torsional vib. of pyranose ring
434.3	438.0	434.8	434.4	435.1	436.4	

Absorbance in cm<sup>-1</sup>.<sup>a</sup> Assymmetric stretching vibration of N—O in NO<sub>2</sub>.

**Table II Percent Moisture Regain of Parent and Chemically Modified PALF**

PALF—ONa		PALF—DNP		PALF—OBz		PALF—OBz—OAC		PALF—O—NO <sub>2</sub>
NaOH (%)	Moisture Regain (%)	Time of Phenylation (h)	Moisture Regain (%)	Time of Benzylation (h)	Moisture Regain (%)	Time of Acetylation (h)	Moisture Regain (%)	Moisture Regain (%)
2	26.16	0	25.35					
4	27.08	1	10.62					
6	28.53	2	10.51	0.5	12.34	1	11.43	20.53
8	29.42	3	9.71					
10	30.61	4	8.83					
		6	8.82					

combined effect of asymmetric N—O stretching vibration in the NO<sub>2</sub> group and absorbed water. The weak band at 1634.9 cm<sup>-1</sup> is due to the absorbed water that disappeared on dinitrophenylation and benzylation. This is in agreement with the moisture regain data shown in Table II. A weak inflection at 1528.7 cm<sup>-1</sup> in PALF—DNP and an intense peak at 1530.5 cm<sup>-1</sup> in PALF—O—NO<sub>2</sub> are attributed to aromatic asymmetric C—NO<sub>2</sub> stretching vibration. The nature of the bands in PALF—O—NO<sub>2</sub> and PALF—DNP undoubtedly reveals the nitration of the aromatic nucleus in lignin as well as the C<sub>6</sub>—OH of the glucose units in the cellulose upon nitration. Bands at different places in the FTIR pattern of parent and modified PALF in the 1431 to 1024.5 cm<sup>-1</sup> regions with varying intensity are almost similar and are due to various vibrational modes of groups as indicated in Table I. The band of medium intensity at 897.9 cm<sup>-1</sup> due to β-glycosidic linkage in the parent PALF underwent shifting to a lower wave number, except PALF—ONa was accompanied by an increase in the intensity. This relates to the rotation of glucose residue around the glycosidic bond<sup>17</sup> and indicates a slow transition from parent to chemically modified PALF. Bands at and beyond 667 cm<sup>-1</sup> corroborate the observations of Blackwell and coworkers.<sup>18</sup>

### pH Determination

The pH values of all the samples except the alkali treated fiber were nearly 6.6 and for PALF—ONa it was 7.5. The latter value entails no quantitative involvement of PALF-hydroxyl groups in the alkali treatment.

### Nitrogen Detection

Lassaigne's test was positive with PALF—DNP and PALF—O—NO<sub>2</sub>. This supports nitration and dinitrophenylation.

## PHYSICOCHEMICAL BEHAVIOR

### Percent Moisture Regain (Extent of Hydrophobicity)

About 0.2 g of each of the parent and modified fibers were placed separately in previously weighed bottles. The bottles were kept in an oven at 50–60°C until a constant weight was obtained. The oven dried samples were then kept in an artificial humidity chamber of 80% relative humidity (RH) for a week. The bottles were weighed at intervals until constant weight.

% moisture regain

$$= \frac{(\text{equilibrium wt of fiber}) - (\text{oven dry wt})}{\text{oven dry wt}} \times 100$$

**Table III Mechanical Strength of Parent and Chemically Modified PALF**

Sample	Strength (kg f/g)
PALF	36
PALF—ONa (4%)	60
PALF—DNP	44
PALF—OBz	34
PALF—O—NO <sub>2</sub>	39
PALF—OBz—OAC	42

**Table IV** Effect of Chemical Behavior of Parent and Chemically Modified PALF

Sample	Percent Solubility					
	0.1N HCl	0.1N NaOH	0.1N H <sub>2</sub> SO <sub>4</sub>	0.1N NaCl	0.1N NH <sub>3</sub>	5% H <sub>2</sub> O <sub>2</sub>
PALF	13.7	25.1	11.4	11.8	5.5	20.6
PALF—ONa	15.3	20.5	13.3	6.3	2.2	12.5
PALF—O—NO <sub>2</sub>	6.6	16.4	8.2	10.8	3.4	11.6
PALF—DNP	9.8	18.6	9.6	9.2	7.2	10.6
PALF—OBz	4.6	8.8	7.6	6.3	3.2	9.4
PALF—OBz—OAc	3.9	9.2	6.9	5.9	3.2	8.6

The data in Table II shows that the reduction in percent moisture regain is significant upon dinitrophenylation and benzylation—acetylation but low upon nitration. The hydrophobicity order follows PALF—DNP > PALF—OBz—OAc > PALF—OBz > PALF—O—NO<sub>2</sub> > PALF > PALF—ONa.

### Mechanical Strength

The mechanical strength of parent and chemically modified fibers was measured in the fiber breaking strength measuring machine (Good Brands and Co. Ltd., London). The data in Table III shows that, except for the benzyolated PALF, all had mechanical strength higher than that of PALF. In particular, the alkali treated fibers showed a significant increase in mechanical strength. The lowering of strength for the benzyolated fiber was probably due to the liberated HCl degrading the cellulose backbone in the triopolymer matrix.

### Chemical Treatment

The behavior of parent and modified fibers toward H<sub>2</sub>SO<sub>4</sub>, HCl, NH<sub>4</sub>OH, NaCl, NaOH, and H<sub>2</sub>O<sub>2</sub> was tested by determining the percentage solubility of the samples. For this purpose the samples were immersed separately in aqueous solution (0.1N) of the reagent for 2 h using a fiber—liquor ratio of 1 : 100 at 60°C. The method adopted was similar to that of Leveau et al.<sup>19</sup> The results of percent solubility are recorded in Table IV. Although PALF—OBz—OAc showed remarkable resistance, other samples had moderate resistance to the chemical reagents.

### CONCLUSION

The results of the studies reveal that under suitable conditions with the use of appropriate chemi-

cal reagents, it is possible to modify the surface characteristics of cheap natural fibers. Primary requisites such as enhanced hydrophobicity, improved mechanical strength, and chemical inertness can be imparted onto the fibers that may perhaps make them suitable for use as reinforcements in FRP. The developments of composites and evaluation of their properties will be reported in separate communications.

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