Chapter 12

BANANA MICROFIBRIL COMPOSITES

Abstract

This chapter deals with the preparation of banana microfibril commingled composites. Banana microfibrils (BMF) have been prepared from banana fiber by steam explosion process. The polarity of the microfibrils has been investigated by solvatochromic and electrokinetic studies. It was observed that microfibril has higher hydrogen bond donating (HBD) than banana fiber. Chemical treatment of the microfibril lowered the HBD value. The results of the empirical polarity parameters determined were found to be consistent with the results of electrokinetic measurements. The effect of microfibril loading on the tensile properties of the composites was analyzed. It was found that tensile properties increase with microfibril loading up to 20%, and then decreased. Microfibrils have been further subjected to oxalic acid hydrolysis. Transmission electron microscope (TEM) analysis of the microfibrils after oxalic acid hydrolysis revealed that the size of the microfibrils has been in the nano range.

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12.1 Introduction
The raw lignocellulosic materials are made mainly of a complex network of three polymers namely cellulose, hemicellulose and lignin. Chemical, thermal or mechanical pretreatments could help the separation of these components. Cellulose is a poly dispersed linear polymer of poly-β (1,4)-D-glucose with a syndiotactic configuration. Cellulose chains aggregate to form microfibrils, long thread like bundles of molecules stabilized laterally by hydrogen bonds between hydroxyl groups and oxygens of adjacent molecules. Steam explosion has been extensively studied and it is used as a pretreatment to separate the main components of the lignocellulosic fiber. It refers to the process of exposing lignocelluloses to high pressure steam. Under severe pressure and temperature conditions of steam explosion, the resulting steam ionization formation causes the accelerated degradation of hemicellulose and lignin, while only a partial degradation of cellulose occurs [1]. Hemicellulose and cellulose degrade through the hydrolysis of glucoside bonds, while lignin degrades through free radical reactions. Hemicelluloses and lignin can be removed from the pretreated solid residue by successive extractions, first with water and then with alkaline aqueous media [1].

Dufresne and coworkers [2-8] have carried out extensive work on separation and characterization of cellulose microfibrils and analyzed the properties of these micro-composites. Stable aqueous suspensions of cellulose microfibrils can be prepared by the acid hydrolysis of biomasses. Depending on the source, the microfibrils offer a wide variety of aspect ratios. The aqueous suspensions of cellulose display a colloidal behaviour. They can be used to process micro composite materials using a polymer as the matrix. Natural fibers which are rich in cellulose can be used as the starting material for the preparation of cellulose microfibrils. Rodriguez et al. [9] prepared
sisal cellulose whiskers reinforced polyvinyl acetate nanocomposites. Statistical analysis of the sisal whisker length and diameter resulted in average values of 250nm and 4nm, respectively. Bondeson et al. [10] isolated nanocrystals from microcrystalline cellulose by acid hydrolysis. With a sulfuric acid concentration of 63.5% (w/w), it was possible to obtain cellulose nanocrystals/whiskers with length between 200 and 400 nm and width less than 10 nm in approximately 2 h with a yield of 30% (of initial weight). Bhatnagar et al. [11] prepared cellulose nanofibers from various sources such as flax bast fibers, hemp fibers, kraft pulp, and rutabaga, by chemical treatments followed by innovative mechanical techniques. The nanofibers thus obtained have diameters between 5 and 60 nm. There are also reports on microfibrils prepared from other natural materials [12-14].

In this study, the preparation of BMF from BF by steam explosion method is described. BMF were characterized by solvatochromic and electrokinetic studies. This is a new venture in literature as no studies has been reported in literature where banana microfibrils were characterized by solvatochromic and electrokinetic studies. Effect of microfibril loading on the tensile properties of the composites was studied. The microfibrils were further subjected to oxalic acid hydrolysis. TEM was used to observe the changes in the morphology after oxalic acid hydrolysis.

12. 2 Results and Discussion
12.2.1 Preparation of banana microfibrils
Steam explosion process, which combines mechanical and chemical actions, causes lignocellulosics to undergo physical and chemical changes which include defibrillation of lignocellulosics into individual fibers and partial depolymerization of hemicellulose and lignin. Hemicellulose and cellulose degrade through the hydrolysis of glucoside bonds while lignin degrades through radical reactions involving its units. Hemicellulose and lignin can
be removed from the pretreated solid residue by successive extractions, first with water and then with bleaching solution.

During steam explosion with 2% NaOH, the steam penetrates into the BF bundles. It removes the natural and artificial impurities, waxes and pectins, causes the dissolution and leaching of fatty acids and removes most of the lignin component of the fiber. Steam explosion processes results in the hydrolysis of hemicellulose within the fiber, the interfibrillar region is likely to be less dense and less rigid. The hydrolysed sugars can be filtered off by washing. After washing, a residue of cellulose and lignin will be left. The solubility of non-cellulosic components depends on the molecular weight of the substances. Here the aim of the pretreatment of the fibers is to decrease the intermolecular binding possibilities, which in turn leads to the increase of solubility of non-cellulosic components. In the presence of alkali solution, the carboxylic groups present in pectin ionize to form sodium carboxylate which is soluble in the solvent medium and can be filtered off. This results in the decreasing tendency of intermolecular hydrogen bond formation. The concentration of alkali solution should be carefully controlled so that it cannot degrade the cellulose content. 2% alkali solution is found optimum to avoid the degradation of cellulose residue.

The second step of the steam explosion process is bleaching treatment. The main aim of bleaching treatment is to remove lignin present in the steam treated pulp. Lignin is believed to be linked with the carbohydrate moiety through two types of linkages. One is alkali sensitive and other alkali resistant. The alkali sensitive linkage forms an ester type combination between lignin hydroxyls and carboxyls of hemicellulose Uranic acid. The ether type linkage occurs through the lignin hydroxyls combining with the hydroxyls of the cellulose. The degradation of lignin leads to the formation of hydroxyl, carbonyl and carboxylic groups. These
groups help in solubilizing the lignin content in alkali medium and there by facilitates the purification of cellulose. After bleaching, the cell walls of the fibers are individualized but the microfibrils are still associated within the cell wall. So a mechanical treatment is necessary to individualize the microfibrils from the cell wall. The mechanical stirring leads to the individualization of the microfibrils, destroying the kinks and twists present in the microfibrils. These kinks are accounted for the amorphous region of microfibrils. The removal of this amorphous region increases the crystallinity index of cellulose residue. The enhanced mechanical properties of the microfibrils are associated with increased crystallinity index, increased surface area and decreased degree of polymerization. The information about the effect of pretreatment and the structural changes of the steam exploded banana fiber can be obtained from SEM studies. Fig.12.1 shows the SEM of BF before steam explosion. From the figure it can be seen that the fibrils are associated in bundles and the surface of the fiber is found to be smooth due to the presence of waxes and oil. Fig. 12.2 (a and b) show the SEM of the BF after steam explosion at two different magnifications. During the steam explosion with alkali at high temperature, the hemicelluloses are hydrolysed and become water soluble. The lignin gets depolymerised. As a result, defibrillation of the fiber occurs, because of the removal of the cementing materials, which can be seen from the SEM micro photograph (Fig. 12.2 (a and b).
Fig. 12.1 SEM of banana fiber before steam explosion

Fig. 12.2 SEM of banana fiber after steam explosion at two different magnifications

Fig. 12.3 (a and b) show the SEM micrograph of the samples after bleaching. Bleaching helps to remove most of the lignin present in the BF, which helps in further defibrillation. Sodium hypochlorite, sodium acetate buffer allow the removal of lignin and tannin. Lignin is rapidly oxidised by chlorine. Lignin oxidation leads to lignin degradation and leads to the formation of hydroxyl, carbonyl and carboxylic groups, which facilitate the lignin solubilisation in alkaline medium.
Mechanical stirring after bleaching helps to disintegrate the fibrils further. Fig. 12.4 (a and b) show the SEM photographs of the microfibrils after mechanical treatment. It can be seen from the SEM that the size of the BF is reduced from 100 µm to 10 µm. Thus steam explosion followed by bleaching helps in defibrillating the fiber.

Acid hydrolysis of the above microfibrils with 8% oxalic acid lowered the size of the BMF to the nano range. Fig. 12.5 shows the TEM of the banana nano fibrils (BNF). From the TEM, we can see that the size of the BNF is about 50 nm.
Fig. 12.6 shows the FTIR spectra of the BF and BMF. In the spectra of BMF, we can observe the disappearance of a number of peaks which indicates the removal of a number of components like hemicellulose, lignin, ester groups, fatty acid groups etc. The band at 1730 cm\(^{-1}\) which is characteristic of hemicellulose is absent in BMF. This is a clear evidence of the removal of hemicellulose during steam explosion. The peak for \(-(\text{C}=\text{O})\) stretch, carboxylic acid \(\sim 1760-1690\) is also disappearing in the spectra. Lignin bands at \(\sim 1650-1250\) and \(\sim 1200-900\) cm\(^{-1}\) are also not discernible in the spectra [15]. The band at 3400 cm\(^{-1}\) is the characteristic of the hydrogen bonded –OH stretching [15]. This band can be seen both for the BF and BMF. This observation is in agreement with the results obtained from SEM studies. SEM studies revealed that the size of the BF is decreased from 100 \(\mu\)m to 10 \(\mu\)m (Fig. 12.1 and 12.4) after steam explosion followed by bleaching. This confirms the removal of many of the components like hemicellulose, lignin, and waxes, which constitutes different types of alcohol and acids like (palmitic, oleaginous, and stearic acid) from the BF. Acid hydrolysis resulted in further reduction of the size of the microfibrils to about 50 nm which can be observed from the TEM (Fig. 12.5).
12.2.2 Solvatochromic studies

Solvatochromic studies are carried out to characterize the surface polarity of the BMF and chemically treated BMF. Fig. 12.7 shows the UV/Vis spectra of BF and BMF when probed with dye 1. The spectra of the BF shows a change in the absorption peak compared with BMF indicating a change in the number of acidic sites. For BF, a bathochromic shift was observed when compared to the BMF. Fig. 12.8 a and b show the UV/Vis absorption spectra of BF and BMF when probed with dyes 1, 2 and 3. The spectra of the BMF show a change in absorption peaks with the three dyes compared with BF indicating a change in the number of acidic and basic sites. This is attributed to the changes in the surface structure of the BF as a result of steam explosion. Iron dye can interact with more acidic groups. The dye becomes protonated when adsorbed on acidic surfaces. It can interact through the cyano group. The typical intramolecular charge transfer (CT) band of the adsorbed dye 1 contributes to the UV/Vis spectra. The indicators 2 and 3 can interact in many ways with surfaces of the cellulose fibrils. Using probe dye molecules 1, 2, and 3, the polarity...
parameters $\alpha$, $\beta$, $\pi^*$, $E_1(30)$ and AN of BMF and chemically treated BMF are calculated using different established Linear Solvation Energy equations. Table 12.1 shows the UV/Vis absorption maxima for the three
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Dyes used on BMF and chemically treated BMF. The $\nu_{\text{max}}$ values for dye 3 are the lowest. The absorption maxima depend on the type of the chemical treatment given to the fibrils. Tables 12.2 and 12.3 contain the Kamlet–Taft polarity parameters calculated for various chemically treated BMF. As evident from the Table 12.2, all the chemical treatments decreased the acidity of the BMF. Acidity $\alpha$ depends on both amount and strength of accessible acidic surface groups on the cellulose surface. The increase in the $\alpha$ value of BMF is due to the changes in the manifold surface properties that make new reaction sites available. After steam explosion followed by bleaching, most of the components of the BF like hemicellulose, lignin, pectin, waxes are removed. The extensive hydrogen bonding network will also be broken and the hydroxyl groups of cellulose become more active as they are free from hydrogen bonding. [26]. The –OH groups on the BF are not accessible as in microfibrils as the cellulose is embedded in the matrix of lignin and hemicellulose. This will give rise to

**Table 12.1** UV/Vis absorption maxima for the three probe dyes used on chemically treated banana microfibrils

<table>
<thead>
<tr>
<th>Samples</th>
<th>$\nu_{\text{max}}$ 1 ($10^{-3}\text{cm}^{-1}$)</th>
<th>$\nu_{\text{max}}$ 2 ($10^{-3}\text{cm}^{-1}$)</th>
<th>$\nu_{\text{max}}$ 3 ($10^{-3}\text{cm}^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Banana fiber</td>
<td>19.7</td>
<td>26.9</td>
<td>18.5</td>
</tr>
<tr>
<td>Banana microfibral</td>
<td>20.3</td>
<td>26.3</td>
<td>17.9</td>
</tr>
<tr>
<td>Silane treated microfibral</td>
<td>19.4</td>
<td>27.2</td>
<td>15.0</td>
</tr>
<tr>
<td>Stearic acid treated microfibral</td>
<td>19.4</td>
<td>26.5</td>
<td>16.2</td>
</tr>
<tr>
<td>Benzoylated microfibral</td>
<td>19.7</td>
<td>26.3</td>
<td>19.1</td>
</tr>
<tr>
<td>KMnO$_4$ treated microfibral</td>
<td>19.2</td>
<td>27.0</td>
<td>15.3</td>
</tr>
</tbody>
</table>
the greater accessibility of the –OH groups at the banana fibril surface. The –OH groups on the BF are not accessible as in fibrils as the cellulose is embedded in the matrix of lignin and hemicellulose. The values of the $\alpha$ term also depend on crystallinity. Amorphous parts have low $\alpha$ values and crystalline parts have high values. Both the strength and the concentration of acidic surface groups contribute to $\alpha$. Therefore, $\alpha$ is a specific parameter which can be significantly changed depending on pretreatment of the BF and basicity of the probe used, because of manifold acid–base interactions.

Table 12.2 Values of the Kamlet –Taft polarity parameters for banana fiber and chemically treated banana microfibrils

<table>
<thead>
<tr>
<th>Samples</th>
<th>$\alpha$</th>
<th>$\pi^*$</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Banana fiber</td>
<td>1.5</td>
<td>0.87</td>
<td>0.43</td>
</tr>
<tr>
<td>Banana microfibril</td>
<td>1.6</td>
<td>0.50</td>
<td>0.57</td>
</tr>
<tr>
<td>Silane treated microfibril</td>
<td>1.27</td>
<td>0.43</td>
<td>1.51</td>
</tr>
<tr>
<td>Stearic acid treated microfibril</td>
<td>1.42</td>
<td>0.61</td>
<td>1.32</td>
</tr>
<tr>
<td>Benzoylated microfibril</td>
<td>1.57</td>
<td>0.53</td>
<td>0.2</td>
</tr>
<tr>
<td>KMnO$_4$ treated microfibril</td>
<td>1.36</td>
<td>0.4</td>
<td>1.44</td>
</tr>
</tbody>
</table>

Steam-explosion followed by bleaching also results in cellulose with an increased degree of crystallinity and crystallites of higher perfection and size [16]. This is due to the reorganization of amorphous and para crystalline cellulose regions, releasing strains that arise due to the interactions with hemicellulose and lignin [16].

For all the samples, $\alpha$ is larger than $\pi^*$. The comparison of the Gutman’s acceptor number (Table 12.3) which is indicative of the electron accepting ability or acidity also show the same trend. The $E_T$ (30) parameter (Table 12.3) reflects the polarity of the environment. This parameter also increases
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after steam explosion followed by bleaching of the BF as explained earlier. BMF shows larger $\beta$-values (0.57) when compared to BF. This is because dye 3 is not always solely sensitive to the acidic surface environment. A low $\beta$ value corresponds to a weak proton affinity of the sample.

Table 12.3  AN and $E_T$ (30) parameters of banana fiber and and chemically treated banana microfibrils

<table>
<thead>
<tr>
<th>Samples</th>
<th>AN</th>
<th>$E_T$ (30)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Banana fiber</td>
<td>62.0</td>
<td>59.0</td>
</tr>
<tr>
<td>Banana microfibrils</td>
<td>70.0</td>
<td>63.0</td>
</tr>
<tr>
<td>Silane treated microfibrils</td>
<td>53.0</td>
<td>55.0</td>
</tr>
<tr>
<td>Stearic acid treated microfibrils</td>
<td>58.0</td>
<td>59.0</td>
</tr>
<tr>
<td>Benzoxylated microfibrils</td>
<td>62.0</td>
<td>61.0</td>
</tr>
<tr>
<td>KMnO$_4$ treated microfibrils</td>
<td>55.0</td>
<td>57.0</td>
</tr>
</tbody>
</table>

Table 12.1 contains the UV/Vis absorption maxima for the three dyes on chemically treated BMF. For chemically treated BMF, the $\nu_{\text{max}}$ values for dye 3 are the lowest. The absorption maxima depend on the type of the chemical treatment given to the BMF. Tables 12.2 and 12.3 contain the Kamlet–Taft polarity parameters calculated for various chemically treated BMF. As evident from the Table 12.2, all the chemical treatments lowered the acidity of the BMF. This can be explained as due to the decrease in the number of free acidic hydroxyl groups on the BMF as a result of chemical treatment. As discussed earlier, acidity $\alpha$ depends on both availability and strength of accessible acidic surface groups on the cellulose surface. But
the dipolarity and the HBA value of the microfibril varied considerably depending upon the type of the chemical treatment.

Treatment with silane decreased the HBD ability or acidity of the BMF, showing the reduction in the number of acidic surface groups when compared with BMF. When the microfibrils are further treated with silane, more coverage of the surface area by silane occurs because of the additional cavities available from the dissolution of hemicellulose and lignin. These multilayers, other than forming ether linkages with the fiber surface, self-condense to give polysiloxanes. This makes additional reaction sites available for the silanol. The polysiloxane bridges are responsible for the low HBD value or acidity.

When the BMF are immersed in the aqueous solution of the vinyl trimethoxy silane, chemical bonds (R₁-Si-O⁻) as well as hydrogen bonds are established between the -OH group of the microfibril surface and R₁-Si(OH)₃ molecules. Formation of these bonds can be explained as follows. Silanes can be represented as R₁Si(OR₂)₃ where R₁ is an aliphatic linkage that serves to attach the functional organic groups to the silicon. OR₂ is a hydrolysable alkoxy group. Moisture hydrolyses the silanes to form silanols. The hydrolyzed silanol forms strong covalent and hydrogen bonds with -OH group of the cellulose BMF.
Fig. 12.9  Scheme showing the interaction of banana microfibrils with silane, R represents the alkyl group

The schematic representation of the reaction between silane and the BMF is represented in Fig.12.9.
Fig. 12.10 shows the SEM of the silane treated microfibrils. From the figure we can observe the coating of siloxanes on the microfibril surface. $\alpha$ value (Table 12.2) of the silane treated microfibril is lower than that of BMF. This indicates lower acidic character of the silane treated microfibril. $\beta$ and $\pi^*$ values are also lower than BMF, which shows lower basic and polarizing character of the silane treated BMF. AN and $E_t(30)$ values show a decrease when compared to the BMF. The HBD ability is lowered due to the presence of siloxane bridges formed as a result of the interaction of the cellulose microfibrils with silane [18]. AN values calculated for these microfibrils which are indicative of the electron accepting ability or acidity also shows the same trend. The $\pi^*$ value is found to be increased due to the dispersion forces between the dye and the siloxane bridges.

In the case of stearic acid treated BMF, the dyes 1 and 2 show sharp absorption bands while dye 3 shows a broad absorption band. The $\alpha$ value is found to be lower than the untreated BMF showing the reduction in the number of acidic sites. The polarisability value is also reduced. In stearic acid treated BMF, the carboxyl group of the stearic acid reacts with hydroxyl group of the fibril through an esterification reaction and hence the treatment reduced the number of hydroxyl groups available for bonding.
with water molecules. Another reason for lower acidity is that the large bulky alkyl groups possibly prevent the dyes from attaching to the polar surface centers of the BMF. The treatment also helped to remove the non-

![FTIR spectra](image)

**Fig. 12.11** FTIR spectra of (a) banana microfibrils (b) stearic acid treated banana microfibrils

crystalline constituents of the microfibrils. This is further proved by FTIR spectra. The FTIR spectra of the stearic acid treated microfibril (Fig. 12.11) shows absorption bands around $\sim 3400\text{cm}^{-1}$, $\sim 1720\text{cm}^{-1}$, $\sim 2800\text{cm}^{-1}$ corresponding to $-\text{OH}$ stretching, ester bond and C-H group. SEM photographs of the stearic treated microfibril surface (Fig. 12.12) shows more fibrillation and roughness. AN value shows a decrease when compared to the untreated BMF due to lower acidic character of the fibril surface. The $\pi^*$ which shows the overall polarity is less for stearic acid treated BMF. The $\beta$ value is also high due to the presence of the alkyl group. The reaction of stearic acid $\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$ with the banana microfibrils can be represented as follows

$$\text{CH}_3(\text{CH}_2)_{16}\text{COOH} + \text{HO- banana microfibril} \rightarrow \text{CH}_3(\text{CH}_2)_{16}\text{COO- banana microfibril}.$$
FTIR spectrum of benzoylated BMF (Fig.12.13) exhibited a number of characteristic observations. The bands around 1950, 1600, and 710 cm$^{-1}$ indicate the presence of aromatic groups and the peaks around 1725 and 1300 cm$^{-1}$ indicate the presence of ester groups [19]. The sodium hydroxide pretreatment before benzoylation results in partial breaking of hydrogen bonding in cellulosic chains and make the fibril surface more reactive for benzoylation.

Fig.12.13  FTIR spectra of (a) banana microfibrils (b) benzoylated microfibrils.
Benzoylated microfibrils have higher acidity when compared to other chemically treated BMF. This is due to the formation of HCl as a result of the excess benzoyl chloride. The benzene ring also plays an important role in enhancing the acidity. The $\pi^*$ value is also high. But HBA, which represents basicity of the system, is low. AN is also high which indicates high acidity when compared to BMF. The $E_T(30)$ value which depends on $\alpha$ and $\pi^*$ is also high. Fig. 12.14 shows the schematic representation interface of the benzoylated microfibrils.

Treatment of banana microfibrils with KMnO$_4$ solution leads to the formation of cellulose manganate complex [19]. The formation of cellulose manganate complex is responsible for the low $\alpha$ value when compared to the BMF. The reaction of BMF with KMnO$_4$ is represented in Scheme 3.1 Chapter 3. The UV/Vis absorption maxima obtained for dye 1, 2, and 3 are at $\lambda_{\text{max}} = 520$ nm, $\lambda_{\text{max}} = 370$ nm and $\lambda_{\text{max}} = 626$ nm. For KMnO$_4$ treated microfibrils, $\alpha$ and $\pi^*$ values are less, but $\beta$ value is higher when compared to the BMF. Fig.12.15 shows the SEM microphotograph of the KMnO$_4$ treated microfibril.
Dye 1, is ideal for locating acidic centres on BF, BMF and chemically treated BMF. Unlike dye 1, dye 2 give sharp UV/Vis absorption bands in almost all cases. All the samples are characterized by the indicator dye 2. The absorption peaks obtained due to 2 are at a lower wavelength than those due to dye 1. The UV/Vis absorption peaks due to 2 are due to π-π* transition.

From the dipolarity (π*) and E⊥ 30 values (Table 12.2 and 12.3), we can see that the polarity of the BMF is reduced after the chemical treatment. The change in polarity of the microfibril will affect the fiber/matrix interface adhesion. Reduced polarity of the microfibril will increase the compatibility with the non polar matrices like PP. On the other hand the increase in polarity of the microfibril will increase the compatibility with polar matrices like polyester.

12.2.3 Zeta potential measurements

The studies of the influence of pH on zeta potential provide valuable information on the nature of the surface of banana fibril and chemically treated banana fibril. The acidity or basicity of the solid surfaces can be determined qualitatively by the pH that corresponds to zero of the zeta
potential (isoelectric point IEP). At this pH, the number of negative charges equals the number of positive ones [20]. The acidity of the surface is always characterised by the IEP. In the case of low IEP values, the number of acidic group dominates. For banana fiber, the IEP value is found to be 2.5, which indicates an acidic surface (Chapter 3, Table 3.4). This is because the natural cellulose fibers are negatively charged, due to the presence of carboxyl and hydroxyl groups [20].

Fig. 12.16 shows the pH dependence on the $\zeta$-potential of BMF and chemically treated BMF. From (Fig. 12.16), it can be seen that BMF shows a negative value of $\zeta$-potential of -22 mV. The IEP value for BMF is found beyond 2.5. As we have only a measuring window from pH ~ 2.5 to ~10, the exact value cannot be determined. As the IEP values of BMF are lower than that of BF, BMF have higher acidity when compared to the BF. This is in agreement with the solvatochromic measurements. The hydrogen bond donating ability $\alpha$ is found higher for BMF (Table 12.2). Acceptor number according to Gutmann, which characterize the strength of Lewis-acid properties of the surface is also found higher for BMF (Table 12.3). If the liquid phase remains constant the electrokinetic potential of microfibrils is determined by the chemical constitution, polarity of the microfibril surface, microstructure of the microfibril (porosity and specific surface) and swelling behaviour in water.
According to Kanamaru [21] the zeta potential of any fiber decreases with increasing adsorption of water. Swelling processes are assumed to expand the inner surface of the fibers. Furthermore, the electrochemical double layer is expected to migrate in this swelling layer and the slipping plane shifts towards the bulk electrolyte. The potential drop in the electrochemical double layer causes the decrease of zeta potential with increasing swelling time [22]. On the other hand, the composition of the electrochemical double layer is influenced by the adsorption of electrolyte ions. Because of the competitive adsorption of water the amount of adsorbed potential-determining ions decreases during the swelling process followed by a simultaneous decrease in the zeta potential, [23]. In this study, BMF are prepared from BF by steam explosion method. The surface potential of the BMF increases as a result of steam explosion because of
the removal of non crystalline components, pectins, waxes, hemicellulose and lignin. An increase in surface charge density on the surface of the BMF is observed because of the higher amount of available -OH groups after steam explosion. Thus increase in crystallinity of the BMF leads to an increase in charge density and solid surface potential. The higher degree of crystallinity accounts for the lower adsorption of water and high zeta potential values of BMF when compared to the BF.

The plot of pH dependence on the $\zeta$-potential for untreated, alkai treated, vinyl triethoxy octyl silane treated and benzoylated BMF are shown in Fig. 12.16. The zeta potential curves show a difference between the untreated BMF and chemically treated BMF. The IEP value is found to be 3 for different chemically treated BMF which indicates a slight difference between various treatments. But compared to the untreated BMF, there is an increase for the IEP values for chemically treated BMF which indicates that chemical treatment reduced the acidity of the BMF surface. This result is also in agreement with solvatochromic measurements. Hydrogen bond donating ability $\alpha$ is found lower for chemically treated BMF than untreated BMF. Gutmann’s Acceptor Number (AN) also shows the same trend. Another effect is the decrease of the zeta potential value with increasing pH for untreated and chemically treated BMF. The process of alkali absorption destroys the hydrogen bonds within the cellulose, opening up the structure. There is a decrease in the supramolecular order in the chain conformation of cellulose. Usually, hydroxyl anions are seen to be responsible for the primary interaction with the cellulosic hydroxy groups in the ordered regions of the structure, while hydrated cations are responsible for the resulting swelling [20]. The removal of non-cellulosic components make the inter-fibrillar region to be less dense and less rigid making the fibrils capable of rearranging themselves. The pH dependence on the $\zeta$-potential of the NaOH (1%) -treated BMF (Fig.12.16) shows an isoelectric
point of 3. The value in the case of the untreated BMF is beyond 2.5 which indicates an increase of acidity, and the treatment with alkali decreases the acidity. Treatment of the BMF with silanes leads to the covering of the microfibrils with siloxane as described earlier. The increase in IEP indicates a decrease in surface acidity compared to untreated BMF. The results are consistent with the acceptor number calculated using solvatochromic measurements presented in Table 12.3. Of all the treatments given, benzoylated microfibril shows the lowest \( \zeta \)-potential value. Benzoylated BMF surface is found to be more acidic than other treated BMF. Solvatochromic measurements also showed the same trend.

12. 2.4 Tensile properties of PP/microfibril composites

The tensile properties of PP/BMF composites with different BMF loading are shown in Table 12.4. It can be seen from the Table that the addition of BMF to PP has resulted in an increase of tensile strength of the composites up to 20% microfibril loading. After 20% addition, the tensile strength of the composite slightly decreases. But tensile modulus increases with BMF loading. This is expected and attributed to poor microfibril/matrix interfacial adhesion resulting from the incompatibility between the polar hydrophilic BMF and non-polar hydrophobic PP matrix. This can be readily understood by the investigation of SEM of the tensile fracture surface of the PP/BMF composites. Fig. 12.17 (a) shows the SEM of the tensile fracture surface of the composite with 25% BMF loading. Fibril pullout can be seen from the SEM which indicates poor microfibril/matrix interfacial adhesion.

Another factor contributing to the poor tensile strength is due to the poor dispersion of the microfibrils at higher microfibril loadings. It is particularly attributed to the strong intermolecular hydrogen bonding between the BMF and their low compatibility with the PP matrix. Fig. 12.17 (b) shows
the SEM of the tensile fracture surface of 25% BMF composites showing
the state of microfibril agglomeration.

**Table 12.4** Effect of banana microfibril loading on the tensile properties of
the PP/microfibril composites

<table>
<thead>
<tr>
<th>Samples</th>
<th>Tensile strength (MPa)</th>
<th>Tensile modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat PP</td>
<td>21± 1</td>
<td>0.87 ± 0.035</td>
</tr>
<tr>
<td>10% BMF composites</td>
<td>18 ± 2.0</td>
<td>2.0 ± 0.50</td>
</tr>
<tr>
<td>15% BMF composites</td>
<td>22 ± 2.5</td>
<td>2.12 ± 0.70</td>
</tr>
<tr>
<td>20% BMF composites</td>
<td>26 ± 2.0</td>
<td>2.31 ± 0.75</td>
</tr>
<tr>
<td>25% BMF composites</td>
<td>25 ± 1.5</td>
<td>2.46 ± 1.1</td>
</tr>
</tbody>
</table>

**Fig. 12.17** SEM of the tensile fracture surface of the PP/microfibril
composites (25% microfibril loading) (a) microfibril pull out
(b) microfibril agglomeration

**12.3 Conclusions**

BMF were prepared from BF by steam explosion method. Empirical
polarity parameters were characterized in terms of the Kamlet-Taft
solvent polarity scale for BMF and chemically treated BMF. The
solvatochromic analysis revealed that HBD ability $\alpha$ is high for BMF. Chemical treatments with stearic acid, KMnO$_4$, silane and benzoyl chloride reduced the acidity as well as polarity of the BMF. FTIR analysis revealed the dissolution of hemicellulose, lignin, ester groups and fatty acids from the BF after steam explosion. This was found to be consistent with SEM and TEM studies which showed the changes in the morphology and the size of the microfibril before and after steam explosion. Electrokinetic studies seem to be in agreement with solvatochromic measurements. IEP value was found to be lower for BMF than BF which indicated increased acidity for the microfibril. Chemical treatments increased the IEP value of the BMF which indicated a lower acidity after the chemical treatment. The effect of microfibril loading on the tensile properties of the composites showed that the tensile strength increased with increase in BMF loading upto 20% and at higher loading a slight decrease is observed due to the agglomeration and the poor dispersion of microfibrils. But the modulus value increased with BMF loading. SEM of the tensile fracture surface of the composites showed the poor dispersion of the microfibrils at higher microfibril loading.

References


