

# Assessment of Color and Contact Angle Changes in Waterborne Stained Wood under Natural Weathering Condition of South Korea's Summer Climate

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This study aimed to develop a waterborne stain (WBS) that protects against weathering and increases resistance of wood to fungi when exposed to heavy rainfall. The WBS was prepared using an antibacterial agent, insect repellent, and copper nanoparticle solution (CN) as a surface coating agent. The WBS was applied on larch and hemlock wood, and changes in color and wettability due to natural and artificial weathering were evaluated. A gray-blue spot developed on the untreated wood surface within 30 d of outdoor exposure, which then spread over the entire wood surface, and the wood eventually turned black. Resistance to fungi increased when CN alone was applied; however, the CN surface was oxidized and turned gray after 30 d and 90 d for larch and hemlock, respectively. The water contact angle was increased due to leaching. The application of CN followed by WBS prevented wood discoloration under ultraviolet light and the wood showed excellent weathering resistance capacity. The prevention of wood discoloration and resistance to fungi by CN were confirmed, which could guide the development of a paint that can prolong protection from weathering of wood exposed to heavy rainfall events.

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## INTRODUCTION

Wood is a sustainable bio-based material that contributes to the achievement of the following sustainable development goals: 12 (Responsible Consumption and Production), 13 (Climate Action), and 15 (Life on Land) of the United Nations (Poohphajai *et al.* 2023). The use of wood products as building materials reduces carbon emissions (Geng *et al.* 2017). In addition, wood can be recycled from construction sites and buildings demolished after their service life has ended (Jahan *et al.* 2022). Wood also has advantages, such as good thermal insulation capacity, low density, high strength, and aesthetic features. However, wood also has disadvantages, including hygroscopicity, flammability, decay due to insect damage, and surface graying due to weathering (Jirouš-Rajković and Miklečić 2021).

Weathering generally refers to the gradual degradation of wood following exposure to external environmental factors (Poohphajai *et al.* 2021). Weathering is influenced by environmental factors, including solar radiation, water, oxygen, temperature, and air pollution (Cogulet *et al.* 2018). Wood comprises cellulose, hemicellulose, and lignin (Gupta *et al.* 2023; Lionetto *et al.* 2012). Lignin is a phenolic compound that absorbs 80-95% of the UV components of sunlight, while holocellulose (5 to 20%) and extractives (2%) absorb the rest (Xie *et al.* 2005). The weathering of uncoated wood is usually associated with biological attack, such as mold and rot, which in turn, change the appearance of wood surfaces (Poohphajai *et al.* 2021). The surfaces of weathered wood products eventually develop green or gray-blue spots and wood turns gray (Ion *et al.* 2023).

The occurrence and growth of mold, rot, and stains caused by fungi are associated with climatic conditions (Isaksson and Thelandersson 2013). Wood's exposure to the outdoor environment has been shown to rapidly change its color and appearance due to weathering, mold, and fungal staining (Bobadiha *et al.* 2021). Scheffer (1971) compared climatic indicators for the decay of wooden structures in different states in the US (Mississippi, Oregon, and Wisconsin) and found that Mississippi had the highest decay susceptibility. Therefore, wood weathering varies depending on the temperature and humidity in a region, and it is essential to develop weathering prevention technology based on the climatic conditions of a region.

Methods of preventing wood decay caused by weathering include wood modifications or application of coatings (paints, varnishes, and stains) (de Meijer *et al.* 2001; Baur and Eastel 2013). Coatings can be divided into waterborne and solvent-borne coatings. However, because of recent regulations on volatile organic compound emissions from paints, the focus has shifted from solvent-borne coatings to the development of waterborne coatings (Cogulet *et al.* 2018).

Acrylic and polyurethane coatings are preferred because of their ability to resist weathering (Rosu *et al.* 2009; Shukla *et al.* 2009). Other methods used to protect wood coating systems from solar irradiation include the use of reflective pigments and application of organic ultraviolet (UV) absorbers, such as benzophenone and benzotriazole (Jirouš-Rajković and Miklečić 2021). The wood component that is most vulnerable to photodecomposition is lignin. Therefore, modification of lignin is necessary to increase its resistance to UV radiation and weathering. The durability and photostability of clear coatings are improved using chromic acid, copper, ferric chloride, titanium, and zirconium compounds as photoprotective primers (Chang *et al.* 1982; Pandey and Pitman 2002; Schmalzl and Evans 2003; Jirouš-Rajković and Miklečić 2021). However, the hexavalent chromium compound, chromic acid, is a health hazard and the use of less toxic copper molybdate and copper (II) amine-based wood preservatives can protect wood from photodecomposition (Schmalzl and Evans 2003).

Therefore, this study aimed to develop a functional stain with mold resistance containing antibacterial agents, insect repellents, and copper nanoparticles to prevent weathering of wood exposed to hot and humid summer conditions in Korea. To determine the weathering resistance capacity of the developed stain, the contact angle and change in color of wood exposed to natural and artificial weathering were evaluated. The findings of this study could be used as a basis for the development of weather-resistant coatings for wood used outdoors during the heavy rainfall events in summer.

## EXPERIMENTAL

### Sample Preparation

To compare change in wood color following exposure to the external environment, two light-colored wood species, larch (*Larix kaempferi*) and hemlock (*Tsuga heterophylla* [Rafinesque] Sargent) were selected. Larch and hemlock were purchased as dried lumber. The surfaces of the supplied lumber were prepared according to the ISO 16474-1 (2013) standard and then cut to pieces with a thickness of 10 mm, width of 70 mm, and length of 150 mm. The samples were equilibrated for 7 d at a temperature of 20 °C ( $\pm 2$  °C) and relative humidity of 65% ( $\pm 2$ %) before application of stain to equalize the initial moisture content. The stain consisted of acrylic waterborne stain with antibacterial and insect repellent additives, as well as copper nanoparticles that can protect lignin in wood from photodegradation and wood weathering during the hot and humid summer conditions (Table 1). The transparent acrylic waterborne stain consisted of a base waterborne stain (42.9%), distilled water (54.7%), BYK 028 (1%), BYK 333 (0.6%), and functional additives (0.8%). The BYK 028 antifoaming and BYK 333 leveling agents were purchased from BYK Additives and Instruments (Geretsried, Germany). As additives to the acrylic waterborne stain, ACTICIDE IPS20 (active substance: 3-iodo-2-propynyl-butylcarbamate) was used as an antiseptic and KONSERVAN P10 (active substance: permethrin pyrethroide) was used as an insect repellent. The stain was prepared by adding 0.8% of each insect repellent. The stain containing the antibacterial agent was labeled “A” and that containing the insect repellent was labeled “B.” Copper nanoparticles (diameters of 180 nm and 500 to 800 nm) were purchased from Guangbo New Nanomaterials Stock Co., Ltd. (Ningbo, China) and prepared in a 10% aqueous solution. The wood samples stained with the copper nanoparticle aqueous solution were referred to as “CN.” After the first application of the copper nanoparticle aqueous solution, two functional stains A and B were subsequently applied to the samples and were referred to as “CN + A” and “CN + B,” respectively. The prepared stains (0.03 mL/cm<sup>2</sup>) were applied to the wood samples twice. After the first round of application, the wood samples were dried for 24 h and then the stains were reapplied. The coated samples were stored indoors for 7 d without exposure to UV radiation, dried, and then subjected to artificial and natural weathering. A flatbed scanner (Plustek OpticBook 4800; Plustek Inc., Santa Fe Springs, CA, USA) with a resolution of 1200 dpi was used to observe change in wood color over time.

### Artificial Weathering Test

A xenon arc weathering tester (Ci3000+ Weather-Ometer; Atlas Materials Testing Technology LLC, Chicago, IL, USA) was used to perform the test according to the ISO 16474-2 (2013) standard. The wood samples were exposed to artificial weathering for a total of 600 h and then configured to facilitate repetition of UV irradiation and water spray cycles of 120 min. One cycle of 120 min consisted of 102 min of UV irradiation and 18 min of UV irradiation + water spraying. Changes in the color of wood samples were recorded every 200 h.

### Natural Weathering Test

The Scheffer climate index, which is used to determine the risk of wood decay according to geographical location, was calculated as shown in Eq. 1. Areas with a Scheffer index of 35 or less have a low risk of decay, whereas areas with a value of 65 or more have a high risk of decay (Scheffer 1971). Kim *et al.* (2011) calculated the Scheffer index for

each region using climate data collected over 10 years (2001 to 2010). The average Scheffer index of Daejeon, a natural exposure area, was 64.1 ( $\pm 11.7$ ), and was classified as a medium-risk area for decay. However, in 2007, Daejeon was classified as an area with a high risk of decay at 79.3. The Scheffer index was calculated following Eq. 1,

$$SCI = \sum_{m=Jan}^{Dec} [(T_m - 2)(D_m - 3)]/16.7 \quad (1)$$

where  $T_m$  denotes the monthly average temperature ( $^{\circ}\text{C}$ ) and  $D_m$  is the number of days with more than 0.25 mm of rainfall.

The Scheffer index was calculated using the daily average temperature and precipitation data in 2020 (Table 1). Constants 2 and 3 in Eq. 1 are values set on the assumption that wood decay cannot proceed if the average monthly temperature is  $2^{\circ}\text{C}$  and the number of rainy days is less than 3 (Kim and Ra 2014). Therefore, for Korea, January to April and October to December of 2020 were classified as periods in which there is almost no decay. The 2020 climate was such that active wood decay occurred from June to August, with the highest decay being observed in August 2020. In addition, the Scheffer index in 2020 was over 65, suggesting that the area had a high risk of decay. Therefore, July was selected as the exposure period for the natural weathering resistance caused by fungi.

**Table 1.** Weather Data and Scheffer Climate Index in 2020

Month	Temperature ( $^{\circ}\text{C}$ )	Total Precipitation (mm)	$(T-2)(D-3)/16.7$	Scheffer Climate Index
Jan	2.7	78.5 (6)	0.13	71.13
Fab	3.6	91.2 (10)	0.66	
Mar	8.5	24.4 (4)	0.39	
Apr	14.6	17.8 (3)	0	
May	18.8	80.4 (9)	6.04	
Jun	24.1	192.5 (12)	11.9	
July	23.6	544.9 (18)	19.43	
Aug	27.5	361.6 (9)	24.47	
Sept	21.2	173.6 (9)	6.89	
Oct	14.2	3.2 (1)	0	
Nov	8.6	13.3 (9)	1.19	
Dec	0.5	4.1 (2)	0	

"()" Indicates the number of days with over 0.25 mm of precipitation

Testing began on July 16, 2020 and ended on November 16, 2020. Korea has four distinct seasons, and wood decay caused by UV radiation and moisture begins during the long rainy season in summer. The coated samples were exposed to the natural environment at the rooftop of the College of Agriculture and Life Sciences Building at Chungnam National University in Daejeon, Korea. The wood samples were randomly mounted on a rack and titled at  $45^{\circ}$  and  $180^{\circ}$  azimuth so that one side of the sample was exposed. The samples were collected, scanned, recolored, and the contact angles measured after 30, 90, and 120 d of exposure to the natural environment.

### Color Measurement

The color change parameters, lightness ( $L^*$ ), red-green tone ( $a^*$ ), and yellow-blue tone ( $b^*$ ) were measured using a colorimeter (Chroma meter CR-410, 5 cm diameter; Konica Minolta Sensing Americas Inc., Ramsey, NJ, USA). Color changes were evaluated

using the CIE  $L^*a^*b^*$  color space system with the three parameters to express colors of the wood samples. The difference in wood color ( $\Delta E$ ) during the exposure period was calculated using Eq. 2. A larger  $\Delta E$  value indicated severe discoloration of wood during the exposure period.

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (2)$$

In Eq. 2,  $\Delta L^*$ ,  $\Delta a^*$ , and  $\Delta b^*$  denote differences between color coordinate values measured at a given time and referenced to the corresponding values of the initial colors.

### Contact Angle Measurement

The contact angles of wood surfaces were measured after the samples were stained to determine variations in the moisture absorption rates based on the exposure environment. The contact angle of wood surfaces was measured using a contact angle analyzer (Phoenix 150, SEO Co., Ltd., Suwon, Korea; frame: 70 frame/s, CCD camera resolution:  $640 \times 480$  pixels) (Kim *et al.* 2022). Wood samples were mounted on the contact angle analyzer and 0.1 mL of distilled water was dropped onto the sample surfaces from a height of approximately 1 cm from the wood surface. Subsequently, the contact angle of each wood sample was measured 10 times, and the average contact angle was calculated. The contact angle was measured every 200 hours for the artificial weathering test and every 30 days for the natural weathering test, and the changes in the contact angle were compared.

## RESULTS AND DISCUSSION

### Color Changes and Wettability of Wood Exposed to Artificial Weathering

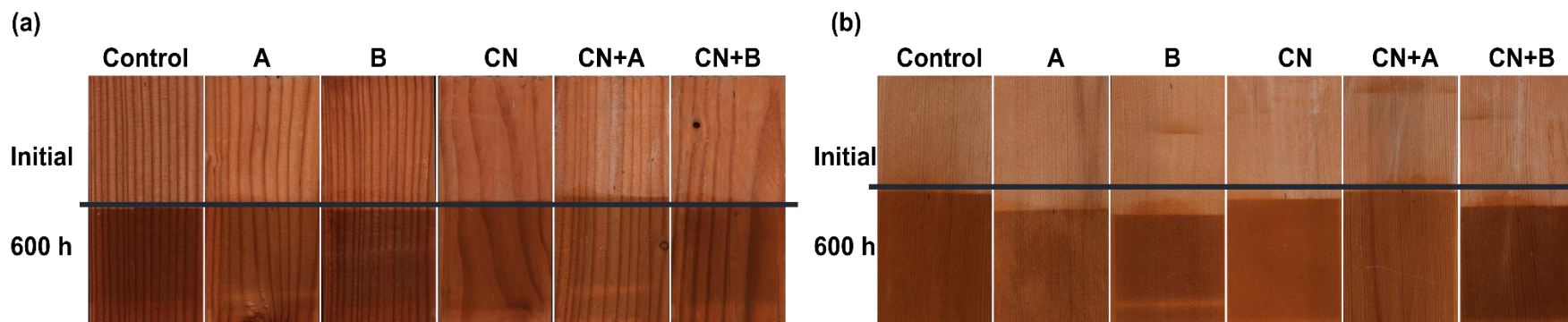
The results of CIE  $L^*$ ,  $a^*$ ,  $b^*$ , and  $\Delta E$  for stained and unstained larch and hemlock wood based on the type of stain used are shown in Table 2. The appearances of wood samples before and after artificial weathering are illustrated in Fig. 1. The color of stained and unstained larch wood after artificial weathering decreased as  $L^*$  shifted toward the dark, and  $a^*$  and  $b^*$  increased, thereby changing the wood color to red and blue. According to a previous study conducted by Cheng *et al.* (2021), larch wood was light yellow before weathering, but it became slightly darker after 492 h of exposure, markedly dark after 1008 h, reddish-brown after 3368 h, and dark red from 3368 h to 5528 h after exposure. The color of larch wood was consistent with the observations made after exposure to artificial weathering, where wood color darkened and turned red over time.

Change in wood color following exposure to UV light causes rapid transformation of chemical components, such as extracts, which leads to the darkening of wood (Wood *et al.* 2000; Kropat *et al.* 2020). The UV light breaks the covalent bonds of the wood polymer compounds and various free radicals are generated, which rapidly combine and react with oxygen. Consequently, photosensitive radicals that cause wood discoloration are generated, and the color of the materials changes, which also occurs with a radical intermediate called hydroperoxide (Muasher and Sain 2006). Regarding  $\Delta E$ , NC exhibited the highest  $\Delta E$  (16.2), followed by CN + B, B, and A, with CN + A exhibiting the lowest  $\Delta E$ . Furthermore, CN + A exhibited the least change in color even after being subjected to weathering using UV light, suggesting that it had a high resistance to UV light.



**Table 2.** Changes in CIE  $L^*$ ,  $a^*$ ,  $b^*$ , and  $\Delta E$  Based on Artificial Weathering Time and Stain Types

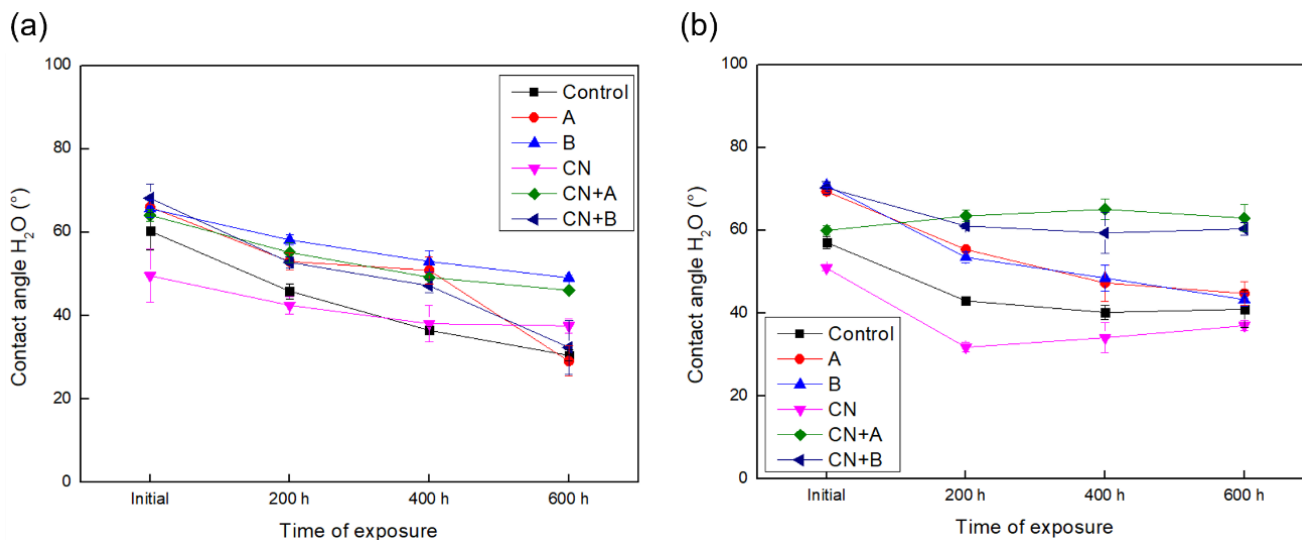
Larch	Initial			200 h				400 h				600 h			
	$L^*$	$a^*$	$b^*$	$L^*$	$a^*$	$b^*$	$\Delta E$	$L^*$	$a^*$	$b^*$	$\Delta E$	$L^*$	$a^*$	$b^*$	$\Delta E$
Control	61.39	10.44	18.56	50.94	12.61	21.15	11.02	45.85	13.42	19.77	15.89	41.81	13.29	16.98	19.88
A	56.04	11.92	19.04	50.03	11.61	19.84	6.28	47.39	13.16	18.52	8.81	47.17	11.5	17.8	9.09
B	56.46	11.19	17.97	45.51	12.51	17.11	10.12	43.64	13.67	18.06	12.12	42.90	12.33	16.39	12.78
CN	58.64	9.87	17.51	48.58	13.04	18.74	10.73	47.76	13.09	18.00	13.36	42.86	12.89	17.72	16.13
CN + A	57.18	10.38	18.68	51.16	10.76	19.18	6.43	50.04	11.7	19.54	7.52	50.1	11.04	18.83	7.66
CN + B	56.77	10.65	19.2	56.75	10.49	18.16	1.13	50.35	11.25	18.5	6.53	44.14	11.68	17.03	12.88
Hemlock	Initial			200 h				400 h				600 h			
	$L^*$	$a^*$	$b^*$	$L^*$	$a^*$	$b^*$	$\Delta E$	$L^*$	$a^*$	$b^*$	$\Delta E$	$L^*$	$a^*$	$b^*$	$\Delta E$
Control	63.07	7.61	17.37	54.45	11.07	22.99	10.87	54.45	11.07	22.99	10.87	47.66	13.15	21.24	16.83
A	60.7	7.82	18.09	56.68	9.21	22.76	6.4	51.37	11.56	21.3	6.4	50.42	11.14	20.06	10.58
B	59.66	7.83	17.91	50.26	10.87	20.43	10.3	49.08	13.13	21.08	10.3	44.88	10.89	18.2	12.35
CN	61.19	6.08	13.14	54.55	9.92	22.4	12.1	47.09	12.11	20.33	12.1	46.81	12.68	20.75	16.98
CN + A	58.67	7.66	17.18	55.23	9.2	21.37	5.73	52.4	10.94	20.93	5.73	52.17	10.64	20.35	8.06
CN + B	59.81	7.7	17.37	61.18	6.19	14.05	4.19	45.18	11.69	18.16	4.19	43.46	11.44	16.93	15.21



**Fig. 1.** Wood samples before and after subsection to 600 h of artificial weathering based on wood species and stains: (a) larch wood and (b) hemlock wood

Stained and unstained hemlock wood also exhibited a color trend similar to that of larch wood. Hemlock wood color turned dark as  $L^*$  decreased, turned red as  $a^*$  increased, and turned blue as  $b^*$  increased. Regarding  $\Delta E$ , NC exhibited the highest  $\Delta E$  (17.0), followed by CN + B, B, and A, with CN + A exhibiting the lowest  $\Delta E$ . CN + A, which was used as a stain additive rather than using copper nanoparticle alone, exerted an inhibitory effect on color change. The result is consistent with the findings of Schmalzl and Evans (2003), who found that the use of copper-based wood preservatives can protect wood from photodegradation. Therefore, copper nanoparticles were added to increase antibacterial effect and resistance to UV light.

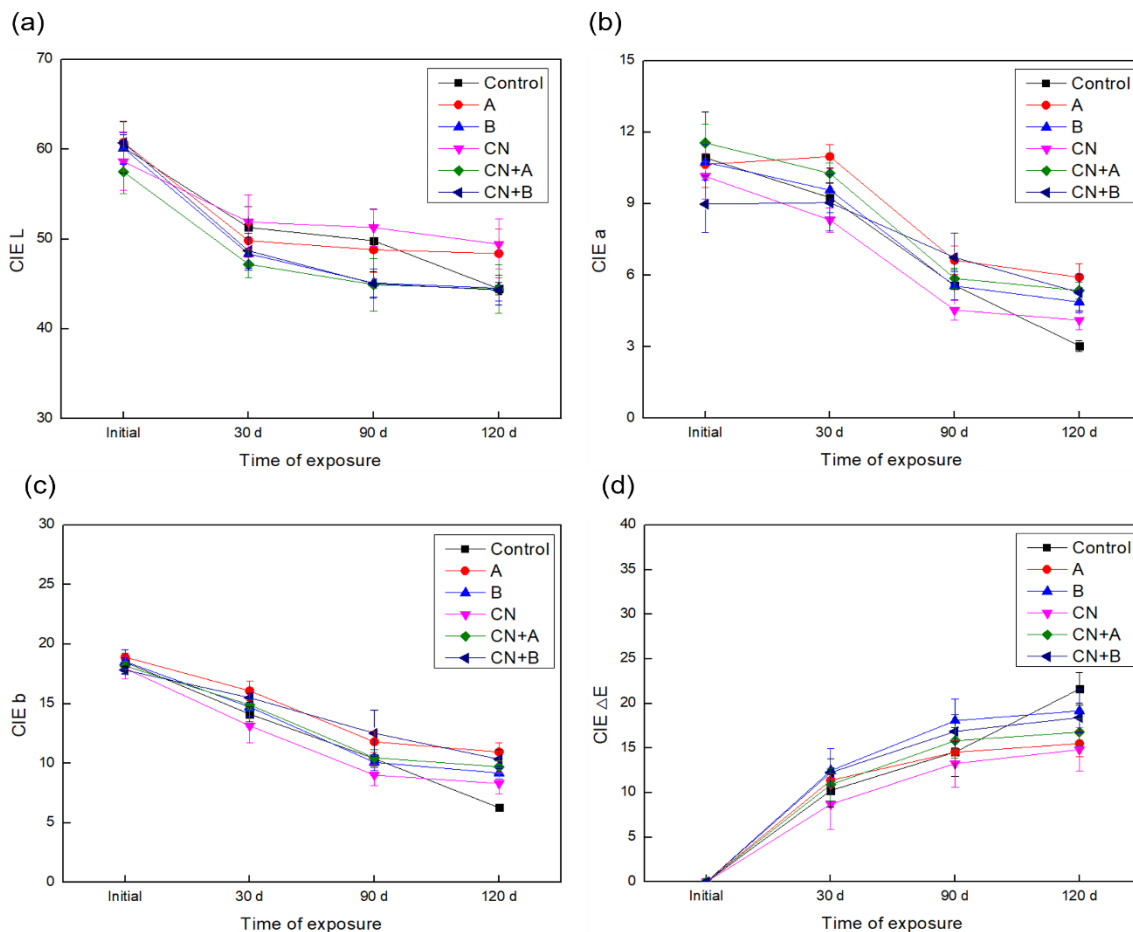
The wettability results of stained and unstained larch and hemlock wood based on the type of stain are shown in Fig. 2. The contact angle of stained and unstained larch wood before exposure to artificial weathering was in the range of 45 to 70°. The CN wood had the lowest contact angle before exposure to artificial weathering, but contact angle increased to 37.6° after 600 h of exposure to artificial weathering, which was higher than that of the control. The contact angles of wood stained with A and CN + B stains decreased rapidly after 400 h, and moisture resistance decreased due to UV light. The contact angles of wood stained with B and CN + A stains were high at 49.1° and 46.1°, respectively, when compared to those of the control. In particular, wood stained with CN + A stain had high resistance to color change upon exposure to UV light and consequently, high moisture resistance. The contact angle of stained and unstained hemlock wood before exposure to artificial weathering was in the range of 50 to 70°. Furthermore, hemlock wood stained with NC exhibited the lowest contact angle before exposure to artificial weathering, which is consistent with the larch wood results. The change in contact angle of wood stained with stains A and B with different additives was similar. The contact angle of wood stained with CN + A stain was greater than 60° after 600 h of exposure to artificial weathering, suggesting a high moisture resistance. According to the results, the most effective stain for larch and hemlock wood under artificial weathering conditions is CN + A, which prevents color change and has a high moisture resistance capacity.



**Fig. 2.** Water contact angles (°) of coated and uncoated wood exposed to artificial weathering: (a) larch wood and (b) hemlock wood

### Color Changes and Wettability of Wood Exposed to Natural Weathering

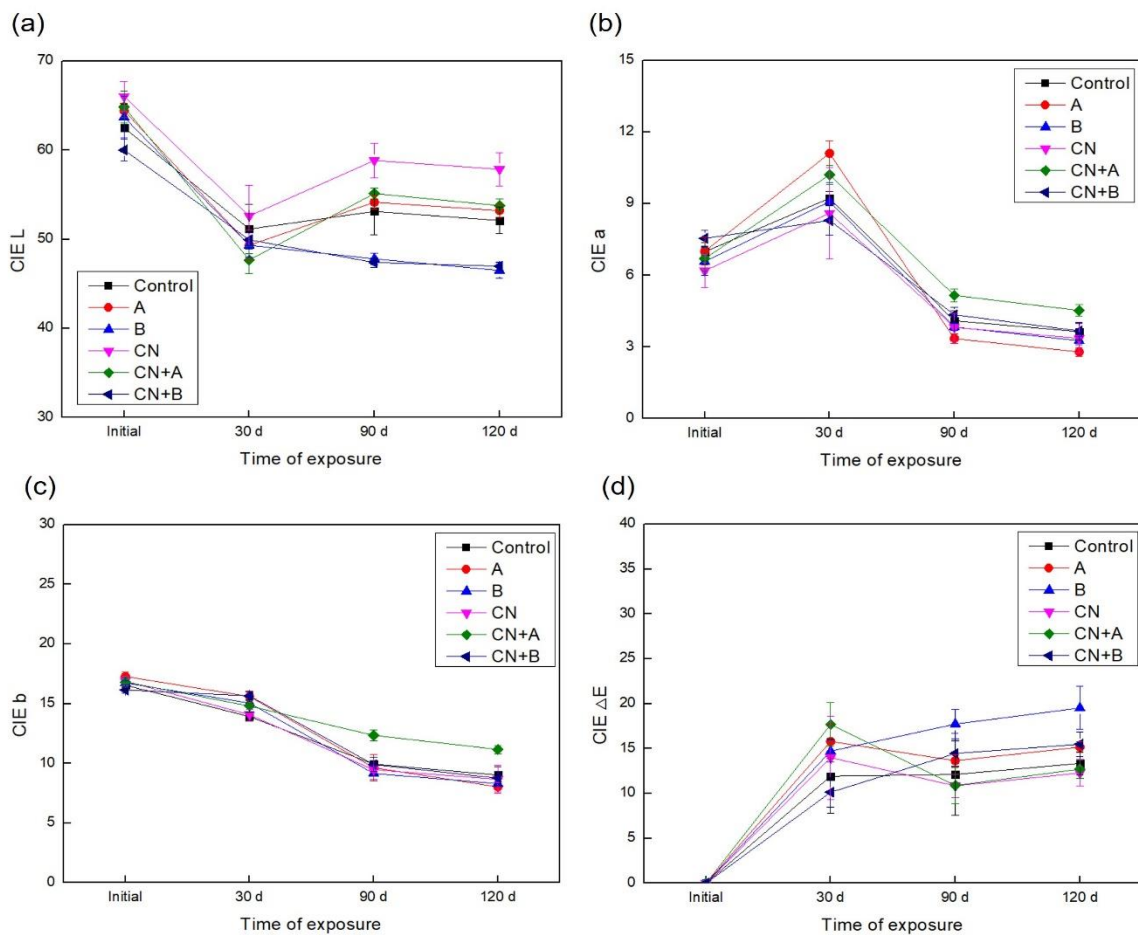
The CIE  $L^*$ ,  $a^*$ ,  $b^*$ , and  $\Delta E$  results of stained and unstained larch and hemlock wood based on the type of stain used are shown in Figs. 3 and 4. The appearances of wood samples before and after exposure to natural weathering are shown in Fig. 5. The  $L^*$  of larch wood decreased rapidly within the first 30 d, but that of wood stained with CN and A stains remained unchanged. The  $L^*$  of larch wood stained with CN + A and CN + B stains decreased, and the color shifted toward the dark region. In addition,  $a^*$  decreased and shifted toward the green region, while  $b^*$  decreased and shifted toward the blue region. The values of  $\Delta E$ , CN, A, and CN + A were less than 17, suggesting a low resistance to color change when compared to the control (21.62). The results are consistent with the findings of Ion *et al.* (2023), who observed that weathered wood surfaces developed green or gray-blue spots, in turn, causing wood to turn gray. Moreover, the lowest decrease in  $L^*$  and the lowest  $\Delta E$  were observed in wood coated with CN stain. According to George *et al.* (2005), wood preservatives can protect wood from photodegradation. Copper-based preservatives reduce photodecomposition of wood by delaying the formation of carbonyl groups and delignification (Temiz *et al.* 2005). The current study's results suggest that CN had an effect on reducing color changes in wood by forming carbonyl groups and delaying delignification.



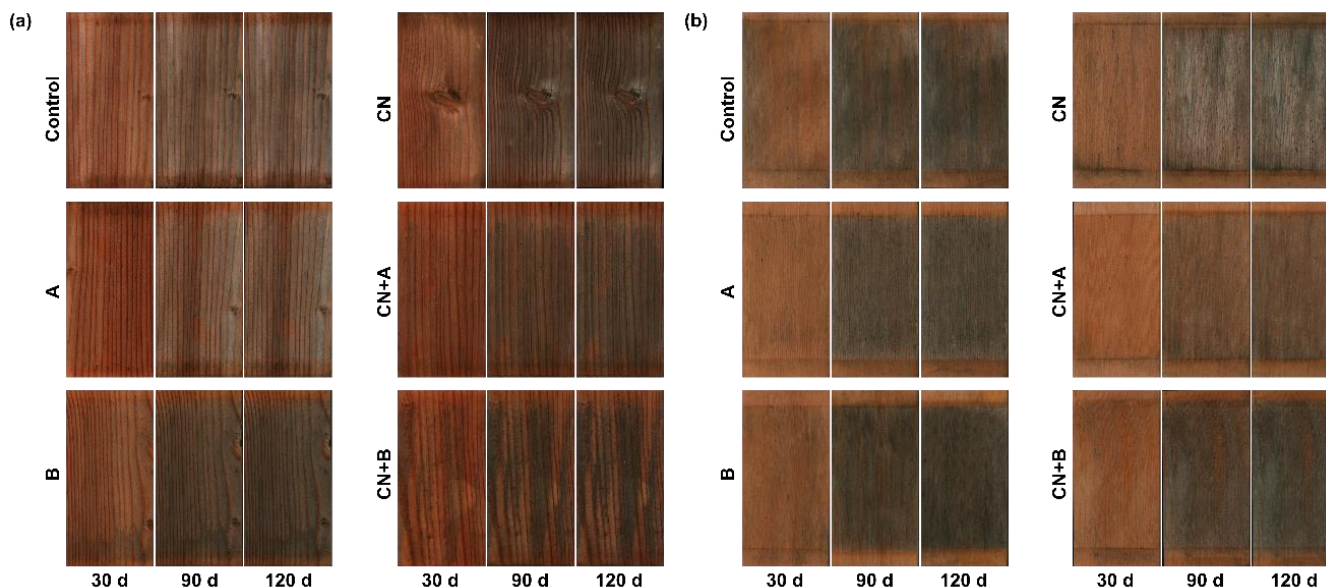
**Fig. 3.** Color coordinates of coated and uncoated larch wood exposed to natural weathering: (a)  $L^*$ , (b)  $b^*$ , (c)  $a^*$ , and (d)  $\Delta E$



The  $L^*$  of hemlock wood decreased rapidly within the first 30 d and then shifted toward the dark region. However,  $L^*$  increased and the color of wood stained with CN and CN + A stains turned lighter and gray after 30 d. The observation could be because CN and CN + A stains contained copper nanoparticles, which prevented formation of dark spots caused by fungi due to the heavy rainfall received during the first 30 d of exposure. In addition, the shifting of wood color toward dark was low, and the color of wood became brighter and was maintained thereafter, suggesting the effect of natural weathering on wood color. Generally, the copper nanoparticles used in this study can act as a reservoir for copper ions, which are gradually released and can induce toxic effects on the fungal cell wall through a Trojan horse mechanism after contact with fungi (Civardi *et al.* 2016; Limbach *et al.* 2017). However, when wood was treated with CN only, a few dark spots were formed, but graying increased rapidly. Therefore, copper nanoparticles should be combined with a solvent-borne stain rather than used alone. CN + A stain confers the advantages of high resistance to fungi even under heavy rainfall conditions, as it can prevent changes in wood color and the occurrence of dark spots on wood surfaces. Further, before the stain was applied, it was confirmed that the aqueous copper-nanoparticle solution used for staining had resistance to blue-stain infestation.



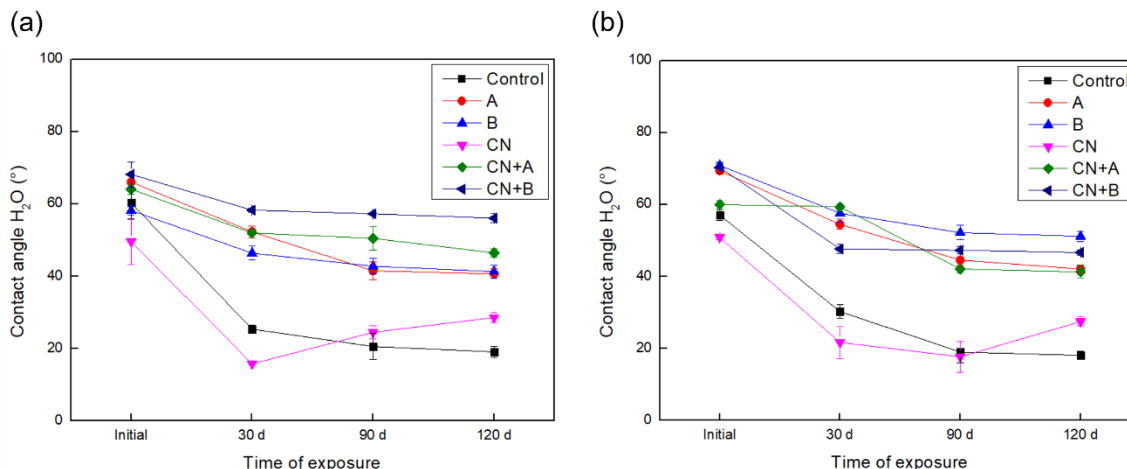
**Fig. 4.** Color coordinates of stained and unstained hemlock wood exposed to natural weathering: (a)  $L^*$ , (b)  $b^*$ , (c)  $a^*$ , and (d)  $\Delta E$



**Fig. 5.** Wood samples before and after 120 d of natural weathering based on wood species and stains: (a) larch wood and (b) hemlock wood

The wettability results of stained and unstained larch and hemlock wood exposed to natural weathering are shown in Fig. 6. The contact angle of wood stained with CN was the lowest before exposure to natural weathering, which is consistent with the results of wood exposed to artificial weathering. The contact angle of wood coated with CN differed between the two species. The contact angle for larch wood initially sharply decreased until 30 d after exposure to natural weathering and then increased. The contact angle for hemlock wood initially sharply decreased until 30 d after exposure to natural weathering, decreased gradually until 90 d after exposure to natural weathering, and then increased again. According to Kim (2012), there are physical processes through which copper is fixed in wood, such as ion–ion, ion–dipole, and dipole–dipole interactions, due to electrostatic attraction. Furthermore, copper is fixed in wood through chemical reactions between reactive groups, such as carbonyl, hydroxyl, and phenyl hydroxyl groups in wood tissues. The copper nanoparticles applied to the wood surfaces deteriorates after exposure to weathering, which results in a rapid decrease in moisture resistance and leaching of nanoparticles by water, thereby exposing wood surfaces and increasing the contact angles. Larch wood stained with CN + A and CN + B stains exhibited higher water resistance after 120 d than wood coated with A and B stains. The result could be attributed to the activation of the wood surface by copper nanoparticles applied to it and enhanced bonding strength following subsequent application of A and B stains, resulting in a higher contact angle than that of wood stained with A and B stains.

The hemlock wood that had been stained with B ( $51.2^\circ$ ) and CN + B ( $46.7^\circ$ ) stains presented large contact angles after 120 days. When exposed to outdoors, B and CN+B formed on the surface to prevent the photodecomposition of lignin, which is caused by ultraviolet rays, and were also effective at preventing lignin loss during rainfall.



**Fig. 6.** Water contact angles (°) of stained and unstained wood subjected to natural weathering: (a) larch wood and (b) hemlock wood

According to the results of the artificial and natural weathering tests, the  $a^*$  and  $b^*$  values of the specimen increased over time in the artificial weathering test, and the color shifted to red and yellow. In contrast, in the natural weathering test, the  $a^*$  and  $b^*$  values of the specimen decreased over time, and the color shifted to green and blue. Therefore, the results of the artificial and natural weathering indicated conflicting outcomes. This was consistent with previous studies showing that artificial weathering conditions did not give rise to blue-stain and mold growth (Kropat *et al.* 2020). In addition, according to a previous study conducted by Ruther and Jelle (2013), the agreement between the results of the artificial and natural weathering test results was relatively low, especially with regard to the biological activity of the natural weathering test.

Korea has four seasons (spring, summer, fall and winter), and high temperatures and heavy rainfall experienced in the summer accelerate the weathering of wood by promoting the development of gray-blue spots on wood surfaces and color changes associated with fungi. Therefore, a functional stain containing antibacterial and insect repellent additives, in addition to copper nanoparticles was developed and applied to wood surfaces to improve resistance to fungi. The formation of gray-blue spots was decreased after application of the copper nanoparticle solution and stain to wood surfaces, which effectively prevented rapid color changes after 120 d. The application of both copper nanoparticle solution and stain can increase wood resistance to fungi during heavy rainfall periods. Therefore, it is necessary to develop a functional stain supplemented with copper nanoparticles to prevent leaching of copper nanoparticles during heavy rainfall seasons.

## CONCLUSIONS

In this study, a waterborne stain for coating wood products used outdoors was developed using fungicides and insect repellents, as well as copper nanoparticles. The stain was applied to larch and hemlock wood surfaces, and the wood subjected to artificial and natural weathering. Color changes and wettability of the wood samples were compared, and the major conclusions are as follows.

1. The most effective way to protect wood from developing gray-blue spots during the heavy rainfall season in summer is to initially apply copper nanoparticles to the wood surfaces and then apply a functional stain containing fungicides.
2. Copper nanoparticles activate wood surfaces and increase wettability and bonding strength with the stain over time. In addition, copper nanoparticles prevent color changes in wood exposed to UV light and exhibit excellent weather resistance capacity.
3. The application of copper nanoparticles alone can prevent the formation of gray-blue spots on wood surfaces, but oxidation of copper rapidly increases graying after 90 d.
4. The stain developed in this study enhances resistance to fungi and prevents changes in wood color under heavy rainfall conditions.

## ACKNOWLEDGMENTS

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