PREPARATION AND CHARACTERIZATION OF CELLULOSE FILMS FROM *FICUS NATALENSIS* BARK CLOTH FIBERS

Hua Wang

Professor, Dr.
College of Textiles, Donghua University
2999 North Renmin Road, Shanghai 201620, China
E-mail: huawang@dhu.edu.cn

Mugaanire Tendo Innocent

PhD Scholar, Engr.
College of Material Science and Engineering, Donghua University
2999 North Renmin Road, Shanghai 201620, China
E-mail: 419019@mail.dhu.edu.cn

*Hafeezullah Memon**†*

Postdoc Fellow, Dr.
E-mail: hm@zstu.edu.cn

Xiaoke Jin

Lecturer, Dr.
E-mail: jinxiaoke13@hotmail.com

*Feichao Zhu***

Lecturer, Dr.
College of Textile Science and Engineering
(International Institute of Silk)
Zhejiang Sci-Tech University
Hangzhou 310018, China
E-mail: zhufeichao1988@126.com

(Received November 2020)

Abstract. In this study, cellulose films were prepared from *Ficus natalensis* bark cloth fibers via phase inversion technique using NaOH/urea/water as the solvent. Films were formed at a concentration of 7 wt. % and 8 wt. % of microcrystalline cellulose (MCC) as isolated from *Ficus natalensis* bark cloth fibers. Their morphology, physiochemical, and mechanical properties were examined with scanning electron microscopy (SEM), Fourier transform IR spectroscopy (FTIR), X-ray diffraction (XRD), thermal gravimetric analysis (TGA), and a microcontrolled electronic universal testing machine. The resultant regenerated cellulose (RC) films exhibited rough surfaces morphologically, good tensile strength (19.85 $\pm$ 0.13 MPa), exhibited a plastic behavior with considerable strains. However, they are thermally stable at higher temperatures up to 280°C. Cellulose films from this study could potentially act as biodegradable packaging materials to upgrade the scope of application of *Ficus natalensis* bark.

Keywords: Biodegradable, cellulose film, *Ficus natalensis*, bark cloth.

* Corresponding author
† SWST member

Wood and Fiber Science, 53(1), 2021, pp. 62-68
https://doi.org/10.22382/wfs-2021-06

INTRODUCTION

Besides being sustainable and ecofriendly, natural materials have also been promising materials for many industrial applications Wang et al (2019). Among them, the tree bark biomass is an emerging class of lignocellulosic materials anticipated as a potential raw material for bio-oil, chemicals, and biodegradable products such as engineered fibers and functional films to minimize dependence on synthetic polymeric material deemed harmful to the environment. Not only are they cheap alternatives but tree barks have a rich chemical composition ranging from extractives with compounds for medicinal applications Pásztory et al (2016) to too long and stiff fibers for application in the textile industry Dou et al (2016). Meanwhile, it is urged that the difficulty involved in separating the bark from xylem (wood) for most tree species is among the significant limitations impeding their utilization because the procedure is considered expensive and time-consuming Jansone et al (2017). In this regard, the bark from *Ficus natalensis* from which bark cloth is designed presents an otherwise better option.

Unlike most tree barks with disposal challenges into the environment, *Ficus natalensis* bark is harvested without harming or damaging the tree. In addition to that, the whole extraction procedure of the bark from the tree is cheap, quick, and straightforward Robertson 2014. Interestingly, the bark from *Ficus natalensis* regenerates in 8 mo toward the next harvest. Moreover, the tree takes around 4 yr for the same harvest of the bark to take place once planted. Furthermore, *Ficus natalensis* is a popular tree species in most communities within the east and southern Africa, but specifically Uganda. Thus, the practice of harvesting the bark from *Ficus natalensis* simultaneously conserves the environment while generating income to communities where the tree grows, and bark cloth is made in Uganda. Just like barks from willow Dou et al (2018) and Norway spruce trees Le Normand et al (2014), Samson and Blank maintained that bark cloth prepared from the bark of *Ficus natalensis* also consists of fibers held in bundles Rwawiire and Tomkova (2017). In all cases, fibers from the tree bark still pose a significant challenge when designing a systematic extraction method. Nonetheless, *Ficus natalensis* bark fibers contain high cellulose content Rwawiire et al (2017), but no study has exploited its use for the application. Herein, biodegradable cellulose films could act as possible packaging materials prepared from *Ficus natalensis* bark cloth fibers and characterized to determine their thermal and mechanical properties

MATERIALS AND METHODS

Preparation and Dissolution of Microcrystalline Cellulose

Microcrystalline cellulose (MCC) was prepared according to our previous method Mugaanire et al (2019). Cellulose at all dimensions, ie macro, micro, and nano, does not dissolve in ordinary organic solvents. Therefore, a hybrid solvent of sodium hydroxide, urea, and water was prepared in a ratio of 7:12:81 by weight, respectively. The total weight of the resultant solution was 70 g. Details are provided in Table 1.

The formation of cellulose films demands that cellulose solutions containing the right viscosity be used. It was thus imperative that several w/w % concentrations of MCC be experimented with to obtain the appropriate viscosity, leading to the formation of MCC films. In this case, various MCC concentrations concerning the total weight of the solvent (70%) were sampled, as depicted in Table 2.

While stirring with a rod, each MCC sample was mixed in the NaOH/urea/water solvent to produce cellulose solutions with varying concentrations. The mixture was then cooled to −18°C in a freezer for approximately 40 min and later

Table 1. Preparation of the NaOH/urea/water solvent system.

Name	Concentration (w/w %)	Weight (g)
Sodium hydroxide	7	4.9
Urea	12	8.4
Water	81	56.7
Total solvent weight	100	70

Table 2. Various concentrations of MCC in NaOH/urea/water system.

MCC sample code	Weight (w/w %)	Weight (g)
A	4	2.8
B	5	3.5
C	6	4.2
D	7	4.9
E	8	5.6

thawed at room temperature. After thawing at room temperature, the resultant cellulose solutions contained air bubbles that would otherwise produce defects in the final films.

To remove air bubbles, centrifugation was performed on each thawed cellulose solution at a speed of 3500 rpm for 15 min at 5°C.

Preparation of Cellulose Films

Regenerated cellulose (RC) films were prepared using the phase inversion technique Wu et al (2017). In brief, the air-free viscous cellulose solutions were spread on glass plates using an alloy spreader and lowered into a coagulation bath half-filled with water at room temperature. After 2 h, the films were removed from the bath, thoroughly washed with distilled water, left to dry overnight at room temperature, and stored for analysis.

In this study, the concentration of cellulose below 7 wt. %, ie samples (A, B, and C) had insufficient viscosity to regenerate films in the coagulation bath. Therefore, cellulose film formation was achieved with samples D and E at MCC concentrations of 7 wt. % and 8 wt. %, respectively. The various stages of the preparation are shown in Fig 1.

Regeneration of cellulose films at higher concentrations was due to the low degree of polymerization of MCC due to the hydrolytic dissolution of paracrystalline regions in bark cloth fibers during preparation with hydrochloric acid.

Characterization of Cellulose Films

The surface morphology of raw bark cloth, scoured bark cloth fibers, bleached bark cloth fibers, and microcrystalline cellulose (MCC) powder were examined with a scanning electron microscope (Quanta 250, Thermo Fisher Scientific, Waltham, MA). IR spectra were generated with a Nicolet® 6700 Fourier Transform IR spectrometer (Thermo Fisher Scientific). Fine powders of raw bark cloth fibers, scoured bark cloth fibers, bleached bark cloth fibers, and microcrystalline cellulose were mixed with potassium bromide (KBr) before Fourier transform IR spectroscopy (FTIR) analysis.

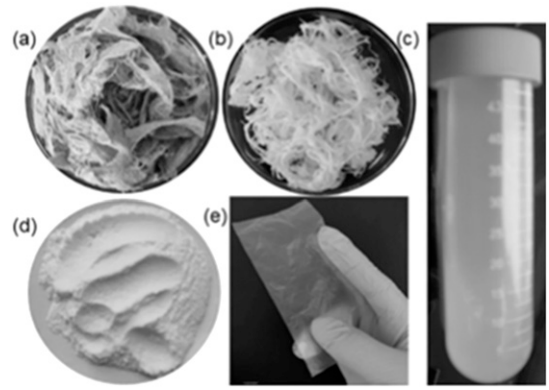

Figure 1. Preparation of cellulose films: (a) bark cloth fibers; (b) alkaline peroxide bleached–bark cloth fibers; (c) degassed viscous cellulose solution; (d) microcrystalline cellulose; (e) regenerated cellulose.

X-ray diffraction (XRD) analysis was performed using an X-ray diffractometer (Rigaku D/Max 2550/PC, Tokyo, Japan) with Cu-Kα radiation ($\lambda = 1.54$ Å) in a 2θ range of 5-60° at a scanning speed of 1° min^{-1}. The crystallinity indices of raw fibers, scoured fibers, bleached fibers, and microcrystalline cellulose samples were calculated based on the empirical method in Eq (1), described earlier (Thygesen et al 2005; Segal et al 1959).

$$\text{C.I} = A = \frac{I_{200} - I_{\text{AM}}}{I_{200}}, \qquad (1)$$

where I_{200} is the peak intensity close to $2\theta = 22.7°$ corresponding to the combined amorphous and crystalline components of the test material and I_{AM} is the diffraction at $2\theta = 18°$ representing the amorphous part of the material only.

The sample thermal stability was studied using a thermogravimetric analyzer (Perkins Elmer TGA 400 (Thermo Fisher Scientific). Approximately 5 mg of each sample was scanned from 30°C to 600°C at a heating rate of 20°C/min under a nitrogen-controlled atmosphere.

Tensile properties of RC films were measured using a microcontrolled electronic universal testing machine (Shenzhen Suns Technology Stock Company, Ltd., Shenzhen, China) at a rate of 10 mm/min at room temperature. Five samples were tested, and the average results for both films, ie MCC concentrations 7 wt. % and 8 wt. %, are presented. The tensile curves were generated using Origin Pro software.

RESULTS AND DISCUSSION

Surface Morphology

The surface morphology of raw bark cloth, scoured bark cloth fibers, bleached bark cloth fibers, microcrystalline cellulose (MCC) powder, and RC film is shown in Fig 2. It can be seen that the MCC particles were heterogeneously dispersed in the solvent, leading to the formation of films with rough surfaces (Fig 2 [d]), as a result of impartial dissolution probably due to a larger particle size of MCC whose length was 90 ± 25 μm and diameter was 17.08 ± 3.3 μm. In addition, there could have been a substantial amount of residual lignin Pang et al (2015) in MCC, which might have also contributed to its incomplete dissolution in the NaOH/urea solvent system.

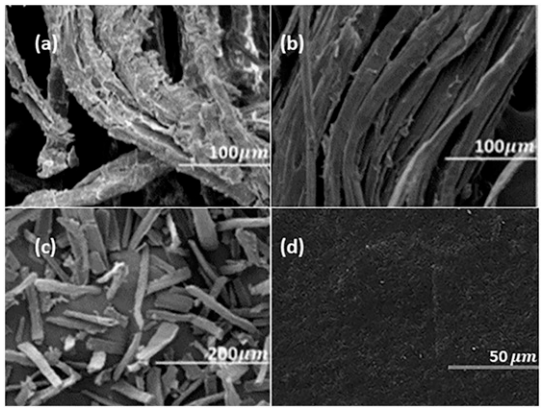

Figure 2. Scanning electron microscopy micrograph: (a) bark cloth fibers; (b) bleached bark cloth fibers; (c) microcrystalline cellulose (MCC); (d) rough surface of MCC.

Fourier Transform Spectroscopy

Interaction between cellulose and NaOH was further investigated using FTIR with spectra shown in Fig 3. Mostly referred to as the "crystallinity peak" Parida et al (2015), the peak at 1430 cm^{-1} assigned to CH stretch in cellulose was observed to have significantly reduced in the RC film. The amorphous band peak intensity at 896 cm^{-1} chiefly ascribed to β-1-4-glycosidic bonds linking up to the sugar units in cellulose also remarkably increased Geng et al (2014). Therefore, it was deduced that the reduction in the crystallinity index of regenerated films was due to amorphous cellulose.

XRD

XRD patterns of the RC were compared with those of the isolated microcrystalline cellulose, as shown in Fig 4. Broad peaks at approximately 12.04° and 20.1° corresponding to (−1 1 0) and (1 1 0) Miller indices were observed, respectively Reddy et al (2017). These peaks are characterized by cellulose II conformation. Therefore, the results indicated a transition of cellulose I into cellulose II during the dissolution process, which could have been due to aggregation or association of the cellulose chains either in the NaOH/urea solvent system or during the formation of the film. It was also observed that the crystallinity index of the RC films significantly decreased to 33.7% compared with the 75.8% of MCC Liu et al (2015) from which such films were prepared. This could be attributed to the fact that the original structure of cellulose and the glycosidic bonds linking the glucose/sugar units together may have partially severed during dissolution and film-forming processes.

Thermal Properties

The initial tiny weight loss below 100°C was due to evaporation moisture absorbed by the RC

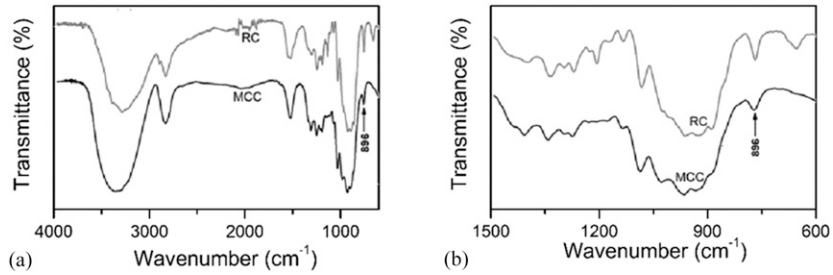

Figure 3. Fourier transform IR spectroscopy analysis of the cellulosic films, ie regenerated cellulose (RC) and microcrystalline cellulose (MCC) in the range of (a) 4000-600 cm^{-1} and (b) 1500-600 cm^{-1}.

membrane (Reddy et al 2017; Kumar et al 2018). Similar to microcrystalline cellulose, the RC film followed a two-step thermal degradation process between temperature ranges of 275-400°C and 450-548°C, respectively, as shown in Fig 5. The first degradation was either due to depolymerization, dehydration, or decomposition of some glycosidic bonds in cellulose Saravana Kumaar et al (2019), whereas the second resulted from the oxidation and breakdown of charred residues. However, its initial decomposition temperature was observed at approximately 282°C, which was slightly lower than the extracted MCC. This decomposition temperature is attributed to the rupture of intra- and intermolecular hydrogen bonds of MCC during dissolution.

Mechanical Properties of the RC Films

To assess the practicability of the regenerated biodegradable films for industrial applications, mechanical properties such as tensile stress and breaking strain (elongation at break) were determined. The stress–strain graphs of the RC films are shown in Fig 6. The films displayed a thermoplastic behavior in which the stress increased rapidly for low strains. It was noted that the tensile stress of membranes regenerated from the bark cloth microcrystalline cellulose was comparatively lower than the pristine cellulose in other studies Pang et al (2015). The slightly lower tensile strength of RC films from MCC was attributed to the insufficient dissolution of MCC by the NaOH/urea solvent system as demonstrated by their surface roughness, as shown previously

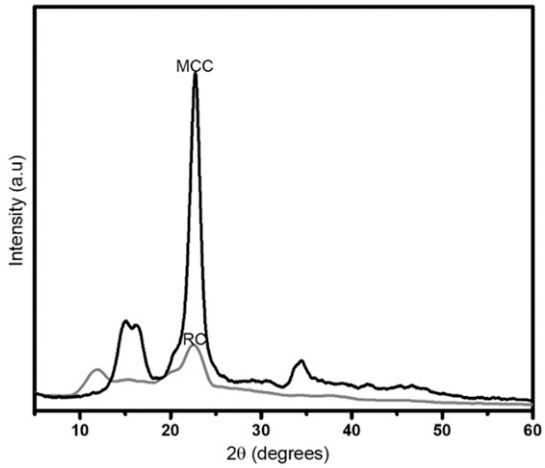

Figure 4. X-ray diffraction of regenerated cellulose (RC) compared with microcrystalline cellulose (MCC).

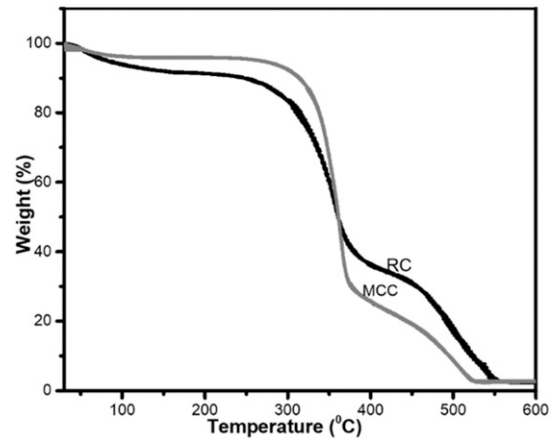

Figure 5. Thermal properties of regenerated cellulose film (RC) compared with microcrystalline cellulose (MCC).

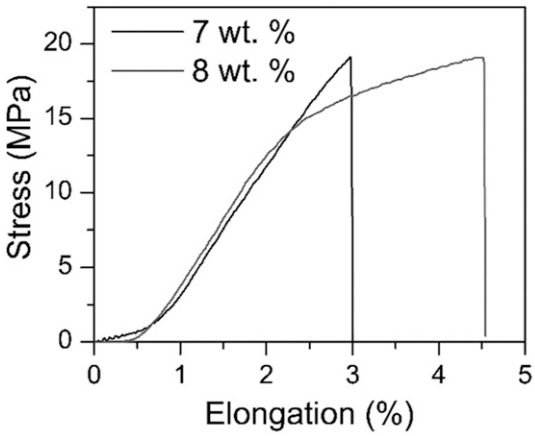

Figure 6. Mechanical properties of regenerated films at a varying concentration of MCC.

in Fig 2(d), scanning electron microscopy micrograph.

In addition, comparative studies have shown that films regenerated with NaOH/urea solvent systems are relatively weaker than other hybrid solvent systems Trache et al (2016) because of a narrow dissolution range Lindman et al (2010). Because bark fibers are known to be highly lignified, residual lignin could have also contributed to the reduced mechanical properties of films regenerated from *Ficus natalensis* bark cloth microcrystalline cellulose. On the other hand, regenerated films from PVC/MCC polymer blends showed exceptional mechanical properties.

CONCLUSIONS

RC films were prepared from 7 wt. % and 8 wt. % microcrystalline cellulose (MCC) as isolated from new sustainable materials, ie *Ficus natalensis* bark cloth fibers in a NaOH/urea/water hybrid solvent via phase inversion. According to results from the scanning electron microscope, films generated from *Ficus natalensis* microcrystalline cellulose were rough. They exhibited good tensile strength (19.85 $\pm$ 0.13 MPa) and elongation between 3 and 4.6%. On the other hand, they were thermally stable at relatively higher temperatures up to 280°C. RC films in this study are potential biodegradable packaging materials.

ACKNOWLEDGMENTS

The outstanding postdoc grant (grant no. 11150331282007) of Zhejiang Sci-Tech University is acknowledged.

REFERENCES

Dou J, Galvis L, Holopainen-Mantila U, Reza M, Tamminen T, Vuorinen T (2016) Morphology and overall chemical characterization of willow (*Salix* sp.) inner bark and wood: Toward controlled deconstruction of willow biomass. ACS Sustain Chem Eng 4:3871-3876.

Dou J, Xu W, Koivisto JJ, Mobley JK, Padmakshan D, Kögler M, Xu C, Willför S, Ralph J, Vuorinen T (2018) Characteristics of hot water extracts from the bark of cultivated willow (*Salix* sp.). ACS Sustain Chem Eng 6: 5566-5573.

Geng H, Yuan Z, Fan Q, Dai X, Zhao Y, Wang Z, Qin M (2014) Characterisation of cellulose films regenerated from acetone/water coagulants. Carbohydr Polym 102:438-444.

Jansone Z, Muizniece I, Blumberga D (2017) Analysis of wood bark use opportunities. Energy Procedia 128: 268-274.

Kumar R, Hynes NRJ, Senthamaraikannan P, Saravanakumar S, Sanjay M (2018) Physicochemical and thermal properties of *Ceiba pentandra* bark fiber. J Nat Fibers 15:822-829.

Le Normand M, Moriana R, Ek M (2014) Isolation and characterization of cellulose nanocrystals from spruce bark in a biorefinery perspective. Carbohydr Polym 111: 979-987.

Lindman B, Karlström G, Stigsson L (2010) On the mechanism of dissolution of cellulose. J Mol Liq 156:76-81.

Liu Z, Sun X, Hao M, Huang C, Xue Z, Mu T (2015) Preparation and characterization of regenerated cellulose from ionic liquid using different methods. Carbohydr Polym 117:99-105.

Mugaanire IT, Wang H, Sun J (2019) Fibrous microcrystalline cellulose from *Ficus natalensis* barkcloth. Eur J Wood Wood Prod 77:483-486.

Pang J, Wu M, Zhang Q, Tan X, Xu F, Zhang X, Sun R (2015) Comparison of physical properties of regenerated cellulose films fabricated with different cellulose feedstocks in ionic liquid. Carbohydr Polym 121:71-78.

Parida C, Dash SK, Pradhan C (2015) FTIR and Raman studies of cellulose fibers of *Luffa cylindrica*. Open J Comp Mater 5:5-10.

Pásztory Z, Mohácsiné IR, Gorbacheva G, Börcsök Z (2016) The utilization of tree bark. BioResources 11:7859-7888.

Reddy KO, Maheswari CU, Dhlamini M, Mothudi B, Zhang J, Zhang J, Nagarajan R, Rajulu AV (2017) Preparation and characterization of regenerated cellulose films using

borassus fruit fibers and an ionic liquid. Carbohydr Polym 160:203-211.

Robertson L (2014) Rethinking material culture: Ugandan bark cloth. *In* Biennial Symposium Proceedings: New Directions: Examining the Past, Creating the Future, September 10-14, 2014, Los Angeles, CA.

Rwawiire S, Tomkova B (2017) Thermal, static, and dynamic mechanical properties of bark cloth (*Ficus brachypoda*) laminar epoxy composites. Polym Compos 38: 199-204.

Rwawiire S, Tomkova B, Militky J, Hes L, Kale BM (2017) Acoustic and thermal properties of a cellulose nonwoven natural fabric (barkcloth). Appl Acoust 116:177-183.

Saravana Kumaar A, Senthilkumar A, Sornakumar T, Saravanakumar S, Arthanariesewaran V (2019) Physicochemical properties of new cellulosic fiber extracted from Carica papaya bark. J Nat Fibers 16:175-184.

Segal L, Creely J, Martin A Jr., Conrad C (1959) An empirical method for estimating the degree of crystallinity of native cellulose using the X-ray diffractometer. Textile Res J 29:786-794.

Thygesen A, Oddershede J, Lilholt H, Thomsen AB, Ståhl K (2005) On the determination of crystallinity and cellulose content in plant fibres. Cellulose 12:563.

Trache D, Hussin MH, Chuin CTH, Sabar S, Fazita MN, Taiwo OF, Hassan T, Haafiz MM (2016) Microcrystalline cellulose: Isolation, characterization and bio-composites application—a review. Int J Biol Macromol 93:789-804.

Wang H, Memon H, Hassan AM, Sohag M, Arshad A (2019) Effect of jute fiber Modification on mechanical properties of jute fiber composite. Materials (Basel) 12:1226.

Wu L, Sun J, Wu M (2017) Modified cellulose membrane prepared from corn stalk for adsorption of methyl blue. Cellulose 24:5625-5638.