3-5 Utilization of Subcritical Water to Separate Components of Biomass

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ABSTRACT

In order to develop a simple method For complete use of biomass, extraction from biomass by subcritical water was investigated. The extraction at 200°C for 15 min gave the highest concentration of reducing sugar and radical scavenging activity in the extracted solution. The residue could be used for materials replacing a part of starch for preparation of biodegradable starch foam. Addition of the residue at 20%(w/w) increased the value of the flexural modulus for the foam plate to 1.7 times of that for the plate using only starch. Both extracted solution and residue after subcritical water could be used effectively.

KEYWORDS

Subcritical water, biomasss, extraction, starch foam

INTRODUCTION

In some Asian and Pacific countries, there is the present condition in which a large amount of waste is not processed, piled on a street, and started to decay. Establishment of the collection system of waste is pressing need and development of a simple technology which processes the accumulated waste is also desired. At the beginning of this research, the possibility of the waste treatment by superheated steam (Suzuki 2005) was investigated for aiming at reducing in quantity of waste and rotten control. However, I had received a suggestion that it is better to focus on extraction of the useful materials from waste. Based on this point, it aimed at by exploring the possibility using all of waste by extracting a useful substance from the waste with using only water and by changing the residue to a new material. In this study, shells of a walnut, *Carya cathayensis sarg*, produced in China was used as a model of waste. The amount of product of the walnut is 7,000 ton a year. The shell of the walnut (WS) is discarded. The composition of the WS is similar to wood biomass, which is still not used in a large amount at present. So, a good technology that can process the WS would be applicable to the wood biomass.

Water can maintain its liquid state in a temperature range from 100 to 374°C under pressurized condition. The water is called as subcritical water and has two characteristics different from water at ambient temperature and pressure. One of the characteristics is a low relative dielectric constant. It is a reason why solubility of hydrophobic substances such as fatty acid to subcritical water was increased while temperature increased (Khuwijitjaru *et al.*, 2002). The other is a high ion product. It makes subcritical water to act as an acidic or basic catalyst. Using the two characteristics, subcritical water have been investigated as a tool for extracting valuable materials from various biomass (Adachi and Kimura). In this study, it was investigated to set the optimal condition to extract a large amount of useful substances from WS by subcritical water and to search a possibility that the residue can be used as a strengthening material by added to starch foam.

MATERIALS AND METHODS

A shell of walnut, *Carya cathayensis sarg* (Fig. 1) which was produced in China, was chosen as a biomass in this study. The shell was ground into the powders with a mortar. The powders were sieved with a screen and the particles whose diameters were less than 0.3 mm were chosen for the following subcritical water treatment. Phenol , sodium chloride, ethanol, 1,1-diphenyl-2-pycryl hydrazyl hydrate (DPPH), sulfuric acid, and other reagents were purchased from Wako Pure Chemical Ind. (Osaka, Japan).

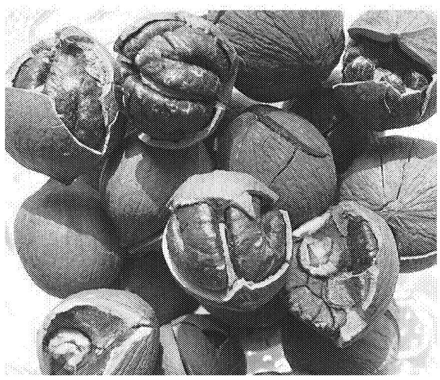


Fig. 1 ***Carya cathayensis sarg***

Hundred milligrams of the powder of WS were put with 7 mL of distilled water in a withstand pressure vessel (10 mL, sus316). The vessel was set in a ceramics furnace (ARF-40K, Asahi-Rika, Chiba, Japan) with a temperature regulator. The temperature was controlled from 160 to 260°C for 15 min or at 200°C for 15 to 60 min. The reaction time was started when the temperature had reached to the desired level. In order to stop the reaction, the vessel was put in ice. After the temperature of the vessel became the ambient one, the reaction solution was taken out from the vessel and filtered with a glass filter. The concentrations of reducing sugar and radical scavenging activity in the filtrate were measured by phenol-sulfuric acid method (Dubois *et al.*, 1956) and DPPH assay (Hata *et al.*, 2008). The residue after the filtration was dried at 105°C in an oven. After dried, the contents of lignin, hemicellulose, and cellulose in the residue were measured. The lignin content was measured by 72%(w/w) sulfuric acid method with some modification (Jerome *et al*, 1945). The contents of holocellulose, which was a sum of hemicellulose and cellulose, were measured by a sodium chloride method with some modification (Wise *et al.*, 1946). The cellulose contents were measured by a modified nitric acid-ethanol method (Xu and Xu, 2006). The hemicellulose contents were calculated by subscription from the holocellulose contents by the cellulose contents.

The dried residue after the treatment by subcritical water (200°C for 15 min) was used for the preparation of biodegradable foam. Firstly, the residue was mixed with corn starch for 3 min.

The contents of the residue in the mixture were 0-20%(w/w) in the base of the dried weight. The total dried weight was 1.0 g. The corn starch included water at 12.6%(w/w). Some water was added to the mixture. The weight of the water added and the weight of the water included in the corn starch were set at 90%(w/w) against the weight of the dried corn starch. Magnesium stearate was added as a release agent at a level of 2.0%(w/w) of the weight of the dried corn starch. The residue, the corn starch, the water, and magnesium stearate were mixed at 74°C until the state of the mixture became like dough. Then the mixture was transferred to an aluminum mold (50 × 20 × 3 mm) in an aluminum plate. Two aluminum plates were set on and below the plate. The three plates was set with a hot press (AH-2001, AS ONE, Osaka, Japan) which was preheated at 170°C, then was heated for 3 min. After that, a foam plate was prepared.

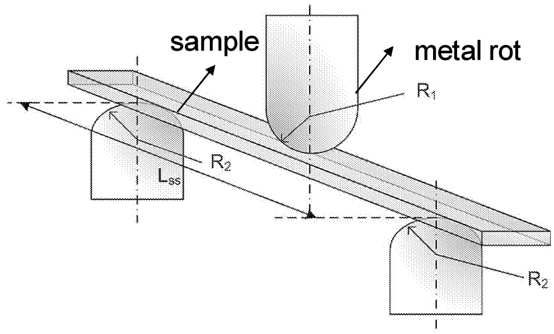


Fig. 2 Three-point bending test

The foam plate prepared was cut into a size of 50 × 10 × 3 mm for the measurement of the mechanical strength. Three-point bending test was performed as shown in Fig. 2 The deflection, δ, [m] and the loaded force, P, [N] were measured. Then the flexural modulus, E, [Pa] and the flexural stress, σ, [Pa] were calculated by the following equations.

$$E = \frac{PL^3}{4\delta bh^3} \qquad (1)$$

$$\sigma = \frac{P_{\max} L}{2bh^2} \qquad (2)$$

The L is the length between two supporting points [m]. The b and h are the width and height of the plate [m]. The P_{max} is the load force at a broken point [N].

RESULTS AND DISCUSSION

Figure 3 shows the contents of reducing sugar extracted by subcritical water (160-260°C, 15 min). The yield of reducing sugar extracted at 200°C was almost 40%(w/w) of WS. When the WS was treated at 200°C, the yield decreased with increasing the treating time. The maximum yield was the one at 15 min. The high yield for radical scavenging activities was achieved by treating at 200 or 220 for 15 min. These results shows that treatment by subcritical water at 200°C for 15 min was most available for production of reducing sugar and radical scavenging activity. The extracted solution could be used for fermentation to produce bioethanol or lactate, which is a substance for biodegradable plastics.

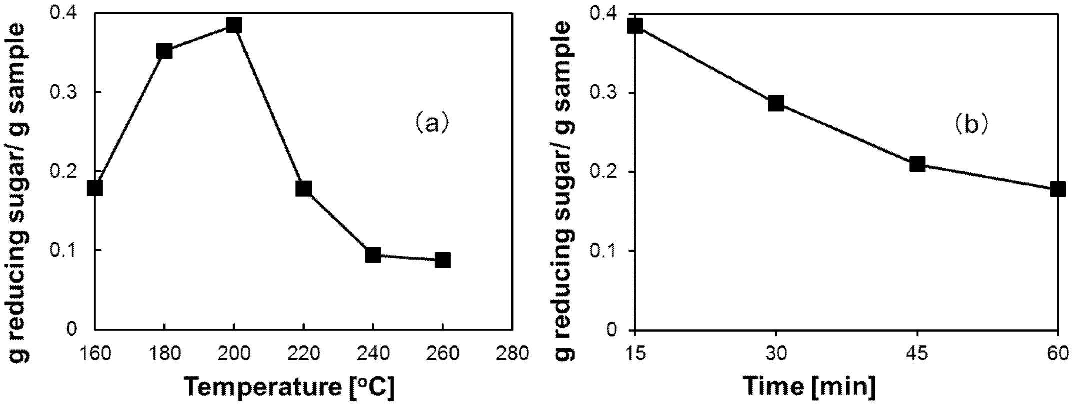


Fig. 3 Changes of reducing sugar content in the extracted solution at various temperatures for 15 min (a) and with various time at 200°C (b).

The weight of the dried residue was 54 mg when 100 mg of WS was treated at 200°C for 15 min. Table 1 shows the contents and weight of compositions in WS and the residue. The weight of hemicellulose in the residue was lower than that in WS, however, the weight of cellulose was almost same. These suggested that the reducing sugar in the extracted solution was come from hemicellulose. The main compositions in the residue were lignin and cellulose (Table 1). The residue could be estimated as a good substance for ligno-cellulose materials.

Table 1 Contents and weights (calculated) of composition in WS and the residue

Composition	WS (100 mg)		Residue (54 mg)	
Cellulose	27.9%	27.9 mg	46.3%	25.0 mg
Hemicellulose	30.2%	30.2 mg	2.6%	1.4 mg
Lignin	39.1%	39.1 mg	50.6%	27.3 mg
Protein	5.1%	5.1 mg	ND	ND
Ash	1.3%	1.3 mg	ND	ND

ND: not detected

Figure 4 shows some starch foam plates which included the residue at the contents (0-20%(w/w)). The color of the plate which was made from the corn starch (0% of the residue) was white. The color became darker with increasing the residue contents. We did not get any plate when the content was over 20%. The plates could be prepared when WS was used instead of the residue until the content was equal and less than 20%. All of the densities of the plate were about 0.36 g/cm3.

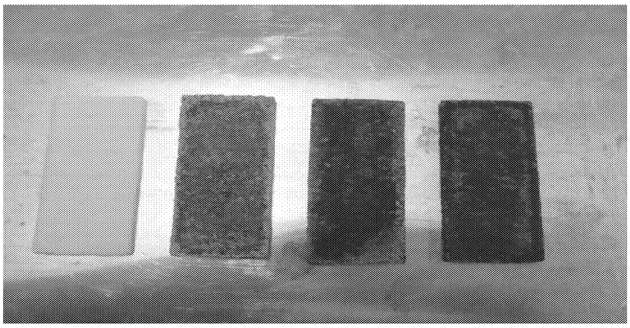
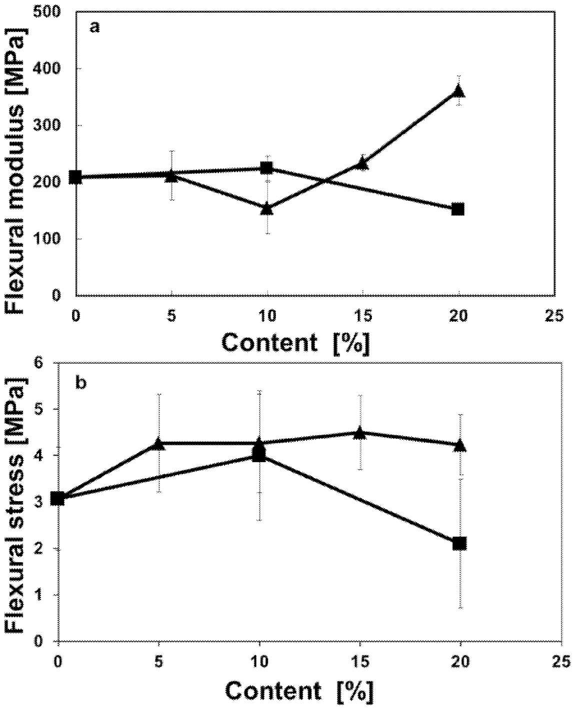


Fig. 4 The optical scans of starch foams (Residue content form left to right is 0%, 5%, 10% and 20%)



content [■] on the foam flexural modulus (a) and flexural stress (b).

Figure 5a) shows the flexural modulus of the prepared foam plate. The value for the plate containing 20% residue was 361 MPa and 1.7 times higher than that for that without the residue. The value is also as same as lignin-starch foam with 20% pure lignin (395 MPa, Stevens *et al.*, 2010). On the other hand, the starch foam plate containing 20% WS showed the lower value than that for the plate containing the starch only. The value was as same as that for the plate containing 10% residue. Both plates included the same content of lignin. It suggested that the content of lignin affected on the value of the flexural modulus. Figure 5b) shows the flexural stress for the plates. The values for the plates containing the residue (5-20%) were higher than that for the plate with the starch only. The values of the flexural modulus and the flexural stress for the plate containing 20% residue were higher than the values for polystyrene foam, 108 MPa and 1.3 MPa, respectively.

Figure 6 shows the cross-section of some foams. The interiors of all foams had large cells with thin walls. Two skin layers on the surfaces of the plates were observed. The thickness of the skin layer increased with increasing the contents of the residue or WS (data not shown). However, the relationship

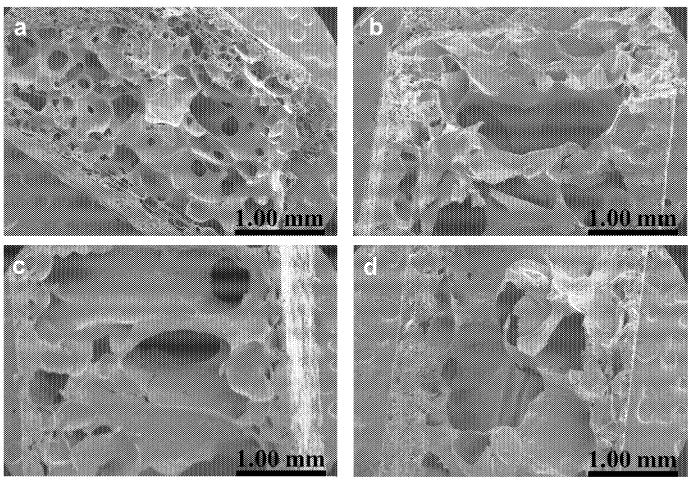


Fig. 6 SEM of cross-section of the foams; (a) corn starch foam, (b) starch foam containing 10% the residue, (c) starch foam containing 20% WS, (d) starch foam containing 20% the residue

between the thickness and the mechanical strength was not significant.

As mentioned above, the extracted solution and the residue after treating WS by subcritical water were available. Especially, this treatment should be attractive for a simple preparation of lingo-cellulose.

CONCLUSIONS AND PERSPECTIVES

A shell of walnut, *Carya cathayensis sarg*, as a model of plant biomass could be treated by subcritical water. The optimal condition was set to get the extracted solution containing a high concentration of reducing sugar and radical scavenging activity and the residue which could replace part of starch for the foam plate and made the plate stronger in the mechanics.

There is a possibility that the residue could be converted to a film like plastics. The trial to investigate the possibility will be done in the next year. For the proposal for practical utilization of subcritical water to convert from waste to useful materials, continuous flow system could have an advantage. In this content, a research to convert from glycerol to lactate will be included in this project. Glycerol is a waste when biodiesel fuelwas produced from food oil waste and lactate is a starting substance to make polylactate, biodegradable plastics.

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