Gaseous Ozone Treatment of Wood: Effect of Treatment Conditions on the Wood Wettability and Phenol-formaldehyde Adhesive Bonding Strength

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Findings of an earlier study, "Improving Wood Surface Wettability through Gas-phase Ozone Treatment of Air-dry Wood," demonstrated that the wood gas-phase ozone treatment enhances the wettability of wood by water, and thus potentially also the spread, absorption, and adhesion of water-based adhesives and coatings to the wood surfaces. This study extends that work by examining the effect of ozone treatment temperature and the wood moisture content on the wettability of ozone treated wood and bonding strength of phenol-formaldehyde (PF) adhesive. In the present study, both air-dry and wetted birch plywood and veneer were ozone-treated at 23 °C, 35 °C, and 55 °C for 10 and 30 minutes. The amount of reacted ozone increased with higher treatment temperature and with an increase in the wood moisture content. However, the reduction in the water contact angle was more pronounced for air-dry wood. Bonding tests showed that the ozone treatments substantially increased the PF adhesive bonding strength, and the bonding strength correlated negatively with the ozone-treated birch veneer water contact angle. The results suggest that both the treatment temperature and moisture content of the wood during the treatment influenced the ozone reactions with wood, and thus on wood wettability and PF adhesive bonding strength (192 / max. 200).

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INTRODUCTION

Ozone (O_3) has strong oxidative properties ($E° = 2.07$ V, 25 ºC), and it reacts readily with organic materials, particularly those containing carbon-carbon double bonds and aromatic compounds resulting in the formation of carbonyl and carboxyl groups (Greene *et al*. 2012; Travaini *et al*. 2015; Epelle *et al*. 2023). In previous work (Korpela *et al*. 2025), air-dry samples of spruce, thermo-modified pine, and birch wood were treated with gaseous ozone using a flow-through ozone reactor, followed by measurements of the water contact angle and the water absorption (Cobb-value) of the wood samples, and by determining their surface free energies using the Owens, Wendt, Rabel, and Kaelble (OWRK) calculation method. Furthermore, water absorption and evaporation rates were measured through water immersion and subsequent drying of the wood samples. The results indicated that ozone treatment increased the woods´ surface energy, and especially its polar component, thus accelerating water spreading and absorption on the wood.. The cause of the observed effects, confirmed by FTIR measurements, was the formation of new carbonyl and carboxyl groups on the wood surface. These findings are consistent with the studies by Safiullina *et al.* (2020) and Mukhametzyanov *et al.* (2021), which demonstrated that ozone treatment can enhance the spreading, absorption, and adhesion of water-based adhesives and coatings on wood surfaces.

The present study extends the previous research by examining how temperature and wood moisture during the ozone treatment affect the wood surface energy and wettability by water, and further, on water-based PF adhesive bonding strength. In general, increasing the ozone treatment temperature may accelerate reactions between ozone and the substrate, but it can also lead to faster ozone decomposition to oxygen, potentially reducing the effectiveness of the treatment (Batakliev *et al.* 2014, Epelle *et al*. 2023).

In dry wood, ozone reactions are believed to occur primarily at the gas–wood interface, resulting in modification of the outer surface of the wood and wood fibers. In contrast, during the treatment of wet wood, water may transport dissolved ozone deeper into the swollen wood and fibers, where it can further react (Mamleeva *et al.* 2020). According to the cited work, ozone reactions in wood with a moisture content above 30 to 40% lead to lignin degradation and the formation of low-molecular-weight, water-soluble acids. Therefore, wood moisture content can influence the chemical composition and surface energy of the treated wood, as well as the depth of the wood surface modification. In principle, ozone treatment could be applied to moist wood, for example in plywood and laminated veneer lumber production, after peeling of the green veneer (moisture content 40 to 60%). As wood planing and sanding are usually done for dry wood, treatment of dry planed or sanded wood would probably be more feasible.

In the present study, both air-dry and wet birch plywood and veneer were treated at 23, 35, and 55 °C using two different treatment times. The ozone treatments and test methods followed those reported in the authors' previous study (Korpela *et al.* 2025). In addition, the effect of ozone treatments on phenol formaldehyde (PF) adhesive bonding strength was examined. The measurements were carried out using the Automated Bonding Evaluation System (ABES) instrument. The findings obtained in this study can help in the evaluation of the practical applicability of ozone treatment for various wood products and can guide the conceptual design of ozone treatments for different applications. To the best of the authors' knowledge, no such results have been published before.

EXPERIMENTAL

The experiments and measurements were performed following the methods described by Korpela *et al.* (2025).

Materials

Sanded 7-ply birch plywood samples (100 mm × 50 mm × 9 mm) were sourced from a Finnish wood product manufacturer. The long axis of the top plies was oriented parallel to the grain. The samples were stored in dry indoor conditions, protected from light, for at least one year. Before the ozone treatment and subsequent measurements, the plywood samples were conditioned for at least two weeks at a relative humidity (RH) of 50 % and a temperature of 23 °C.

Additionally, rotary cut birch veneer samples (140 mm x 140 mm x 10 mm) were prepared for treatment and bonding performance assessments. The samples were stored in dry indoor conditions, protected from light, for at least two years. Before the ozone treatments, the veneer samples were conditioned for 24 hours at a relative humidity (RH) of 50% and a temperature of 23 °C.

The bonding performance was assessed using a commercial phenol-formaldehyde (PF) adhesive, which is used industrially for plywood bonding.

Water absorption tests were carried out using Milli-Q water. Surface energy was determined using Milli-Q water, analytical-grade formamide (Merck KGaA, Germany), and 99.8% ethylene glycol (Sigma-Aldrich Co., USA).

Ozonation

The ozonation treatments of the air-dry and water-soaked birch plywood and veneer samples were carried out using VTT's (Espoo, Bioruukki) laboratory ozonation equipment, consisting of an ozone generator (Emery-Trailigaz Model Sorbios, USA) and a flow-through ozonation reactor (Ø 235 mm, height 395 mm). Water soaking of the samples was done by immersing the sample in Milli-Q water (23 °C) for 20 min. In the ozone treatments, five wood samples were placed in the bottom of the reactor followed by directing an ozone-oxygen mixture (10% ozone and 90 % oxygen) in the chamber. The flow rate of the gas mixture through the reactor was two liters per minute. Temperature of the gas flow was adjusted to 22, 35, and 55 ± 2 °C by using a water bath. After each treatment, the amount of reacted ozone was determined from potassium iodide solution by titration with sodium thiosulfate. After treatment, the samples were stored at RH 50% and 23 °C for two weeks before measurements.

Contact Angle Measurement and Determination of Surface Free Energy

Water contact angle measurements were conducted on tangential wood surfaces of five parallel birch plywood and veneer samples using an Attention Theta Optical Tensiometer (Biolin Scientific, Sweden) at 23 °C and 50% relative humidity (RH), with Milli-Q water (droplet volume: 4.0 μL) as the probe liquid. The measurements were conducted parallel to the wood grain, *i.e.*, the camera observed the droplet from a direction perpendicular to the grain. The measurement points on the wood surfaces were selected to evenly represent both earlywood and latewood. The reported results for birch plywood and veneer were the averages of the water contact angle 0.7 seconds and 1.4 seconds after the droplet application, respectively. The shorter measuring time for the veneers contact angle was due to almost instant spreading of the water droplets on the ozone-treated veneers.

The surface energy measurements for birch plywood samples were conducted with three test liquids: water, ethylene glycol, and formamide. Surface free energy values and dispersive (non-polar) and polar components were calculated using the Owens, Wendt, Rabel, and Kaelble (OWRK) method. The reported surface energies are averages of five parallel determinations with each test liquid. In contrast to the previous study, surface energy determinations were performed without diiodomethane, because its rapid spreading on the wood surface caused uncertainty in the contact angle measurements.

Cobb Test

Water absorption of plywood samples was measured using a modified Cobb test. In the performed tests, a rubber sealing ring and a metal cylinder were placed on the surfaces of pre-weighed wood samples (RH 50%, 23 °C), with the base area of the cylinder and the sealing ring being 10 cm². Then, a 2 kg weight was placed on top of the cylinder to improve sealing between the wood and the cylinder. Finally, 10 ml of Milli-Q water was added to the cylinder. After 120 seconds, the wood sample and the cylinder were turned upside down, and the extra water was wiped off the wood surface with blotting paper. The sample was then weighed, and the amount of absorbed water in g/m² was calculated. The reported results are the averages of three parallel measurements.

Bond Strength Measurement

Birch veneer and phenol-formaldehyde (PF) adhesive interaction was evaluated using an Automated Bonding Evaluation System (ABES) apparatus (Adhesive Evaluation Systems, Inc., Corvallis, OR, USA) in accordance with ASTM D7998-19 (2019). The PF adhesive, applied at a spread rate of approximately 100 g/m², was spread on a 5 × 20 mm² area at one end of the birch veneer specimens (20 × 117 mm²). The assembly time for the specimens was approximately 50 s. Adhesive bonds were cured by pressing for 160 s at 130 °C under a pressure of 2.0 MPa. Before testing, the bonded specimens were cooled for 10 s to reach a temperature of approximately 25 °C. Lap-shear strength tests were then conducted, and the reported results represent the average of 9 to 12 replicates.

RESULTS AND DISCUSSION

Figure 1 shows the effect of temperature on the amount of consumed ozone (wt%) during the treatment of air-dried and water-soaked birch plywood. Ozone consumption was calculated based on the weight of air-dry sample weight (23 °C, RH 50%), and it is defined as the total amount of ozone that has either reacted with the wood or undergone decomposition. During the treatment, the flow rate of the ozone–oxygen mixture (10% ozone, 90% oxygen) through the reactor was maintained at 2 L/min. According to the results, increased ozone treatment temperature enhanced ozone reactions in the treatments of both air-dry and water-soaked birch plywood. This is possibly not only due to the accelerated reactions between wood and ozone, but possibly also due to intensified decomposition of ozone molecules at an elevated temperature. Unfortunately, in the present study, only the total ozone consumption could be determined. The higher ozone consumption observed for the water-soaked plywood can be explained by partial dissolution of ozone in water and its transport deeper into the water swollen wood, where it can further react.

Figure 2 shows how the temperature of ozone treatments of air-dry and water-soaked birch plywood samples affected the water contact angle of the plywood surfaces. Before the measurements, the samples were conditioned for two weeks at 23 °C and RH 50%. According to the results, ozone treatment had a more pronounced effect on reducing the water contact angle in air-dry birch plywood compared to water-soaked plywood. It is possible that, in air-dried birch plywood, the effects of ozone took place in the outermost surface layer, resulting in a strong decrease of the water contact angle; whereas, in water-soaked plywood, reactions may occur partly deeper within the water-swollen fibers and wood (Mamleeva *et al.* 2020).

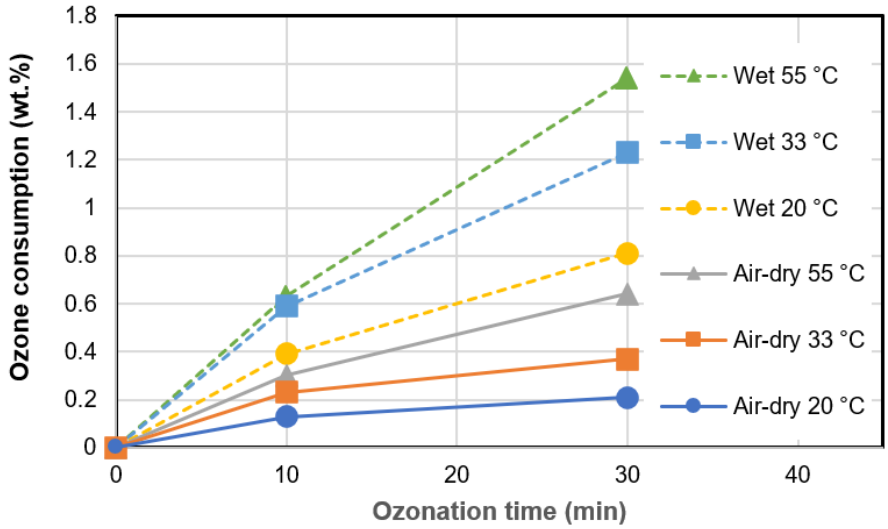

Fig. 1. Effect of temperature on ozone consumption (wt.%) in birch plywood (air-dried and water-soaked) ozone treatments. Ozone consumption was calculated based on the weight of air-dry sample weight (23 °C, RH 50%), and it is defined as the total amount of ozone that has either reacted with the wood or undergone decomposition.

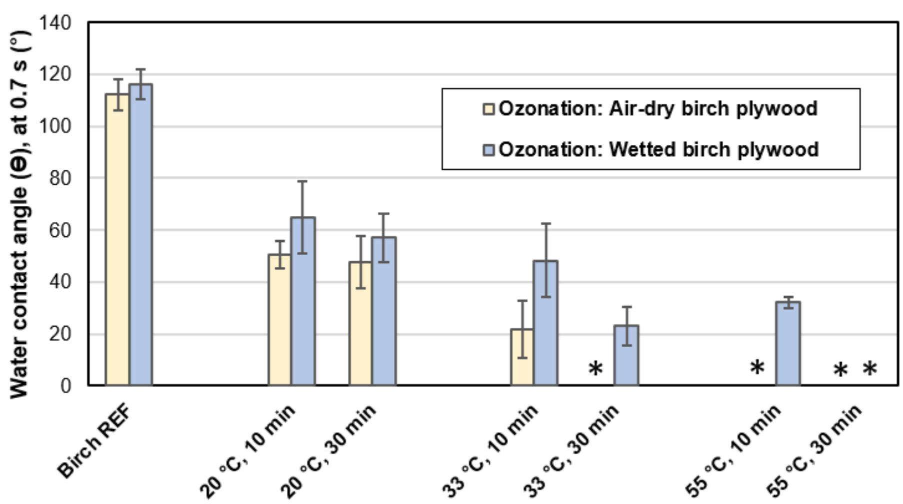

Fig. 2. Effect of ozone treatment temperature on the water contact angle of birch plywood. Samples for which the water contact angle could not be measured at 0.7 s, due to rapid droplet spreading and absorption, are indicated by *.

Figure 3 shows the effect of ozone treatment temperature and time on the surface birch plywood water absorbency measured using the modified Cobb method. In the case of the ozone treated samples, the Cobb values exhibited considerable variation. This was partly attributed to uncontrolled water spreading beneath the rubber gasket pressed on the plywood surface. Nevertheless, the measured Cobb values indicating increased water absorption are in line with the decreased water contact angle. (Note: The used modified Cobb method does obviously work better with such smooth wood surfaces, in which the water contact angle is relatively high).

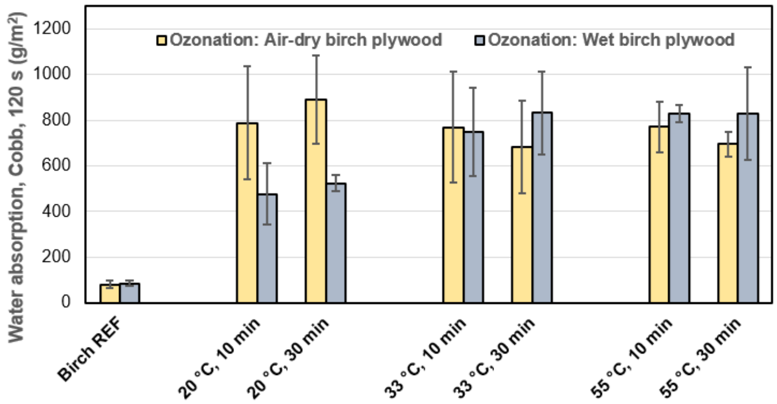

Fig. 3. Effect of ozone treatment on the water absorption (Cobb test) of birch plywood

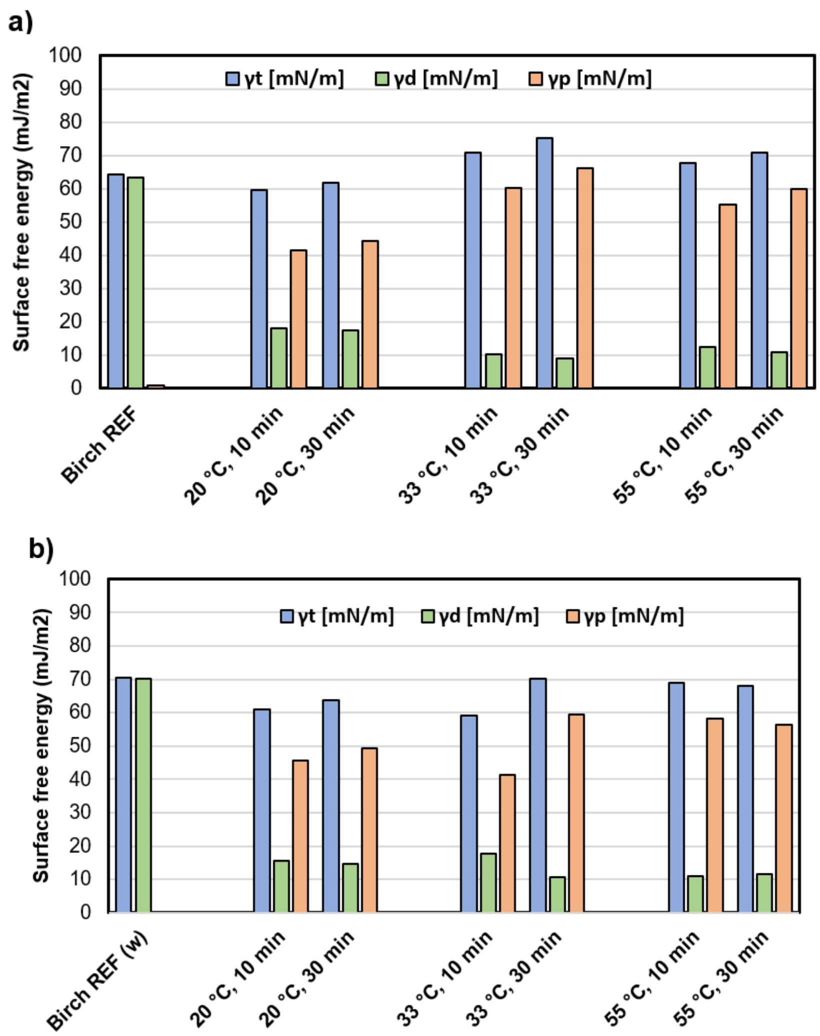

Fig. 4. Surface free energy (γt) and its dispersive (γd) and polar (γp) components of (a) air-dry or (b) wet birch plywood after ozone treatments at different temperatures and exposure times, determined using the OWRK method

Ozone treatments of both air-dry and water-soaked birch plywood decreased the dispersive component and correspondingly increased the polar component of the surface free energy of the plywood (Fig. 4). The results of air-dry wood ozone treatments are in line with those of the previous study (Korpela *et al*. 2025). The magnitude of the changes in ozone treatments of air-dry and water-soaked plywood was approximately same. The effect of the ozone treatments on the surface energy disperse and polar components intensified with increased treatment time (10 min to 30 min), while the influence of increased treatment temperature was not entirely consistent.

The ozone treatments´ influence on the birch veneer water contact angle, as well as PF adhesive bonding strength (MPa), are shown in Table 1. The contact angle results are in line with those of birch plywood presented in Fig. 2. Also, in the case of veneer ozone treatment, water soaking of the wood samples prior to ozone treatment resulted in a substantial increase in ozone consumption during the treatment. The effects of ozone treatments on water-soaked veneer were unfortunately somewhat counterintuitive, for reasons that could not be clarified.

The PF adhesive bonding strength results show that ozone treatments resulted in a clear and consistent increase in the bonding strength, indicating improved spread and absorption of the PF adhesive on the ozone-treated veneer surfaces (Table 1). As shown in Fig. 5, a clear negative correlation existed between the observed decrease of water contact angle and the increase in the PF adhesive bonding strength. Overall, the water contact angle and PF adhesive bonding strength results support the hypothesis of the previous (Korpela *et al*. 2025) and the present studies, according to which ozone treatments can potentially be used to improve water-based adhesives and coatings spread, absorption and adhesion on wood surfaces. The presented findings are also in agreement with those reported earlier by Safiullina *et al*. (2020) and Mukhametzyanov *et al.* (2021).

Table 1. Effect of Air-dry and Water-soaked Birch Veneer Ozone Treatments on the Veneers' Water Contact Angle and PF Adhesive Bonding Strength

	Amount of consumed O_3 (wt%)	Water contact angle, 1.4 sec	PF adhesive bonding strength (MPa)
Birch veneer REF	-	120 (±3)	6.0 (±0.8)
Air-dry 23 °C, 10 min	0.38	31 (±4)	7.8 (±0.8)
Air-dry 35 °C, 10 min	0.63	11 (±4)	8.2 (±0.6)
Air-dry 35 °C, 30 min	0.95	6 (±2)	8.3 (±0.7)
Wet 23 °C, 10 min	0.93	54 (±8)	7.5 (±0.6)
Wet 35 °C, 10 min	1.19	72 (±5)	7.3 (±0.6)
Wet 35 °C, 35 min	3.33	34 (±8)	7.9 (±0.3)

The findings of a previous study (Korpela *et al*. 2025), together with the present results, suggest that ozone treatment provides a means to improve the adhesion of water-based coatings and adhesives to wood. Such improvements could facilitate the broader use of water-based systems in the wood products industry. Nevertheless, the general applicability of the method requires further validation. It is well established that porous, low-density woods can absorb adhesives even excessively, creating "starved" of "dry" bond lines, which in turn increases the required application amounts (g/m²) to achieve sufficient bonding strength (Chandler *et al.* 2005; Frihart 2005; Kamke and Lee 2007).

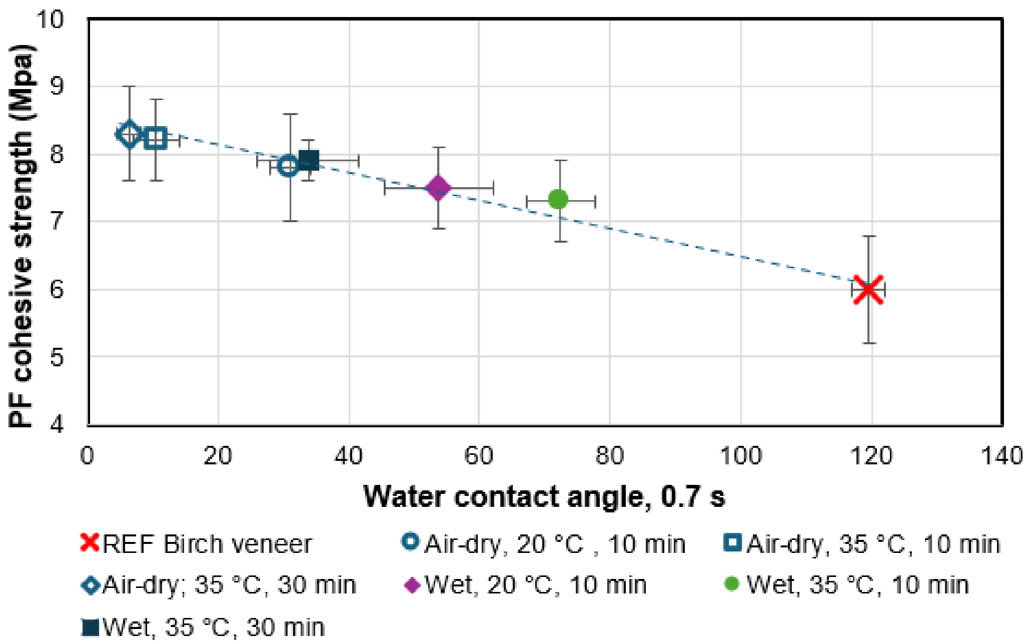

Fig. 5. Relationship between PF adhesive bonding strength and water contact angle for untreated and ozone-treated birch veneers

The risk of excessive penetration of adhesives and coatings in ozone treated wood is likely lower when the treatment is applied to dry wood, as under such conditions the effects of the treatment are confined to the wood outermost surface layer. An additional potential advantage of air-dry wood treatment is that it preserves the original composition and strength of the wood under the outermost wood surface layer, thereby contributing to the strength of the glue-bonded joint. The ozone treatment of air-dry wood also reduces ozone consumption, improving both process efficiency and environmental performance

In both this and the preceding study (Korpela *et al.* 2025), ozone treatments were performed using a flow-through laboratory reactor, which was originally designed for papermaking pulp ozone treatments. During the trials, a mixture of ozone and oxygen was passed through the reactor at a constant flow rate. Under these conditions, only a fraction of the ozone reacted with the wood samples. In practice, ozone treatments of wood could potentially be carried out in a closed reactor with recovery and circulation of unreacted ozone, thereby reducing ozone consumption and improving process efficiency. Further research and development is needed to evaluate the technical and economic feasibility of different ozone treatment process options.

CONCLUSIONS

1. Ozone treatment of both air-dry and water-soaked birch wood enhances bonding strength with water-based PF adhesive. This improvement is primarily attributable to the formation of new lignolytic and cellulosic functional groups, including carboxyl, carbonyl, and hydroxyl groups, on the wood fibers, which promote better wetting and interaction of both water and PF adhesive with the wood surface
2. Ozone treatment of air-dry birch veneer is more effective than that of water-soaked veneer in improving birch plywood wetting by water and increasing PF adhesive bond

strength. Increase of the treatment time from 10 min to 30 min, temperature from room temperature to 35 °C, boosted the effects.

3. Ozone treatments could support the adoption of environmentally friendly water-based adhesives and coating materials in the wood products industry. Further studies are still required to assess the feasibility of different industrial ozone treatment process options and the potential advantages of ozone treatment in the gluing and coating of various wood products.

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