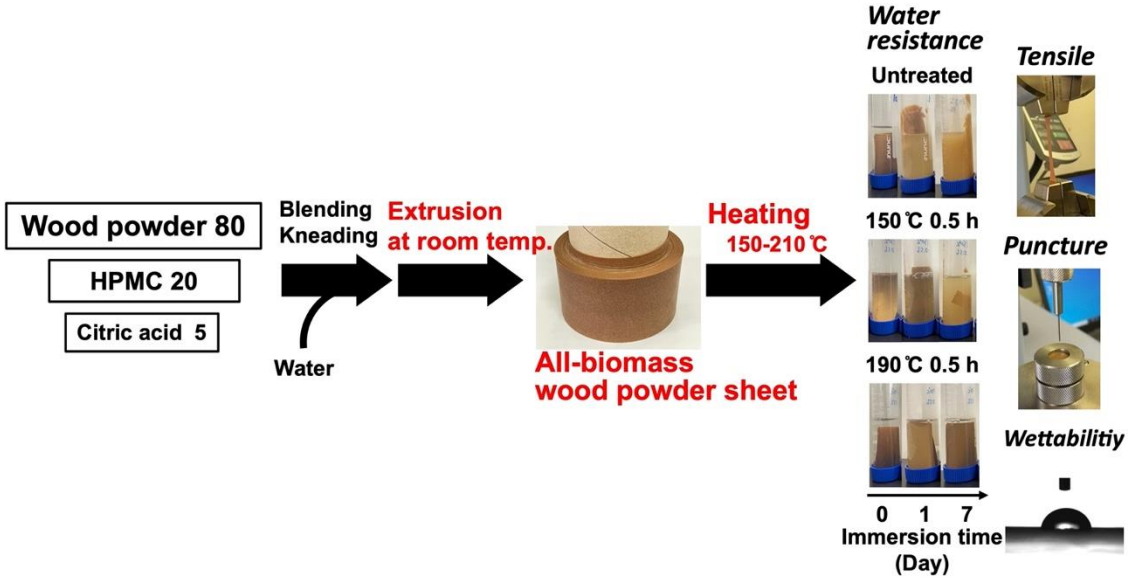
Physical Properties of Wood Powder Sheets Extruded with Hydroxypropyl Methylcellulose and Citric Acid after Heating

Hiroyuki Hiratsuka, Xiangyu Tao, Yuki Tokunaga, and Hiroshi Nonaka *

*Corresponding author: nonaka@bio.mie-u.ac.jp

DOI: 10.15376/biores.20.1.1900-1914

GRAPHICAL ABSTRACT



Properties of Wood Powder Sheets Extruded with Hydroxypropyl Methylcellulose and Citric Acid after Heating

Hiroyuki Hiratsuka, Xiangyu Tao, Yuki Tokunaga, and Hiroshi Nonaka *

Plastic products generally have excellent thermal plasticity and water resistance. However, their adverse environmental effects have become a severe problem. To overcome these problems, a 100% plant-derived plastic substitute material was developed by mixing wood powder, hydroxypropyl methylcellulose (HPMC), and citric acid solution, followed by vacuum extrusion and heating to insolubilize the HPMC. In this study, the effect of heating on physical properties was investigated. The extruded wood powder sheets were heated under a wide range from 0.5 to 5 h at 150 to 210 °C, which covers the conditions required for esterification between HPMC and citric acid. Water absorption, tensile strength, puncture resistance, and wettability were then tested. The sheet became tolerant of water and developed slightly higher tensile strength upon adequate heating, although it was more easily punctured when rewetted. Excessive heating at 210 °C was found to damage the sheet. The overall activation energy, calculated from the weight loss during heating, was as low as 46 kJ/mol, indicating that the dehydration and crosslinking of HPMC could occur easily. The curing process improved the water resistance and did not considerably worsen other physical properties; therefore, the possibility of using wood powder/HPMC/citric acid composite sheets has potential.

DOI: 10.15376/biores.20.1.1900-1914

Keywords: Wood powder; Hydroxypropylmethyl cellulose; Cellulose derivative; Citric acid; Extrusion; Cross-linking; Biomass composite; Water resistance; Tensile strength; Curing

*Contact information: Graduate School of Bioresources, Mie University, 1577 Kurimamachiya-cho, Tsu, Mie 514-8507, Japan; *Corresponding author: nonaka@bio.mie-u.ac.jp*

INTRODUCTION

Petroleum-based plastics have significant disadvantages because they are not biodegradable under environmental conditions. In recent years, the use of these products in numerous applications has increased, leading to severe environmental pollution and ecological issues (Napper and Thompson 2023). In contrast, biomass materials have the potential to reduce environmental and ecological problems and can be degraded by common physical and biochemical processes. However, biomass itself is not thermoplastic and cannot be molded without plastic support, as in the case of wood-plastic composites. As a result, relatively few plastic products, such as drinking straws and cutlery, have been replaced with paper or wood.

In recent years, the authors have demonstrated that wood powder and other types of biomass powders, such as bamboo and spent coffee grounds, can be molded by wet extrusion into a practical all-biomass composite material using hydroxypropyl

methylcellulose (HPMC), thereby eliminating the need for petroleum-derived resins and starches, which are food sources (Kawamura *et al.* 2018; Matsuoka and Nonaka 2020; Matsuoka and Nonaka 2021; Nonaka 2023). The HPMC, also called hypromellose, is a cellulose derivative that contains partially *O*-methylated and *O*-(2-hydroxypropylated) residues, which make it water-soluble. It is obtained by treating natural cellulose with caustic soda and then alkylating the targeted hydroxyl groups of the cellulose with etherifying agents, such as ethylene oxide (Mašková *et al*. 2020). It is a creamy-white, tasteless, odorless, and nontoxic powder that has been approved as a safe ingredient by various agencies worldwide, including the Pharmaceuticals and Medical Devices Agency in Japan, the European Food Safety Authority in the European Union (EFSA Panel on Additives and Products or Substances used in Animal Feed (FEEDAP) *et al.* 2020), and the Food and Drug Administration in the United States The HPMC has attracted the attention of a vast array of industrial demands in food packaging (Lai *et al*. 2021) and in pharmaceutical components, where it serves as a nanocarrier for the controlled release of chemical compounds and living cells for medical treatments (Mašková *et al*. 2020; Grosskopf *et al*. 2022).

All-biomass composite materials developed by extrusion molding have low water resistance due to using a water-soluble polymer, HPMC. It becomes slimy when it comes into contact with water that makes it breaks down. The HPMC must be rendered insoluble in water after extrusion molding to overcome this drawback. Chemical crosslinking, which induces interaction networks among molecules, can improve the physical properties of biomass products. Formaldehyde and epichlorohydrin are well-known cross-linkers for polysaccharides (Kuniak and Marchessault 1988; Kulkarni *et al.* 1999), but from the viewpoint of the environmental hazards they lead to toxicity; thus natural compounds are preferred to them (Girl 1997; Ma and Harris 1988). Tricarboxylic acid known as citric acid is a natural compound found in citrus fruits and it is a non-toxic and inexpensive chemical. Focusing on the eco-friendly properties, citric acid has been used as a chemical for crosslinking wood-derived materials (Umemura *et al*. 2011), starch (Zhang *et al*. 2023), carboxymethyl cellulose (CMC) (Wang *et al*. 2021), and HPMC (Novaes *et al*. 2022).

Based on the studies, the authors used citric acid as a crosslinking agent for an all-biomass composite material and reported that the water resistance of the wood powder sheet was extruded when the ratio of cedar wood powder to HPMC was 7:3 (Tao and Nonaka 2021). The water resistance of wood powder sheets might change their physical properties due to crosslinking. Therefore, it is necessary to elucidate how the crosslinking modification using citric acid affects the mechanical properties in order for the material to be used as applications such as containers derived from all-biomass sheets instead of petroleum-based plastics. To achieve the justification required for the applications, herein, the goal was to clarify optimal crosslinking temperature and time range to maintain outstanding mechanical properties.

In this study, sheets made from cedar wood powder were prepared using reduced amounts of HPMC compared to previous studies, and a citric acid solution was employed in a vacuum extrusion molding machine. The sheets were heated (cured) under a wide range of times and tempeartures from 0.5 to 5 h at 150 to 210 °C, covering the conditions required for esterification between HPMC and citric acid. The study investigated the tensile strength and puncture resistance of the extruded sheet, along with its water absorption and contact angle after heat treatment. In addition, to understand the mechanistic processes of crosslinking between biomass components, the overall activation energy, including the crosslinking associated reaction, was calculated from the weight loss.

EXPERIMENTAL

Materials

Cedar wood powder with particle size less than 91 µm was purchased from Naka Wood Co., Ltd. (Tokushima, Japan). When measured in the laboratory, the cedar wood powder consisted of 70% holocellulose, 45% α-cellulose, 32% acid-insoluble lignin, and 0.2% acid-soluble lignin. The HPMC (Metolose®, 90SH-4000) was purchased from Shin-Etsu Chemical Co., Ltd. (Tokyo, Japan). Citric acid was purchased from Fujifilm Wako Pure Chemical Co. (Wako Special Grade, Osaka, Japan). The materials were used as purchased without purification or dilution.

Preparation of Wood Powder Sheet with HPMC and Citric Acid

In prepartion for the sheet formation, 50 g of citric acid was dissolved in 1150 g of water. Wood powder (800 g), HPMC powder (200 g), and a citric acid solution were blended in a mixer. The mixed material was kneaded and extruded with a die 80 mm wide and 0.4 mm thick using a vacuum extrusion molding machine typically used for extruding ceramic powders. The extrusion temperature was at 13 °C and the extrusion speed was 0.91 m/min as one layer. The extruded sheets were passed over a conveyor under hot air at 40 °C, then rolled and dried using a drum dryer at 68 °C (Fig. 1). The thickness of the sheet after drying was approximately 0.3 mm.

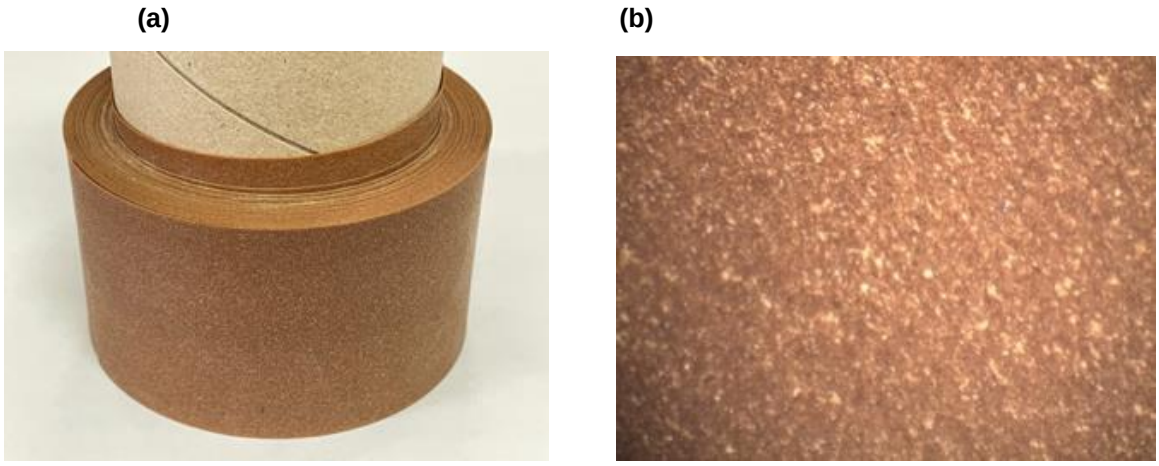


Fig. 1. (a) Appearance of rolled wood powder sheet and (b) the sheet surface (x10)

Heat Treatment of Wood Powder Sheet

The wood powder sheet was cut into samples having dimensions of 100 mm × 80 mm and heated at 105 °C for 1 h. This process was intended to bring the sheets to a state of absolute dryness. The sheets were then heated to higher temperatures, as listed in Table 1. Heating promotes the insolubilization of HPMC due to crosslinking of HPMC *via* citric acid through dehydration and it prevents wood powder from breaking apart in water.

The weight loss of each sample was calculated using Eq. 1. The mean of the two measurements was calculated for each sample. Data are shown as means ± standard deviations (SDs) of five measurements. Data represent two independent experiments,

$$Weight\ loss(\%) = \left(\frac{W_0 - W}{W}\right) \times 100 \quad (1)$$

where W_0 is the initial weight (g) of the sheet after drying at 105 °C for 1 h and W is the weight (g) after heating at the indicated temperature and time (Table 1).

Table 1. Heating (Curing) Temperature and Time Durations Used for the Wood Powder Sheets

Temperature (°C)	Time (h)		
105*	1		
150	0.5	1.5	5
170			
190			
210			
*105 °C was indicated as an untreated (solely dried) sample			

Reaction Kinetics During Heating of Wood Powder Sheet

Kinetic analysis was used to determine the overall activation energy using the weight data during heating. Assuming that the reaction is first order, as shown in Eq. 2, the rate constant k for the reaction at each temperature was calculated from the slope of the simple linear regression between ln (W_0/W) and the crosslinking time t (Eq. 3):

$$\frac{dW}{dt} = -kW \quad (2)$$

$$ln\left(\frac{W_0}{W}\right) = kt \quad (3)$$

The activation energy, E_a, is related to the rate constant in the Arrhenius Eq. 4. The E_a was calculated from the slope of the Arrhenius plot, the linear regression between $ln\ k$ and ($-1/T$),

$$k = Aexp\left(\frac{-E_a}{RT}\right) \quad (4)$$

where R is the gas constant (8.3145 J/mol K) and T is the heating temperature (K).

Water Absorption Test

The swelling of the sheets in water was evaluated based on water absorption. After heat treatment, the sheet samples with dimensions of 60 mm × 20 mm were immersed in distilled water at 25 °C. The weight of the sheets was measured after 1, 3, 5, and 24 h. Data are shown as means ± SDs of five measurements. Water absorption (%) was calculated as weight gain (%) using Eq. 5,

$$Water\ absorption(\%) = \left(\frac{W_w - W_0}{W_0}\right) \times 100 \quad (5)$$

where W_w is the weight of wet samples after immersion in water.

Tensile Strength Test

Dumbbell-shaped specimens with the reduced dimensions of JISSK7161-2 (2014) and ISO 527-2 (2012) type 1 BA were cut from the rolled wood powder sheet using an SD lever-type cutter (SDL-200, Dumbbell Co., Ltd., Japan) (Fig. 2a). The sheet thickness was measured by digital micrometer (Mitutoyo, Japan) prior to the test, and the tensile test was performed using a compact table-top universal/tensile tester tensile (EZ-LX, Shimadzu Ltd, Japan) under room temperature (25 to 30 °C, 60% to 80% relative humidity). The span

and test velocities were set as 60 mm and 10 mm/min, respectively. Data were recorded using the software (Trapezium X, V 1.4.0, Shimadzu Ltd., Japan). Data are shown as means ± SDs of five measurements.

Needle Penetration Test

The wood powder sheet cut from the roll was fixed using a cylindrical jig, and a needle penetration test was performed at a speed of 50 mm/min until penetration was achieved (EZ-LX, Shimadzu Ltd., Japan) (Fig. 2b). The sheet thickness was measured using a digital micrometer before testing. The maximum load (N) was measured, and data are shown as means ± SDs of five measurements.

Contact Angle Measurement

The contact angle of the samples was measured using a contact angle meter (LSE-ME3, NiCK Corporation, Japan) with a pendant drop of 2 µL distilled water for 10 s. The data were recorded with i2win software (NiCK Corporation, Japan) and analyzed by the θ/2 method. Data are shown as means ± SDs of five measurements.

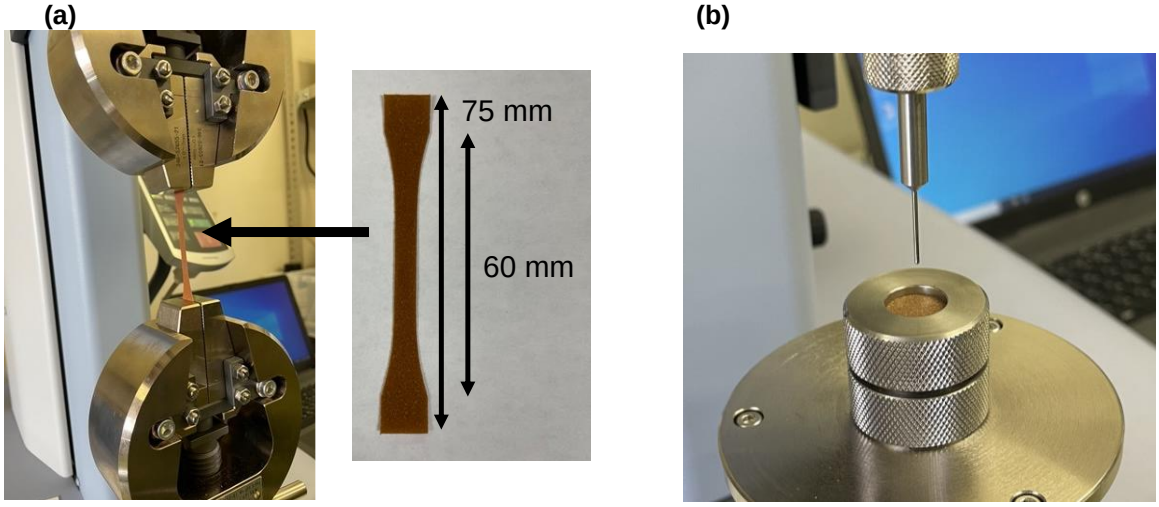


Fig. 2. (a) Tensile test of dumbbell-shaped specimens and (b) Needle penetration test on wood powder sheet

RESULTS AND DISCUSSION

Crosslinking of Wood Powder Sheet by Heat Treatment

The sheet was extruded with a lower HPMC ratio (Wood: HPMC = 8:2) than 7:3 in a previous study (Tao and Nonaka 2021). The change was made with a goal to reduce the cost of the product. Extrusion using this composition was successful. Heat treatment was conducted from 0.5 to 5 h at 150 to 210 °C, covering the conditions needed for esterification between HPMC and citric acid after heat treatment for 1 h at 105 °C in order to remove some water including the sheets. As shown in Fig. 3, the weight of the wood powder sheets decreased over time with increasing temperature.

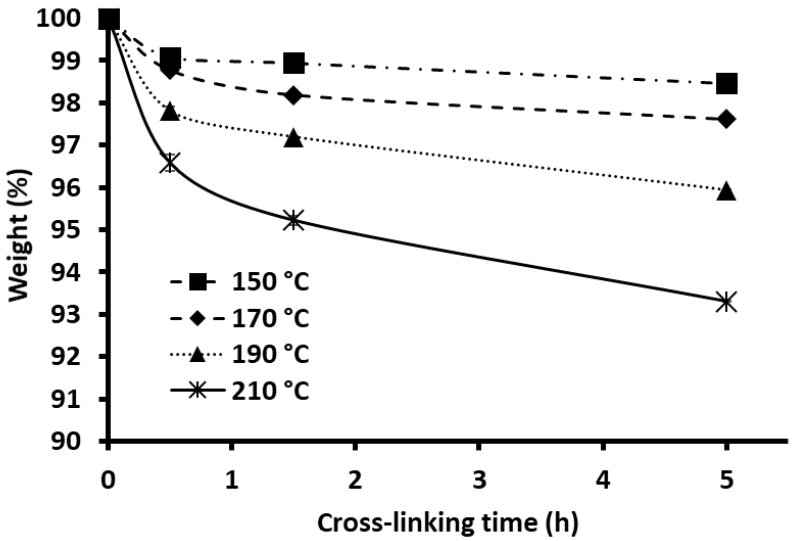


Fig. 3. Weight decrease of the wood powder sheets during heating at 150 to 210 °C for 0.5 to 5 h

Apparent Activation Energy During Heating

The wood powder, HPMC, and citric acid solution were blended, kneaded, and extruded, meaning that the wood powder was bound with a binder of HPMC and citric acid. Most of the citric acid is thought to be dispersed in the binder along with HPMC. Therefore, in this temperature range, it would be natural to consider the dehydration associated with esterification between HPMC and citric acid as the main factor in weight loss, although a small amount of weight loss could be attributed to pyrolysis. Assuming that this weight loss is a first-order reaction, the rate constant was calculated for each heating temperature (Fig. 4a). Based on the Arrhenius plot of the rate constants (Fig. 4b), the overall activation energy was calculated to be 46 kJ/mol.

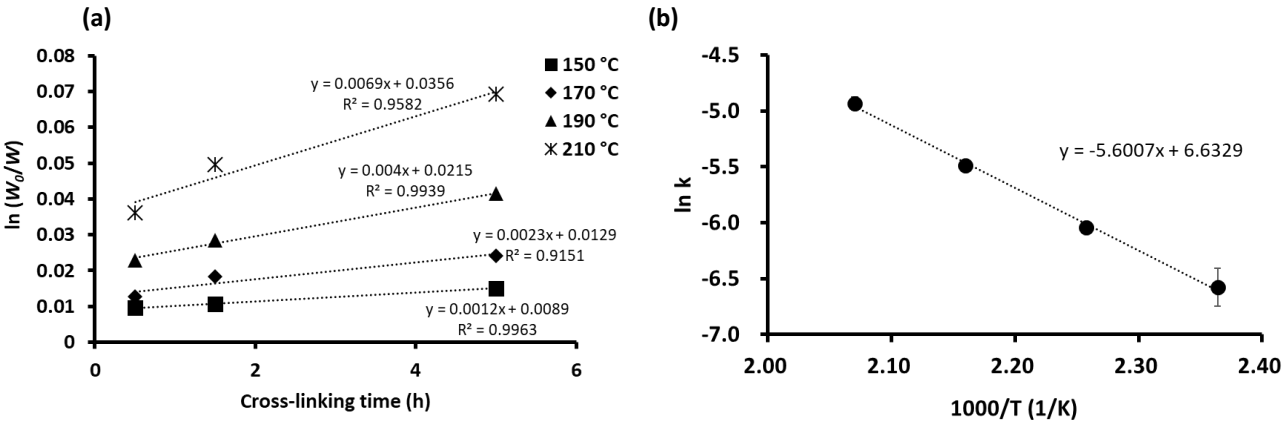


Fig. 4. Kinetic analysis on dehydration during heating of wood powder sheets based on the weight decrease: (a) Linear regression of *ln* (W/W_0) as a function of crosslinking time, (b) Arrhenius plot to determine overall activation energy

The activation energies of esterification under sodium hypophosphite conditions have been reported to be 48.6 kJ/mol for starch and 63 kJ/mol for cellulose (Christian *et al.* 2008; Li *et al.* 2015), which are of the same order of magnitude as the present values. The obtained result was similar to the activation energy for crosslinking of starch,

indicating that water-soluble HPMC reacted more readily with citric acid than crystalline cellulose. Although some of the citric acid is naturally in contact with the wood powder surface, and crosslinking between citric acid and wood powder components, such as hemicellulose, should also occur (Azeredo *et al.* 2015; Shao *et al.* 2019), this is considered a minor reaction compared to the crosslinking of HPMC by citric acid.

Water Absorption of the Crosslinked Sheets in Water

The suppression of swelling and degradation due to water absorption is the most important factor in regard to the crosslinking of wood powder sheets extruded with HPMC. When used as potential applications such as food containers, it is assumed that foods contain some water. Thus, the water stability of the sheets was evaluated by immersion as a strict condition. The weight gain of the samples in water was measured until equilibrium was reached. Figure 5a shows the water absorption percentages of the samples immersed in deionized water for 24 h.

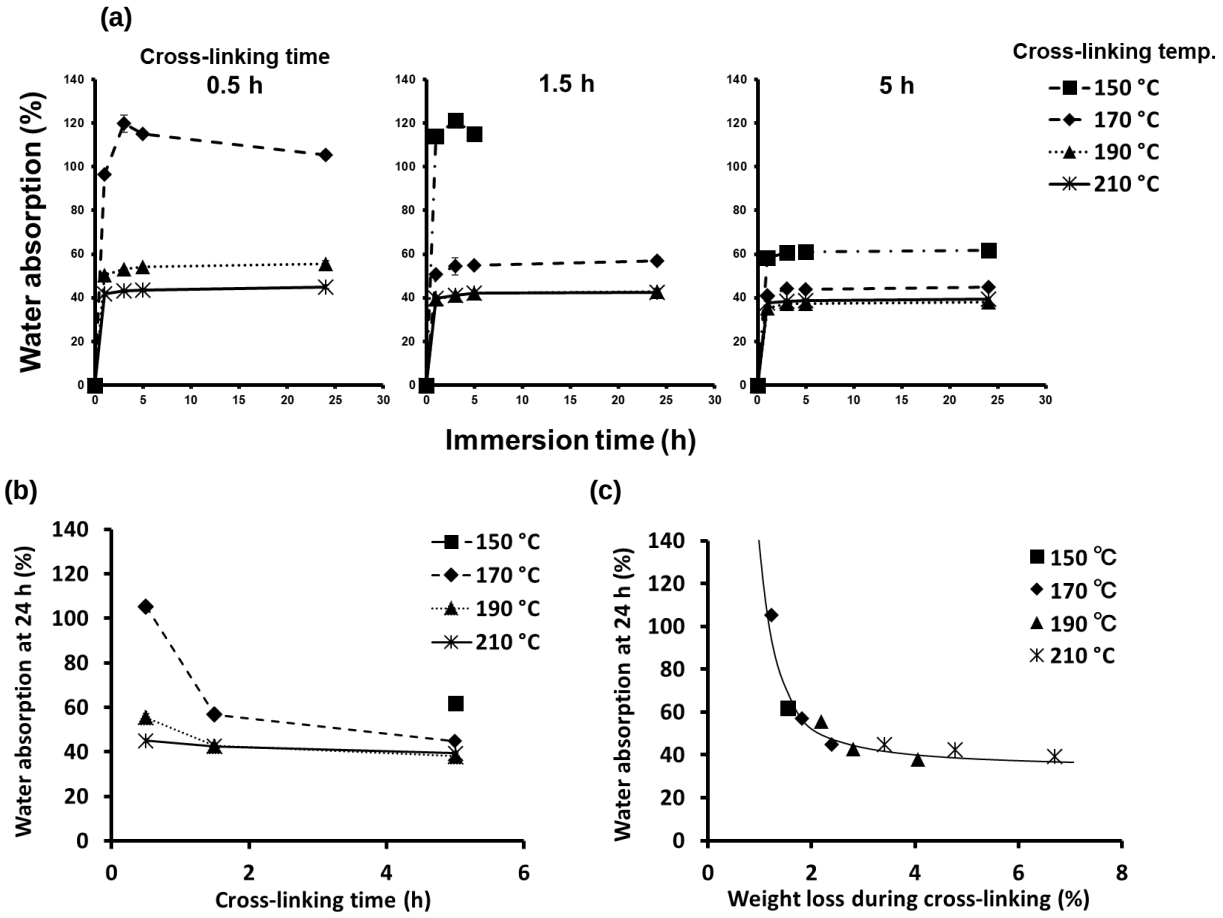


Fig. 5. (a) Water absorption for 24 h of the wood powder heated at 150 to 210 °C for 0.5 to 5 h; There are no data shown for the wood powder sheet heated at 150 °C for 0.5 h because it disintegrated in the water. (b) Relationship between the heating time and water absorption at 24 h as shown in Fig. 5a, (c) Relationship between weight loss (Fig. 3) and water absorption at 24 h (Fig. 5a). There are no data shown for the wood powder sheet heated at 150 °C for 0.5 and 1.5 h because the sample could not be removed from water at 24 h due to disintegration.

The samples that were heated at 150 °C for 0.5 h, disintegrated in water quickly, and the water absorption could not be measured. Similarly, the samples that were heated at 150 °C for 1.5 h vastly swelled and could not be taken out at 24 h for measurement. The other samples quickly absorbed water in 1 h, maintained their shape, and did not change their weight considerably until after 24 h. The samples heated at 150 °C for 5 h, 170 °C for 1.5 h, and 190 °C for 0.5 h showed a decrease in water absorption to 50% to 60%. The water absorption in the samples heated at 170 °C for 5 h, 190 °C for 1.5 h, and 210 °C for 0.5 h decreased to around 40% (Fig. 5b). These phenomena indirectly indicate that the degree of crosslinking increased as the heat treatment became severe.

Figure 5c shows the relationship between the weight loss (Fig. 3) and water absorption at 24 h. The figure indicates that there was a turning point in regard to water absorption at a weight reduction ratio of approximately 2%. It was found that the temperature 150 °C was too low to make the sheet stability to water. This process required several hours to complete. When the weight loss exceeded 2%, the water absorption ratio seemed to saturate at approximately 40% and did not appear to fall below 40%. The weight of the sheet decreased when it was heated for a longer time (Fig. 3). This indicates that the esterification and crosslinking of HPMC were still progressing; however, there was no further improvement in the water resistance. After heating the wood powder sheet, it never disintegrated into water, but it had a water capacity of 40%. Wood powder and crosslinked HPMC absorb water because they are hydrophilic cellulose-based materials, and it is estimated that many voids in the sheet can absorb water. Although these sheets, which would be used as food containers *etc.*, are not designed to be used in water, they maintained the water stability for more than one week (Fig. S1).

Tensile Strength of the Crosslinked Sheets

The mechanical properties of the sheet were influenced by the crosslinking of HPMC. The sheets untreated (just dried at 105 °C) or heated at 150 to 210 °C for 0.5 to 5 h were conditioned at 70 °C and a relative humidity of 90% for 24 h, and then the tensile strength was measured (Fig. 6a). The untreated sheets exhibited a sufficient tensile strength. Most of the heated wood powder sheets showed a slight increase in tensile strength (from 50 to approximately 60 MPa), suggesting that the crosslinked HPMC had a higher adhesive strength as a wood powder binder. In contrast, the tensile strength of the sheets treated at 190 °C for 5 h or 210 °C for 1.5 h and 5 h tended to decrease despite esterification and crosslinking. Figure 6b shows the relationship between the weight loss due to heating and the tensile strength. There are optimal heating conditions from the perspective of tensile strength. Under the severe heating conditions, the crosslinked HPMC probably became less hydrophilic because of dehydration with citric acid and had weaker hydrogen bonds with the wood powder, which decreased the tensile strength.

Dumbbell-shaped samples were dipped in deionized water to investigate the tensile strength when wet for 24 h. The specimens were then immediately subjected to tensile testing. The wet tensile strength was found to be much lower than that shown in Fig. 6a; however, the sheets heated under the nine conditions (Fig. 6c) were still strong enough to be tested. Increasing the temperature and time also improved the wet tensile strength. The severe heating conditions, 210 °C for 1.5 to 5 h, decreased the strength similarly as observed in Fig. 6b.

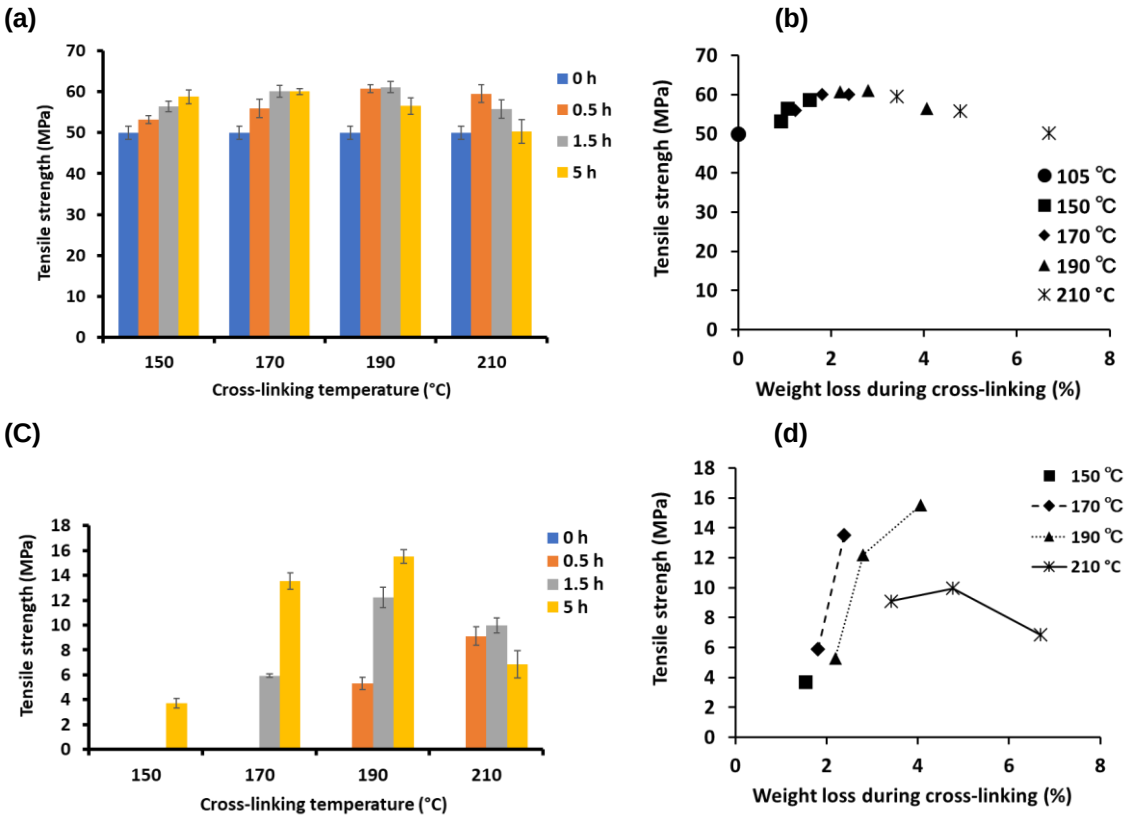


Fig. 6. (a) Tensile strengths of the wood powder sheets heated at each condition after conditioning at 70 °C and 90% RH for 24 h. The sample at 0 h is the sample solely dried at 105 °C; (b) Relationship between weight loss by heating (Fig. 3) and the tensile strength (Fig. 6a). (c) Tensile strengths of the wood powder sheets heated at each condition after immersing in water for 24 h; (d) Relationship between weight loss by heating (Fig. 3) and the wet tensile strength (Fig. 6c)

Puncture Resistance of the Crosslinked Sheets

This study considered possible applications of biomass-derived products to replace plastic products, including food containers. Applications such as food containers and coffee cup lids require small areas to withstand large forces. To evaluate the mechanical properties of the crosslinked sheets stored at room temperature, a puncture resistance test was performed using a cylindrical jig at a constant speed to penetrate a specific spot on the samples (Sun *et al*. 2023). Figure 7a shows the puncture resistance of the crosslinked sheets. The stress decreased as the heating conditions became more severe (Fig. 7b). This may be due to a decrease in the elasticity of non-crosslinked HPMC. The HPMC was expected to crosslink and become brittle with increasing heating temperature and when the time was longer. Moreover, air permeability of the application as a contaner is crucial for preventing or slowing the deterioration of the food or ingredients contained within. To support this property, the air permeability was tested for both sides of two test pieces, which were the unteated sheets and the sheets cured at 210 °C for 5 h by using a Gurley type densometer (No. 158, TOYOSEIKI, Japan) in accordance with the modified ISO 5636-5 (2013). As a result, air did not penetrate both sheets, showing that the air permeabilities were very low compared to that of paper (approximately 29.6 seconds per 100 mL) at least. Thus, the applications made from the sheets can have a potential to prevent the deterioration of the foods.

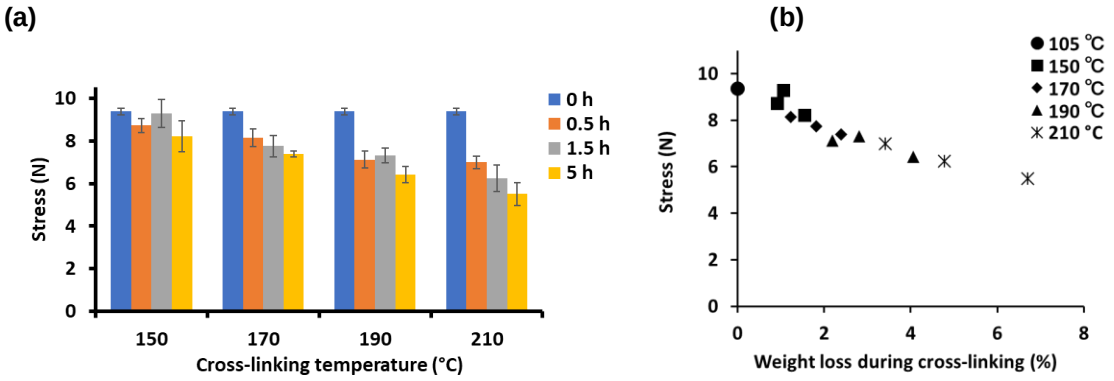


Fig. 7. (a) Puncture resistances of the wood powder sheets heated at each condition in an indoor environment; (b) Relationship between weight loss by heating (Fig. 3) and the puncture stress (Fig. 7a)

Contact Angle Measurements

Contact-angle measurements were performed to determine the wettability of the sheet surfaces. Images of the water droplets on the crosslinked sheets are shown in Fig. S2; the obtained angles are shown in Fig. 8a.

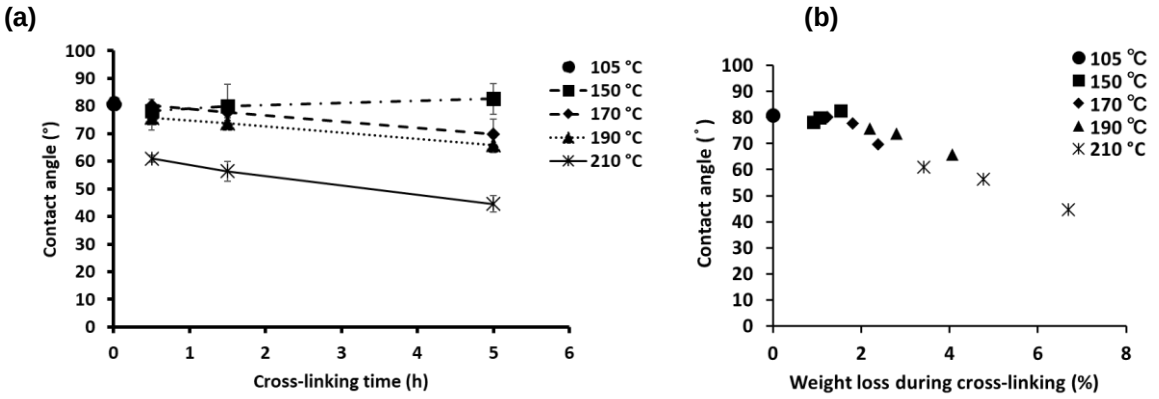


Fig. 8. (a) Contact angles of the wood powder sheets heated at each condition in an indoor environment; (b) Relationship between weight loss by heating (Fig. 3) and the contact angle (Fig. 8a)

Untreated sheet maintained a contact angle of 80 °. Interestingly, sheets prepared by heating at 150 °C also maintained a contact angle of 80 °. The contact angles of the samples at the crosslinking temperatures of 170 and 190 °C were similar with respect to their reduction in contact angles with the increase of crosslinking time. Contact angles of the crosslinking temperature 210 °C decreased to 60 ° despite the treatment time of 0.5 h, compared to contact angle 80 ° of the untreated sheet. Figure 8b shows a clear relationship where the contact angle decreased as the heating conditions became more severe. The observed decrease in contact angle seemed unexpected compared to reduction in water absorption in Fig 5c. This discrepancy may be considered to be due to the reduction of water-soluble HPMC. When treated at 105 and 150 °C, HPMC was still uncrosslinked or less-crosslinked; swelling by water affected the contact points within the structure and tended to retain as droplets. On the other hand, when the sheets were treated with severe

conditions, the decrease in water-soluble HPMC is thought to have reduced the water retention capacity, resulting in a lower contact angle. Since the sheets were composed of wood powder and HPMC, whether crosslinked or not, the material was basically hydrophilic and not water repellent.

This study shows appropriate temperature and time conditions for maximizing the water resistance and tensile strength of wood powder sheets extruded with HPMC and citric acid as a cross-linker. Moreover, the indirect activation energy calculated from the weight loss associated with dehydration suggests that this material readily induced crosslinking. Therefore, this study suggests that easy crosslinking using citric acid could facilitate the industrialization of wet extrusion of biomass powder.

CONCLUSIONS

In this work, all-biomass composite sheets were successfully prepared by mixing wood powder, HPMC, and citric acid solution (the ratio was 8:2:0.5, respectively), followed by extrusion using a vacuum extrusion molding machine. Because this sheet disintegrates in water, the sheet was cured at 150 to 210 °C for 0.5 to 5 h. The new findings were as follows:

1. The kinetics of the crosslinking reaction based on weight loss for dehydration were pseudo-first-order with an activation energy of 46 kJ/mol. The crosslinking of the wood powder sheets including HPMC and citric acid was able to occur easily.
2. Heating at 150 °C for 1.5 h was insufficient to prevent swelling and disintegration in water. Heating at temperatures higher than 170 °C effectively improved water resistance and suppressed the swelling of the sheet in water. The tensile strengths of the sheets increased slightly upon heating.
3. The weight loss caused by heating can determine the intensity of heat treatment. Excessive heating converged the water absorption approximately 40%, resulting in a decrease in tensile strength. Optimal heating conditions were estimated to be in the range of 170 to 190 °C for 0.5 to 5 hours.
4. Heating decreased the puncture resistance and contact angle in an indoor environment.

ACKNOWLEDGMENTS

The authors are grateful for the support provided by the Environment Research and Technology Development Fund (JPMEERF20221C03) of the Environmental Restoration and Conservation Agency, Ministry of the Environment of Japan.

REFERENCES CITED

Azeredo, H., Kontou-Vrettou, C., Moates, K. G., Wellner, N., Cross, K., Pereira, H.F. P., and Waldron, K. W. (2015). "Wheat straw hemicellulose films as affected by citric acid," *Food Hydrocoll.* 50, 1-6. DOI: 10.1016/j.foodhyd.2015.04.005

Christian, S., Beate, R., and Ortwin, B. (2008). "Kinetic data for the crosslinking reaction of polycarboxylic acids with cellulose," *J. Soc. Dye. Colour.* 113(12), 346-349. DOI: 10.1111/j.1478-4408.1997.tb01861.x

EFSA Panel on Additives and Products or Substances used in Animal Feed (FEEDAP), Vasileios, B., Giovanna, A., Maria, d. L.-A. B., Henrik, C., Birgit, D., Mojca, K. D., Maryline, K., Marta, L., Secundino, L. P., *et al.* (2020). "Safety and efficacy of hydroxypropyl methyl cellulose for all animal species," *EFSA Journal* 18(7), article e06214. DOI: 10.2903/j.efsa.2020.6214

Girl, K. A. (1997). "Genetic toxicology of epichlorohydrin: A review," *Mutat. Res.* 386, 25-38. DOI: 10.1016/S1383-5742(96)00042-7

Grosskopf, K. A., Labanieh, L., Klysz, D. D., Roth, A. G., Xu, P., Adebowale, O., Gale, C. E., Jons, K. C., Klich, H. J., Yan, J., *et al.* (2022). "Delivery of CAR-T cells in a transient injectable stimulatory hydrogel niche improves the treatment of solid tumors," *Sci. Adv.* 8(14), article ID eabn8264. DOI: 10.1126/sciadv.abn8264

ISO 527-2 (2012). "Plastics – Determination of tensile properties - Part 2: Test conditions for moulding and extrusion plastics," International Organization for Standardization, Geneva, Switzerland.

ISO 5636-5 (2013). "Paper and board – Determination of air permeance (medium range) – Part 5: Gurley method," International Organization for Standardization, Geneva, Swizerland.

JIS K7161-2 (2014). "Plastics – Determination of tensile properties - Part 1: General principles," Japanese Standards Association, Tokyo, Japan.

Kawamura, K., Abera, T., and Nonaka, H. (2018). "Extrusion molding of cellulosic fibers using cellulose derivative," *Japan Tappi J.* 72(3), 321-327. DOI: 10.2524/jtappij.72.321

Kulkarni, R. A., Soppimath, S. K., Aminabhavi, M. T., Dave, M. A., and Mehta, H. M. (1999). "Urea-Formaldehyde crosslinked starch and guar gum matrices for encapsulation of natural liquid pesticide [*Azadirachta indica* A. Juss.(Neem) Seed oil]: Swelling and release kinetics," *J. Appl. Polym. Sci.* 73(12), 2437-2446. DOI: 10.1002/(SICI)1097-4628(19990919)73:12<2437::AID-APP12>3.0.CO;2-7

Kuniak, L., and Marchessault, R. (1988). "Study of the crosslinking reaction between epichlorohydrin and starch," *Starch* 24(4), 110-116. DOI: 10.1002/star.19720240404

Lai, W., Zhao, S., and Chiou, J. (2021). "Antibacterial and clusteroluminogenic hypromellose-graft-chitosan-based polyelectrolyte complex films with high functional flexibility for food packaging," *Carbohydr. Polym.* 271, article ID 118447. DOI: 10.1016/j.carbpol.2021.118447

Li, S., Helan, X., Lingjuan, K., and Yiqi, Y. (2015). "Non-toxic crosslinking of starch using polycarboxylic acids: Kinetic study and quantitative correlation of mechanical properties and crosslinking degrees," *J. Polym. Environ.* 23, 588-594. DOI: 10.1007/s10924-015-0738-3

Ma, T. H., and Harris, M. M. (1988). "Review of the genotoxicity of formaldehyde," *Mutat. Res.* 196(1), 37-59. DOI: 10.1016/0165-1110(88)90027-9

Mašková, E., Kubová, K., Raimi-Abraham, T. B., Vllasaliu, D., Vohlídalová, E., Turánek, J., and Mašek, J. (2020). "Hypromellose – A traditional pharmaceutical excipient with modern applications in oral and oromucosal drug delivery," *J. Control Release* 324, 695-727. DOI: 10.1016/j.jconrel.2020.05.045

Matsuoka, T., and Nonaka, H. (2020). "Wet extrusion of wood powder using a cellulose derivative production of pipe-shaped material 'Wood straw'," *Japan Tappi J.* 74(5), 516-524. DOI: 10.2524/jtappij.74.516

Matsuoka, T., and Nonaka, H. (2021). "Development of coffee residue products by wet extrusion molding," *J. Jpn. Inst. Energy.* 100(6), 55-61. DOI: 10.3775/jie.100.55

Napper, E. I., and Thompson, C. R. (2023). "Plastics and the environment," *Annu. Rev. Environ. Resour.* 1(48), 55-79. DOI: 10.1146/annurev-environ-112522-072642

Nonaka, H. (2020). "3D biomass molding without using oil-based plastics – Wood straw as an example," *Nippon Enerugi Gakkai Kikanshi Enerumikusu* 99(1), 27-32. DOI: 10.20550/jieenermix.99.1_27

Nonaka, H. (2023). "Extrusion molding of biomass powder with cellulose derivatives," *Glycoforum* 26(6), article A22. DOI: 10.32285/glycoforum.26A22

Novaes, D. S., Oliveira, V. P., and Petri, S. F. D. (2022). "Hydroxypropyl methylcellulose-sugarcane bagasse adsorbents for removal of 17α-ethinylestradiol from aqueous solution and freshwater," *Environ. Sci. Pollut. Res. Int.* 42, 63936-63952. DOI: 10.1007/s11356-022-20345-4

Shao, H., Sun, H., Yang, B., Zhang, H., and Hu, Y. (2019). "Facile and green preparation of hemicellulose-based film with elevated hydrophobicity *via* cross-linking with citric acid," *RSC Advances* 9(5), 2395-2401. DOI: 10.1039/c8ra09937e

Sun, X., Ji, R., Zhang, Y., Li, Y., and Wang, P. (2023). "Preparation of a TPU-based flexible stab-resistant composite membrane filled with SiO_2 and SBR nanoparticles," *ACS Appl. Polym. Mater.* 6, 1790-1799. DOI: 10.1021/acsapm.3c02618

Tao, X., and Nonaka, H. (2021). "Wet extrusion molding of wood powder with hydroxy-propylmethyl cellulose and with citric acid as a crosslinking agent," *BioResources* 16(2), 2314-2325. DOI: 10.15376/biores.16.2.2314-2325

Umemura, K., Ueda, T., and Kawai, S. (2011). "Characterization of wood-based molding bonded with citric acid," *J. Wood Sci.* 58, 38-45. DOI: 10.1007/s10086-011-1214-x

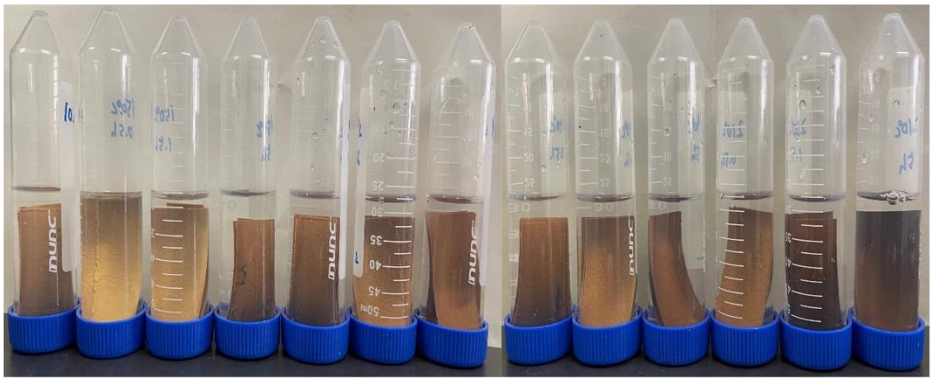
Wang, H., Ma, R., Huang, Z., Liu, X., Wang, T., and Chen, K. (2021). "Preparation and characterization of carboxymethylcellulose based citric acid crosslinked magnetic aerogel as an efficient dye adsorbent," *Int. J. Biol. Macromol.* 181, 1030-1038. DOI: 10.1016/j.ijbiomac.2021.04.078

Zhang, J., Han, Y., Ben, Z., Han, T., and Yin, P. (2023). "Effect of branched polyethyleneimine and citric acid on the structural, physical and antibacterial properties of corn starch/chitosan films," *Int. J. Biol. Macromol.* 231, article ID 123186. DOI: 10.1016/j.ijbiomac.2023.123186

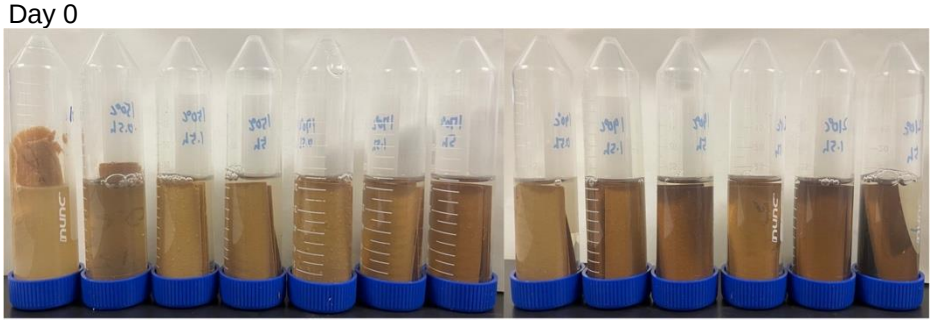
Article submitted: October 8, 2024; Peer review completed: November 9, 2024; Revised version received and accepted: December 23, 2024; Published: January 10, 2025.
DOI: 10.15376/biores.20.1.1900-1914

APPENDIX

Temperature (°C)	105	150			170			190			210		
Heating time (h)	1	0.5	1.5	5	0.5	1.5	5	0.5	1.5	5	0.5	1.5	5

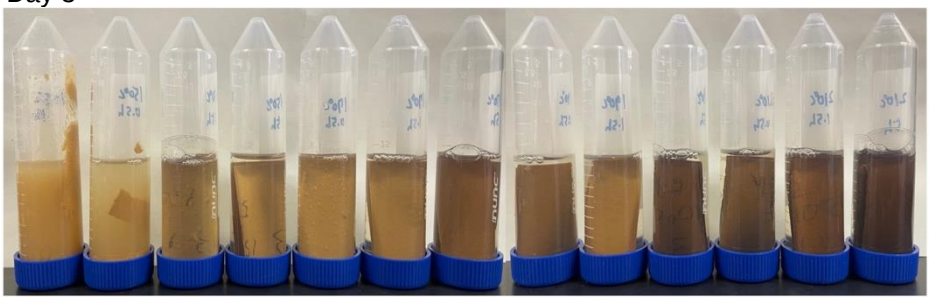


Day 0



Day 1

Day 3



Day 7

Fig. S1. Photos of the water stability of the sheets for 1 week. About 1 g of wood powder sheets were completely immersed in distilled water at 25 °C for 1 week.

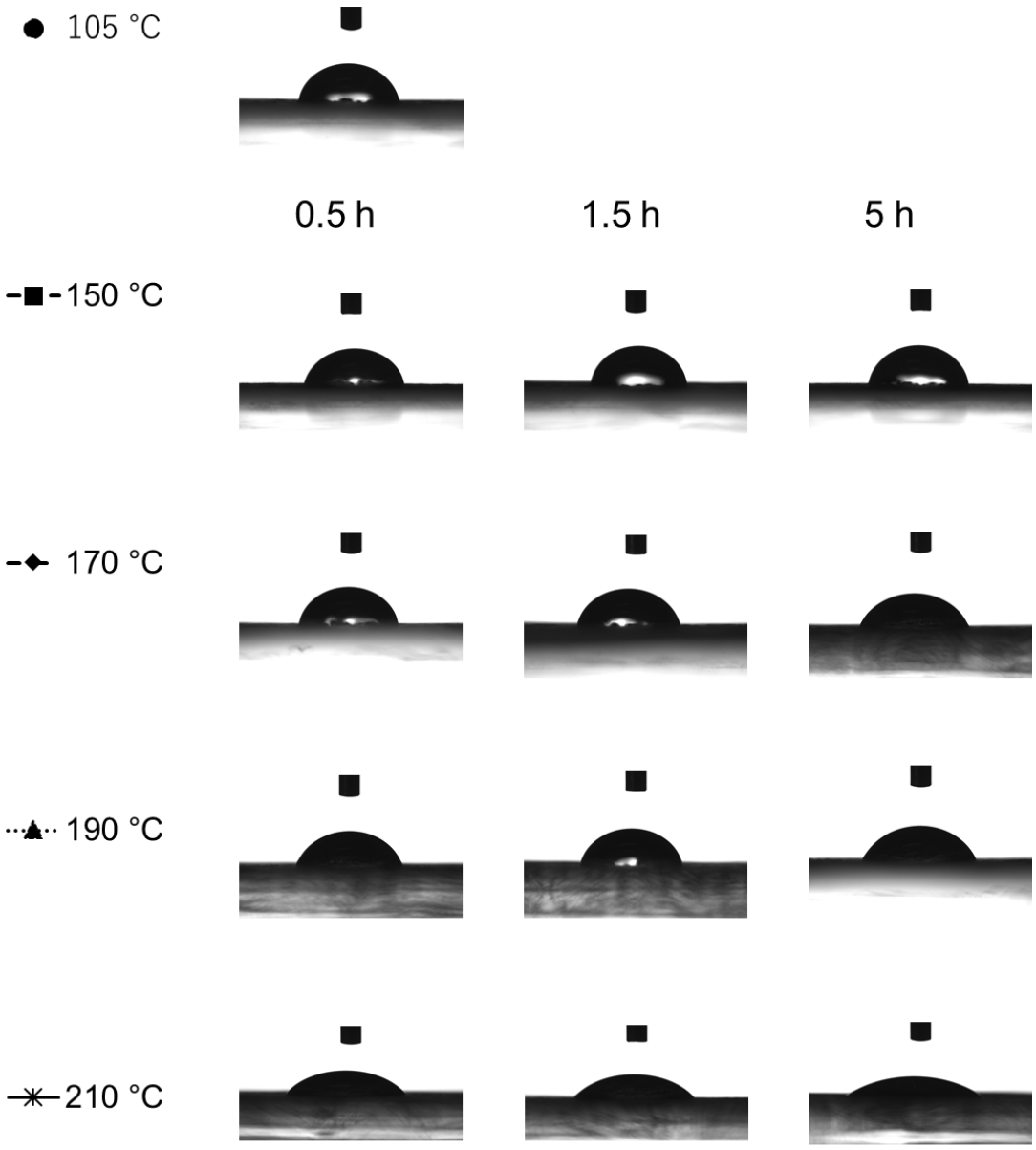


Fig. S2. Photos of the contact angles for the wood powder sheets heated at each condition