FABRICATION AND CHARACTERISATION OF STARCH/NANOCELLULOSE BIONANOCOMPOSITE FILMS

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ABSTRACT

In this work we developed starch/nanocellulose bionanocomposite films by solution casting method. The nanocellulose (NC) was extracted from the leaves of pineapples that remained agro-waste after harvesting pineapple fruit by using the method steam explosion. The influences of NC on the structural, physical and thermal properties of starch films were studied. Thermal stability of films were analysed by using thermogravimetric analysis and found that the addition of NC improved the thermal stability of starch film. The incorporation of cellulose nanoparticles favoured plasticization and increased the rigidity in TPS films, as well as the thermal stability. The aim of this work was to obtain bio-based thermoplastic starch films for replacing petroleum-derived ones in packaging industry, especially for short-life applications.

ABBREVIATIONS USED

- NP -Nano Particles
- NC -Nanocellulose
- SEM -Scanning Electron Microscopy
- TEM -Transmission Electron Microscopy
- TGA -Thermo Gravimetric Analysis
- DSC -Differential Scanning
- FTIR - Fourier transform infrared spectrometry
- NFCs -Nano fibrillated cellulose
- NCCs -Nano crystalline cellulose
- BNCs -Bacterial nanocellulose
- WVP -Water Vapor Permeability

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CHAPTER 1

INTRODUCTION

1.1 AN INTRODUCTION TO NANOTECHNOLOGY

In recent years, the use and application of nanomaterials has increased in a wide range .It includes medical field, optical application, energy harvesting devices, storage electronics etc. Nano materials can be defined as these substances which have at least one dimension that have a size range between 1nm and 100nm.The smaller size of these materials causes their broad-unique applications. Nowadays, the influence of nano technology unavoidable in the basic science to prototype applications. Their nanometer size provides them with unique properties which helps them to be further modified into the required applications. [1]

1.2 CLASSIFICATION OF NANO MATERIALS

According to Siegel, nanomaterials are classified on the basis of the entity which is nano sized. This classification is based on the number of dimensions of the material that is not confining to the nano scale range. On the basis of this nano materials are classified [2] as;

i. Zero dimensional nanomaterials
ii. One dimensional nanomaterials
iii. Two dimensional nanomaterials
iv. Three dimensional nanomaterials

- Zero dimensional nanomaterials

In zero dimensional nano materials, all the dimensions are measured within the nano scale. The most common examples are the nanoparticles. These 0D nanoparticles can be crystalline or amorphous, and they may be single crystalline or poly crystalline. They are composed of single

or multichannel elements. Seen individually or by incorporating in a matrix .It may be metallic ceramic or polymeric.

Eg: Quantum dots.

- One dimensional nanomaterial

In 1D nano materials, one dimension is outside the nano scale range. This leads to needle like or rod like structures.1D nanomaterials include nano wire, nano tube, nano rod etc.1D nanomaterials can be crystalline or amorphous, single crystalline or poly crystalline. They may be chemically pure or impure. May be ceramic, polymeric or metallic, seen either alone or by embedding within another medium.

- Two dimensional nanomaterials

In 2D nanomaterials two dimensions are outside the nanometer scale. That is they exhibit plate like shapes.2D nanomaterials includes nanofilms, nanolayers and nanocoatings.Two dimensional nanomaterials can be amorphous/ crystalline. They can be made in various chemical compositions. They are used as single layer or multilayer structures. Most often they are seen as deposited on a substrate in a surrounding matrix material. These materials may be crystalline, amorphous and may be polymeric, metallic or ceramic

Eg: Quantum well

- Three dimensional nanomaterials

3D nanomaterials or bulk nanomaterials are not confined to the nanoscale in any dimension. Thus they have three arbitrary dimensions above 100nm.In terms of nanocrystalline structure, bulk nanomaterials can be composed of multiple arrangement of nanosize crystals, most typically in different orientations.3D nanomaterials can contain dispersions of nanoparticles, bundles of nanotubes & nanowires as well as multi nanolayers.

1.3 **PROPERTIES OF NANOMATERIALS**

The physical & chemical properties of substances changes abnormally when considered them in the nano level. The nanomaterials have unusual mechanical, electrical, optical

And magnetic properties. [3]

- ✓ Nanostructured semiconductors are known to show various non-linear optical (NLO) properties.
- ✓ Materials such as gold, which is chemically inert at normal scales, can serve as potent chemical catalysts at nano scales.
- ✓ Nano sized metallic powders have been used for the production of gas tight materials, dense parts and porous coatings.
- ✓ Nanostructured metal clusters and colloids of mono- or plurimetallic composition have a special impact in catalytic applications.
- ✓ Opaque substances become transparent (copper)
- ✓ Nanophase ceramics are of particular interest because they are more ductile at elevated temperatures as compared to the coarse-grained ceramics.
- ✓ Nanostructured metal-oxide thin films are receiving a growing attention for the realization of gas sensors with enhanced sensitivity and selectivity.

1.4 **IMPORATANCE OF NANOCELLULOSE REINFORCED STARCH POLYMER COMPOSITES**

Plastic based food packaging are nowadays generating serious environmental issues due to the accumulation of plastic waste in surroundings. In recent years, there is a growing need for replacing petroleum based plastics like polyethylene and polypropylene, as these are low biodegradable, non-renewable and significant carbon foot print [4,5].A number of materials like paper, plastic, aluminum foils, steel are used worldwide for packaging food materials. Among this the application of petro based plastic packaging is proliferated due to its better mechanical characteristics and copiousness.

Food products are available in many forms such as liquid, semi-solid or solid which makes it necessary to pack them sufficiently. Efficient packaging provides protection against undesirable pollutants, atmospheric moisture, dust and microbial contamination.[6] Packaging of materials include its nutrient details, manufacturing and expiry informations, price which makes it convenient for customers. In order to make the food products demandable in the

market, they must be packed in a material with enough strength and properties to keep the quality and safety of foods.

In industries, different packaging materials were used to provide safety features for food materials. Metal was preferred for packaging in the initial stages due to its light weight, heat and moisture resistance, and excellent malleability features. Further, paper packaging were recommended for a wide range of applications; but due to their low moisture barrier and insignificant mechanic strength. After that plastic was used as packaging materials. Globally, the plastic consumption was reported to be exceed 700 million annually.[7] Due to the consumption of highest volumes of plastics, packaging industries became the primary source of plastic waste accumulation into the environment inn an alarming rate. Consumers are increasingly demanding biodegradable food packaging with minimal amount of synthetic preservatives and for developing new products from sustainable raw materials.

Thus to overcome this constant environment issue triggered by non-biodegradable plastics many natural biopolymers like polylactic acid, polyhydroxy alkanoates, polysaccharide based plastics, proteins have been investigated as an effective substitution to conventional plastics. Large number of bio polymers from diverse sources such as agro-based, microbial, synthetic biopolymers were used for bio degradable. Among these biodegradable polymers, starch satisfies all the principal aspects to be a future green material to replace non-biodegradable plastic.[8,9]

Easy availability of starch and its annual renewable nature make sit a perfect base material for the broad spectrum of industrial application. Starch has wide applications in food industry most often as a thickening agent (for modifying the viscosity, texture etc.), for water retention (swelling properties) so, there is an increasing demand for starch.[10] Maize is the main source of starch isolation. Potato, wheat, rice and cassava can also be used.

Starch is a common biopolymer which bears several advantages due to its non-toxicity, transparent, odorless, semi permeability to moisture, overwhelming biodegradability, abundance, sustainability, ease of handling, and the possibility of being blended with other polymers[11]. However the challenge for using starch like biopolymer is poor processibility, low mechanical strength, its brittle behavior, low resistance towards water (high water absorption capacity) and they act as microbial food which prevent its application in food packaging.[12,13] Due to the brittle behavior and lack of mechanical integrity in starch –based films, researchers have been done starch modifications by the addition of modifiers or

reinforcing materials into the film to enhance the thermal, mechanical and microbial attack on films.[14,15,16] Starch modification can be achieved by the blending of starch with other biopolymers or by using novel preparation techniques. Starch based films have been applied for the packaging of various food items such as bakery foods, fruits and vegetables, meat etc[17]. Modified starch, are classified into the following categories based on the modifying agents and physicochemical characteristics:[18]

- Derivatized: Chemically modified with modifying agents like acetyl, phosphate, hydroxypropyl
- Cross-linked: Chemically modified using epichlorohydrin, trimetaphosphate;
- Pregelatinized: Physically modified by extrusion or drum drying:
- Dextrinized: Physical modification by irradiation, heat or chemical modification by using oxidizing agents, acid hydrolysis or enzymatic modification by amylolytic enzymes.

Adequate packing uses two different approaches.[19]

1. Uses of edible source as a coating material for vegetable's or fruit surface
2. Materialistic approach which would be further divides as
    a. Thin edible film
    b. Gel conversion.

Biopolymers especially different kind of starch, chitosan, whey, gums and microbial gums (xanthan gum, cellulose)are highly recommended for coating and packaging needs either alone or by blending to improve mechanical properties.

Biopolymers have the ability to undergo gelation upon the addition of multivalent cations, which leads to a cross linking and aggregation when both are in contact with cations. During the reticulation process, a strong network occurs via gelation due to the exchange of divalent ions .This in turn will leads to a stronger matrix in terms of mechanical properties and structure.

The ionic crosslinking in biopolymers can successfully produce aerogels which is typically produced by the sol gel technique. This aerogels are used for intelligent food packaging applications.

Modification starch by chemical, physical and enzymatic means provides a choice for enhancing the film characteristics. Fabrication of starches with by introducing functional

groups reduces the hydrophilic behavior of starch films thereby improving its compatibility with other polymers.

Nowadays, much focus was given on cellulose nanofiller reinforcement to the starch based polymer. Cellulose is abundant, biodegradable, and biocompatible with other polymers. Hence it can be used for many applications. Attempts for the nano reinforcement using nanocellulose is considered as an efficient strategy for enhancing the water barrier resistance, mechanical strength properties, gas permeability etc.

Cellulose nanofibers has an increasing concern due to its fascinating properties like increased surface to volume ratio, low density, light weight, high mechanical strength and the ability to form strongly porous mesh compared to the commercial fibers. Moreover they are low cost, easily available [20]and ecofriendly fibers because they consume less energy during the manufacturing phase and they are easily to recycle via combustion. Reinforcement of starch based films with nano fibers or nano crystals provide a good strategy for manufacturing bio composites with better mechanical characteristics, application in biomedicine, pharmaceuticals etc. Therefore it is notable to incorporate cellulose nanocrystals or nanofibers in starch- based films to investigate the improvised industrial applications.

1.5 NATURAL FIBERS

The word "natural fiber was used to explain different types of fibers that are produced naturally by plants, animals, and minerals.It is composed of three main components namely 1)Lignin 2)Cellulose 3)Hemi cellulose.Traces of other minor components like extractives pectin and pigments are also present. Due to this reason natural fibers are also called cellulosic or lignocellulosic fibers. Different types of fibers have different cell structure and composition, hence the structure and composition of natural fibers are very complicated. Each fiber consists of several elements and parts which are referred to as composites. Rigid micro-sized cellulose (mainly cellulose and lignin) are embedded into this composite in a soft matrix.[21]

1.6 CELLULOSE

Cellulose is one of the most abundant [22,23,24]and renewable biopolymers on earth .It is seen in most of the natural fibers, mainly in plant based materials and serves as the reinforcing phase in plant structures. These materials are naturally occurred as microfibrils linked together to form cellulose fibers.It is a semi crystalline high molecular weight nanopolymer .It has a typical crystal length of 20-2000nm.The interaction of the microfibrils interact with H-bonds and van der Waals attraction.This results in the structural scaffolding of the fiber cell wall.Scanning and transmission electron microscopy has revealed the appearance of needle like cellulose particle similar to crystalline structure of native fibers.The high water insolubility of cellulose is the main focus of many investigations.Nano cellulose produced from cellulose are considered as a nanobiomaterial with various applications in medical,food and pharmaceutical field. [25]

1.7 **NANOCELLULOSE**

Nanocellulose are divided into three types:[26]

I. Nanofibrillated cellulose(NFCs)
II. Nanocrystalline cellulose(NCCs)
III . Bacterial nanocellulose(BNCs)

BNCs are synthesized by the *Gluconoacetobackerxylinius* family of bacteria.It is cultivated in the culture medium as microfibrils by the bottom up approach.NFCs and NCCs are obtained by the top down approach like physical, chemical, enzymatic methodologies for extracting and isolation.[27

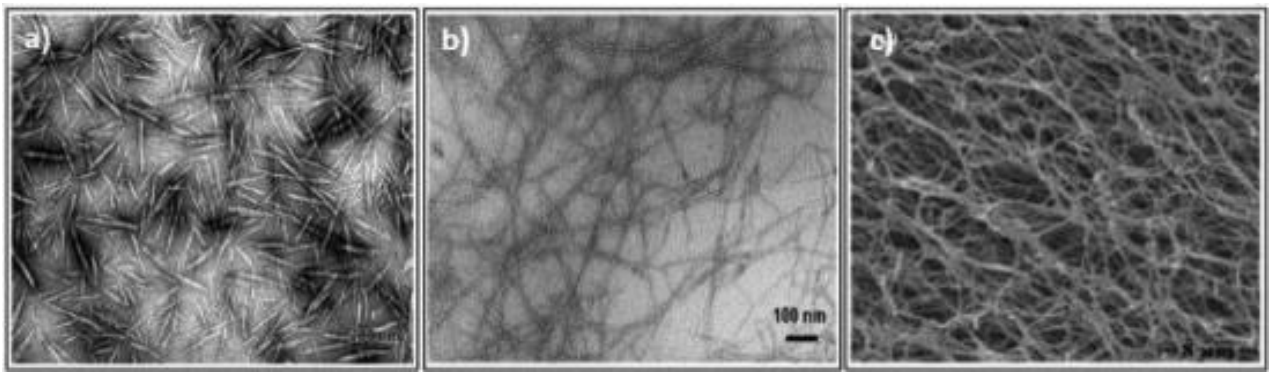


Fig 1:Comparison of microscopic images of (a) nanocrystalline cellulose (b)nanofibrillated cellulose (c)bacterial nanocellulose.(Adapted from[20])

1.8 **BIONANOCOMPOSITES**

A polymer nanocomposite is defined as a polymer that is reinforced with a filler in which the filler size has atleast one dimension smaller than 100nm. The nano composites is now known as a ‘nano structured hybrid material’ ,due to the reinforcement of the polymer with the nano structural properties of the filler.According to Siqueira and et al, bio nanocomposites are defined in two ways [28,29]

- Nano filler material is made upo from renewable nano particles(NCCs,BNCs,NFCs)reinforced petroleum derived polymers
  Eg: PP, PE
- Nano filler made up from inorganic or synthetic nanofillers (nanoclay,ZnO_2 nano particles) reinforced biopolymers.
  Eg: Starch, PLA, PHA

1.9 **NANOCELLULOSE REINFORCED STARCH BASED NANOCOMPOSITES**

Bio plastics is defined as a material that are made up of 100% renewable material. One of the widely used bio plastic is starch. Starch has gained a huge attention because it can substitute conventional petroleum based plastics mainly for disposable applications [30].But its usage is highly hindered due to their low mechanical strength .Brittleness, poor water sensitivity etc. One of the method for overcoming these problems is by reinforcing them with nanocellulose. It has been proven to enhance the mechanical strength and water barrier properties.[31]

1.10 SCOPE OF THE STUDY

Nanocellulose enriched starch biocomposites can effectively be used to extend the shelf life and thereby the quality of food. Due to the low mechanical properties and WVP characteristics limits the application of natural biopolymers.The application of nanotechnology in such packaging may improve the mechanical properties of with new active properties. Nanocomposites in food packaging are designed to enhance food shelf-life during processing and handling.[32]

Montoya et al. [33] wrapped mango into starch/bacterial nanocellulose films at 5 ◦C with 75% RH for five days. The study concluded that starch-based biodegradable film preserved the physical and chemical integrity of the fruit. Potato starch film reinforced with 5% CNC resulted in improved rigidity, thermal stability, and water resistance; therefore, it appears to be a better alternative for short-life applications into the packaging industries [34].

Syafri et al. [35] prepared Beng Kuang starch and hyacinth nanocellulose biocomposites followed by ultrasonic incubation for 15 to 30 min. Ultrasonication vibration improved the thermal stability and moisture resistance of biocomposites, indicating their potential utilization as eco- friendly packaging bags.

The accumulation of petro based plastic materials in the earth is a major environmental hazard. Therefore this biodegradable packaging could be a replacement for the petro based packaging. A poor soluble drug, Methotrexate (MTX), has significant therapeutic effects for treating bowel inflammation disease, including ulcerative colitis and Chron's disease, and colorectal cancer [36] . Nanotechnology supports drug delivery by producing nanoscale substances, therefore used as carriers [37]. Nanocellulose enriched high amylose starch films were applied with 4 ml MTX by the dripping process. Reported data indicated that nanocomposite films had the potential to increase MTX release with a burst release varies from 40.84 to 64.13% within the first 15 min of testing, suggested a vital strategy to reduce the oral bioavailability problems of poorly soluble drugs. High swell ability, crystallinity, hydrophilicity, and porous behavior of nanocellulose fibers facilitated the improved diffusion of drugs via polymer matrix [38]. Further, for the sustained release of dimethyl phthalate, Patil et al. [39] formulated nanocomposites using gelatinized corn starch and CNFs. They concluded that reinforcement of starch with CNFs hampered the initial release of dimethyl phthalate; however, the overall release was higher, and 85–90% of the drug was released within seven days.

CHAPTER 2

REVIEW OF LITERATURE

- Sneh Punia Banger, William Scott Whiteside conducted a simple and green synthesis for replacing petroleum based plastic with starch based films. Nanocellulose was isolated from lignocellulosic fibers.The mechanical properties , thermal properties ,barrier properties morphological characteristics, rheological properties and biodegradability of the films were studied.
- The work by R A Ilyas,S M. Sopuan,M R. Ishak , E S Zainudin, M S N Atikahprovided an overview of the progresses made in the area of plasticized starch reinforced with nanocellulose.They substantiate the significant influence of the nanocellulose source on the properties of nanocellulose.The article comprises of two parts . The first part agrees with the processing and characterisation of cellulose nano composites.The second part deals with the new development of the method in different applications.
- S M Noorbakhsh-Soltani, M Zerafat, S Sabbagi conducted a comparative study of gelatin and starch based nano-composite films modified by nano cellulose and chitosan for food packaging applications.For this purpose, nanocellulose were incorporated into starch matrices and gelatin. Chitosan were used to improve the antifungal, water proof and mechanical properties.The work is designed and analazed using response surface methodology. Nano cellulose were prepared by acid hydrolysis and were incorporated into the base matrix by wet processing. DSC/TGA and air permeability test was performed. Transparency in UV-Visible , water contact angle, tensile strength test, food preservation test are also performed on the films. Increasing the nanocellulose composition to 10% leads to increase in the tensile strength. They also revealed that increasing the chitosan composition from 5% to 30% can enhance food preservation upto 15 days.
- In the work by Susana Mali, Maria Victoria E. Grossmann, Maria A. Garzia , Miriam N.Martino, Noemi E.Zaritzky –uarm starch were produced by the thermal gelatinization of starch suspensions. The films were characterized bu SEM,DSC,TMA,XRD,Water Vapor Permiability (WVP)and polarized light microscopy. From the DSC and polarized light microscopy the starch gelatinization for film formation was complete.The Tg temperatures of films with glycerol were lower

than the control films as measured by DSC and TMA.This work showed and increase of water vapor permeability of yam starch films with an increase in glycerol content.

- The work by Razali M.O. Syafiq, Salit.M. Sapuan and Mohd R.M.Zuhri exhibited the effect of cinnamon essential oils in the thermal, morphological and inflammability properties of nanocellulose fiber reinforced starch biopolymer composites. The thermal stability of CEO/SPN/SPS biopolymer composites was remarkably improved with increasing the CEO loadings on comparing to the thermal stability of unfilled compound. The surface of the control film without cinnamon essential oil displayed a smooth and uniform texture without any traces of crack. The presence of CEO in the SPN/SPS bio films had affected the structures of the SPS matrix. An increase in surface coarseness can be seen with CEO concentrations. The linear burning rate were also increased by the increase in CEO concentrations.
- The work carried out by Mayer Fazeli, Meysam Kely, Esmaeil Biazar on the preparation and characterization of starch based composite films reinforced by cellulose nano fibers. As a solution to the highly hydrophilic nature and poor mechanical properties of films, they made a nanocomposite of thermoplastic starch (TPS) as matrix and cellulose nanofiber as a (CNF) as reinforcement. The TPS/CNF was prepared by the polymer solution casting method. The characteristics of the films were studied by Atomic Force Microscopy (AFM), Oxygen Transmission Rate (OTR), X Ray Diffraction, Water Vapor Transmission Rate(WVTR).The TPS films with 0.4 weight percentage CNF showed an improvement in tensile strength .The elastic modulus and tensile strength upto 170% and 80% respectively. Above 0.5 weight percentage of CNF, the tensile strength began to deteriorate . The OTR and WVTR shows an increase in water barrier properties . The SEM and TEM was employed to study the morphology of nanofibers. The topography of the nanocomposite was studied by AFM .
- A Nazrin,S.M.Sapuan,M.Y.M Zuhri,R.A.Ilyas,R.Syafiq,S.F.K.Sherwani reinforced Thermo Plastic Starch,Poly Lactic Acid and Polybutylene Succinate with nanocellulose for food packaging applications. Nanocellulose as a natural fiber incorporated into the TPS,PLS,PBS,as a reinforcement material to overcome their weakness.

CHAPTER 3

OBJECTIVES OF THE STUDY

- To extract nanocellulose from pineapple leaves
- Characterisation of nanocellulose
    - TEM
    - FTIR
- Preparation of starch films from starch powder and nanocellose
- Characterisation of films
    - Scanning Electron Microscopic Analysis (SEM)
    - Fourier Transform Spectroscopic Analysis(FTIR)
    - Thermogravimetric Analysis (TGA)

CHAPTER 4

MATERIALS AND METHODS

4.1 MATERIALS

Potato starch powder, fresh *Hibiscus sabdariffa* flower collected from local area, pineapple *Ananas comosus* leaves(kew variety), sodium hydroxide (NaOH), sodium chlorite ($NaClO_2$) solution, acetic acid, glycerol, Potassium bromide (FTIR grade ≥ 99%) were purchased from sigma Aldrich. All chemical reagents included in this work have been of scientific grade and were used without any further treatment or chemical modification.

4.2APPARATUS USED

- Glass beakers
- Measuring Jars
- Watch glass
- Magnetic Stirrer

4.3 EXTRACTION OF NANOCELLULOSE FROM PINEAPPLE LEAVES

The method that we adopted for the extraction of nanocellulose from pineapple leaf fiber (PLF) involves the steam explosion, one of the effective method used in the literature[7,33]. Fresh pineapple leaves were washed with distilled water and chopped in to small pieces. Leaves were dried in an air oven at 80°C. The dried leaves were powdered by using a grinder and treated with 3 N NaOH solution under pressure in an autoclave. After the alkaline treatment washed the suspension using distilled water until the neutral conditions attained. The process of steam explosion process was repeated 3 times. The steam exploded fibers were then bleached in an autoclave until the suspension of cellulose fiber attains white color. The bleaching solution was prepared by mixing sodium hypochlorite ($NaClO_2$, 4% w/v) with the mixture of acetic acid and NaOH (2% w/v). The suspension was then centrifuged and washed several times with water until the solution was neutral. The cellulose fiber suspension was then homogenised

using a homogeniser and sonicated using a probe sonicator at 60 W for about 10 minutes at reduced temperature.

4.4 PREPARATION OF FILMS

.

Sample Code	PS Wt%	NC Wt%
S	100	0
S/NC	95	5
S/NC	90	10

Table1: Sample code and composition of Starch, NC and HFE in different filmogenic solution

5g potato starch powder (S) was dispersed in 100ml distilled water using a magnetic stirrer keeping the temperature of solution at 40°C. Glycerol (40wt% of dry base) was then added to the hot starch solution and stirred for 2 minutes. After the complete dissolution of starch, temperature was raised to 90°C. The film forming solution was then homogenized using a homogeniser *(*Ika Ultra-Turrax T 25) and heated to at 90 °C for 10 min. The filmogenic solution was then poured in to a teflon sheet and dried in an oven at 55°C for 24 hours. The dried films were peeled off.

4.5 CHARACTERISATION TECHNIQUES

4.5.1 Scanning Electron Microscopy (SEM)

SEM the technique used for the surface morphological and topographical studies and also for compositional analysis[

40].Samples were mounted on aluminum stubs with sticky double-side carbon tape. No special treatment was applied to the specimens and no coating was needed. Examination was performed by a Carl Zeiss EVO 18 scanning electron microscope.

4.5.2 Fourier transform infrared spectrometry (FTIR)

FTIR orginates from the vibrational motion of the molecule.The technique is used for the characterisation of organic, inorganic and biological compounds. The band intensities are proportional to the concentration of the compound and hence qualitative estimations are

possible.FTIR spectres of synthesised samples were recorded with the technique of thin transparent tablets with potassium bromide for spectroscopy. The solid samples are dispersed in KBr or polyethylene pellets depending on the region of interest. The recordings were made in wave numbers from 4000 to 400 cm-1 on the FTIR spectrophotometer (Thermoscientific Nicolet iS50).

4.5.3 Thermal Analysis(TGA and DTG)

Thermogravimetric analysis (TGA) measures weight changes in a material as a function of temperature (or time) under a controlled nitogen atmosphere atmosphere. Its principle uses include measurement of a material's thermal stability, filler content in polymers, moisture and solvent content, and the percent composition of components in a compound. A TGA analysis is performed by gradually raising the temperature of a sample in a furnace as its weight is measured on an analytical balance that remains outside of the furnace. In TGA, mass loss is observed if a thermal event involves loss of a volatile component. Chemical reactions, such as combustion, involve mass losses, whereas physical changes, such as melting, do not. The weight of the sample is plotted against temperature or time to illustrate thermal transitions in the material – such as loss of solvent and plasticizers in polymers, water of hydration in inorganic materials, and, finally, decomposition of the material.,

Derivative Thermo Gravimetry (DTG) is a type of thermal analysis in which the rate of material weight changes upon heating is plotted against temperature and used to simplify reading the weight versus temperature thermogram peaks which occur close together.Analysis was performed by a Simultanous Thermal Analyser STA 8000.

CHAPTER 5

RESULT AND DISCUSSION

Colourless-homogeneous-thin films was obtained. From the observations all the films were slightly opaque in nature.

5.1 CHARACTERISATION OF NANOCELLULOSE

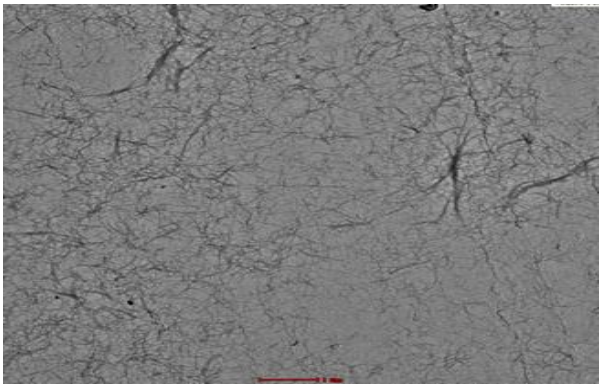


Figure 2: TEM image of nanocellulose extracted from PLF.

TEM image of NC isolated from PLF is shown in the figure 1. The TEM image confirmed the formation of nanocellulose after the various treatments like steam explosion, bleaching and acid treatment. The diameter of the NC ranging between 10–100nm showing that the combination of different processing steps in the autoclave resulted in the effective defibrillation of cellulose present in PLF and complete removal of lignin and hemiellulose present in the raw fiber[35] that was confirmed by FTIR analysis.

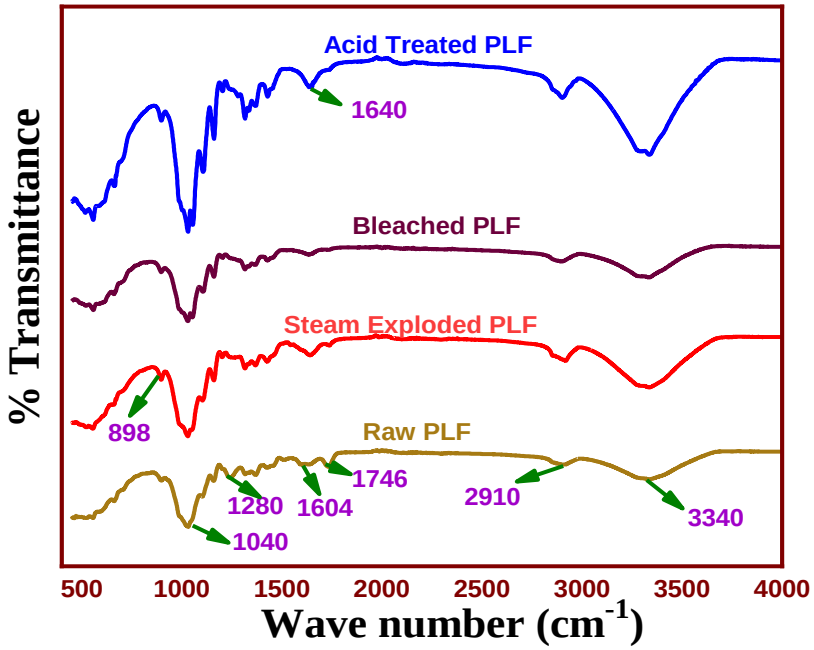


Figure 3: FTIR spectra of PLF after various treatments.

Figure 3 represents FTIR spectra of Raw PLF, steam exploded PLF, Bleached PLF and acid treated PLF. The characteristic peaks corresponding to cellulose, lignin and hemicellulose can be analysed from the spectrum. The peak at 898cm^{-1} attributed to the presence of glycosidic linkage in polysaccharides[36]. The peak at 1040 cm^{-1} ascribed to the presence of C- O-C glucopyranose ring skeleton in cellulose that was found in the spectra of all the PLF samples. This reveals that treatments of PLF fiber could not change the structure of cellulose. It has been revealed from the spectra that the intensity corresponding to the peak increased at 1040 and 1640cm^{-1} during each processing step in the extraction of NC, implying an increase in the amount of cellulose present in the sample after various treatments (steam explosion, bleaching and acid treatment). The decrease in intensity of characteristic peaks at 1280, 1604 and 1746 cm^{-1} attributed to the total removal of hemicellulose and lignin from raw PLF by the successive treatments. Hemicellulose and lignin were removed from the raw fiber by hemicellulose solubilization and lignin de- polymerization. The increase in intensity of peaks around the region 3340 cm^{-1} after each treatment corresponds to the more exposure of the hydroxyl groups of the cellulose molecules.

5.2 SCANNING ELECTRON MICROSCOPY

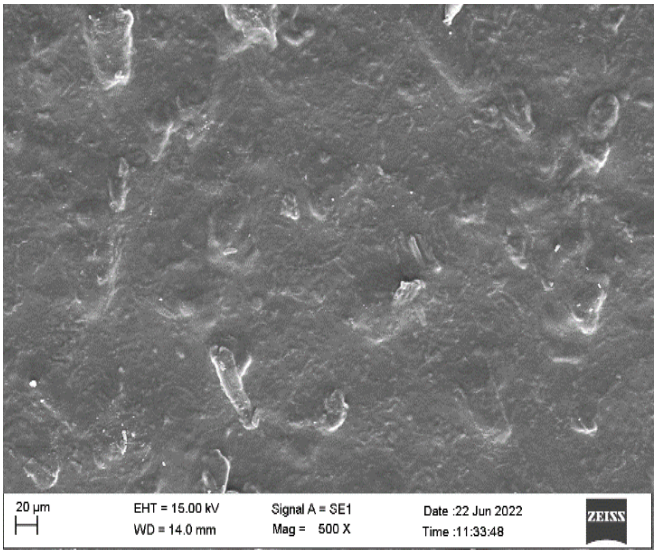


Fig 4 (a)

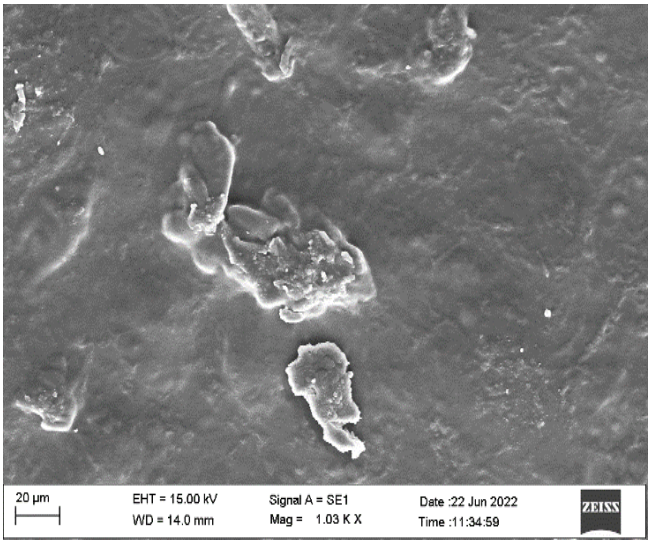
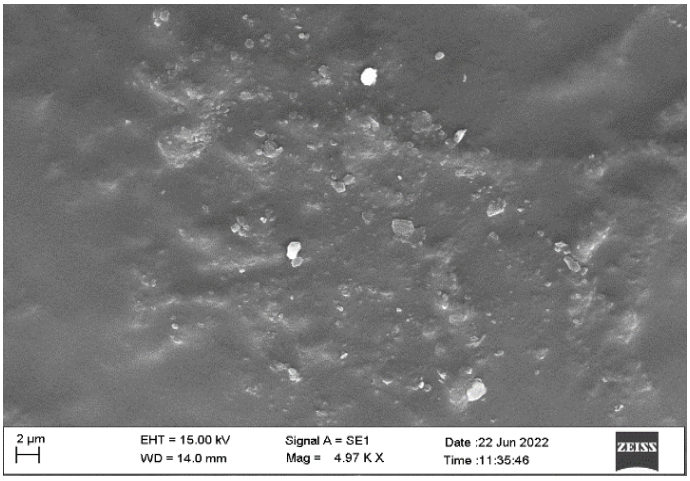
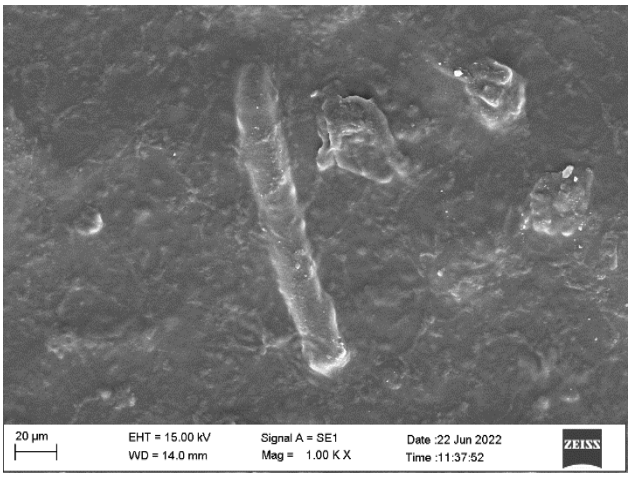


Fig 4(b)



4(c)



4(d)

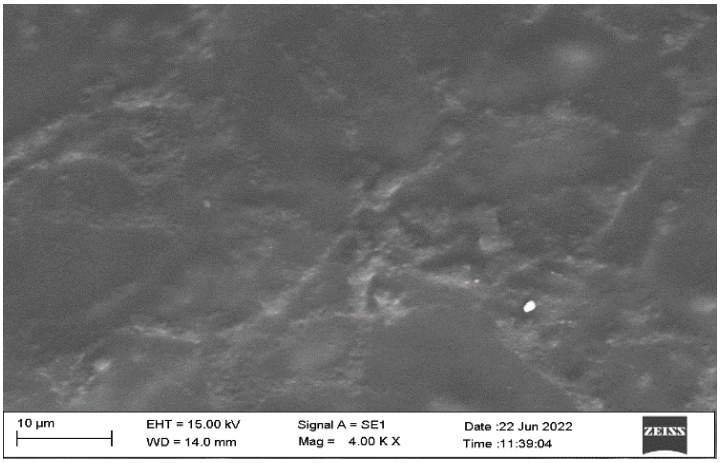


Fig4(e)

Figure 4(a,b) :Starch films reinforced with 5% nanocellulose ;Fig4(c,d,e):Starch films reinforced with 10% nanocellulose

Scanning Electron Microscopy technique is used for surface morphological and topographical studies and also for compositional analysis. No special treatment was applied to specimens and no special coating was needed. Examination was performed by a Carl Zeiss EVO 18 scanning electron microscope under an EHT of 15.00kV.

From the images the films with 10% weight of nanocellulose showed smooth surfaces .The homogeneous matrix of the films is a good indicator of its structural integrity, and consequently good mechanical properties would be expected.

5.3 THERMOGRAVIMETRIC ANALYSIS

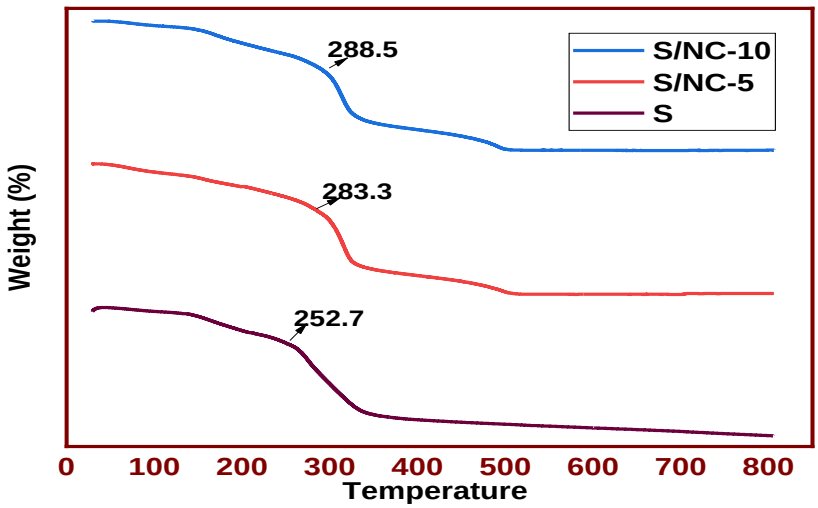


Fig5:a)TG Analysis of starch films with 5% nanocellulose and with 10% nanocellulose

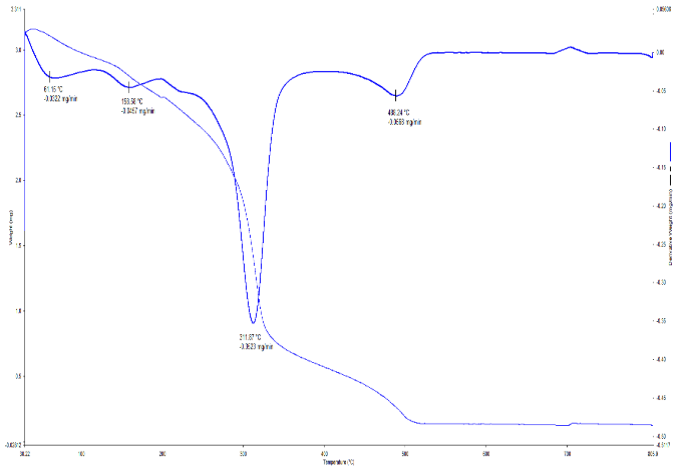


Fig5(b)

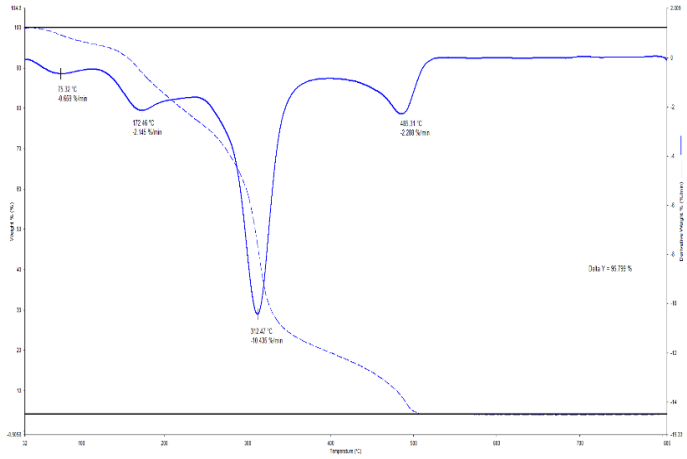


Fig5(c)

Figure 5 DTG of starch films with 5% nanocellulose (Fig 5.b) and DTG of starch films with 10% nanocellulose(Fig5.c)

Thermal Gravimetric Analysis tests are performed on the sample. The sample was analysed in oxygen atmosphere with the instrument SIMULTANEOUS THERMAL ANALYZER STA 8000.Figure 5 (a) shows the TG curves of sample A (with 5% nanocellulose) and sample(with 10% nanocellulose).Figure5(b,c) shows the combined representation of TG and DTG curves.

In figure a small mass reduction was observed with increasing in temperature due to moisture and volatiles evaporation. From 240^0C to 340^0 C a significant mass reduction and decomposition was observed. Thermal degradation and thermal stability of starch films (S, S/NC) were represented by TGA and DTG curves Figure (7(a) and (b). Thermal analysis was performed to evaluate the effect of NC and HFE on thermal stability of different films. For all film samples there occurred small weight change at the first stage ascribed to the evaporation of water molecules[11]. Thereafter, the samples exhibited high thermal stability, keeping their mass almost unchanged up to 252°C, 283°C, and 288°C respectively for S, S/NC-5 and S/NC-10films. In addition , the presence of a single peak in the DTG curve revealed the good compatibility of all the components in the filmogenic solution.

CHAPTER 6

CONCLUSION

In this work starch binanocomposite films were developed from starch powder and nanocellulose extracted from pineapple leaves. Nano cellulose fibers were used as the nanofiller for the fabrication of nanocomposites film by using the method of solution casting. The nanocellulose fibers were extracted from pineapple leaves by using the method of steam explosion followed by bleaching and acid treatment FTIR spectra of Raw PLF, steam exploded PLF, Bleached PLF and acid treated PLF showed that treatments of PLF fibre could not change the structure of cellulose[37]. It has been revealed from the spectra that the intensity corresponding to the peak increased at 1040 and 1640cm^{-1} during each processing step in the extraction of NC, implying an increase in the amount of cellulose present in the sample after various treatments (steam explosion, bleaching and acid treatment). SEM analysis prepared films revealed that the incorporation of CNC gives more homogeneous surfaces.. The addition of nanocellulose improved the thermal stability of starch films. The addition of NC has a significant effect on the degradation temperatures of films at different weight loss.

CHAPTER 7

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