ORIGINAL ARTICLE

The effects of cellulose nanofibers compounded in water-based undercoat paint on the discoloration and deterioration of painted wood products

Tomoko Shimokawa[1*], Yukako Hishikawa[1], Eiji Togawa[1], Hajime Shibuya[1], Masahiko Kobayashi[2], Atsuko Ishikawa[2], Xin He[3], Hironari Ohki[3] and Kengo Magara[1]

Abstract

Cellulose nanofibers (CNFs) have many potentials as filler to improve the properties of the other materials. We have developed the novel paints containing CNFs, and which controlled the discoloration of wood products. To clarify the discoloration mechanism of wood panels using an undercoat paint containing CNFs, prepared by an integrated process from *Cryptomeria japonica*, the composites and films made of CNFs and acryl resin that was a raw material for the paints were prepared. Observation of the surface of the CNFs/acryl resin composite film by atomic force microscopy showed that the fibers and the resin were uniformly mixed. The composite film prevented light transmittance in the ultraviolet (UV) light region, as well as oxygen gas permeation. The permeability coefficient of the oxygen gas decreased to 60% with the addition of 1.5 wt% of CNFs to the acryl resin. The addition of CNFs also increased the breaking stress by approximately 1.5 times compared with the acryl resin film. Electron spin resonance (ESR) analysis after UV irradiation resulted in the lowest radical formation of a piece of wood wrapped in the CNFs/acryl resin composite compared with the acryl-coated specimen and the wood as it was. Therefore, the CNFs composite film shielded the UV rays and oxygen more effectively than the original acryl resin, making it difficult for these factors to reach the wood's surface, and thus, perhaps suppressing the generation of radicals from the wood. These actions would suppress the production of coloring substances caused by the radicals, resulting in the suppression of discoloration. Furthermore, the increase in the film's strength by the addition of CNFs would have enhanced the stability of overall the paints with a CNF-containing undercoat. These effects might have contributed not only to the prevention of discoloration but also to the prevention of the occurrence of minute cracks caused by various weather deterioration factors.

Keywords: Cellulose nanofiber, Paint, Acryl resin, Discoloration, Radical

Introduction

Cellulose nanofibers (CNFs) made from pulp are an environmentally friendly material that originates from wood, which is a renewable resource. By finely loosening pulp fibers, a suspension containing CNFs can be obtained [1–4]. Since CNFs have been reported to have some notable characteristics, such as being lightweight, high strength, many studies have made efforts to combine them with resins and other industrial materials at the nano-level, leading to the improvement of the physical characteristics of the composites [1–3]. Some products that utilize CNFs have already become available on the market. Thus,

*Correspondence: tshimo@ffpri.affrc.go.jp
[1] Department of Forest Resource Chemistry, Forestry and Forest Products Research Institute, 1 Matsunosato, Tsukuba, Ibaraki 305-8687, Japan
Full list of author information is available at the end of the article

CNFs are an industrially valuable, promising material for use in an eco-friendly society.

To spread the social implementation of CNFs, it is important to broaden the selection range of CNF manufacturing methods. Currently, CNFs are mainly produced on a large scale with pulp as a raw material by paper companies. When the reduction of manufacturing costs is the priority, it is appropriate to use papermaking pulp produced on a large scale. By contrast, when broadly considering the flow of local wood biomass resources and the expansion of industrial fields, the development of small-scale manufacturing processes also becomes important since the local biomass resources are often available on a small and medium scale [5]. To manufacture CNFs by taking advantage of local resources, it has been necessary to establish a pulp-manufacturing method and a nanosizing process using easy-to-handle manufacturing equipment that can use raw materials obtained on a small and medium scale. We constructed an integrated CNF manufacturing process using Japanese cedar (*Cryptomeria japonica*) [6–8], which is the most planted tree species in Japan's artificial forests [9], as the raw material. At the first of this process, the cedar pulp from wood chip was prepared by soda–anthraquinone cooking; then, the enzymatic pretreated pulp was processed by bead milling [4]. While confirming the safety of the obtained CNFs water suspension [10], we examined the development of various applications and confirmed the effectiveness of the CNFs, when adding it in a wood paint [11, 12].

The life cycle of wood products is greatly affected by weather deterioration factors, such as sunlight, wind and rain, temperature, and humidity changes [13]. Wood paint plays a major role in suppressing these deterioration factors; thus, the improvement of its properties may contribute to the maintenance of the esthetic appearance of wood products. Several research studies have been carried out to improve the properties of the coating film, such as increasing the viscosity and texture of the coating film by adding CNFs [11, 14, 15]. Using the CNFs water suspension prepared by the integrated process, a CNF-containing wood paint blended with a water-based acryl resin emulsion (CNFs/acryl resin composite) was prepared. Then, the test wood panels coated with the CNFs/acryl resin composite were subjected to an accelerated weathering test to examine the influence of the coating film due to weather deterioration factors. As a result, the test panels using the CNF-containing paint as the topcoat acquired fewer surface defects than the case in which the paint without CNFs was used for coating. Additionally, the accelerated weathering test with the CNF-containing paint (Fig. 1) as the undercoat resulted in fewer surface defects and less discoloration than in the case where the paint without CNFs was used for coating or the case without the undercoat [11, 12].
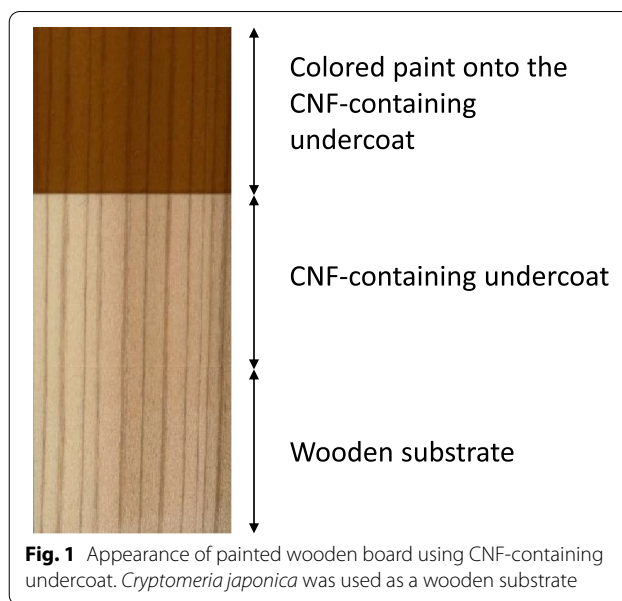

Fig. 1 Appearance of painted wooden board using CNF-containing undercoat. *Cryptomeria japonica* was used as a wooden substrate

In wood products, the beauty of the grain and the color of the wood itself are important considerations, and to express the texture of the wood, highly transparent paints are often used. However, especially in the case of light-colored wood, such as cypress, the color tone changes due to aging [16, 17]. By applying the undercoat paint containing the CNFs, the original wood color tone was shown to be maintained when transparent topcoat paint was used [12]. This function contributes to the widespread use of wooden products, such as indoor and outdoor wooden walls and wooden tableware, which take advantage of the intrinsic beauty of the wood. For clarifying the mechanism by which the discoloration of wood is suppressed using an undercoat paint containing CNFs, the CNFs/acryl resin composite and the resin coating film not containing CNFs were prepared. We investigated the properties of these coating films and the factors that suppressed the discoloration.

Experimental

Materials

Cutting chips (approximately $4 \times 3 \times 0.5$ cm) of air-dried Japanese cedar (*C. japonica*) were used as the raw material for the cedar pulp preparation. A 25 wt% NaOH aqueous solution was purchased from Kobayashi Chemistry Co. Ltd., Fukuoka, Japan. Anthraquinone (2% NaOH solution containing 22% of anthraquinone (1,4-dihydro-9,10-dihydroxyanthracen) as solid content) was donated by Kawasaki Kasei Chemicals Co. Ltd., Kanagawa, Japan. Peracetic acid preparation, Persan MP2-J, was purchased from Kanto Chemical Co. Inc., Tokyo, Japan. Hydrogen

Shimokawa *et al. Journal of Wood Science*   (2021) 67:74

Page 3 of 10

peroxide solution used for the hydrogen peroxide bleaching was obtained from Fujifilm Wako Pure Chemical Co. Ltd., Osaka, Japan. Aqueous acryl resin emulsion, having a glass transition temperature of -8 °C, a viscosity of 800 mPa·s, and a non-volatile component of 45%, was from GenGen Co. Ltd. Cellulizer CL was purchased from Nagase ChemteX. Co. Ltd., Osaka, Japan.

Preparation of cedar pulp

Based on the previous report [7, 10], the cedar pulp was bleached with oxygen, peracetic acid, and hydrogen peroxide after soda–anthraquinone cooking. A quantity of 5 kg (dry matter, (DM)) of cedar chips was placed in a 55 L-capacity vertical rotary autoclave (No. 2615, Kumagai Riki Co. Ltd., Tokyo, Japan) and 15 kg of a cooking solution containing sodium hydroxide ((NaOH), 24% per DM of chips) and anthraquinone (0.1% per DM of chips) was added. The water content in the chips was subtracted from the preparation of the cooking solution. After cooking at 170 °C for 150 min and being allowed to cool, the chips were squeezed with a rotary squeezing dehydrator (RP-1, Kato Tekkou Co. Ltd., Gunma, Japan) to a solid content of approximately 50%. The obtained pulp was returned to the autoclave, and 10 kg of 1% NaOH aqueous solution was added. After sealing the autoclave, oxygen gas was added at 0.7 MPa, and the autoclave was treated at 90°C for 60 min while rotating. After the oxygen treatment, the pulp was dehydrated with the rotary squeezing dehydrator and then made into slurry with 3% water. This slurry was defibrated using a slush pulper (No. 2534, Kumagai Riki Co. Ltd.) and was then knot-removed and washed using a flat screen (No. 2625, Kumagai Riki Co. Ltd.) equipped with a 50/1000-inch-wide slit. The washed pulp was collected by a 300-mesh screen and dehydrated with a centrifuge (H-130G, Kokousan Co. Ltd., Saitama, Japan). The washed oxygen-bleached pulp was placed in a slush pulper to make 3% slurry. The pH of the slurry was adjusted to 4.5 with phosphoric acid, and then the peracetic acid was added to 6% per DM of the pulp. After bleaching at 70 °C for 60 min with stirring, NaOH was added to adjust the pH to 7. Then, the slurry was dehydrated with a rotary squeezing dehydrator, defibrated with an integrator (No. 2531, Kumagai Riki Co. Ltd.), washed with a flat screen equipped with an 8/1000-inch-wide slit, and dehydrated with a centrifuge. The dehydrated pulp was put into the slush pulper again, and the slurry concentration was adjusted to 3% with water. Then, the pH was adjusted to 10.5 with NaOH, and 1.5% of hydrogen peroxide was added per DM of the pulp; then, the mixture was bleached at 70 °C for 60 min. After washing with a flat screen with an 8/1000-inch-wide slit, the pulp was dehydrated to a pulp concentration of approximately 30% using a centrifuge.

The brightness of the obtained pulp was measured using a spectral reflectance meter (Elrepho 2000A, Datacolor, NJ, USA).

Preparation of CNFs water suspension

The pulp after bleaching was made into 2.4 wt% slurry using ion-exchanged water. The endoglucanase-rich enzyme preparation (Cellulizer CL) was added at a rate of 2 mg (equivalent to protein) per 1 g (DM) of the pulp, and then, the enzymatic reaction was carried out at pH 4–5 and 55 °C for 6 h. The amount of protein contained in the enzyme preparation was quantified by a Quick Start Bradford Protein Assay (Bio-Rad Laboratories Inc., CA, USA) using bovine gamma globulin as a standard. The reaction was terminated by heating at 110 °C to inactivate the enzyme, and the obtained pulp suspension was defibrated to nano-level with a circulating bead mill (LMZ-2, Ashizawa Finetech Co., Ltd., Chiba, Japan). Zirconia beads of φ1 mm were used to defibrate, and the bead mill filling rate in the vessel was set at 85%. A total of 40 kg of the pulp suspension after the enzymatic pretreatment was passed through a vessel that had a peripheral bead speed of 12 m/s at a flow rate of 3 L/min. The entire amount was passed once in a batch system. Then, the one-pass processed product was returned to the apparatus, and the defibration process under a circulate operation was carried out for an amount of time equivalent to 14 passes. The resultant was used as the CNFs water suspension.

CNFs/acryl resin composite preparation

A prototype of the CNF-containing undercoat paint was prepared by combining the water-based acryl resin emulsion with the CNFs water suspensions. Two suspensions were mixed so that the content of the resin-derived non-volatile component in the mixture was 9 wt% and the concentration of the CNFs was 1.5 wt%. A 50-g mixed suspension was prepared, and the mixture was agitated at 10,000 rpm for 10 s using a homogenizer (AM-11, Nihonseiki Kaisha Ltd., Tokyo, Japan). Additional CNF-containing composites were also similarly prepared, with concentrations of 0.5 wt% and 1 wt%.

Film preparation

Especially ordered polyethylene apparatuses with separable bottoms and sides (Kyoto Jushi-Seiko Co., Ltd., Kyoto, Japan) were used to obtain the self-supporting films. The composites prepared by mixing were left to stand overnight at room temperature before use to defoam the bubbles that had been generated by stirring. Each 10 g of composite was gently cast into the apparatus that was 7 cm in diameter (0.26 g of composite/cm^2). To prepare the films for the light transmittance analyses,

Shimokawa *et al. Journal of Wood Science*   (2021) 67:74

Page 4 of 10

the apparatuses that were 4.5 cm in diameter were also used with the same amount per unit area. The films were prepared by drying in a room at 24 °C for at least seven days, and then they were carefully peeled from the apparatuses. The thicknesses of the films were measured using a thickness gauge (NO. 7331, Mitutoyo Co. Ltd., Kanagawa, Japan).

Atomic force microscopy (AFM)

The surface properties of the films, including CNFs, were observed using an SPM-9700HT scanning prove microscope (Shimadzu Co. Ltd., Kyoto, Japan). A portion of the diluted specimen was dried at room temperature on a clean mica substrate. The images were scanned in a tapping mode using silicon micro-cantilevers (OMCL-AC200TS, Olympus Co. Ltd., Tokyo, Japan). To observe the surface condition of the film on the wood panel, a CNFs/acryl resin composite was applied to the cedarwood board with a spray-type coating apparatus to a thickness of the dried film should be approximately 10 μm. After the painted film had dried, it was cut out with a cutter so that the thickness of the base wood was 1 mm or less, and it was fixed to the sample holder with a double-sided tape for AFM observation.

The sizes of the images were 1×1 μm or 2×2 μm, and flattening of the image processing was only carried out before measuring the thickness of the fibers. The average fiber thickness was calculated from the measured values at 157 locations.

Light transmittance

The light transmittance of each film was determined from 220 to 850 nm using a Shimadzu UV-2400 spectrometer equipped with an integrating sphere attachment ISR-2200 (Shimadzu Co. Ltd.). The measurement was carried out in duplicate, and the average value of the light transmittance at 365 nm was obtained.

Tensile testing

The tensile strength and elongation-at-break for the films were assessed using a testing machine, EZ-Graph (Shimadzu Co. Ltd.), with a 500-N load cell. The films were cut into strips of 10×50 mm. The strips were aged at 22 °C and 50% RH for at least two days prior to measuring. The initial gauge length was 10 mm, and the crosshead speed was 100 mm/min. The results are expressed as the means of the four to five specimens.

Oxygen gas permeability

A film for the measurement of the oxygen gas permeability was mounted on a differential pressure gas permeameter (BT-3, Toyoseiki Co. Ltd., Tokyo, Japan). Using oxygen gas of 99.9% or more, the measurement

was carried out at a test temperature of 23 °C. The gas pressure on the high side was 100 kPa, and the permeation area had a diameter of 30 mm. The average value was calculated for each of the three films. The analyses were carried out at the Chemicals Evaluation and Research Institute, Tokyo, Japan.

Electron spin resonance (ESR) spectrometric measurement

An air-dried wood sample (DM of 94.4%) of approximately $1 \times 1 \times 30$ mm was cut out from cypress and adjusted to 15 mg. A film was formed by adding 4.13 g of acrylic resin or CNFs/acryl resin composite to a homemade apparatus that had a diameter of 4.5 cm; this was dried at 45 °C. Four pieces of wood samples of the adjusted weight were placed on the dried membrane; then, 1.5 g of each suspension was added so that the pieces of wood were immersed; they were then dried at 45 °C. Next, a further 1.5 g of the suspension was added and dried to obtain the film-coated wood specimens. The film was extracted from the apparatus, and the coated specimen was carefully cut out, taking care not to peel off the coating around the wood sample. Since the weight of the coated wood specimen with the CNFs/acryl resin composite was 95 mg, the weight of an acryl resin-coated wood specimen was also adjusted to 95 mg by excising the resin film remaining around the piece of wood. Since the weight of the wood specimen was 15 mg, 80 mg of the resin film samples was also prepared using some sheets that were obtained by cutting each of the CNFs/acryl resin composite film and the acrylic resin film to a size of approximately $2 \times 2 \times 30$ mm; the weight was adjusted by excising each of the resin pieces. Another set of specimens was prepared with the same weight as the coated wood specimens, and ESR analyses were performed in duplicate.

The ESR (JES FA200, JEOL Co. Ltd., Tokyo, Japan) measurement was performed using a quartz test tube with a diameter of 5 mm. After setting the specimen in the test tube, it was treated with ultraviolet (UV) irradiation for 2 min using an ultra-high pressure mercury lamp (USH-500SH, Ushio Inc., Tokyo, Japan). Immediately after the UV irradiation, the radicals were measured by ESR, and the changes in radical formation before and after irradiation with each specimen were compared. Using manganese (Mn) as a standard, the spectra were measured with 336 ± 7.5 mT, modulation amplitude of 0.35 mT, time constant of 0.1 s, microwave output of 1 mW, and the measurement time was 1 min.

Results

Properties of the pulp and CNFs

The brightness of the pulp prepared from the cedar chips was 76%. Figure 2 shows an AFM observation image of
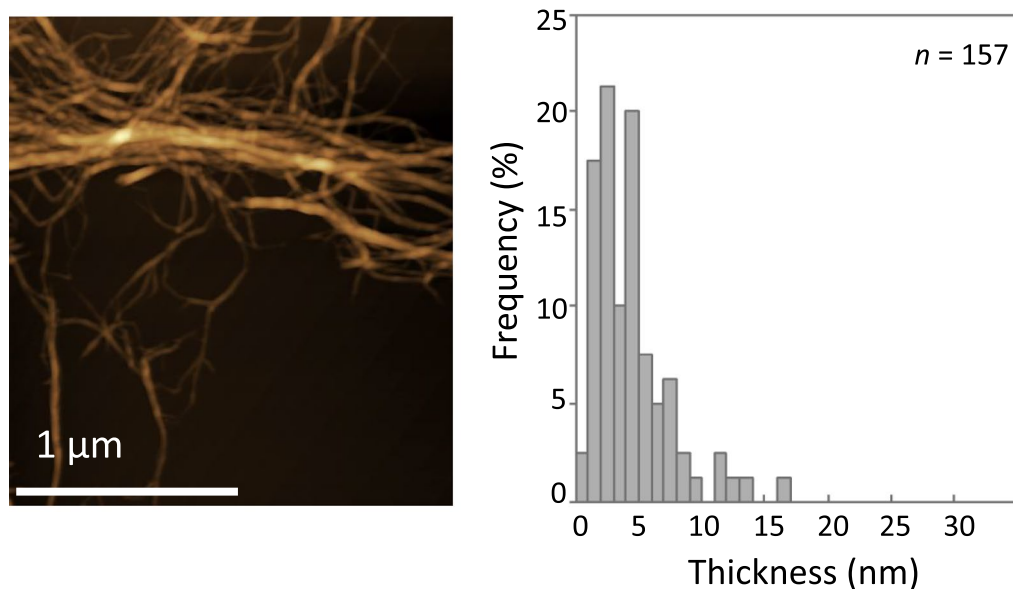
Fig. 2 Atomic force microscopy image and thickness distribution histogram of CNFs derived from *Cryptomeria japonica*

the CNFs. The prepared CNFs were not uniformly dispersed as unit fibers, which were reported to be approximately 3 nm in thickness [1–3]. The average thickness of the fibers constituting the cedar CNFs was 6.5 nm, with a wide distribution range.

Surface observation of the composite film

Figure 3 shows a surface observation of an acryl resin film (Fig. 3a) and a CNFs/acryl resin composite film (Fig. 3b) by AFM. In the CNFs/acryl composite film, nanofibers were confirmed, whereas they were not detected in the surface of the film made of acryl resin alone. It was also shown that they were uniformly mixed with the acryl resin at the nano-level. Figure 3c shows the surface of the CNFs/acryl resin composite applied to a wood board.

Although the CNFs/acryl resin composite was spray-painted onto the wood board, the CNFs and acryl resin were uniformly mixed and solidified. Both fibers and resin were confirmed on a part of the surface of the composite film.

Properties of the CNFs/acryl resin composite film

A thin, transparent film was prepared from the suspension of acryl resin emulsion. The CNFs/acryl resin composite film, prepared using a suspension of the same weight per unit area, was thicker and less transparent than the acryl resin film.

Figure 4 shows the light transmittance of the films. The average film thickness of the acryl resin film was 13 µm, the film thickness of the 1 wt% CNFs/acryl resin
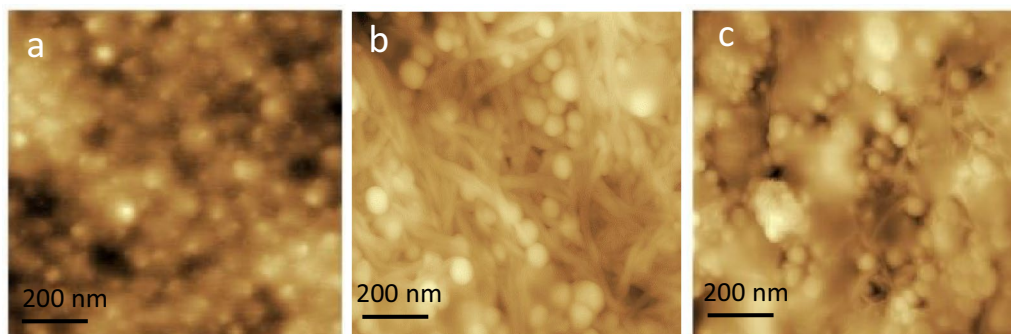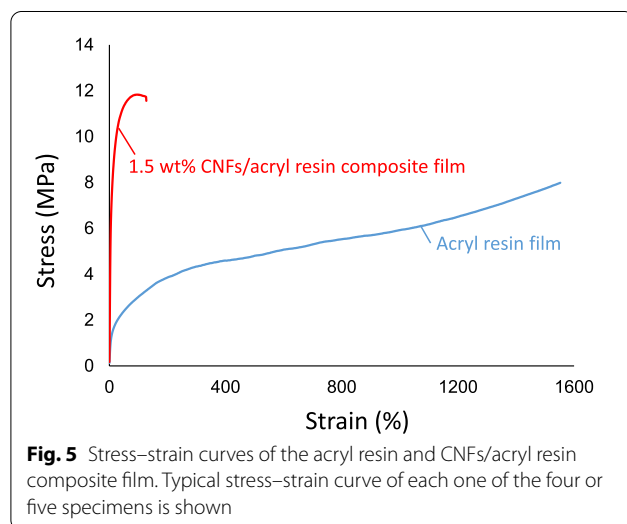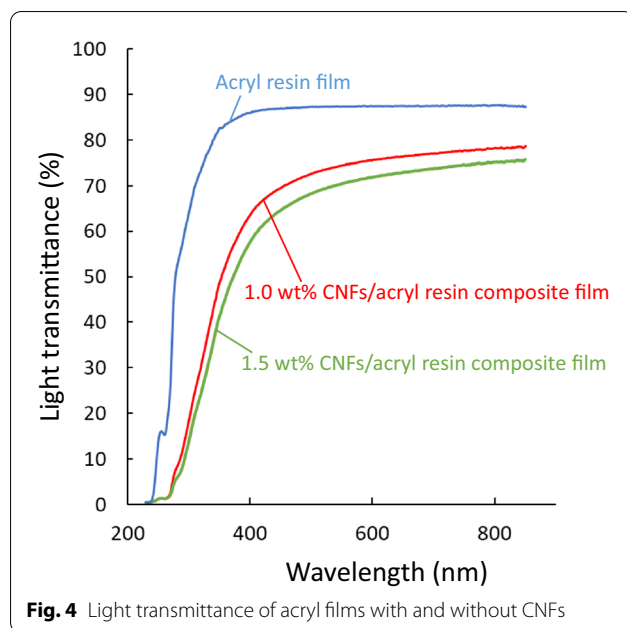

Fig. 3 Atomic force microscopy images of acryl films with and without CNF. Acryl resin film (**a**) and CNFs/acryl resin composite film (**b**) on a mica substrate and the composite film applied to a wood board with a spray-type coating apparatus (**c**)

Shimokawa *et al. Journal of Wood Science*   (2021) 67:74

Page 6 of 10

Fig. 4 Light transmittance of acryl films with and without CNFs

Fig. 5 Stress–strain curves of the acryl resin and CNFs/acryl resin composite film. Typical stress–strain curve of each one of the four or five specimens is shown

composite film was 24 µm, and that of the 1.5 wt% CNF-containing acryl resin film was also 24 µm. In the UV light region, the light transmittance of the CNF-containing film tended to be lower, and the average of each light transmittance value at 365 nm was 82.8% for the acrylic resin film, while the value for the 1.0 wt% CNF-containing film was 55.3%, and that for the 1.5 wt% CNF-containing film was 47.6%.

The mechanical properties of the films were evaluated using tensile testing. Figure 5 shows the typical stress–strain curves of the acryl resin film and the 1.5 wt% CNF-containing acryl resin composite film. Both properties of the breaking stress and the elongation-at-breakage of the films differed by the addition of CNFs. The average value of the breaking stress increased by approximately 1.5 times from 7.62 ± 0.57 MPa to 11.5 ± 0.35 MPa by the addition of CNFs to the acrylic resin films. By contrast, the elongation of the CNFs/acryl resin composite film was significantly restricted compared with that of the acryl resin film. The average value of the elongation-at-break of the CNFs/acryl composite film was $131\% \pm 12.2\%$, and that of the acryl resin alone was $1498\% \pm 158\%$.

Table 1 shows the results of the oxygen permeability. The average thickness of the acryl resin film was 0.204 ± 0.02 mm and that of 1.5 wt% CNF/acryl resin composite film was 0.276 ± 0.03 mm. When the films were prepared with the same weight per unit area, the CNF-containing film was thicker than the acryl resin film, as described above. When the values of the oxygen gas permeability were compared without considering the film's thickness, the value of the CNF-containing film was less than half of that of the acryl film. The value of the gas permeability coefficient, considering the thickness of the membrane, was also decreased to 60% with the addition of CNFs, indicating that the addition of CNFs made it difficult for oxygen gas to permeate.

Table 1 Oxygen gas permeability of CNFs/acryl resin composite film

	Thickness of the films (mm)	Oxygen gas permeability		Oxgen gas permeability coefficient
		$mol/(m^2 \cdot s \cdot Pa)$	$cm^3/(m^2 \cdot 24\ h \cdot atm)$	$mol \cdot m/(m^2 \cdot s \cdot Pa)$
CNFs/acryl resin composite film	0.276	3.85×10^{-12}	756	1.06×10^{-15}
Acryl rein film	0.204	8.80×10^{-12}	1.73×10^3	1.78×10^{-15}

CNF content was 1.5 wt%

Average of 3 independent measurements are shown

Shimokawa *et al. Journal of Wood Science*   (2021) 67:74

Page 7 of 10

Radical measurement by ESR

The results for the radical measurements before UV irradiation and immediately after UV irradiation are shown in Fig. 6. The largest amount of radical was generated from the unpainted wood specimen after UV irradiation, followed by the acryl resin-coated wood specimen. The amount of radical generated was the lowest for a piece of wood wrapped in a CNFs/acryl resin composite. No significant amounts of radical generation were observed from the acryl resin alone nor the CNFs/acryl resin composite itself before and after UV irradiation under the same experimental conditions (data not shown). The addition of CNFs resulted in a suppression of the radical generation from the wood sample under UV irradiation.

Discussion

The CNFs prepared in this study had a wide fiber thickness distribution range and remained a subtle partially thick structure, resulting in a white to pale yellow of the produced CNFs water suspension. Although such properties of CNFs, a uniform composite was obtained by a simple homogenizing treatment of the CNFs water suspension and the aqueous acryl resin emulsion, and no fiber lumps or coagulated substances were found in the dried film. Previous research found that the fiber length of pulp prepared by soda–anthraquinone cooking was shorter than that of kraft pulp [8, 18] when the degree of polymerization was evaluated as the pulp viscosity measured by the capillary–viscometer method using cupriethylenediamine solution according to TAPPI T230 om-13 "Viscosity of pulp (capillary viscometer method)". The CNFs water suspension produced from a soda–anthraquinone cooked cedar pulp showed low viscosity [8]. The low-viscosity CNFs water suspensions were easy to

mix uniformly when they were blended with a highly viscous water-based resin emulsion.

As reviewed by Sharma et al. (2019) [19] and Phanthong et al. (2018) [20], nanocellulose has been employed as a filler in the polymer matrix due to its excellent mechanical properties. The tensile strength of the acryl resin film also increased by adding CNFs in this study; the strength of coating film combined with CNFs apparently improved. The CNFs should have acted as an excellent reinforcing agent.

In this study, some nanosized fibers were found on the surface of the cast film prepared from the CNFs/acryl resin composite. In addition, the fibers were also detected on the surface of the film spray-painted on the wood board. Although the surface of the spray-painted coating was uneven compared to the films formed on the flat, clean mica substrate, some nanofibers were found on the film's surface. The spray-painting operation was faulted for the uneven surface of the film. Both nanofibers and resin were observed on the surface of the coated film, instead of the fibers settling on one side of the film or entangled to form a lump, indicating that the CNFs/acryl resin composite maintained uniformity during film formation.

The generation of phenoxy radicals by the photooxidation reaction of lignin and the subsequent formation of colored structures such as quinones are considered one of the principal causes of discoloration in wood products that are related to deterioration by weather [13, 21–23]. The discoloration of lignin due to photooxidation is also one of the yellowing factors in lignin-rich [21] and lignin-containing pulps [24]. Several radical generation models have been proposed using lignin model compounds and related compounds [21, 23, 25]. According to a review by
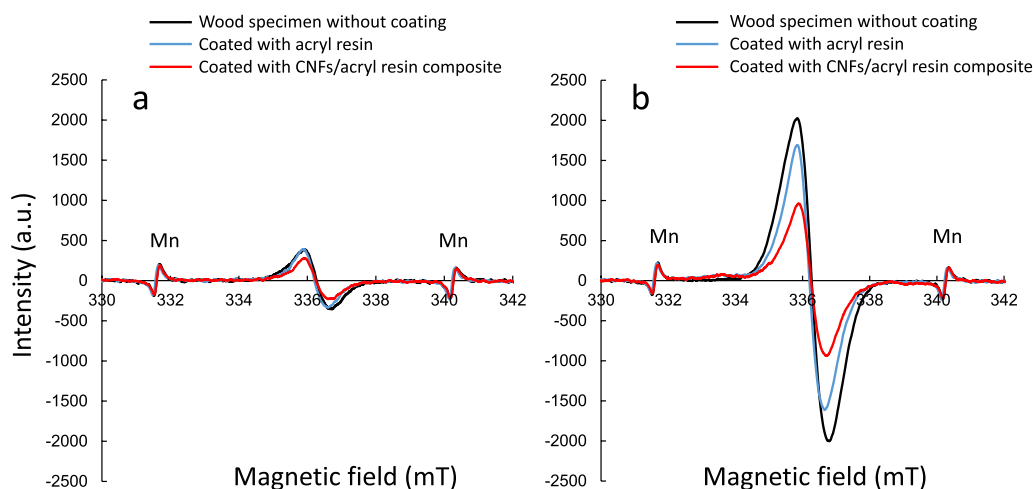

Fig. 6 Electron spin resonance spectra of before (**a**) and after (**b**) 2 min of UV irradiation. Mn was used as a standard

Shimokawa *et al. Journal of Wood Science*   (2021) 67:74

Page 8 of 10

Paulsson and Parkås (2012) [21], the fast phase of photo yellowing of lignin-rich pulps has been attributed to oxidation of free phenolic groups and/or hydroquinones and catechols to photoproducts of mainly quinoid character, and the phenoxy radicals are significant intermediates. Kringstad and Lin (1970) [23] reported the discoloration of lignin on light exposure and oxygen and showed the generation of free radicals near ultraviolet (UV) light using ESR analysis. Thus, UV irradiation, the presence of oxygen, and the generation of radicals seemed to play a role in wood discoloration.

The light transmission of the CNFs/acryl resin composite film in the UV region was first investigated. As a result, the CNF composite film prevented the transmission of UV rays more effectively than the acryl films. Films prepared with the same amount of acryl resin water suspension or CNFs/acryl resin composite per unit area were thicker in the CNFs composite film. The thickening of the film may have also affected the lower UV transmittance of the CNFs composite film. The oxygen gas permeability of the film containing the CNFs was then investigated, which revealed a reduced gas permeability coefficient. When another type of acryl resin (viscosity of approximately 250 mPa·s) was tested, the oxygen gas was also shielded by the composite film. The gas permeability coefficient of the CNFs/acryl composite film was 4.45×10^{-16} (mol·m/m^2·s·Pa) and that of the acryl resin alone was 7.02×10^{-16} (mol·m/m^2·s·Pa) in the additional test. The oxygen barrier properties of nano-fibrillated cellulose material-based films are well known [26, 27]; thus, the oxygen barrier performance of the CNF-containing films seemed to be a solid property. The CNFs/acrylic resin composite film effectively prevents oxygen permeation, indicating that it may prevent wood surface oxidation.

Since the generation of radicals was thought to be related to UV rays and oxygen, it was expected that protecting against these factors would reduce the number of radicals. ESR analysis after UV irradiation detected the generation of radicals from the wood specimen (Fig. 6b). Because the formation of phenoxy radicals has been reported in photooxidation reactions such as lignin [21, 23], the detected radicals were presumed to be phenoxy radicals. In the specimen coated with the CNFs/acryl resin composite, the number of radicals generated following UV irradiation was lower than in the specimen coated with acryl resin alone or the wood itself, under the same experimental conditions. This effect can be caused by the CNFs/acryl resin composite film preventing UV rays and oxygen gas transmission.

The effect of suppressing the wood discoloration using the CNFs/acryl resin composite was significant when a transparent topcoat paint was applied to wood products, taking advantage of the characteristics of the wood grain or a light color [12, 28]. The presumed wood discoloration suppression mechanism when CNFs/acryl resin composite was used as the undercoat and a transparent topcoat was applied on top of it was consequently as follows: the CNFs composite film shielded the UV rays and the oxygen more effectively than the original acryl resin film, making it difficult for these factors to reach the wood's surface; thus, the generation of radicals from the wood was reduced. This action might have prevented the production of coloring substances caused by the radicals, resulting in the reduction of discoloration. Furthermore, the film's increase in strength by the addition of CNFs would have supported the enhanced stability of the whole coating films with a CNF-containing undercoat. These effects could have helped to prevent not only discoloration but also minute cracks caused by various weather deterioration factors.

In our previous work, the accelerated weathering test indicated the prevention of color change from light to dark of the test wood panels when transparent paints were applied to the topcoat with the CNFs/acryl resin composite as the undercoat. On the one hand, the CNF-containing undercoat also prevented the fading of the dark-colored topcoat [12, 28]. Because UV transmittance has been reported to be related to the color [29, 30], the dark (for example, brown) coating film colored with some pigments showed a lower UV transmittance than the transparent acryl coating film (data not shown). Therefore, the discoloration suppression mechanism when the dark-colored topcoat was used seemed slightly different from the mechanism when the transparent topcoat was applied. The mechanism of the fading prevention of the dark-colored topcoat by the CNFs/acryl resin undercoat requires further investigation. Although the effect of CNFs/acryl resin composite undercoat on UV irradiation suppression would be limited when the dark-colored topcoat was used, by preventing the permeation of oxygen, some effects in reducing the amount of radical generation might have been expected. Additionally, the acryl resin coating also cracked owing to photodegradation triggered by the radicals [31]. The stabilization of the entire coating film because enhanced strength of the undercoat paint due to the addition of CNFs might have suppressed the occurrence of cracks in the coating film, preventing the pigment from being leached and fading of the dark-colored paint.

Still, a few areas need to be investigated, such as the properties of CNF-containing paints and the long-term effect of CNF-containing coating films installed outside. By accumulating research, the use of CNFs and painted wood products should become more popular. Improving the function of wood paints and the quality of painted

Shimokawa *et al. Journal of Wood Science*   (2021) 67:74

Page 9 of 10

wood products using CNFs can increase the demand for the raw wood required to make CNFs and wood products.

Authors' contributions
TS designed the study, collected data, interpreted the results, and drafted the manuscript. YH prepared the composite films and provided advice on oxygen gas permeability. ET contributed to prepare cedar pulp and measured the strength of the films. HS analyzed CNFs by AFM. MK provided advice on ESR analysis. AI provided advice on weather resistance of coating film. XH and HO provided advices on weather resistance of coating film and the properties of acryl resins. KM participated in designing the study, prepared cedar pulp, and supervised the manuscript. All authors have read and approved the final manuscript.

Availability of data and materials
Data generated or analyzed during this study are included in this published article.

Declarations

Competing interests
TS, KM, XH, and HO have a patent on CNF-containing paints (Japanese Patent No. 6745747).

Author details
[1]Department of Forest Resource Chemistry, Forestry and Forest Products Research Institute, 1 Matsunosato, Tsukuba, Ibaraki 305-8687, Japan. [2]Department of Wood Improvement, Forestry and Forest Products Research Institute, 1 Matsunosato, Tsukuba, Ibaraki 305-8687, Japan. [3]Gen Gen Corporation, 74 Aza Nakanoori, Kamori, Tsushima, Aichi 496-0005, Japan.

References
1. Isogai A (2013) Wood nanocelluloses: fundamentals and applications as new bio-based nanomaterials. J Wood Sci 59:449–459
2. Moon RJ, Martini A, Bairn H, Simonsen J, Youngblood J (2011) Cellulose nanomaterials review: structure, properties and nanocomposites. Chem Soc Rev 40:3941–3994
3. Yano H (2019) Cellulose nanofibers—an abundant sustainable bioresource in japan- (in Japanese). J Jap Solar Energy Soc 45(4):55–58
4. Shimokawa T, Ikeda T, Magara K, Togawa E, Masaya N, Otsuka Y, Nojiri M, Takao T, Ogawa M, Nyakayama E, Hyayashi N (2020) Cellulose nanofiber production from bamboo by enzymatic pretreatment for wet milling process using bead mill aiming at application to food materials (in Japanese). Bull For Forest Prod Res Inst 19:341–348
5. Shimokawa T, Magara K (2021) Manufacturing and utilization of cellulose nanofibers using Kamaishi/Otuchi region model (in Japanese). Kanto J Forest Res 72(1):141–144
6. Hayashi N, Shimokawa T, Nojiri M, Shibuya M, Magara K, Kubo S, Togawa E, Fujisawa S, Kobayashi M, Kiguchi M (2017) Development of a system for integrated production of cellulose nanofibers from Sugi (in Japanese). In: Forestry and Forest Products Research Institute, Results of the 3rd Midterm Plan, pp38–39, https://www.ffpri.affrc.go.jp/pubs/seikasenshu/dai3ki/documents/p38-39.pdf. Accessed 13 May 2021
7. Magara K (2016) Cellulose nanofiber manufacturing technology demonstration project (in Japanese). Seibutushigen 10(3):2–13
8. Shimokawa T, Togawa E, Nojiri M, Shibuya H, Kuroda K, Tanaka R, Ishikawa A, Kobayashi M, Kanbayashi T, Magara K, Ohki H, Ka K (2019) Compatibility of cellulose nanofibers produced by wet milling with enzymatic pretreatment for undercoat paint (in Japanese). In: 15th Biomass Science Conference, Koriyama, 11–13 December 2019. https://doi.org/10.20550/jiebiomassronbun.15.0_37
9. Forestry Agency, Ministry of Agriculture, Forestry and Fisheries, Japan (2020) In: Annual report on forest and forestry in Japan Fiscal Year 2019 (Summary). https://www.rinya.maff.go.jp/j/kikaku/hakusyo/r1hakusyo/attach/pdf/index-1.pdf. Accessed 13 May 2021, p.33.
10. Shimokawa T, Hayashi N (2017) Safety evaluation for the use of nano-sized cellulose derived from Sugi (in Japanese). Kagaku Kogyo 68(1):53–58
11. Ishikawa A, Kataoka A, Ohki H, Ka K, Itou T, Shimokawa T, Hayashi N, Magara K, Kobayashi M, Kanbayashi T, Kiguchi M (2019) Characteristics of varnish blended with cellulose nanofiber produced by enzymatic treatment and wet milling (in Japanese). Wood Prot 45:68–76
12. Ka K, Ohki H, Shimokawa T, Hayashi N, Magara K, Ishikawa A, Kataoka A, Kobayashi M, Kanbayashi T (2020) Using cellulose nanofiber for the development of weather resistant wood-paint (in Japanese). Coating Technol Assoc 55:356–365
13. Kataoka Y (2017) Weathering and surface protection of wood—weathering mechanism-(in Japanese). Wood Prot 43:58–68
14. Kuma S, Enjoji T, Taguri Y, Hoaki K, Hirai T, Yano M, Fukumoto Y (2018) Research on paints with cellulose nanofibers (I). Development of environmentally preferable wood paints (in Japanese). Rep Ind Technol Center Saga 2018:41–45
15. Toisawa K, Sasaki R (2020) Characterization of water-based paint and coating film with cellulose nanofiber (in Japanese). Hyoumengijyutu 71(5):59–63
16. Mitsui K (2004) Changes in the properties of light-irradiated wood with heat treatment. Holz Roh Werkst 62:23–30
17. Yamamoto K, Kataoka A, Furuyama Y, Matsuura T, Kiguchi M (2007) The effect of irradiation wavelength on the discoloration of wood (in Japanese). Mokuzai Gakkaishi 53(6):320–326
18. Magara K, Togawa E, Kubo S, Shimokawa T (2021) Preparation of raw materials for cellulose-nanofiber blending water-based paints. Jap Tappi J 75(6):553–568
19. Sharma A, Thakur M, Bhattacharya M, Mandal T, Goswami S (2019) Commercial application of cellulose nano-composites-a review. Biotechnol Rep 21:e00316. https://doi.org/10.1016/j.btre.2019.e00316
20. Phanthong P, Reubroycharoen P, Hao X, Xu G, Abudula A, Guan G (2018) Nanocellulose: extraction and application. Carbon Res Conversion 1:32–43
21. Paulsson M, Parkås J (2012) Light-induced yellowing of lignocellulosic pulps-mechanisms and preventive methods. BioResouces 7(4):5995–6040
22. Leary GJ (1968) Photochemical production of quinoid structures in wood. Nature 217:672–673
23. Kringstad KP, Lin SY (1970) Mechanism in the yellowing of high-yield pulps by light. Structure and reactivity of free radical intermediates in the photodegradation of lignin. Tappi 53(12):2296–2301
24. Fjellström H, Höglund H, Paulsson M (2007) Light-induced yellowing of mechanical and chemimecanical pulp sheets—influence of wood raw material, process and aging method. Nordic Pulp Paper Res J 22(1):117–123
25. Takagi H, Forsskåhl I, Perakyla H, Omori S, Dence CW (1990) Studies on the mechanism of the photoyellowing of bleached mechanical and chemimechanical pulps. Holzforschung 44(3):217–222

Shimokawa *et al. Journal of Wood Science*   (2021) 67:74

Page 10 of 10

26. Wang J, Gardner DJ, Stark NM, Bousfield DW, Tajvidi M, Cai Z (2017) Moisture and oxygen barrier properties of cellulose nanomaterial based films. ACS Sustain Chem Eng 6:49–70
27. Aulin C, Gällstedt M, Lindström T (2010) Oxygen and oil barrier properties of microfibrillated cellulose films and coatings. Cellulose 17:559–574
28. Ishikawa A, Shimokawa T, Kobayashi M, Kanbayashi T, Magara K, Ohki H, Ka K, Ito T (2020) Development of paint for wood using CNF (in Japanese). In: Cellulose nanofibers manufactured from local forest resources, Forestry Forest Prod Res Inst, p 10–11. https://www.ffpri.affrc.go.jp/pubs/chukiseika/4th-chuukiseika29.html. Accessed 1 June 2021.
29. Wilson CA, Gies PH, Niven BE, McLennan A, Bevin NK (2008) The relationship between UV transmittance and color-bisual description and instrumental measurement. Textile Res J 78:128–137
30. Gies PH, Roy CR, Toomey S, McLennan A (1998) protection against solar ultraviolet radiation. Mutation Res 422:14–22
31. Okamoto S (1989) Study about photodegradation of acrylic resin paint films by ESR spectrometer (in Japanese). Shikizai 62:404–410

Publisher's Note

Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.