DEVELOPMENT AND CHARACTERIZATION OF NATURAL GUM BASED NANOCOMPOSITE

By

MEGHANA ROSE JOSEPH

(2017-17-006)

THESIS

Submitted in partial fulfillment of the
requirement for the degree of

MASTER OF SCIENCE IN FORESTRY

Faculty of Forestry
Kerala Agricultural University

DEPARTMENT OF NATURAL RESOURCE MANAGEMENT
COLLEGE OF FORESTRY
VELLANIKKARA, THRISSUR – 680656
KERALA, INDIA
2019

DECLARATION

I hereby declare that the thesis entitled **"DEVELOPMENT AND CHARACTERIZATION OF NATURAL GUM BASED NANOCOMPOSITE"** is a bonafide record of research done by me during the course of research and that this thesis has not previously formed the basis for the award of any degree, diploma, fellowship or other similar title, of any other University or Society.

Vellanikkara

MEGHANA ROSE JOSEPH
(2017-17-006)

3

Dr. S. Gopakumar
Professor
Department of Natural Resource Management
College of Forestry
Kerala Agricultural University
Vellanikkara, Thrissur, Kerala

CERTIFICATE

Certified that the thesis, entitled **"DEVELOPMENT AND CHARACTERIZATION OF NATURAL GUM BASED NANOCOMPOSITE"** is a record of research work done independently by **Ms. MEGHANA ROSE JOSEPH (2017-17-006)** under my guidance and supervision and that it is not previously formed the basis for the award of any degree, diploma, fellowship or associateship to her.

Vellanikkara

Dr. S. Gopakumar
Major Advisor
Advisory Committee

CERTIFICATE

We, the undersigned members of the Advisory Committee of Ms. **MEGHANA ROSE JOSEPH (2017-17-006)**, is a candidate for the degree of Master of Science in Forestry, agree that this thesis entitled **"DEVELOPMENT AND CHARACTERIZATION OF NATURAL GUM BASED NANOCOMPOSITE"** may be submitted by her in partial fulfillment of the requirement for the degree.

Dr. S. Gopakumar
(Chairman, Advisory Committee)
Professor
Department of Natural Resource Management
College of Forestry
Kerala Agricultural University
Vellanikkara, Thrissur, Kerala.

Dr. K. Vidyasagaran
(Member, Advisory Committee)
Professor and Head
Department of Natural Resource Management
College of Forestry
Kerala Agricultural University
Vellanikkara, Thrissur, Kerala.

Dr. E.V. Anoop
(Member, Advisory Committee)
Professor and Head
Department of Forest Products and Utilization
College of Forestry
Kerala Agricultural University
Vellanikkara, Thrissur, Kerala

Dr. Nandakumar Kalarikkal
(Member, Advisory Committee)
Director,
International and Interuniversity Centre for Nanoscience and Nanotechnology,
Mahatma Gandhi University,
Kottayam, Kerala.

AKNOWLEDGEMENT

With great pleasure, I express my deep gratitude and obligation towards my supervising teacher **Dr. S. Gopakumar**, *Professor, Department of Natural Resource Management, who took a great risk by allowing me to study and work on an interdisciplinary subject, nanotechnology. I'm deeply moved by his efforts in taking forest nanotechnology to a next level and appreciate his amiable support and constant evaluation regarding the research so that I was able to finish my work within time.*

I extent my gratitude to **Dr. Nandakumar Kalarikkal,** *Director, IIUCNN for his guidance and allowing me to work at the international institute of great reputation with all the support and help from which I have greatly benefited throughout my period of research. Besides being a scientist of great reputation, he has always found time for patiently listening to my problems and helping me in all possible ways.*

I'm extremely grateful **to Prof. Dr. Sabu Thomas,** *Hon.Vice-Chancellor, Mahatma Gandhi University, who magnanimously allowed the use of his polymer lab and all the facilities available there widened my knowledge in the field of nanotechnology through his lectures. His hard-working spirit, multi-tasking and erudite knowledge have profound influence on me.*

I take this opportunity to render my thankfulness to **Dr. K. Vidyasagaran,** *Dean, College of Forestry for the academic support and the facilities provided to carry out the research work at the institution.*

I thank **Dr. E.V. Anoop**, *Professor and Head, Department of Forest Products and Utilization, for allowing me to use the Wood Science lab and helping me with my queries in bamboo processing and other wood related queries.*

I extend my sincere gratitude to **Dr. Hanna J Maria** *and* **Mr. Avinash R Pai**, *my mentors at IIUCNN, for helping me with my research and widening the horizon of* *knowledge by clearing my doubts and supporting in my quest regarding the subject and providing me with valid opinions and support throughout my time at the institute.*

I offer my special thanks to, **Mr. Vishnu R,** *Scientist, for his patience in clarifying my doubts and his support and encouragement through out the research. I acknowledge his optimistic thoughts and his interest in research which always inspired me to do my work better.*

I'm thankful to **Dr. Adarsh C.K., Mr. Pavin Praize Sunny, Ms. Vijayalakshmi K.P,** *my seniors for their support during the course of my research.*

I am grateful to research scholars **Nizam, Sisanth, Jesiya, Juvairia, Jibin and Prajitha** *for their encouragement throughout the work. I thank them for the great moments we had in the lab and institute.*

Words cannot express my deepest sense of appreciation to my classmates, **Harilal, Latha, Gayathri***,* **Jobin, Sarmishta, Wahiba, Anush** *and* **Sachin** *who have accompanied me to the field and helped me with the various aspects of my research work. I am indebted to all of them for the wonderful relation we share.*

I would like to thank the non- teaching staff, **Sindhu Chechi, Sujatha Chechi** *for their timely help in making available the resources required for the work.*

Last, but never the least, I would like to thank my family, my father **Dr. Joseph M.J** *who always inspired me with the world of scientific research and has always been a source of inspiration for me to carry out research on nanotechnology. My mother* **Dr. Sherly M.D** *who supported me in all possible ways to complete this research work. and my siblings* **Dr. Haritha Therese Joseph** *and* **Manu Joseph Makkolil** *who supported me and helped me.*

Above all I owe it all to Almighty for being my light at the need and giving me the health and strength to undertake this task and enabling me to complete it.

DEDICATED TO
MY FAMILY AND
FRIENDS

CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF PLATES

INTRODUCTION

1. INTRODUCTION

The Global Green New Deal initiated by the United Nations Environment Programme (UNEP) define greening of economy as "process of reorganizing businesses and infrastructure in order to bring better returns on natural, human and economic capital assets, together with cutting the greenhouse emissions, minimizing the use of natural resources, creating less waste and reducing social disparities". The Three main paths through which the wood and forestry sectors could be included in the green economy objectives are by means of biomass energy, green infrastructure and building and the particular role of forests as carbon sinks. The first two is related to the forest products whilst the last one is usually related to the resources. The increased use renewable biomaterials can be considered as a positive contribution to climate change mitigation as their usage can directly influence the use of non-renewable energy. The sequestration of carbon by the renewable biomaterials gives an additional benefit (FAO, 2009). Nanotechnology is one of the growing sciences that could contribute broadly to the green economy.

Nanotechnology is the study and application of minute particles that works extremely well across many areas, like chemistry, polymer science, biology, forestry, physics, materials science, engineering, environmental science etc for the betterment of the products or perhaps developing new materials. The broad range of application of polymer nanocomposites using glass, plastic and other synthetic components makes it one of the faster growing modern-day technologies. Nanocellulose continues to be considered as a potential material in the present times with regards to developing environmentally friendly materials and bettering the particular mechanical properties of synthetic compounds. Nanocellulose being produced from natural sources such as pineapple leaf fibre, bagasse, rice husk, cotton, coconut fibre, bamboo etc offers great potential. Forest sector has been a great source for natural fibres which are abundant source of cellulose, lignin along with other natural polymers. Cellulose is being isolated from potent forest weed species *Lantana camara,* from fast growing bamboo species and from trees such as Eucalyptus spp., Casuarina spp., *Melia dubia* etc which often are widely-used in paper and pulp industries.

Typically, the biopolymers obtained from natural resources have shown tremendous possibility to replace the fossil derived plastics and other non-degradable materials. The tree gums and other natural biopolymers are yet to be studied in these aspects. Not many studies have been done to characterize these types of materials obtained from natural resources at a chemical level to study their possibility of making materials and products. Based on the BCC research 2018 – 2019, the worldwide bioplastics market will be reaching 2.7 million metric tons by 2023 from 1.6 million metric tons in 2018, while the particular global market for biodegradable polymers hiked upto 484.7 kilotons in 2017 and in addition will be increasing up to 984.8 kilotons by 2022 (BCC research, 2018-2019). Biopolymers reinforced with nanocellulose have been the current trend of research with regard to developing edible films and packing materials.

A typical nanocomposite material is made up of reinforcement such as fillers (fibres, particles, flakes etc) embedded within a matrix (ceramics, polymers, metals,). Nanocellulose is probably the most| commonly used reinforcing material used in the preparation of biodegradable materials. The nanocellulose used for reinforcing can be taken from bamboo, jute, hemp, flax etc. The majority of the so-called biodegradable nanocomposites which make use of synthetic matrices like epoxy resin, metal oxides etc has its own adverse effect. However, after the particular| use of these products, their degradability in the environment is questionable. A completely biodegradable composite can be obtained if the matrix material is coming fromna renewable resource. For example, nanocomposites are developed from cassava starch and oil palm mesocarp cellulose nanowhiskers (Compos *et al*., 2017), Coconut micro fibre is used for improved reinforcement in natural rubber (Bibinbal *et al.,* 2017). Various other bio matrices used in this regard are agar starch and polylactic acid (PLA), chitosan, etc.

Bionanocomposites are materials, developed and fabricated from natural biodegradable polymers with organic or inorganic additives present in nanometer scale. Such kind of materials are capable for developing hybrid components for various biomedical applications that comprises of drug delivery, biosensors, and tissue engineering, where they are applied and designed to disappear itself from the body after use. Bionanocomposites are also being used in food packaging industries (Talegaonkar *et al*., 2016), bioplastic (Lagaron and Lopez, 2011), edible coatings for vegetables and fruits, etc. Water soluble biodegradable film made out of PVA/PVOH is used for making water soluble small dose product packets for agrochemicals, detergents, water treatment chemicals and dyes. Pre-measured water-soluble packaging provides ease-of usage and helps to prevent human exposure to the product being packed. Other than packaging use, the water-soluble films are also used for embroidery applications and for making laundry bags. Rapidly disintegrating drug delivery films for oral doses are also some of the particular applications of water dissolvable edible films (Takeuchiet *et al*., 2013).

Natural fibres are renewable and environmentally friendly materials; they have low density, reduced price and acceptable mechanical properties. Bamboo nanocellulose is one the widely used reinforcing material for the preparation of biodegradable products as it is an easily available and renewable natural resource. Resin extracted from forest trees has variety of uses based on the properties of the resin. Usage of these gum-resins as a suitable natural polymer matrix for the preparation of bionanocomposite can become a value addition of the resins. The physical properties of the resins and gums like pleasant smell, sticky nature, viscous properties etc may get incorporated into the composite. Along with some chemical modification to resins or gum the material can be made hydrophobic to make composite which can be utilized for packaging application.

Not much works has been done using natural gums and resins from tree species as a suitable natural polymer for the preparation of bionanocomposites along with the nanofibres. Since both the reinforcing material and the matrix are biodegradable as well as renewable resource, it has huge potential in the green economy. This study is hence proposed to throw light on these possibilities.

Being an edible polysaccharide with appealing properties such as film forming ability, babul gum extracted from *Acacia nilotica* (L.) Delile can become a suitable matrix for the nanocellulose. Considered as one of many agroforestry crops and a non-timber forest product raised in northern India, the biodegradable films made out of it can be viewed as a value addition of the gum. As an edible material, the gum along with other combinations can be used for edible coating of fruits and vegetables. The objective of this study is to develop and characterize a natural gum-based nanocomposite as well as to ascertain its selected mechanical and thermal properties.

REVIEW OF LITERATURE

2. REVIEW OF LITERATURE

The researches on biodegradable packing and biomedical materials has gained momentum in the recent time due to the apprehension on the pollution caused by non-degradable plastic packaging materials developed from the petrochemicals. The materials used in biomedical field also need our attention as these materials are required in abundant and non-degradable materials used in this regard cause serious environmental problems. Being annually renewable and environmentally friendly; polysaccharides, proteins and other abundant natural resources are potential replacement for plastic. Nanotechnology, which make use of particles at nano-scale has bought tremendous development in this field. The gradual replacement of petroleum-based packing materials is being achieved through the application of nanotechnology in natural resources and bio-based compounds.

2.1 BIOPOLYMERS

Biopolymers, considered as good alternative to plastic made from petroleum due to their decomposing ability, abundance and renewability (Liu *et al.,* 2005). These are biodegradable polymers composed of covalently bonded monomers forming a new molecule chain. Thus, biopolymers have the capability to degrade in the environment by the activity of microorganisms present in the surroundings leaving behind organic by-product like water and carbon dioxide which are non-toxic towards environment (Othman, 2014). The environmentally-friendly nature and the possibility in biomedical and food packaging application are the main reason for the increase in attention of biopolymers (Briassoulis, 2004). Natural polymer-based product packaging materials have great significance for ensuring stability, high food quality, safety being an innovative packaging and processing technology. The unique benefits of the natural biopolymer packaging facilitate to make products which can be used utilized for individual packing associated with particulate foods, drug delivery, carriers for functionally active substances, and dietary supplements. In active packaging the condition of the packaging are developed so as to prolong the shelf-life, enhance the safety or to add sensory properties by indicating particular changes that occurred to the material inside, while preserving the quality and standard of the foodstuff (Vermeiren *et al.*, 1999). Additionally, the edible films can be used to develop a soluble packaging for premixed food ingredients or additives that can perform as a distinct layer associated with individual food portion (Harnkarnsujarit and Li, 2017).

There are wide varieties of polymers which range from familiar synthetic plastics like polystyrene and natural biopolymers such as DNA, polysaccharides, proteins etc which are of fundamental to biological structure and function. Generally, polymers which are being widely-used as matrices that are obtained from renewable resources can be classified into three groups: (1) natural polymers such as starch, protein, cellulose, natural gums (2) synthetic polymers obtained from natural monomers, such as PLA and (3) polymers made through microbial fermentation, such as Polyhydroxy butyrate (PHB).

Although biopolymers meet environmental concerns, they also have reasonable restrictions with regards to the performance such as thermal resistance, barrier and mechanical properties, associated with costs. In order to make it more effective, numerous research efforts were developed to enhance the properties associated with the biopolymers. Through the studies carried out, nanocomposite is considered to be a promising route to enhance the mechanical and barrier properties of biopolymers. By means of composite production, many attributes of polymers from renewable resources can be enhanced (Eichhorn *et al.*, 2010).

2.2 NATURAL GUMS

The natural gum polysaccharides with interesting nanostructures and their chemical nature which are being applied in different aspects of water, food, biotechnology, energy, environment and medicine industries, have gained a lot of interest in the recent time. The gum because of their availability, renewability, diversity and impressive properties as 'green' bio-based renewable materials. Most of the gum obtained from variety of tree resources are non-toxic, edible, biodegradable and can be modified chemically according to the applications. The non-food applications of many important commercially available natural gums for the green synthesis and stabilization of metal/metal oxide nano particles, development of electrospun fibers, biosensors, synthesis of hydrogels, antimicrobial and biomedical applications are growing research interest in the recent years. The polysaccharides obtained from botanical, microbial, seaweed, and animal, origins etc are also comparable with the alike properties of tree gum exudates (Padil *et al.,* 2018).

Gum arabic is used as edible coatings which can delay ripening in tomatoes upto 20 days during storage at 20 ◦C without any negative effects on postharvest standards (Ali *et al.*, 2013). Apandi *et al.* (2013) has described a one pot method of synthesizing edible plastic by using gum Arabic as binder along with starch. In this method sorbitol and glycerol were used as plasticizers.

Gums are a group associated with plant products, formed mostly due to the breakdown of plant cellulose through a process known as gummosis. Large number of plant families produces gum but exploitation is restricted to a few tree species of Combretaceae, Sterculiaceae and Leguminosae families for commercial purposes. The major gum producing trees are *Acacia nilotica* (babul), *A catechu* (khair), *Butea monosperma* (palas), Steruculia *urens* (kullu), *Lannea coromandelica* (lendia), *Azadirachta indica* (neem), *Anogeissus latifolia* (dhawra) and *Bauhinia retusa* (semal). Gums are also being extracted from seeds of certain plants such as guar, tamarind, *Cassia tora* etc. Guar gum is one of the well-known seed based natural gum which is being used in pharmaceutical, textile and food industries.

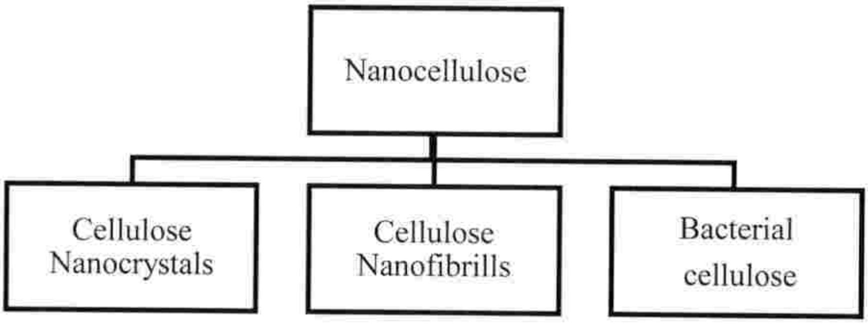
Natural gums contain of polysaccharides or their derivatives which are soluble in water or at least become soft and swollen when combine with water. On the other hand, these are not soluble in organic solvents. They decompose completely when temperature is increased without melting and tend to become charred. Most gums come from plants in a liquid form. They get dried up into tear-shaped, translucent, amorphous, bodies or flakes on contact with air.

Acacia nilotica (L.) Delile (syn. *Vachellia nilotica*) (Babul tree) is one of the major gum-producing acacia species present in the Indian subcontinent. It is often increasingly recognized as a potential commodity having varied pharmacological and commercial applications. Babul gum obtained from *Acacia nilotica* is closely related to gum arabic (*Acacia senegal*) which has commercial value and has been utilized from ancient times (Rukshana and Kazi, 2015). In a work done by Bhushette and Annapure in 2017, the physicochemical, thermal, functional and rheological attributes of *A. nilotica* (ANG) were verified and compared with commercially existing Arabic gum (AG). The presence of arabinose, galactose, and rhamnose in ANG and AG was determined from the sugar composition of the gums. However, ANG shows good resemblance with AG and can be replaced for varied applications in food as well as pharmaceutical industries.

2.3 NANOCELLULOSE

Nanocellulose is one of the environmentally friendly filler added to the composite as reinforcing agent to enhance the mechanical, thermal and barrier properties of biocomposites. Nanocellulose can be extracted from various type of biomaterials. Natural resources such as pineapple leaf fibre, bagasse, rice husk, cotton, coconut fibre, bamboo are being used for extracting nanocellulose applying different methods. Cellulose particles with at least one dimension in the range of 1–100 nm can be identified as nanocellulose. The dimension, composition, and attributes of nanocellulose depend upon the production conditions.

2.3.1 Types of nanocellulose



Based on the type of synthesis and conditions, which can determine its dimensions, composition and properties, the nanocellulose can be classified in to three types: Cellulose nanocrystals (CNC), Cellulose nanofibres (CNF), Bacterial cellulose (BC) (Asim, 2017). The CNC and CNF are products of top down approach of nanocellulose extraction whereas the BC is a product of bottom up approach, which makes it costly to produce on a large scale. Cellulose nanocrystals (CNCs) are commonly produced through acid hydrolysis of cellulosic materials dispersed in water. Usually, for this process concentrated sulfuric acid is used for making CNC which dissolves the amorphous parts of cellulose and the crystalline regions are left alone resulting in short, rod-shaped particles (Lu and Hsieh, 2012), while the CNF particles are obtained by the high pressure grinding of the pulp resulting in branched, longer and entangled network.

Bacterial nanocellulose (BNC) is obtained by the action of bacteria. *Acetobacter xylinum* is an example of bacteria used in this regard. BC is the purest form as it is made by joining molecules by molecules and there will not be any other binding materials like lignin, hemicellulose etc. The water absorbency, porosity, biodegradability in both dry and wet states, porosity of BNC makes it an potential component in varied applications (Kalia *et al.*, 2011).

2.3.2 Methods of extraction

Nanocellulose can be extracted based on the requirement and purpose for which is needed. Cellulose nano fibers can be obtained by three types of processes: (1) mechanical treatments (e.g., milling, homogenization and grinding); (2) chemical treatments (e.g., TEMPO oxidation); and (3) a combination of chemical and mechanical treatments.

Usually prior to the mechanical extraction a pre-treatment is done in order to reduce the consumption of energy and for increasing the production during the process. These pre-treatments can be done by various methods such as enzymatic hydrolysis where enzymes such as laccase which can degrade the lignin and hemicellulose contents without affecting the cellulose content; Alkaline- acid treatment where the fibres are treated with sodium hydroxide, hydrochloric acid to remove the lignin and hemicellulose; Ionic liquid treatment where fibres are treated with organic salts with certain properties that can be used as solvents of cellulosic materials. Li *et al.* (2012) treated sugarcane bagasse with 1-butyl-3-methylimidazolium chloride as ionic liquid followed by the high-pressure homogenization technique to make nanocellulose.

Mechanical process of nanocellulose include high pressure homogenization, microfluidization, Grinding, Cryocrushing, high intensity ultrasonication, Ball milling process (Zhang *et al.*, 2015). The pre-treated fibres or pulp are subjected to any one of the above process to get nanocellulose.

In chemical means various chemical catalyst are used for eg: TEMPO-mediated oxidation in which - 2,2,6,6-tetramethyl-1-piperidinyloxy radical (TEMPO) is used as an oxidation catalyst. The mechanically treated fibres are subjected to acid treatment to produce CNC. Acids such as sulphuric acid, hydrobromic acid, nitric acid are normally recommended for the CNC extraction. These acids remove the amorphous region present in the cellulose resulting in cellulose nano crystals (CNC).

An environmentally friendly method given by Abraham *et al.* (2013) with certain modifications. In the bleaching action, the absence of elemental chlorine which causes strong environmental problems is achieved by using $NaClO_2$. Several recent researches have used steam explosion to extract and fibrillate nanocellulose. Cellulose nanofibers of diameter in range 10 to 50 nm were obtained from wheat straw by applying alkali steam explosion technique combined with high shear homogenization (Kaushik and Singh 2011). Treated banana fibres along with alkaline-assisted steam explosion followed by bleaching and acid hydrolysis procedures, yielded cellulose microfibers with an average diameter of 1 μm (Deepa *et al.*, 2011). Cellulose nanocomposites with nanofibres isolated from pineapple leaf fibres are used in medical field. The nanocellulose was extracted from pine apple leaf by steam explosion method. It is said to be an effective method for the separation of nanofibres from biomass. Further, pineapple leaf fibres were used to isolate cellulose nano fibres with widths in the range of 5 to 60 nm using 2% NaOH and 11% oxalic acid assisted steam explosion along with bleaching process (Cherian *et al.*, 2010).

2.3.3 **Applications of nanocellulose**

Nanocellulose is considered to be potential material of modern times as it is being used in variety of fields such as electronics, medical, automobile, packaging, construction, and wastewater treatment applications (Mohammed *et al.*, 2018). In paper industry nanocellulose are being added for improving the strength parameters and to improve the quality of the paper than the same achieved through conventional refining process. Nanocellulose are being widely added as filler in composites to improve thermal, mechanical and other properties as well. Nanocellulose are being added to biodegradable polymers to increase the strength and rate of degradation. (Spence *et al.*, 2011). Due to its non-toxicity and biocompatibility, it is widely being used in biomedical researches and application. Wound healing scaffolds (Waghmare *et al.*, 2018), capsule encapsulation material, carrier for immobilization of enzymes etc are some of the supplication in biomedical field. One of the other promising application areas of cellulosic nanoparticles is barrier membranes due to its sustainability which can gradually replace the nondegradable materials used for the same application. Nanocellulose is observed to improve the excellent oxygen gas barrier properties of gelatin (Mondragon *et al.*, 2015).

2.4 BIONANOCOMPOSITES

Bio-nanocomposites are multiphase arrangement comprising of two or more components which are continuous phase or matrix such polymers or other materials and a discontinuous nano dimensional phase or nanofiller (<100 nm). The nano-sized fillers enhance the structural role in which they will work as reinforcement to improve the mechanical and barrier properties by combining with the matrix. The matrix tension is transmitted to the nanofillers through the boundary between them (Azeredo *et al.*, 2011; Othman, 2014). The discontinuous stage is normally harder and stronger compared to the continuous phase and is called the 'reinforcement' or 'reinforcing material', like: glass, natural fibres, flakes, fillers etc whereas the continuous phase is named as the 'matrix' such as polymers, metals, ceramics etc (Jose *et al.*, 2012). There are remarkable changes in the physical and mechanical properties such as the tensile strength, Young's module, shear strength, tensile strength of polymers mainly due to the addition of inorganic solid nanoparticles (typically in the form of fibres, flakes, spheres or other fine particles) as fillers and are explained by the huge surface area, which increases the interaction between the nanoparticle and the polymer (Šupová *et al.*, 2011). The boundary region between two phases in contact is known as interface. The composition, properties or structure of the interface may vary throughout the region and could also differ in composition, structure or properties of either of the two contacting phases (Schwartz, 1984), fibre and matrix. The physical and chemical factors has a crucial role at the interfacial region that exert a considerable influence in controlling the properties associated with reinforced composites. The interfacial interaction depends particularly on aggregation, fibre aspect ratio, strength of interactions, fibre alignment etc.

Development of completely natural based bionanocomposites with the addition of nanoparticles as fillers for the improvement of properties for packing application are explained by many authors. Dubey *et al.*, 2017 made environmental-friendly polymer nanocomposite material from PLA-Nano zinc oxide in different levels (0. 1, 0.3 and 0. 5%) of concentration. Neem essential oil were incorporated into the chitosan by solution cast approach to enhance the properties of the bionanocomposite film such as mechanical, barrier properties, thermal stability etc (Sanuja *et al.,* 2015). Completely biodegradable biocomposite films were developed from agar and mulberry pulp nanocellulose were the agar film properties such as mechanical and water vapor barrier properties were improved considerably by the addition of CNC (Reddy and Rhim, 2014). The green composite may be used for mass production of consumer goods with short life cycles of one or two years (nondurable) or products indented for one term or short-term use prior to disposal. A wide range of natural and synthetic biodegradable resins are usually available for using in green composites. Incorporation of nanocellulose improved the water vapour permeability (WVP) of the alginate films nanocomposites significantly showing a 31% decrease mainly due to 5 wt% NCC loading (Huq *et al.,* 2012). Bionanocomposite films are also prepared from agar and nanocellulose extracted from paper-mulberry pulp, in which the mechanical and thermal properties have improved after adding nanocellulose. (Reddy and Rhim, 2014). Completely biobased nanocomposite was developed with cellulose whiskers and chitosan as the matrix in which the tensile properties of the composite in dry and wet states increased from 85 to 120Mpa and 9. 9 to 17. 3 Mpa respectively (Li *et al.,* 2009).

Concentration of fibres in the matrix plays an important role in deciding the mechanical properties of the fibre reinforced polymer composites (Kutty and Nando, 1991). As the concentration of fibres is increased to a higher level, the tensile properties steadily improve to give strength higher than that of the matrix. Reactive nanofillers incorporated in biopolymers can function as sensors. Bio-nanocomposite materials used for the function of biosensor exhibit the ability to respond to contamination of food materials, modifications in our surroundings such as temperature, humidity, and levels of oxygen as well as to degradation (Azeredo *et al.*, 2012; Bouwmeester *et al.*, 2009).

2.5 APPLICATIONS OF WATER-SOLUBLE FILMS

Wate soluble edible film has got wide potential in biomedical and packaging field. The water-soluble films can be applied for separate packaging of small portions of food or agrochemicals that have got a one-time application. In biomedical field water soluble films are being used for wound dressing and wound healing application and also is a potential material for capsule coverings instead of the normal gelatin formulation that is available in the market. Fast dissolving oral films used for drug delivery are developed as an alternative to syrups and capsules for paediatric and geriatric patients (Arun *et al.*, 2010). It can aid patients unable to swallow tablets or hard gelatin capsules easily. In edible packaging the films can improve the organoleptic properties of packaged foods as long as they contain various components (flavorings, colorings, sweeteners). (Kadajji and Betageri, 2011)

2.6 CHARACTERIZATION TECHNIQUES

The basic characterization required to check the properties of the packaging material developed includes FTIR, UTM, TGA, Water vapour permeability, SEM, transparency, contact angle, antimicrobial properties ETC. The fiber characters like the length, thickness etc will be studied with the help of SEM (Scanning electron microscope/microscopy). After extracting nanofibres, it is mixed with the resin in different ratios of fibre to resin using agitator so that both are mixed evenly and a good composite is formed. The characterization of composite film will be done by using SEM by studying the change in the properties of the individual components in the composite. The mechanical properties like elasticity, tensile strength, shearing strength etc will be tested using UTM (Universal testing machine) and thermal properties by using thermogravimetric analysis (Khalil *et al.*, 2014) by obtaining temperature-mass curve and degradability rate.

MATERIALS AND METHODS

3. MATERIALS AND METHODS

The main objective of this study was therefore to develop a babul gum-based water-soluble film reinforced with nanocellulose isolated from bamboo fibre for improving the mechanical and thermal properties of the films suitable for the applications. For this, cellulose nano fibre were isolated from bamboo fibres and characterized by using sophisticated techniques such as Fourier transform infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray diffraction (XRD).The babul gum-based films reinforced with cellulose nano fibres were prepared by following solution casting method (Reddy and Rhim, 2014) and their thermal and mechanical properties were tested using TGA and UTM respectively.

3.1 MATERIALS

The babul gum is obtained from the tree *Acacia nilotica* .L Delile (Syn. *Vachellia nilotica*) present in the deciduous forests of peninsular India. The material required the experiment was obtained from local markets of Khandwa, Madhya Pradesh. And the bamboo required for extracting nanocellulose was obtained from Bambusetum of Kerala Forest Research Institute, Veluppadam, Thrissur. Chemicals used for isolating nanocellulose and for nanocomposite preparation include Sodium hydroxide, Acetic acid, Oxalic acid, Sodium hypochlorite, Sodium sulphide, Sodium carbonate, all of analytical purity.

3.2 ISOLATION OF NANOCELLULOSE FROM BAMBOO

For the isolation of fibres, 6-year-old culm of *Bambosa Bambos* was harvested and cut at three nodes apart using hydraulic cutter and the bamboo skin was removed with help of skin and knot removing instrument. The bamboo pieces were then sliced into small pieces with the help hand knife. And was dried in hot air oven at 45-50°C for 24hrs. In steam explosion method, the fibres treated with chemicals were kept in autoclave at high temperature and pressure was suddenly released to defibrillate the fibre for the extraction of nanocellulose.

3.2.1 Kraft process

Kraft process is widely used in paper and pulp industries for removing the lignin content before the preparation of cellulose fibre. The dried bamboo fibres was soaked in Sodium hydroxide (103.2gm), Sodium sulphide (25.2gm) and Sodium carbonate (34.2 gm) for 1L solution. This mixture is known as white liquor. The beaker containing fibres soaked in white liquor was kept in vertical autoclave for 2 hrs at 10-15 bar pressure at 100° C. The lignin that gets separated in this process was kept aside and the fibres were taken for further treatments.

3.2.2 Alkali treatment

The Kraft treated fibre was then treated with 5% NaOH at 10 bar pressure for 1hr. This process was repeated 2 times. After each step, new solution of NaOH was used to soak the fibre. The lignin in the fibre gets dissolved in the solution and was removed in each step.

3.2.3 Bleaching

The alkali treated fibres were bleached using solution A and solution B. Solution A consisted of 250ml Sodium hypochlorite and 750ml distilled water. Solution B consisted of 74ml Acetic acid, 26g NaOH and 900 ml distilled water. Both the solutions were mixed in 1:1 ratio and the alkali treated fibres were soaked in the solution and autoclaved at 10 bar pressure for 1 hour. The process was repeated 5 times. After the beaker has taken out from the autoclave during each bleaching step, the bleaching solution was removed and new solution was poured into the beaker.

Plate 1. Bamboo processing

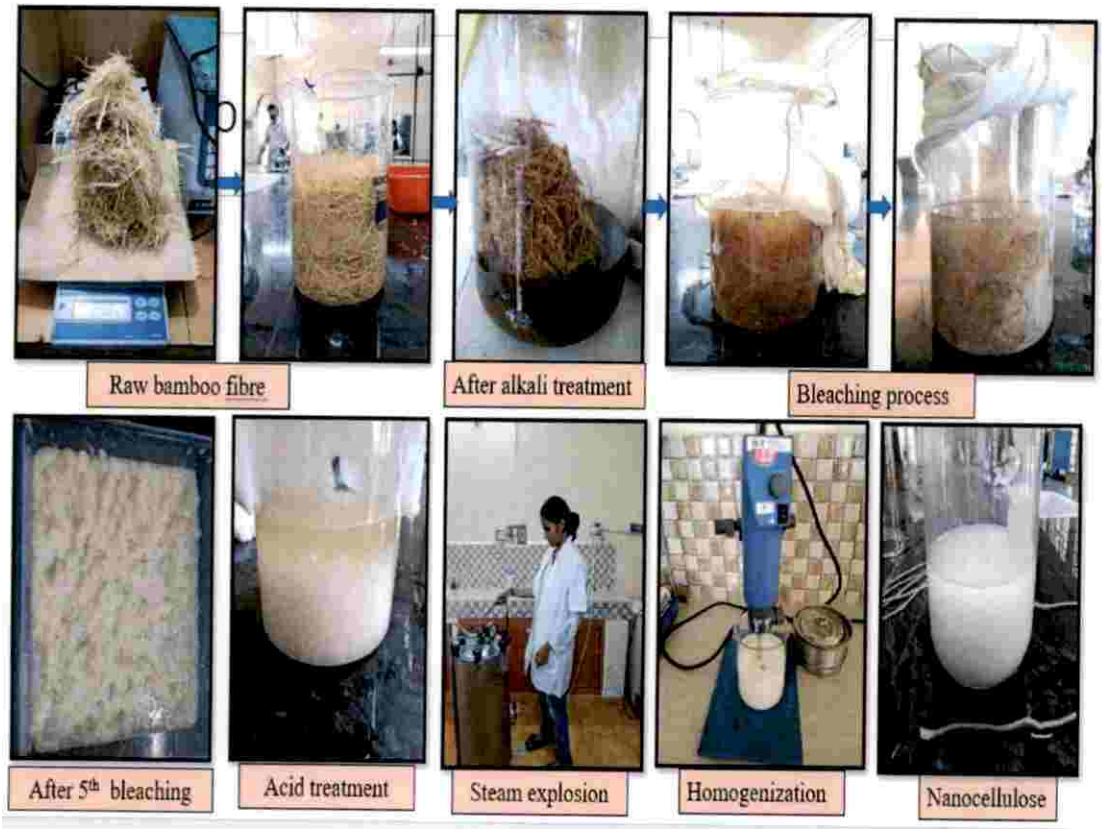


Plate 2. Nanocellulose extraction

3.2.4 Acid treatment

The bleached fibres were washed with distilled water till the pH became neutral. Oxalic acid was used for acid treatment of the fibres. 10g of oxalic acid was mixed in 100ml distilled water for obtaining 10% oxalic acid and it was poured to the beaker containing washed fibres after bleaching. The beaker was kept in autoclave and steam explosion was carried out. When the pressure inside the autoclave reached 10 bar it was maintained as such for 10 minutes and the pressure was suddenly released. This process was repeated 10 times.

3.2.5 Homogenization

Homogenization was done after washing the acid treated fibres using distilled water till the pH reached neutral. Homogenization was done using IKA®- T25 digital ULTRA TURRAX® homogenizer at 10000 rpm for 15 min. The sample was kept in air tight containers till further characterization.

3.3 CHARACTERIZATION OF NANOCELLULOSE

The nanocellulose isolated using steam explosion from bamboo was characterized using various methods like SEM, TEM, XRD, TGA, FTIR to study in detail about its chemical, thermal, crystalline properties etc.

3.3.1 Fourier transform infrared spectrometry (FT-IR) analysis

FTIR spectroscopy was used to investigate the chemical bonds via vibrations in the infrared frequencies in range of 400 cm^{-1} to 4000 cm^{-1} (Model: Thermo Nicolet, Avatar 370). Atoms or molecules present in the materials are in continuous motion with regard to one another. The subtle interactions with the surrounding atoms or molecules impose the stamp of individuality in the spectrum of each compound. Each chemical bond with several vibrational modes can absorb several frequencies with different intensities. They vibrate about some mean position. IR spectrum of a compound is the superposition of absorption bands of specific functional groups. IR absorption has numerous applications in qualitative and quantitative analysis. The stretching vibrations cause stronger absorptions of IR radiation than the bending vibrations. The absorbed frequencies are characteristics of chemical bonds hence it can be used for the identification of functional groups. Graph was plotted with wavenumber vs transmittance using Origin Pro software for further analysis.

3.3.2 Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) is a method used for high resolution surface imaging. Surface imaging of the material is done using an electron beam. The advantages of SEM over light microscopy is that SEM has much larger depth of field and greater magnification. The morphology of the cellulose fibres at different stages of isolation was observed using Scanning Electron Microscopy (SEM) analysis in JEOL Model JSM - 6390LV/ JED-2300. Samples were gold sputtered in an argon atmosphere. Analysis was carried out at 20KV with 20 μm magnification.

3.3.3 X-Ray Diffraction

The diffraction patterns were obtained at diffraction angles between 5° and 50° with a scanning rate of 0.4°/min at room temperature using XRD analysis. The diffraction patterns were obtained at diffraction angles between 5° and 50° with a scanning rate of 0.4°/min at room temperature. The degree of crystallinity (DC) of bamboo fiber and the CNF was calculated using following equation (1) (Hasan *et al.*, 2019)

$$DC = [(I_{200} - I_{AM})/I_{200}] \text{ x } 100 \tag{1}$$

where I_{200} is the intensity of the 0 0 2 peak (at $2\theta = 22^\circ$) and I_{AM} denotes the intensity of the peak at $2\theta = 16^\circ$. And crystallite size (D) of the fiber was calculated with Scherrer equation (Reddy and Rhim, 2014)

$$D = K\lambda/\beta_{1/2} \cos \theta \tag{2}$$

where K is a constant (0.94), $\beta_{1/2}$ is the full width at the half maximum of the deflection peak (FWHM), θ is Bragg's angle and λ is the X-ray wavelength ($\lambda = 0.1546$ nm).

3.3.4 Transmission Emission Microscopy (TEM)

The determination of shape and size of cellulose nanofibres is an important challenge and transmission electron microscopy (TEM) is one of the most powerful tool used in this regard. The TEM image of steam exploded nanocellulose was taken using JEOL JEM-2100 electron microscope.

3.3.5 Thermogravimetric Analysis (TGA)

The degradation of the material according to varying temperatures was determined using TGA analysis at 0-400°C temperature range. The degradation of the material was recorded. Weight (%) vs Temperature (°C) graph was plotted using Origin Pro 8 software.

3.4 PREPARATION OF NANOCOMPOSITE

Babul gum and babul gum based nanocomposite film were prepared using solution casting method following the method of Reddy and Rhim (2014). Babul gum film was prepared by dissolving 3g of babul gum in 100 ml of distilled water with sorbitol as plasticizer. The solution was heated at for 30 min at 85°C on magnetic stirrer (IKA® C-MAG HS 7) and was sieved through white cloth to remove the impurities and plasticizer was added and again stirred for 5min. The solution was casted on to a petridish lined with OHP sheet. The sample was kept for overnight drying at 35°C in hot air oven. The concentration of gum and plasticizer was standardized through preliminary tests that has been carried out.

38

3.4.1 Standardization of sorbitol

The standardization of sorbitol was done by taking 10%, 50%, 80% (w/v) of sorbitol to the weight of the gum taken. (Table:1) The plasticizer was added to the gum solution and was casted in a petridish and kept for overnight drying in hot air oven at 35°C. the film formation, stickiness of the film, ability to peel off the film etc were noted.

Table: 1 Combinations gum and nanocellulose used in the experiment

No.	Combinations
1	3g Gum + 10% sorbitol
2	3g Gum + 10% sorbitol + CNF 1%
3	3g Gum + 10% sorbitol + CNF 3%
4	3g Gum + 10% sorbitol + CNF 5%

3.5 CHARACTERIZATION OF NANOCOMPOSITE

3.5.1 Thermal stability

Thermal properties of bamboo fiber, CNF, babul gum and babul gum/CNF composite films was determined using a thermogravimetric analyzer (Perkin & Elmer). TGA analysis provide details about the thermal stability of the material ie, temperature at which the material is stable or there is no change in mass. In this material characterization technique, mass of a material is measured against function of time or temperature. The temperature range at which test should be conducted is determined by looking into the nature of the material. TGA gives the upper temperature beyond which the material starts to degrade. The range used in this experiment is from 0 to 400°C, as the material is completely organic. Around 10mg of the sample was used for conducting the test. The graph obtained from TGA analysis is plotted as weight against temperature using Origin Pro8 software. The char content and the weight loss (%) were measured using the TGA curve. Thermal stability denotes the ability of a material to retain the required properties such as strength, toughness, or elasticity at a given temperature.

3.5.2 Mechanical properties

The tensile and elastic properties of the nanocomposite film was tested using the Universal testing machine (Tinius Olsen) model H50KT, at cross head speed of 10mm/min, according to ISO 527 on dumbbell shaped specimens of size 75x10 mm. Tensile properties such as elastic modulus (EM), elongation at break (E), and tensile strength (TS) of each film samples were evaluated (Rhim, 2011).

3.5.3 Scanning Electron Microscopy (SEM)

SEM images of nanocomposite was taken to see the alignment of bamboo fibres in the gum matrix, observed using SEM analysis in JEOL Model JSM - 6390LV/ JED-2300.

3.5.4 Contact angle

The contact angle of the samples were tested using Phoenix model contact angle analyzer. Films were cut into 2 cm × 2 cm size and a drop of distillated water was used for the analysis of hydrophilicity of the sample. The value of contact angle was measured and expressed in degrees.

3.5.5 Moisture content of the films

Moisture content (MC) present in babul gum and gum/CNF films was found out through oven dry method (Rhim and Wang, 2013), with slight modifications. The films were cut into square pieces of 3 cm × 3 cm and later dried at 105 ◦C for 24 hrs

40

using a drying oven. The MC was calculated from the weight loss and expressed as percent moisture content.

3.5.6 Water solubility of the films

Water solubility of babul gum films was measured by following the method of Zhang *et al.*, (2016) with slight modification. Film samples of size 2 cm × 2 cm put into the beakers were dried at 90 ◦C for 12 hours, and the weigh was taken. These samples were immersed in 50 ml of distilled water for at 25 ◦C for 20 minutes. Subsequently, the undissolved pieces were poured on to filter paper and the residues were dried at 90 ◦C for 12h until constant weight was obtained. Water solubility of Babul gum films was calculated using Eq. (3):

$$\text{WS (\%)} = \frac{m_1 - m_2}{m_1} \text{ X } 100 \qquad (3)$$

where m_1 and m_2 are the initial and final dried weight of Babul gum film samples, respectively.

3.5.7 Statistical Analysis

Measurements of films for each property were analysed with three replicates individually prepared film samples as the experimental units, and mean values with standard deviations (SD) were calculated. One-way analysis of variance (ANOVA) was performed, and the significance of each mean property value was determined ($p < 0.05$) with the Duncan's multiple range test using SPSS, a statistical analysis computer program for Windows.

Plate 3. Nanocomposite preparation

Plate 4. Films made using solvent casting method

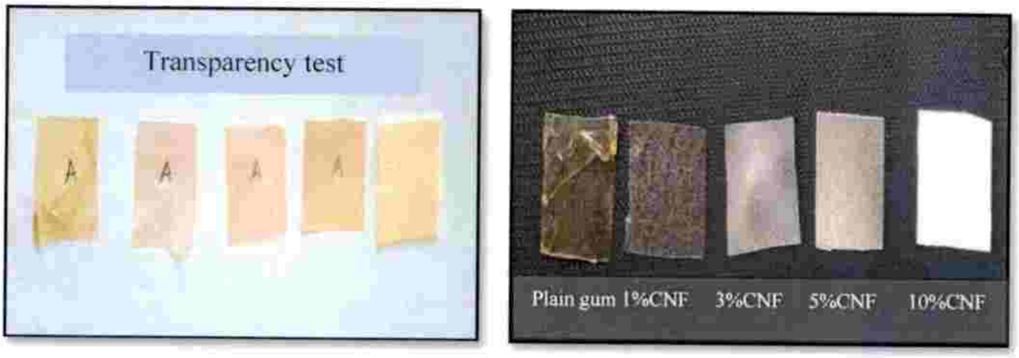


Plate 5. Plain gum film and Nanocomposite films with difference concentration of CNF

RESULTS AND DISCUSSION

4. RESULTS AND DISSCUSSION

4.1 CHARACTERIZATION OF NANOCELLULOSE

4.1.1 Fourier-transform infrared spectroscopy analysis (FT-IR)

Fourier-transform infrared spectroscopy analysis was used for understanding the chemical changes that has occurred in raw bamboo fibre after alkali treatment, bleaching and acid treatment. The analysis was taken at a range of 650 cm^{-1} to 4000 cm^{-1}. The gradual chemical changes that has occurred during nanocellulose extraction starting from the basic raw material to the final nanocellulose was analyzed from the FTIR graph by identifying peaks for different functional groups present. From the graph (Fig.1) it is evident that there are variations in the FT-IR peaks of raw fibre and CNF due to the formation and removal bonds during the course of extraction.

The typical peaks at the range of 900cm^{-1}-2000cm^{-1}can be attributed to that of a carbohydrate. Strong band at 3312 cm^{-1} are due to the stretching vibration of hydroxyl groups (-OH). The decrease in intensity of hydroxyl group in the CNF when compared with raw fibre is due to the alkali treatment which reduces the hydrogen bonding as given by Reddy and Yang (2005). Band at 2894 cm^{-1} could be due to C-H stretching. Bands at 1639 cm$^{-1,}$1509 cm^{-1},1428 cm^{-1},1370 cm^{-1} and 1160 cm^{-1} corresponded to absorbed water, aromatic asymmetric stretching of lignin, bending vibration of CH_2 groups, C-H groups of aromatic rings and C-O-C linkages in lignin. Furthermore, absorption peak that can be seen around 1024 cm^{-1} was assigned to C–O–C pyranose ring stretching vibration as given by Mandal and Chakrabarty (2011) and the vibrational peak at 896 cm^{-1} was due to characteristic of glycosidic bonds. Some peaks at 1509 cm^{-1},1428 cm^{-1}, 896 cm^{-1} tends to disappear or decrease in intensity after the bleaching. It is mainly due to the removal cementing compounds such as lignin, hemicellulose, pectin etc present in the raw fibre in agreement with previous studies (Mondragon *et al.*, 2015; Yang, *et al.*, 2017).

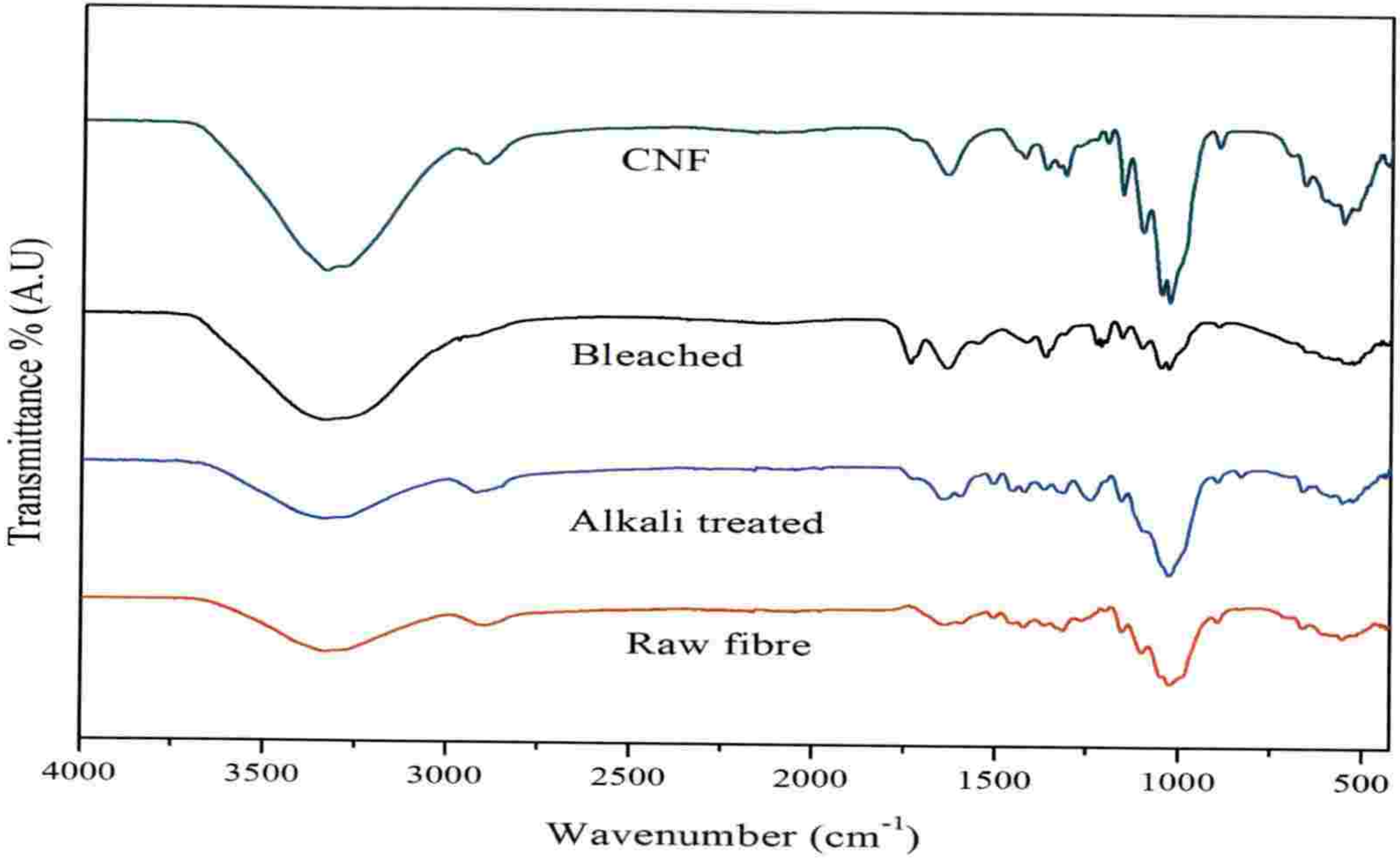


Figure 1. FT-IR spectra of (A) Raw fibre (B) Alkali treated fibre (C) Bleached fibre (D) CNF

45

4.1.2 X-Ray diffraction analysis (XRD)

The X-ray patterns of bamboo raw fibre and cellulose nano fibre extracted from bamboo are given in Fig 2. The crystalline nature of the cellulosic material and raw fibre was analyzed through X-ray diffraction. The degree of crystallinity of bamboo fibre and its CNF estimated using Scherrer equation (Eq.1) were 41% and 54.46 %, respectively. There has been an increase in the crystallinity of the fibre in each stages of isolation. The increase can be due to the removal of lignin, hemicellulose and other compounds from the fibre. The crystallite size of bamboo raw fibre and that of nanocellulose (calculated with Eq .2) are found to be 1.99 nm and 3.8 nm respectively which was in confirmaion with the works of Mohammed *et al.*,2018; Hasan *et al.*, 2019 using the same method. The crystallite size of nanocellulose can be confirmed from the TEM images. The changes in cryslallite size of cellulose fibres after acid treatment has been reported by Maiti *et al.*, 2013.

Table 2. Degree of crystallinity of raw bamboo fibre and CNF

Angle (2θ)	**Intensity (I) (a.u)**	**Degree of crystallinity (%)**
Raw bamboo fibre		
16.22	4147.20	41%
21.68	7030	
CNF		
16	4057.50	54.46%
22.18	8910	

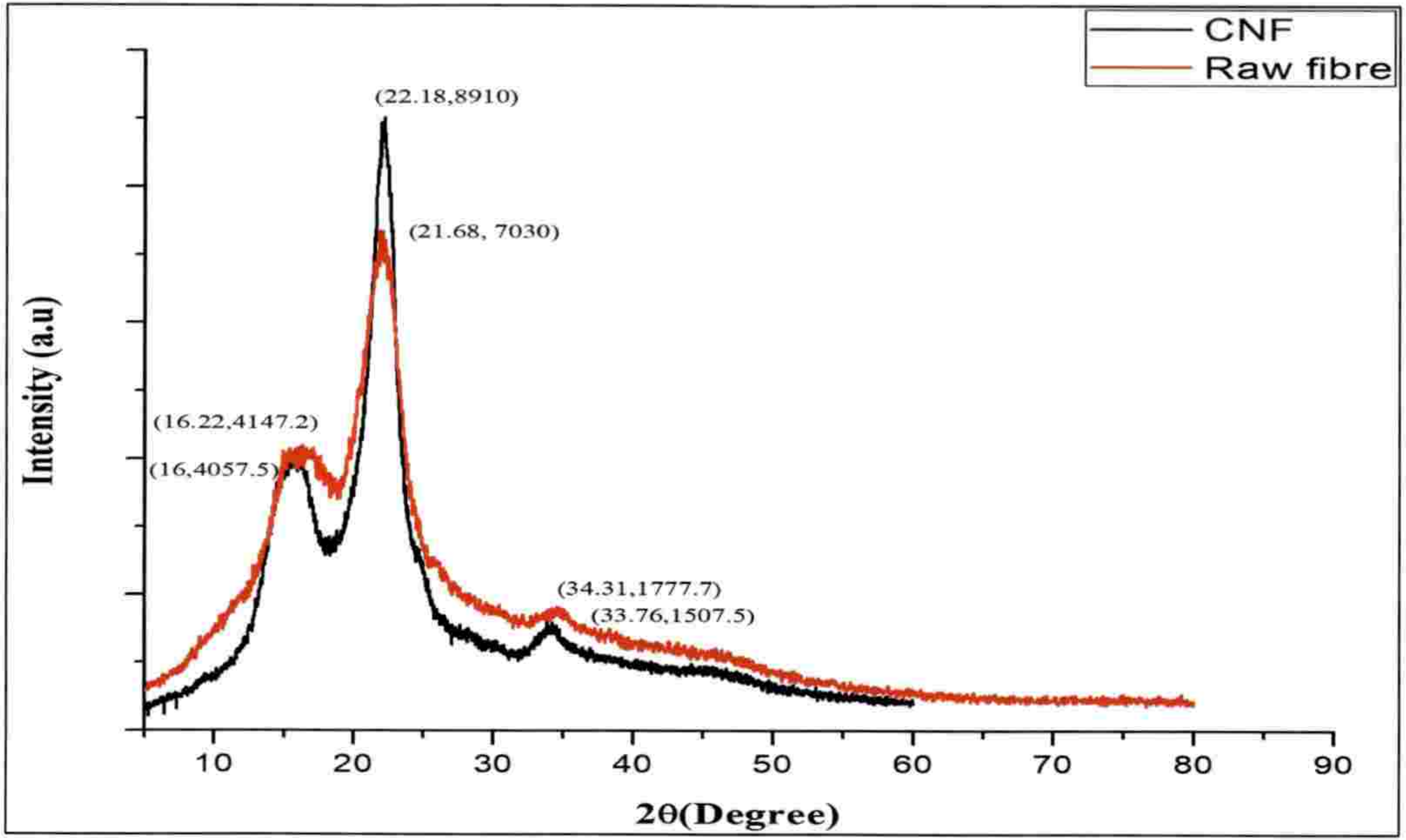


Figure 2. XRD patterns of Raw bamboo fibre and Nanocellulose

47

4.1.3 Thermogravimetric analysis (TGA)

TGA is used for the study of thermal characteristics of the material. It measures the weight loss of the material as a function of temperature. The thermal properties of raw bamboo fibre and that of cellulose nanofiber was tested using TGA analysis. There are two important weight loss regions at 50-100°C and 200-350°C. The initial weight reduction occurred at a temperature range of 50-100°C can be attributed to the removal of water molecules and other low molecular weight compounds (Saelee *et al.*, 2016). The major thermal degradation occurred at a temperature range of 250-350°C. As described by Yang, *et al.* (2017), it is mainly due to the disintegration and pyrolysis of the three major component of the material such as cellulose, hemicellulose, and lignin present. At this range cleavage of glycocidic linkage of cellulose occurs. A distinct decrease in weight occurs at a temperature of about 270° C which can be explained with the lower thermal stability of hemicellulose which makes it decompose before cellulose and lignin. The presence of acetyl groups explains the lower thermal stability of hemicellulose. (Deepa *et al.*, 2011).

From Fig .3 and Table. 3 The rate of degradation of CNF occurs at 265 °C and reach maximum at 311.6 °C while the degradation of untreated fibre becomes evident at 215 °C and the rate of degradation reaching its peak at 296.2 °C. As explained by Mandal and Chakrabarty (2011), the early onset of degradation of the raw fibre is attributed to the low degradation temperatures of non-cellulosic constituents such as lignin, hemicellulose. In the CNF, i.e., pure cellulose, however, the removal of all these non-cellulosic materials helps to make the cellulose structure denser and more compact and hence the rise in the onset temperature of degradation. At 350 °C 41.1% of the raw fibre and 24.7% of the CNF residue remains. In spite of the initial low temperature degradation of non-cellulosic constituents, the high percentage of raw fibre residue at 350 °C, when compared to CNF is probably due to the presence of more amount of crystalline cellulose I having parallel orientation. Before acid hydrolysis the cellulose contains more of less crystalline cellulose II (having antiparallel orientation) and amorphous cellulose. The further hike in percentage of residue in case of CNF after the first step of degradation can be attributed to amorphous and crystalline regions of cellulose which are intrinsically flame resistant (Roman and Winter, 2004).

Table 3. Peak temperature (°C) of 5%, 10%, 15%, 20%, 25% mass loss of raw fibre and CNF

	Peak temperature (°C)				
Sample	**5% weight loss**	**10% weight loss**	**15% weight loss**	**20% weight loss**	**25% weight loss**
Raw fibre	215	263.3	277.7	287.6	296.2
CNF	265.8	292	302	307.6	311.6

4.1.3 Morphology of raw, alkali treated and acid treated fibres

The morphology of the raw, alkali treated and acid treated fibres was observed using Scanning Electron Microscopy (SEM) and Transmission Emission Microscopy (TEM) analysis. The scanning electron micrographs of bamboo nanocellulose were used to study the morphology of the material. SEM images taken at different stages of extraction process helped to understand the changes that has occurred during the process in the fibre morphology. From the SEM image of raw fibre (Plate. 7) it has been noted that the surface is rough and the particles are intact and the parallel arrangement of the fibres are visible. During further process of alkali treatment (Plate. 8) the particles started to defibrillate due to the removal of other organic particles such as the non-cellulosic cementing compounds which holds the fibre intact. The size of the particles are reduced after the alkali treatment. In previous studies it has been shown that during the alkali treatment most of the lignin and hemicellulose were

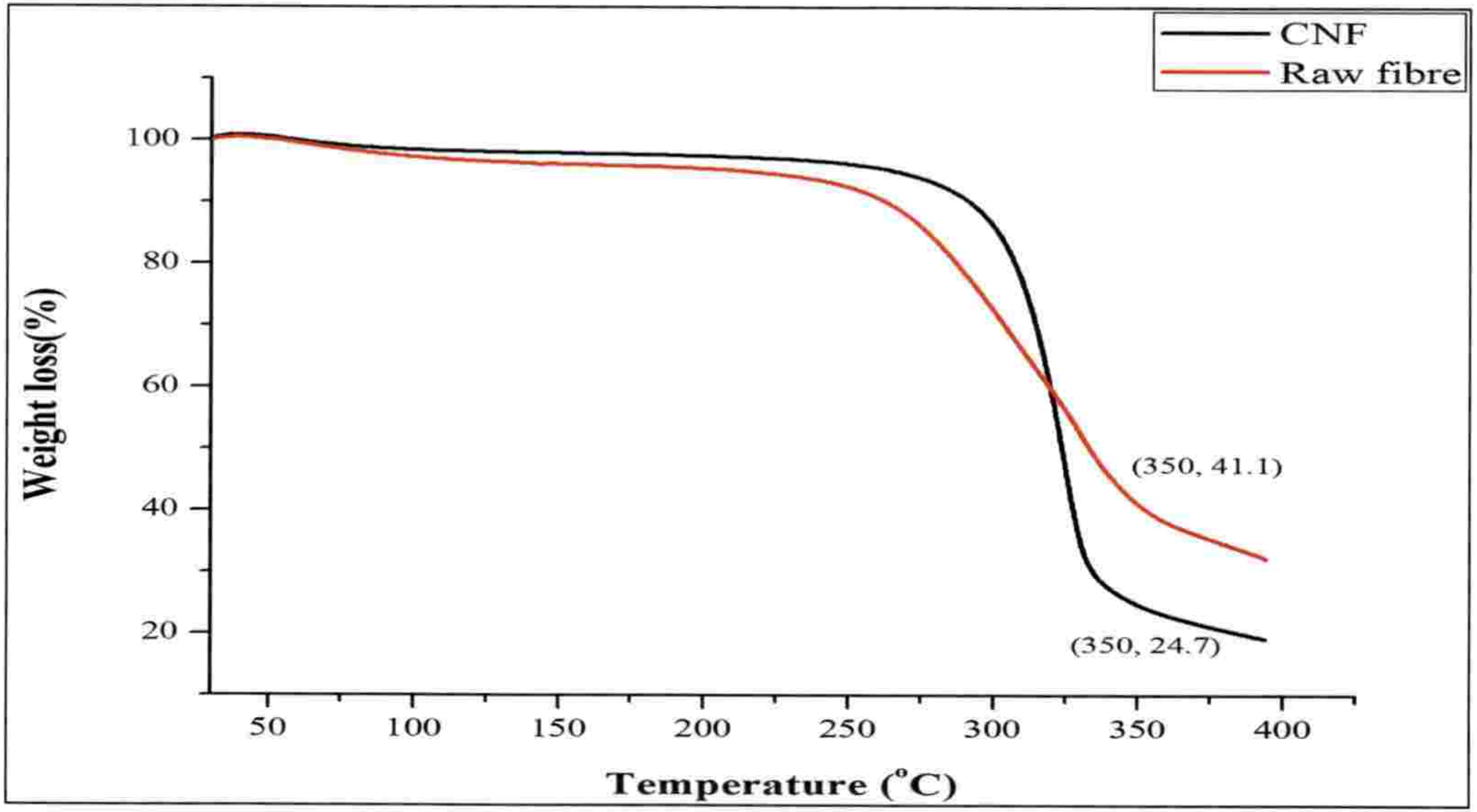


Figure 3. TGA graph of CNF and raw fibre

removed. During the bleaching step most of the non-cellulosic particles are removed and further defibrillation of the fibre occurs which result in reduced size and network like alignment of the fibre. After the steam explosion size of the fibres are reduced due to the hydrolysis effect of the mild acid used. The fibres form a smooth surface and adhere to each other as seen the SEM images. (Plate. 9,10)

The TEM images were used to verify the nanostructure of the fibre. The TEM images of cellulose nano fibres revealed a network arrangement in size ranging from 1-100nm. The nanofibers were obtained after the steam explosion followed by homogenization of bamboo fibres which reduced the particle size further than that of raw and bleached fibres. It has been observed that the size of the nanoparticle varies with raw material used and type of extraction method adopted. The TEM images (Plate.6) established that the diameters of most of the CNFs were less than 100 nm. The aspect ratio (fibril length to the diameter ratio) is an important parameter in determining reinforcing ability of the nanofiber (Cherian *et al.*, 2010). These images showed CNFs that were slightly agglomerated due to the re-bonding of the hydroxyl groups present in the chains (Chirayil *et al.*, 2014).

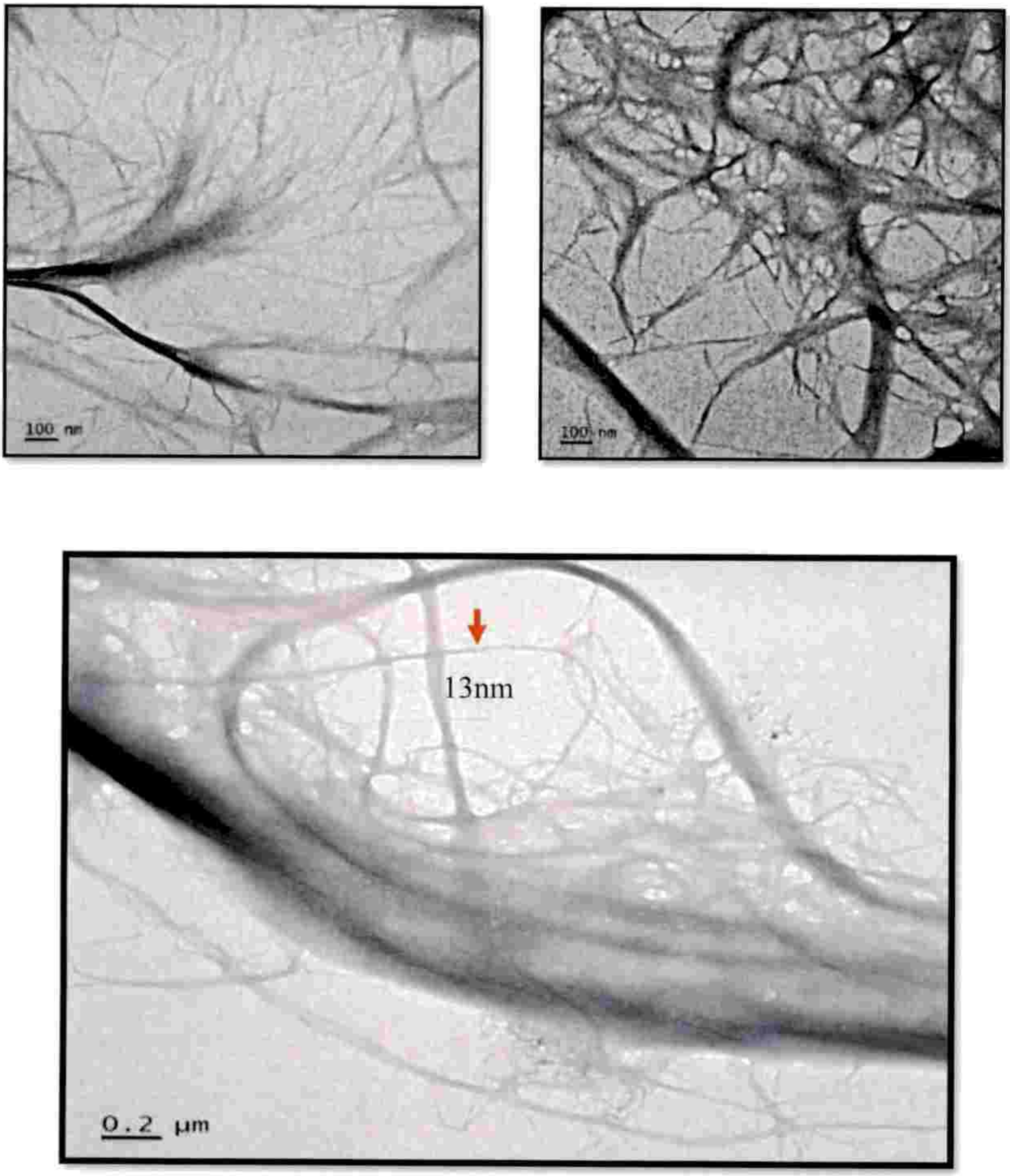


Plate 6. TEM images of CNF

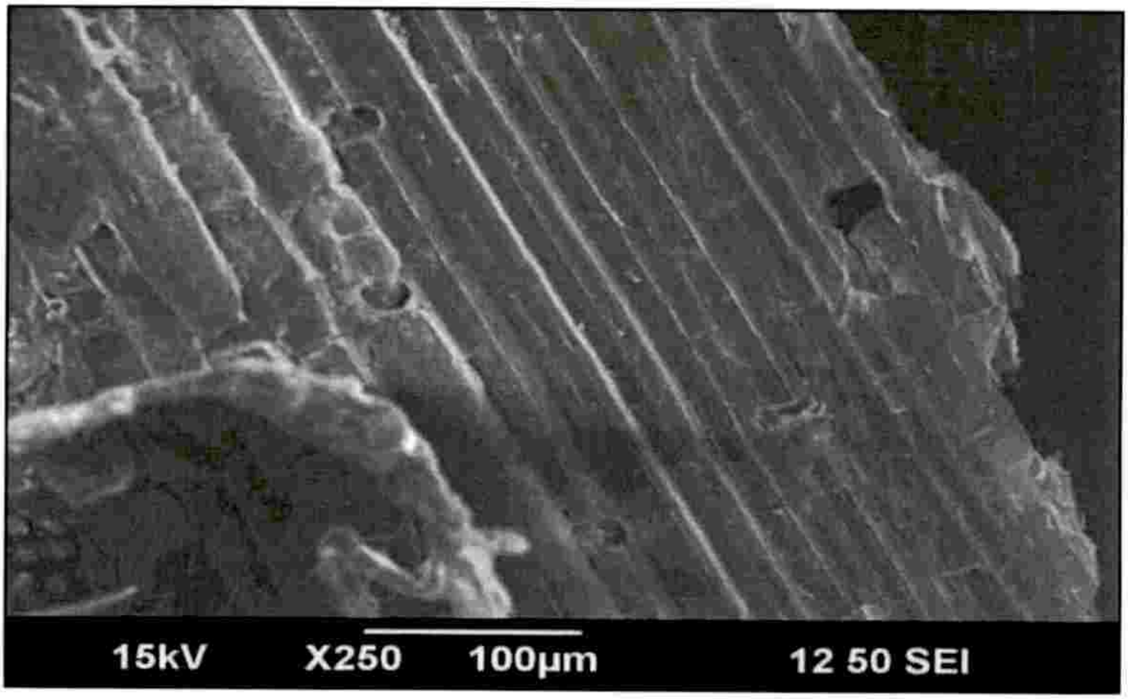


Plate 7. SEM image of raw bamboo fibre

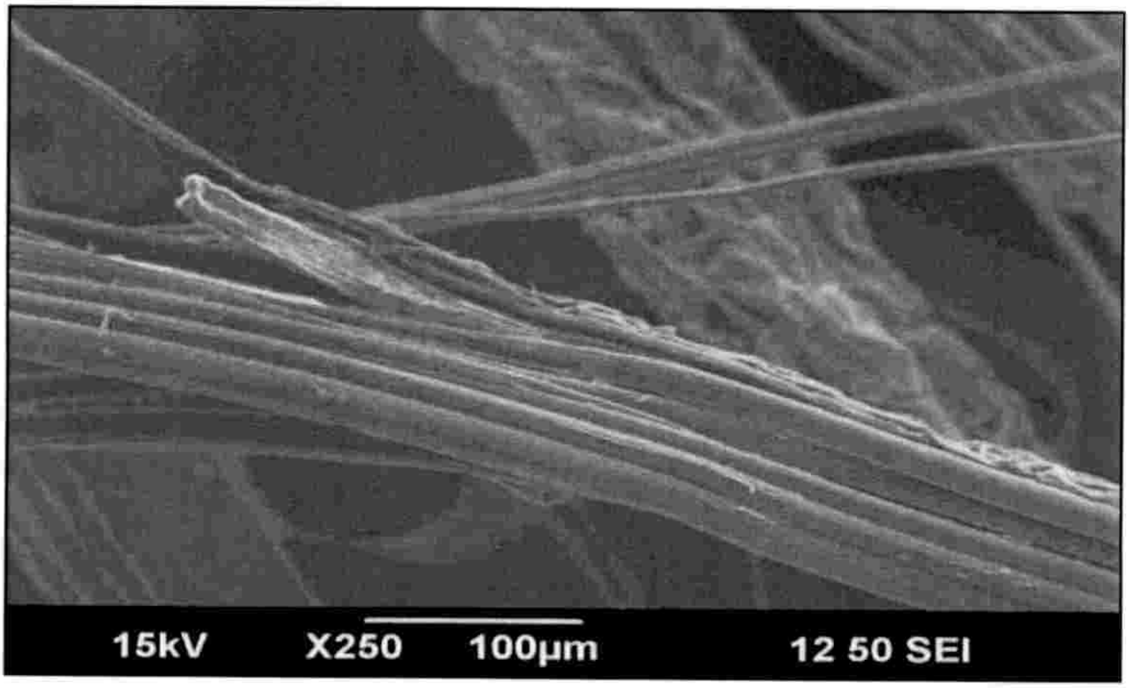


Plate 8. SEM image of alkali treated fibre

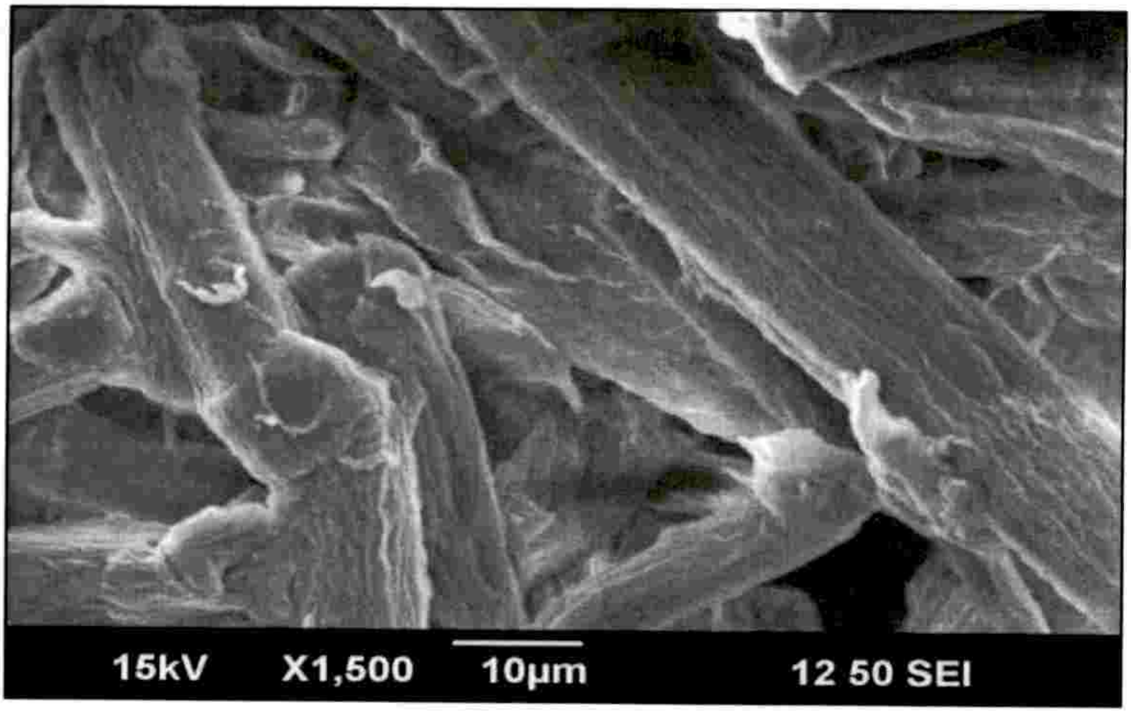


Plate 9. SEM image of bleached fibre

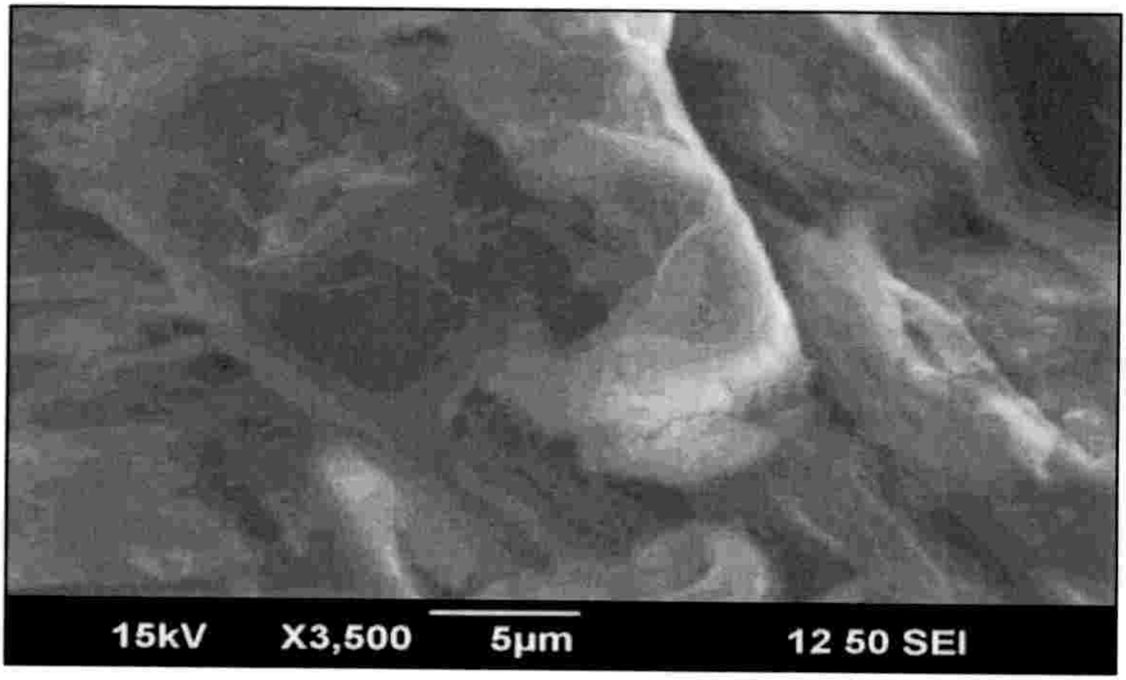


Plate 10. SEM image of steam exploded fibre

54

4.2 STANDARDIZATION OF PLASTICIZER

Sorbitol was used as plasticizer for preparing the films. The concentration of sorbitol was standardized using trial and error method and the characteristics of the films obtained were noted for further experiment.

Table 4. Standardization of sorbitol for composite preparation

Concentration of Sorbitol used for film making	**Characteristics of the film formed using solvent casting technique**
10%	Non-sticky, Film formation, can be peeled from petridish, semi transparent
50%	Sticky, not able to peel off even after completely dried, semi transparent
80%	Sticky, not able to peel off even after completely dried, semi transparent

4.3 CHARACTERIZATION OF NANOCOMPOSITE

4.3.1 Thermogravimetric Analysis

Mainly three distinctive weight loss regions can be seen in the TGA of babul gum and CNF nanocomposite (Fig.4). The initial region at a temperature of 80–150 ◦C was mostly due to the moisture evaporation (weak physical and strong chemically bound water) with the weight loss of about 15 wt%. The second degradation occurred at around

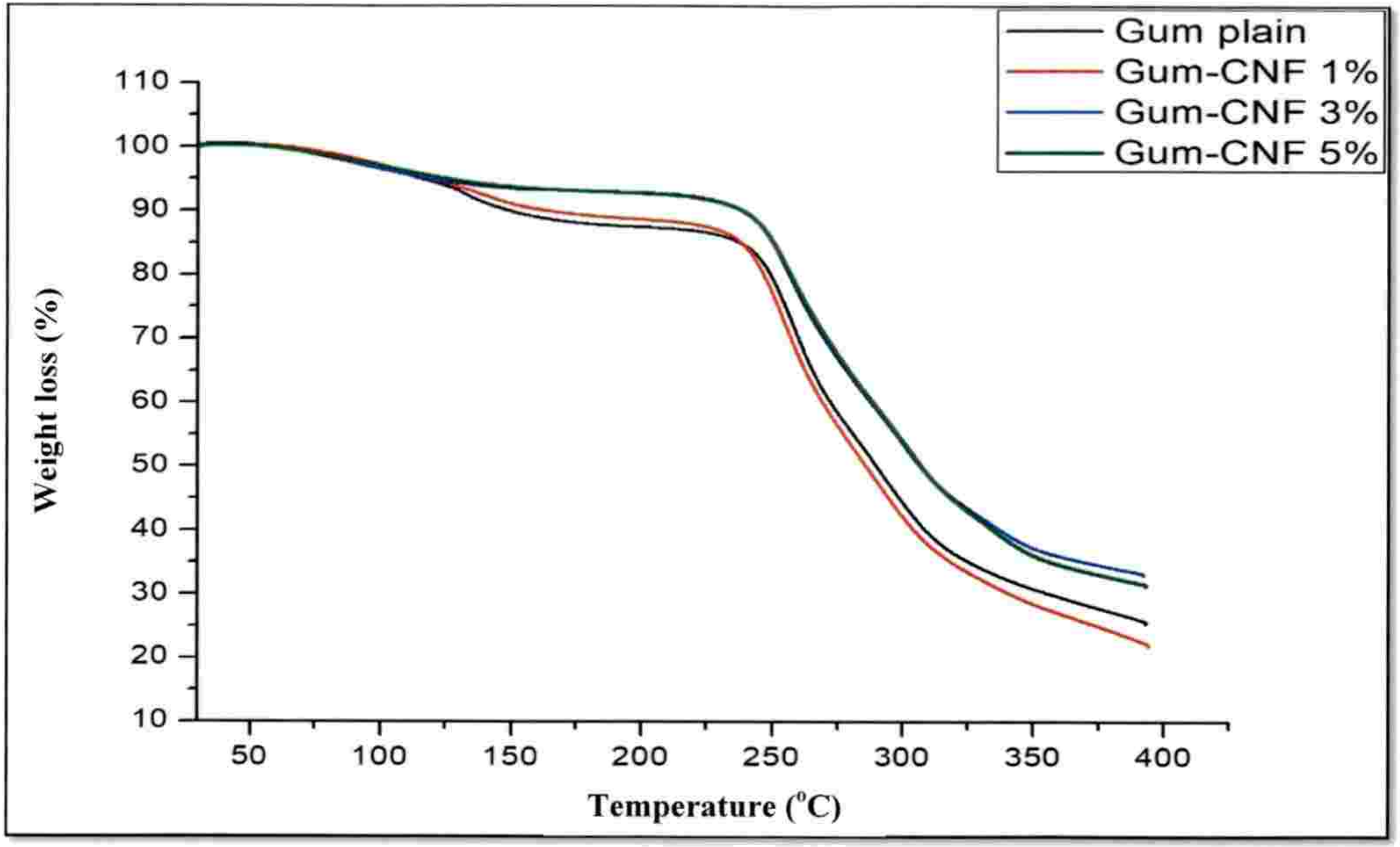


Figure 4. TGA graph of Gum plain, Gum-CNF 1%, Gum-CNF 3%, Gum-CNF 5%

190–250 ◦C, which can be explained by the volatilization of plasticizer used. The third and the obvious weight loss occurred above 300 ◦C, which was due to the thermal degradation of the biopolymer chain.

Table 5. Peak temperature (°C) of 5%, 10%, 15%, 20%, 25% mass loss of plain gum film and composites

	Peak temperature (°C)				
Sample	**5% Mass loss**	**10% Mass loss**	**15% Mass loss**	**20% Mass loss**	**25% Mass loss**
Gum plain	115.7	149	238	249.3	255.1
Gum + CNF 1%	119.4	163.8	238	246.8	252.3
Gum + CNF 3%	118.5	238.8	250.2	256.5	262.6
Gum + CNF 5%	125.7	238.9	250.5	257	263.5

It was clear from the TGA analysis that in smaller loading of CNF there is not much change in thermal stability of the composite material but in higher loading of CNF into the babul gum matrix at 3%, 5% there is an increased thermal property. In Table. 5 the gradual reduction in weight and corresponding temperature are given. The thermal stability of the composites showed an increase than the pristine gum film, however there was no significant difference between the change of the concentration of CNF in the film and the thermal stability. Although an obvious increase in the thermal stability was visible with higher loadings of CNF, this increase in the composite can be due to the formation of hydrogen bond between the gum molecules and CNF resulting in improved thermal properties. Normally the CNF has more thermal stability than the raw fibre, hence the composite formation results in an improved property. Similar thermal degradation performance were found in the nanocrystalline cellulose reinforced in agar matrix given by Reddy and Rhim (2014).

4.3.2 Mechanical properties of plain gum film and composite films

Table 6. Mechanical properties of Babul gum/CNF films

No.	Sample ID	Tensile Strength (Mpa)	Elongation at break (%)	Elastic Modulus (Mpa)
1	Gum plain	0.37 ± 0.06^{a}	46.85 ± 0.74^{a}	4.76 ± 0.40^{a}
2	Gum-CNF1%	0.47 ± 0.07^{a}	27.12 ± 0.64^{b}	15.28 ± 0.55^{b}
3	Gum-CNF3%	1.70 ± 0.16^{b}	29.59 ± 1.12^{c}	35.75 ± 0.41^{c}
4	Gum-CNF5%	2.71 ± 0.16^{c}	17.47 ± 0.99^{c}	56.43 ± 0.32^{d}
5	Gum-CNF10%	3.65 ± 0.26^{d}	13.71 ± 0.57^{d}	71.68 ± 0.36^{e}

*Each value is the mean of three replicates with the standard deviation. Any two means in the same column followed by the same letter are not significantly ($p > 0.05$) different as per Duncan's multiple range test.

A significant change in the mechanical property can be seen between pristine gum film and the composite. An increase in the thickness of the composite is noted due to the increase in the solid content. The tensile strength of the composite was found to increase with increasing concentration of CNF in the gum matrix (Fig.5). It can be due to the strong interfacial interaction of the hydrogen or ionic bonds between the CNF and the babul gum matrix (Siqueira *et al.*, 2010). A remarkable reinforcing effect can be seen when the cellulose nanofibers are uniformly dispersed in the polymer gum matrix. Tensile test results indicate efficient stress transfer from matrix to fiber.

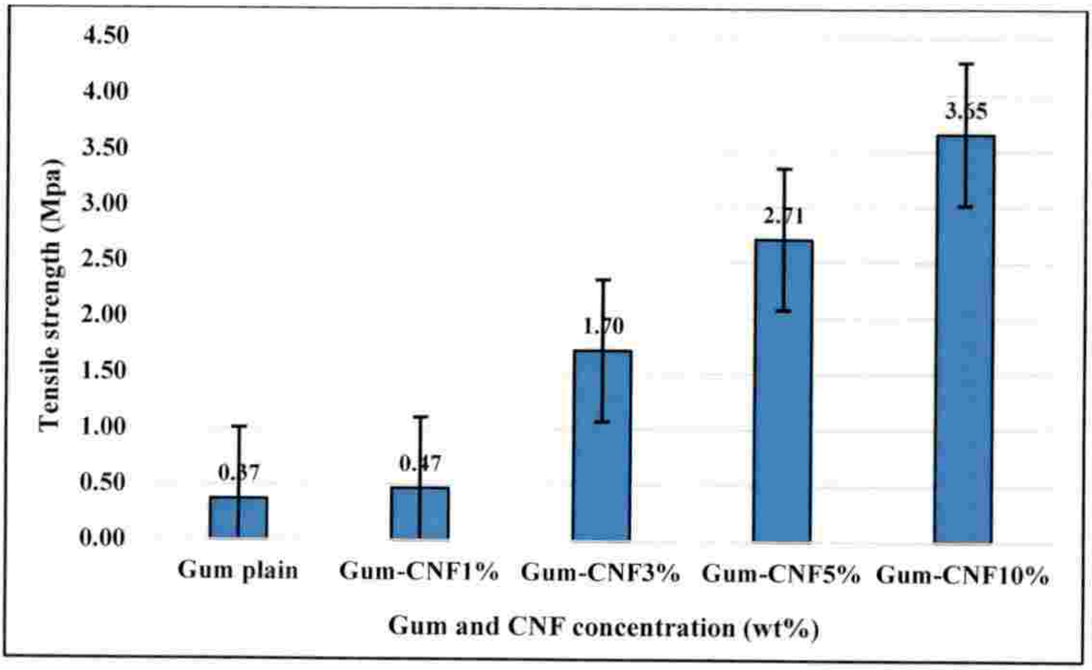


Figure 5. Tensile Strength of plain gum film and gum film loaded with different concentration of CNF (1%, 3%, 5%, 10%)

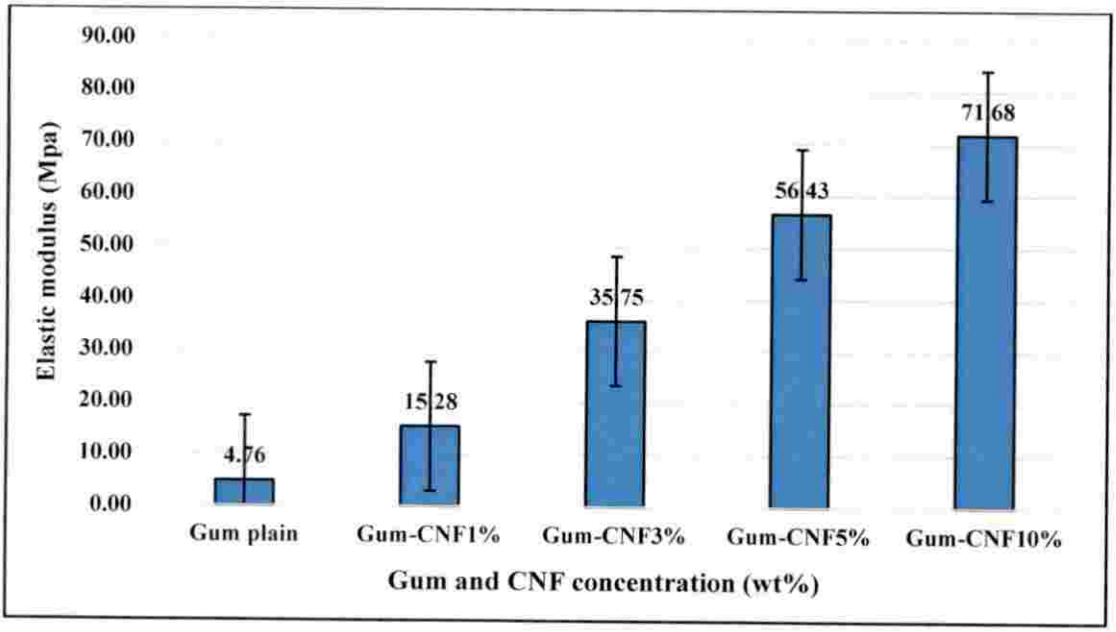


Figure 6. Elastic Modulus of plain gum film and gum film loaded with different concentration of CNF (1%, 3%, 5%, 10%)

The degree of stiffness of a film measured by the elastic modulus of the biocomposite film increased gradually with the amount of the CNF. The stiffness of the composite increased 93% more than the pristine babul gum film when 10 wt% of the CNF was added. This again is mainly due to the nanofiller with high elastic modulus. Both tensile strength and elastic modulus of the nanocomposites were improved with the addition of fillers according to several previous findings of Abdollahi *et al.*, 2013; Reddy and Rhim, 2014.

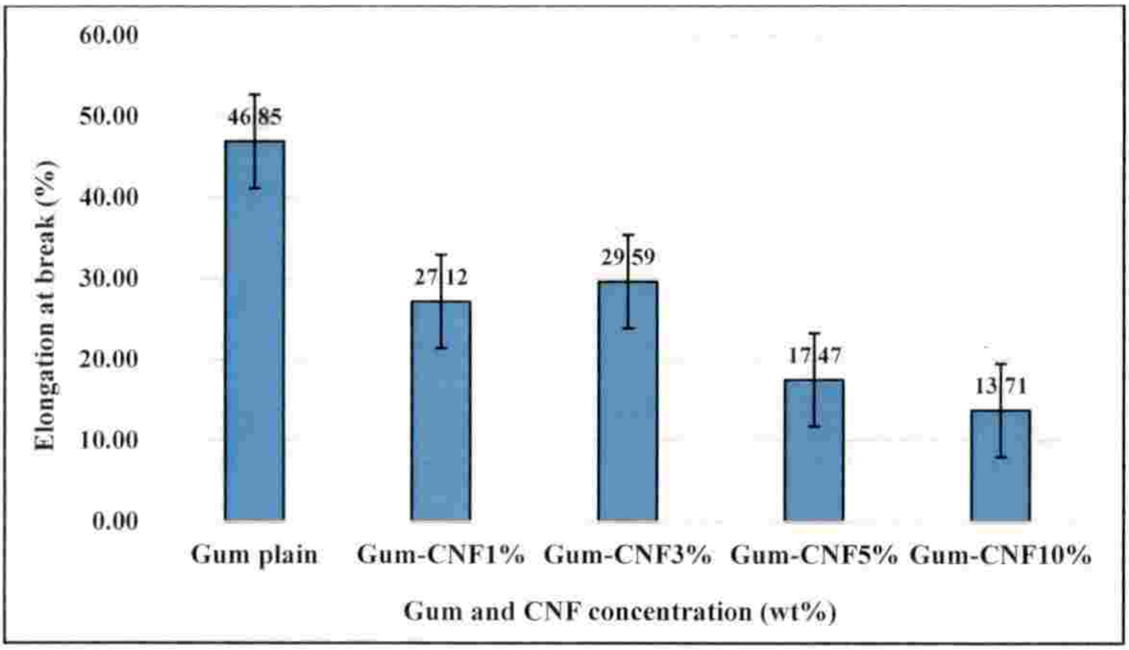


Figure 7. Elongation at Break graph of plain gum film and gum film loaded with different concentration of CNF (1%, 3%, 5%, 10%)

The elongation at break (E), which studies the flexibility or ductility, of babul films also varied depending on the amount of CNF. The change in pattern of E in gum/CNF composite films was inversely proportional to the tensile strength of the same, as it decreased with increase in the CNF content. The decrease in the flexibility of the composite film at high concentration of the filler can be due to the restricted

60

mobility of polymer strand caused by the increased stiffness of the film (Azeredo *et al.*, 2010).

The elasticity of the material was found to be decreasing with increasing concentration of CNF. The elasticity is higher for the plain gum film than the composite. The elastic modulus difference between gum-CNF5% and gum-CNF10% was less when compared to that between other combinations. The fibers are likely to be well compatible in babul gum matrix due to the fact that both gum and the fibers surface contain reactive hydroxyl functional groups and the hydrogen bonding between phases can occur. The interaction between these can induce an effective stress transfer from the matrix to CNF and the better mechanical properties can be achieved. The stress-strain graph Fig. 8 reveals that the varying mechanical properties can be standardized according to the purpose.

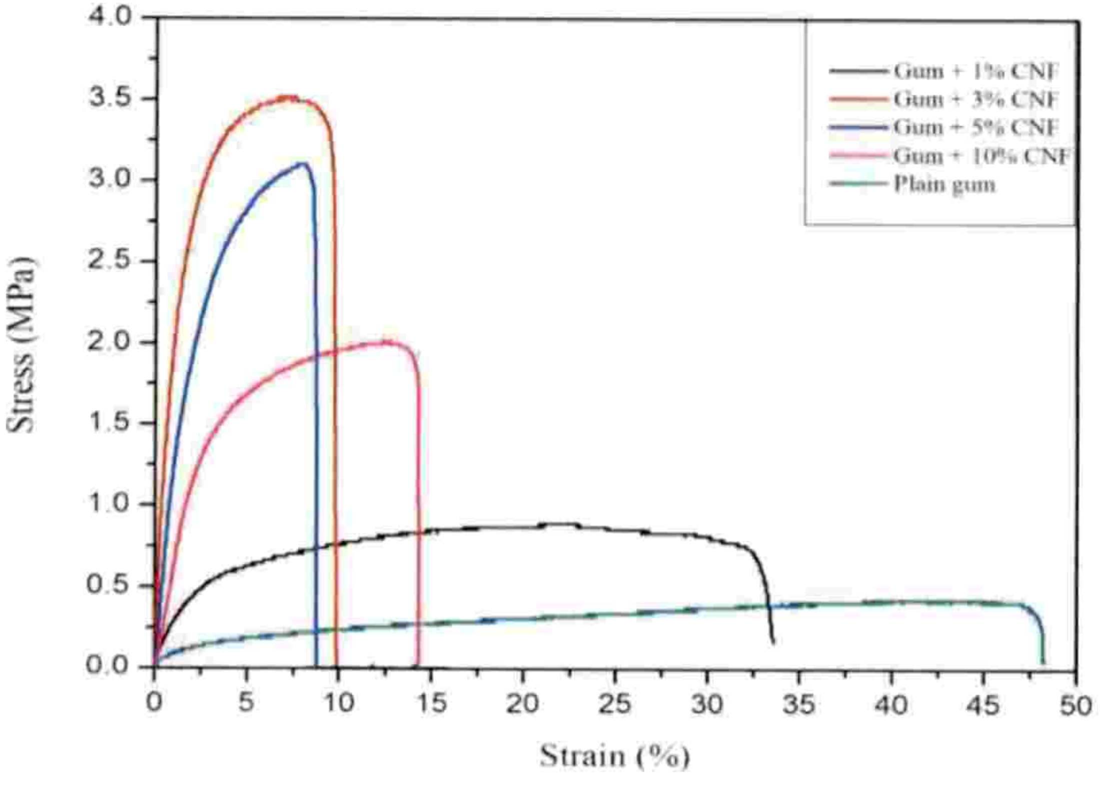


Figure 8. Stress-strain graph of plain gum film and composites

4.3.3 Contact angle (CA)

Table 7. Contact angle of the plain gum film and composites

Sample ID	Contact Angle (Deg.)
Plain gum	47.29 ± 0.7^{b}
Gum+CNF1%	55.21 ± 1.4^{a}
Gum+CNF3%	59.16 ± 2.9^{a}
Gum+CNF5%	66.32 ± 0.9^{c}
Gum+CNF10%	80.01 ± 1.4^{d}

Contact angle is usually tested to understand the hydrophobicity and wettability of surfaces of the nanocomposite materials especially used for biomedical and packing applications. The hydrophilicity of the cellulose nanofibers used for making composite is mainly due to the presence of abundant OH groups. The cellulose nanofibers used for making composite is hydrophilic due to the presence of abundant OH groups. In this experiment the contact angle was increased to 55.21 from 47.29 when 1% CNF was added to the plain gum. This can be due to the interaction of -OH groups in CNF and the same in gum matrix resulting in decrease of -OH group thereby hydrophilicity. It is certain that -OH groups at the surface region of nanocellulose play a major role in adhesion and wettability phenomena, especially regarding the interactions with water and other hydrogen-bonding materials (Hubbe *et al.*, 2015).

The babul gum contains arabinose as its major constituent and the compound contains many reactive hydroxyl groups which results in hydrogen bonds there by reducing the hydrophilic nature of the material. The contact angle was found to be increasing with increasing the concentration of CNF added to the gum matrix. This can be explained by the air area fraction and the surface roughness of the nanostructured

62

composite which increases with increasing amount of nanocellulose which is explained by Jonoobi *et al.*, 2010; Wu *et al.*, 2014 . It is found that there can be an increase in the contact angle of the cellulosic based composite than the neat cellulosic material or other added fillers as given by Szewczyk *et al.*, 2019. The aspect ratio differs with CNC and CNF and the contact angle is found to decrease in composite made out of agar and CNC than the neat film (Reddy and Rhim, 2014). The increase in contact angle after addition of CNF is also reported by Abdollahi *et al.* (2013).

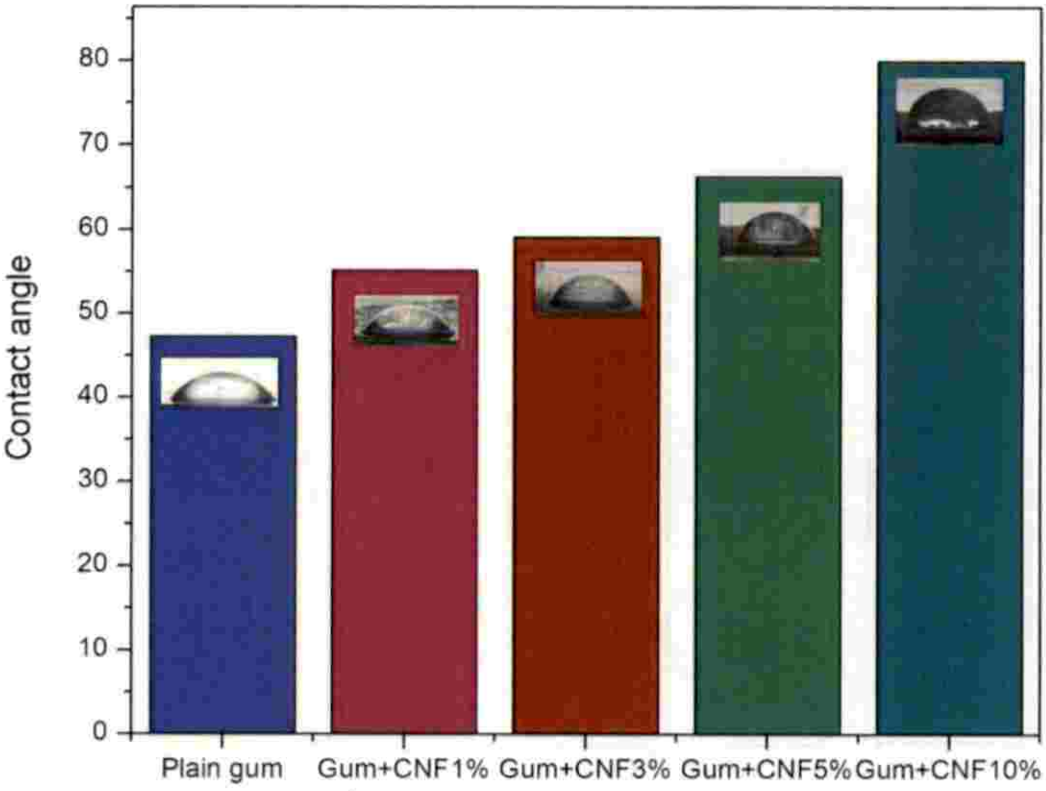


Figure 9. Contact angle of Plain gum film and nanocomposite

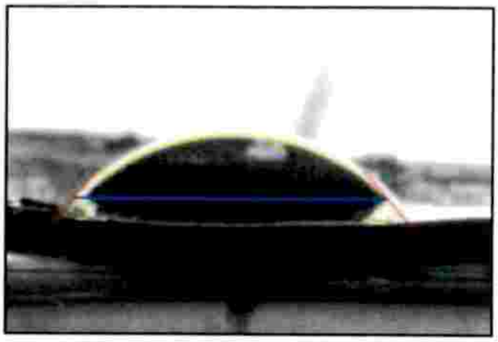


Plate 11. Contact angle of Gum plain

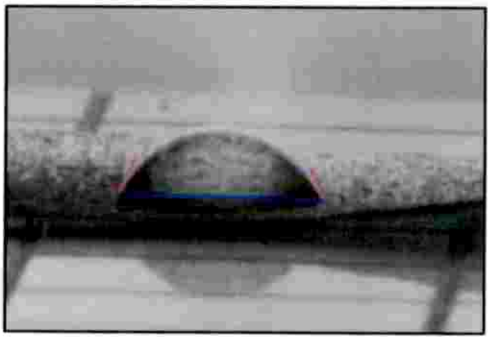


Plate 12. Contact angle of Gum-CNF 1%

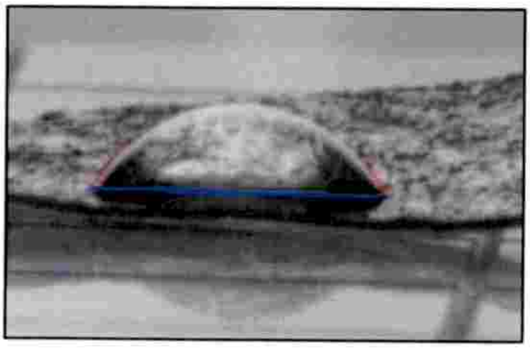


Plate 13. Contact angle of Gum-CNF 3%

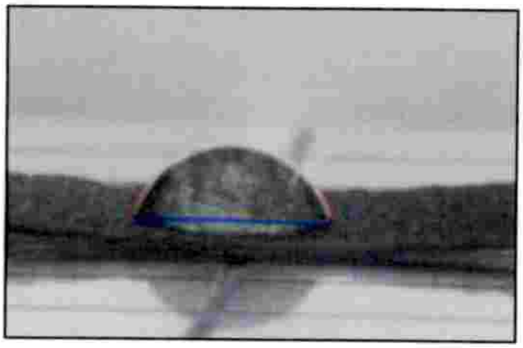


Plate 14. Contact angle of Gum-CNF 5%

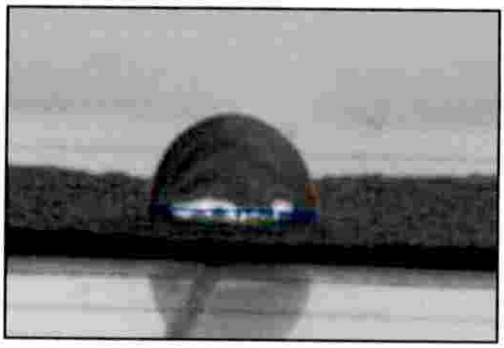


Plate 15. Contact angle of Gum-CNF 10%

4.3.4 Moisture content and water solubility of plain gum film and composites

Table 8. Moisture content of plain gum film and composites

No.	Sample ID	Moisture Content (%)
1	Gum plain	$3.19 \pm .03^{a}$
2	Gum + CNF 1%	$2.88 \pm .03^{b}$
3	Gum + CNF 3%	$3.37 \pm .06^{ac}$
4	Gum + CNF 5%	$3.18 \pm .12^{a}$
5	Gum + CNF 10%	$3.46 \pm .05^{c}$

Table 9. Water solubility of plain gum film and composites

No.	Sample ID	Water solubility (%)
1	Gum plain	$99.69 \pm .074^{a}$
2	Gum-CNF 1%	$98.16 \pm .21^{b}$
3	Gum-CNF 3%	$96.4 \pm .45^{c}$
4	Gum-CNF 5%	$94.33 \pm .45^{d}$
5	Gum-CNF 10%	$95.67 \pm .27^{c}$

Water sensitivity is one of the important parameters measured for packaging as well as biomedical materials. The moisture content and water solubility of the plain gum and composites varies significantly ($p<0.05$). The moisture content tends to increase than the plain gum film but does not show any pattern regarding the increase or decrease (Table 8). Water solubility is one of the important properties of biodegradable films used for food packaging applications and biomedical fields where water activity is high or when the film must be in contact with water. The plain babul gum film was found to be completely soluble in water (99.69 ± .07%) which is due to the hydrophilic nature of the gum. The addition of CNF into the gum matrix reduced the solubility which can be attributed to the hydrogen bond formation between the nanocellulose and the gum matrix. The strong interaction however was seen upto a limit as the solubility was found to increase when there is an addition of CNF beyond 5%. The hydroxyl and carboxyl groups present in the CNF and gum contribute to the cohesiveness affecting the solubility and moisture content (Abdollahi *et al.*, 2013).

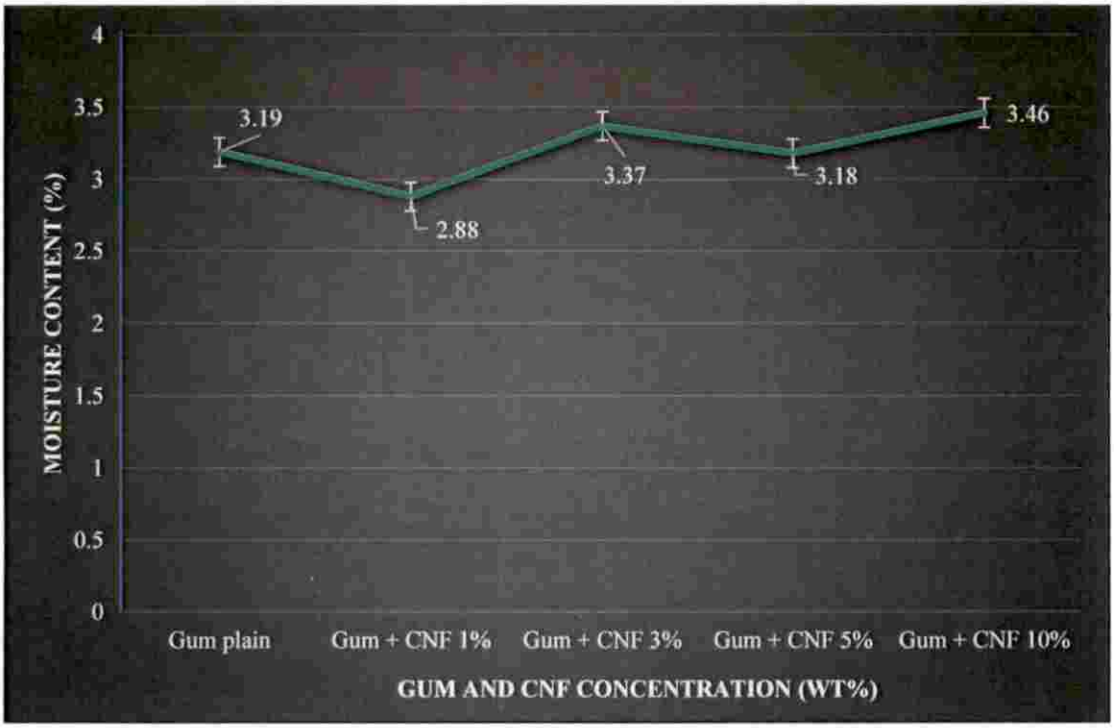


Figure 10. Moisture content of plain gum film and composites

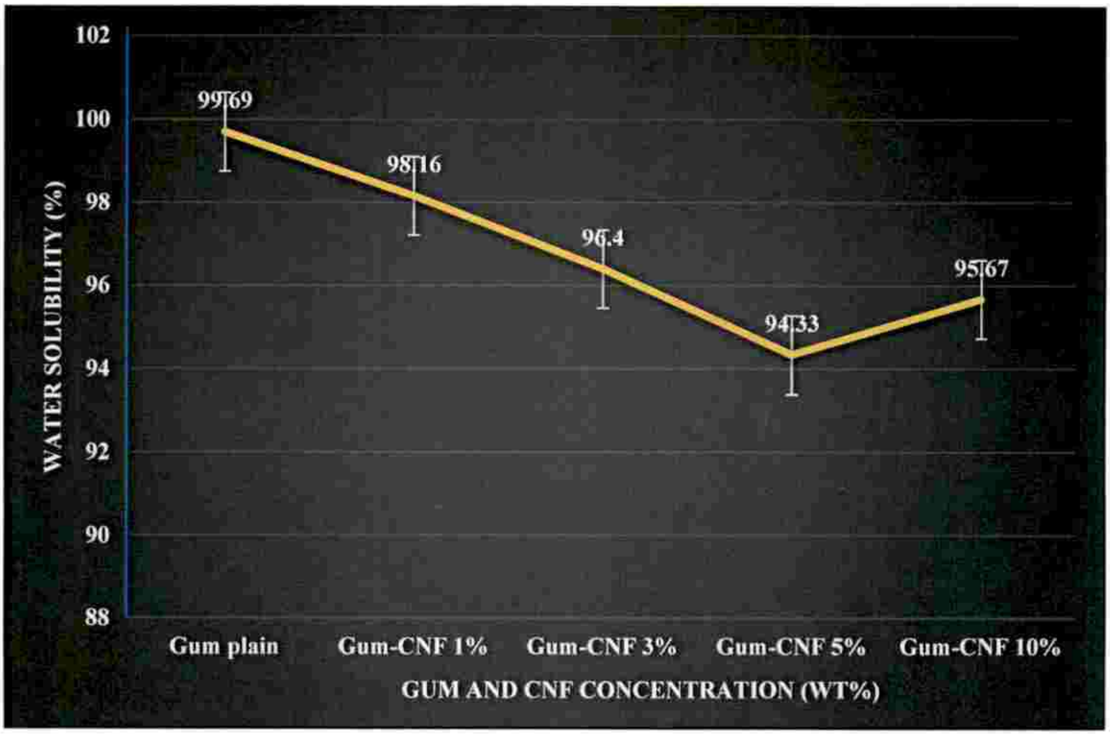


Figure 11. Water solubility of plain gum film and composites

4.3.5 Morphological studies of composite

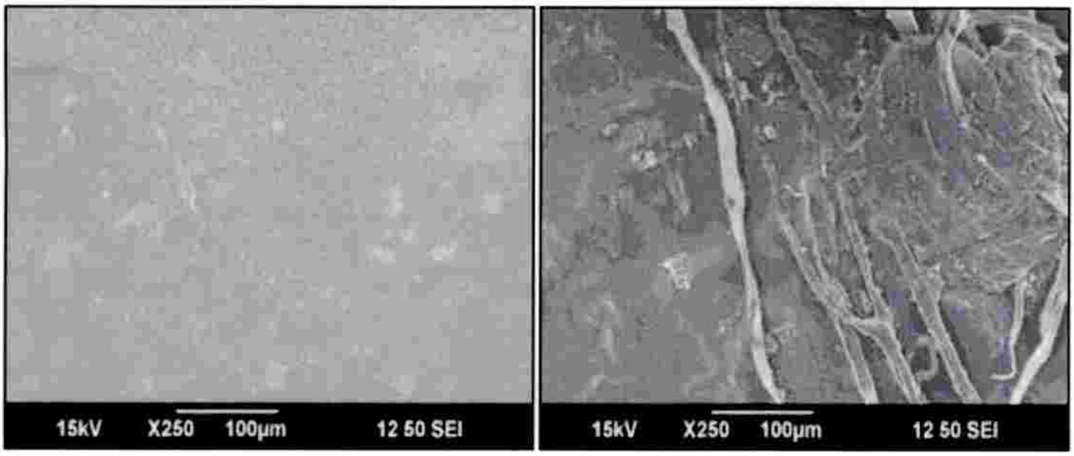


Plate 16. Scanning electron microscope image of plain gum film and nanocomposite

Plate 17. Optical microscope image of CNF dispersed in Gum matrix

The Scanning Electron Microscopy images (Plate. 16) and the optical microscope images (Plate. 17) of CNF-Gum composite shows the alignment of nanofibers in the gum matrix forming the bionanocomposite. In some parts agglomeration of fibres can be seen. As shown in the SEM images, the plain babul gum film showed smooth surface and the CNF particles in the composite films are well dispersed in the gum matrix. The degree of smoothness and transparency of the film surface depend on the CNF concentration and the dispersion of the CNF in gum matrix. The network of CNF embedded in the matrix with hydrogen bonds results in improved mechanical properties for the composite than the pristine gum films.

4.3.6 Fourier-transform infrared (FTIR) spectroscopy analysis

The FTIR analysis of Babul, CNF and gum-CNF composite (Fig.12) revealed that there are interaction between the gum matrix and the CNF resulting in the formation of composite. The broad peak with strong intensity in Babul gum at 3319 cm^{-1} might be due to intra-inter O-H bond of sugars present in the gum. The peaks at 2927 cm^{-1} and 1620 cm^{-1} reveals the C-H bond stretching and carboxyl groups (COO-) stretching respectively (Bhushette and Annapure, 2017). The change in intensity of the O-H stretching at the range of 3500 cm^{-1} to 3000 cm^{-1} indicates the intraction between the gum and CNF. The variation in the intensity and number of peaks in the range of 1460 cm^{-1} -1237 cm^{-1} and 480 cm^{-1} - 620 cm^{-1} also reveals an interaction between gum and CNF.

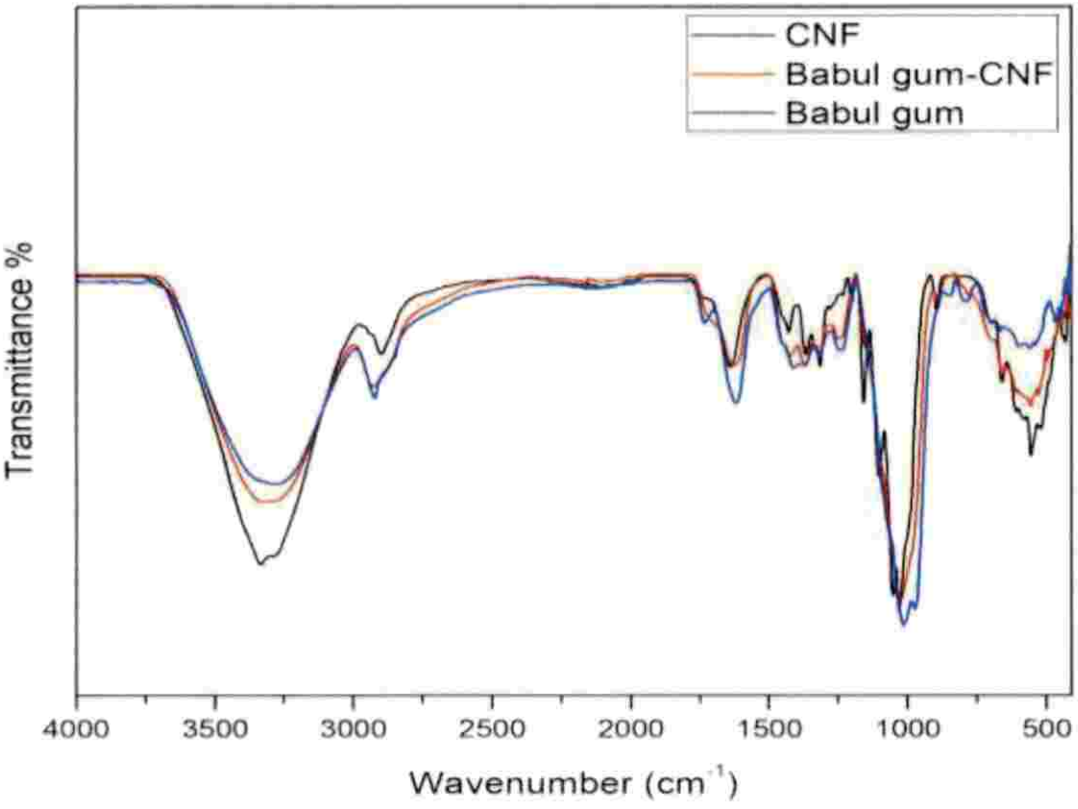


Figure 12. FT-IR spectra of CNF, Babul gum and CNF-Babul gum composite

4.3.6 Future line of work

- The films made from babul gum composite can be further standardized with different plasticizers and different types of nanocellulose ie, Nanocrystals (NCC) and the properties can be compared.
- The antimicrobial properties of the film can be tested and can be improved by the addition of ZnO nanoparticles, Graphene oxide etc so that the material can be further tested for food packaging application.
- The water vapour permeability of the composite film can be tested to understand the barrier properties.
- Standardization of procedures for extracting nanocellulose from forest-based resources pulp yielding trees, fibres obtained from natural resources can be considered, as nanocellulose is one of the important materials used in present day research. The demand for nanocellulose and other cellulosic materials are increasing and the production of the material in large scale through quality researches can be profitable.
- The gum and resins collected from forest-based resource can be subjected to chemical analysis using various testing methods like HPLC, TGA, FT-IR etc, so that it can be utilized by the industries according to their need and thereby widening the market of such products.
- The medicinal uses of the resin and gums can be utilized effectively by the preparation of scaffolds, oral strips etc which can help in drug delivery without side effects as the basic constituents are from natural resource.
- Natural gums along with modified nanocellulose as reinforcement can be analyzed for various wood-based industries, coatings, packing industries etc

- Nanocellulose and lignin can be extracted from any plant material with reasonable amount of the same. Hence the potential woody weeds such as *Lantana camara*, *Senna spectabilis* which are abundantly available in forest areas can be used for this purpose.

SUMMARY

5. SUMMARY

Completely biodegradable edible nanocomposite was developed from babul gum obtained from *Acacia nilotica* (L.) Delile reinforced with Cellulose nanofiber (CNF) isolated from bamboo using steam explosion and was characterized using SEM, FTIR, TEM, TGA, XRD etc to study various parameters.

- The FTIR studies of the nanocellulose showed that there are changes in the chemical composition of the materials at each stage during the extraction.
- The XRD results revealed that the nanocellulose extracted from bamboo has got higher crystallinity than the raw bamboo fibre. ie, 54.46% and 41% respectively.
- The TGA analysis showed that the CNF has higher temperature resistant than the raw fibre. The degradation temperature for 25% mass loss was recorded as 296.2°C for raw fibre while 311.6°C for CNF
- The SEM and TEM images revealed the network pattern of the cellulose nanofiber and the morphological analysis were made possible.
- The nanocellulose was successfully reinforced in babul gum matrix and different combinations (1%, 3%, 5%, 10%) of CNF.
- The TGA analysis revealed that the composites had more thermal stability than the plain gum film.
- The tensile and elastic modulus of the composite increased significantly ($p>0.05$) when the concentration of CNF increased in the gum matrix, while the elastic property got reduced with the addition of CNF.
- The contact angle was found to be increasing with increasing the concentration of CNF added to the gum matrix resulting in less hydrophilic composite with high CNF content.

- The moisture content and water solubility of the plain gum and the composite were tested and the results showed that the strong interaction between gum and CNF was seen upto a limit as the solubility was found to increase when there is an addition of CNF beyond 5%.
- Experimental results show that when the nanocellulose was added to the babul gum as reinforcement the properties improved.

REFERENCES

6. REFERENCES

Abdollahi, M., Alboofetileh, M., Behrooz, R., Rezaei, M. and Miraki, R. 2013. Reducing water sensitivity of alginate bio-nanocomposite film using cellulose nanoparticles. *Int. J. of Biol. Macromol.* 54: 166-173.

Abraham, E., Deepa, B., Pothen, L.A., Cintil, J., Thomas, S., John, M. J., Anandjiwala, R. and Narine, S.S. 2013. Environmental friendly method for the extraction of coir fibre and isolation of nanofibre. *Carbohydr. Polym.* 92(2): 1477-1483.

Ali, A., Maqbool, M., Alderson, P.G. and Zahid, N. 2013. Effect of gum arabic as an edible coating on antioxidant capacity of tomato (Solanum lycopersicum L.) fruit during storage. *Postharv. Biol. and Technol.* 76: 119-124.

Apandi, N.A.A., Razak, N.S.A., Masri, M., Yusoff, S.F. and Lazim, A.M. 2013. A Preliminary Study on Gum Arabic as a Binder in Preparation of Starch Based Edible Plastic. *Int. J. on Adv. Sci.* 3(2): 148-150.

Arun A., Chandra, A., Sharma, V. and Pathak, K., 2010. Fast dissolving oral films: an innovative drug delivery system and dosage form. *Int J ChemTech Res*. 2(1): 576-83.

Asim, M. 2017. Nanocellulose: Preparation and application. In: *Cellulose-reinforced nanofibre composites: production properties and application.* Elsevier, Amsterdam, pp. 261-276.

Azeredo, H. M. C., Capparelli M., and Habig, T. 2011. Nanocomposites in Food Packaging – A Review. In: *Advances in Diverse Industrial Applications of Nanocomposites,* Intech open publishers, London, pp.57-78.

16

Azeredo, H.M., Mattoso, L.H.C., Avena-Bustillos, R.J., Filho, G.C., Munford, M.L., Wood, D. and McHugh, T.H. 2010. Nanocellulose reinforced chitosan composite films as affected by nanofiller loading and plasticizer content. *J. of Food Sci.* 75(1): N1-N7.

Azeredo, H.M., Miranda, K.W., Rosa, M.F., Nascimento, D.M. and de Moura, M.R. 2012. Edible films from alginate-acerola puree reinforced with cellulose whiskers. *Food Sci. and Technol.* 46(1): 294-297.

BCC [Business Communications Company] 2018. BCC [online]. Available: https://www.bccresearch.com/market-research/plastics/biodegradable-polymers-global-markets-and-technologies.html [24 Aug 2018].

Bhushette, P.R. and Annapure, U.S. 2017. Comparative study of Acacia nilotica exudate gum and acacia gum. *Int. J. of Biol. Macromol.* 102: 266-271.

Bipinbal, P K., Thomas, Teena., Joseph, Joseph., Narayanankutty, Sunil. 2017. Restructuring of coir to microfibers for enhanced reinforcement in natural rubber. *Polym. Compos.* 11:1-37.

Bouwmeester, H., Dekkers, S., Noordam, M.Y., Hagens, W.I., Bulder, A.S., De Heer, C., Ten Voorde, S.E., Wijnhoven, S.W., Marvin, H.J. and Sips, A.J., 2009. Review of health safety aspects of nanotechnologies in food production. *Reg. Toxicol. and Pharmacol.* 53(1), pp.52-62.

Briassoulis, D. 2004. An overview on the mechanical behaviour of biodegradable agricultural films. *J. of Polym. and the Environ.* 12(2): 65-81.

Campos, A., Rodrigues, V.B., Luchesi, B.R., Francys K.V., Correa, A.C., Luiz, H.C., Marconcini, J.M. 2017. Bionanocomposites produced from cassava starch and oil palm mesocarp cellulose nanowhiskers. *Carbohydr. Polym.* 175: 330-336.

Cherian, B.M., Leão, A.L., de Souza, S.F., Costa, L.M.M., de Olyveira, G.M., Kottaisamy, M., Nagarajan, E.R. and Thomas, S. 2011. Cellulose nanocomposites with nanofibres isolated from pineapple leaf fibers for medical applications. *Carbohyd. Polym.* 86(4): 1790-1798.

Cherian, B.M., Leão, A.L., de Souza, S.F., Thomas, S., Pothan, L.A. and Kottaisamy, M. 2010. Isolation of nanocellulose from pineapple leaf fibres by steam explosion. *Carbohydr. Polym.* 81(3): 720-725.

Chirayil, C.J., Joy, J., Mathew, L., Mozetic, M., Koetz, J. and Thomas, S. 2014. Isolation and characterization of cellulose nanofibrils from Helicteres isora plant. *Ind. Crops and Prod.* 59: 27-34.

Deepa, B., Abraham, E., Cherian, B.M., Bismarck, A., Blaker, J.J., Pothan, L.A., Leao, A.L., De Souza, S.F. and Kottaisamy, M. 2011. Structure, morphology and thermal characteristics of banana nano fibers obtained by steam explosion. *Bioresour. Technol.* 102(2): 1988-1997.

Dubey, S.P., Thakur, V.K., Krishnaswamy, S., Abhyankar, H.A., Marchante, V. and Brighton, J. L. 2017. Progress in environmental-friendly polymer nanocomposite material from PLA: Synthesis, processing and applications. *Vacuum*. 146: 655-663

Eichhorn, S.J., Dufresne, A., Aranguren, M., Marcovich, N.E., Capadona, J.R., Rowan, S.J., Weder, C., Thielemans, W., Roman, M., Renneckar, S. and Gindl, W. 2010. current international research into cellulose nanofibres and nanocomposites. *J. of Mater. Sci.* 45(1): 1-33.

FAO. 2009. The Forest Sector in the Green Economy. Geneva Timber and Forest Discussion paper-54, United Nations Publications. pp.1-9.

Gopakumar, D.A., Arumughan, V., Pottathara, Y.B., KS, S., Pasquini, D., Bračič, M., Seantier, B., Nzihou, A., Thomas, S., Rizal, S. and HPS, A.K. 2019. Robust Superhydrophobic Cellulose Nanofiber Aerogel for Multifunctional Environmental Applications. *Polymers*. 11(3): 495.

Harnkarnsujarit, N. and Li, Y., 2017. Structure–property modification of microcrystalline cellulose film using agar and propylene glycol alginate. *J. of Appl. Polym. Sci.* 134(47): 45533.

Hasan, M., Gopakumar, D.A., Arumughan, V., Pottathara, Y.B., Sisanth, K.S., Pasquini, D., Bracic, M., Seantier, B., Nzihou, A., Thomas, S. and Rizal, S., 2019. Robust Superhydrophobic Cellulose Nanofiber Aerogel for Multifunctional Environmental Applications. *Polymers.11*(3).

Hubbe, M.A., Gardner, D.J. and Shen, W. 2015. Contact angles and wettability of cellulosic surfaces: A review of proposed mechanisms and test strategies. *Bioresources*. 10(4): 8657-8749.

Huq, T., Salmieri, S., Khan, A., Khan, R.A., Le Tien, C., Riedl, B., Fraschini, C., Bouchard, J., Uribe-Calderon, J., Kamal, M.R. and Lacroix, M. 2012. Nanocrystalline cellulose (NCC) reinforced alginate based biodegradable nanocomposite film. *Carbohyd. Polym*. 90(4): 1757-1763.

Jonoobi, M., Harun, J., Mathew, A.P., Hussein, M.Z.B. and Oksman, K. 2010. Preparation of cellulose nanofibers with hydrophobic surface characteristics. *Cellulose*. 17(2): 299-307.

Jose, J.P., Thomas, S., Kuruvilla, J., Malhotra, S.K., Goda, K. and Sreekala, M.S. 2012. Advances in polymer composites: Macro-and microcomposites—State of the art, new challenges, and opportunities. In: *Polymer Composites*: *Vol. 1*. Wiley: Weinheim, Germany. pp. 3-16.

19

Kadajji, V.G. and Betageri, G.V. 2011. Water soluble polymers for pharmaceutical applications. *Polymers.* 3(4): 1972-2009.

Kalia, S., Dufresne, A., Cherian, B.M., Kaith, B.S., Avérous, L., Njuguna, J. and Nassiopoulos, E. 2011. Cellulose-based bio-and nanocomposites: a review. *Int. J. of Polym. Sci.* 2011: 1-35.

Kaushik, A. and Singh, M., 2011. Isolation and characterization of cellulose nanofibrils from wheat straw using steam explosion coupled with high shear homogenization. *Carbohyd. Res*. 346(1): 76-85.

Khalil, H.P.S.A., Davoudpour, Y., Aprilia, N.S., Mustapha, A., Hossain, S., Islam, N. and Dungani, R., 2014. Nanocellulose-Based Polymer Nanocomposite: Isolation, Characterization and Applications. *Nanocellul. Polym. Nanocompos*. 2014 (11): 273-309.

Kutty, S.K. and Nando, G.B. 1991. Short kevlar fiber–thermoplastic polyurethane composite. *J. of Appl. Polym. Sci.*. 43(10): 1913-1923.

Lagaron, J.M. and Lopez-Rubio, A. 2011. Nanotechnology for bioplastics: opportunities, challenges and strategies. *Trends in Food Sci. Technol*. 22(11): 611-617.

Li, J., Wei, X., Wang, Q., Chen, J., Chang, G., Kong, L., Su, J. and Liu, Y. 2012. Homogeneous isolation of nanocellulose from sugarcane bagasse by high pressure homogenization. *Carbohyd. polym.* 90(4): 1609-1613.

Li, Q., Zhou, J. and Zhang, L. 2009. Structure and properties of the nanocomposite films of chitosan reinforced with cellulose whiskers. *J. of Polym. Sci. Part B: Polym. Phys.* 47(11): 1069-1077.

Liu, W., Misra, M., Askeland, P., Drzal, L.T. and Mohanty, A.K. 2005. 'Green'composites from soy based plastic and pineapple leaf fiber: fabrication and properties evaluation. *Polymer*. 46(8): 2710-2721.

Lu, P. and Hsieh, Y.L. 2012. Preparation and characterization of cellulose nanocrystals from rice straw. *Carbohyd. Polym*. 87(1): 564-573.

Maiti, S., Jayaramudu, J., Das, K., Reddy, S.M., Sadiku, R., Ray, S.S. and Liu, D. 2013. Preparation and characterization of nano-cellulose with new shape from different precursor. *Carbohyd. polym*. 98(1): 562-567.

Mandal, A. and Chakrabarty, D., 2011. Isolation of nanocellulose from waste sugarcane bagasse (SCB) and its characterization. *Carbohyd. Polym*. 86(3): 1291-1299.

Mohammed, N., Grishkewich, N. and Tam, K.C. 2018. Cellulose nanomaterials: Promising sustainable nanomaterials for application in water/wastewater treatment processes. *Environ. Sci. Nano*. 5(3): 623-658.

Mondragon, G., Peña-Rodriguez, C., González, A., Eceiza, A. and Arbelaiz, A. 2015. Bionanocomposites based on gelatin matrix and nanocellulose. *Eur. Polym. J*. 62: 1-9.

Othman, S.H. 2014. Bio-nanocomposite materials for food packaging applications: types of biopolymer and nano-sized filler. *Agric. and Agric. Sci. Proc*. 2: 296-303.

Padil, V.V., Wacławek, S., Černík, M. and Varma, R.S., 2018. Tree gum-based renewable materials: Sustainable applications in nanotechnology, biomedical and environmental fields. *Biotechnol. adv*.36(7):1984-2016

Reddy, J.P. and Rhim, J.W. 2014. Characterization of bionanocomposite films prepared with agar and paper-mulberry pulp nanocellulose. *Carbohyd. Polym.* 110: 480-488.

Reddy, N. and Yang, Y. 2005. Structure and properties of high quality natural cellulose fibers from cornstalks. *Polymer*. 46(15): 5494-5500.

Rhim, J.W. and Wang, L.F. 2013. Mechanical and water barrier properties of agar/κ-carrageenan/konjac glucomannan ternary blend biohydrogel films. *Carbohyd. Polym.* 96(1): 71-81.

Roman, M. and Winter, W.T., 2004. Effect of sulfate groups from sulfuric acid hydrolysis on the thermal degradation behavior of bacterial cellulose. *Biomacromol*. *5*(5):1671-1677.

Rukshana I. and Kazi L. K. 2015. Acacia nilotica gum : An underutilized food commodity. *Int. J. of Curr. Res*. 7: 14280-14288.

Saelee, K., Yingkamhaeng, N., Nimchua, T. and Sukyai, P. 2016. An environmentally friendly xylanase-assisted pretreatment for cellulose nanofibrils isolation from sugarcane bagasse by high-pressure homogenization. *Ind. Crops and Prod.* 82: 149-160.

Sanuja, S., Agalya, A. and Umapathy, M.J. 2015. Synthesis and characterization of zinc oxide–neem oil–chitosan bionanocomposite for food packaging application. *Int. J. of Biol. Macromol.* 74: 76-84.

Schwartz, M.M. 1984. Composite materials handbook (2nd Ed.). McGraw-Hill Book Company, New York, 651p.

92

Siqueira, G., Curvelo, A.A. and Dufresne, A. 2010. Extrusion and characterization of functionalized cellulose whiskers reinforced polyethylene nanocomposites. *Polymer*. 50(19): 4552-4563.

Spence, K., Habibi, Y. and Dufresne, A. 2011. Nanocellulose-based composites. In *Cellulose fibers: bio-and nano-polymer composites*. Springer, Berlin, Heidelberg, pp. 179-213.

Šupová, M., Martynková, G.S. and Barabaszová, K. 2011. Effect of nanofillers dispersion in polymer matrices: A review. *Sci. of Adv. Mater*. 3(1): 1-25.

Szewczyk, P., Ura, D., Metwally, S., Knapczyk-Korczak, J., Gajek, M., Marzec, M., Bernasik, A. and Stachewicz, U. 201. Roughness and fiber fraction dominated wetting of electrospun fiber-based porous meshes. *Polymers*. 11(1): 34.

Takeuchi, H., Yamakawa, R., Nishimatsu, T., Takeuchi, Y., Hayakawa, K. and Maruyama, N. 2013. Design of rapidly disintegrating drug delivery films for oral doses with hydoxypropyl methylcellulose. *J. of Drug Deliv. Sci. and Technol*. 23(5): 471-475.

Talegaonkar, S., Sharma, H., Pandey, S., Mishra, P.K. and Wimmer, R. 2016. Bionanocomposites: Smart biodegradable packaging material for food preservation. In: *Food Packaging*. Academic press, Cambridge, pp. 79-110.

UNEP [United Nations Environmental programme]. 2009. Global Green New Deal. Pittsburgh G20 Summit, Green economy initiative. pp.1-14.

Vermeiren, L., Devlieghere, F., van Beest, M., de Kruijf, N. and Debevere, J.1999. Developments in the active packaging of foods. *Trends in food sci. & technol*. 10(3): 77-86.

Waghmare, V.S., Wadke, P.R., Dyawanapelly, S., Deshpande, A., Jain, R. and Dandekar, P. 2018. Starch based nanofibrous scaffolds for wound healing applications. *Bioactive mater.* 3(3): 55-266.

Wu, C.N., Saito, T., Yang, Q., Fukuzumi, H. and Isogai, A. 2014. Increase in the water contact angle of composite film surfaces caused by the assembly of hydrophilic nanocellulose fibrils and nanoclay platelets. *Appl. Mater. & interfaces*. 6(15): 12707-12712.

Yang, W., Cheng, T., Feng, Y., Qu, J., He, H. and Yu, X. 2017. Isolating cellulose nanofibers from steam-explosion pretreated corncobs using mild mechanochemical treatments. *Bioresources*. 12(4): 9183-9197.

Zhang, L., Tsuzuki, T. and Wang, X., 2015. Preparation of cellulose nanofiber from softwood pulp by ball milling. *Cellulose.* 22(3): 1729-1741.

Zhang, P., Zhao, Y. and Shi, Q., 2016. Characterization of a novel edible film based on gum ghatti: Effect of plasticizer type and concentration. *Carbohyd. Polym.* 153: 345-355.

DEVELOPMENT AND CHARACTERIZATION OF NATURAL GUM BASED NANOCOMPOSITE

By

MEGHANA ROSE JOSEPH

(2017-17-006)

ABSTRACT

THESIS

Submitted in partial fulfillment of the
requirement for the degree of

Master of Science in Forestry

Faculty of Forestry
Kerala Agricultural University

DEPARTMENT OF NATURAL RESOURCE MANAGEMENT
COLLEGE OF FORESTRY
VELLANIKKARA, THRISSUR – 680656
KERALA, INDIA
2019

7. ABSTRACT

Natural gum based bionanocomposite film using babul gum obtained from *Vachellia nilotica* .L and cellulose nanofibrils (CNF) extracted from bamboo culms via steam explosion cum acid treatment was developed for biomedical and packaging applications. Alkali treatment (using NaOH) followed by bleaching (using sodium hypochlorite) of chopped bamboo culms resulted in removal of impurities like pectin, lignin, hemicellulose and other organic compounds. Steam coupled acid treatment of the bleached cellulose pulp resulted in the depolymerization and defibrillation of the fibres to produce cellulose nanofibrils. The structural, morphological, chemical, and thermal properties of CNF were analysed using Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Fourier Transform Infrared Spectroscopy (FT-IR), X-Ray Diffraction (XRD) and Thermogravimetric Analysis (TGA). TEM and SEM images showed that the CNF was composed of network like structure of long fibrils of nanocellulose having the size of few micrometres in length and 50-60 nm in width. The CNF had a crystallinity of 54.46% which was greater than that of the raw bamboo fibre (41%). The chemical composition of the raw fibre and the CNF was analysed by FT-IR micrographs. TGA showed that the CNF was thermally more stable than the raw fibre and the results of peak temperature of 10 and 20% weight loss of raw fibre and CNF substantiated the same. The effect of CNF content (1, 3, 5, and 10 wt% based on gum) on the thermal, mechanical, water solubility, contact angle, and moisture content of nanocomposites was studied. Properties of babul gum film such as mechanical properties were improved significantly ($p<0.05$) by combining with CNF. The TGA analysis revealed that the composites had more thermal stability than the pristine gum film. The tensile and elastic modulus of composites increased significantly ($p<0.05$) when the concentration of the CNF increased in the gum matrix, while the elastic property decreased with the addition of CNF. The contact angle was found to be increasing with increasing the concentration of CNF added to the gum

matrix resulting in less hydrophilic composite with high CNF content. The moisture content tested for the composite films showed no significant difference with the addition of CNF. Water solubility tested showed around 90-95% of the film was dissolved completely in water. The CNF obtained from bamboo fibre can be used as reinforcing agent for the preparation of bio-nanocomposites and they can have a high potential for the development of completely biodegradable edible films which can be used for biomedical applications and packaging.