様　式　Ｃ－１９、Ｆ－１９－１、Ｚ－１９　（共通）

KAKENHI 科研費

科学研究費助成事業　　研究成果報告書

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研究課題名（和文）Extraction of cellulose nanofiber from rice fiber for food packaging application using environmental friendly method

研究課題名（英文）Extraction of cellulose nanofiber from rice fiber for food packaging application using environmental friendly method

研究代表者

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交付決定額（研究期間全体）：（直接経費）　　2,100,000円

研究成果の概要（和文）：グリーン法によるセルロースの取得と籾殻から得られるセルロースを使用した包装材料の製造の2つの主な目的。
最初の目的では、NaOHのグリーン法と弱酸前処理の組み合わせを使用してセルロースを取得し、塩素系法を使用している市販の溶媒と比較しました。グリーン法を使用して得られたセルロースは、塩素化法と比較してサイズが小さかった。
セルロースは、包装目的の前にデンプンフィルムの強度と特性を改善するためにデンプンで強化されました。強化セルロース-デンプンマトリックスは、デンプンの機械的特性を向上させ、高い結晶化度と熱特性を実現します。

研究成果の学術的意義や社会的意義
Utilisation of untapped biomass resources by adopting green recovery method for cellulose extraction devoid the use of organic solvents, cheaper in cost and reduce amount of waste generated in the mill. Understanding and mechanisms of extraction process was documented for the scientific community.

研究成果の概要（英文）：The research project stated to achieve two main objective which are to obtain cellulose through green methods and production of packaging materials using cellulose obtained from rice husk.
In the first objective, cellulose was successfully obtained using combination of green methods of NaOH and weak acid pretreatment and compared with the commercial solvent used which is using chlorinated methods. The cellulose obtained using green methods was smaller particle in size as compared to chlorinated methods.
In second objective, cellulose was reinforced with starch in order to improve the strength and properties of starch film prior to packaging purposes. The reinforced cellulose-starch matrix increase the mechanical properties of starch with high crystallinity and thermal properties obtained.

研究分野：Pretreatment, material science

キーワード：rice husk　pretreatment　total free chlorine　cellulose　packaging

様　式　Ｃ－１９、Ｆ－１９－１、Ｚ－１９（共通）

１．研究開始当初の背景

The research project stated to achieve two main objective which are to obtain cellulose through green methods and production of packaging materials using cellulose obtained from rice husk. In the first objective, cellulose was successfully obtained using combination of green methods of NaOH and weak acid pretreatment and compared with the commercial solvent used which is using chlorinated methods. The cellulose obtained using green methods was smaller particle in size as compared to chlorinated methods. In second objective, cellulose was reinforced with starch in order to improve the strength and properties of starch film prior to packaging purposes. The reinforced cellulose-starch matrix increase the mechanical properties of starch with high crystallinity and thermal properties obtained.

２．研究の目的

An environmentally friendly strategy for the extraction of cellulose by integrated high pressure steam assisted total free chlorine method from rice fibre (straw,husk and bran) will be develop. This strategy is employed with the aims to increase the yield of cellulose obtained as compared to chemical extraction methods and reduce the disruption of fibre surface due to the harsh methods applied.

３．研究の方法

The project will be divided into three (2) stages;
i) Extraction of cellulose from rice fiber (straw, husk, and bran) using proposed environmental friendly method
Sample of rice fiber (straw, husk, and bran) will be collected from nearby rice-processing mill. Physicochemical analysis characteristic of the fiber will be carried out. Parameter of pretreatment that will be focus are ratio of solid to liquid during pretreatment, temperature and pressure of high pressure steam vessel, concentration of acid and alkaline used and retention time. The quality extracted CNF will be compared with commercial CNF obtained from hardwood or other biomass.

ii) Nanocellulose fiber biocomposite for food packaging standard
A blending commercial polymer/CNF will be prepared by melt blending using internal mixer at certain ratio of polymer/CNF, different temperature, time and rotation speed. For analysis of the biocomposite food packaging, mechanical properties analysis will be carried out.

４．研究成果

The results obtained from each chlorine and non-chlorine treatment RH after delignification are shown in Fig. 1. For delignification by NaOH, the treated RH was recovered on the basis of 400 g of initial dry RH. About 160 g of RH was recovered after delignification (5% of NaOH at 120°C for 45 min consecutively), which was equivalent to 40% of mass recovery. During this process, about 60% of loss, which was estimated in the form of lignin, hemicellulose, pectin, wax, and silica removal from raw RH. The lignin, cellulose, and hemicellulose content after delignification was 17.52%, 53.07%, and 17.89%, respectively, indicating 29.92% of lignin removal, yielding more cellulose constituents for further extraction. Effective treatment is aimed to disintegrate the lignin, cellulose, and hemicellulose complex matrix of RH by initially solubilizing lignin and hemicellulose before the cellulose fraction can be extracted. Lignin is associated with cellulose and hemicellulose that are deposited in the cell wall for mechanical strength, so NaOH treatment is initially introduced to remove noncellulosic constituents, such as lignin, hemicellulose fraction, pectin, and wax on the RH surface (Fig 2). The effect of NaOH treatment on the RH appearance. The color changes observed as the former NaOH solution extracted turned to black liquor could be associated with pigmentation of the lignin fraction removed from the RH. Simultaneously, the irregular rod-like shape of RH ruptured after NaOH treatment. The average 10 mm length of raw RH decreased to a length range of 5–8 mm after NaOH treatment.

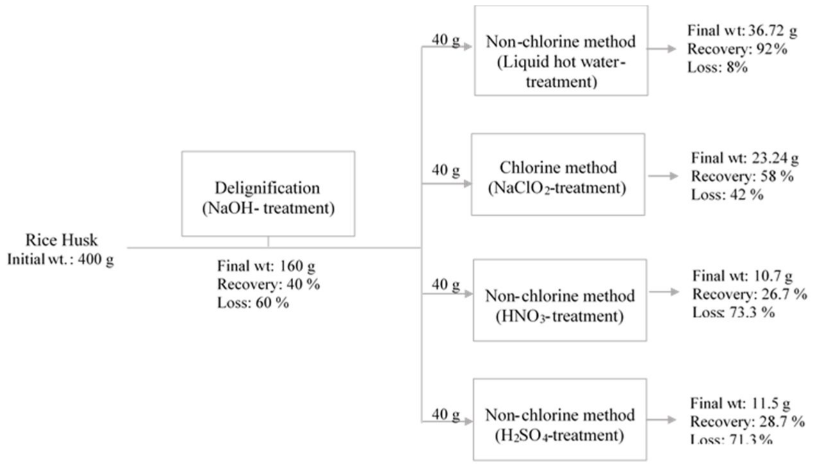

Fig 1: Mass of treated rice husk recovered after each pretreatment process

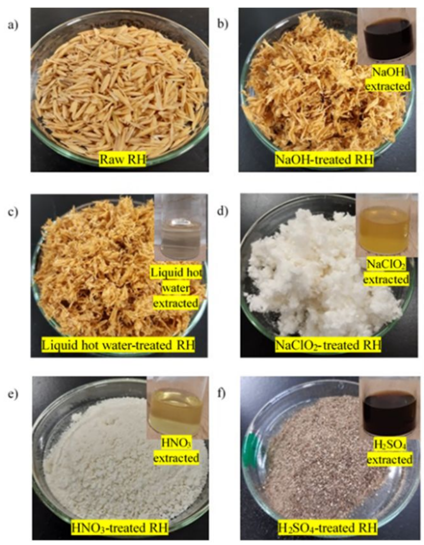

Fig 2: Photograph of RH-lignocellulosic dissolution and cellulose bleaching extraction process

TGA and DTG results are shown in Fig. 3a–b, and the thermal analysis is given in Table 2. Raw RH showed an endothermic peak at ~334.6°C, where ~46.13% of weight loss occurred. TGA curves for raw RH (Fig 3a) show four thermal degradation patterns translated into weight loss (%). Stage 1 is associated with a small weight loss due to the evaporation of water because of the hydrophilic character of lignocellulosic at 30°C–100°C. Moisture and other volatile materials evaporate during this stage. In stage 2, hemicellulose is decomposed at 200°C–300°C in raw RH only. In stage 3, cellulose depolymerization begins at a decomposition temperature 320°C–400°C because of the dehydration and decomposition of glycosidic linkages with major weight loss occurring rapidly and distinct peaks in DTG at 334.6°C. In stage 4, at a temperature beyond 400°C, lignin and silica decompose with a small weight loss, leading to the formation of char residue after 600°C.

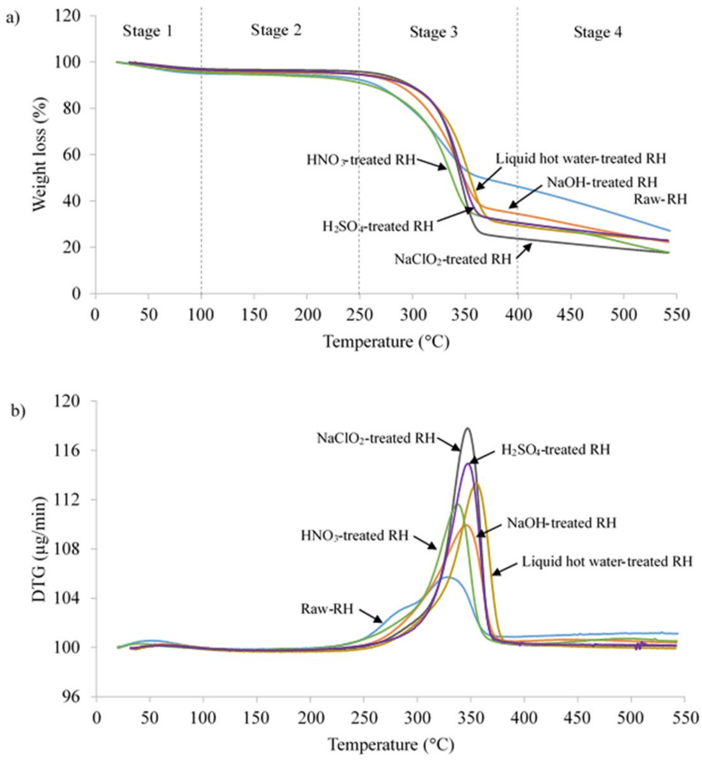

Fig. 3. Thermal analysis profile a) TGA and b) DTG treated RH with different stage of decomposition

The crystallinity of cellulose polymers is closely linked to hydrogen bonds and van der Waals forces between cellulose molecules in the crystallites of cellulose. Typically, crystalline cellulose–associated peaks are obtained in commercial cellulose spectra at 2θ = 15°–17°, 22.5°, and 35°, indicating a high degree of crystallinity in the cellulose I structure (Campano et al., 2017). Figure 4 shows intense peaks of cellulose in raw and treated RH. It is expected that treated RH has higher cellulose crystallinity due to more hydrogen bonding, which causes treated RH to be more densely packed with close intertwining of fibrils. The crystallinity of hot-water-, $NaClO_2$-, HNO_3-, and H_2SO_4-treated RH was higher compared to raw RH and NaOH-treated RH. An increase of 3.28%–40.8% in the CrI of treated RH because of the applied delignification, bleaching, and acid hydrolysis, which facilitate partial removal of lignin and hemicellulose during chemical treatment compared to the initial CrI of raw RH (56.31%). The characteristic diffraction peaks of typical cellulose at 2θ = 22.5° in all treated RH samples, indicating a highly crystalline cellulose I structure.

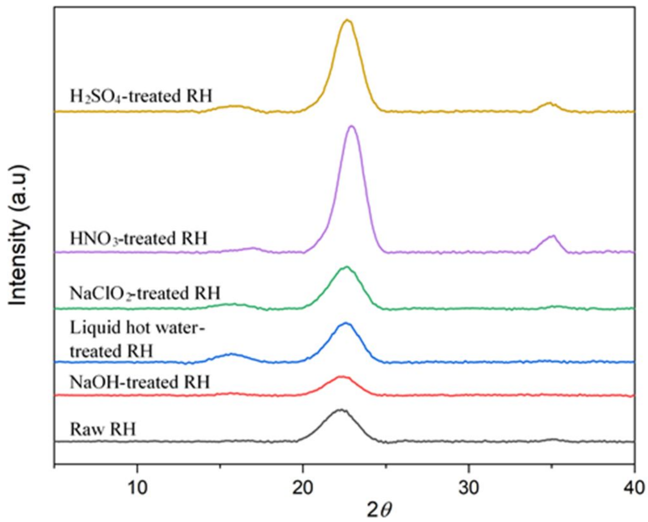

Fig 4: XRD pattern of rice husk under different treatment

As a conclusion, this is an environment-friendly process of cellulose extraction from RH through successive combination treatment of NaOH delignification with hydrolysis using weak acid mixtures containing HNO_3 under mild conditions. HNO_3 treatment showed an increment (2.01–fold) in the cellulose content and some enhancement in the crystallinity of cellulose (up to 40.8%). A slight increase was observed in thermal properties from 334.6°C to 339.3°C. This process will provide an in-depth understanding of the effectiveness of acid hydrolysis in extracting cellulose from rice husk.

5．主な発表論文等

〔雑誌論文〕　計1件（うち査読付論文　0件／うち国際共著　1件／うちオープンアクセス　0件）

1．著者名 Hafid Halimatun Saadiah、Omar Farah Nadia、Zhu Jiangyu、Wakisaka Minato	4．巻 260
2．論文標題 Enhanced crystallinity and thermal properties of cellulose from rice husk using acid hydrolysis treatment	5．発行年 2021年
3．雑誌名 Carbohydrate Polymers	6．最初と最後の頁 117789～117789
掲載論文のDOI（デジタルオブジェクト識別子） 10.1016/j.carbpol.2021.117789	査読の有無 無
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

〔学会発表〕　計3件（うち招待講演　0件／うち国際学会　3件）

1．発表者名 Halimatun Saadiah Hafid, Minato Wakisaka
2．発表標題 Cellulose nanofiber production from rice husk using green acid hydrolysis for high crystallinity
3．学会等名 8th International Joint Symposium on Applied Engineering and Sciences (SAES, 2020)（国際学会）
4．発表年 2020年

1．発表者名 Halimatun Saadiah Hafid, Minato Wakisaka
2．発表標題 Cellulose nanofiber production from rice husk using green acidhydrolysis for high crystallinity
3．学会等名 The 9th Joint Conference on Renewable Energy and Nanotechnology (JCREN 2020)（国際学会）
4．発表年 2020年

1．発表者名 Halimatun Saadiah Hafid, Minato Wakisaka
2．発表標題 Effect of drying conditions on the mechanic properties of long grain rice kernel
3．学会等名 The 9th Joint Conference on Renewable Energy and Nanotechnology (JCREN 2020)（国際学会）
4．発表年 2020年

〔図書〕　計0件

〔産業財産権〕

〔その他〕

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6．研究組織

	氏名 （ローマ字氏名） （研究者番号）	所属研究機関・部局・職 （機関番号）	備考

7．科研費を使用して開催した国際研究集会

〔国際研究集会〕　計0件

8．本研究に関連して実施した国際共同研究の実施状況

共同研究相手国	相手方研究機関