CHAPTER 7
DEVELOPMENT OF BIO-NANOCOMPOSITS OF POLY (VINYL ALCOHOL) REINFORCED WITH CELLULOSE NANOCRYSTALS ISOLATED FROM SAGO SEED SHELLS

Abstract

The present chapter deals with the optimisation of cellulose nanocrystals isolated from sago seed shells, being used as reinforcement in PVA matrix. The bio-nanocomposite films developed were characterized by FTIR, ATR-FTIR, XRD, DSC, TG, UV-Visible, SEM, and AFM. Mechanical and biodegradability studies were also carried out. FTIR & ATR-FTIR analyses show the incorporation CNCs into the PVA matrix. This is further supported by XRD and DSC. TG analysis shows a slight increase in thermal stability for lower concentration of CNCs. UV-visible spectra exhibited no reduction in the transparency of composite film compared to neat PVA film. SEM and AFM further support the distribution of CNCs into the matrix. Among the composites 0.75 wt.% CNCs showed the highest tensile strength. Biodegradation through weight loss, tensile strength and SEM show increase in biodegradability of bio-nanocomposites compared to neat PVA.
7.1 INTRODUCTION

Composites having desirable properties have been used in diverse fields in many applications. Traditionally composites are filled with macro sized fillers like carbon black, silica, glass fibres, natural fibres etc. Nanocomposites are multi-phase materials, in which one of the constituents has dimension less than 100 nm, thus nanoparticles give ample opportunities for the development of high performance composites [1]. Polymer nanocomposites consist of thermoplastics, thermosets or elastomers, reinforced with small quantities of nano sized particles. Due to the high specific surface area, nanocomposites present a large volume of interphase, with properties different from those of the bulk, which can impart remarkable properties to composites [2]. Thus the uniform distribution of nanoparticles leads to a very large matrix-filler interfacial area, changing the molecular motion, relaxation behaviour and thus ensuring better thermal and mechanical properties [3,4]. Therefore, replacement of traditional composites by nanocomposite materials has grown up during the last two decades to overcome the limitations of the traditional composites.

Cellulose is one of the most abundant natural biopolymers, can produce nanomaterials like microfibrillated cellulose (MFC) or nanofibrillated cellulose (NFC) by mechanical force and naocellulose or nanowhiskers by acid hydrolysis. The impressive mechanical properties, reinforcing capability, abundance, low weight, crystalline cellulose having axial elastic modulus than Kevlar, reactive surface -OH groups, amenable for modification and biodegradability make them ideal candidates for the processing of polymer nanocomposite at low filler loadings [5,6]. Bio-nanocomposites are composites reinforced with renewable nanoparticles like cellulose whiskers or MFC and petroleum-derived polymers like PP, PE,
epoxies, etc., or biopolymers like PLA and PHA reinforced with synthetic or inorganic nanofillers like carbon nanotubes, nanoclay etc [1,7]. When both the matrix and nano reinforcement are biodegradable, we can also have green bio-nanocomposites.

As already discussed in previous chapters, PVA is a well-known synthetic polymer of great industrial value with many desirable characteristics. PVA degrades in microbial active environments within 5–6 weeks [8]. PVA and PVA-based composites are used in a wide range of applications, including filtration materials [9], paper coatings [10], films [11,12], mats [13] and packaging materials [14], as well as in medical field [15]. However, the low mechanical strength and integrity of PVA demand the use of reinforcing agents, for example, carbon nanotubes, cellulose nano fibres, chitin whiskers etc [8]. Since PVA is biodegradable, the growing emphasis on environmental awareness and search for new material focus on eco-friendly materials which are renewable, recyclable, sustainable and triggered biodegradable [16].

PVA and CNCs being hydrophilic both can be processed in an aqueous medium. Interaction between matrix and filler gets improved, dispersion of filler will be easy and moreover, the composite will be environmental friendly.

Ramaraj and Poomalai 2005 prepared PVA composites reinforced with different wt.% of coconut shell powder by aqueous mixing. Weight loss measurements showed that the biodegradability increased as the filler content increases [17]. Bana and Banthia 2007 studied the effect of Piyasal wood waste as filler in PVA containing glutaraldehyde as crosslinking agent, the biodegradability tests showed that wood dust increased the biodegradability of composites [18]. The same authors in 2011 added maleic anhydride-
modified wood dust as reinforcement in PVA by solvent casting, and studied their properties. The results also showed that the presence of wood dust enhanced the biodegradability of polymer composites [19].

Cellulose whiskers were isolated from cotton linter using acid hydrolysis by Roohani et al.2008 and used as filler in PVA. The effect of PVA having different molecular weights and degree hydrolysis on whisker addition was studied by conditioning the composite at various moisture contents. The results showed that reinforcing effect increased when the degree of hydrolysis of the matrix increases. This leads to an increase in the glass transition temperature, decrease of both the melting point and degree of crystallinity of the polymeric matrix in dry atmosphere. But increase in $T_g$ was observed under humid condition on whiskers addition irrespective of degree of hydrolysis [20]. The effect of spherical nanocellulose, isolated from cotton linter and linen was studied by Ibrahim et al.2010, as reinforcement in PVA. Nanocomposite containing 20% of nanocellulose particles from linen increased the mechanical properties, while 40 and 60% resulted decreases in the tensile strength. The elongation at break of nanocomposite from linen is in the range 26.8–108.53%, but at 40% nanocellulose content, composites showed lower value than neat PVA [21].

Zhang et al.2011 used pan milling process to separate cellulose from bleached hardwood pulp fibers, used as reinforcement in PVA along with water and formamide as plasticizer. The tensile strength of cellulose/PVA composites increased from 8.8 MPa to 16.4 MPa, while elongation at break increased from 76.8% to 374%, when pan-milling cycles of cellulose increased. The composite exhibited enhanced thermal stability and better biodegradability [22]. Commercial MCC was used to isolate nanocellulose by Cho and Park in 2011 and used as reinforcement in PVA. The results showed
that as nanocellulose increases, tensile modulus and strength improved, but decreased for 7 wt.% of nanocellulose. DMA analysis showed improvement in storage modulus at 3 wt.% of nanocellulose. Thermal stability of the nanocomposite improved as the nanocellulose content increased up to 7 wt.% [23].

Ooi et al. 2012 prepared films reinforced with Rambutan skin waste flour in PVA by solution casting, with and without cross linker in presence of glycerol as a plasticizer. Biodegradability through weight loss showed that, weight loss of non-cross linked films was higher than those of cross linked films [24]. Lexmeshwar et al. 2012 studied the effect of modified cellulose using 2-(trifluromethyl) benzoylchloride by base catalysed reaction in PVA matrix. Soil burial test showed that composites have good biodegradation behaviour [25]. Zoltan et al. 2012 prepared composites of PVA containing bacterial cellulose (BC) and chitosan (CTS) as fillers. Biodegradation results showed a relative high degradation of the BC/CTS/PVA film than BC/PVA [26].

Fortunati et al. 2013 isolated CNC from Okra bahmia (Abelmoschus Esculentus) bast fibres and used as reinforcement in PVA. UV-visible spectra between 300 and 450 nm exhibited reduction in transmission, while at 650 nm showed constant transmission level of about 92%. TG indicated that maximum degradation rate was reduced with the addition of CNC to the PVA matrix up to 5 wt.% content. Moreover, at 5 wt.% cellulose content there was direct mechanical interaction between the PVA and cellulose structures [27]. Corn cob was used to isolate CNC using sulphuric acid at 45 ⁰C for different times by Alves et al. 2013 and studied their reinforcing capability in PVA. The composite containing nanocellulose with 60 minute hydrolysis duration showed an increase in tensile strength of 140.2% with 9 wt.% of CNC.
Moreover, visually the incorporation of CNC did not affect the transparency or homogeneity of the polymeric matrix [28]. Fortunati et al. 2013 prepared PVA bio-nanocomposites reinforced with CNC extracted from commercial MCC and from natural fibres, Phormium tenax and Flax. Thermal analysis of composites showed that, CNC promotes the crystallization of the PVA matrix and TG showed that maximum degradation rate reduced with the addition of 5 wt.% CNC. Moreover, CNCs resulted in an increase in tensile strength of about 45% for MCC derived CNC-PVA and flax derived CNC-PVA composites compared to the PVA matrix. All CNC-PVA composites remain transparent and showed saturation level after the first 18–24 h of water absorption [29].

Mizanur et al. 2014 isolated cellulose crystals (CC) from jute by chemical treatment followed by hydrolysis with 40% sulphuric acid and used as reinforcement in PVA. The tensile strength and modulus increased with CC up to 9% and decreased at higher loading [30]. Commercial MCC was used by Voronova et al. 2015 to isolate CNC and used as reinforcement in PVA. The results showed that thermal stability of CNC-PVA composites enhanced with CNC content of 8–12 wt.%, decreased when more than 12 wt.% CNCs content was used [31].

Since the morphologies of cellulose nanocrystals depend to a large extent on the source and method of preparation, this in turn determines the reinforcing ability of nano particle. Cellulose nanocrystals prepared from other sources can be tried to check its reinforcing ability. Fillers will have large impact on the physio-chemical properties of composite when the reinforcing ability changes. Therefore, the main objective of the present chapter is to investigate the effect of cellulose nanocrystals as reinforcement in PVA by developing bio-nanocomposites.
7.2 RESULTS AND DISCUSSION

7.2.1 Fabrication of bio-nanocomposite film

Solution casting technique was used for the fabrication of bio-nanocomposites. Since cellulose nanocrystals contain negative charges due to considerable grafting during sulphuric acid hydrolysis, they form stable suspension in aqueous medium. Therefore can be easily processed in water along with PVA, which is also water soluble. The detailed method of fabrication has already been given in Chapter 3.2. Bio-nanocomposites fabricated are listed in Table 7.1.

<table>
<thead>
<tr>
<th>Wt. of PVA (g)</th>
<th>Wt. % of CNC relative to PVA (g)</th>
<th>Composite films</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0</td>
<td>5PVA</td>
</tr>
<tr>
<td>5</td>
<td>0.5</td>
<td>5PVA-0.5CNC</td>
</tr>
<tr>
<td>5</td>
<td>0.75</td>
<td>5PVA-0.75CNC</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>5PVA-1CNC</td>
</tr>
</tbody>
</table>

7.2.2 FTIR and ATR-FTIR analyses

Figure 7.1 (a) shows the FTIR spectra of the PVA and Figures 7.1 (b), (c) and (d) show ATR-FTIR spectra of bio-nanocomposite. From Figure 7.1 (a) the frequency at 3404 cm\(^{-1}\) is due to the stretching vibration of its side hydroxyl groups, 2921 cm\(^{-1}\) is due to CH\(_2\) group stretching vibrations, 1712 cm\(^{-1}\) is due to C=O from residual acetate group or oxidation during manufacturing process present in the PVA. Frequency at 1435 cm\(^{-1}\) is attributed to O-H or C-H bending, or CH\(_2\) deformations. Frequency at 1093
cm$^{-1}$ is due to C-O stretching vibrations and 844 cm$^{-1}$ is due to skeletal and CH$_2$ rocking and they are characteristic of neat PVA.

**Figure 7.1** (a) FTIR spectra of PVA, (b) ATR-FTIR spectra of 5PVA-0.5CNC, (c) ATR-FTIR spectra of 5PVA-0.75CNC and (d) ATR-FTIR spectra of 5PVA-1CNC.

Comparing the **Figures 7.1** (a) with (b), (c) and (d), stretching frequency at 3404 cm$^{-1}$ of neat PVA get shifted to 3276, 3270, 3260 cm$^{-1}$ for PVA-0.5CNCs, 5PVA-0.75CNCs, 5PVA-1CNCs respectively, indicating the disruption of hydrogen bond existed in PVA film and possibility of formation of new hydrogen bond between -OH groups of PVA and CNCs due to sonication [27,29,32]. Moreover, the frequency at 1093 cm$^{-1}$ does not make any shift, because the sulphuric acid hydrolysis will introduce sulphate group on cellulose nanocrystals, which in turn impart repulsive effect. The intensity of the band in the region of 1093 cm$^{-1}$ increased with the addition of CNC to
the PVA matrix because of the contribution of C-O stretching from the cellulosic component [33].

7.2.3 XRD analysis

Figure 7.2 shows the XRD patterns of 5PVA film and 5PVA-CNC bio-nanocomposites. It was found that the XRD pattern Figure 7.2 (a) of 5PVA film contains a narrow peak at 2θ=19.4° and peaks at 2θ=22.0° corresponding to the semi crystalline nature of pure PVA [34].

![XRD patterns of (a) 5PVA film, (b) 5PVA-0.5CNC, (c) 5PVA-0.75CNC and (d) 5PVA-1CNC.]

From Figure 7.2 (b-d), it can be observed that diffractograms of the nanocomposite display the superposition of the characteristic peaks of the two components [31]. All the composites show strong peak at 2θ=19.4, 22.0 corresponding to PVA, suggesting that the crystal structure of PVA is essentially maintained even with the introduction of CNCs. Moreover, nanocomposites contains a diffraction peak at 2θ=11.5° due to the presence of
cellulose nanocrystals and becomes more pronounced when the CNCs concentration is increased [11,35]. The slight increase in crystallinity of PVA due to superposition of the peaks is further supported by DSC analysis.

7.2.4 Differential scanning calorimetry (DSC)

Figure 7.3 shows the DSC curves obtained for 5PVA film and 5PVA-CNCs bio-nanocomposites. Since PVA is a semi crystalline polymer, it has strong inter- and intra-chain interactions through hydrogen bonds in its structure [8]. Glass transition temperature (\(T_g\)), melting temperature (\(T_m\)) and heat of fusion (\(H_f\)) were determined for all the samples on the first heating scan. CNCs are highly crystalline and hence do not show any glass transition temperature (\(T_g\)) and no \(T_m\) for cellulose since it degrades prior to melting. As a result DSC thermogram mainly shows the PVA behaviour [36].

![DSC curves](image)

**Figure 7.3** DSC curves of (a) 5PVA film, (b) 5PVA-0.5CNC, (c) 5PVA-0.75CNC and (d) 5PVA-1CNC
From Figure 7.3 (a) 5PVA film exhibits sharp endothermic curve, with peak at 224.7 °C. There is also a specific heat increment observed around 75 °C, corresponding to $T_g$ [11]. From Figure 7.3 (b-d) $T_g$ values of nanocomposites are 76 °C for 5PVA-0.5CNC, 76.5 °C for 5PVA-0.75CNC and 77 °C for 5PVA-1CNC respectively. The $T_g$ values are slightly shifted to higher temperatures due to competitive interactions between PVA, water and CNC surface, ie., PVA/CNC and water/CNC interactions tend to shift $T_g$ towards higher temperature [20,37]. From Figure 7.3 (b-d) the melting temperatures are found to be 224.5, 224.2, and 224.1 °C for 5PVA-0.5CNC, 5PVA-0.75CNC and 5PVA-1CNC respectively. As the CNCs content increases the melting temperatures show a slight decrease indicating the incorporation of CNCs into the PVA matrix due to interactions between the CNCs and polymer matrix [8,20,31]. Crystalline domains are formed, by restriction in the polymer chains due to the interactions between CNCs and matrix [11,31]. This may lead to changes in crystallinity of host polymer matrix, because CNCs are able to promote the crystallization of the PVA matrix acting as heterogeneous nucleating agents [29]. The degree of crystallinity ($X_p$) of the composites was calculated using the Equation 7.1

$$X_p \, (\%) = \frac{\Delta H_f}{w \times \Delta H_f^0} \times 100 \quad \text{Equation 7.1}$$

Where ($\Delta H_f$) obtained from the area under the melting endotherms of each sample and $w$ is the weight fraction of the polymer in the composite. The value 161.6 Jg$^{-1}$ was used for the heat of fusion of 100% crystalline PVA ($\Delta H^0_f$) [20]. $T_g$, $T_m$ and the degree of crystallinity ($X_p$) are presented in Table 7.2. The degree of crystallinity was found to be slightly increased with the increase in CNC content [39].
Table 7.2  $T_g$, $T_m$ and degree of crystallinity ($X_p$) of 5PVA and PVA-CNC bio-nanocomposites.

<table>
<thead>
<tr>
<th>Polymer/bio-nanocomposite</th>
<th>$T_g$ ($^\circ$C)</th>
<th>$T_m$ ($^\circ$C)</th>
<th>$H_f$ (Jg$^{-1}$)</th>
<th>$X_p$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5PVA</td>
<td>75</td>
<td>224.7</td>
<td>54.3</td>
<td>33.6</td>
</tr>
<tr>
<td>5PVA-0.5CNC</td>
<td>76</td>
<td>224.5</td>
<td>56.0</td>
<td>34.87</td>
</tr>
<tr>
<td>5PVA-0.75CNC</td>
<td>76.5</td>
<td>224.2</td>
<td>58.04</td>
<td>36.17</td>
</tr>
<tr>
<td>5PVA-1CNC</td>
<td>77</td>
<td>224.1</td>
<td>58.25</td>
<td>36.04</td>
</tr>
</tbody>
</table>

7.2.5 Thermogravimetry (TG)

TG was used to study the thermal performance of 5PVA film and PVA-CNC bio-nanocomposite. All the films exhibited three distinct weight losses, initial weight loss in the region 70-140 $^\circ$C is due to evaporation of water, consistent with similar observations [11,31].

![Figure 7.4 TG curves of (a) 5PVA film, (b) 5PVA-0.5CNC, (c) 5PVA-0.75CNC and (d) 5PVA-1CNC.](image)
From Figure 7.4 (a) for neat 5PVA, the second stage degradation occurs at the range of 254-340 °C, due to decomposition of side chain of PVA mainly involving dehydration reactions and the formation of volatile products. From Figure 7.4 (b-d), the second stage degradation temperatures for nanocomposites are in the range of 257-346, 260-350, and 258-346 °C for 5PVA-0.5CNC, 5PVA-0.75CNC, and 5PVA-1CNC respectively. The onset thermal decomposition temperature \( T_{on} \) of PVA-CNC composites shifted slightly towards higher temperature, suggesting that the composite films had higher thermal stability mainly because of the presence of the crystal structure and interaction between CNCs and PVA [23,31,37]. The formation of additional hydrogen bonds between PVA and CNC, improves the decomposition temperature \( T_{on} \) in the second stage decomposition of composites. Among nanocomposite 5PVA-0.75CNC has slightly higher \( T_{on} \) due to higher interaction between CNCs and matrix. This is further supported by tensile strength measurement also. Above 500 °C, TG curves of all samples became flat, and mainly the residue remains. The third stage decomposition for 5PVA and for composites was found to be almost the same, which can be well understood from the DTG curves. The results obtained are presented in Table 7.3.

Figure 7.5 shows the DTG curves of 5PVA and bio-nanocomposites. From Figure 7.5 (b-c) the DTG\(_{\text{max}}\) of the PVA-CNCs composites shifted slightly to a higher temperature compared to that of pure PVA [Figure 7.5 (a)]. But for 5PVA-1CNC, the DTG\(_{\text{max}}\) was found to be slightly lower than the 5PVA-0.75CNC may be due to reduced interfacial adhesion accounting possible agglomeration. The DTG curve temperature can also be used as a measure of thermal stability, as all the DTG\(_{\text{max}}\) of composites move to higher temperatures after the addition of CNCs, indicating that CNCs improve the thermal stability of the composites [23,35].
Figure 7.5 DTG curves of (a) 5PVA film (b) 5PVA-0.5CNC, (c) 5PVA-0.75CNC and (d) 5PVA-1CNC

The decomposition temperature corresponding to the maximum weight loss shows that the thermal decomposition behaviour of the composites is similar to that of the pure PVA. DTG results of 5PVA and bio-nanocomposites are also presented in Table 7.3

Table 7.3 TG and DTG results of 5PVA and PVA-CNC bio-nanocomposites

<table>
<thead>
<tr>
<th>Polymer/Bio-nanocomposite</th>
<th>Second stage decomposition</th>
<th>Third stage decomposition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_{on}$ $^\circ\text{C}$</td>
<td>$T_{max}$ $^\circ\text{C}$</td>
</tr>
<tr>
<td>5PVA</td>
<td>254</td>
<td>340</td>
</tr>
<tr>
<td>5PVA-0.5CNC</td>
<td>257</td>
<td>346</td>
</tr>
<tr>
<td>5PVA-0.75CNC</td>
<td>260</td>
<td>350</td>
</tr>
<tr>
<td>5PVA-1CNC</td>
<td>258</td>
<td>346</td>
</tr>
</tbody>
</table>
7.2.6 **UV-Visible spectra**

The light transmittance (Tr) of the composite films were studied by recording the UV-Visible spectra from 200 to 900 nm, which are shown in Figure 7.6. The bio-nano composites films exhibited higher Tr values at the visible region (400–800 nm) than the ultraviolet region (200–400 nm). The Tr values of 5PVA and bio-nanocomposite films are 80-85% in the region 400 to 900 nm, indicating their good transparency.

![UV-Visible spectra graph](image)

**Figure 7.6** UV-Visible spectra of (a) 5PVA film, (b) 5PVA-0.5CNC, (c) 5PVA-0.75CNC and (d) 5PVA-1CNC.

From Figure 7.6 (b-d) it can be clearly observed that there is no much reduction in transparency of composites films especially in 400-900 region, because particles are too small to scatter visible light [27,29]. Moreover, bio-nanocomposites have shown no shift in bands, indicating no
charge transfer or chemical change takes place during the incorporation of CNCs [40].

7.2.7 SEM analysis

Figure 7.7(a) shows fractured surface image of 5PVA, (b) 5PVA-0.75CNC and (c) 5PVA-1CNC. The fracture surface morphological character of the prepared pure 5PVA film and 5PVA-CNC composites have been investigated by SEM analysis by dipping in liquid nitrogen and the images are shown as Figure 7.7.

Figure 7.7 Fractured surface SEM images of (a) 5PVA, (b) 5PVA-0.75 CNCs and (c) 5PVA-1CNC.

From Figure 7.7 (a) homogenous structure with smooth surface is observed for PVA film. From Figure 7.7 (b) evidences for uniform
dispersion can be observed. The small CNCs appear as white dots, which are distributed evenly throughout the matrix, but rough texture was observed at higher CNC concentration for 5PVA-1CNC [Figure 7.7 (c)] [11,20,41].

7.2.8 AFM analysis

Figures 7.8 (a-d) exhibit the AFM height images of 5PVA film and 5PVA-CNC bio-nanocomposites.

Figure 7.8 AFM height images (a) 5PVA film, (b) 5PVA-0.5CNC, (c) PVA-0.75CNC and (d) 5PVA-1CNC.

Figure 7.8 (a) AFM height image of 5PVA has light coloured regions which corresponds to crystalline regions and dark coloured corresponding to amorphous regions, indicating its semi crystalline nature,
which may arise from the random distribution of polymeric chains in an amorphous matrix [42]. Figures 7.8 (b-d) show some bright coloured spots and it becomes more pronounced when CNC concentration increases. This clearly reveals the surface morphological change during the incorporation of CNC into PVA.

Figure 7.9 AFM 3D images (a) 5PVA film (b) 5PVA-0.5CNC (c) PVA-0.75CNC and (d) 5PVA-1CNC

Figures 7.9 (a-d) represents the AFM 3D images of 5PVA film and bio-nanocomposites. Figure 7.9 (a), shows the AFM 3D image of 5PVA film, contains both amorphous and crystalline regions. Surface morphological changes of bio-nanocomposite films are visible in Figure 7.9 (b-d). As the concentration of CNC increases there is remarkable change in the surface due to the incorporation of CNC. For 5PVA-1CNC, from Figure 7.9 (d) more agglomerated structures were observed, which is further supported by SEM image Figure 7.8 (c)
7.2.9 Mechanical properties

7.2.9.1 Tensile strength

The mechanical behaviour of 5PVA film and bio-nanocomposites were evaluated, the tensile strength values are graphically represented in Figure 7.10. It is well known that the mechanical properties of composites depend on nature of the matrix, reinforcement and on their interfacial adhesion. Pure film gives an average tensile strength of 32 MPa. Among the bio-nanocomposite 5PVA-0.75CNC has the highest tensile strength of 55 MPa, at higher loading the tensile strength is found to be decreasing. The enhancement in tensile strength is due to uniform distribution and better filler matrix interaction. Increase in tensile strength of PVA reinforced with nanocellulose has been reported in number of earlier studies [11,21,28,35,43,44].

![Graph showing tensile strength of 5PVA film and bio-nanocomposites.](image)

**Figure 7.10** Tensile strength of 5PVA film and bio-nanocomposites.
The uniform distribution is further supported by SEM analysis also [Figure 7.7 (b)]. Since PVA is hydrophilic in nature, there is a strong interfacial bonding between hydroxyl groups of CNCs with polymer, resulting in an increase in tensile strength of the composite film. The reinforcing ability of CNCs is attributed to the formation of rigid CNC networks, in which stress transfer is facilitated by hydrogen bonding between the CNCs. Van der Waal’s interactions also shown to play a significant role. But CNC-CNC interactions can also lead to aggregation during the nanocomposite fabrication [45]. Therefore, at higher filler loading the tensile strength decreases. The formation of rigid network resulting from strong interactions between adjacent whiskers through hydrogen bonding was responsible for the mechanical behaviour of cellulose whiskers reinforced composites or the percolation of network held by hydrogen bonds. As degree of hydrolysis of PVA increases more –OH group in PVA chain results in the stronger PVA-CNC interaction [46].

7.2.9.2 Elongation at break

Figure 7.11 exhibits the elongation at break of 5PVA and bio-nanocomposites. The elongation at break is affected by the volume fraction of the added reinforcement, the dispersion in the matrix, and the interaction between the reinforcement and the matrix.
It can be seen from the graph as the CNC content increases the elongation at break decreases [46]. The reduced elongation at break with the addition of filler in the polymer, is a common phenomenon observed in thermoplastic composites [27].

7.2.10 Biodegradation studies

7.2.10.1 Weight loss

Biodegradability evaluation is very important for eco-friendly materials for their commercial application. There are methods like enzymatic, microbial and soil burial which are used for monitoring the biodegradation. Evaluation by soil burial is mostly based on the weight loss of materials referring to the erosion of molecules from the solid phase. The indoor soil burial test carried out in plastic trays sprinked with water helps the microorganism to grow and degrade the bio-nanocomposites. The molecules
leached from the bio-nanocomposite films might be CNCs or PVA metabolites such as low molecular organic acids and ketonic compounds. These molecules can be easily degraded by microorganisms. Figure 7.12 shows the weight loss of 5PVA and bio-nanocomposite after soil burial for 60 days.

![Figure 7.12](image)

**Figure 7.12** Weight losses during biodegradation of 5PVA and bio-nanocomposites

As shown in Figure 7.12 all the bio-nanocomposites exhibited increased weight loss than neat PVA, indicating their better biodegradability [19,22]. Since cellulose component in the nanocomposites films is consumed by the microorganisms faster than PVA there is faster disintegration of bio-nanocomposites [47]. The soil burial test provides indirect indications of biodegradation. Since the number of micro-organism that degrades PVA were limited, microbial attack occurs, especially in environments containing continuous contamination by the polymer [48]. Eventhough, soil burial is an
easy and efficient method, the difficulties in removing the soil adhered on the surface and inside the sample, which are difficult to extract without damaging the specimens may cause error in assessing the residual mass [49].

7.2.10.2 Tensile strength

Figure 7.13 shows the tensile strength values of 5PVA and bio-nanocomposites before and after soil burial.

![Figure 7.13 Tensile strength of 5PVA film, bio-nanocomposites before and after soil burial](image)

It has been found that invariably there is decrease in tensile strength of neat 5PVA film and bio-nanocomposites after soil burial. The reduction in tensile strength is due to the erosion of filler particle due to biodegradation and physical deterioration of the composites.
7.2.10.3 SEM analysis

The surface morphological characters of the neat 5PVA film and bio-nanocomposites have been investigated by SEM analysis and the images are shown Figure 7.14. SEM images after biodegradation is a useful method to analyse the level and extent of biodegradation.

Figure 7.14 (a) SEM surface images of 5PVA before soil burial, (b) 5PVA film after soil burial, (c) 5PVA-0.5CNC after soil burial, (c) 5PVA-0.75CNC after soil burial and (d) 5PVA-1CNC after soil burial.
From **Figure 7.13** (a), the surface SEM image of neat 5PVA film exhibit homogenous with smooth surface having no characteristic surface defects. From **Figure 7.14** (b) that of 5PVA after soil burial shows evidences for biodegradation, due to heterogeneous and uneven surface. All bio-nanocomposites presented morphological modifications after the soil burial test. In comparison with the surface images of the neat PVA films, bio-nanocomposites are considerably destroyed which can be clearly observed from **Figures 7.14** (c-e). The microbial attack on the sample surface leads to massive surface erosion, increase in surface roughness, formation of cracks, grooves and voids seen, which increase as the CNC concentration increases [50–52]. The SEM micrographs add testimony to the results obtained from tensile strength after biodegradation.

### 7.3 CONCLUSION

Bio-nanocomposites reinforced with cellulose nanocrystals isolated from sago seed shells have been developed and optimised for better properties. The FTIR and ATR-FTIR give evidence for the incorporation of CNCs into the PVA matrix through hydrogen bonding, having lower –OH stretching frequency than PVA. XRD shows the super position of peaks for bio-nanocomposites. DSC analysis of bio-nanocomposite shows that, there is slight increase in crystallinity due to interaction between PVA and CNC. Moreover, they show marginal increase in glass transition temperature and slight decrease in melting temperatures. XRD and DSC results support each other. The uniform distribution is supported by SEM and surface morphological changes during the reinforcement with different amount of CNC were shown by AFM analysis. TG data reveals the increased thermal stability in the second stage decomposition for 5PVA-0.75CNC and almost same stability for bio-nanocomposites at the third stage. Among the bio-
nanocomposites 5PVA-0.75CNC has shown highest mechanical strength and showed 71.8% increase in tensile strength than neat PVA film. The improved mechanical properties of the composites have been attributed to the uniform distribution of cellulose nanocrystals in PVA matrix and decreased at higher concentration due to possible agglomeration. Moreover, bio-nanocomposites film showed good transparency and there is no reduction in the transparency by the addition of CNCs. The biodegradability studies through weight loss, tensile strength and SEM analysis show that, bio-nanocomposites have better biodegradability than neat PVA.
REFERENCES


