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Nanocellulose from Diseased Coconut Wood Biomass

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Abstract

Cellulose is the most widespread biopolymer on earth. In biosynthesis, cellulose polymers aggregate to form substructures, microfibrils, which in turn aggregate to form cellulose fibers. By applying effective methods these fibers can be disintegrated into cellulose substructures with micro- or nano-size dimensions. This article covers some aspects related to the sources of cellulose micro- and nanofibers and the most important methods for their isolation. One of these methods, acid hydrolysis, was experimentally used to obtain cellulose nano-fibers from diseased coconut wood biomass. They were studied by Thermogravimetric analysis (TGA), X-ray diffractometer (XRD) and Scanning electrom microscope (SEM).

The 'Replanting and Rejuvenation of Coconut Gardens' was the sponsored scheme of the Coconut Development Board with an objective to eliminate all disease- affected coconut palms in eight districts of Kerala state in India. The main components of the scheme included cutting and removal of all old, unproductive and disease-hit palms followed by a replanting exercise. The present work was carried out under the Board sponsored project entitled "Diversified uses of diseased coconut wood".

Keywords: diseased coconut wood, cellulose, microcrystalline cellulose, nanocellulose.

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Introduction

One of primary uses of coconut timber is for building construction. Coconut timber is suitable for housing components like trusses, purloins, walls, joists, doors, window frames and jalousies. Low density coconut wood materials (from the centre of the stem) is used only in non-load structures like walls and panels while high density coconut wood (from the perimeter of the stem) can be used for load-bearing structures like trusses and joints. However, the actual availability of wood from coconut stem is much less as compared to the round wood logs of other species of wood as the core portion which accounts for about 60% consists of soft wood having low density and it has presently no value as wood for any purpose other than a poor quality fire wood. The ratio of the soft to hard portion of the trunk varies from the stump height to the top portion. There is a growing concern for the use of diseased coconut stems as those are produced in large quantities from the plants affected by the root wilt disease.

The term "coconut wood" has been established for the material of the coconut palm stem. Unlike conventional trees, palms, like many other monocotyledons, have vascular fibre bundles scattered in a yellowish parenchymatic ground tissue. These bundles contain the water and nutrient transport system (xylem vessels and phloem) as well as thick-walled fibres giving the stem its strength, and paratracheal parenchymatic cells. The ground parenchyma has mainly a storage function and contains starch among other things. The anatomical features result in a rather non-homogenous distribution of physical properties both over cross-section and height, and thus in a very non-homogenous raw material. From the economic and environmental point of view, it is practical to process and add value to a potentially useful resource rather than see it go to waste and pose a hazard to the environment. From the forest conservation perspective, increased used of coconut wood could potentially reduce the pressure exerted on natural forests by providing alternative or complementary raw material for different purposes. There are also significant prospects for income and employment generation to be derived from increased utilization of diseased coconut wood. This prospect is both socially and economically attractive since more than 80% of coconut landholdings in our country are owned by small farmers.

In the last years emergent technologies have opened new opportunities in many fields, including cellulose and cellulose nano composites preparation. Understanding the complexity of these cellulose structures is essential for the development of similar structures but with fundamentally different properties for engineering applications. Their unique properties continue to attract attention of researchers from different disciplines. Though, in general, age did not affect the strength properties significantly, over-mature palms and significantly higher modulus of elasticity values than lower age palms. Strength properties of coconut wood from over-mature palms compare quite well with that of other structural timbers. Stem wood from wilt-diseased palms, of adequate density, can also be used for construction purposes.

In literature nano-fibers are often referred as "nanowhiskers" or "nano-crystals". Despite their dimensions in the nano-scale level these crystallites have been named "microfibrils" or "microcrystallites". The term "nano-fibers" can be defined as long flexible particles consisting of elementary assemblies of distinct polymer units that have diameters in the order of tens of nanometers, whereas the term "whiskers" is used to designate elongated crystalline rod-like nano-particles. The cell wall of wood fibers consists of repeated crystalline structures resulting from the aggregation of cellulose chains (microfibrils). These microfibrils are surrounded by an amorphous matrix of hemicelluloses and lignin. The cell wall can be divided into several layers (Fig. 1): a middle lamella (ML), primary cell wall (P), secondary cell wall (S) (secondary wall is divided further into S1, S2 and S3 layer) and warty layer (W). These layers are different from each other in terms of structure and chemical composition.

The structure and the morphology of cellulose have been the subject of a large amount

Figure 1. Composition of wood cell wall and cellulose microfibrils consisting of crystalline and amorphous regions

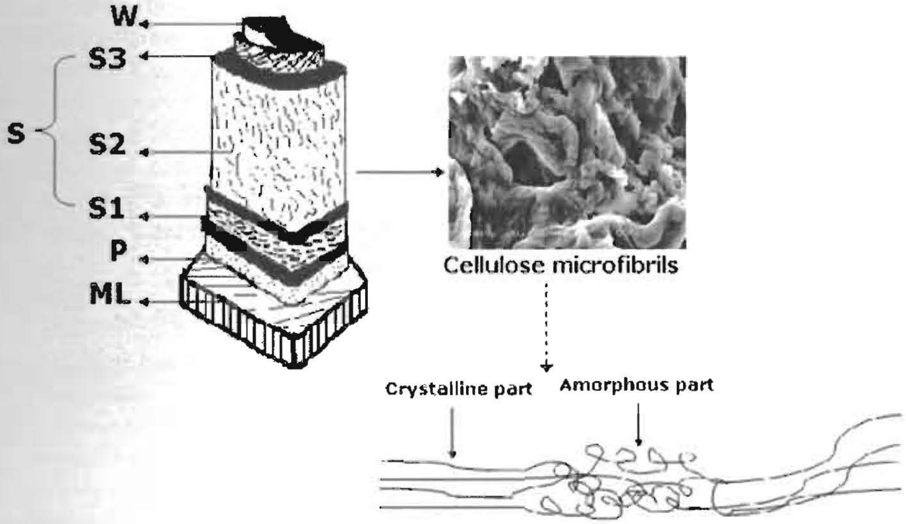
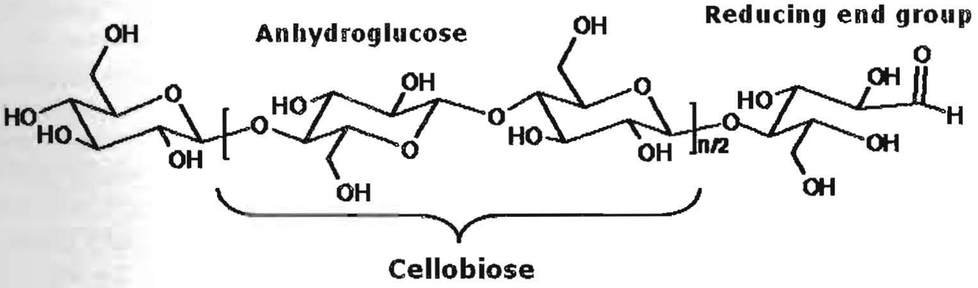


Figure 2. Chemical structure of cellulose



of work. Cellulose has a complex architecture distributed on many levels. The native cellulose molecule consists of linear glucan chains with repeating (1-4)-β-glucopyranose units (Fig. 2). In nature, cellulose chains have polymerization degree (DP) of approximately 10000 glucopyranose units in wood cellulose and 15000 in native cellulose cotton.

Each repeating unit of cellulose contains three hydroxyl (-OH) groups. These hydroxyl groups and their ability to form hydrogen bonds play a major role in directing the crystal packing and also governing the physical properties of cellulose. In cellulosic plant fibre, cellulose is present in an amorphous state, but also associates to crystalline domains through both inter-molecular and intra-molecular hydrogen bonding. The properties of cellulose including good mechanical properties, low density, biodegradability, and availability from renewable resources have become increasingly important and have contributed to a rising interest in this material. The main reason in using cellulose nano-fibers in composite materials is due to the potentially high stiffness of the cellulose fibers for reinforcement. Chemical and mechanical treatments of the cellulose fibrils result in chemical and mechanical changes on the fibre cells and surface, which affect the properties of the fibre composites. Acid hydrolytic processes are also used to degrade amorphous cellulose in forming cellulose nanofibres. Traditionally, cellulose crystallites from cellulosic materials were prepared using hydrochloric acid (HCl) and sulphuric acid (H_2SO_4) hydrolysis, and cellulose whiskers were also obtained from microfibrils by acid hydrolysis. Acid hydrolysis leads to the isolation of micro and nano-fibers with a high degree of crystallinity by removing the amorphous regions of the raw cellulose material. Applying this method a negatively charged surface of the cellulose fibers can be obtained, through the esterification of hydroxyl groups by the sulfate ions. The time and temperature of hydrolysis reaction as well as acid concentration are the factors that are playing an important role concerning the morphology and the dimensions of the obtained fibers.

Cellulose nano-fibers and the composite materials reinforced with this kind of fillers have found many potential applications in important fields like electronic and electrical industry, constructions, biomedicine and cosmetics, paper industry, packaging, building materials, textile industry and others. The fact that almost any cellulose material could be considered as a potential source for isolation nano-cellulose structures represents another important advantage in using cellulose elements as reinforcing phase in polymeric matrix composites. Despite of these attractive characteristics, cellulose fibers have also a few disadvantages due to their polar and hydrophilic character. These limitations make them poorly compatible with non-polar matrices, such as polyolefins, and induce loss of mechanical properties of composite material upon moisture adsorption. Cellulose nano-fibers can be submitted to specific surface modification in order to avoid these drawbacks. Nanocellulose can also be used to make aerogels/foams, either homogeneously or in composite formulations. Nanocellulose-based foams are being studied for packaging applications in order to replace polystyrene-based foams. Svagan et al. showed that nanocellulose has the ability to reinforce starch foams by using a freeze-drying technique. The advantage of using nanocellulose instead of wood-based pulp fibers is that the nanofibrills can reinforce the thin cells in the starch foam.

Microcrystalline cellulose (MCC) has attracted attention as a potential starting material for the cellulose reinforced nanocomposites. MCC has been used as a universal filler and binder for the extrusion process and consists of aggregated bundles of crystallites with different particles. The origin of the raw materials and the production method can decisively influence the characteristics of MCC.

Materials and Methods

The diseased coconut wood was collected from Central Coir Research Institute (Coir Board), Alleppey, Kerala. The hardwood portion of the tree includes mainly the stem region. The hard portion occupies 55% of the cross sectional area at the stump height of about 10 metre from ground level to 20% at a level two metres below the origin of the leaves. And according to the figure given below, a length of 10.04 m is said to be the hardwood portion. Soft wood refers to the crown portion which includes the leaves, bud, inflorescence, etc. (fao.org) (Figure 3), it involves a length of 4.04 m. The utilization of both the hard wood portion (Fig.4 (a)) and the soft wood portion (Fig.4 (b)) is important for the complete utilization of the diseased coconut palm. As per the figure given below an average length of 3.6 meter is said to be totally unusable. But the present study focuses on the utilization of all the portions of the coconut palm. Fig. 3.

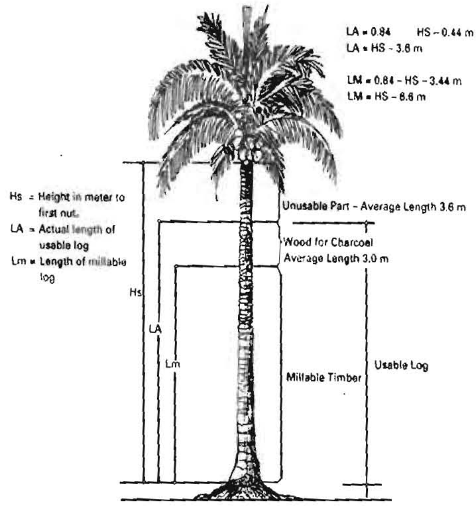


Figure 4. Diseased coconut wood (a) Hardwood (b) Softwood

Figure 4(a)

Figure 4(b)

The diseased coconut wood samples were cut in to pieces and dried at 60^{0}C and then powdered mechanically/manually. The powdered sample was oven dried at 105^{0}C for 1 hour to make it moisture free and was used for the study.

Extraction of Nanocellulose

Extraction of Nanocellulose was carried out in three steps:

1) Extraction of cellulose:

Diseased coconut wood sawdust was extracted in a soxhlet extractor using ethanol and toluene (1:2) for 6 h. The sample was finally allowed to air dry thoroughly. The material then was kiered in an autoclave using a solid: liquid ratio of 1:20 with 2% sodium hydroxide solution for 3 hours. The resultant product was washed thoroughly with water followed by 0.1% acetic acid. The pulp thus obtained was bleached with sodium chlorite (0.7%) and buffer solution to get a maximum brightness. This material was then boiled for 2 hrs using 5% w/v sodium bisulphate solution. Then it was treated with 17.5% NaOH solution. Filtered and washed with distilled water and dried at 60^{0}C in a vacuum oven until a constant weight.

2) Extraction of microcrystalline cellulose from cellulose:

The alpha-cellulose thus obtained was hydrolyzed by 2.5 N HCl, keeping the solid-liquid ratio of 1:20 and it was refluxed at 105^{0}C ± 2^{0}C for 15 minutes. After hydrolysis, the material was washed thoroughly with 1% ammonium hydroxide solution followed by washing with distilled water, and then air-dried. The final material was MCC; which was powdered and stored.

3) Extraction of Nanocellulose:

One grams of dried MCC were taken in a two-neck flask equipped with a mechanical stirrer and a condenser. HBr 40 ml (2 M) was added slowly with continuous stirring. The stirring was maintained at 100^{0}C for 4 hours. The solution was then cooled to room temperature, and it was treated with an ultrasonic liquid processor for 1 hour. The obtained suspension was centrifuged (6000 rpm) for 20 min and washed five times in distilled water. The solidified samples were freeze-dried for 48 hours, and then the crystalline linear nanocellulose powder was collected.

Morphological properties

0.01 gm each of cellulose, microcrystalline cellulose and nanocellulose was placed on the carbon coated cylindrical steel stub, and sputtered with Platinum (JEOL JFC – 1600 Auto fine coater, Japan). The surface morphology was examined using the Scanning Electron Microscope (SEM) (JEOL JSM - 6380LV, Tokyo, Japan) system with an accelerating voltage of 15 and 20 keV.

XRD Analysis

An X-ray diffractometer (XRD) with Bragg-Brentano geometry was used (Bruker AXS D8 Advance) for the study using Cu Kα radiation (λ=1.54 Å). The 2θ angle was scanned between 3 and 80^0. The crystallinity index was calculated as, CrI= $(I_{002}-I_{am})/I_{002}$, where I_{002} is the overall intensity of the peak at 2θ about 22^0 and I_{am} is the intensity of baseline at 2θ about 18^0.

Thermal Properties

The thermal decomposition behavior of the materials was measured by thermogravimetric analyzer (TGA) (Mettler Toledo TGA/ SDTA851^e, Japan). Tests were carried out in an inert atmosphere under nitrogen at a scan rate of 10^0C/min over a temperature range of 25^0C to 700^0C. A sample of 5 to 10 mg was used for each run. The weight change was recorded as a function of the heating temperature.

Results and Discussion

Morphological properties

Figures 5(a) to 5(c) depict the SEM images of Cellulose extracted from diseased coconut palm wood, Microcrystalline Cellulose from extracted cellulose and Nanocellulose from extracted Microcrystalline Cellulose respectively. Figure 5(a) clearly reveals the shape and size distribution of the micron size cellulose. These well separated microfibrils have lengths of 15-50 µm and diameters of 10-20 µm. The Figure 5(b) clearly shows the micro fibrils extracted from cellulose by the acid hydrolysis using HCl. The Figure 5(c) clearly shows the nano fibrils isolated into individual crystallites and dispersed uniformly showing a needle shaped structure. A dramatic change was observed in the particle size of 2 M HBr treated microcrystalline cellulose. A reduction in the length and diameter of the MCC by acid hydrolysis was clearly detected. The exposed parts of nanocellulose are needle shaped, with a diameter of around 100 nm (Figure 5(c)). SEM images also revealed that the diameter of nanocellulose was thicker at the middle than at the ends.

XRD Analysis

The structure and crystallinity in the cellulose were studied using XRD. The XRD patterns obtained from cellulose, MCC and nanocellulose are shown in Figure 6(a) to Figure 6(c). In these curves, the peaks are observed at 2θ=20.277, 21.521 and 21.960. The intensity of the peaks was observed to be higher in nanocellulose, indicating that the nanocellulose samples are more crystalline than MCC. On the other hand, there is a decrease in diffraction intensity (around 18^0) in the amorphous region of nanocellulose which may be attributed to the less ordered region of cellulose.

Figure 5. SEM images of (a) Cellulose extracted from diseased coconut wood, (b) Microcrystalline cellulose from the extracted cellulose, and (c) Nanocellulose from Microcrystalline cellulose (MCC)

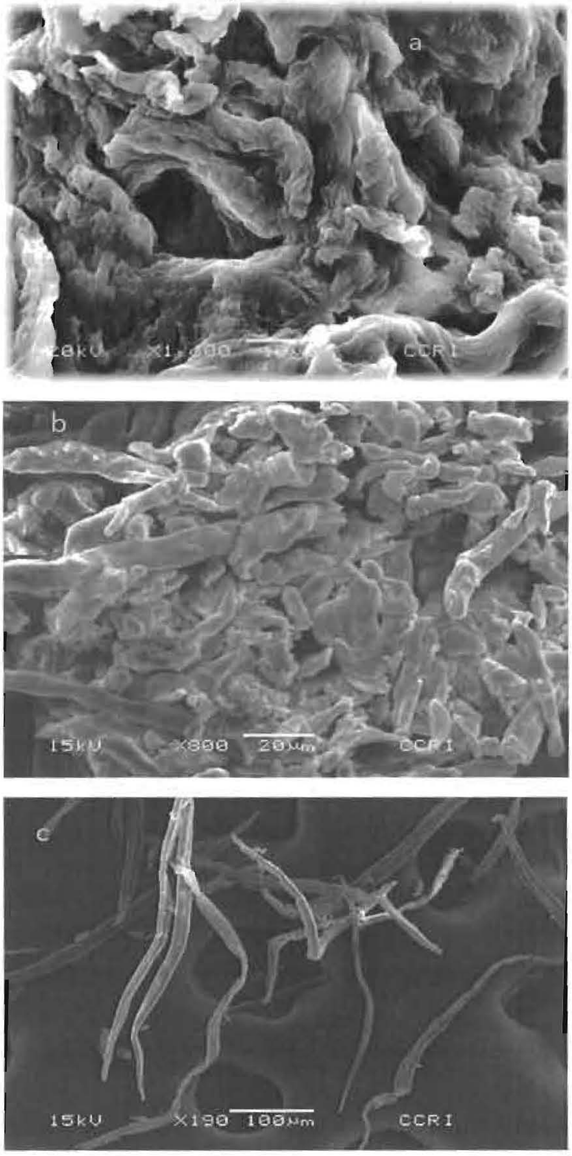
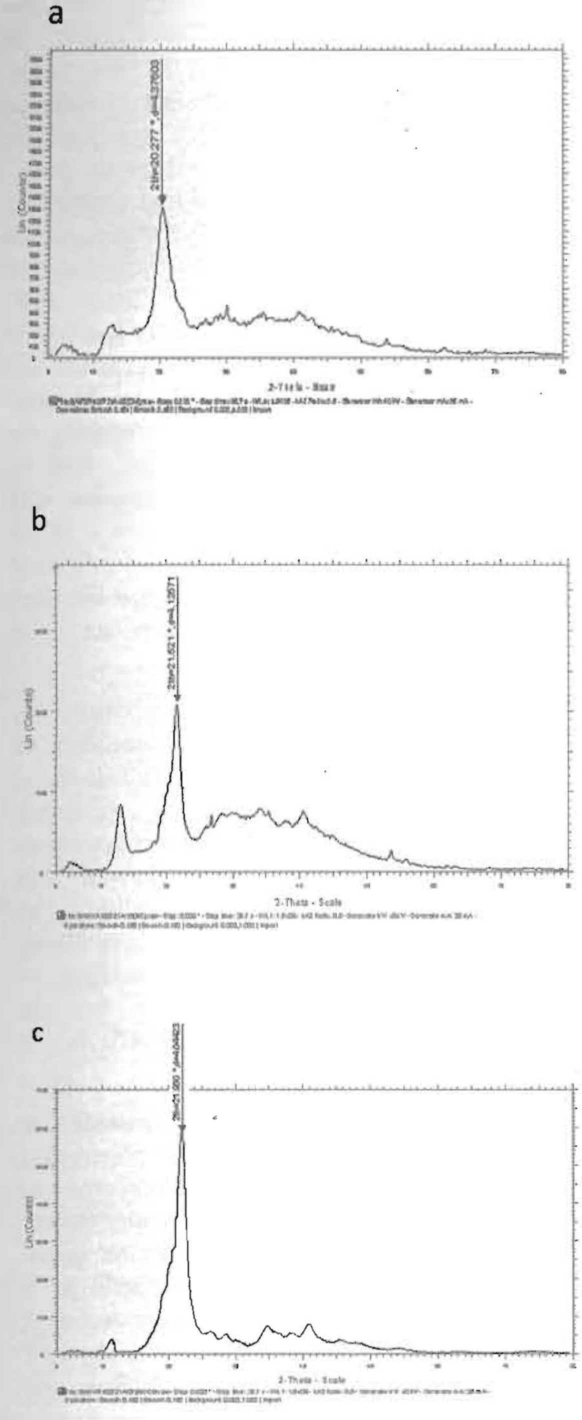


Figure 6. XRD datas of (a) Cellulose extracted from diseased coconut palm, (b) Microcrystalline cellulose from extracted cellulose, and (c) Nanocellulose from extracted Microcrystalline cellulose



The crystalline of cellulose extracted from diseased coconut palm, Microcrystalline Cellulose from extracted cellulose, and Nanocellulose from extracted Microcrystalline cellulose are shown in Table 1.

Table 1. Crystalline of Cellulose, MCC & Nanocellulose

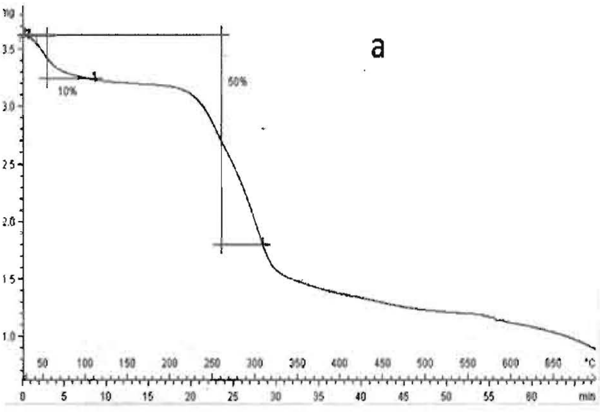
Sample	Crystallinity, X_c
Cellulose	0.1123
MCC	0.1636
Nanocellulose	0.1803

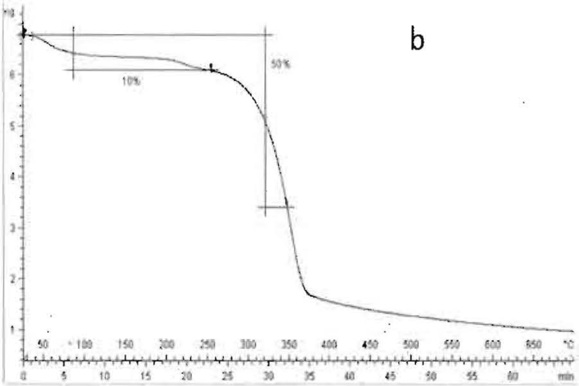
The X_c of cellulose was initially observed as 0.1123 which after acid hydrolysis showed a significant increase in MCC & Nanocellulose. This result indicates that after dissolving or degrading of the accessible amorphous regions, the crystalline regions still remain confirming the crystalline of nanocellulose.

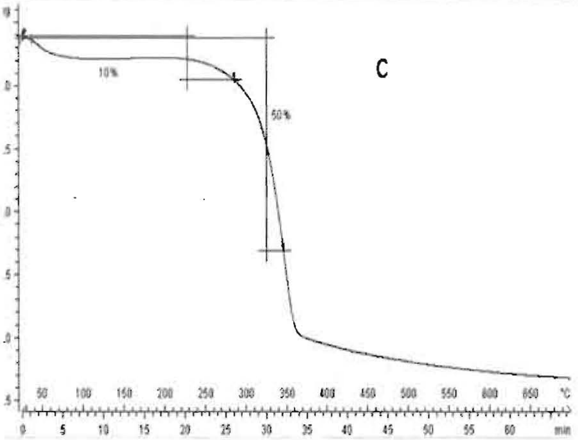
Thermal Properties

The TGA results of cellulose, microcrystalline cellulose and nanocellulose have been furnished in Figures 7(a) to 7(c).

Figure 7. TGA datas of (a) Cellulose extracted from diseased coconut wood, (b) Microcrystalline cellulose from extracted cellulose, and (c) Nanocellulose from extracted Microcrystalline Cellulose







The temperatures at 10% weight loss (T_{10}) and 50% weight loss (T_{50}) of cellulose, MCC and nanocellulose are shown in Table 2. From the TGA for MCC it was observed that the temperatures at 10 % weight loss (T_{10}) and 50 % weight loss (T_{50}) increased from 250^0 to 350^0C. After acid hydrolysis with 2 M HBr, the T_{10} of nanocellulose increased to 275^0C, and the T_{50} increased to 356^0C. From the results it is observed that there is an increase in crystallinity of the nanocellulose which in turn increases its thermal stability.

Table 2. TGA of cellulose, MCC and Nanocellulose

Sample	T_{10} (^{0}C)	T_{50} (^{0}C)
Cellulose	110	325
MCC	250	350
Nanocellulose	275	356

Conclusion

MCC and Nanocellulose could be extracted from cellulose in diseased coconut wood. By means of TGA, XRD and SEM it was possible to characterize the cellulose, MCC and nanocellulose. XRD tests showed that the crystallinity was comparatively higher in nanocellulose as compared to the other celluloses studied. The nanocellulose obtained after 2 M HBr hydrolysis of MCC was observed to have greater thermal stability than MCC. Crystalline cellulose has interesting mechanical properties for use in material applications. Its tensile strength is about 500MPa, similar to that of aluminium. Its stiffness is about 140–220 GPa, comparable with that of Kevlar and better than that of glass fiber, both of which are used commercially to reinforce plastics. In semi-crystalline polymers, the crystalline regions are considered to be gas impermeable. Due to relatively high crystallinity, in combination with the ability of the nanofibers to form a dense network held together by strong inter-fibrillar bonds (high cohesive energy density), it has been suggested that nanocellulose might act as a barrier material.

Nanocellulose can also be used to make aerogels/foams, either homogeneously or in composite formulations. Nanocellulose-based foams are being studied for packaging applications in order to replace polystyrene-based foams. Svagan et al. showed that nanocellulose has the ability to reinforce starch foams by using a freeze-drying technique. The advantage of using nanocellulose instead of wood-based pulp fibers is that the nanofibrills can reinforce the thin cells in the starch foam.

There is potential of nanocellulose applications in the area of paper and paperboard manufacture Nanocelluloses are expected to enhance the fiber-fiber bond strength and, hence, have a strong reinforcement effect on paper materials. Nanocellulose may be useful as a barrier in grease-proof type of papers and as a wet-end additive to enhance retention, dry and wet strength in commodity type of paper and board products.

Other applications

- Freeze-dried nanocellulose aerogels used in sanitary napkins, tampons, diapers or as wound dressing.
- The use of nanocellulose as a composite coating agent in cosmetics e.g. for hair, eyelashes, eyebrows or nails
- A dry solid nanocellulose composition in the form of tablets for treating intestinal orders
- Nanocellulose films for screening of biological compounds and nucleic acids encoding a biological compound
- Filter medium partly based on nanocellulose for leukocyte free blood transfusion
- A buccodental formulation, comprising nanocellulose and a polyhydroxylated organic compound
- Powdered nanocellulose has also been suggested as an excipient in pharmaceutical compositions
- nanocellulose in compositions of a photo reactive noxious substance purging agent

The diseased coconut wood biomass could therefore be utilized for extraction of cellulose which could be used for different applications including the high end use for nanocellulose.

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References

Al-Shouiman Salim S. Furfural from Some edible plants grown in Saudi Arabia, *Journal of J. King Saud Unvi* 10, Science (2) 119-125 (A.H.1428/1998)

Bondeson D., Mathew A., Kristiina Oksman. 2006. Optimization of the isolation of nanocrystals from microcrystalline cellulose by acid hydrolysis. *Cellulose.* 13(2): 171-180.

Central Plantation Crops Research Institute (CPCRI), Kasaragod. Mycoplasma diseases of coconut with special reference to root (wilt) disease. *Indian Phytopath.* 52 (4): 335-353 (1999)

Chattopadhyay H., Sarkar p.B.1946, New Method for estimation of cellulose, *proe Natl Inst Sci India* 12 (1): 23-46.

David N.S. Hon and Nobuo Shiraishi. 2000. Wood and cellulosic chemistry 2nd edition. 282pp.

Dong S.P. and Roman M. 2007. Fluorescently labeled cellulose nanocrystals for bioimaging applications. *Journal of the American Chemical Society,* 129(45): 13810-13811.

Eichhorn S.J., Dufresne A., Aranguren M., Marcovich N.E., Capadona J.R., Rowan S.J., Weder C., Thielemans W., Roman M., Renneckar S., Gindl W., Veigel S., Keckes J., Yano H., Abe K., Nogi M., Nakagaito A.N., Mangalam A., Simonsen J., Benight A.S., Bismarck A., Berglund L. A., and Peijs T. 2010. Review: *current international research into cellulose nanofibres and nanocomposites. Journal of Materials Science,* 45(1): 1- 33.

Hoenich N. 2006. Cellulose for medical applications: past, present and future. *BioResources,* 1(2): 270-280.

Hubbe M.A., Rojas O.J., Lucia L.A., and Sain M. 2008. Cellulosic Nanocomposites: A review. *BioResources,* 3(3): 929-980.

Kamel S. 2007. Nanotechnology and its applications in lignocellulosic composites, a mini review. *EXPRESS Polymer Letters,* 1(9): 546-575.

Laka M. and Chernyavskaya S. 2007. Obtaining microcrystalline cellulose from softwood and hard wood pulp, *BioResources,* 3(3): 583-589.

Moran J.I., Alvarez V.A., Cyras V.P., Vazquez A. 2008. Extraction of cellulose and preparation of nanocellulose from sisal fibers. *Cellulose.* 15(1): 149-159.

Perssoa JR A., Manchila IM., and Sato S. 1997. Acid Hydrolysis of Hemicellulose from Sugar cane Bagasse. *Brazilian Journal of chemical engineers.* 14(3): 632-636.

Ramjagtheesh R., Karthikeyan G., Rajendran L., Johnson I., Raghuchander T. & Samiyappan R. (2012), Root (wilt) disease of coconut palms in South Asia- an overview. 45 (20): 2485-2493

Rauganna S. 1977. Manual of analysis of fruits & vegetables products. CFTRI, New Delhi 324pp. AACC Method 1962, 52-11

Sadasivam **S.** and Manickam A. 1996. Biochemical Methods. 2nd ed. New age, 14pp.

Sarwar Hahan M., Lee Z.Z.,Yongoan JJIN *et al* 2006. Organic Acid Pulping of Rice Straw: *Turk J. Agric. For Cooking,* 30: 231-239.

Sjöström E. 1993. Wood Chemistry: Fundamentals and Applications. 2nd ed Academic Press Inc., San Diego, USA. 54pp.

Sun-Young Lee, D Jugan Mohan, In Aeh Kang, Geum-Hyun Doh, Soo Lee and Seong OK Han. 2009. Nanocellulose Reinforced PVA Composite Filims Effects of Acid treatments of Filter Loading. *Journal of Fibers & polymers,* 10(1): 77-82.

Vogels Aurthur I. 1957. Text Book of Practical Organic Chemistry including Qualitative Organic Analysis, 3rd ed. DSC Lond, DIC FRIC. 299pp.

Wegner T.H., Winandy J.E., and Ritter M.A. 2005. Nanotechnology opportunities in residential and non residential construction. *2nd International Symposium on Nanotechnology in Construction, Bilbao, Spania.* 101-110pp.

Zimmermann T., Bordeanu N., and Strub E. 2010. Properties of nanofibrillated cellulose from different raw materials and its reinforcement potential. *Carbohydrate Polymers*, 79(4): 1086-1093.