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Isolation and characterization of cellulose nanowhiskers from *Acacia caesia* plant

Seena K. Thomas[1,2] | P. M. Sabura Begum[1] | C. D. Midhun Dominic[3] | Nisa V. Salim[4] | Nishar Hameed[5] | Sanjay Mavinkere Rangappa[6] | Suchart Siengchin[6] | Jyotishkumar Parameswaranpillai[6]

[1]Department of Applied Chemistry, Cochin University of Science and Technology, Kochi, India

[2]Postgraduate Department of Chemistry, Sree Sankara College, Ernakulam, India

[3]Department of Chemistry, Sacred Heart College, Cochin, India

[4]Faculty of Science, Engineering and Technology, Swinburne University of Technology, Hawthorn, Victoria, Australia

[5]Factory of the Future, Swinburne University of Technology, Hawthorn, Victoria, Australia

[6]Natural Composites Research Group Lab, King Mongkut's University of Technology North Bangkok (KMUTNB), Bangkok, Thailand

Correspondence
Jyotishkumar Parameswaranpillai, Natural Composites Research Group Lab King Mongkut's University of Technology North Bangkok (KMUTNB) 1518 Pracharaj 1, Wongsawang Road, Bangsue, Bangkok 10800, Thailand.
Email: jyotishkumarp@gmail.com

Suchart Siengchin, Natural Composites Research Group Lab, King Mongkut's University of Technology North Bangkok (KMUTNB), Bangkok, Thailand.
Email: suchart.s.pe@tggs-bangkok.org

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Abstract

Acacia caesia (L.) Willd (soap bark) fiber is an abundant natural resource, that is rich in cellulose. The study reports the effective utilization of underutilized *Acacia caesia* fiber for the isolation of nanocellulose whiskers. The nanocellulose whiskers were isolated successfully from *Acacia caesia* fibers by following alkali, bleaching, and sulfuric acid treatment. The obtained nanocellulose whiskers were carefully investigated for its chemical composition, structure, morphology, crystallinity, and thermal stability. The chemical composition and Fourier transform infrared spectra of nanocellulose whiskers showed the elimination of the non-cellulosic parts present in the raw *Acacia caesia* fibers. The X-ray diffraction analysis showed an upsurge in the crystallinity of the cellulose fibers after the chemical treatments. The isolation of nanocellulose whiskers from *Acacia caesia* raw fiber was confirmed by electron microscopy analysis. The thermogravimetric analysis showed remarkably high char residue for the nanocellulose whiskers compared to raw fibers. Based on the properties of nanocellulose whiskers, it can be concluded that the nanocellulose whiskers produced from *Acacia caesia* raw fibers are potential reinforcing material for developing high-performance green composites.

1 | INTRODUCTION

Nanocellulose has gained enormous interest among researchers in academia and industry owing to its easy availability, renewability, cheap, lightweight, good rigidity, easy processing, eco-friendly, biodegradability, nontoxic, good thermo-mechanical properties, large surface area, and lower thermal expansion.[1,2] With the recent technological advancement, the isolation of nanocellulose from plant fibers attracted more attention.[3–5] Plant fibers consist of cellulose, hemicellulose, pectin, lignin, and wax. Plant fibers such as flax (71.0), hemp (70.2–74.4), ramie (68.6–76.2), pineapple (70.0–82.0) and sisal (67.0–78.0) have very high cellulose content.[6] Many natural fibers such as *Helicteres isora* (*east Indian screw tree*),[7] sugarcane bagasse,[2] wood, bamboo, wheat straw fibers, flax fibers,[8] cotton,[9] banana,[10] banana peel,[11] Jute,[12] coconut husk fibers,[13] wheat straw and soy hulls,[14] water hyacinth,[15] and oil palm[16] have been used for the isolation of cellulose. Cellulose is poly(β-D-glucopyranose) and the monomer units are connected by β-1-4-linkages. The degree of polymerization in cellulose is ca. 2000 and in nature, it exists as cellulose fibers rather than cellulose molecules.[17] The cellulose component offers strength and rigidity to the plant fibers and it exists in microfibrils along with hemicellulose and lignin in the cell wall of the plants.[18] Several methods are available for the isolation of nanocellulose from the plant fibers such as high-pressure homogenization,[19] steam explosion,[20] ultrasonic technique,[21] enzymatic pre-treatments,[22] and chemical treatments.[2,23,24]

High-pressure homogenization is a common mechanical treatment method used to isolate cellulose from raw natural fibers. In this method raw fibers are passed through the homogenizer at high pressure and high viscosity, causing fiber fibrillation. The disadvantages of this method are high energy consumption, clogging, low aspect ratio, and poor thermomechanical properties. However, this method is environmentally friendly and is used for the industrial production of cellulose fibers.[19,25–27] Steam explosion is an effective method for the extraction of nanocellulose from raw natural fibers. Here chemically treated fibers are subjected to high pressure in an autoclave. The rapid release of pressure cause fiber fibrillation. The process is repeated multiple times for good results. The advantage of this method is that it is a sulfur-free process and hence less hazardous. The drawbacks of this process are low pulp yield, wastage of chemical reagents, corrosion of apparatus, and high energy consumption.[12,20,26,28] Recently, the ultrasonication method has become more popular for the fibrillation of natural fibers. In the ultrasonic technique, the fibers soaked in distilled water were subjected to ultrasonication. The hydrodynamic forces generated from the ultrasound is used for the fiber fibrillation. This method is relatively simple and environmentally friendly. However, ultrasonication has many drawbacks such as low thermal stability and crystallinity of the prepared nanocellulose fibers and also chemical pre-treatment is necessary for effective fiber fibrillation.[29–31] In enzymatic pre-treatments, the raw fibers were treated with enzymes like cellulase, ligninase, xylanase, pectinase, laccase, and so forth. The action of these enzymes results in the degradation of hemicellulose, lignin, and pectin. Enzymatic technology ensures effective and green synthesis of cellulose fibers. The major limitation of this technique is the cost of enzymes.[32–35]

Different chemical agents like sulfuric acid, hydrochloric acid, phosphoric acid, and so forth, are commonly used for the extraction of nanocellulose from natural fibers.[36–40] Among the various chemical methods, sulfuric acid hydrolysis is the most commonly used method for the extraction of cellulose from plant fibers. Hydrochloric acid is also used for the acid hydrolysis of raw natural fibers. The thermal stability and the yield of nanocellulose produced by hydrochloric acid hydrolysis is better than sulfuric acid, however, the generated nanocellulose may flocculate in the absence of any surface charge.[27,39] Phosphoric acid is an another commonly used acid for the extraction of nanocellulose. The nanocellulose obtained by this method forms a stable suspension and is also thermally stable.[40]

Previous studies have shown that sulfuric acid hydrolysis of natural fibers can produce cellulose nanocrystals or long cellulose nanofibrils from different cellulose sources and hydrolysis conditions.[41,42] Jiang et al.[24] showed that the sulfuric acid hydrolysis of pure rice straw cellulose resulted in highly crystalline rod-like cellulose nanocrystals (CNCs) with 90% crystallinity. Later Jiang et al.[43] utilized sulfuric acid hydrolysis for the extraction of CNCs from tomato peels. The CNCs have cellulose Iβ structure with 80.8% crystallinity. Morais et al.[44] isolated nanocellulose from raw cotton linter using sulfuric acid hydrolysis. The percentage crystallinity of raw cotton linter is 64%, and this value increases to 90% for nanocellulose whiskers. Azani et al.[45] prepared CNC form oil palm frond using sulfuric acid hydrolysis. The CNCs have 90 nm long, and 6 nm diameter with a crystallinity index value of 60%. Recently Septevani et al.[46] synthesized nanocellulose from oil palm empty fruit bunch via sulfuric acid treatment. Thus, studies revealed the successful extraction of nanocellulose from raw natural fibers by sulfuric acid hydrolysis treatment. It is important to point out that the nanocellulose produced from various plant sources are used in many potential applications such as super adsorbent for wastewater

treatment, transparent films, food packaging industries, and biomedical materials.[17,46–48]

Plants are abundant however their characteristic properties are different due to the difference in their structural features; therefore, it is worth to extract and characterize nanocellulose from different plant species. *Acacia caesia (Incha)* is a widely grown tree in the Western Ghats, India.[49] It is easily available, biodegradable, low cost, and ecofriendly. It belongs to the family Mimosaceae and grows up to 15 m tall. *Acacia caesia* is famous for its medical value and is widely used as a natural body scrubber. Leaves are used for the treatment of asthma, and skin diseases.[49,50] The wood is used for making furniture, boats, and so forth. *Acacia caesia* is an agro-waste after its application as a scrubber or after some ayurvedic treatment. Even though *Acacia caesia* fibers are known for centuries, it is underutilized in commercial high-performance applications.

Among the various methods used for the extraction of nanocellulose, the chemical method is most attractive because it is cheap, highly effective, and fast process.[10] Also, chemical treatment of the plant fibers can effectively modify the physical structure together with the improvement in thermomechanical properties. Moreover, chemical treatment will reduce the hydrophilicity of the fibers thus enhances the interfacial interaction between the fibers and polymer.[13,16,51–54] As per literature, the extraction of nanocellulose from *Acacia caesia* fibers has not been reported to date. In this work, an attempt has been made to isolate cellulose nanowhiskers from *Acacia caesia* raw fiber by alkali treatment, bleaching, and acid hydrolysis.

2 | MATERIALS AND METHODS

2.1 | Materials

The raw *Acacia caesia (L.) Willd* stem fibers (soap bark) were obtained from the local market in Ernakulam, Kerala, India. The chemicals such as NaOH, H_2O_2, and H_2SO_4 were purchased from Merck for the chemical treatment of *Acacia caesia* fibers.

2.2 | Methods

2.2.1 | Preparation of cellulose nanowhiskers from *Acacia caesia*

Acacia caesia fibers were powdered well and about 50 gm of the sample was treated with 1000 ml 20 wt% NaOH with stirring for 24 h. The fibers were then washed well in distilled water and the procedure was repeated four times to remove most of the lignin, wax, and pectin content from the fiber. The alkali treated fibers were bleached with 200 ml 20% H_2O_2 and 40 ml 10% NaOH solution with stirring for 24 h. The bleaching was repeated four times or until the fibers become white. Later bleached fibers were thoroughly washed with distilled water and dried at room temperature. The dried fibers were treated with 64 wt% H_2SO_4 at 45°C with stirring for 1 h. Finally, the fibers were washed thoroughly with distilled water until the pH of the sample is neutral. The cellulose exists as alternate crystalline and amorphous regions. Acid hydrolysis helps the dissolution of non-crystalline (amorphous) parts.

2.2.2 | Characterization of cellulose nanowhiskers

The chemical composition of *Acacia caesia* fibers was measured in accordance with ASTM standards. The ASTM standards D 1103-55T, D 1104-56, D1106-56, and D 4442-92 were used for the evaluation of cellulose, hemicellulose, lignin, and water content respectively.[7] FTIR spectrum of the treated and untreated fibers was recorded using Avtar 370 spectrometer (Thermo Nicolet, USA). The powdered fibers were mixed thoroughly with KBr and pressed to form KBr pellet. KBr was used for making sample pellets because it is transparent for the light in the IR range. The sample pellet was scanned from 400 to 4000 cm^{-1}. Bruker, D8 advance rotaflex diffraction meter was used to record the X–ray diffraction pattern of raw fibers and cellulose nanowhiskers using CuKα radiation at a $\lambda = 1.5406$ Å. Scanning electron microscopic (SEM) images were taken with a JEOL-JSM 5800 scanning electron microscope to study the microstructural characteristics of the fibers. The fibers were sputtered with gold before SEM analysis. The nanoscale morphology of the cellulose nanowhiskers was taken using JEOL JEM3010 transmission electron microscope (TEM). The thermal behavior of the raw fibers and cellulose nanowhiskers was measured using a Perkin Elmer, Diamond TG/DTA. The experiments were carried out at 30–700°C at a constant heating rate of 20°C/min.

3 | RESULTS AND DISCUSSION

3.1 | Chemical composition of *Acacia caesia* fibers

The chemical composition of *Acacia caesia* fibers is given in Table 1. The raw *Acacia caesia* fibers have a

TABLE 1 Chemical composition of *Acacia caesia* fibers

Samples	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Moisture (%)
Acacia caesia raw fibers	54.08	21.52	18.14	5
Cellulose nanowhiskers	92.35	0.32	0.395	7

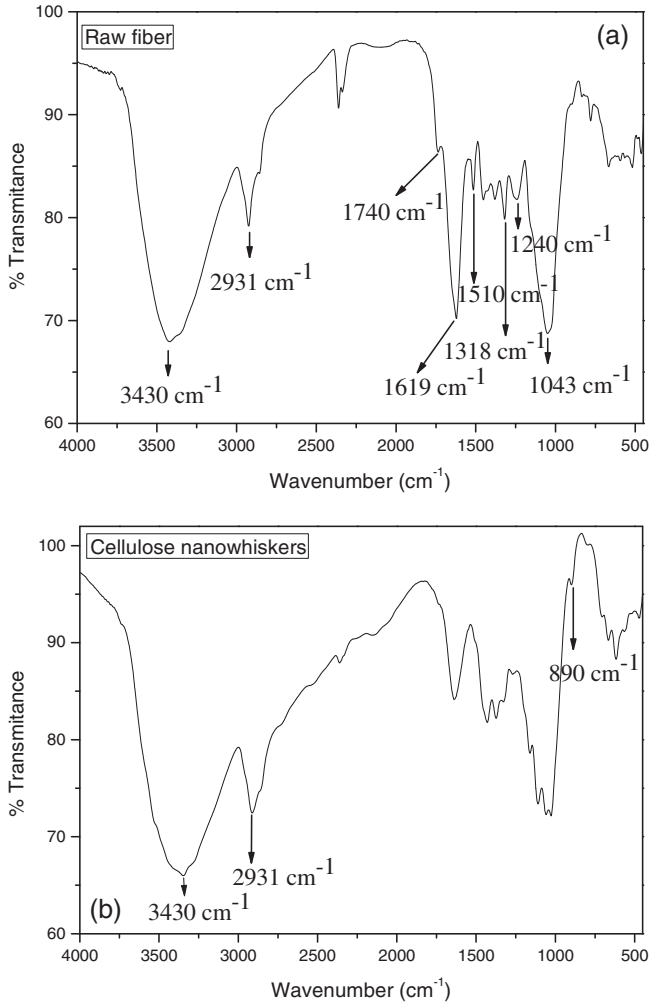

FIGURE 1 FTIR spectrum of (a) raw *Acacia caesia fiber*, and (b) prepared cellulose nanowhiskers

cellulose content of 54.08%, hemicellulose content of 21.52%, lignin content of 18.14%, and water content of 5%. While that of treated *Acacia caesia* fibers have a cellulose content of more than 92%. On the other hand, a substantial reduction of hemicellulose and lignin is observed after the chemical treatment. The increase in cellulose and the decrease in hemicellulose and lignin in the treated fibers confirms the removal of non-cellulosic parts from the raw *Acacia caesia* fibers.

3.2 | Fourier transform infrared spectroscopy (FTIR) studies

The FTIR spectra provide an easy understanding of the structural features of plant fibers. The FTIR spectra of raw *Acacia caesia* fiber and prepared cellulose nanowhiskers are given in Figure 1(a, b). The peaks position of the raw fiber is shown in Figure 1(a). The broad band/peak at 3430 cm^{-1} represents the OH stretching vibrations of the cellulose.[16] The peak at 2931 cm^{-1} corresponds to C—H stretching vibrations of cellulose.[19] These two peak positions are common for cellulose nanowhiskers and raw fiber. The shoulder at 1740 cm^{-1} in the raw *Acacia caesia* fiber is due to the presence of hemicellulose and lignin and is absent in cellulose nanowhiskers demonstrating the elimination of hemicellulose and lignin from the raw fibers during the chemical treatment.[2,8] The peak at ca. 1619 cm^{-1} is associated with the absorbed water molecules.[55] The band at 1510 cm^{-1} corresponding to the stretching vibrations of lignin is disappeared in the case of cellulose nanowhiskers indicating the dissolution of lignin from the raw fibers during the chemical treatment.[15] The band at 1240 cm^{-1} corresponds to hemicellulose and lignin, is vanished in the prepared cellulose nanowhiskers further confirms the elimination of lignin and hemicellulose from the nanocellulose.[56,57] The peak at 1043 cm^{-1} is assigned to the ether linkage from lignin or hemicellulose in the raw fiber.[7] This peak is absent in the prepared cellulose nanowhiskers due to the dissolution of lignin or hemicellulose from the fibers after the chemical treatments. The appearance of a new band at 890 cm^{-1} in the prepared cellulose nanowhiskers corresponds to β-glycosidic linkages of glucose units in cellulose, represent an upsurge in the cellulose content in the treated fiber.[2] Thus, the FTIR study reveals the removal of non-cellulosic parts from the natural fiber during the chemical treatment and the major content of the prepared nanofiber is cellulose.

3.3 | X-ray diffraction (XRD) studies

The crystallinity of cellulose nanowhiskers is critical for polymer reinforcements as it provides strength and

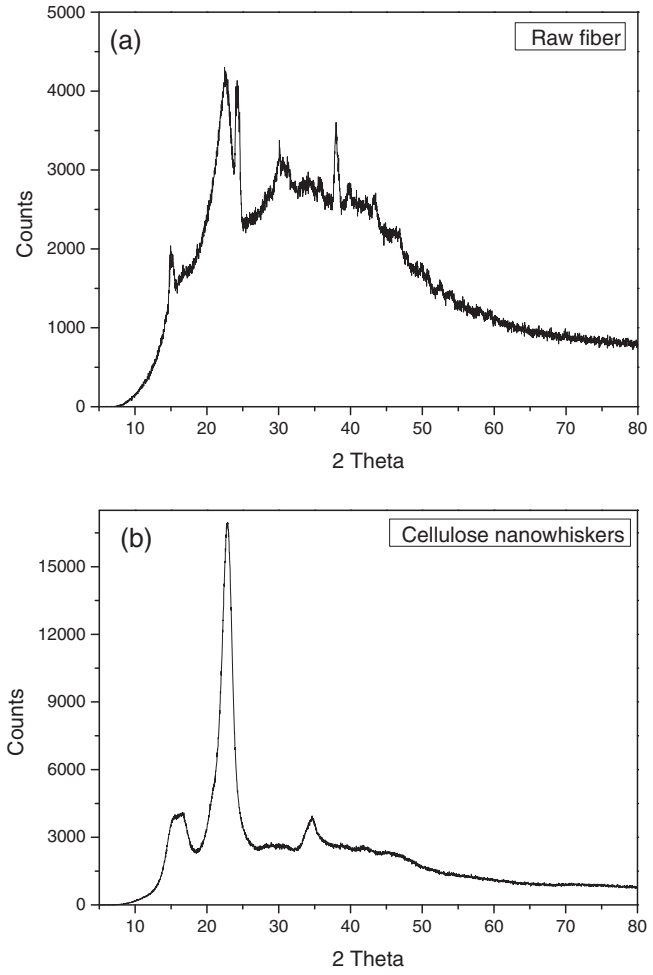

FIGURE 2 XRD pattern of (a) raw *Acacia caesia* fiber, (b) cellulose nanowhiskers

stiffness to the composites. The crystalline behavior of the raw fiber and cellulose nanowhiskers were investigated by XRD. The XRD pattern of raw fiber and prepared cellulose nanowhiskers are shown in Figure 2(a, b). The XRD of the samples tested shows two broad diffraction patterns at $2\theta = 16^\circ$ and $2\theta = 22.6^\circ$, representing cellulose I structure.[8,19] This indicates that the crystalline structure of the fiber did not change during chemical treatment.[11] The diffraction peak at $2\theta = 22.6^\circ$ corresponds to crystalline cellulose. From Figure 2, the intensity of the crystalline peak increases with chemical treatment, the intense peak proposes the removal of the noncellulosic part from the raw natural fibers. These results suggest an increase in the crystallinity of the cellulose nanowhiskers.[58] The crystallinity index (*Ic*) of the raw fiber and prepared cellulose nanowhiskers was calculated using the following Equation.[8,59]

$$Ic = \frac{[I(200) - I(am)]}{I(200)} * 100, \quad (1)$$

where $I_{(200)}$ is the peak intensity at $2\theta = 22.6^\circ$ and I_{am} is the intensity minimum between 200 and 110 plane (I_{am}, $2\theta = 18^\circ$).

The *Ic* of the raw fiber and prepared cellulose nanowhiskers are given in Table 2. The crystallinity of the raw fiber is lowest because it is embedded in the amorphous matrix. On the other hand, the crystallinity remarkably increases after the chemical treatments in prepared cellulose nanowhiskers. The treatments cause the dissolution of the amorphous phase. That means the increase in the crystallinity is due to the removal of the non-crystalline component from the fiber. It is reported that the alkali treatment causes the dissolution of some of the amorphous portion of the fibers.[60] This causes the rearrangement of the crystalline phase and the remaining amorphous phase. The bleaching followed by the acid hydrolysis removes the remaining amorphous phase. This is because during acid hydrolysis treatment the hydronium ions penetrate into the fiber causing the hydrolytic cleavage of glycosidic bonds of cellulose, allowing the dissolution of non-crystalline part and hence resulting in highly ordered crystallites.[60,62] The high value of crystallinity provides strength and stiffness and will be more effective as a reinforcement with the polymer matrix. The crystallinity index (*Ic*) of the raw fiber and prepared nanocellulose from various sources are given in Table 2.

3.4 | Morphology of the nanocellulose whiskers

The SEM images of *Acacia caesia* fibers at the various stages of chemical treatment are given in Figure 3(a–d). From the micrographs, it is clear that the chemical treatment reduced the fiber dimension from macro to nanoscale. Figure 3(a) showed an irregular structure of raw *Acacia caesia fibers* with an average diameter of ca. 50 μm. The uneven surface of the raw fiber is due to the presence of cementing materials such as hemicellulose, lignin, pectin, and wax. The treatment with NaOH removed some part of the cementing material and hence a reduction in the diameter of the fibers is observed. After NaOH treatment, the fiber becomes more rough and the fiber diameter reduced to ca. 10 μm. The bleaching of the alkali-treated fiber surface with NaOH and H_2O_2 further reduced the size of the fibers to ca. 300 nm, because of the defibrillation of the fibers. Finally, after the sulfuric acid treatment, the crystalline rod-like nanocellulose whiskers are observed (Figure 3(d)) in the form of a classic web-like network structure.[58] As stated in the XRD studies, the acid hydrolysis causes the hydronium ion to penetrate into the fibers resulting in the hydrolytic cleavage of glycosidic bonds of cellulose and also removed

TABLE 2 Crystallinity index (*Ic*) of the raw fiber and prepared cellulose nanowhiskers from various sources

Samples	Method of treatment	Raw fibers (Ic)	Nanocellulose (Ic)	Reference
Acacia caesia	Chemical treatment	56.67%	79.65%	Current work
Helicteres isora	Chemical treatment and steam explosion	38.0%	90.0%	7
Wood	Chemical-ultrasonic process	56.0%	71.0%	8
Bamboo	Chemical-ultrasonic process	55.5%	64.9%	8
Rice straw	Chemical-ultrasonic process	50.9%	63.4%	8
Flax	Chemical-ultrasonic process	78.3%	81.6%	8
Cotton fiber	Chemical treatment	77.0%	91.0%	9
Banana Fiber	Chemical treatment	60.05%	80.13%	10
Jute fiber	Steam explostion	46.32%	62.54%	12
Coconut fibers	Chemical treatment	38.9%	65.9%	13
Wheat straw fibers	Chemical treatment	57.5%	77.8%	14
Soy hulls	Chemical treatment	59.8%	69.6%	14
Sugarcane bagasse	High pressure homogenization	60.0%	36.0%	19
Wood fibers	Ultrasoniaction	52.74%	69.34%	30
Curaua fibers	Enzymatic treatment (pectinase)	68.2%	69.7%	34
Alfa fiber	Chemical-ultrasonic process	45.0%	75.0%	37
Rice husk	Chemical treatment	44.1%	54.2%	43
Arecanut husk fiber	Chemical treatment	37.0%	73.0%	60
Sugar palm fibers	Chemical treatment	55.8%	85.9%	61

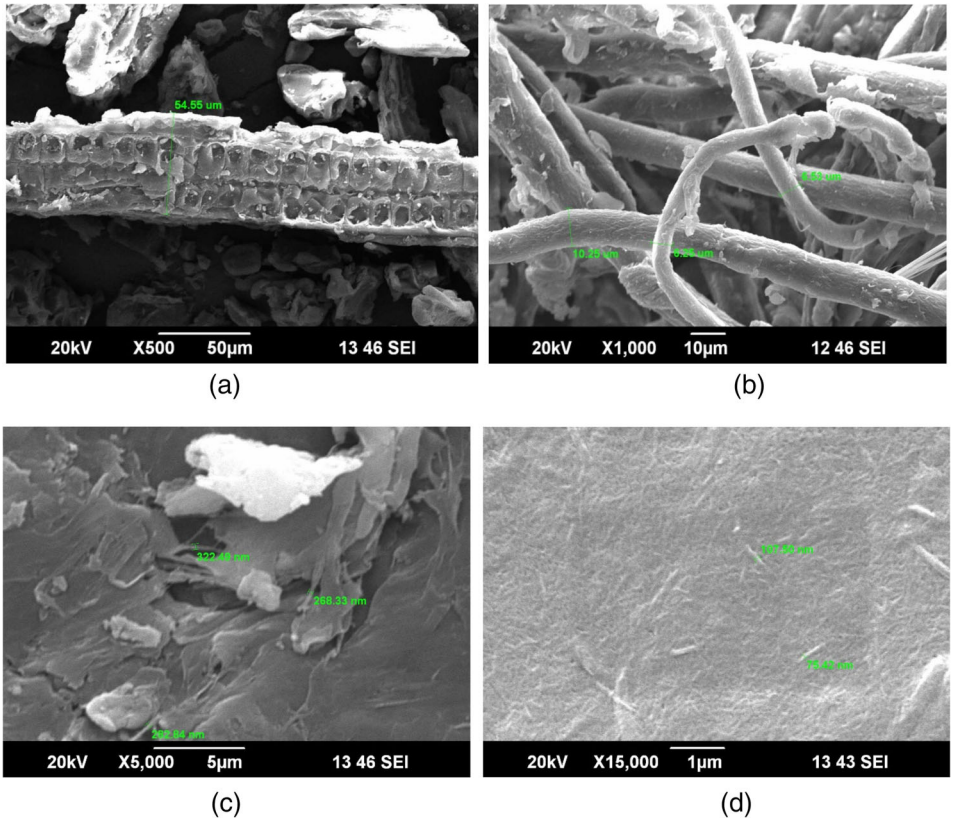

FIGURE 3 SEM images of (a) raw *Acacia caesia*, (b), NaOH treated *Acacia caesia*, (c) bleached *Acacia caesia* and (d) H_2SO_4 treated *Acacia caesia* [Color figure can be viewed at wileyonlinelibrary.com]

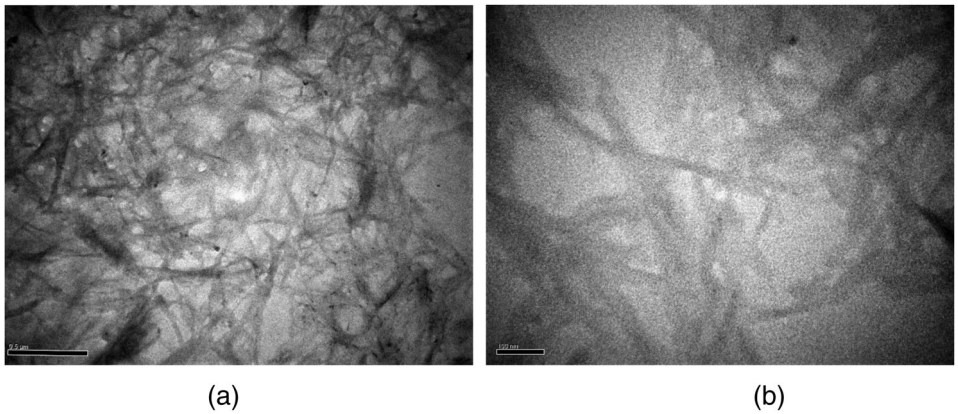

FIGURE 4 TEM image of cellulose nanowhiskers (a) lower resolution (scale bar- 0.5 μm) (b) higher resolution (scale bar- 100 nm)

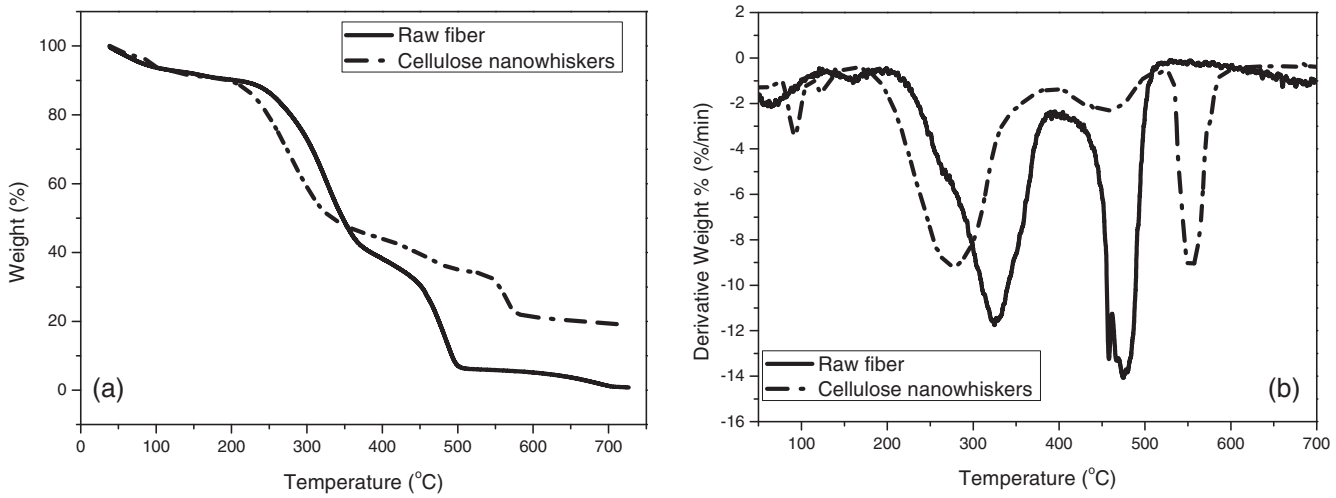

FIGURE 5 TGA (a) and DTG (b) curve of raw fiber and cellulose nanowhiskers

the rest of the binding materials.[60] Thus, highly ordered crystallites are formed. For a better understanding of the morphology of the nanocellulose whiskers, TEM images are taken. TEM images of the highly ordered crystallites of nanocellulose are shown in Figure 4(a, b). Nanocellulose whiskers with ca. 30 nm are observed from the TEM images. Thus the TEM images confirm the dissolution of hemicellulose, pectin, wax, and other cementing materials from the raw fibers with alkalisation, bleaching, and acid hydrolysis resulting in the nanowhiskers.[7] These results suggested that the nanocellulose whiskers are successfully obtained after chemical treatments.

3.5 | Thermogravimetric analysis

Thermal stability of raw *Acacia caesia* fiber and prepared cellulose nanowhiskers is studied for the understanding of the thermal degradation behavior of raw *Acacia caesia* fiber and cellulose nanowhiskers. The thermogravimetric analysis curve and derivative thermogram of raw *Acacia caesia* fiber and cellulose nanowhiskers are shown in Figure 5(a, b). The degradation of raw fiber and treated fiber took place in multiple steps, suggesting the presence of different fiber components which decompose at different temperatures. The weight loss at 100°C is because of the evaporation of moisture content present in the raw *Acacia caesia* fiber and cellulose nanowhiskers. The degradation at 120°C in cellulose nanowhiskers may be due to chemisorbed water or intermolecularly H-bonded water in the cellulose nanowhiskers.[2] Interestingly, from the TGA and DTG curve, the moisture absorption is more in the case of cellulose nanowhiskers. This is because the moisture may get entrapped in the open spaces created on the removal of the non-cellulosic part with the acid hydrolysis. Other than the minor degradation at 100°C, the raw *Acacia caesia* fibers and cellulose nanowhiskers show two major degradation steps and are reflected in the DTG curve. The first major degradation at ca. 300 °C is due to the decomposition of cellulose, hemicellulose, and some portion of the lignin.[11,15,63]

A careful examination of the results revealed that the first major degradation temperature of the cellulose nanowhiskers decreases to lower temperatures after the chemical treatments. This is because the acid hydrolysis dissolves both the amorphous phase and the crystalline phase making them more susceptible to thermal degradation.[16] It may also due to the reduction in the molecular weight of the cellulose caused by the chemical treatments.[2] The degradation at 480°C is due to the decomposition of lignin along with the carbonaceous residue.[60,61,64–66] The mass loss of the oxidative degradation of lignin and other carbonaceous residue is reduced from ca. 30% to ca. 10% in cellulose nanowhiskers and the degradation temperature shifted to higher temperatures with chemical treatment. These results indicate the removal of the amorphous components from the raw *Acacia caesia* fiber during the chemical treatment supporting the chemical composition, FTIR, XRD, SEM and TEM results. It is important to add that the prepared cellulose nanowhiskers show a remarkably high char residue of ca. 20% compared with untreated fiber (ca. 1%), this is owing to the presence of sulfate groups in cellulose nanowhiskers, here the sulfate groups act as a flame retardant.[16]

4 | CONCLUSION

The important conclusions of the present work are as follows.

- Cellulose nanowhiskers are isolated from *Acacia caesia*, a common medicinal plant by following alkali, bleaching, and sulfuric acid hydrolysis treatment.
- Chemical composition and FTIR analysis of prepared cellulose nanowhiskers confirmed the dissolution of non-cellulosic part from the raw *Acacia caesia* fiber during the chemical treatment.
- XRD studies showed high crystallinity for cellulose nanowhiskers compared to raw fibers.
- SEM and TEM images demonstrated the formation of the nanosized rod-like structure of cellulose.
- Thermal studies revealed the higher char residue for the prepared cellulose nanowhiskers. Thus, the prepared cellulose nanowhiskers possesses high crystallinity and good thermal stability.

The future work of this research is about the potential utilization of cellulose nanowhiskers for various composite applications.

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ORCID

Jyotishkumar Parameswaranpillai https://orcid.org/0000-0002-3809-8598

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