Effects of Heat Treatment on Environmental Stability and Dissolution Behavior of Citric Acid-Containing Wood Flour Sheets

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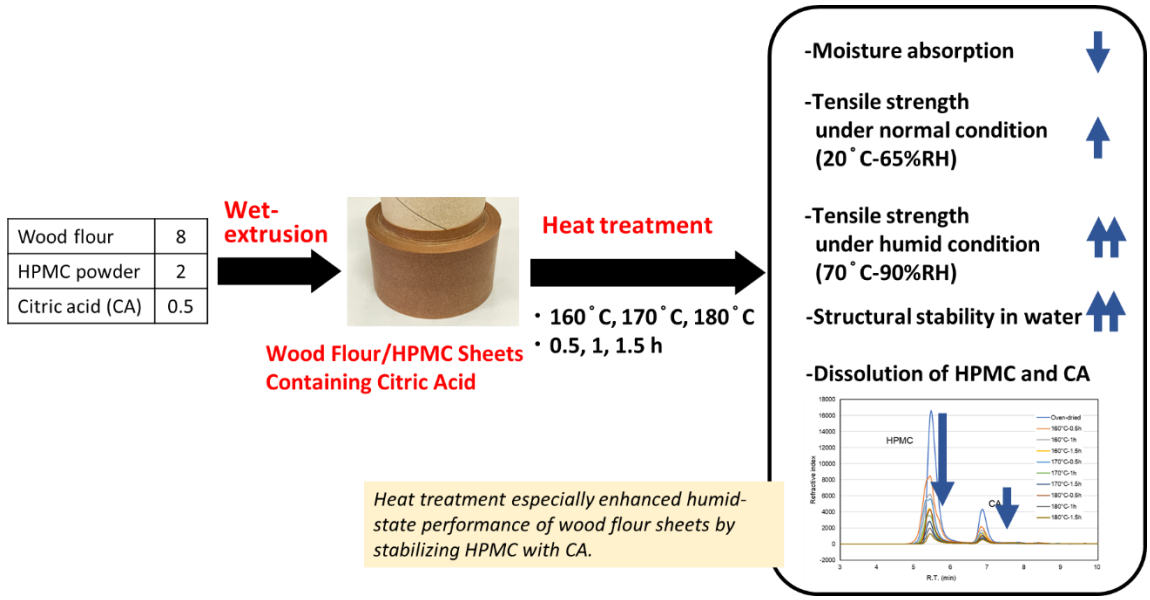
GRAPHICAL ABSTRACT



Effects of Heat Treatment on Environmental Stability and Dissolution Behavior of Citric Acid-Containing Wood Flour Sheets

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

Wood flour sheets were prepared by wet extrusion molding using hydroxypropyl methylcellulose (HPMC) and citric acid (CA) as a molding aid and crosslinking agent, respectively. The effects of heat treatment (160 to 180 °C, 0.5 to 1.5 h) on moisture absorption, tensile properties, water stability, and dissolution behavior of CA and HPMC were investigated. Moisture absorption decreased from approximately 9% to 8% at 20 °C and 65% relative humidity (RH), and from approximately 15% to 12% at 70 °C and 90% RH. The tensile strength measured at 20 °C and 65% RH remained nearly constant regardless of the heat-treatment severity, whereas the tensile strength at 70 °C and 90% RH was significantly improved by the heat treatment. Water immersion tests showed that the heat-treated sheets exhibited improved structural stability and reduced water absorption compared to the oven-dried control. HPLC analysis revealed that the dissolution ratios of both CA and HPMC decreased markedly with increasing heat treatment severity. The simultaneous reduction in CA and HPMC dissolution suggests that heat treatment promoted CA-mediated crosslinking and insolubilization of HPMC within the sheet structure. These changes contributed to improved water stability and retention of mechanical properties under high-temperature/high-humidity conditions, thereby enhancing the overall environmental stability of the wood flour sheets.

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Keywords: Wood powder; Hydroxypropyl methylcellulose; Cellulose derivative; Wet extrusion molding; Citric acid crosslinking

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INTRODUCTION

Wood is a renewable and abundant lignocellulosic resource that is widely used for wood products and paper. It is increasingly viewed as a potential feedstock for the production of functional materials (Zhang *et al.* 2026) and bio-based chemicals (Isikgor and Becer 2015). Unlike thermoplastic polymers, wood does not exhibit thermoplastic behavior; therefore, it cannot be directly molded into durable products. To overcome this limitation, wood flour is commonly combined with thermoplastic polymers to produce wood–plastic composites (WPCs) (Klyosov 2007; Gardner *et al.* 2015; Mitaľová *et al.* 2024; Khan *et al.* 2025). WPCs have been extensively studied and commercialized for applications, such as decking materials, outdoor construction products, and other wood-like materials.

Polyethylene (PE) and polypropylene (PP) are widely used as matrix polymers, and industrially compostable polymers such as polylactic acid (PLA) (Peltola *et al.* 2014) and poly(butylene adipate-co-terephthalate) (PBAT) (Yu *et al.* 2025) have also been investigated. In addition, thermoplastic starch (Agnantopoulou *et al.* 2012), sucrose (Kajikawa *et al.* 2020), and other bio-based substances have been explored as alternatives to synthetic polymers for wood-based molded materials.

WPCs are typically processed at temperatures approaching or exceeding 200 °C depending on the melting point of the plastics used. Such high processing temperatures can cause thermal degradation of wood components (Gardner *et al.* 2015; Mitaľová *et al.* 2024), resulting in discoloration, generation of volatile degradation products, and undesirable odors. In addition, the amount of wood flour that can be incorporated into WPC formulations is inherently limited (Samyn 2024), because higher loadings markedly reduce the melt flow and impair processability.

Previously, Matsuoka and Nonaka (2020) developed a wet extrusion molding process that operates at ambient temperature using hydroxypropyl methylcellulose (HPMC), a water-soluble cellulose derivative, as a molding aid in the wet stage and as a binder in the dry stage. They demonstrated that wood flour can be molded into pipe-shaped products through wet extrusion followed by drying, establishing a low temperature processing route that avoids thermal degradation during molding. HPMC is widely used in food, pharmaceutical, and industrial applications (Matilla *et al*. 2026) owing to its excellent film forming ability (Ghadermazi *et al.* 2019), water solubility, and thermal gelation behavior (Fairclough *et al.* 2012; Yoo and Um 2013). These properties make HPMC a promising binder for wood flour based molded materials.

To improve the water stability of wet-extruded materials, Tao and Nonaka (2021) introduced citric acid (CA) as a bio-based cross-linking agent. They reported that the heat treatment of wood flour/HPMC composites containing CA markedly improved water stability. In particular, the products heated at 170 °C for 30 min maintained their shape and hardness during water immersion, whereas untreated products readily disintegrated. These results suggest that the heat treatment promoted the formation of a water-insoluble structure within the sheets. Subsequently, Hiratsuka *et al.* (2025) investigated the effects of heat treatment on the properties of wood flour/HPMC sheets containing CA over wide temperature ranges (150, 170, 190, and 210 °C) and durations (0.5, 1.5, and 5 h). For simplicity, the wood flour/HPMC sheets are hereafter referred to as wood flour sheets. They demonstrated that the weight loss increased with the severity of heat treatment and could be used as an integrated indicator of treatment conditions. Relationships between weight loss and water absorption, tensile strength, and contact angle have also been reported. However, detailed information on the environmental stability of the heat-treated composite sheets under practical conditions is limited.

This study focused on practical heat-treatment conditions within the temperature range of 160 to 180 °C and investigated the effects of heat treatment on the environmental stability and dissolution behavior of wood flour sheets. Particular attention was paid to moisture absorption, tensile properties under controlled temperature and humidity conditions, structural stability during water immersion, and the dissolution behavior of CA and HPMC to provide further insight into the stabilization mechanism of the heat-treated sheets.

EXPERIMENTAL

Materials

Japanese cedar (*Cryptomeria japonica*) wood flour (particle size < 91 μm; Naka Wood Co. Ltd., Tokushima, Japan) was used as the raw biomass material. HPMC (90SH-4000, Shin-Etsu Chemical Co., Ltd., Tokyo, Japan) (degree of substitution of methoxy group (-OCH_3): 1.4, molar substitution of hydroxypropoxy group (-$OCH_2CHOHCH_3$): 0.20) was used as a binder to facilitate wet extrusion molding. Citric acid monohydrate (purity: 99.5%) (FUJIFILM Wako Pure Chemical Corp., Osaka, Japan) was used as a crosslinking agent. Distilled water was used for all the experiments.

Preparation of Wood Flour Sheets

Wood flour sheets were prepared according to the method described by Hiratsuka *et al*. (2025). Wood flour, HPMC powder, water, and CA were mixed in a weight ratio of 8:2:11.5:0.5. The raw materials were premixed using a Henschel mixer and subsequently processed using a kneading vacuum extrusion molding machine (Miyazaki Iron Works Co., Ltd., Saga, Japan). The extruded sheet was continuously dried on a drum dryer maintained at 70 °C and collected in roll form. The resulting sheets had a thickness ranging from 0.3 to 0.4 mm.

Verification of Oven-Drying Conditions

To confirm the suitability of oven drying for determining oven-dry weight, wood flour sheet specimens were placed in a drying oven maintained at 105 °C for up to 12 h. Specimens were weighed at regular intervals during the drying process. Data were shown as means ± SDs of two measurements.

Heat Treatment of Wood Flour Sheets

The wood flour sheets were cut into specimens measuring 100 mm in length. Prior to heat treatment, the specimens were oven-dried at 105 °C for 1 h to obtain their oven-dry weights. The oven-dried specimens were subsequently heat-treated at 160, 170, or 180 °C for 0.5, 1.0, or 1.5 h in a drying oven under atmospheric conditions to promote esterification and crosslinking reactions involving CA. The specimen weight was measured before and after the heat treatment to evaluate the weight loss associated with the crosslinking process.

Moisture Absorption under Controlled Temperature and Humidity Conditions

The heat-treated wood flour sheet specimens were conditioned at 20 °C and 65% relative humidity (RH) for 48 h in a constant climate cabinet (LHU-144, ESPEC Corp., Japan), with reference to the standard conditioning atmosphere specified in ISO 187:2022 and its corresponding Japanese standard, JIS P 8111:1998, which are widely adopted for conditioning cellulose-based materials. After conditioning, the specimens were weighed. The conditioned specimens were subsequently exposed to 70 °C and 90% RH for 48 h in the same climate chamber. This condition was independently established as an accelerated hygrothermal exposure condition (such as the lid for hot drink) for comparative evaluation of the environmental stability. After conditioning, the specimens were weighed immediately. The moisture absorption ratios at 20 °C-65%RH and 70 °C-90%RH were calculated as follows,

$$\text{Moisture absorption (\%)} = ((W_h - W_d) / W_d) \times 100 \quad (1)$$

where W_d is the oven-dry weight of the specimen and W_h is the specimen weight after conditioning under each condition. Data were shown as means ± SDs of five measurements.

Tensile Testing

Tensile test specimens were prepared from wood flour sheets using a Super Dumbbell Cutter (SDMK-1000-D, Dumbbell Co., Ltd., Japan) mounted on a lever-type specimen cutting machine (SDL-200, Dumbbell Co., Ltd., Japan). The Super Dumbbell Cutter used for preparing the specimens complied with standards: JIS K7161-2-1BA. The geometry of each specimen is illustrated in Fig. 1. Tensile tests were conducted using a compact tabletop universal testing machine (EZ-LX; Shimadzu Corp., Kyoto, Japan). The grip separation distance was set to 60 mm and the crosshead speed was 10 mm/min. Five replicate specimens were tested under each condition and the average tensile strength was reported. Tensile strength (σ) was calculated as follows,

$$\sigma \text{ (MPa)} = P / A \quad (2)$$

where σ is the tensile strength (MPa), P is the maximum load (N), and A is the original cross-sectional area of the specimen (mm²). Data were shown as means ± SDs of five measurements.

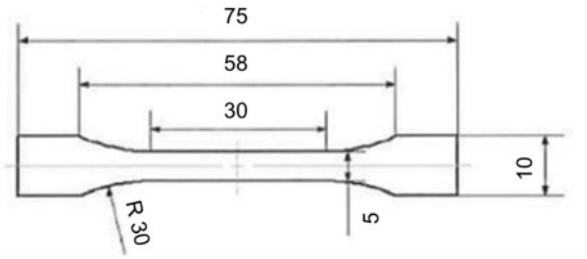

Fig. 1. Dimensions of the dumbbell-shaped specimen used for tensile testing

Water Immersion Test of Heat-Treated Sheets

According to an in-house methodology, approximately 0.5 g (oven-dry basis) of each specimen was immersed in 50 mL of distilled water. Prior to immersion, the specimens were oven-dried at 105 °C and weighed. The immersion test was conducted at 25 °C using a laboratory shaker (BC-730, AS ONE Corp., Japan) installed in a temperature-controlled chamber. The specimens were continuously agitated during the immersion. After 24 h, the specimens were removed from the water and excess surface water was gently removed before weighing. Water absorption was calculated using Eq. 3,

$$\text{Water absorption (\%)} = ((W_1 - W_0) / W_0) \times 100 \quad (3)$$

where W_0 is the oven-dry weight before immersion and W_1 is the weight of the specimen after 24 h of immersion. The dimensional stability and appearance of the immersed sheets were evaluated visually after the immersion test. Five replicate specimens were analyzed for each treatment condition. Data were shown as means ± SDs. After the water absorption measurements, the immersion solutions were collected and subjected to high-performance liquid chromatography (HPLC) analysis.

Analysis of Dissolved Citric Acid and Hydroxypropylmethylcellulose

The water-soluble components extracted from the sheets were analyzed using an HPLC system equipped with a refractive index (RI) detector and a Shodex SUGAR SH1011 column. A 3.0 mmol/L aqueous perchloric acid ($HClO_4$) was used as the mobile phase at a flow rate of 1.0 mL/min. The relative dissolution ratios of CA and HPMC were evaluated based on the corresponding peak areas. The peak area obtained from the oven-dried control sheet was defined as 100%, and the relative dissolution ratio was calculated using Eq. 4,

$$\text{Relative dissolution ratio (\%)} = (A_i / A_{OD}) \times 100 \quad (4)$$

where A_i is the chromatographic peak area of CA or HPMC obtained from the immersion solution of each heat-treated sample and A_{OD} is the corresponding peak area obtained from the oven-dried control sheet.

RESULTS AND DISCUSSION

Weight Loss During Heat Treatment

To establish a reference dry weight, the wood flour sheets were dried at 105 °C for 12 h and the weight change was monitored (Fig. 2(a)). The sheet weight decreased significantly during the first hour of drying and remained nearly constant thereafter. Therefore, the weight after drying at 105 °C for 1 h was adopted as the oven-dry reference weight for subsequent experiments.

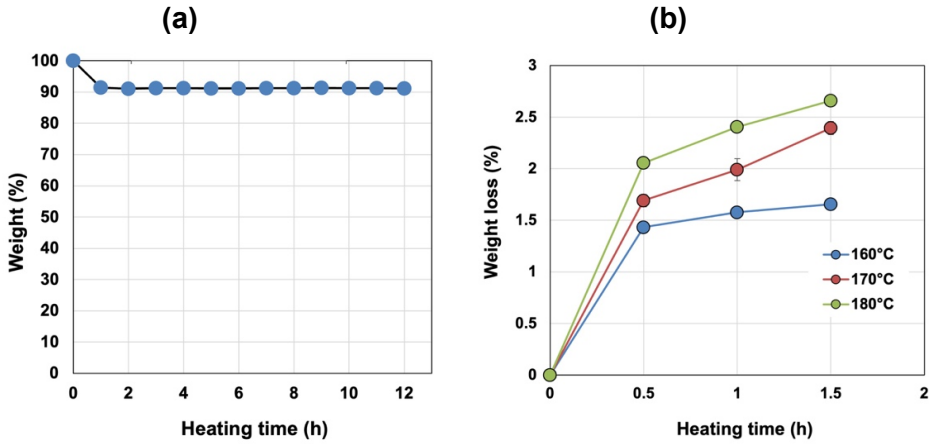

Fig. 2. (a) Changes in specimen weight during oven drying at 105 °C. The initial specimen weight was defined as 100%, and data are presented as mean ± SD (n = 2). (b) Weight loss of wood flour sheets during heat treatment at 160, 170, and 180 °C. Data are presented as mean ± SD (n = 5). Error bars smaller than the data-point symbols are not visible.

Figure 2(b) shows the weight loss of the wood flour sheets during heat treatment at 160, 170, and 180 °C. The weight loss increased rapidly during the initial 0.5 h of heating and then increased gradually with prolonged treatment time. The extent of weight loss depended strongly on the heating temperature. After 1.5 h of treatment, the weight loss reached 1.7%, 2.4%, and 2.7% at 160, 170, and 180 °C, respectively. Similar weight loss levels were obtained under different temperature–time combinations. For example, the

samples treated at 170 °C for 1 h and 180 °C for 0.5 h exhibited weight losses of approximately 2.0%. The samples treated at 170 °C for 1.5 h and 180 °C for 1 h showed nearly identical weight losses of approximately 2.4%. These results suggest that a comparable extent of thermal modification under different heat treatment conditions.

The observed weight reduction is considered to be mainly associated with dehydration accompanied by esterification reactions involving CA and the surrounding HPMC matrix (Fig. 3), because wood flour, HPMC (Ford 1999; Matsuoka *et al.* 2022) and CA (Wyrzykowski *et al.* 2011) underwent only limited thermal decomposition within the temperature range employed in this study. Previous studies have suggested that CA reacts with HPMC through esterification, which results in crosslinking and reduced water solubility (Sebti *et al.* 2003; Marani *et al.* 2015; Tao and Nonaka 2021). It is expected that the majority of CA coexists with HPMC within the matrix and crosslinks upon sufficient heating to form water-insoluble HPMC (Fig. 3). The remaining CA present on the surface of the wood flour may react with wood components (cellulose, hemicellulose, and lignin); however, this reaction is considered to be minor compared to the crosslinking reaction between HPMC and CA. Unfortunately, as we previously reported (Tao and Nonaka 2021), it is difficult to confirm the formation of ester linkage or the disappearance of -OH and -COOH group in wood flour sheets using FT-IR analysis. As proposed in our previous study (Hiratsuka *et al.* 2025), weight loss can serve as a useful integrated parameter for evaluating the overall progress of HPMC crosslinking and water insolubilization during heat treatment (Marani *et al.* 2015). In the following sections, the relationships between weight loss and changes in sheet properties, including moisture absorption and tensile properties, are examined to clarify the effects of heat treatment.

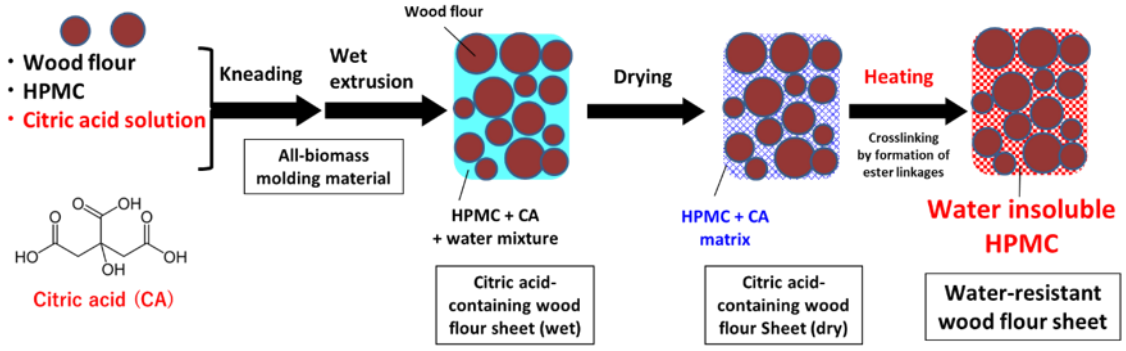

Fig. 3. Wet-extrusion molding of CA-containing wood flour sheets and the insolubilization upon heating

Moisture Absorption of Heat-Treated Sheets

Figure 4(a) shows the moisture absorption of the heat-treated wood flour sheets after conditioning under ambient conditions (20 °C – 65%RH) and high-temperature/high-humidity conditions (70 °C – 90%RH). Moisture absorption decreased with increasing heat-treatment severity under both humidity conditions. Under the 20 °C – 65%RH condition, moisture absorption decreased from approximately 9.0% for the oven-dried sheet to about 7.8% for the sheet treated at 180 °C for 1.5 h. A larger reduction was observed under the 70 °C – 90%RH condition, where moisture absorption decreased from approximately 14.6% to 11.9% over the same treatment range. These results indicate that the heat treatment effectively reduced the hygroscopicity of the wood flour sheets, particularly under high-humidity conditions.

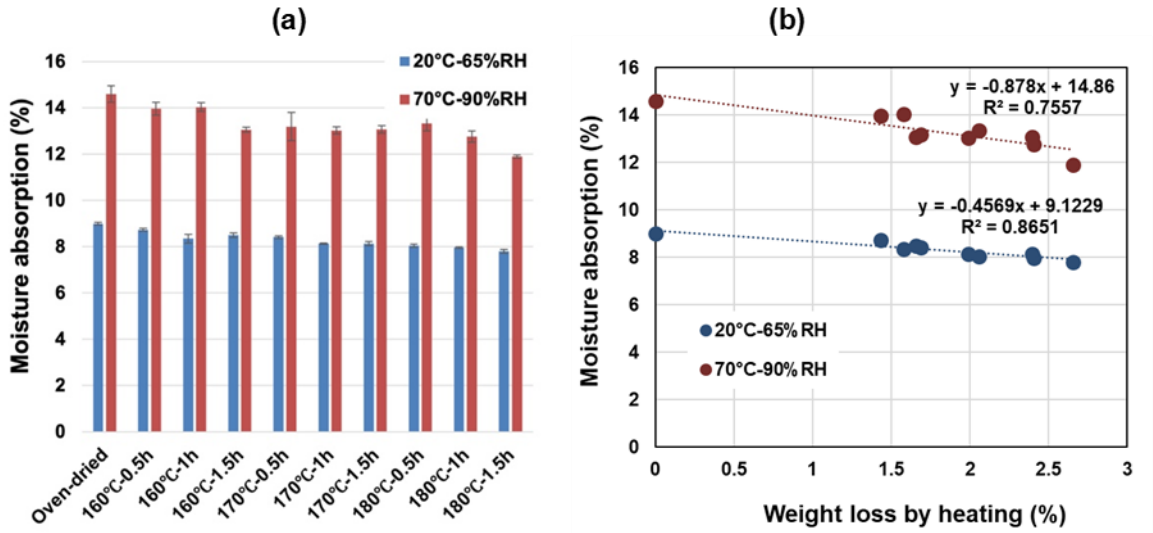

Fig. 4. (a) Moisture absorption of heat-treated wood flour sheets conditioned at 20 °C-65%RH and 70 °C-90%RH, and (b) relationships between weight loss during heat treatment (Fig. 2) and moisture absorption.

Figure 4(b) shows the relationship between the weight loss during heat treatment and moisture absorption. Negative correlations were observed under both humidity conditions. The coefficients of determination (R^2) were 0.8651 and 0.7557 for the 20 °C-65%RH and 70 °C-90%RH conditions, respectively. In addition, the slope of the regression line was steeper under the 70 °C-90%RH condition (−0.8780) than under the 20 °C-65%RH condition (−0.4569), indicating that moisture absorption was more sensitive to the progress of thermal modification under high-humidity conditions.

The reduction in moisture absorption is likely associated with esterification reactions involving CA, which reduce the number of accessible hydrophilic hydroxyl groups and restrict to enhance hydrophobicity (Shao *et al.* 2019; Nongnual *et al.* 2024). Although weight loss does not directly represent the degree of crosslinking, the observed correlations suggest that the thermal reactions contributing to weight reduction also contribute to the improved moisture resistance.

Tensile Strength of Heat-Treated Sheets

Figure 5(a) shows the tensile strength of the heat-treated wood flour sheets after conditioning at 20 °C-65%RH and 70 °C-90%RH. Under 20 °C-65%RH conditions, all heat-treated samples exhibited higher tensile strengths than the oven-dried control. The average tensile strength of the heat-treated samples was 71.8 MPa, whereas the control sample showed a tensile strength of 61.6 MPa.

Figure 5(b) shows the relationship between weight loss during heat treatment and tensile strength. Under the 20 °C – 65%RH condition, all the heat-treated samples exhibited similar tensile strengths, regardless of weight loss. These results indicate that the heat treatment improved the tensile strength of the sheets; however, further increases in weight loss had little influence on the tensile strength under ambient conditions.

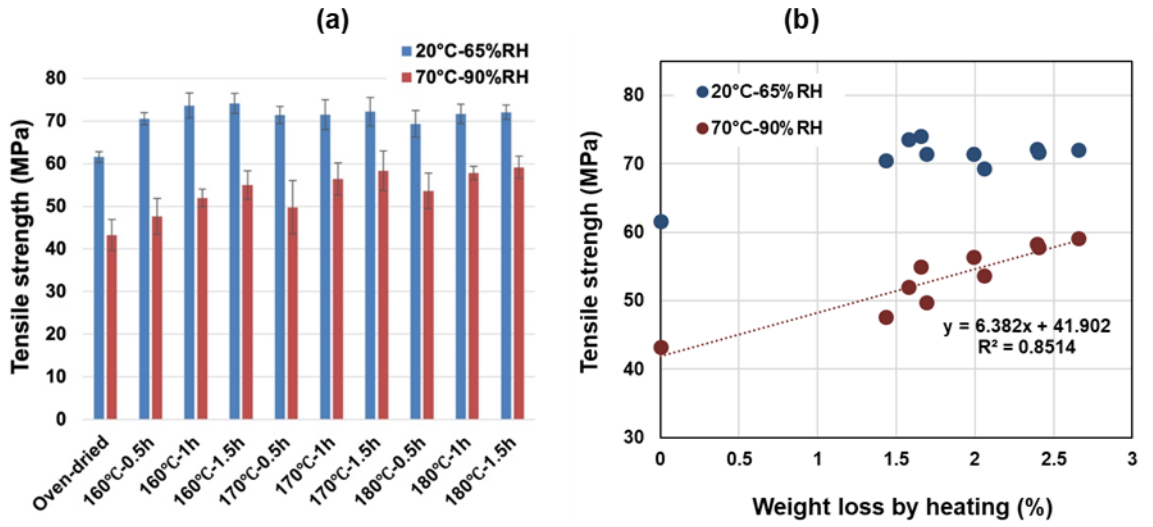

Fig. 5. (a) Tensile strength of heat-treated wood flour sheets conditioned at 20 °C – 65%RH and 70 °C – 90%RH, and (b) relationship between weight loss during heat treatment (Fig. 2) and tensile strength

In contrast, under 70 °C – 90%RH conditions, the tensile strength increased with increasing weight loss, showing a strong positive linear relationship (R^2 = 0.8514). The tensile strength increased from 43.3 MPa for the control sample to approximately 59.2 MPa for the samples exhibiting the highest weight loss. The improvement in the tensile strength under high-temperature/high-humidity conditions was consistent with the reduction in moisture absorption, as shown in Fig. 4.

As shown in Fig. 4(b), moisture absorption decreased more markedly with increasing weight loss under 70 °C – 90%RH than under 20 °C – 65%RH. Samples exhibiting greater weight loss absorbed less moisture and experienced less water-induced plasticization of the sheet structures. Consequently, the tensile strength was better retained even after exposure to 70 °C – 90%RH. These findings support the hypothesis that CA-mediated crosslinking contributes primarily to the retention of mechanical properties under humid conditions rather than increasing tensile strength under ambient conditions. A similar high-humidity performance has been reported for paper products (Widsten *et al.* 2014).

Stability and Dissolution Behavior of Heat-Treated Sheets in Water

Figure 6(a) shows the appearance of the wood flour sheets after immersion in distilled water for 24 h. The oven-dried sheet completely lost its original shape during immersion and could not be recovered intact. Similarly, the sheet treated at 160 °C for 0.5 h became extremely soft and fragile after immersion, making it impossible to recover the specimen intact. In contrast, the sheets treated at higher temperatures and/or for longer durations largely retained their original shapes after immersion. Sheets treated at 170 and 180 °C generally retained their original shape after immersion, indicating that heat treatment substantially improved water stability.

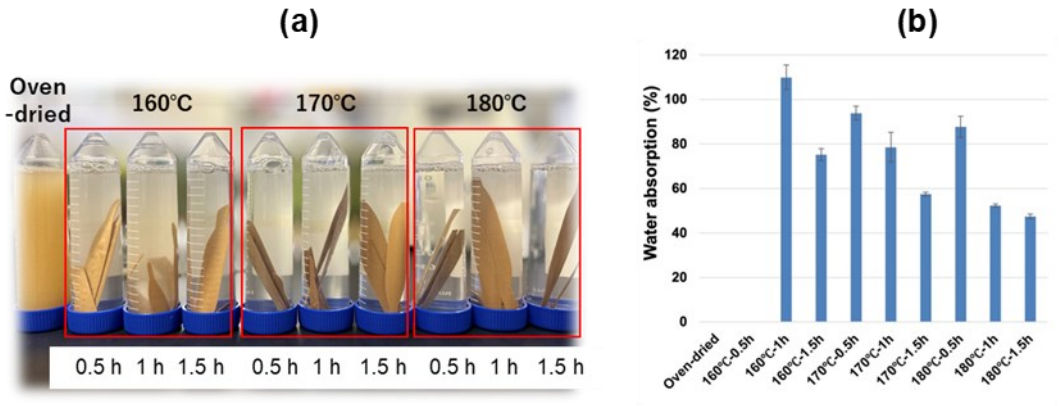

Fig. 6. (a) Structural stability of heat-treated wood flour sheets, and (b) water absorption after soaking in distilled water for 24 h

The water absorption values of the recovered sheets are presented in Fig. 6(b). Water absorption decreased with increasing heat treatment severity. The highest water absorption among the recovered sheets was observed for the sheet treated at 160 °C for 1 h, whereas the lowest value was observed for the sheet treated at 180 °C for 1.5 h. In general, increasing the treatment temperature and duration reduced the water uptake, indicating the suppression of swelling in the sheet structure. Similar improvements in wet stability have been reported for starch-CA adhesives (Liu *et al*. 2024), soy protein-CA adhesives (Hao *et al*. 2023), and wheat straw pulp-CA to enhance drainage (Huang *et al*. 2024). The improvement in structural stability is consistent with the moisture absorption behavior shown in Fig. 4 and the tensile strength retention under high-temperature and high-humidity conditions, as shown in Fig. 5. The samples that absorbed less moisture also exhibited lower water uptake during immersion and better sheet morphology retention. These results suggested that heat treatment reduced the water sensitivity of the sheet structure and improved its resistance to water-induced deterioration, possibly through the insolubilization of HPMC within the sheet matrix.

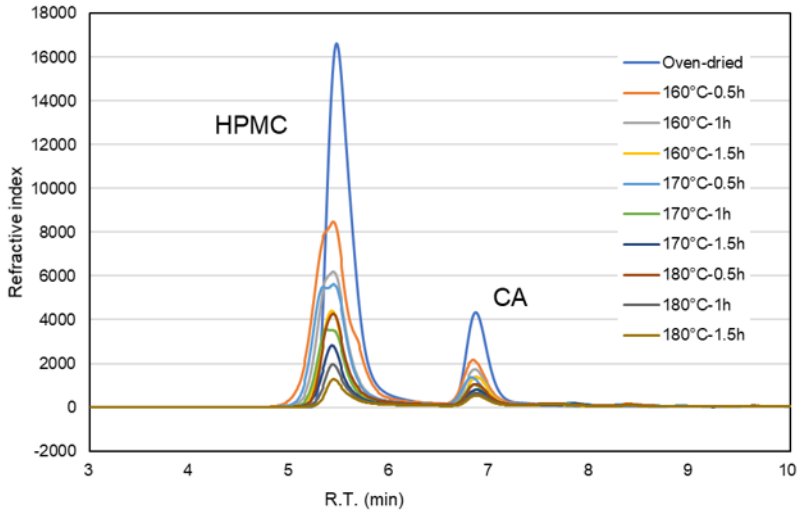

Fig. 7. HPLC chromatograms of CA and HPMC dissolved from heat-treated wood flour sheets after soaking in distilled water for 24 h

To clarify the mechanism responsible for the improved structural stability, the dissolution behaviors of CA and HPMC during water immersion were investigated using HPLC. Figure 7 shows the HPLC chromatograms of the immersion solutions obtained from heat-treated wood flour sheets. Two major peaks were observed at retention times of approximately 5.4 and 6.9 min and were assigned to dissolved HPMC and CA, respectively, based on comparison with standard solutions. The oven-dried control sheet exhibited the largest peak areas for both components. As the heat treatment temperature and duration increased, the peak areas of both HPMC and CA gradually decreased, indicating that the amounts of water-extractable HPMC and CA were reduced by heat treatment. A decrease in the unbound CA has also been reported in corrugated boards treated with CA (Widsten *et al.* 2014).

The relative dissolution ratios of CA and HPMC calculated from the chromatographic peak areas are shown in Fig. 8(a). Both dissolution ratios decreased with increasing heat-treatment severity, and the lowest values were observed for the sheets treated at 180 °C for 1.5 h.

These results indicated that heat treatment progressively reduced the water-extractable fractions of both CA and HPMC. Figure 8(b) shows the relationship between the relative dissolution ratios of CA and HPMC. Lower dissolution ratios of CA were generally accompanied by lower dissolution ratios of HPMC, indicating that the heat treatment simultaneously reduced the water-extractable fractions of both components.

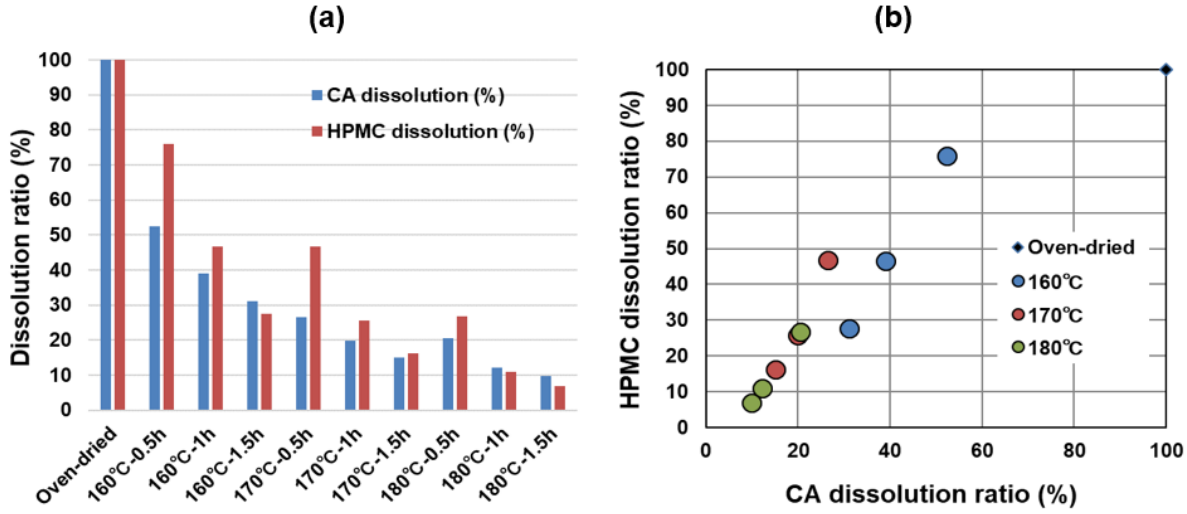

Fig. 8. (a) Relative dissolution ratios of CA and HPMC for heat-treated wood flour sheets. (b) Relationship between the dissolution ratios of CA and HPMC

The decrease in extractable CA may be attributed primarily to esterification reactions with hydroxyl groups in HPMC (Sebti *et al.* 2003; Marani *et al.* 2015; Tao and Nonaka 2021), although reactions with hydroxyl groups in wood components may also occur as well as to the thermal decomposition of free CA during heating (Barbooti and Al-Sammerrai 1986). The dehydration and decarboxylation reactions have been reported previously (Wyrzykowski *et al.* 2011). Furthermore, the reduction in HPMC dissolution suggested that HPMC became increasingly insoluble upon heat treatment.

The simultaneous decrease in the dissolution ratios of CA and HPMC supports the hypothesis that heat treatment promotes CA-mediated crosslinking and insolubilization of HPMC within the sheet structure. Crosslinkers other than CA have also been used to modify methylcellulose hydrogels (Bonetti *et al.* 2023). This stabilization is consistent with the improved structural stability in water shown in Fig. 6, and may also explain the improved retention of tensile strength under high-temperature and high-humidity conditions, as shown in Fig. 5.

CONCLUSIONS

1. Heat treatment within the range 160 to 180 °C reduced the hygroscopicity of CA-containing wood flour sheets prepared by extrusion molding with HPMC. Moisture absorption decreased from approximately 9% to 8% at 20 °C – 65%RH, and from approximately 15% to 12% at 70 °C – 90%RH.
2. Heat treatment improved the tensile performance. Under 20 °C – 65%RH conditions, tensile strength increased from 61.6 MPa for the oven-dried control to approximately 72 MPa for the heat-treated sheets, but it showed little dependence on heat-treatment severity. In contrast, tensile strength under 70 °C – 90%RH conditions increased from 43.3 MPa to approximately 59 MPa with increasing heat-treatment severity, demonstrating improved mechanical stability under humid conditions.
3. Heat treatment reduced the dissolution of both CA and HPMC and improved their structural stability in water. The simultaneous decrease in CA and HPMC dissolution suggests that CA-mediated insolubilization of HPMC contributes to the enhanced environmental stability of the sheets.
4. The heat treatment at 180 °C for 1.5 h provided the optimal performance of the wood flour sheet, yielding low moisture absorption, high tensile strength, and a low dissolution rate of CA and HPMC in water.

ACKNOWLEDGMENTS

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Conflict of Interest

The authors declare that they have no conflict of interest.

Use of Generative AI

Generative artificial intelligence (AI) was used during the preparation of this manuscript to assist with English language editing, text refinement, and organization of manuscript sections. All scientific interpretations, experimental results, and conclusions were reviewed and validated by the authors, who assume full responsibility for the accuracy and integrity of the manuscript.

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