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Monitoring the surface aging of wood through its pits using atomic force microscopy with functionalized tips

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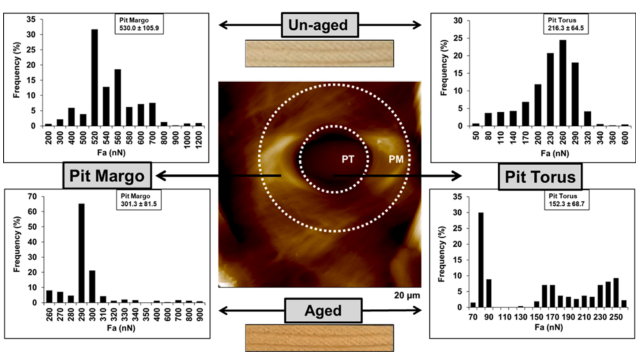
GRAPHICAL ABSTRACT



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ABSTRACT

Wood aging is a topic of great interest due to its impact on wood performance and durability as a construction material. Therefore, it is important to develop accurate methods to monitor aging and understand its mechanisms. Atomic force microscopy (AFM) is a powerful tool to study the changes in materials properties in the nanoscale. We aim in this paper at developing an accurate AFM-based method to understand the wood aging phenomenon by studying the surface changes of wood pits as they are the most susceptible wood structures to aging. For this objective, surface adhesion measurements were performed to detect any chemical changes on the surface of wood structures by estimating the relative adhesion force (RAF). The results showed that unfunctionalized AFM tips should not be used for monitoring aging as they fail to simply differentiate between the different wood structures (cell wall, lumen, pit torus and pit margo) as the RAF values were around 10 for the four structures. With a focus on pit structures (torus and margo), AFM tips functionalized with hydroxyl groups showed significantly different RAF values for torus and margo suggesting the ability of these tips in detecting possible chemical changes. The RAF values of torus and margo were around 216 and 530 for unaged wood, respectively. This indicates that, for the first time, the use of functionalized tips does not only improve the interaction between the tips and wood in general but also improves the sensitivity to its different structures. This also allowed monitoring wood aging as the RAF values for torus and margo dropped to 152 and 301 upon aging,

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respectively. This work suggests that using AFM tips with different functional groups, such as carboxyl, acetyl, methoxyl, and hydroxyl groups can bring a more thorough understanding of wood aging.

1. Introduction

Wood as a constructing material can be traced back to the ancient Egyptian time [1]. In the recent decades, the rising demand on developing and utilizing sustainable and renewable resources has made wood more attractive [2]. Wood, however, is vulnerable to long-term use due to aging, which involves irreversible changes of certain physical, chemical and mechanical properties under external conditions [3], such as temperature [4], humidity [5], UV light [6], chemical treatment [7], and mechanical stresses [8,9] and others. Therefore, an established knowledge on the possible changes of wood properties during aging is of great importance, especially for material engineers who seek to understand the fundamental mechanisms of aging in order to design materials of desired properties, performance, and lifetime.

Several degradation mechanisms, which could happen in polymeric composites during aging, have been thoroughly investigated [10] and they are assumed to be triggered by different external variables. For instance, intensive and cyclic stress loading could lead to matrix cracking, which tends to trigger phase separation and microstructural changes [8]. In addition, chemical degradation such as (hygro)-thermal degradation, oxidation, and hydrolysis could take place in the presence of high oxygen and moisture content in combination of heat [5,11]. When investigating the aging phenomenon of wood as a natural polymeric composite, a wide range of wood properties have been studied [12]. Extensive research has reported that wood aging causes changes in (1) physical properties, including morphology and density [13,14], hydroscopic behavior [15] and other properties [16] 2) mechanical properties, such as bending/compression/tensile strength, MOR, MOE, etc [17] and (3) chemical properties which mainly resulted in changes in the content of wood components [18]. How exactly aging causes these changes is not yet fully understood as different aging mechanisms seem to act simultaneously, which makes it very challenging to study the individual effects separately [11]. Therefore, the changes in the chemical properties of the major wood polymers, e.g. cellulose, hemicelluloses and lignin, which are distributed in different locations down to the nanoscale need to be further investigated, which could give us a more thorough understanding of wood aging.

Many techniques have been used to monitor wood properties as a function of aging (or treatment). However, these methods have mostly focused on the macroscopic changes in wood [19,20]. Atomic force microscopy (AFM), with a nanoscale resolution, is a powerful technique to study the micro/nanostructure of wood/fiber surface [21–24]. This technique is widely applied for surface imaging, estimation of micromechanical properties, and chemical characterization of surfaces [25–28]. For instance, AFM has been used to monitor the variation in wood surface polarity by measuring the adhesion between AFM tips and wood surface over different anatomies mainly at cell wall and cell lumen. The adhesion significantly varied depending on the polymer proportions in the characterized anatomies [26]. To achieve more significant variation, functionalized AFM tips with different groups, such as —OH, or C—H_3, on their surfaces have been used [29]. This variation, however, was actually overestimated as it was also induced by surface roughness [27,30].

In this study, Norway spruce (*Picea abies*) specimens were subjected to laboratory aging treatment simulating the environmental effects that may result in permanent changes of properties. To improve the applicability of AFM as a technique to monitor wood aging, we hypothesize that measuring the adhesion between functionalized AFM tips and wood pits is an accurate approach to monitor wood aging as it is more significant in these wood anatomies.

2. Materials and methods

2.1. Preparation of wood samples

Ten samples of wood (dimensions of 45 × 6.5 × 10 mm) were cut in the radial direction from air-dried Norway spruce (*Picea abies*). All samples were cut from similar locations to minimize any possible variation.

2.2. Accelerated aging of the wood samples

Five of the ten wood samples were subjected to an accelerated aging treatment in a UV climate chamber (QUV/Spray Accelerated Weathering Tester, Q-Lab, USA). The treatment included two steps of a total of 11 cycles following the standard EN 927−6. The first step is one cycle of 24-h water spraying at 45°C followed by 10 cycles of UV radiation at 60°C (6 h per cycle). A UV-A 340 lamp with an irradiation of 0.89 W/m^2/nm was used.

2.3. Sample preparation for the AFM measurements

A cubic sample (5 mm) was cut from each unaged and laboratory-aged sample (a total of ten samples, 5 unaged and 5 aged). Each sample was glued on an AFM disc sample holder and a smooth radial surface was prepared using a diamond knife (Diatome, DiS-Galetzka, Germany) mounted on a microtome (HM360 HistoServe, 1 mm/s, knife angle 45°, cutting angle 5°). The cutting counts for all samples were identical. All samples were then vacuum dried for 24 h and stored in a desiccator for one week before the AFM adhesion force measurements were performed to avoid any transient effect induced by aging of a freshly cut surface.

2.4. AFM adhesion measurements

The relative adhesion force was determined by force measurements conducted in an environmental chamber where nitrogen gas was continuously blown. This allows controlling the humidity and minimizing any induced adhesion due to the existence of water molecules on the sample surface. The wood sample after glued to the AFM disc was mounted on the AFM hot stage, which was set at a constant temperature of 30°C (Model 332, Lake Shore Cryotronics, USA). Using the AFM camera, the tip was located over the earlywood part of the wood sample surface. A topographic scan was performed using the instrument (Agilent Technologies 5500 with multipurpose closed loop scanner) at first in order to locate the different wood anatomies, i.e. cell wall (CW), cell lumen (CL), pit torus (PT) and pit margo (PM). Two types of AFM tips were used in this work: standard AFM tip mounted on a silicon nitride cantilever (Multi75Al-G, Nanoandmore, Germany) and chemically modified tip grafted with hydroxyl groups (ST-PNP—OH, Nanoandmore, Germany). The adhesion force measurements were carried out based on the obtained pull-off force via force–distance curve. The actual value depends on the deflection sensitivity and the force constant of the cantilever. All these values were calibrated using the thermal noise method. The measurements were conducted within an area of 1 × 1 μm^2 with a measurement size of 4 × 4 (16 locations) at the targeted regions. There were a total of ca. 200 measurements for each region per sample.

2.5. Polarized light microscopy

The surface of the unaged and Laboratory-aged wood samples was imaged using a light microscope (Zeiss Axioplan, Zeiss, Germany) to monitor the changes in the anatomies of wood surface upon aging.

2.6. ANOVA analysis

The collected relative adhesion force values were analyzed with a one-way ANOVA test. A significance level of $\alpha = 0.05$ was set for comparison among i) different wood anatomies; ii) AFM tip types. All Correlation was assessed using Pearson's correlation (p value).

3. Results and discussion

Wood pits are one of the most representative microstructures in both softwood and hardwood [31]. They function as conductive tunnels, enabling the transportation of liquids and gases laterally and vertically through the pit membrane, which exists between adjacent cell walls. Torus-margo type of pits are generally possessed by softwood species such as Norway Spruce (Fig. 1). These pits appear to be similar in composition to primary cell walls and consists of two distinct areas. The outer margo area (PM) with porous cellulose elementary-formed structure, allowing low-resistance transfer of water between tracheids, and the center torus (PT) with a thick tightly woven and impermeable structure (Fig. 1) [32–34].

Due to the permeability difference between PT and PM, pit membrane is considered as a "safety valve" to control the flow of liquids and gases brought by external environmental conditions [32]. The direct contact and continuous deflection during this process introduce irreversible structural deformation and chemical degradation in both pit margo and torus [35,36]. Such degradation/deformation can be clearly observed in Norway spruce samples upon artificial aging (Fig. 2). Characteristic tracheid to tracheid pitting in the earlywood was observed (Fig. 2(A)). Upon aging, the pit-containing regions were partially destroyed or degraded while the cell walls were mostly maintained intact (Fig. 2(B)). While wood cell walls with their rigid layered structure contribute to the majority of mechanical strength of wood, pits tend to be more vulnerable to external aging conditions, such as humidity, heat, UV radiation and any contaminant particles. As a result, wood pits can be considered as aging sensors.

Qualitative and quantitative analysis of surface aging by means of AFM-based adhesion force measurements has already been discussed with smooth and homogeneous polymeric materials [37,38], but not much has been done with wood. In this study, we aim at developing an accurate quantitative AFM-based method to monitor wood aging by measuring the adhesion forces at the wood pits as suggested earlier that they are more susceptible to aging compared to other wood structures. Towards that goal, we aimed at first investigating the sensitivity of AFM in general in detecting the differences in the chemical properties of the different wood structures through adhesion force measurements. To perform the measurements, a region with the target wood structures was selected by imaging the wood surface (Fig. 3). The difference in the brightness is a result of the difference in the height of the different wood structures. From the height profile of the AFM image, the thickness of cell wall and cell lumen can be estimated as ca. 2∼3 μm, 25−30 μm, respectively, which are comparable to similar reported values in the literature [39].

The adhesion force measurements were then performed on each of the four wood structures (CW, CL, PT, and PM) at 20 locations (16 measurements per location) using an unfunctionalized AFM tip (around 200 measurements per wood structure per sample) (Fig. 4). An identical relative adhesion force (RAF) of 11.8 was obtained when measuring the surface of CW and CL. However, the results for the wood pit structures slightly varied; a relatively lower adhesion force of 10.3 ± 1.8 was obtained for PT while a higher value of 12.4 ± 2.8 was obtained for PM. To statistically determine if there is actually a significant difference between the measured RAF results, ANOVA analysis was performed (Table 1). No significant difference in the RAF values was observed when it comes to CW and CL as the estimated p-value was more than 0.05 (p-value of 0.905). However, a p-value of 0.002 was obtained between the PT and PM adhesion force values indicating a significant difference. It still seems that the use of unfunctionalized AFM tip fails to distinguish the surface polarity difference between the different wood structures in contrary to few reports in the literature [29]. One of the reasons that there was no clear difference in the RAF values between the different wood structures is the low RAF values (ca. 10) for all the structures indicating a poor interaction between the AFM tip and the wood surface in general. This also implies that AFM using unfunctionalized tips would most probably fail to detect small microstructural changes upon aging.

In an effort to increase the sensitivity of the adhesion measurements, we aimed to maximize the interaction between the AFM tips and wood structures through the use of functionalized AFM tips with high polarity such as hydroxyl groups. As a result, the difference in the RAF between the different wood structures (Pit torus and margo) was more significant. To explore this possibility, the adhesion measurements were performed on the PT and PM surfaces using a hydroxyl-functionalized tip and the results were compared to those obtained using the unfunctionalized tip (Table 2). The results showed that RAF increased significantly from 10.3 to 216.3 and from 12.4 to 530.0 for PT and PM, respectively, upon the use of hydroxyl-functionalized tip. More interesting is the significant difference in the RAF between PT and PM with the use of hydroxyl-functionalized tips as also implied by the drop in the p-value from 0.002 to $7.9 * 10^{-7}$. It is important to mention that this significant difference in RAF was not a result of the difference in surface roughness as the roughness of PT or PM was not different using the different tips (Table 2). In conclusion, the RAF results could imply that AFM with hydroxyl-functionalized tips can be used to detect possible wood chemical and physical changes upon aging.

To explore the possibility of using hydroxyl-functionalized AFM tips to detect wood changes upon aging, the adhesion measurements were performed on PT and PM surfaces of aged wood samples and compared to the previous results for the unaged wood. The wood samples were

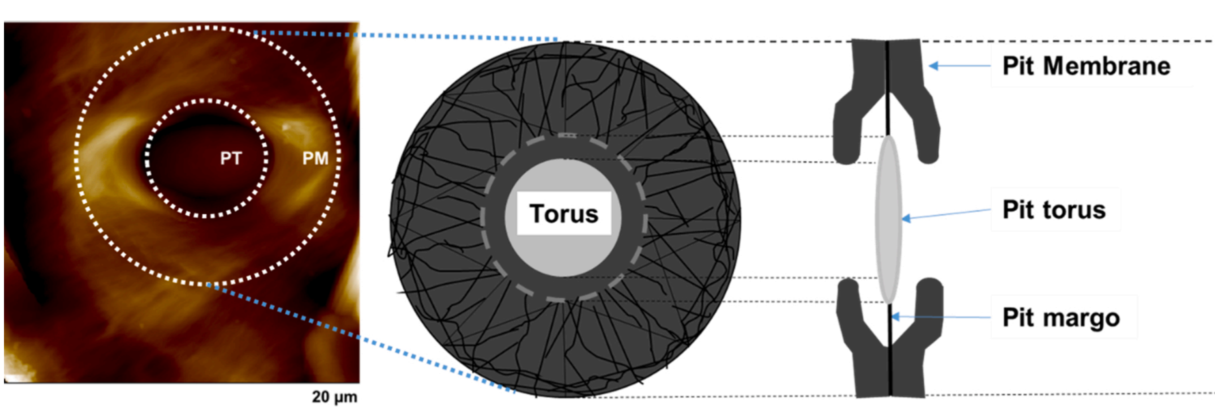

Fig. 1. AFM topography and schematic of a pit with a torus-margo structure in the earlywood of Norway Spruce.

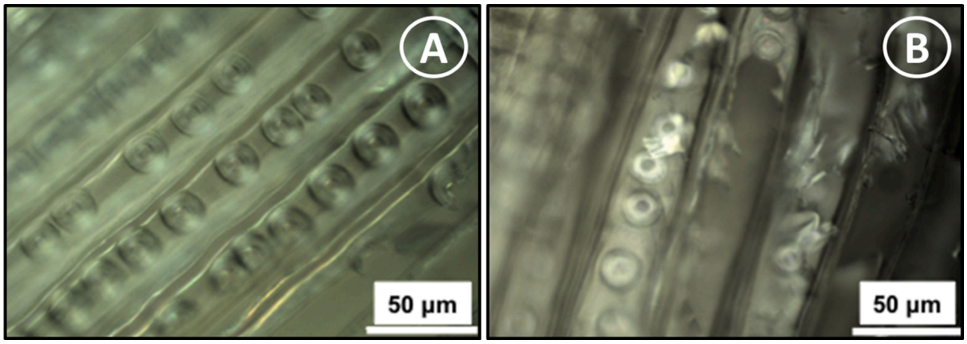

Fig. 2. Light microscopic images of earlywood wood pits in the (a) unaged (b) aged Norway Spruce.

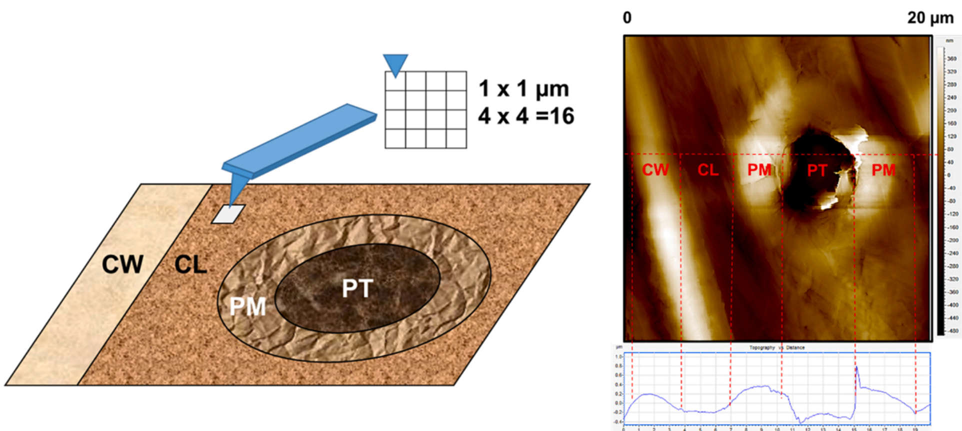

Fig. 3. AFM topography of cell wall (CW), cell lumen (CL), pit torus (PT) and pit margo (PM) in the earlywood of untreated Norway Spruce.

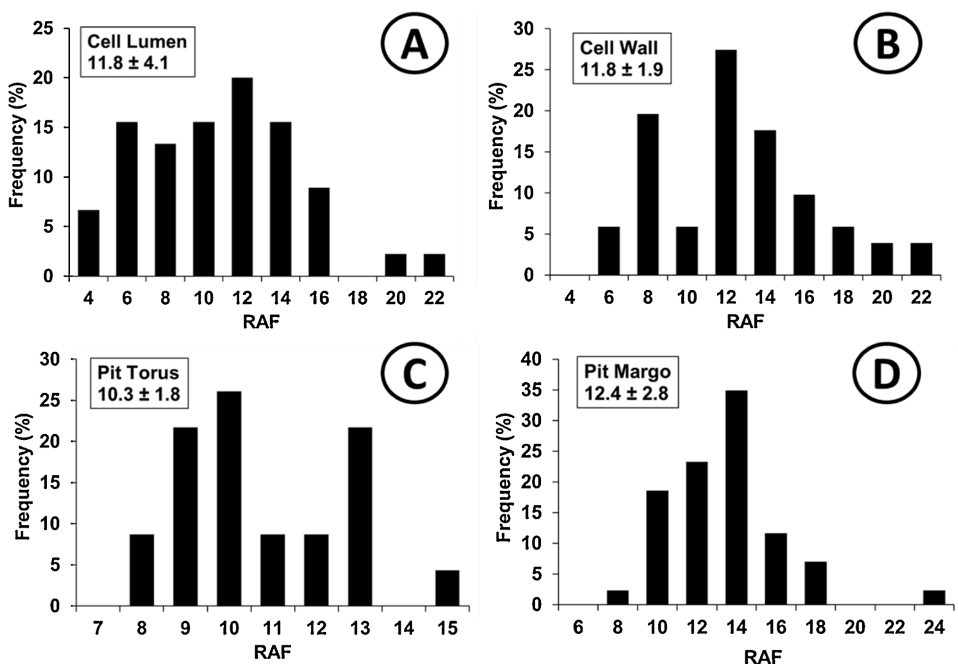

Fig. 4. Histograms of adhesion values obtained for (A) Cell lumen (B) Cell wall (C) Pit torus (D) Pit membrane using non-functional AFM silicon tips. The measurements were conducted under condition of 30 °C, N_2.

artificially aged using an equipment, which is designed to simulate the conditions of outdoor or indoor weathering. It is a combination of mild heating, water spraying, and cyclic UV-radiation. Upon aging, the wood surface became darker, which is one of the typical changes due to UV-radiation [40] (Fig. 5). When it comes to the RAF results, the distribution of the RAF values was significantly affected by the treatment. The relative standard deviation of the RAF obtained with PM increased from 0.2 and 0.3 for the unaged PM and PT to 0.3 and 0.5 for the aged PM and

Table 1
Summary of RAF, surface roughness and p value for the different wood structures for the untreated samples.

Wood Structure	Pit Torus	Pit Margo	Cell Lumen	Cell wall
RAF	10.3 ± 1.8	12.4 ± 2.8	11.8 ± 4.1	11.8 ± 1.9
Surface Roughness (nm)	9.8 ± 1.7	14.3 ± 1.5	10.9 ± 1.6	12.0 ± 2.2
p-value	0.002		0.905	

Table 2
Summary of RAF, surface roughness and p value for the different pit parts using hydroxyl-functionalized and unfunctionalized tips.

Tip	Unfunctionalized		Hydroxyl-Functionalized	
Wood Structure	Pit Torus	Pit Margo	Pit Torus	Pit Margo
RAF	10.3 ± 1.8	12.4 ± 2.8	216.3 ± 64.5	530.0 ± 105.9
Surface Roughness (nm)	9.8 ± 1.7	14.3 ± 1.5	8.8 ± 1.6	15.5 ± 1.5
p-value	0.002		$7.9 * 10^{-7}$	

PT, respectively. This indicates that the artificial aging process increases its heterogeneity. Most importantly, both the PT and PM displayed weaker interaction with the functionalized AFM tip upon treatment as the RAF values decreased by ca. 45 % and 30 %, respectively (Table 3). This indicates that wood upon artificial aging becomes less hydrophilic possibly due to the degradation of cellulose and hemicelluloses [3]. The p-values confirm the significant difference between the RAF values for the unaged and aged wood. These results confirm that the use of hydroxyl-functionalized tips are not only able to detect the differences between wood structures but also any changes could happen to them as a results of aging. It is also clear from the results that PM is more susceptible to aging than PT as the RAF value dropped more significantly upon treatment. This is also evident from the significantly lower p-value for the aged and unaged PM compared to the aged and unaged PT. We, therefore, recommend to study aging by performing the adhesion measurements on PM for maximum accuracy and sensitivity.

During aging, wood undergoes different chemical changes because of its complex nature. For instance, lignin in the cell wall is the most sensitive component to UV light due to its aromatic structure [3,40]. Cellulose degradation also was reported to be taken place as a result of UV transferring from lignin. Moreover, hemicellulose thermal degradation takes place and is mainly responsible for the color change happens on the wood surface [3]. These combined processes lead in general to a gradual hydrophobization of wood surface as shown earlier (Fig. 5 and Table 3). To have a more thorough understanding of wood aging, we recommend the use of AFM tips with different functional groups such as carboxyl, acetyls, methoxyl, in addition to hydroxyl groups used in this study to show what kind of wood components forms or degrade during aging.

4. Conclusions

In this work, AFM-based method was developed and tested to characterize wood surface changes due to treatment simulating ageing. Both

Table 3
Summary of RAF, surface roughness and p-value for the different pit parts for the aged and unaged samples.

Wood Structure	Pit Torus		Pit Margo	
Sample	Unaged	Aged	Unaged	Aged
RAF	216.3 ± 64.5	152.3 ± 68.7	530.0 ± 105.9	301.3 ± 81.5
Surface Roughness (nm)	8.8 ± 1.6	9.3 ± 2.8	15.5 ± 1.5	16.1 ± 2.1
p-value	~0 (2.2×10^{-57})		~0 (6.4×10^{-249})	

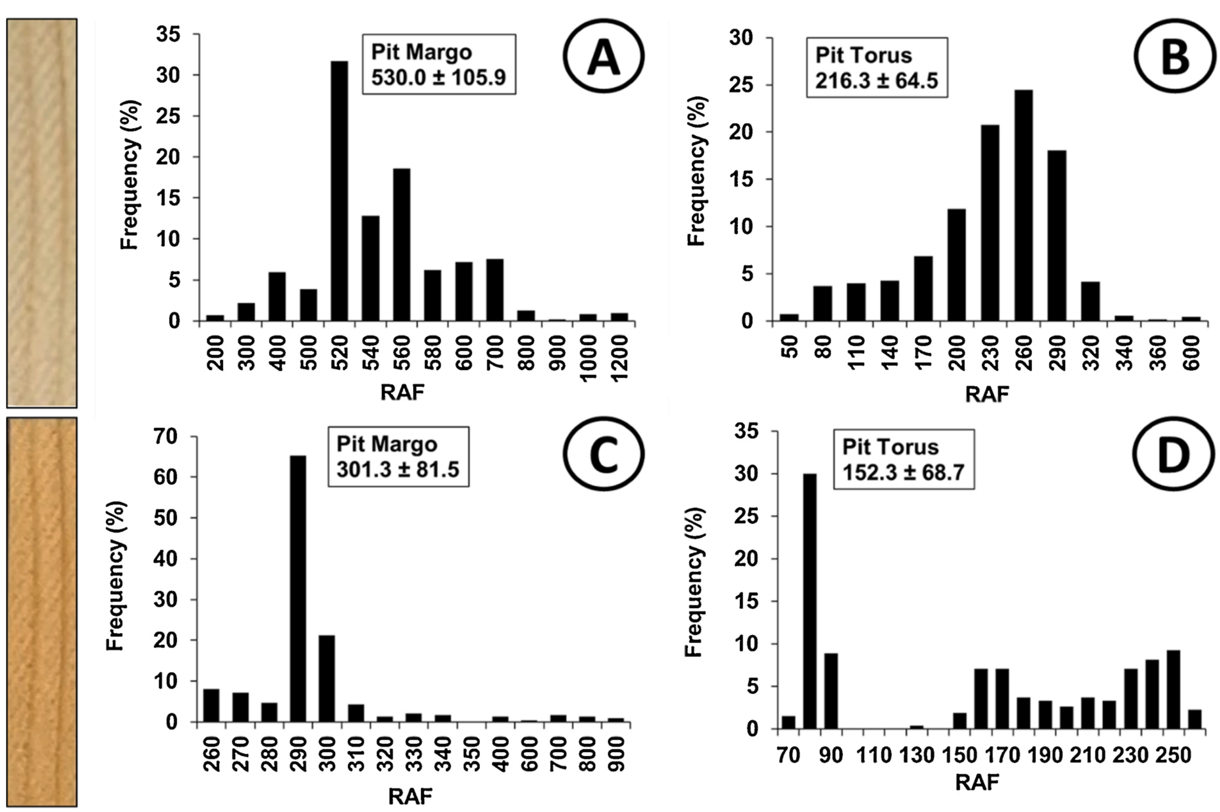

Fig. 5. Histograms of adhesion values obtained for (a) PM and (b) PT in the unaged Norway Spruce; (c) PM and (d) PT in the aged Norway Spruce using OH-functional tips. The measurements were conducted under condition of 30 °C, N_2.

unfunctionalized and hydroxyl-functionalized tips were used to measure the relative adhesion force (RAF) between the tips and targeted surface located at different characteristic anatomies, and wood pits were found more suitable for monitoring aging at earlier stage. Standard tips without any functionalization were not sensitive enough to detect minor aging, while O—H modified tips were preferable as the contrast in obtained RAF between unaged and aged samples was larger, which was also proven statistically by the calculated p values using ANOVA. Note that the variation in RAF was not a result of the difference in surface roughness. Combined artificial aging treatment in this work led to hydrophobization of wood surface, which was validated by the decreased RAF values for both pit margo and torus. It can be stated that measuring adhesion between the functionalized AFM tip and wood pits provides a possibility to monitor wood aging.

CRediT authorship contribution statement

Jia Mao: Conceptualization, Methodology, Investigation. **Hatem Abushammala:** Methodology, Investigation. **Bohumil Kasal:** Supervision, Writing - review & editing.

Declaration of Competing Interest

The authors report no declarations of interest.

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References

[1] M. Bramwell, The International Book of Wood: Mitchell Beazley, Available online at https://books.google.ae/books?id=Mgp_QgAACAAJ, 1976.
[2] Robert L. Youngs, Every age, the age of wood, Interdiscip. Sci. Rev. 7 (3) (1982) 211–219, https://doi.org/10.1179/isr.1982.7.3.211.
[3] Katalin Kránitz, Walter Sonderegger, Claus-Thomas Bues, Peter Niemz, Effects of aging on wood: a literature review, Wood Sci. Technol. 50 (1) (2016) 7–22, https://doi.org/10.1007/s00226-015-0766-0.
[4] Dick Sandberg, Peer Haller, Parviz Navi, Thermo-hydro and thermo-hydro-mechanical wood processing: an opportunity for future environmentally friendly wood products, Wood Mater. Sci. Eng. 8 (1) (2013) 64–88, https://doi.org/10.1080/17480272.2012.751935.
[5] Keisuke Toba, Hiroyuki Yamamoto, Masato Yoshida, Crystallization of cellulose microfibrils in wood cell wall by repeated dry-and-wet treatment, using X-ray diffraction technique, Cellulose 20 (2) (2013) 633–643, https://doi.org/10.1007/s10570-012-9853-7.
[6] Antoine Cogulet, Pierre Blanchet, Véronic Landry, Wood degradation under UV irradiation: a lignin characterization, J. Photochem. Photobiol. B, Biol. 158 (2016) 184–191, https://doi.org/10.1016/j.jphotobiol.2016.02.030.
[7] E. Franceschi, I. Cascone, D. Nole, Thermal, XRD and spectrophotometric study on artificially degraded woods, J. Therm. Anal. Calorim. 91 (1) (2008) 119–123, https://doi.org/10.1007/s10973-007-8372-5.
[8] Susanne Reichel, Michael Kaliske, Hygro-mechanically coupled modelling of creep in wooden structures, part I: mechanics, Int. J. Solids Struct. 77 (2015), https://doi.org/10.1016/j.ijsolstr.2015.07.019.
[9] Susanne Reichel, Michael Kaliske, Hygro-mechanically coupled modelling of creep in wooden structures, Part II: influence of moisture content, Int. J. Solids Struct. 77 (2015) 45–64, https://doi.org/10.1016/j.ijsolstr.2015.07.029.
[10] Accelerated Aging of Materials and Structures: The Effects of Long-Term Elevated-Temperature Exposure (1996). Washington, DC: The National Academies Press. Available online at https://www.nap.edu/catalog/9251/accelerated-aging-of-materials-and-structures-the-effects-of-long.
[11] Tetsuya Inagaki, Heinz W. Siesler, Katsuya Mitsui, Satoru Tsuchikawa, Difference of the Crystal structure of cellulose in wood after hydrothermal and aging degradation: a NIR spectroscopy and XRD study, Biomacromolecules 11 (9) (2010) 2300–2305, https://doi.org/10.1021/bm100403y.
[12] R. Wagenführ, Holzatlas: Fachbuchverlag Leipzig, Available online at, 2007, https://books.google.ae/books?id=hXCGAAAACAAJ.
[13] Juan Guo, Haibin Zhou, Jasna S. Stevanic, Mengyu Dong, Min Yu, Lennart Salmén, Yafang Yin, Effects of ageing on the cell wall and its hygroscopicity of wood in ancient timber construction, Wood Sci. Technol. 52 (1) (2018) 131–147, https://doi.org/10.1007/s00226-017-0956-z.
[14] Asaf Oron, Nili Liphschitz, Benjamin W. Held, Ehud Galili, Micha Klein, Raphael Linker, Robert A. Blanchette, Characterization of archaeological waterlogged wooden objects exposed on the hyper-saline Dead Sea shore, J. Archaeol. Sci. Rep. 9 (2016) 73–86, https://doi.org/10.1016/j.jasrep.2016.06.049.
[15] Luis Esteban, Francisco Garcia Fernández, Antonio Casasús, Paloma Palacios, Joseph Gril, Comparison of the hygroscopic behaviour of 205-year-old and recently cut juvenile wood from Pinus sylvestris L, Ann. For. Sci. (2006) 63, https://doi.org/10.1051/forest:2006010.
[16] Takunori Noguchi, Eiichi Obataya, Kosei Ando, Effects of aging on the vibrational properties of wood, J. Cult. Herit. 13 (2012) S21–S25, https://doi.org/10.1016/j.culher.2012.02.008.
[17] Walter Sonderegger, Katalin Kránitz, Claus-Thomas Bues, Peter Niemz, Aging effects on physical and mechanical properties of spruce, fir and oak wood, J. Cult. Herit. 16 (6) (2015) 883–889, https://doi.org/10.1016/j.culher.2015.02.002.
[18] Christelle Ganne-Chédeville, Anna-Stiina Jääskeläinen, Julien Froidevaux, Mark Hughes, Parviz Navi, Natural and artificial ageing of spruce wood as observed by FTIR-ATR and UVRR spectroscopy, Holzforschung 66 (2) (2012) 163–170, https://doi.org/10.1515/HF.2011.148.
[19] Jia Mao, Barbara Heck, Hatem Abushammala, Günter Reiter, Marie-Pierre Laborie, A structural fibrillation parameter from small angle X-ray scattering to quantify pulp refining, Cellulose 26 (7) (2019) 4265–4277, https://doi.org/10.1007/s10570-019-02386-0.
[20] Hatem Abushammala, Jorge F. Pontes, Gustavo H. Gomes, Anayancy Osorio-Madrazo, Rossana M.S.M. Thiré, Fabiano V. Pereira, Marie-Pierre G. Laborie, Swelling, viscoelastic, and anatomical studies on ionic liquid-swollen Norway spruce as a screening tool toward ionosolv pulping, Holzforschung 69 (9) (2015) 1059–1067, https://doi.org/10.1515/hf-2014-0292.
[21] Xu Cheng, Karl W. Putz, Charles D. Wood, L. Catherine Brinson, Characterization of local elastic modulus in confined polymer films via AFM indentation, Macromol. Rapid Commun. 36 (4) (2015) 391–397, https://doi.org/10.1002/marc.201400487.
[22] Kirstin Casdorff, Tobias Keplinger, Ingo Burgert, Nano-mechanical characterization of the wood cell wall by AFM studies: comparison between AC- and QI^{TM} mode, Plant Methods 13 (1) (2017) 60, https://doi.org/10.1186/s13007-017-0211-5.
[23] Jia Mao, Anayancy Osorio-Madrazo, Marie-Pierre Laborie, Preparation of cellulose I nanowhiskers with a mildly acidic aqueous ionic liquid: reaction efficiency and whiskers attributes, Cellulose 20 (4) (2013) 1829–1840, https://doi.org/10.1007/s10570-013-9942-2.
[24] Jia Mao, Hatem Abushammala, Nicole Brown, Marie-Pierre Laborie, Comparative assessment of methods for producing cellulose I nanocrystals from cellulosic sources, Nanocelluloses: Their Preparation, Properties, and Applications, American Chemical Society (ACS Symposium Series, 1251) vol. 1251 (2017) 19–53.
[25] Kirstin Casdorff, Tobias Keplinger, Markus Rüggeberg, Ingo Burgert, A close-up view of the wood cell wall ultrastructure and its mechanics at different cutting angles by atomic force microscopy, Planta 247 (5) (2018) 1123–1132, https://doi.org/10.1007/s00425-018-2850-9.
[26] Stephan Frybort, Michael Obersriebnig, Ulrich Müller, Wolfgang Gindl-Altmutter, Johannes Konnerth, Variability in surface polarity of wood by means of AFM adhesion force mapping, Colloids Surf. A Physicochem. Eng. Asp. 457 (2014) 82–87, https://doi.org/10.1016/j.colsurfa.2014.05.055.
[27] X. Jin, B. Kasal, Adhesion force mapping on wood by atomic force microscopy: influence of surface roughness and tip geometry, R. Soc. Open Sci. 3 (10) (2016) 160248, https://doi.org/10.1098/rsos.160248.
[28] M. Obiols-Rabasa, G. Oncins, F. Sanz, Th.F. Tadros, C. Solans, B. Levecke, et al., Investigation of the elastic and adhesion properties of adsorbed hydrophobically modified inulin films on latex particles using Atomic Force Microscopy (AFM), Colloids Surf. A Physicochem. Eng. Asp. 524 (2017) 185–192, https://doi.org/10.1016/j.colsurfa.2017.04.048.
[29] Jérôme Colson, Laurin Andorfer, Tiina Elina Nypelö, Bernd Lütkemeier, Frank Stöckel, Johannes Konnerth, Comparison of silicon and OH-modified AFM tips for adhesion force analysis on functionalised surfaces and natural polymers, Colloids Surf. A Physicochem. Eng. Asp. 529 (2017) 363–372, https://doi.org/10.1016/j.colsurfa.2017.06.017.
[30] K. Meine, K. Kloß, T. Schneider, D. Spaltmann, The influence of surface roughness on the adhesion force, Surf. Interface Anal. 36 (8) (2004) 694–697, https://doi.org/10.1002/sia.1738.
[31] Monica Ek, G.öran Gellerstedt, Gunnar Henriksson, Wood Chemistry and Wood Biotechnology, Available online at, De Gruyter, Berlin, Boston, 2016, https://www.degruyter.com/view/title/34117.
[32] Brendan Choat, Alexander R. Cobb, Steven Jansen, Structure and function of bordered pits: new discoveries and impacts on whole-plant hydraulic function, New Phytol. 177 (3) (2008) 608–625, https://doi.org/10.1111/j.1469-8137.2007.02317.x.
[33] Josef Bauch, Heide Berndt, Variability of the chemical composition of pit membranes in bordered pits of gymnosperms, Wood Sci. Technol. 7 (1) (1973) 6–19, https://doi.org/10.1007/BF00353374.
[34] Daniela Altgen, Barry Goodell, Jody Jellison, Mark Lessard, Holger Militz, A new approach for the study of the chemical composition of bordered pit membranes: 4Pi and confocal laser scanning microscopy, Am. J. Bot. 100 (2013), https://doi.org/10.3732/ajb.1300004.
[35] Susanne M. Jutte, John F. Levy, The structure and degradation of bordered pits in gymnosperm tracheids as revealed by the scanning reflection electron microscope,

Acta Bot. Neerl. 20 (5) (1971) 453–466, https://doi.org/10.1111/j.1438-8677.1971.tb00730.x.
[36] Martina Meincken, Philip D. Evans, Nanoscale characterization of wood photodegradation using atomic force microscopy, Holz Als Roh- Und Werkst. 67 (2) (2009) 229–231, https://doi.org/10.1007/s00107-008-0305-x.
[37] Matteo Chiesa, Chia-Yun Lai, Surface aging investigation by means of an AFM-based methodology and the evolution of conservative nanoscale interactions, Phys. Chem. Chem. Phys. 20 (29) (2018) 19664–19671, https://doi.org/10.1039/C8CP03454K.
[38] Anna Tarasova, Paul Hamilton-Brown, Thomas Gengenbach, Hans Griesser, Laurence Meagher, Colloid probe AFM and XPS study of time-dependent aging of amine plasma polymer coatings in aqueous media, Plasma Process. Polym. 5 (2008) 175–185, https://doi.org/10.1002/ppap.200700054.
[39] Dietrich Fengel, Manfred Stoll, Über die Veränderungen des Zellquerschnitts, der Dicke der Zellwand und der Wandschichten von Fichtenholz-Tracheiden innerhalb eines Jahrringes, Holzforschung 27 (1) (1973) 1–7, https://doi.org/10.1515/hfsg.1973.27.1.1.
[40] Mon-lin Kuo, Ninghe Hu, Ultrastructural Changes of Photodegradation of Wood Surfaces Exposed to UV, Holzforschung 45 (5) (1991) 347–353, https://doi.org/10.1515/hfsg.1991.45.5.347.