CHAPTER 4

RESULTS AND DISCUSSION

This chapter is essentially to present the outcome of the experiments carried out on raw PJFs and various chemically modified PJFs. The characterisation of raw and various chemically treated PJFs are discussed separately. The micrographs, plots, photographs and tables have been used in support of the test results in each category.

The detailed discussion on the results is presented in the various sections with suitable reasons. The test results of characterisation of raw PJFs are reported in the sections 4.1. The results of characterisation of optimally treated PJFs and various chemically modified PJFs are discussed in detail in the sections 4.2 and 4.3, respectively. Further, the raw PJFs derived parameters are analyzed for paper production process which is detailed in section 4.4.

4.1 CHARACTERIZATION STUDY OF RAW PJF

4.1.1 Anatomy of Prosopis Juliflora (PJ) Bark and Fiber

Examination of the PJ bark and fiber under a polarized microscope revealed the existence of several thin dark tangential layers of collapsed phloem alternating with several successive cylinders of phloem fibers as shown in Figure 4.1 (a) & (b). The PJFs were cleaved into thick blocks by wavy dilated phloem rays. There were about 15 successive cylinders of fibers
in the bark. The fiber blocks were smaller and less prominent in the outer zone and they became gradually wider and thicker in the inner zone.

Figure 4.1  (a) & (b) Transverse section of the PJ bark showing several successive cylinders of fibers. CPh-Collapsed Phloem, PhFi-Phloem fibers
Figure 4.1 (c) to (e) (continued)
Figure 4.1 (e) to (e) Transverse section of phloem showing outer blocks and inner portion of the bark showing wider blocks of fiber and disintegrated phloem (PhR- Phloem ray, Scl- Sclereids, CPh- Collapsed phloem, PhFi-Phloem fibers)

Figure 4.1 (f) (GFi) - Gelatinous fibers enlarged
(g) Figure 4.1(g) Transverse section of fibers stained with phloroglucinal its show lignification of the primary wall (PW- Primary Wall)

(h) Figure 4.1(h) Gelatinous fibers as seen under polarised light microscope (PW- Primary Wall)
Figure 4.1(i)  The PJF as viewed under a polarized microscope (CL-Cell Lumen, PW- Primary Wall, SW- Secondary Wall, S₁, S₂, and S₃- Wall layers)

The outer and inner blocks of the fibers are 30 μm and 40 μm thick, respectively. Outer blocks of the PJF were 60–100 μm wider whereas the inner blocks were 200–300 μm wider as illustrated in Figures 4.1 (c) to (e).

The PJFs belonged essentially to gelatinous or mucilaginous type that consisted of an outer primary wall which was highly lignified while the secondary wall had mucilaginous substance. When the PJF was stained with toluidine blue, its outer primary wall appeared dark green in color while the inner secondary wall appeared purple in color as represented in Figure 4.1 (f).
However, the primary wall of the PJF appeared red in color because it took up the phloroglucinal stain due to the presence of lignin while the secondary wall remained unstained as shown in figure 4.1 (g).

When the PJFs were stained and observed under a polarized microscope, the primary walls appeared bright blue in color while the secondary walls remained either colorless or differently colored as indicated in Figure 4.1(h).

The diameter and thickness of the primary and secondary walls of the single PJF were 20 μm, 5–8 μm and 10–12 μm, respectively as seen in the Figure 4.1 (i). Whereas the diameters of single fibers derived from other bark are 17.8–21.6 μm, 17–22.8 μm, 15.9–20.7 μm, 17.7–21.9 μm and 28.1–35 μm for flax, hemp, jute, kenaf and ramie, respectively (Perry 1975). The S1, S2 and S3 layers of the PJF were not very distinct and the cell lumen was approximately 8 μm in diameter.

4.1.2 XRD Analysis

The spectrum corresponding to the PJF shows a well-defined diffraction peaks at the following angles viz. 2θ = 15.07° and 22.67° as shown in Figure 4.2. The observation of a major crystalline peak of PJF originate at 2θ diffraction angles of 15.07° (1 1 0) and 22.67° (2 0 0), which corresponds to the crystallographic plane family of cellulose-I. The CI which is a measure of the amount of crystalline cellulose with respect to the global amount of amorphous materials was determined using Segal empirical method (Segal et al 1959).

The CI value for the PJF was found to be 46%, which is much lower than that determined for jute (71%) and hemp (88%) (Mwaikambo & Ansell 2002). Using Scherer’s equation in 3.3, the CS of the PJF was found to
be 15 nm, which is much greater than that determined for the flax fiber (2.8 nm) and quite closer to the ramie fiber (16 nm) (Reddy & Yang 2005 b). The crystallite size strongly believed to reduce the moisture absorption capacity and chemical reactivity of the raw PJF.

Figure 4.2 X-ray spectrum of the PJF

4.1.3 Determination of the Mechanical Properties of the PJFs

Mechanical properties of bark fibers depend largely on the cell wall structure (S₁, S₂, and S₃) and the chemical composition. The S₁ layer is very important for the transverse elastic modules of fibers and the bulk of the central S₂ layer contributes to the mechanical strength of the fiber in the longitudinal direction (Sjostrom 1993, Han et al 2007).

Tensile strength of the PJFs was found to be 558 ± 13.4 MPa with 1.77 ± 0.04% of strain rate, while the tensile strengths of other bark fibers viz. flax, hemp, jute, and ramie are 500–900 MPa, 690 MPa, 370 ± 134 MPa, and 915 MPa, respectively (Bolton 1994, Perry 1975, Saha et al 2010, Seki et al
2011). The calculated Young’s modulus of the PJF was 31.52 ± 1.18 GPa higher than the vakka, date, palm, coconut, banana, sisal and quite closer to bamboo fibers (Rao & Rao 2007).

The PJF consist of highly crystalline cellulose fibrils spirally wound in a matrix of amorphous hemicellulose and lignin. The oriented microfibril angle (ω) of the PJF was 10.64° ± 0.45° with axis of the fiber as derived from the global deformation (Charlet et al 2009) as mentioned in Equation (4.1)

\[ \varepsilon = \ln \left( 1 + \frac{NL}{L_\omega} \right) = -\ln(\cos \omega) \quad (4.1) \]

It is worth mentioning that jute, flax, hemp and banana fibers had a microfibril angle of 8.1°, 5°, 6.2° and 11 to 12°, respectively (Perry 1975, Kulkarni et al 1983). Finally, the fiber-matrix interfacial shear strength was determined as 5.3 ± 0.26 MPa. This is the primary factor that indicates the stress transfer from matrix to fiber in a composite structure. The specific mechanical properties of the PJF are significant because of the good mechanical properties are combined with a low density.

4.1.4 Thermal Analysis of the PJF

Thermal analysis of the natural fibers gives a good description of their thermal stability. Initial degradation of the PJF started at 63.4°C which resulted in a weight loss which is presumably due to the vaporization of water in the fiber. The PJF underwent 10% degradation at a temperature of 149°C when the initial temperature was set at 33°C. It was thermally stable at around 217°C in that a significant peak observed at 219°C fell in the range of 200°C to 300°C TG and DTG curve as shown in Figure 4.3 that corresponded to the thermal depolymerisation of hemicellulose.
A prominent peak at 331.1° C indicated the possible decomposition of α-cellulose. However, the similar peak was observed at 321° C, 308.2° C, 298.2° C and 309.2° C for bamboo, hemp, jute and kenaf fibers, respectively (Yao et al 2008). Structurally lignin has a complex composition of aromatic rings with several branches and hence its decomposition generally occurs at a very low weight loss rate within the whole temperature range from ambient to temperatures higher than 700° C (De Rosa et al 2010 and Yang et al 2007).

![Graph](image)

**Figure 4.3** TG and DTG curves of the PJF

Remaining two peak values viz. 480.6° C and 676.6° C may be a consequence of oxidative degradation of the charred residue. The apparent activation energy $E_a$ was determined to understand the detailed kinetic parameter of the fiber (Das & Chakrabarty 2008) from detailed Broido’s equation in 4.2.
\[
\ln \left[ \ln \left( \frac{1}{y} \right) \right] = -\left( \frac{E}{R} \right) \left[ \left( \frac{1}{T} \right) + K \right]
\]

where \( R \) is the gas constant (8.32 J/mol K), \( T \) is the temperature in Kelvin, \( y \) is the normalized weight \((w_t/w_0)\), \( w_t \) denotes the weight of the sample at any time \( t \), while \( w_0 \) indicates the initial weight. The kinetic activation energy \((E_a)\) 76.72 kJ/mol was interpolated from the plot of \( \ln[\ln(1/y)] \) vs. \( (1/T) \) as illustrated in Figure 4.4. This general range might offer a comparatively narrower range of activation energy for understanding fiber decomposition for polymer composite with respect to previously reported values i.e., 60–170 kJ/mol for wood decomposition (Di Blasi 2002).

![Figure 4.4 Broido’s plot of the PJF](image-url)
4.1.5  Morphological Analyses

Morphological analyses of the PJFs were essentially conducted using the phloem tissue. The phloem parenchyma and rays are clearly shown in Figure 4.5 and the PJF cells assumed irregular circular configuration with the intact cell walls running in both directions.

![Figure 4.5](image)

**Figure 4.5**  Ultramicroscopic structure of the PJF as viewed under a scanning electron microscope (R-rays)

4.1.6  Chemical Analysis of the PJFs

The principle chemical constituents of the natural fibers cell walls are embedded with semicrystalline polysaccharides of cellulose, branched amorphous polymer of hemicellulose and high complex aromatic structure of lignin. The cellulose content of the PJFs was 61.65% which is believed to act as fasten which can withstand hydrostatic pressure gradients of the fibers. The PJF had hemicellulose content of 16.41% whose degradation usually leads to
disintegration of fibers into cellulose microfibrils resulting in lower strength because of the linking effect (Morvan et al 1990).

The wax content of the PJF was 0.61% as opposed to 2.3% and 0.3% in the cases of the hemp and okra bark fibers, respectively which may generate poor interfacial bond between fibers and polymer matrices. Higher lignin content (17.11%) of the PJF can potentially contribute to the excellent rigidity when compared to other bark fibers. The chemical composition of other bark fibers was obtained from the published literatures (Alam & Arifuzzaman Khan 2007, Arifuzzaman Khan et al 2009, Jayaramudu et al 2010, Mwaikambo & Ansell 2002, Reddy & Yang 2009, Sathishkumar et al 2012, Yan & Pickering 2008) and used for the purpose of comparison as shown in Table 4.1.

**Table 4.1 Comparison of chemical compositions of the PJF with bark fibers of other plants**

<table>
<thead>
<tr>
<th>Name of Fiber</th>
<th>Cellulose (wt.%)</th>
<th>Hemicelluloses (wt.%)</th>
<th>Lignin (wt.%)</th>
<th>Wax (wt.%)</th>
<th>Moisture content (wt.%)</th>
<th>Density (kg/m³)</th>
<th>Ash (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PJF</td>
<td>61.65</td>
<td>16.14</td>
<td>17.11</td>
<td>0.61</td>
<td>9.48</td>
<td>580</td>
<td>5.2</td>
</tr>
<tr>
<td>Jute</td>
<td>72</td>
<td>13</td>
<td>13</td>
<td>-</td>
<td>12.6</td>
<td>1460</td>
<td>-</td>
</tr>
<tr>
<td>Flax</td>
<td>81</td>
<td>14</td>
<td>3</td>
<td>-</td>
<td>10</td>
<td>1500</td>
<td>-</td>
</tr>
<tr>
<td>Ramie</td>
<td>76</td>
<td>15</td>
<td>1</td>
<td>-</td>
<td>8.0</td>
<td>1500</td>
<td>-</td>
</tr>
<tr>
<td>Hemp</td>
<td>74</td>
<td>18</td>
<td>4</td>
<td>2.3</td>
<td>10.8</td>
<td>1480</td>
<td>-</td>
</tr>
<tr>
<td>Kenaf</td>
<td>53.14</td>
<td>14.33</td>
<td>8.18</td>
<td>-</td>
<td>-</td>
<td>1400</td>
<td>-</td>
</tr>
<tr>
<td>Hop stem</td>
<td>84 ± 1.6</td>
<td>-</td>
<td>6.0 ± 0.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.0 ± 0.1</td>
</tr>
<tr>
<td>Okra</td>
<td>60-70</td>
<td>13.1-16.7</td>
<td>0.6-0.7</td>
<td>0.3</td>
<td>7.5-17</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
4.1.7 FTIR Analysis

FTIR spectra with classical peaks of the PJF are presented in Figure 4.6. It is noteworthy that the peaks of whole PJF appeared at 3437 and 896 cm\(^{-1}\) while the peak of the whole kenaf fiber (core and bast) projected at 3390 and 1190 cm\(^{-1}\) corresponding to O–H stretching and O–H bending frequencies (Khalil et al 2010). In the PJF, the O–H stretching peak was seen at 3437 cm\(^{-1}\) and C–H stretching peak existed at 2922 cm\(^{-1}\). For the PJF, a peak that appeared in 3342 cm\(^{-1}\) was due to cellulose; O–H stretching of \(\alpha\)-cellulose was represented by the band of 3432 cm\(^{-1}\) for Grewia tilifolia (Jayaramudu et al 2010).

The 1057 cm\(^{-1}\) peak indicate the C–O–C (ester) group in the PJF. Carbonyl stretching C–O for acetyl groups in hemicellulose and aldehydic group of lignin are represented by the peaks at 1734 cm\(^{-1}\) to 1616 cm\(^{-1}\). The carbonyl region was predicted at 1710 cm\(^{-1}\) in the case of hemp fiber (Pracella et al 2006). Two bands at 1643 and 1742 cm\(^{-1}\), respectively were assigned to the free and esterified carboxyl groups in mulberry bark (Liu et al 2010) whereas a small peak at 1517 cm\(^{-1}\) indicated C=C stretching of aromatic ring of the lignin in okra fiber (De Rosa et al 2011).

![Figure 4.6 FTIR spectrum of the PJF in the frequency of 400–4000 cm\(^{-1}\).](image-url)
4.2 CHARACTERIZATION STUDY OF OPTIMALY ALKALI TREATED PJFs

4.2.1 The Optimally Alkali Treated PJFs (optimally APJF)

Alkali treatment of the PJFs performed with 5% (w/v) NaOH for 60 min soaking time caused favourable changes in chemical properties especially relatively higher (wt.%) cellulose content and lower amorphous contents as shown in Table 3.1.

4.2.2 XRD Analysis

X-ray diffractograms of the optimally APJF and raw PJFs are shown in Figure 4.7. The diffractograms show peaks exhibited at 20=15.07°, 16.9° and 22.67° that are characteristic diffraction pattern of cellulose-I. It also showed higher crystallographic plane. The CI of raw and optimally APJFs was 46% and 73%, respectively.

Figure 4.7 Diffractograms of raw and optimally APJFs
The alkali treatment has enhanced CI value by 58.6 %, possibly due to diminishing amorphous content of the fiber and the rearrangement of the crystalline regions. The CS of optimally APJFs was 16.03 nm which reduces the moisture absorption capacity and chemical reactivity of the fiber.

4.2.3 Tensile Properties of the Optimally APJFs

Cellulose is principally responsible for mechanical strength of natural fiber because of its specific properties such as high degree of polymerization and linear orientation (Thakur & Singha 2010). The tensile strength of raw PJF was found to be 558 ± 13.4 MPa. Influence of alkali treatment on O-H bonds formation in ubiquitous cellulose chains structure improved the tensile strength of optimally APJFs up to 638 ± 9.12 MPa.

Removal of non-cellulosic substances from cellulose-hemicellulose lignin network is known to enhance the tensile strength of natural lignocellulosic fibers (Pejic et al 2008). It is worth mentioning that treatment of the date palm fiber imparted the maximum tensile strength (Alawar et al. 2009). Similarly, 61% increase in tensile strength was seen with kenaf fibers that were treated using NaOH (0.35% w/v) for 16 hours. This change in tensile properties is attributed to interacting factors such as the rupture of alkali sensitive bonds existing between the cellulose and hemicellulose and the stress transfer between interfibrillar regions (Mukherjee et al 1993).

The increase in tensile strength was assumed to result from increased intermolecular interaction and increased crystallinity in cellulose which was supported by X-ray diffraction (Williams et al 2011). However, diameter of the optimally treated PJFs was reduced to 23.58%. It is worth mentioning that alkali treatment of the PJFs make cell wall to swell inward thereby reduces the fiber diameter and improves crystalline packing which eventually increases the tensile strength (Syahrizul 2012).
Nevertheless elongation of the optimally APJFs marginally increased from 1.77 ± 0.04 % (raw) to 2.89 ± 0.01 %. Removal of hemicellulose makes interfibrillar region of the fiber to become less denser and less rigid, to get rearranged along tensile deformation, thus a better load sharing result between the fibers and higher stress develop when the fibers are stretched.

Further, there was a reduction in Young’s modulus (30%) of the optimally APJFs because of the reduction in stiffness of the fiber due to partial elimination of hemicellulose, wax, gum and cementing materials that ensure cohesion between cellulose microfibrils (Bledzki & Gassan 1999) and decreases the resistance of cellulose microfibrils to stretching (Rong et al 2001).

The similar observation has been made in the case of single curaua fiber after alkali treatment (Gomes et al 2004) and nearly 10.4% of tensile modulus was reduced compared to untreated century fiber (Obi Reddy et al 2013 b). The density of the optimally APJFs increased to 0.648 g/cm³ which is obviously less than the synthetic fiber. It is tempting to conclude that the optimally APJFs could be used as reinforcements in making light weight composite structures.

4.2.4 Thermal Analysis

Thermogravimetry is one of the most widely used techniques to monitor the composition and structural dependence on the thermal degradation of natural cellulose fiber (Hagedorn et al 2003). Thermal degradation profiles of the optimally APJFs and raw PJFs were determined from the TG & DTG thermogram as represented in Figure 4.8. As expected the two stages of degradation are evident in both the profiles which corresponded to temperature regions for different constituents like moisture
evaporation (upto 100°C) and degradation of hemicellulose (220-300°C), cellulose (300-375°C) and lignin (300-500°C).

![TG and DTG thermograms of raw and optimally APJFs](image)

**Figure 4.8 TG and DTG thermograms of raw and optimally APJFs**

The depolymerization of hemicellulose usually occurs between 180 and 350°C, the random cleavage of the glycosidic linkage of cellulose between 275 and 350°C and the degradation of lignin between 250 and 500°C (Kim et al 2006). The initial peak at 66.2°C in raw and 60.7°C for the optimally APJF data obviously represent the loss of moisture and other volatiles at the first degradation which is observed between room temperature and 100°C. Nearly 5.5°C reduction in temperature observed with the optimally APJFs suggests decrement in hydrophilicity.

Further, the next peak which was seen around 300°C (13.72% of weight loss) denotes degradation of hemicellulose. Nevertheless, degradation of cellulose happens at around 351.3°C (40.85% of weight loss) and a prominent peak appears at the temperature corresponding to the maximum
degradation rate. Moreover, optimal alkali treatment increases the cellulose degradation temperature (332°C to 351.3°C) which is due to retention and improvement of the structural order and reduction in the amorphous content. A greater crystalline structure essentially requires a higher degradation temperature (Yang & Kokot 1996). The residual char at almost 999°C was slightly higher for the optimally APJFs than for the raw PJF.

### 4.2.5 Surface morphology analysis

Surface morphology of the raw and optimally APJFs was studied by SEM to understand the changes caused due to alkali treatment which can considerably remove impurities. The electrographs of raw and optimally APJF were represented in the Figure 4.9 (a) & (b). Roughness of the surface of the optimally APJFs which improved due to presence of the multi cellular wall structure is expected to promote good interfacial bonding between the fibers and matrix if composites are made with these fibers as reinforcement (Mwaikambo and Ansell 2002).

![Surface morphology analysis](image)

(a) Figure 4.9 (Continued)
Figure 4.9  SEM morphology of (a) Raw PJFs (b) Improved surface of optimally APJFs

4.2.6  Chemical analysis of the optimally APJFs

The fibers derived from plants primarily have prearranged entity of cellulose made up of linear polymer consisting of D-anhydroglucose (C₆H₁₁O₅) units joined together by β-1, 4-glycosidic linkages. The effect of optimal alkali treatment conditions influenced the degree of swelling and hence the degree of lattice transformation of the native cellulose from 61.65 (wt.%) (raw) to 72.27 (wt.%). Virtually 17.23% (wt.%) of improvement in cellulose content was seen in the optimally treated PJFs.

The hemicellulose content of the optimally APJFs reduced from 16.14 to 4.02 (wt.%) with an increase in treatment time since hemicellulose has a lower molecular weight than cellulose and is much more sensitive to the action of NaOH at room temperature. The alkali treatment also caused a
change in lignin content from 17.11 to 12.09 (wt.%). Interestingly, the low wax content (0.10 wt.%) and moisture content (6.36 wt.%) of the optimally APJFs can enable its use as reinforcement in polymer matrices by offering higher interfacial bonding. An increase in ash content (from 5.2 wt.% to 13.22 wt.%) typically shows the elimination of amorphous elements from the optimally APJFs.

4.2.7 Elemental Analysis

The elemental analyzer is an intensification apparatus to identify the weight loss in a natural fiber through the estimation of carbon content. The carbon content in the raw PJF was 15.47 % ± 0.62 % and that of the optimally APJF was 20.14 % ± 0.38%. The elemental analysis of raw and optimally APJFs suggested that the weight loss cloud be due to leaching of hemicellulose and lignin.

4.2.8 FTIR Analysis

The FTIR spectra showing the structural changes that happen during the alkali treatment are illustrated in Figure 4.10. A broad absorption peak in 3437 cm⁻¹ corresponds to the characteristic O-H stretching vibration and hydrogen bond of the hydroxyl groups. One of the most visible differences between the spectra is the modification of the signal at 1734 cm⁻¹, characteristic of the stretching of unconjugated C-O groups present in hemicellulose (Uma Maheswari et al 2013). The subsistence of the wax or wax like gist is observed in unsymmetrical vibrations at 2355 cm⁻¹ and 2928 cm⁻¹ is assigned to the less ordered band of the alkyl chain (Guo et al 2006).
The bands observed at 1537 cm$^{-1}$ to 1375 cm$^{-1}$ pronounced to the aromatic skeletal vibrations, ring breathing with C-O stretching in lignin. A strong peak at 1057 cm$^{-1}$ is ascribed to the C-O and O-H stretching vibration pertaining to polysaccharide in cellulose. A peak observed at 896 cm$^{-1}$ corresponds to the presence of $\beta$-glycosidic linkages between monosaccharides. Noticeable observation in optimally APJFs bands at 2355 cm$^{-1}$, 1734 cm$^{-1}$, 1537 cm$^{-1}$ and 1375 cm$^{-1}$ typically indicate the diminished content of wax, hemicellulose and lignin due to influence of the alkali treatment.

4.3 CHARACTERIZATION STUDY OF VARIOUS CHEMICALLY MODIFIED PJFs

4.3.1 Crystal Structure of the Modified PJFs

X-ray diffractograms as illustrated in Figure 4.11 are meant for investigation of the crystallinity of the modified PJFs. The noticeable major
crystalline peak for various treated PJFs occurred in 2θ = 22.67° and well defined peaks present at 2θ = 15.07°, 2θ = 16.9° corresponded to the typical diffraction of cellulose-I. The minimum intensity peaks were observed at 2θ = 18.12°. However the fiber contains a higher percentage of amorphous fractions (lignin, pectins, hemicellulose, and amorphous cellulose).

The CI of the raw and various treated PJFs as evaluated by Eq.(1) is shown in the following order: SPJF (88.70%)>BPJF (87.43%)>PPJF (74.67%)>optimally APJF (73%)>Raw PJF (46%). This order suggests improved CI mainly due to two reasons. Firstly, the treatments may have caused removal of some of the hemicellulose and non-crystalline region of the fiber thereby increasing the presence of relative crystalline cellulose. Secondly, there may be a rearrangement of the crystalline regions in such a way that the fiber acquires a more crystalline nature (Pan et al 2009).

![X-ray diffractograms of the raw and chemically modified PJFs](image_url)
4.3.2 Thermal Stability of Modified PJFs

Thermogravimetric performance of various modified PJFs is as in TG and DTG curves depicted in Figure 4.12 (a) & (b). Typically two main stages of degradation were observed in all the chemically modified and raw PJFs. The initial degradation noticed between 32° to 100°C could be due to evaporation of moisture from the fiber and second major degradation proceeded from about 220° to 400°C.

The temperature region of 220°–300°C associated to thermal depolymerization of hemicellulose with different weight loss of SPJF (9.45%), BPJF (11.32%), PPJF (10.94%), optimally APJF (13.72%) and raw PJF (16.54%). The strong promising peaks at 351.4°, 357.2°, 363°, 365.3° and 332.2°C assigned the depolymerization of cellulose with corresponding weight loss of SPJF (47.31%), BPJF (45.22%), PPJF (42.32%), optimally APJF (40.85%) and raw PJF (38.58%), respectively. The crystalline structure contained strong intramolecular and intermolecular hydrogen bonding which required higher energies to break down (Placet 2009).

Moreover, all chemical modifications were stipulated imperative progress in thermal stability of PJFs as in the order: SPJF (10%)>BPJF (9.27%)>PPJF (7.52%)>optimally APJF (5.77%) compared to raw PJFs, which could be due to retention and improvement of the structural order and reduction in the amorphous content. In general, the lignin degradation takes place over a broader temperature range of 200° to 500°C.

The weak bonds break at the temperature range from 200° to 300°C whereas at higher temperature the cleavage of strong bonds in aromatic rings occurs (Dorez et al 2013). However, the residue at 500°C was marginally higher in the case of chemically modified PJFs than the raw PJFs. Taken together, these findings clearly show that the chemically modified PJFs can
preferably be used as reinforcement in polymer matrices whose processing temperature is below 250°C.

Figure 4.12  (a) TG curves of various modified PJFs (b) DTG curves of various modified PJFs
4.3.3 Morphological analysis of the modified PJFs

SEM study was employed to monitor the changes in surface morphologies and its micrographs of modified PJFs were presented in Figure 4.13 (a) to (c), respectively. Raw PJFs contain impurities, wax, fatty substance and globular protrusions called “tyloses” (Bismarck et al 2000). On the other hand, during optimally alkali treatment, sodium interacted with the fiber surface and resulted in dramatically increases the surface roughness and removal of wax substance, impurities as clearly depicted in Figure 4.9 (b).

(a)

(b) Figure 4.13 (Continued)
Figure 4.13 Surface micrographs of (a) BPJF (b) PPJF (c) SAJF

However the peroxide, permanganate and stearic acid treated surface of the PJFs showed highly improved surface roughness through maximum elimination of globular fatty deposit from the fiber surface. As a consequence, the adhesion between fibers and matrix got improved.

4.3.4 Chemical Composition of the Modified PJFs

The principal chemical constituents of the natural fiber cell walls are embedded with semicrystalline polysaccharides of cellulose, branched amorphous polymer of hemicellulose and high complex aromatic structure of lignin. The chemical composition of modified and raw PJFs is listed in Table 4.2. The raw and various chemically modified PJFs were found to contain different levels of cellulose: SPJF>BPJF>PPJF>optimally APJF>raw.

The improved cellulose content and diminished amorphous (hemicellulose & lignin) content and higher moisture resistance properties in all the modified PJFs resulted in a tendency for highly packed crystalline order. Relatively higher density of the modified PJFs in comparison to the
raw fibers could be due to (i) densification of walls of fiber as a result of the removal of impurities (less dense fats and waxes) by solvents and (ii) filling of the pores with grafted molecules (Varma et al 1989). The various chemical treatments and their reactions are as shown in Scheme 13 (a) to (d). The Properties of raw and chemically modified PJFs were listed in Table 4.3 for comparative study.

**Scheme 13a (Alkali treatment)**

**Scheme 13b (Potassium permanganate treatment)**

**Scheme 13c (Benzoyl peroxide treatment)**
Scheme 13d (Stearic acid treatment)

Table 4.2 Chemical composition of the raw and chemically modified PJFs.

<table>
<thead>
<tr>
<th>Name of the treatment</th>
<th>Cellulose (%wt)</th>
<th>Hemicellulose (%wt)</th>
<th>Lignin (%wt)</th>
<th>Wax (%wt)</th>
<th>Moisture content (%)</th>
<th>Density (g/cm³)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw</td>
<td>61.65</td>
<td>16.14</td>
<td>17.11</td>
<td>0.61</td>
<td>9.48</td>
<td>0.580</td>
<td>Saravanaku mar et al 2013</td>
</tr>
<tr>
<td>Optimally APJF</td>
<td>72.27</td>
<td>4.02</td>
<td>12.09</td>
<td>0.10</td>
<td>6.36</td>
<td>0.648</td>
<td>Saravanaku mar et al 2014 a</td>
</tr>
<tr>
<td>BPJF</td>
<td>82.09</td>
<td>2.6</td>
<td>9.12</td>
<td>0.07</td>
<td>4.67</td>
<td>0.921</td>
<td>Saravanaku mar et al 2014b</td>
</tr>
<tr>
<td>PPJF</td>
<td>78.84</td>
<td>3.32</td>
<td>11.67</td>
<td>0.09</td>
<td>5.88</td>
<td>0.744</td>
<td>Saravanaku mar et al 2014b</td>
</tr>
<tr>
<td>SPJF</td>
<td>82.16</td>
<td>2.3</td>
<td>9.06</td>
<td>0.06</td>
<td>4.61</td>
<td>0.933</td>
<td>Saravanaku mar et al 2014b</td>
</tr>
</tbody>
</table>
Table 4.3 Properties of raw and chemically modified PJFs for comparative study.

<table>
<thead>
<tr>
<th>Name of the treatment</th>
<th>Tensile strength MPa</th>
<th>Young’s modulus GPa</th>
<th>Elongation (%)</th>
<th>CI (%)</th>
<th>CS (nm)</th>
<th>Cellulose degradation Temperature (°C)</th>
<th>Thermal stability (%)</th>
<th>SEM observation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw PJF</td>
<td>558 ± 13.8</td>
<td>31.52 ± 1.18</td>
<td>1.77 ± 0.04</td>
<td>46</td>
<td>15</td>
<td>331.1</td>
<td>-</td>
<td>Assume irregular circular configuration</td>
</tr>
<tr>
<td>Optimally APIF</td>
<td>638 ± 9.12</td>
<td>9.45 ± 0.35</td>
<td>2.89 ± 0.01</td>
<td>73</td>
<td>16.03</td>
<td>351.3</td>
<td>5.77</td>
<td>Multicellular wall structure</td>
</tr>
<tr>
<td>BPJF</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>87.43</td>
<td>16.1</td>
<td>363</td>
<td>9.27</td>
<td>Tyloses removed</td>
</tr>
<tr>
<td>PPJF</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>74.67</td>
<td>16.05</td>
<td>357.2</td>
<td>7.52</td>
<td>Tyloses removed</td>
</tr>
<tr>
<td>SPIF</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>88.70</td>
<td>16.12</td>
<td>365.3</td>
<td>10</td>
<td>Tyloses removed</td>
</tr>
</tbody>
</table>

4.3.5 FTIR study of the modified PJFs

The typical functional groups of the raw and modified PJFs in the form of infrared spectrum are as shown in Figure 4.14. The hydrophilicity of raw and modified PJFs is evidenced by broad absorption band in the 3700-3100 cm\(^{-1}\) region which is associated with the \(-\text{OH}\) stretching of \(\alpha\)-cellulose. The intensity peak at 2850 cm\(^{-1}\) attributed to C–H (aldehyde) and highly notified peak at 2355 cm\(^{-1}\) is seen only in raw PJF and disappeared in the spectra of all the modified PJFs that are exemplified by C=O stretching (wax). A peak signal at 1734 cm\(^{-1}\) in the raw fiber is due to their acetal and uronic ester groups of the hemicellulose (Uma Maheswari et al 2013).

The noticeable peak at 1734 cm\(^{-1}\) which is the most evident in diminished region of hemicellulose in each spectrum could be due to the chemical modifications. Two gradually decreasing peaks in all the modified PJFs observed at 1635 cm\(^{-1}\) and 1508 cm\(^{-1}\) corresponds to C=C stretching of lignin and C=C aromatic symmetrical stretching, respectively. An absorption peak at 1429 cm\(^{-1}\) was assigned to CH in plane deformation with aromatic ring stretching. However, the band region at 1381 cm\(^{-1}\) to 1373 cm\(^{-1}\) cm suggested CH bending of lignin and the peak 1313 cm\(^{-1}\) represented the CH\(_2\) wagging.
A well decreasing peak noticed in the modified PJFs spectrum at 1255 cm⁻¹ indicates the CH bending of hemicellulose. This perfect peak visualized only for the modified PJFs shows leaching of hemicellulose. The two peaks at 1157 cm⁻¹ and 1109 cm⁻¹ appeared can be ascribed to asymmetric C–O–C stretching of lignin and the strong vibration peak at 1051 cm⁻¹ is attributed to symmetric CO stretching of lignin. The spectrum peak at 896 cm⁻¹ represented ß-glycosidic linkages between the monosaccharides. As the peaks in each spectrum at 2355 cm⁻¹, 1734 cm⁻¹ and 1508 cm⁻¹ strongly confirmed that the reduction of wax, hemicellulose and lignin contents was caused due to the chemical modifications of the PJFs.

![Image of the FITR spectrum of the raw and chemically modified PJFs](image)

**Figure 4.14 FITR spectrum of the raw and chemically modified PJFs**

### 4.4 THE DERIVED PARAMETERS OF THE PJFs SUITABLE FOR PAPER PRODUCTION

#### 4.4.1 Anatomical Description

The fibers are macerated to measure the length from the micrographs are shown in figure 4.15 (a) to (c). The average lengths of the PJFs were 1.62 ± 0.01 mm. These fibers are uniformly thick with gradually tapering ends. In paper making, the PJFs can act as the cell elements that impart mechanical strength to the paper sheet.
Figure 4.15 (a), (b), and (c) Macerated fibers showing average length

4.4.2 Assessment of Fiber Derived Parameters

The raw PJFs were assessed for their suitability for paper production. Fibers are the cells that are very important for paper production, and therefore, the properties of the fibers are very important; by maceration technique, the separated fibers were measured. Also the fiber dimensions were (Cell Lumen, Primary Wall & Secondary wall) measured from transverse section of bark of PJ as shown in Figure 4.16. Further with the aid of PJFs essential dimensions the derived parameters are obtained and compared to other raw fibers which are indicated in Tables 4.3 & 4.4.
Figure 4.16 Transverse section of bark of PJ

The average fiber length of PJFs was 1.62 ± 0.01mm which is higher than corn stalk, cotton stalk, kenaf and shorter than softwood fibers (2.7-4.6 mm). The length of the PJFs was longer than that of *Eucalyptus grandis* (1.06 mm), which is traditionally used in pulp and paper production. The PJFs lumen diameter was found to be about 8 ± 0.2 μm, which was close to the normal range when compared with hardwood fibers whose diameter is approximately 20–40 μm (Atchison 1987).

On the other hand wall thickness of the PJFs was higher than other fibrous species. The physical properties of a pulp sheet are closely related to the morphological properties of the pulp fiber (Young 1981). The PJFs have a very good slenderness ratio (81.50). This results in comparatively more satisfactory pulp tear and bursting strength for printing and writing process
(Cappelletto et al 2000 and Law et al 2001). The strength properties of the papers are positively correlated with the slenderness ratio (Ates et al 2008).

Table 4.4 PJFs dimensions compared with other nonwood fibers

<table>
<thead>
<tr>
<th>Fiber dimension</th>
<th>Length (mm)</th>
<th>Diameter (μm)</th>
<th>Lumen diameter (μm)</th>
<th>Cell wall thickness (μm)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PJFs</td>
<td>1.62 ± 0.01</td>
<td>20 ± 0.04</td>
<td>8 ± 0.2</td>
<td>7 ± 1.01</td>
<td>-</td>
</tr>
<tr>
<td>Wheat straw</td>
<td>0.74</td>
<td>13.2</td>
<td>4.0</td>
<td>4.6</td>
<td>Deniz et al 2004</td>
</tr>
<tr>
<td>Corn stalk</td>
<td>1.32</td>
<td>24.3</td>
<td>10.7</td>
<td>6.8</td>
<td>Usta et al 1990</td>
</tr>
<tr>
<td>Tobacco straw</td>
<td>1.07</td>
<td>26.8</td>
<td>16.3</td>
<td>5.3</td>
<td>Eroglu et al 1992</td>
</tr>
<tr>
<td>Cotton stalk</td>
<td>1.32</td>
<td>29.3</td>
<td>23</td>
<td>3.6</td>
<td>Eroglu et al 1992</td>
</tr>
<tr>
<td>Rye straw</td>
<td>1.15</td>
<td>14.7</td>
<td>4.2</td>
<td>1.1</td>
<td>Usta &amp; Eroglu 1987</td>
</tr>
<tr>
<td>Kenaf</td>
<td>1.29</td>
<td>22.1</td>
<td>12.7</td>
<td>4.3</td>
<td>Ververis et al 2004</td>
</tr>
<tr>
<td><em>Eucalyptus grandis</em></td>
<td>1.06</td>
<td>19.21</td>
<td>12.20</td>
<td>3.20</td>
<td>Dutt &amp; Tyagi 2011</td>
</tr>
<tr>
<td>Coniferous</td>
<td>2.7 – 4.6</td>
<td>32-43</td>
<td>-</td>
<td>-</td>
<td>Atchison 1993</td>
</tr>
<tr>
<td>Deciduous</td>
<td>0.7 – 1.6</td>
<td>20 – 40</td>
<td>-</td>
<td>-</td>
<td>Atchison 1993</td>
</tr>
<tr>
<td><em>Arundo donax</em></td>
<td>1.22 ± 0.07</td>
<td>17.3 ± 2.4</td>
<td>8.5 ± 2.4</td>
<td>4.4 ± 0.8</td>
<td>Ververis et al 2004</td>
</tr>
<tr>
<td>Bamboo</td>
<td>2.30</td>
<td>15.1</td>
<td>6.9</td>
<td>4.17</td>
<td>Deniz &amp; Ates 2002</td>
</tr>
<tr>
<td>Reed</td>
<td>1.39</td>
<td>13.5</td>
<td>7</td>
<td>3.2</td>
<td>Kirci et al. 1998</td>
</tr>
<tr>
<td>Sunflower stalk</td>
<td>128</td>
<td>22.1</td>
<td>15.6</td>
<td>3.3</td>
<td>Eroglu et al 1992</td>
</tr>
<tr>
<td><em>Panicum virgatum</em></td>
<td>1.15 ± 0.10</td>
<td>13.1 ± 2.8</td>
<td>5.8 ± 3.9</td>
<td>4.6 ± 0.9</td>
<td>Ververis et al 2004</td>
</tr>
</tbody>
</table>
Table 4.5 PJFs derived values compared with other nonwood fibers

<table>
<thead>
<tr>
<th>Name of the fiber</th>
<th>Slenderness ratio</th>
<th>Flexibility coefficient</th>
<th>Rigidity coefficient</th>
<th>Runkel ratio</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PJFs</td>
<td>81.50</td>
<td>40.01</td>
<td>39.97</td>
<td>0.80</td>
<td>-</td>
</tr>
<tr>
<td><em>Arundo donax</em></td>
<td>70.5</td>
<td>49.2</td>
<td>23.90</td>
<td>0.91</td>
<td>Ververis et al 2004</td>
</tr>
<tr>
<td><em>Panicum virgatum</em></td>
<td>87.7</td>
<td>44.2</td>
<td>35.12</td>
<td>1.5</td>
<td>Ververis et al 2004</td>
</tr>
<tr>
<td>Wheat straw</td>
<td>53.13</td>
<td>33.04</td>
<td>34.02</td>
<td>2.23</td>
<td>Tutus et al 2010</td>
</tr>
<tr>
<td>Corn stalk</td>
<td>54.32</td>
<td>44.03</td>
<td>27.98</td>
<td>1.27</td>
<td>Tutus et al 2010</td>
</tr>
<tr>
<td>Tobacco straw</td>
<td>39.92</td>
<td>28.60</td>
<td>36.10</td>
<td>2.57</td>
<td>Tutus et al 2010</td>
</tr>
<tr>
<td>Cotton stalk</td>
<td>32.60</td>
<td>63.30</td>
<td>18.10</td>
<td>0.57</td>
<td>Tutus et al 2010</td>
</tr>
<tr>
<td>Rye straw</td>
<td>37.90</td>
<td>60.80</td>
<td>19.80</td>
<td>0.65</td>
<td>Tutus et al 2010</td>
</tr>
<tr>
<td>Kenaf</td>
<td>58.3</td>
<td>57.5</td>
<td>19.45</td>
<td>0.67</td>
<td>Ververis et al 2004</td>
</tr>
<tr>
<td><em>Eucalyptus grandis</em></td>
<td>55.18</td>
<td>63.5</td>
<td>16.65</td>
<td>0.52</td>
<td>Tutus et al 2010</td>
</tr>
</tbody>
</table>
If the slenderness ratio of a fibrous material is lower than 70, it is considered invaluable for quality pulp and paper production (Bektas et al 1999 and Young 1981). The slenderness ratio of the PJFs was found to be 81.50, and so it can be considered highly valuable for quality pulp and paper production. Depending on cell wall thickness, rigidity coefficient (Eroglu 1998), and elasticity coefficient (Istas et al 1954) are also considered to be very important parameters for evaluating the strength properties and fiber quality. The calculated rigidity coefficient of the PJFs was 39.97. Especially higher rigidity ratio gives lower paper strength properties especially lower burst, tear and tensile indices (Bektas et al 1999). The flexibility coefficient of the PJFs was 40.01.

The fibers with a flexibility coefficient between 50 and 70, can easily be flat and give good paper with high strength properties (Istas et al 1954). Generally, the suitability of a fiber for pulp and paper production is largely determined by its runkel ratio. The lower runkel ratio of PJFs (0.80) is considered better for papermaking (Lessard & Chouinard 1980). However the ratio between fiber length and cell wall thickness (F-factor) provides a measure of fibers flexibility and influences paper strength properties such as bursting and tensile strength (Tutus et al 2010). A high length to cell wall thickness ratio gives high tensile strength and modulus of elasticity of paper.

F-factor values for the PJF are in the range of 235.06 ± 32.85. On the other hand F-factor of unbeaten softwood fibers was 1170 for Western White pine (Pinus monticola) and 1030 for Grand fir (Abies grandis). Nevertheless the F-factor of unbeaten hardwood fibers was 207 for American beech (Fagus grandifolia) and 403 for Paper Birch (Betula papyrifera) (Horn 1974).

Compared to wood fibers, F-factor of the PJFs was quite close to the hardwood fibers and relatively lower than softwood fibers. Finally the
derived values of the PJFs especially the slenderness ratio with a low runkel ratio can play a vital role in paper production and possibly offer increased mechanical strength, thus making it suitable for writing, printing, wrapping, and packaging purposes.

4.5 SUMMARY

The PJFs belonged to gelatinous or mucilaginous type that consisted of an outer primary wall which was highly lignified while the secondary wall had mucilaginous substance. The chemical composition, microfibril angle and mechanical properties of the PJFs were identified and are found to be quite close to the existing natural fibers. The alkali treatment of PJFs was optimized with 5 % (w/v) NaOH and 30 min. The optimally alkali treated PJFs posses relatively higher cellulose content and lower amorphous contents which altogether improved the physicochemical properties. And the various chemically modified PJFs showed the relatively higher level of chemical compositions and thermal stability. The assessment of PJFs derived parameters reveled especially the slenderness ratio with a low runkel ratio can play a vital role in paper production. Finally, all the potential properties of the PJFs are reported in chapter 5.