Chapter 5

Green nanocomposites of polylactic acid reinforced with isolated nanocellulose

This chapter is under final revision in Green Chemistry journal as Green nanocomposites from agricultural resources: Preparation and its various characterisations

The part of the chapter has been published in Carbohydrate Polymers by Cordeiro & Abraham et al as Assessment of the changes in the cellulosic surface of micro and nanobanana fibres due to saponin treatment. Carbohydrate Polymers 98 (2013) 1065–1071

Summary

The chapter deals with the development of sustainable novel ‘green nanocomposites’ by reinforcing nanocellulose (CNF) which is isolated from banana bast fibre by steam explosion process in a biodegradable matrix, poly-L-lactic acid (PLA). Surface modification of the CNF by amino propyl triethoxy silane (APTES) and a naturally extracted surfactant, saponin, were carried out in order to find a system that would give maximum compatibility between matrix and filler. The procedure to attain uniform dispersion and maximum reinforcement of CNF in PLA matrix was assessed, and the spectroscopic, mechanical, thermal and biodegradation properties of the compression molded nanocomposites were analysed. Saponin modified nanocomposites were found to exhibit superior mechanical properties compared to its untreated counterpart. It was found to have an edge over the untreated and silane treated fibre composites.
5.1 Introduction
A great deal of academic research and development is focused on exploring new ways to develop environmentally friendlier polymer composites for a variety of application [1]. Among the different bio-polymers, studies in polylactic acid (PLA) and cellulose nano fibres have garnered great attention [2]. The increasing commercial availability of PLA coupled with their improved properties make them ideal candidates as the matrix of choice in the preparation of green composites. Reinforcing PLA with cellulose nano fibres will enhance its physical properties and thermal stability along with retaining the biodegradability. It is also interesting to study the incorporation of chemically modified reinforcements to improve the toughness and thermal stability of the resulting PLA/cellulose nanocomposites [3]. In the present study, PLA based biodegradable nanocomposites are prepared with banana nano fibril (CNF) as the reinforcement. Chemical modification of the CNF by silane coupling agent and a naturally extracted surfactant namely saponin (a complex organic compound) which is extracted from soapnuts has been carried out and its effect on the mechanical, thermal and biodegradation properties of the nanocomposites have been analysed.

5.2 Results and Discussions
5.2.1 The surface modification of the CNF
The surface modification of the CNF by amino propyl triethoxy silane (APTES) and saponin were carried out by the experimental procedure described in 2.2.3.1 and 2.2.3.2 respectively. The modification of the CNF by APTES was done with the aim to improve the compatibility between the matrix and the filler by providing silanated cellulose nanofibres (CNF) and is reported by various researchers [4,5]. It is hypothesized that silination will
improve the dispersion of CNF in organic solvents. It is further hypothesized that the addition of silanated CNF filler will promote miscibility and interfacial adhesion with the polylactic acid matrix, ultimately enhancing mechanical performance and thermal stability of the resultant composites. In this study, successful silination was confirmed by the results of Fourier transform infrared spectroscopy (FTIR).

**Fig. 5.1** Life cycle analysis of the prepared saponin treated green nanocomposites

The surface modification of the CNF by *saponin*, a naturally extracted surfactant from soapnut fruit was done to provide saponin modified cellulose nanofibres (CNF). To best of our knowledge, this reaction has not been exploited for the modification of CNF and preparation of PLA-based composites. The extraction method for the *saponin* from soapnut fruit is clearly discussed in the literature [6]. Fig. 5.2 demonstrates the proposed mechanism of interaction between CNF and chromosaponin of the saponin extract.
It is hypothesized that the main component of the *saponin* extract, chromosaponin, has made hydrogen bonded interaction with the nanocellulose. The aromatic ring present in chromosaponin with polar groups act as a bridge between the hydrophilic nanocellulose and hydrophobic PLA. The resultant surface modified nanocellulose enhances the filler-matrix interaction in PLA-nanocellulose composite and thereby its various properties.

The morphologies of both modified and unmodified CNF were observed by scanning electron microscopy (SEM) and atomic force microscopy by means of scanning probe microscopic (SPM) methods. In addition, PLA/CNF nanocomposites were characterized by using tensile and impact measurements, thermal and biodegradation and SEM and SPM methods. The CNF become more hydrophobic with surface treatment. The FTIR spectra of the untreated and chemically modified CNF which is shown in Fig. 5.3 support the existence of the proposed mechanism. Finally, the role of CNF in improving the properties of PLA has also been discussed in detail. In addition, the mechanical, thermal and biodegradation studies of the composite were conducted.

The FT-IR spectroscopic analyses of untreated, silane and saponin treated CNF were done as per the procedure described in 2.2.7 to confirm the effect of chemical modifications on the nanofibres. Fig. 5.3 represents the FTIR spectra of the different samples. All the samples have two main transmittance regions. In the preliminary observation of the three spectra, it is clear that the FTIR of the treated CNFs and untreated CNF are entirely different.
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Fig.5.2 Proposed reaction representation of saponin/cellulose interaction

Fig.5.3 FT-IR analysis of the treated and untreated CNF
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5.2.2 FTIR analysis

FTIR of untreated CNF has the characteristic peaks at 3300 cm$^{-1}$ which represents the density of the hydroxyl groups, C-H (2875 cm$^{-1}$), stretching and bending peaks of the hydroxyl group of absorbed water (1660 cm$^{-1}$), 1432 cm$^{-1}$ (CH$_2$ stretching), C-O-C (1170 cm$^{-1}$) [7]. The other main peak at 1041 cm$^{-1}$ is associated with the C–O stretching and C–H rock vibrations of cellulose [8]. APTES treated fibre shows the strong peaks at 1454 cm$^{-1}$ and 1363 cm$^{-1}$. The stretching and bending peaks of the hydroxyl group at 1648 cm$^{-1}$ is completely absent in APTES fibres which shows that the hydroxyl groups of CNF has been used up for the modification with silane. The region between 600 cm$^{-1}$ and 1400 cm$^{-1}$ is responsible for characteristic features of -Si-O- bonds. The increased intensity of the 1454 cm$^{-1}$, 1363 cm$^{-1}$, 1079 cm$^{-1}$ and 1740 cm$^{-1}$ peaks are the other differences of the spectrum of APTES treated CNF from untreated CNF. The very high intensity of these bands after the treatments suggested that the grafting of silane onto cellulose as well as the intermolecular condensation between adjacent adsorbed –Si–OH groups were substantially enhanced. The peak at 1454 cm$^{-1}$ is responsible for the ethoxyl (–O–C$_2$H$_5$) groups of APTES [9].

Silanised cellulose reveals transmittance peaks at around 670 cm$^{-1}$ which could be attributed to Si-O-C stretching bond. A weak peak found at 847 cm$^{-1}$ corresponds to a Si-O-C bond and a broad peak that appeared in the range of 995–1112 cm$^{-1}$ could be due to the presence of asymmetric stretching of Si-O-O-Si or Si-O-O-O-C (1031 and 1060 cm$^{-1}$) bond [10]. Such transmittance band for Si-O-O-O-Si is an indication of the existence of polysiloxanes deposited on the cellulose fibres but the band for Si-O-O-O-C assures a condensation reaction between the cellulose of the fibres and silane. New transmittance bands are found at 1234, 1282, 1320, 1364, 1375 and 2132 cm$^{-1}$.
in APTES treated fibres. These bands are possibly from the C-O-Si stretching of newly formed bonds. Again, there is a sharp peak found at 896 cm\(^{-1}\), which could be assigned to Si-O-OH. This confirms the fact that -OH group of silanol reacts with cellulose or undergoes condensation reaction. All the reactions will facilitate to increase the compatibility between the matrix PLA and CNF and thereby increases the properties of the resultant composite.

Saponin treated CNF show characteristic peaks at 3392, 2992, 2100, 1750, 1647, 1454, 1363 and 1180 and 1100 cm\(^{-1}\). Saponin is composed of a series of complex aromatic skeletal rings resembling to chromosaponin. The stretching vibrations of the C=C bond and C=O bonds in the chromosaponin is responsible for the unique transmittance peak at 1647 cm\(^{-1}\) in saponin treated CNF. The intensity of this peak suggests that this group is in interaction with the hydroxyl groups of cellulose. The methoxy group is a side chain group of the chromosaponin molecule. The stretching of the C-OH is responsible for the peak of 1113 cm\(^{-1}\). The broad intense bands around 1180 and 1100 cm\(^{-1}\) reassigned to the stretching of the saponin–O–cellulose and saponin–O–saponin bonds, respectively. The strong increase in the intensity of these bands after the treatments suggests that the grafting of saponin onto cellulose as well as the intermolecular condensation between adjacent adsorbed Ar–OH groups were substantially enhanced to get a compatible interaction with PLA. The increase of the -OH concentration is evident from the increased intensity of the peak at 3392 cm\(^{-1}\) of the saponin treated CNF compared to the untreated CNF. This increase in the concentration of hydroxyl density is due to the hydroxyl groups present in the aromatic moieties. It has been concluded that the silane can provide a continuous path of covalent bonds between the fibre surfaces which will enhance the hydrophobic nature of fibre surface. This behavior will lead to better PLA-cellulose interaction during the composite preparation.
Interesting points in the study is the resemblance of the FTIR spectra of the naturally extracted saponin treated cellulose and the silane treated cellulose in the surface modification analysis.

5.2.3 Inverse Gas Chromatography (IGC) analysis

Inverse gas chromatography (IGC) has been conducted for untreated and saponin treated CNF as per the procedure described in 2.2.22. The sample cellulose nanofibres which are obtained by the sequential steam explosion coupled with alkali treatment and acid hydrolysis [11] were subjected to saponin treatment. This treatment provokes high changes in composition and morphology in the nanofibres by the removal of the natural and artificial impurities, and lignin and non-cellulosic polysaccharides extraction. The nanofibres show high content in crystalline cellulose and small dimension [12].

From Table 5.1, it can be observed that the $\gamma_s^D$ decreases linearly with the increase of temperature, that is frequently observed in lignocellulosic materials [12,13]. Cellulose nanofibres presented a smaller decrease in the $\gamma_s^D$ with temperature, compared to the microfibres. This can be due to the higher structural organization – high crystallinity [11] presented by these fibres, and consequently a smaller entropic dependence on the temperature than presented by microfibres [14].
Table 5.1 Dispersive component of the surface energy, $\gamma^D_S \, (\text{mJ/m}^2)$ and acid and base surface characteristics ($K_a$ and $K_b$), of the cellulose nanofibre before and after saponin treatment

<table>
<thead>
<tr>
<th></th>
<th>Untreated cellulose nanofibres</th>
<th>Saponin treated cellulose nanofibres</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma^D_S , (\text{mJ/m}^2)$</td>
<td>293 K</td>
<td>298 K</td>
</tr>
<tr>
<td></td>
<td>46.22</td>
<td>45.64</td>
</tr>
<tr>
<td>$K_a$</td>
<td>0.09</td>
<td>0.09</td>
</tr>
<tr>
<td>$K_b$</td>
<td>0.14</td>
<td>0.14</td>
</tr>
<tr>
<td>$K_b/K_a$</td>
<td>1.56</td>
<td>1.56</td>
</tr>
<tr>
<td>(0.997)</td>
<td>(0.997)</td>
<td>(0.997)</td>
</tr>
</tbody>
</table>

Table 5.2 Heat of adsorption ($Q_{\text{ads}}; \, \text{kJ/mol}$) for non-polar and polar probes onto banana fibres before and after saponin treatment

<table>
<thead>
<tr>
<th>Probe ($Q_{\text{ads}}; , \text{kJ/mol}$)</th>
<th>n-octane</th>
<th>Tetrahydrofuran</th>
<th>Ethyl acetate</th>
<th>Acetonitrile</th>
<th>Ethanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated cellulose nanofibres</td>
<td>40.17</td>
<td>27.11</td>
<td>32.46</td>
<td>25.14</td>
<td>45.25</td>
</tr>
<tr>
<td>Saponin treated cellulose nanofibres</td>
<td>42.90</td>
<td>19.63</td>
<td>24.14</td>
<td>30.21</td>
<td>71.68</td>
</tr>
</tbody>
</table>

From Tables 5.1 and 5.2, it can be observed that $\gamma^D_S$ for the saponin coated fibres is higher compared to the untreated fibres surface. The $\gamma^D_S$ for nanofibres change from 45.64 to 56.04 mJ/m$^2$, at 298 K. The increase in
\( \gamma_S^D \) demonstrate the effective coating of the surfactant molecules in nano fibre surfaces during the treatment process. This attachment of saponin molecules in the cellulose surface (Fig. 5.2) provokes an increase in the \( \gamma_S^D \) temperature dependence. The effect is more pronounced with the reduction in the size of the cellulosic fibers and one can suggest more saponin molecules attachment in the increased surface of the nanofibres. This more extended coating of the nanofibres is due to the morphologic factors (namely surface area) and to chemical surface properties (namely \( \gamma_S^D \) and acid/base characteristics). The change in the dispersive component of the fibre surface can be also evaluated by heat adsorption parameter (Q_{ads}) using a non-polar probe. The Q_{ads} value obtained for the n-octane was 38.94 and 40.17 kJ/mol and it increased to 39.90 and 42.90 kJ/mol after saponin treatment, for micro and nanofibres, respectively. The same tendency was observed by the calculated \( \gamma_S^D \) values (Tables 5.1 and 5.2). Since, as the n-alkane probes are able to interact only through dispersion interactions, the increase in the \( \gamma_S^D \), for saponin modified fibres, is an indication that the fibres became more hydrophobic, after saponin treatment.

5.2.4 Morphological analysis by SEM and SPM

The scanning electron micrographic (SEM) analysis of the CNF and the tensile fracture surfaces of the nanocomposites are shown in Fig.5.4. Fig.5.4 (A) reveals that the nanofibres are agglomerated in the micrometer (1-5 \( \mu \)m) range in the dry form. SEM picture will not give the CNF in nanometer dimension since it is taken in the dried agglomerated condition. Ultrasonication to the CNF dispersion just before it mixing with PLA matrix during the composite preparation stage minimizes this agglomeration. Fig.5.4 (B), (C) and (D) shows the tensile fracture surface of the untreated
and APTES treated and saponin treated nanocomposites respectively. The difference in the compatibility and interfacial adhesion between the untreated and treated CNF and PLA is clearly seen from these images. The SEM of the nanocomposites with saponin treated CNF shows a very smooth surface.

**Fig. 5.4** SEM of (A) cellulose nanofibril and tensile fracture surfaces of (B) PLA/untreated CNF (C) PLA/APTES treated CNF (D) PLA/saponin treated CNF
Saponin treated CNF are well dispersed in the matrix, whereas the untreated fibres show some agglomeration. The fibre has been covered with a thin layer of the matrix linking the fibre surface to the matrix, and thus better stress transfer could be expected for saponin treated nanocomposites. As seen in Fig.5.4 (B), the surface was cracked throughout the matrix and appeared to have an uneven appearance along with fibre pullouts and voids, whereas in Fig.5.4 (C) and (D), the surfaces are smoother. Thus enhanced adhesion between the saponin treated CNF and PLA is clearly demonstrated from the fractographic analysis of these tensile samples. The improved dispersion leads to better wetting between the CNF and the PLA which will lead to a significant increase in the properties of the saponin treated nanocomposites. It can be seen that the surface morphologies of APTES treated nanocomposites have some resemblance in characteristics with the saponin treated nanocomposite. In the untreated CNF nanocomposites, there is a continuous fracture between the matrix and nanofibre, with a buildup of particles along the length of the nanofibre that is not observed in the SEM of
the saponin treated CNF nanocomposites. In conclusion, the SEM analysis of the tensile fracture surfaces indicated that the matrix-fibre interface was better in saponin treated nanocomposite than the untreated counterparts.

Fig. 5.5 is the Scanning probe micrographic (SPM) image of the surface of the 2% saponin treated CNF reinforced PLA nanocomposite. The SPM image shows well-dispersed arrangement of CNF in the nanocomposite. The determination of the diameter of the nanoparticle gives a value (50 ± 10 nm) which is more precise than the one determined from SEM observation. The topography image shows that the CNF is partly protruded from the PLA matrix, most probably due to differences in expansion between the matrix and the filler. The compatibility between the matrix and the treated CNF is clearly demonstrated in this morphological analysis. This leads to better stress transfer between the matrix and the nanofibre which is discussed in mechanical properties section.

5.2.5 Tensile properties of the nanocomposites

The tensile properties of the treated and untreated PLA-nanocellulose composite was done as per the procedure described in the experimental section 2.2.12.1 and are shown in Fig.5.6 (a) and (b). From the Fig.5.6 (a), it is clear that the tensile strength of all the composites show a lower value than the tensile strength of neat PLA. But the tensile modulus increases with the addition of CNF which reveals that the incorporation of CNFs into the matrix provides effective reinforcement. Usually, the orientation of fibres in composites influences the tensile strength of fibre-reinforced composites. The better the fibres are aligned, the higher the strength values can be. Since the composite preparation is through compression molding, the orientation of the CNF is random and has no contribution to the tensile strength properties. On the other hand, the decrease in the mechanical strength upon subsequent
loading has a contribution from the inadequate orientation and subsequently the lack of wetting of the fibre with the matrix, which leads to easy composite failure. Park and Balatinecz [15] reported that the ultimate strain decreased as the fibre content increased because of the decreased deformability of the matrix, which was restricted by the rigid particles. The contribution from the crystallinity of the composite has also some contribution to the decrease in the tensile strength of the composite. The PLA is a semicrystalline polymer, and it is predicted that the crystallinity of the PLA will increase with the addition of cellulosic reinforcements [16]. These crystalline regions then could act as physical crosslinks or filler particles, which could subsequently increase the modulus substantially. The increased modulus of the composites compared to pure PLA might be an indication that the crystallinity is higher for composites. However, during the fabrication of the composites, the cooling rate is fast, it is considered that the matrix is mostly amorphous, and the crystallinity may be primarily due to transcrystallinity of the PLA on the fibre surface. Thus during composite fabrication, the transcrystallinity of the PLA induced by the fibres can be believed to be the reason for the increased modulus. Thus, the addition of CNF increases the modulus, but the tensile strength of the untreated CNF reinforced PLA composite shows a gradual decreases with the filler percentage in comparison with neat PLA.

To study the effect of silane and saponin modification of the fibre, we have prepared 4% CNF/PLA nanocomposites and compared its mechanical strength with its untreated counterpart (4% CNF reinforced nanocomposites) by analyzing the tensile and impact properties. Tensile properties of the untreated and modified composites with 4% nanocomposites are shown in Fig.5.6 (b). It is apparent from Fig.5.6 (b) that there is a significant increase
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in the tensile modulus along with tensile strength when surface modified fibre has been used for reinforcement. In natural-fibre-reinforced composites, weak adhesion may result from poor dispersion and incompatibility between the hydrophilic natural fibres and the hydrophobic polymer. But when modification is carried out to increase the compatibility of the matrix and the fibre, the resulting composite has an appreciable increase in its modulus and strength value. It is clearly demonstrated in the Fig.5.6 (b) and the result shows that with the increase in the proportion of CNF, the interaction sites between the matrix and filler increases. Moreover, the filler-filler interaction result in a crosslinking effect and this cross linking is highest for untreated CNF reinforced composites [17]. The surface modification decreases the filler-filler interaction contributing to an increase with modulus and the strength of composites.

![Fig.5.6 (a) Tensile properties of untreated PLA nanocomposites](image)
Since the CNF orientation is random throughout the composite samples and the extent of modification is higher on the surface of the nanofibre which is being used to make chemical interaction with the PLA during the composite formation, the intensity of the interaction between the matrix and the nanofibre is high. Fig. 5.2 shows the proposed reaction mechanism between nanofibres and saponin which results in imparting hydrophobic characteristics to the saponin modified CNF. It is reported that the compatibility between the cellulose nanofibre and polymer matrix is increased with the silane treatment [18]. The silane and saponin moieties enhance the hydrophobicity of the fibres making the filler and matrix compatible in the modified composites. Tensile modulus of the silane and saponin treated nanocomposites (4%) are higher than that of the neat PLA and the untreated counterpart which is evident from the Fig.5.6 (b). The tensile strength of the untreated nanocomposite (4%) shows a lower value than the neat PLA as discussed earlier but in the case of
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silane and saponin treated nanocomposites both the tensile strength and the modulus are higher. Thus the tensile properties of the nanocomposites of 4% CNF with modifications gives better results than their respective untreated counterpart. This reveals that the incorporation of surface modified CNF into the matrix of PLA provides effective reinforcement between the nanofibre and the PLA. As discussed earlier, composite reinforced with untreated filler shows an increasing tendency in tensile modulus but a reverse order in tensile strength with filler concentrations. But the CNF with silane and saponin treatments show better results for both tensile modulus and tensile strength. As discussed in the SEM and FTIR analysis, the matrix-fibre interface was better in saponin and silane treated CNF than the untreated nanocomposites. This result also supports the higher tensile strength and moduli for nanocomposites of treated CNF.

5.2.6 Notched impact strength of the nanocomposites

The notched impact strength of the treated and untreated PLA-nanocellulose composite was done as per the procedure described in the experimental section 2.2.12.1 and the results for an average value of 5 tested samples are shown in Fig.5.7. The impact strength of the PLA/CNF composite changes little after the addition of a 2% fibre. Two factors need to be considered to develop sufficient stress-transfer properties between the matrix and the fibre [19]. First, the hydroxyl groups present near the fibre surface should be strongly interacting with the fibre surface through covalent bonding with the matrix. This means that hydroxyl groups present in PLA can interact with the hydroxyl groups on the fibre surface. Second, the polymer chains of PLA should be long enough to permit entanglements with the filler in the interphase. Fig.5.7 shows that after the addition of CNF, the impact strength of the PLA composite improves significantly. It is reported that the cellulose fibres act as efficient nucleating
agents for the crystallization of PLA and consequently increase the crystallization rate of PLA [20]. This will increase the impact strength of the resultant composite. Usually, good filler/matrix interfacial adhesion provides an effective resistance to crack propagation during impact tests. In Fig.5.7, even after the addition of 2% CNF, the impact strength of the composite remains nearly the same in comparison with neat PLA. This finding is in accordance with the results of Rowell and coworkers [21].

The predominant mechanism of energy absorption is crack propagation in the notched Izod test. Cracks are initiated at points of high stress concentrations such as fibre ends, defects, or the interface region, where the adhesion between the two phases is very poor. Generally, the toughness of short-fibre-reinforced composites can be influenced by a number of factors, such as the intrinsic matrix properties, fibre volume fraction, and interfacial bond strength. The surface modification of the fibre has a significant role in the impact properties of the PLA/CNF composite. The silane and saponin composite with 4% filler shows impact strength as comparable with the 8% untreated PLA/CNF composite. This means that the stress transfer between the matrix and filler is sufficiently improved by the surface modification. This study demonstrates that CNF can be successfully used as a reinforcing filler material in a biodegradable polymer such as PLA. Compression molded CNF/PLA nanocomposites shows significantly higher mechanical properties compared with those of the neat resin of the PLA as a result of reinforcement by CNF. The naturally extracted surfactant, saponin, is a good candidate for the surface modification of CNF for getting PLA nanocomposites with superior mechanical properties.
Fig.5.7 Impact strength analysis of chemically modified PLA nanocomposites

![Impact strength analysis of chemically modified PLA nanocomposites](image)

Fig.5.8 Thermogravimetric analysis of the PLA nanocomposites

![Thermogravimetric analysis of the PLA nanocomposites](image)

5.2.7 Thermal degradation analysis of the nanocomposites

The thermal degradation properties of the PLA, nanocellulose and the nanocomposites are done as per the procedure described in 2.2.14 and are shown in Fig.5.8. The recommended processing temperature of PLA is
200°C and both CNF and composites were able to withstand this temperature. The thermal analysis of the CNF reveals that its decomposition started at 270°C and continues until 360°C and the maximum weight loss was at 330°C. At 350°C almost all cellulose was pyrolyzed, and the solid residuals were left (9.5 wt.%). The slight decrease in weight for all materials below 100°C is due to the moisture content and it is higher in CNF. This graph also shows that the APTES treated composites started to degrade earlier than untreated CNF and saponin treated composites.

Recently Dongyan et al reported enhanced thermal behaviour of cellulose nanowhiskers on electrospun poly (lactic acid) (PLA) nanocomposites [22]. From the TGA graph it is clear that the saponin composites exhibited improved thermal stability than the other two nanocomposites. Another major finding from the thermal analysis is that there was no degradation taking place in either CNF or PLA composites resulting in large weight reductions in the temperature region where PLA is either processed or used, 25–220°C. The untreated composite starts to degrade at 310°C which indicates the compatibility and interfacial bonding between the PLA and CNF. The silane treated composite shows the thermal stability up to 305°C and saponin composite at 315°C. The main observed feature is the further increase in the thermal stability of the saponin nanocomposites due to the stable interfacial bonding between the CNF and PLA. The aromatic structure on the saponin backbone and the enhanced interaction between the saponin treated CNF and PLA matrix makes them more resistant to thermal degradation. The presence of silanols and the increased percentage of the oxygen atom in the silane treated composites make them more susceptible to thermal degradation. The thermal stability of the nanocomposites are in the order of APTES treated < untreated < Saponin treated composites.
The TGA performed to investigate the thermal stability of the produced materials showed that both nanofibrils and composites were thermally stable in the region between 25°C and ~300°C. The thermal analysis also showed that the saponin treated nanocellulose was able to improve the thermal stability of the PLA/CNF composite material to a considerable extent. The results from the thermal analysis indicated that the naturally extracted surfactant used in this study had a higher level of interaction with the PLA matrix as well as with CNF. As a result the amount and type of surfactant used to modify CNF have to be tailored for the biopolymer matrix used. The thermal analysis also indicated that saponin treated CNF have a large potential in improving the thermal properties of biopolymers.

5.2.8 Biodegradation analysis of nanocomposites

The biodegradation analysis of the PLA nanocomposites are done as per the procedure described in 2.2.18. PLA is fully biodegradable and the degradation occurs by hydrolysis to lactic acid, which is metabolised by micro-organisms to water and carbon dioxide. When biodegradation methods are considered, composting is the most preferred disposal route. Enhanced biodegradation of the nanocomposite materials may occur in the presence of the soil compost, a complex biological environment, in which microbial diversity is relatively high and where there is an increased degradation potential [23]. For the biodegradation study we placed neat PLA matrix and 4% CNF reinforced composites of untreated, silane and saponin treated samples. Biodegradation starts within two weeks under composting conditions, and the material fully degrades within 9-10 weeks. Ultimately, the success of composting is based on the microbial transformation of the composite material into an environmentally acceptable end product. In an environment of high humidity and a temperature of around 25-30°C, PLA polymers were found to degrade
rapidly [24]. Therefore, for the present study, temperature and moisture content of the soil was maintained at 25°C and ~60% respectively. In the biodegradation of PLA, moisture susceptibility is the primary driving force towards degradation and involves four steps, namely, water absorption, ester cleavage forming oligomers, solubilization of oligomer fractions, and diffusion of soluble oligomers by bacteria [25]. It was found that the onset of PLA degradation occurred as early as 2 weeks and was marked by the embrittlement of the samples. The slower degradation rate in the composites is due to the resistance in water uptake and diffusion through the composite compared to pure PLA, which readily takes up water. However, the weight loss was not very significant for PLA or the composites until 4 weeks in compost soil. The SEM image of the untreated and saponin treated (4%) nanocomposites after four weeks of biodegradation are shown in Fig. 5.9 (a) and (b) respectively. The deterioration of the biodegradable matrix (PLA) and reinforced CNF which is comparatively stable than PLA is clear from the figure. The crystalline part of the PLA was more resistant to degradation than the amorphous part which is initially subjected to the enzymatic attack [26].

![SEM image of untreated and saponin treated nanocomposite after four weeks of biodegradation](image)

**Fig. 5.9** SEM of (a) untreated and (b) saponin treated nanocomposite after four weeks of biodegradation
In Fig. 5.10, the residual weight percentage (Rw %) of the composites as a function of time (in days) in compost soil is shown. It was seen after the 70 days in the compost soil, the nanocomposites also showed marked degradation. After 30 days, all the samples showed rapid increase in degradation. The figure shows that the silane treated nanocomposites have a lower rate of degradation than the untreated and saponin treated nanocomposites. The saponin is naturally extracted which shows an increased rate for biodegradation than silane treated counterparts. This leads to the conclusion that PLA/untreated CNF nanocomposites are more susceptible to water and thereby more biodegradable followed by saponin and silane treated nanocomposites.

5.3 Conclusion

The chapter dealt with the goal of making sustainable novel ‘green nanocomposites’ by reinforcing nanocellulose (CNF) which is isolated from banana bast fibre by steam explosion process in a biodegradable matrix, poly-L-
lactic acid (PLA). The uniqueness of this study is that the resources for the green composites, even the surfactant is from naturally renewable sources, the matrix polylactic acid is from *corn*, fibres from *banana plant* and the surfactant saponin is from *sapindus tree*.

The surface modification of the CNF by *saponin*, a naturally extracted surfactant from soapnut fruit was done to compare the effect of modification on PLA matrix by a commercially available silane, APTES. The mechanism of interaction between CNF and chromosaponin of the saponin extract suggest that the main component of the *saponin* extract, chromosaponin, has made hydrogen bonded interaction with the nanocellulose. The aromatic ring with polar groups acts as a bridge between the hydrophilic nanocellulose and hydrophobic PLA. The resultant surface modified nanocellulose enhanced the filler-matrix interaction in PLA-nanocellulose composite and thereby it’s various properties.

The addition of untreated CNF increases the modulus, but the tensile strength of the untreated CNF reinforced PLA composite shows a gradual decreases with the filler percentage in comparison with neat PLA. There is a significant increase in the tensile modulus along with tensile strength when surface modified fibre has been used as reinforcement. For the notched impact strength, the silane and saponin composite with 4% filler gives impact strength as comparable with the 8% untreated PLA/CNF composite. The surface modification decreases the filler-filler interaction and increases the filler-matrix interaction and hence the modulus and the strength of the treated composites are high. For the thermal degradation analysis, the presence of silanols and the increased percentage of the oxygen atom in the silane treated composites make them more susceptible to thermal degradation. The thermal stability of the nanocomposites are in the order of APTES treated < untreated < Saponin treated
composites. The thermal analysis also indicated that saponin treated CNF have a large potential in improving the thermal properties of biopolymers.

The biodegradation analysis by soil composting proves that the silane treated nanocomposites have a lower rate of degradation than the untreated and saponin treated nanocomposites. The saponin is naturally extracted which shows an increased rate for biodegradation than silane treated counterparts. This leads to the conclusion that PLA/CNF with untreated nanocomposites are more susceptible to water and thereby more biodegradable followed by saponin and silane treated nanocomposites.

The advantages of these materials have been proved by the enhanced physical properties of the prepared nanocomposites. CNF as reinforcements in PLA provides interesting alternatives for the production of low-cost and ecologically friendly nanocomposites. The superior reinforcing function of treated CNF and PLA will expand the practical application of thermoplastic based materials as replacements for traditional petrochemical plastics [27].

5.4 References


