Abstract

The major findings of the investigations on sago seed shells such as its composition, isolation of microcrystalline cellulose and cellulose nanocrystals have been summarised in this chapter. The fabrication of green composites of PVA reinforced with microcrystalline cellulose, bio-nanocomposites reinforced with cellulose nanocrystals and their characterisation using spectral, thermal, X-ray diffraction, morphological, mechanical properties and biodegradation have been consolidated. The utilization of bio-nanocomposites as barrier membrane has also been summarized. The scope for future studies based on the results of the present work has also been discussed.
Biomasses have been serving the civilisation from time immemorial in a number of fields, now investigated and exploited for the development of nanomaterials in diverse application. Biomasses are composed of polymers, oligomers, monomers, and other nonpolymerisable simple organic compounds, metallic salts etc. The major constituents present are cellulose, hemicellulose, lignins, pectins, extractives, inorganic compounds etc. Therefore, they are also referred as lignocellulosics. Among this cellulose, which is the most abundant biopolymer attracted much attention in recent years. The outstanding aspect of bio-mass or lignocellulosic material is their wide varieties which give ample opportunities in diverse fields. Traditionally they find use in households, production of charcoal, isolation various compounds and potential reinforcement in composites. Composite industries use different parts of plants and fruits of many agricultural crops as fillers. This gives non-food commercial applications to underutilized renewable materials. Another commercially important product obtained is microcrystalline cellulose (MCC) used in a number of fields. Since each application needs specific requirement, compositional analysis of biomass gains much momentum.

Synthetic polymers are considered to be the important gift of modern sciences and technology to mankind. They become unavoidable in our life owing to their wide range of applications in many fields such as packaging, agriculture, food, consumer products, medical appliances, building materials, industry, aerospace materials etc. However, the non-biodegradability has become the serious concern and severe environmental problems, including the difficulties in waste disposal have raised serious concerns all over the world. Therefore, the search for biodegradable polymer gains importance. Unfortunately, the degradable polymers available are associated with inferior
physical properties in terms of strength and dimensional stability, and above all most of them are expensive.

Therefore, there has been increasing demand for environment friendly materials with high performance at affordable costs in recent years with emphasis on renewable, recyclable, sustainable and triggered biodegradability. Since polymer alone cannot meet all the desirable properties they are often blended to achieve the required properties giving composites. Composites containing nanoparticle is another thrust area, they exhibit improved strength and stiffness, reduced gas and water vapour permeability and other intriguing desirable properties, opening opportunities for new high performance materials. Bio-nanocomposites, nanocomposites having biodegradable fillers like cellulose nanomaterials brought revolutions in material science in past few years.

Since PVA is the only carbon-carbon backbone polymer which is water soluble and biodegradable under both aerobic and anaerobic conditions, has the potential of being used as the matrix to produce biodegradable composites. Any source containing cellulose can be used for the isolation cellulose nanomaterials. There are two categories of cellulosic nanomaterials including microfibrillated cellulose and cellulose nanocrystals (CNC). The main objective of this study is to explore the possibility of using underutilised agricultural waste material sago \((Cycas circinalis)\) seed shells for the isolation of MCC and CNC. Moreover, MCC and CNC can be potentially used as filler in PVA to fabricate green and bio-nanocomposite.

Chapter 1 gives an account of general background of composites, natural fiber reinforced composites and nanocomposites. Special reference is given to cellulose nanomaterials and use of PVA as the matrix. Chapter 2 covers a review on MCC reinforced composites, isolation of nanocellulose
and cellulose nanomaterial reinforced composites. The materials and various experimental techniques used in the investigations are briefly discussed in Chapter 3.

Since there are no report on the composition of the sago seed shells, establishing the composition is necessary to decide the feasibility of getting cellulose in reasonable amount. Chapter 4 gives an account of establishing the composition of sago seed shells, isolation of microcrystalline cellulose and their characterisation. ASTM methods were employed to establish the composition of sago seed shells, extractives were determined by ASTM D1107-96, klason lignin was determined by ASTM D1106-96, holocellulose was isolated by method described by Wise et al 1946, α-cellulose determined as per ASTM D 1103-60, hemicellulose by difference between holocellulose and α-cellulose and Ash content by T 211 om 02. The results obtained are presented in the table below

<table>
<thead>
<tr>
<th>Name of component</th>
<th>Extractives</th>
<th>Klason lignin</th>
<th>Holocellulose</th>
<th>α-Cellulose</th>
<th>Hemicellulose</th>
<th>Ash content</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight %</td>
<td>8.2±1</td>
<td>23.6±0.8</td>
<td>59.0±1.2</td>
<td>36.5±1</td>
<td>22.5±1</td>
<td>9.2±0.2</td>
</tr>
</tbody>
</table>

Analyses show that it has reasonably good lignin content and high cellulose, therefore sago seed shells can be used as a potential source for the extraction of cellulose.

FTIR spectra show the presence of lignin, holocellulose and α-cellulose. TG also reveals the presence of holocellulose and α-cellulose. Sago seed shells are having reasonably good α-cellulose content compared with other agricultural waste materials. Therefore, α-cellulose isolated has been converted into MCC by treating with 2.5N HCl. α-Cellulose and MCC exhibited similar FTIR spectra, but –OH stretching frequency was found to
be slightly less for MCC. TG shows similar decomposition temperatures for MCC and α-cellulose, but a well-defined curve was obtained for MCC. XRD pattern of α-cellulose exhibited cellulose I structure, but small amount of cellulose II was also present in MCC and the degree of crystallinity was found to be increased due to the removal amorphous regions. SEM analysis of MCC reveals the presence of aggregated and non-aggregated fibres, further supported by TEM. AFM analysis of MCC shows the presence of some spherical shapes with non-uniform and rough surfaces. TEM and AFM results reveal the microstructural behaviour of isolated MCC.

Since MCC is hydrophilic in nature and only very few reports are available on MCC reinforced composites, composites are fabricated using MCC as the filler. Therefore, PVA which is hydrophilic, water soluble and biodegradable is the most suitable matrix to form composite with MCC. The development of green composites of MCC reinforced PVA and their optimisations for better properties are presented in chapter 5. Green composites of PVA reinforced with MCC have been developed by solution casting into a glass plate and their composition was optimised for better properties. The prepared film was labelled as 5PVA-1MCC, 5PVA-2MCC, 5PVA-3MCC, which contains 1, 2 and 3 weight % of MCC relative to PVA weight. The FTIR, ATR-FTIR, XRD and DSC analyses supports the incorporation of MCC into the matrix. TG also substantiates the incorporation by showing increased onset thermal decomposition temperature for 5PVA-1MCC than neat PVA. The tensile strength of 5PVA-1MCC composite films increased slightly due to uniform distribution of particles in the polymer matrix and decreased at higher loading due to possible agglomeration. The uniform distribution and agglomeration are further supported by SEM and AFM analysis. The composites have good transparency, however slightly lower than glass.
The morphology of cellulose nanomaterials depends on the nature of source and method of preparation. Eventhough, large number of sources have been used for the isolation of CNC, there are only very few reports for their isolation from seed shells. Isolation of cellulose nanocrystals from sago seed shells and their characterisations are given in Chapter 6. CNCs have been successfully isolated from sago seed shells by sulphuric hydrolysis. FTIR spectra of CNCs reveal similar frequencies as that of α-cellulose. XRD pattern shows the co-existence of cellulose I and cellulose II with crystallite size of 9.4 nm. TEM analysis showed that the isolated CNCs contain networked structures and almost spherical shaped particles having 10-15 nm in size. The reductions in size during acid hydrolysis were revealed by SEM. The size of nanoparticle from AFM analysis was found to be approximately 50 nm, containing almost spherical shape and other shaped CNCs. DLS measurement shows that the CNCs have an average particle size of 50.4±3.1nm and zeta potential of -37.8 mV. CNCs exhibited lower onset decomposition temperature and different degradation behaviour compared to α-cellulose as shown by TG.

The fabrication of bio-nanocomposites of PVA reinforced with CNCs and their properties are presented in Chapter 7. Since CNCs have very high modulus they can be effectively used as reinforcement in polymers to fabricate bio-nanocomposites. Bio-nanocomposites were fabricated by solution casting into a glass plate and optimised for better properties. The prepared film was labelled as 5PVA-0.5CNC, 5PVA-0.75CNC, 5PVA-1CNC, which contains 0.5, 0.75 and 1 wt.% of CNC relative to PVA weight. The FTIR and ATR-FTIR show the interaction of CNC with the matrix through hydrogen bonding. XRD pattern shows the super position of peaks for bio-nanocomposites. DSC analysis of bio-nanocomposites shows that, there is slight increase in crystallinity of PVA due to interaction between
PVA and CNCs. 5PVA-0.75CNC exhibited slight increase in onset decomposition temperature as revealed by TG. The uniform distribution was also supported by SEM. The surface morphological changes during the reinforcement were shown by AFM analysis. Among the bio-nanocomposites 5PVA-0.75CNC has shown highest mechanical strength of 55 MPa, while neat film has 32 MPa. Improvement in mechanical properties of the bio-nanocomposite is due to the uniform distribution of CNCs in PVA matrix. The tensile strength decreased at higher concentration due to agglomeration. Moreover, there was no reduction in the transparency of bio-nanocomposite by the addition of CNCs. The biodegradability studies by weight loss, tensile strength and SEM analysis show that bio-nanocomposites have better biodegradability than neat PVA.

The development of bio-nanocomposites as barrier membrane for packaging application is explored in chapter 8. Bio-nanocomposite has been developed as barrier membrane for packaging applications. The barrier properties of the membrane like water vapour transmission rate, moisture uptake and gas barrier properties were examined. Water vapour transmission rate and moisture uptake were found to be decreased as the CNC concentration increases, which show the resistance to moisture. However, bio-nanocomposite shown slight increase in oxygen transmission rate. Since the bio-nanocomposites meet the packaging requirements, the fabricated barrier membranes can be effectively used in place of PVA for better packaging application in consumer and agricultural fields. Many packaging applications demand certain barrier properties as well as mechanical resistance, therefore 5PVA-0.75CNC found to be better.
OUTLOOK

The present work gives opportunities for future investigators to look many aspects of green composites and bio-nanocomposites. Some recommendations for future research include:

- The oxygen transmission rate of bio-nanocomposites can be improved using hydrophobic nanoparticles. Moreover, this may also leads to further increase in water resistance while maintaining the other desirable properties like mechanical, thermal and biodegradability.

- Further investigations can be carried out on another cellulose source which has not been so far exploited.

- Cellulose can be isolated by other methods, since method of isolation has influence on the property of cellulose, MCC and CNC.

- MCC and CNC can be successfully used as filler in other hydrophilic matrices.

- MCC and CNC can be suitably modified and used as filler in different hydrophobic matrices.
APPENDIX

Refereed Journals


Conference Proceedings


Presentations
