

## Article

# Coatings Adhesion on Chemically Modified Scots Pine (*Pinus sylvestris* L.) Woods

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**Abstract:** Synergizing coating and wood modification is a promising concept to develop wood products that have multi-qualities that include excellent dimensional stability, durability, and weathering resistance. However, the nature of the modified substrate is a critical parameter for coating adhesion. Chemical modification of wood impacts the physicochemical properties of the wood, which could in turn impact the adhesion of coatings. Therefore, this study investigated the adhesion of seven different coatings to *Pinus sylvestris* L. woods chemically modified through esterification with acetic anhydride (acetylated), etherification with 1,3-dimethylol-4,5-dihydroxyethyleneurea (DMDHEU), and esterification with sorbitol/citric acid formulation (SorCA). The selected coatings include water-based and solvent-based examples with different binder constituents that include acrylate, alkyd, natural oil, and hybrids. Coating adhesion to the modified wood was evaluated in terms of crosscut resistance to detachment, wear-resistant hardness, and pull-off strength. Chemical modifications yielded positive impacts on coating adhesion compared to unmodified wood. Coatings adhered better to acetylated and DMDHEU-modified *P. sylvestris* wood than on SorCA-modified wood. Solvent-based coatings had higher adhesion strength on the acetylated, DMDHEU-modified, and unmodified woods than water-based coatings. On the other hand, water-based coatings mostly adhered better to SorCA-modified wood compared to solvent-based coating. Overall, the coating of chemically modified *P. sylvestris* wood is promising for the development of an enhanced wood protection system.



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**Keywords:** adhesion; coatings; wood modification; *Pinus sylvestris*

## 1. Introduction

Despite the widely acknowledged benefits of wood, which include renewability, carbon reservoir, aesthetics, etc., moisture-related and durability problems are major drawbacks for its use as a building and construction material [1]. Natural wood is prone to dimensional instability, biodeterioration and weathering degradation. Thus, adequate wood protection mechanisms are needed to ensure long-term maximization of its beneficial attributes [1]. Coating modified wood is a promising integrated approach to resolving the above-mentioned drawbacks [2] and can be tailored to create a new paradigm in wood protection. Different wood modification technologies, such as thermal, resin impregnation, and chemical modifications, have been successfully used, to varying degrees, to improve wood's dimensional stability, resistance to biodegradation, and to a certain extent its weathering resistance [3]. These wood modification technologies are well elucidated in the literature [4–9].

Coatings are used to protect natural wood properties against degradation caused by moisture intrusion, biological attack, photoirradiation, chemically and mechanically induced damages, etc., [1,10,11]. Substrate coatibility and coating performance depend on the substrate's nature as well as the coating type. Essentially, coating adhesion to wood is vital to its finish quality and service life [12]. Likewise, the physicochemical nature of wood is fundamental to the development of the wood–coating adhesion interface [13]. Chemical

modification alters the physical and chemical properties of wood, which could in turn impact coating adhesion. It is therefore important to establish the coatability of chemically modified wood substrates.

Chemical modification of wood through acetylation (esterification with acetic anhydride) and etherification with 1,3-dimethylol-4,5-dihydroxyethyleneurea have been extensively researched and are now commercially available wood modification processes. Likewise, esterification of wood with a sorbitol and citric acid formulation has been well researched but remains pending commercialization [3]. Nevertheless, coatings adhesion on woods modified with these chemical modification processes still require further exploration, hence the focus of this study. Furthermore, the possibility of achieving improved wood properties through a synergy of chemical modification and coating would broaden the opportunities for wood utilization by delivering unique wood products with characteristics that include dimensional stability due to hydrophobization, durability against biodeterioration, and weathering resistance.

## 2. Materials and Methods

### 2.1. Wood Samples

Scots pine (*Pinus sylvestris* L.) wood was sourced from northern Germany. Modified *P. sylvestris* woods were derived from three different chemical modification processes: esterification with acetic anhydride (acetylated), etherification with 1,3-dimethylol-4,5-dihydroxyethyleneurea (DMDHEU), and esterification with sorbitol and citric acid (SorCA). Unmodified *P. sylvestris* wood was used as reference in this study. The mean densities and moisture contents (MC) of the *P. sylvestris* woods were 520 kg/m<sup>3</sup> and 2.13% MC for acetylated samples, 560 kg/m<sup>3</sup> and 9.63% MC for DMDHEU-modified samples, 580 kg/m<sup>3</sup> and 4.42% MC for SorCA-modified, and 610 kg/m<sup>3</sup> and 10.68% MC for unmodified reference samples. Boards of *P. sylvestris* wood were sent to Accsys<sup>®</sup> in Arnhem, The Netherlands for acetylation. The mean weight percent gain (mWPG) of the selected acetylated boards used in this study was 30%. DMDHEU and SorCA modifications were performed at the Wood Biology and Wood Products Laboratory, Georg-August-University, Göttingen, Germany. Both DMDHEU and SorCA modification processes involved a dual-phase process consisting of vacuum-pressure impregnation followed by high-temperature curing. Briefly, vacuum-pressure impregnation of *P. sylvestris* wood with 25% DMDHEU solution was conducted at 5 kPa vacuum for 4 h, followed by 800 kPa pressure for 10 h and a final vacuum of 5 kPa for 20 min. Thereafter, the DMDHEU-impregnated samples were climatized at (20 ± 2) °C and (65 ± 5)% relative humidity (RH) for 168 h before curing at 120 °C for 48 h. A 30% SorCA solution consisting of sorbitol/citric acid ratio 1:3 (v/v) was vacuum-pressure impregnated into *P. sylvestris* wood samples at 5 kPa vacuum for 2 h and 1000 kPa pressure for 4 h. Thereafter, the SorCA-impregnated samples were kept in laboratory conditions for 4 weeks before high-temperature curing rising to 140 °C over a 24 h period. The mWPGs for the cured DMDHEU- and SorCA-modified *P. sylvestris* woods were 28% and 23%, respectively. The modified and unmodified *P. sylvestris* woods are hereafter classified under the *P. sylvestris* wood type.

### 2.2. Coatings

Seven coatings were investigated in this study. Details regarding reference codes, formulation, properties, and the manufacturers' recommended application rates are presented in Table 1. Coats DL8170 and AG7016 were supplied by Doerken Coatings GmbH & Co. KG, Herdecke, Germany, while H210, H230, H320, H415, and H430 were supplied by Koch & Schulte GmbH & Co. KG, Linden, Germany.

**Table 1.** Coatings formulation basis, properties, and application rates.

Coat	Ref. Code	Formulation		Density (g/cm <sup>3</sup> ) *	Dynamic Viscosity (mPa·s) *	Spread Rate (mL/m <sup>2</sup> )
		Basis	Binder(s)			
WoodColor m 6.15 W 100 delta glazes 8170 walnut	DL8170	Water	Pure acrylate	0.98	3596 at 30 rpm SP-3	80–150
Wood preservative glaze (thin film glaze) KS 7940 ruby grey	H210	Solvent	Alkyd resin	0.85	77.8 at 60 rpm SP-1	80–110
Leonardo Hydrolasur (hybrid glaze) KS 7940 ruby grey	H230	Water	Hybrid: Pure acrylate-alkyd resins	0.89	10.7 at 60 rpm SP-1	80–110
Hydrostop H <sub>2</sub> O natural grey KS 7940 ruby grey	H320	Water-oil complex	Alkyd resin and natural oils	0.84	11.4 at 60 rpm SP-1	80–120
Lignolan weather protection paint KS 0275 Swedish red	H415	Water	Pure acrylate	0.97	1556 at 30 rpm SP-3	100–150
Lignolan Swedish house paint KS 0275 Swedish red	H430	Water	Alkyd resin	0.93	3408 at 30 rpm SP-3	100–150
Wood Color m 6.15 W 100 RAL7016 Anthracite Grey	AG7016	Water	Pure acrylate	1.06	2796 at 30 rpm SP-3	80–150

\* As determined in this study at  $21 \pm 1$  °C and viscosity measurement time of 1 min using IKA ROTAVISC lo-vi viscometer (IKA-Werke GmbH & Co. KG, Staufen, Germany).

### 2.3. Test Panel Preparation and Coating Application

Planned wood samples of 15 mm × 50 mm × 300 mm (thickness × width × length) were obtained from each *P. sylvestris* wood type. All test samples were conditioned in standard climate ( $20 \pm 2$  °C and  $65 \pm 5\%$  RH) until constant mass, i.e., mass change less than 0.2% at 24 h interval as prescribed in the DIN EN 927-5:2006 standard [14]. Before coat application, test panels were cleaned by brushing off any dirt, dust, or debris. For application uniformity, each coating was applied in two layers at a 100 mL/m<sup>2</sup> spread rate per layer. Coating application was carried out using a fine synthetic fiber-based brush—AquaSol 1526 flat brush (Wistoba GmbH & Co. KG, Bad Lauterberg im Harz, Germany). The AquaSol 1526 brush is suitable for water-based, solvent-based, and glaze coatings. The manufacturers' recommended time intervals between applications of coat layers (recoatable time) were observed as stated in Table 2. All coated substrates (see Appendix A) were cured in standard climate for 2 weeks.

**Table 2.** Coatings dry-to-touch and recoatable times based on manufacturers' specifications.

Coat	DL8170	H210	H230	H320	H415	H430	AG7016
Dry-to-touch	1 h	6 h	20 min	12 h	1 h	2 h	1 h
Recoatable	4 h	24 h	1 h	Within 8 h *	4 h	6 h	4 h

\* 7 h was adopted in this study.

### 2.4. Dry Film Thickness Measurement

The dry film thickness of coatings was measured using a TQC PIG device (SUPERPIG SP1000-78, mtv Messtechnik, Erfstadt, Germany) equipped with a cutter, a 50× magnification microscope with rotating gradient scale 0.00–2.50 mm, and a thickness measurement range of 2–2000 µm. Three black lines perpendicular to the wood's longitudinal axis, one approximately 30 mm away from each end and one around the mid-section, were drawn on the surface of each coated *P. sylvestris* wood type (see Appendix A). A SUPERPIG cutter with 45° cutting angle was used to make two approximately 30 mm cuts across the drawn black lines, cutting down to the substrate. In accordance with the SUPERPIG thickness determination procedure, counts of graduation marks over the cut area for measurement as seen through the device's microscope were multiplied by a corresponding cutter multiplication factor of 20 to obtain the dry film thickness of each coating. Twelve thickness measurements were performed per coated *P. sylvestris* wood category.

### 2.5. Assessment of Coating Resistance to Detachment in Dry State: Crosscut Test

The detachment resistance of fully cured coatings on *P. sylvestris* wood types was assessed via a crosscut adhesion test in accordance with the DIN EN ISO 2409:2013 standard [15]. A cutting blade with a 20° to 30° edge guided by a 2 mm cross-cut plate (MTV Messtechnik oHG, Erfstadt, Germany) was used to cut six parallel incisions that were subsequently crosscut by six perpendicular incisions on each coated *P. sylvestris* wood type (see Appendix A). A pressure-sensitive tape with its long axis oriented in the grain direction of the coated *P. sylvestris* wood was plastered over the crosscut incisions. The tape was smoothed into place to dispel air and ensure firm attachment, particularly at the intersection of the incisions. Within 5 minutes of tape attachment, the tape was rapidly pulled from the free end back upon itself at an angle as close to 60° as possible. Squares at the crosscut intersection were visually assessed for loss of coatings and graded according to DIN EN ISO 2409:2013 categorization [15]. Four crosscut incisions were made and evaluated per coated *P. sylvestris* wood category.

### 2.6. Determination of Coating Wear-Resistant Hardness

The wear resistance of each coating on each *P. sylvestris* wood type was determined using a hardness test rod equipped with a 0.75 mm probe and a 20 N capacity spiral steel spring (HPS, MTV Messtechnik oHG, Erfstadt, Germany). With the aid of the spiral spring, the hardness rod was pretensioned at an incremental unit of 1 N. The probe of the pretensioned hardness rod was fixated onto the coated surface and pull-driven along the wood grain direction. For each *P. sylvestris* wood type, the hardness probe drive process was repeated for every pretension force increment until slight damage to the coating was observed. The pretension force at which coating damage occurred was recorded as the wear-resistant hardness. Six wear-resistant hardness determinations were made per coated *P. sylvestris* wood category.

### 2.7. Determination of Coating Wet Adhesion Strength: Pull-Off (Tensile) Test

Wet adhesion strength is a measure of coating resistance to detachment under a simulated humidity load. The wet adhesion strength of each coating on each *P. sylvestris* wood type was evaluated via a pull-off test in accordance with the DIN EN ISO 4624:2016 standard [16]. Five aluminium dollies were glued using Araldite® adhesive onto each coated *P. sylvestris* wood type and cured in laboratory conditions for 48 h. A ring-like groove was cut around each glued dolly to isolate the coated area under the attached dolly from the lateral strength of other coated parts of the substrate surface (see Appendix A). To simulate the humidity load for accelerated weakening of the coating adhesion, 0.5 mL deionized water was dosed into each ring-like groove while allowing a penetration period of 2 h before conducting the pull-off test. The pull-off strength in terms of maximum tensile pull-off force relative to the dolly area was determined using a PosiTest® Pull-Off Adhesion Tester equipped with an actuator, a hydraulic pump, and a pressure gauge (Model 3500, DeFelsko Corporation, New York, NY, USA). The pull-off testing procedure with the PosiTest Adhesion Tester was carried out following the manufacturer's instructions. A qualitative assessment of the dolly and substrate was made to determine the fracture pattern (see Appendix A). The pull-off adhesion strength, in megapascals (MPa), and, where applicable, the estimated cohesive fractures within the wood or coatings (to nearest 5%) were recorded. Ten pull-off strength determinations were made per coated *P. sylvestris* wood category.

### 2.8. Statistical Analysis

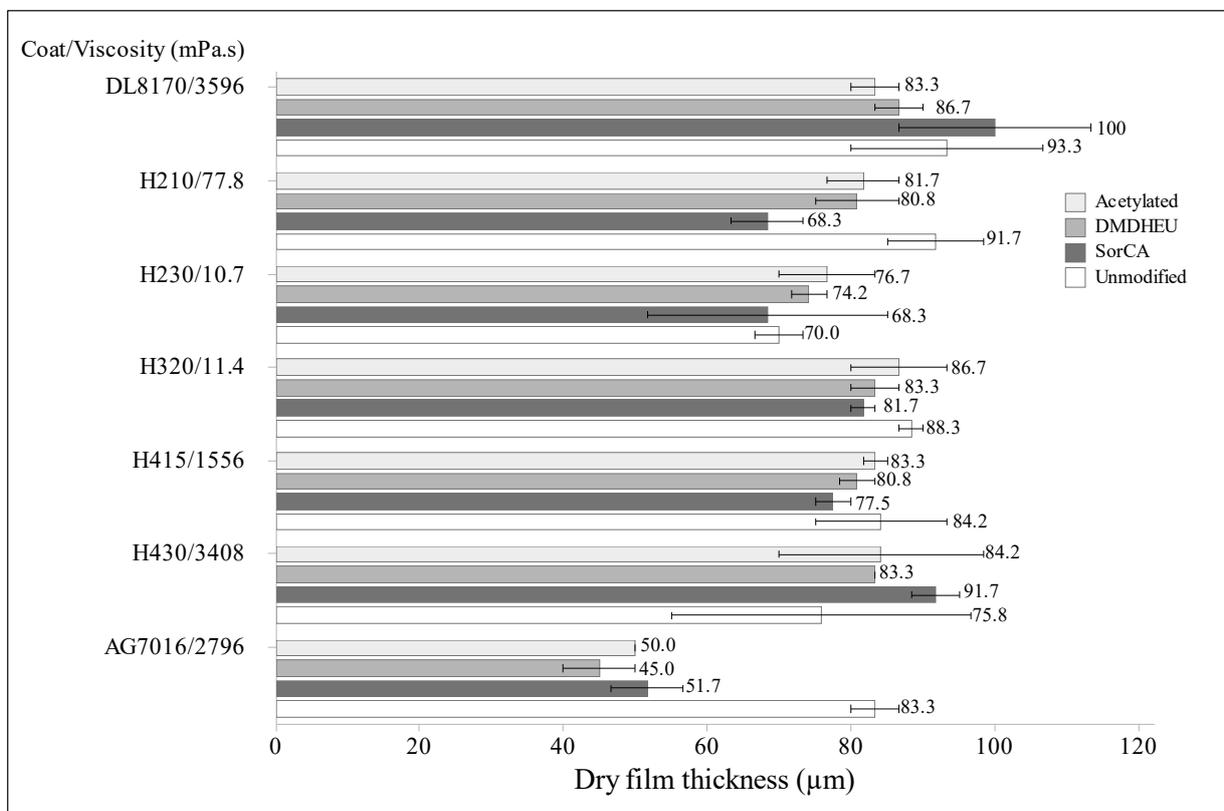
Factorial analysis of variance (ANOVA) was performed to determine the interaction and main effects of wood and coatings on the dry film thickness, wear-resistant hardness, and pull-off strength of the coated *P. sylvestris* wood types. Assumptions of normality and homoscedasticity of data were validated using a Q-Q plot of fitted linear model residuals and a scatterplot of residuals versus predicted values from the fitted model,

respectively. For potential outliers, statistical analysis was conducted at instances including and excluding the outliers. For wear-resistant hardness, the statistical significance of the coefficients was the same with and without the outliers, hence the outliers were retained. On the other hand, for dry film thickness and pull-off strength, the outlier effect influenced the statistical significance of the coefficients, hence the outliers were excluded. Due to the obtained significant wood type and coating interaction effect on the wear-resistant hardness and pull-off strength, the independent variables were concatenated. A one-way ANOVA was performed based on the concatenated variable. Pairwise mean comparisons were conducted using the Tukey post hoc test. All statistical analysis was performed using R programming software (RStudio 2023.06.1 Build 524, Posit Software, PBC, Boston, MA, USA).

### 3. Results and Discussion

#### 3.1. Dry Film Thickness

Coating thickness influences its toughness and wear-resistant properties [17] and also impact its adhesion to the substrate [18]. Therefore, it is important, particularly for comparative assessment, to determine the thicknesses of coatings. As obtained in this study, the dry film thickness was mostly influenced by the coating type; only in a few cases (mostly involving SorCA) was the dry film thickness on modified wood significantly lower than that of unmodified wood. The obtained mean dry film thickness ranged from 45  $\mu\text{m}$  to 100  $\mu\text{m}$  (Figure 1). The observed dry film thickness variations are attributable to the coating formulation basis and viscosity. Based on the results obtained in this study, coatings with any or a combination of three characteristics—higher viscosity, solvent-based, or water–oil complex-based—are mostly found to have higher dry film thicknesses, suggesting limited coating penetration into the wood during the penetration phase, i.e., the period between coating application and curing. Usually, the higher the coating viscosity, the thicker the dry film thickness, as per the results obtained in this study (Figure 1).



**Figure 1.** Dry film thicknesses of coatings on modified and unmodified *P. sylvestris* L. woods. Note: Data labels are mean values and bars are one standard error from the mean.

De Meijer [18] pointed out that coating penetration into wood is contingent on its viscosity. The author further noted that wood's selective absorption of water or solvent from a coating would increase the coat viscosity, thereby limiting the actual coat penetration. Zigon et al. [19] also reported higher coat film thickness for more viscous coatings on differently pretreated beech woods. An exception to the trend of viscosity's effect on dry film thickness as observed in this study was coat AG7016, which had high viscosity (2796 mPa·s) but a thinner dry film thickness (45.0–51.7  $\mu\text{m}$ ) on modified *P. sylvestris* woods. Compared to other high viscosity coatings, coat AG7016 also recorded a substantial difference in mean dry film thickness on modified compared to unmodified (83.3  $\mu\text{m}$ ) *P. sylvestris* wood. While its dry film thickness tends to suggest deeper penetration of coat AG7016 into the modified wood samples, such a claim is considered premature and inconclusive in this study, pending penetrability investigation in our other studies. Regarding the effect of coating formulation, considering the dry film thicknesses of coats H210 and H230 (68.3  $\mu\text{m}$ ) on SorCA-modified *P. sylvestris* wood, it is plausible to assume better penetration of SorCA-modified wood by less viscous alkyd binder-based coatings. De Meijer [18] noted that alkyd binders possess better penetration capacity than acrylic dispersions. However, the natural oil constituent in the binder for coat H320 could limit the coating penetration despite its low viscosity and alkyd constituent in the binder system, hence the thicker coat dry film obtained. Nonetheless, a penetrability study is also required and planned in our further studies to substantiate the assumptions of coating penetration into SorCA-modified wood. Penetrability assessment is usually based on fluorescence microscopy involving dye mixing with a binder or coating, which could impact the binder or coating properties [18]. Such interference would impact coating adhesion, which is the focus of this study, hence a penetration investigation was not conducted in this study. Based on the outcome of factorial ANOVA, the difference in dry film thickness attributable to the interaction effect between a *P. sylvestris* wood type and a coating was not significant ( $p > 0.05$ ), whereas the main effects of *P. sylvestris* wood type and coat were statistically significant ( $p < 0.05$ ) (Table 3). Based on Tukey post hoc analysis for the main effects of *P. sylvestris* wood types, pairwise mean comparison of dry film thickness was significant ( $p_{\text{adj}} < 0.05$ ) only for the recorded difference between unmodified vs. SorCA-modified samples (Table 3). Other pairwise mean comparisons for dry film thickness based on the main effects of *P. sylvestris* wood types were not significantly different ( $p_{\text{adj}} > 0.05$ ). The pairwise mean comparison based on coating main effect revealed that the dry film thickness of coat AG7016 was significantly different from all other coatings ( $p_{\text{adj}} < 0.05$ ), and the difference between coats H430 vs. H320 was statistically significant ( $p_{\text{adj}} < 0.05$ ) (Table 3). Thus, the dry film thickness significantly depends on the coating properties and to a limited extent on the wood modification.

### 3.2. Coating Resistance to Detachment in Dry State: Crosscut Adhesion Grading

Mostly, coatings on modified woods attained the same or closely comparable resistance to detachment as those on unmodified wood. Between the modified woods, coating resistance to detachment was usually better on acetylated and DMDHEU-modified samples than on SorCA-modified wood. Based on DIN EN ISO 2409 categorization, crosscut adhesion of coatings on the different *P. sylvestris* wood types ranged from grade 4 (about 65% coat detachment) to grade 0 (no detachment) (Table 4). The DIN EN ISO 2409 grades 1, 2, and 3 correspond to about 5%, 15%, and 35% coat detachment, respectively. The effect of wood modification on the coating resistance to detachment was not drastically pronounced except for coats H230 (about 65% detachment) and AG7016 (about 15% detachment) on SorCA-modified *P. sylvestris* woods, and coat H415 (about 15% detachment) on acetylated *P. sylvestris* wood. A major influencing factor for coating resistance to detachment is the mechanism of adhesion to the substrate, which also depends on coating properties, substrate nature, and coating penetration. Water-based coatings usually bond to wood via mechanical interlocking, while solvent-based coatings can bond to wood by mechanical and chemical means [12,20]. Hence, to better understand coating resistance to detachment

on the modified woods, our subsequent investigations will include evaluation of the mechanism(s) of coating adhesion on the modified woods.

**Table 3.** Factorial ANOVA and Tukey post hoc results for dry film thickness of coating on *P. sylvestris* L. wood type.

Factorial ANOVA					
Source of Variation	df	Sum of Squares	Mean Squares	F Value	Pr(>F)
<i>P. sylvestris</i> wood type	3	1044	348.0	4.107	0.0164 *
Coat	6	5550	924.9	10.917	$4.48 \times 10^{-6}$ ***
<i>P. sylvestris</i> wood type $\times$ Coat	18	1734	96.3	1.137	0.3745
Residuals	26	2203	84.7		
Tukey Post Hoc Analysis <sup>1</sup>					
Group Comparison	Difference	Lower	Upper	<i>p</i> adj	
<i>P. sylvestris</i> wood type main effect					
Unmodified-SorCA	11.79	1.89	21.70	0.015 *	
Coat main effect					
AG7016-DL8170	−29.49	−44.69	−14.29	$2.83 \times 10^{-5}$ ***	
AG7016-H210	−23.13	−37.81	−8.44	$5.57 \times 10^{-4}$ ***	
H430-H230	16.62	1.42	31.82	0.025 *	
AG7016-H230	−14.79	−29.47	−0.11	0.047 *	
AG7016-H320	−27.50	−42.18	−12.82	$4.88 \times 10^{-5}$ ***	
AG7016-H415	−23.96	−38.64	−9.28	$3.50 \times 10^{-4}$ ***	
AG7016-H430	−31.41	−46.61	−16.22	$1.03 \times 10^{-5}$ ***	

Significance codes: \*\*\*  $p < 0.001$ , \*  $p < 0.05$ . <sup>1</sup> Only group pairs with statistically significant differences are presented.

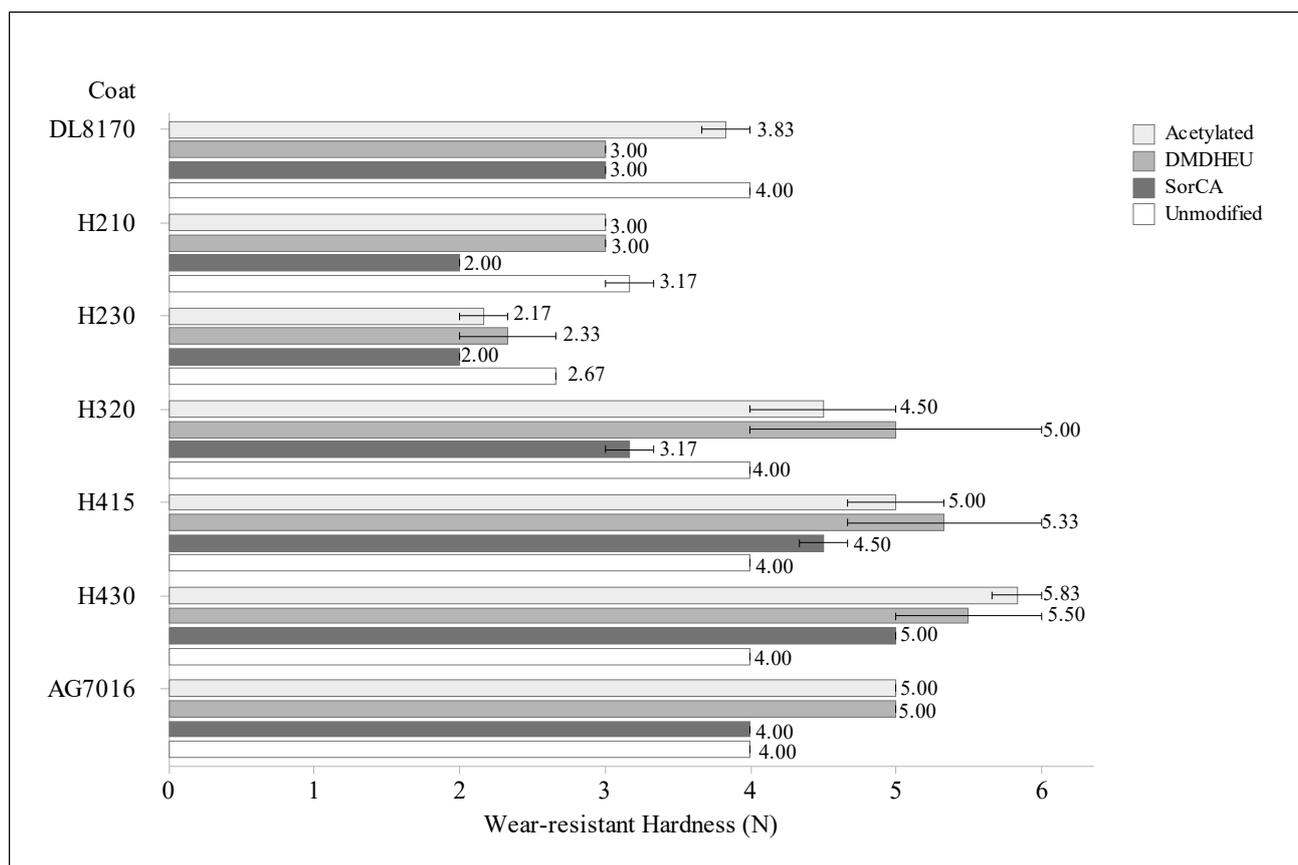
**Table 4.** Crosscut adhesion grade of coatings on *P. sylvestris* wood types according to DIN EN ISO 2409 categorization [15].

Coat	<i>P. sylvestris</i> Wood Type			
	Acetylated	Modified DMDHEU	SorCA	Unmodified
DL8170	0	0	1	0
H210	0	0	1	0
H230	0	1	4	0
H320	0	0	1	0
H415	2	0	0	0
H430	1	1	1	1
AG7016	1	0	2	0

### 3.3. Wear-Resistant Hardness of Coatings

During service life, it is expected that coatings on wood would encounter mechanical wear to a degree dependent on use application. Such mechanical wear could lead to scratches and consequently diminish coatings' ability to protect the wood [1]. Based on the results obtained in this study, both wood modification and coating type had varied effects on the wear resistance of coatings on *P. sylvestris* wood. For most of the investigated coatings, wear-resistant hardness was higher on modified woods than on unmodified samples. Also, coatings mostly attained higher wear-resistant hardness on acetylated and DMDHEU-modified samples than on SorCA-modified samples (Figure 2). The obtained wear-resistant hardness of coatings on the modified *P. sylvestris* woods can be classified into three categories. The first category comprises coats H415 and H430, both having recorded higher mean wear-resistant hardness, 4.50 N–5.83 N, for all modified woods, compared to 4.00 N for each coated unmodified wood sample. The second category comprises coats H320 and AG7016, which recorded higher mean wear-resistant hardness,

4.50 N–5.00 N, only on acetylated and DMDHEU-modified wood samples, compared to 4.00 N for unmodified samples. On SorCA-modified wood, coat H320 recorded lower mean wear-resistant hardness, 3.17 N, while no effect (i.e., same hardness) was observed for coat AG7016 compared to unmodified coated wood samples. The third category comprises coats DL8170, H210, and H230, which recorded lower mean wear-resistant hardness, 2.00 N–3.83 N, for all modified wood samples, compared to 2.67 N–4.00 N for corresponding unmodified coated wood samples (Figure 2).



**Figure 2.** Wear resistant hardness of coatings on modified and unmodified *P. sylvestris* L. woods. Note: Data labels are mean values and bars are one standard error from the mean.

The results of factorial ANOVA revealed that the effect of interaction between *P. sylvestris* wood types and coatings was significant ( $p < 0.05$ ) on the coating wear-resistant hardness (Table 5). However, Tukey post hoc analysis based on individual (within) coat interaction with *P. sylvestris* wood types revealed that only the differences in wear-resistant hardness obtained for coat H320 on SorCA- vs. DMDHEU-modified wood, and coat H430 on acetylated vs. unmodified wood samples, were statistically significant ( $p \text{ adj} < 0.05$ ) (Table 5). Other pairwise mean comparisons for wear-resistant hardness based on the interaction effect did not yield significant differences ( $p \text{ adj} > 0.05$ ). Considering the few significant pairwise mean differences for the wood–coating interaction effect, Tukey post hoc analysis was evaluated to gain insight into the main effects of *P. sylvestris* wood types (Table 5). Coatings on both acetylated and DMDHEU-modified woods exhibited significantly higher ( $p \text{ adj} < 0.05$ ) wear-resistant hardness than those on unmodified woods. The wear-resistant hardness of coatings on SorCA-modified woods was significantly lower ( $p \text{ adj} < 0.05$ ) than those on acetylated and DMDHEU-modified woods but not significantly lower ( $p \text{ adj} > 0.05$ ) than those on unmodified woods (Table 5). The wear-resistant hardness of coatings on acetylated and DMDHEU-modified woods was not significantly different ( $p \text{ adj} > 0.05$ ).

**Table 5.** Factorial ANOVA and Tukey post hoc results for wear-resistant hardness of coatings on *P. sylvestris* L. wood types.

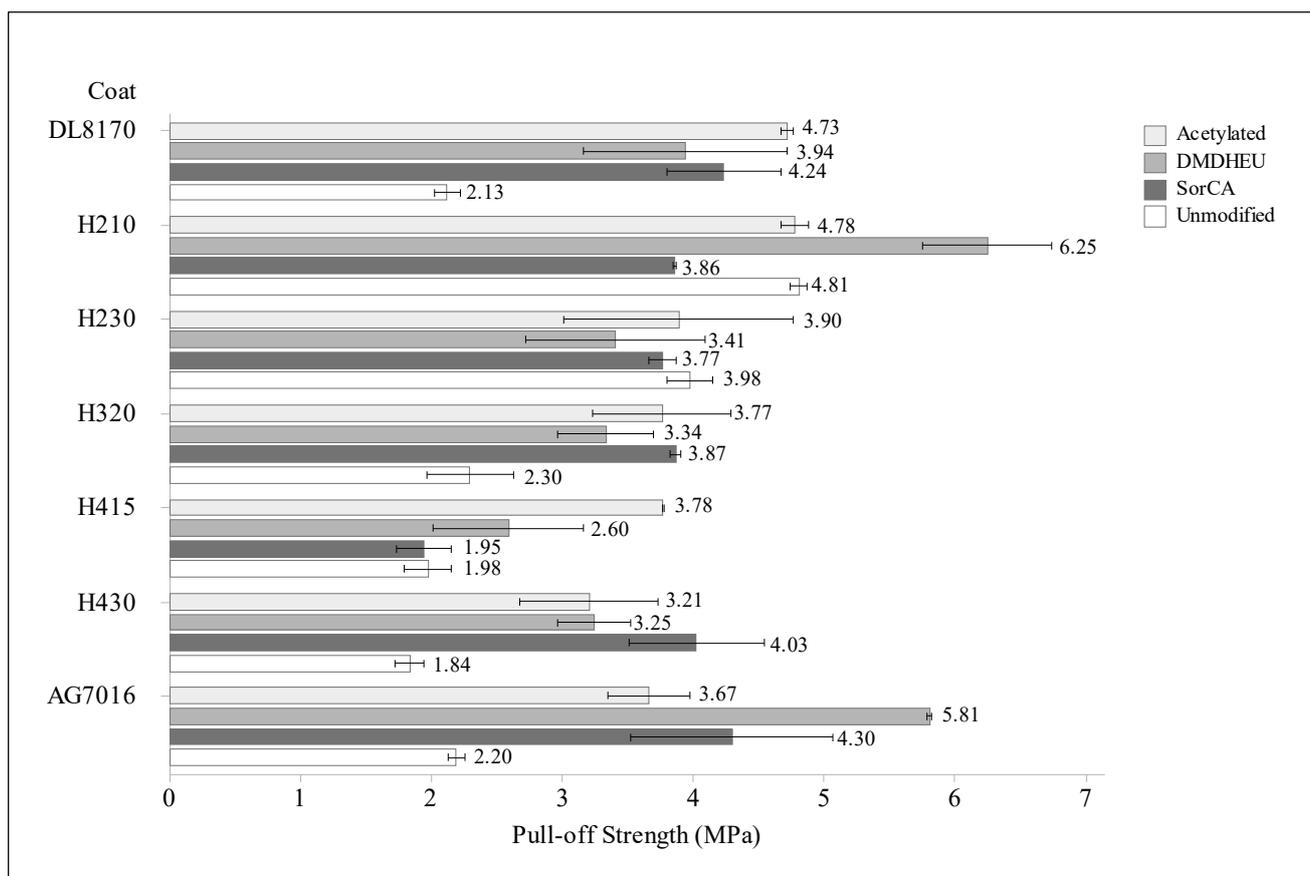
Factorial ANOVA					
Source of Variation	df	Sum of Squares	Mean Squares	F Value	Pr(>F)
<i>P. sylvestris</i> wood type	3	6.46	2.15	12.92	$1.761 \times 10^{-5}$ ***
Coat	6	51.86	8.64	51.86	$6.989 \times 10^{-14}$ ***
<i>P. sylvestris</i> wood type $\times$ Coat	18	8.98	0.50	2.99	$4.536 \times 10^{-3}$ **
Residuals	28	4.67	0.17		
Tukey Post Hoc Analysis <sup>1</sup>					
Group Comparison	Difference	Lower	Upper	<i>p</i> adj	
<i>P. sylvestris</i> wood type $\times$ within-coat interaction effect					
H320 * (SorCA—DMDHEU)	−1.83	−3.51	−0.16	0.021 *	
H430 * (Unmodified—Acetylated)	−1.83	−3.51	−0.16	0.021 *	
<i>P. sylvestris</i> wood type main effect					
SorCA-Acetylated	−0.81	−1.23	−0.39	0.000 ***	
SorCA-DMDHEU	−0.79	−1.21	−0.36	0.000 ***	
Unmodified-Acetylated	−0.50	−0.92	−0.08	0.015 *	
Unmodified-DMDHEU	−0.48	−0.90	−0.05	0.022 *	

Significance codes: \*\*\*  $p < 0.001$ , \*\*  $p < 0.01$ , \*  $p < 0.05$ . <sup>1</sup> Only group pairs with statistically significant differences are presented.

### 3.4. Coating Wet Adhesion (Pull-Off) Strength: Effects of Coating and Wood Modification Types

Wood coatings are most vulnerable under wet conditions, as adhesion at the wood-coating interface declines significantly [18]. The pull-off method is regarded as a test of the practical adhesion of a coating to a substrate [21]. The results obtained in this study showed that the coatings' pull-off strengths on modified *P. sylvestris* woods were mostly higher than, while a few were comparable to, those on unmodified woods. The only exception was the pull-off strength of coat H210, which was about 20% lower on SorCA-modified compared to unmodified wood (Figure 3). The mean pull-off strengths obtained in this study ranged from 1.84 MPa–6.25 Mpa (Figure 3).

Excluding SorCA-modified wood, the solvent-based coat H210 recorded higher pull-off strengths than the water-based coatings, which is consistent with the comparison of the pull-off strengths of solvent-based versus water-based (both acrylic and alkyd binder based) coatings reported by De Meijer [18]. Miklečić et al. [12] and Jaić et al. [20] also reported higher adhesion strengths for solvent-based coatings in comparison to water-based coatings on hornbeam and ash woods, and beech wood, respectively. Findings in this study showed that chemical modification of wood improved coating adhesion in contrast to other wood modification methods, such as reported cases of reduced coating adhesion on thermally modified woods [12,22–24]. Liptáková et al. [13] noted that coating adhesion on wood is primarily influenced by interactions of surface forces at the phase boundary. Therefore, studying the surface force interactions at the modified wood-coating phase boundary will enable better understanding of the mechanism by which the investigated wood modifications impacted coating adhesion, hence this is planned for our further studies.

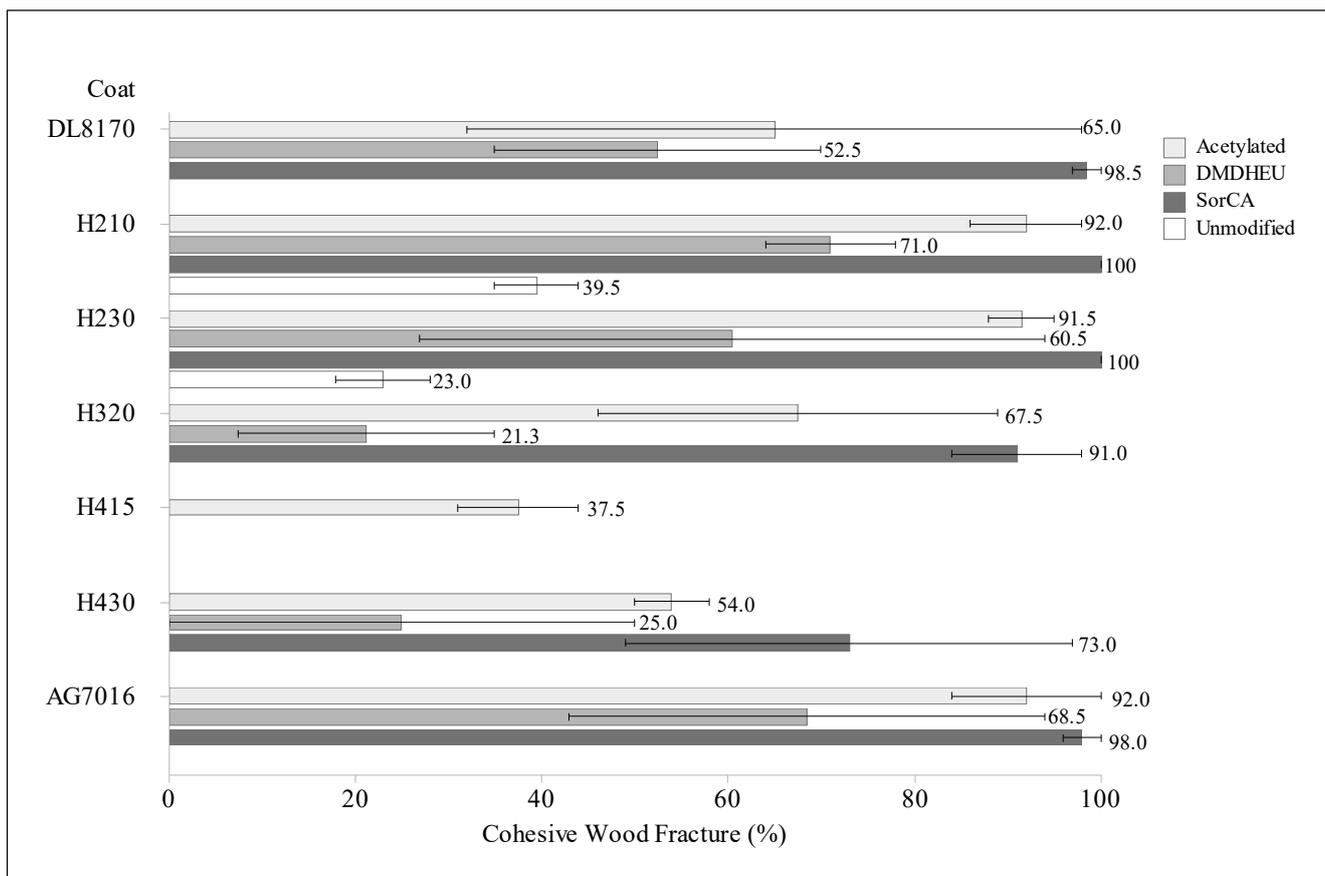


**Figure 3.** Pull-off strength of coatings on modified and unmodified *P. sylvestris* L. woods. Note: Data labels are mean values and bars are one standard error from the mean.

### 3.5. Coating Wet Adhesion (Pull-Off) Strength: Fracture Pattern

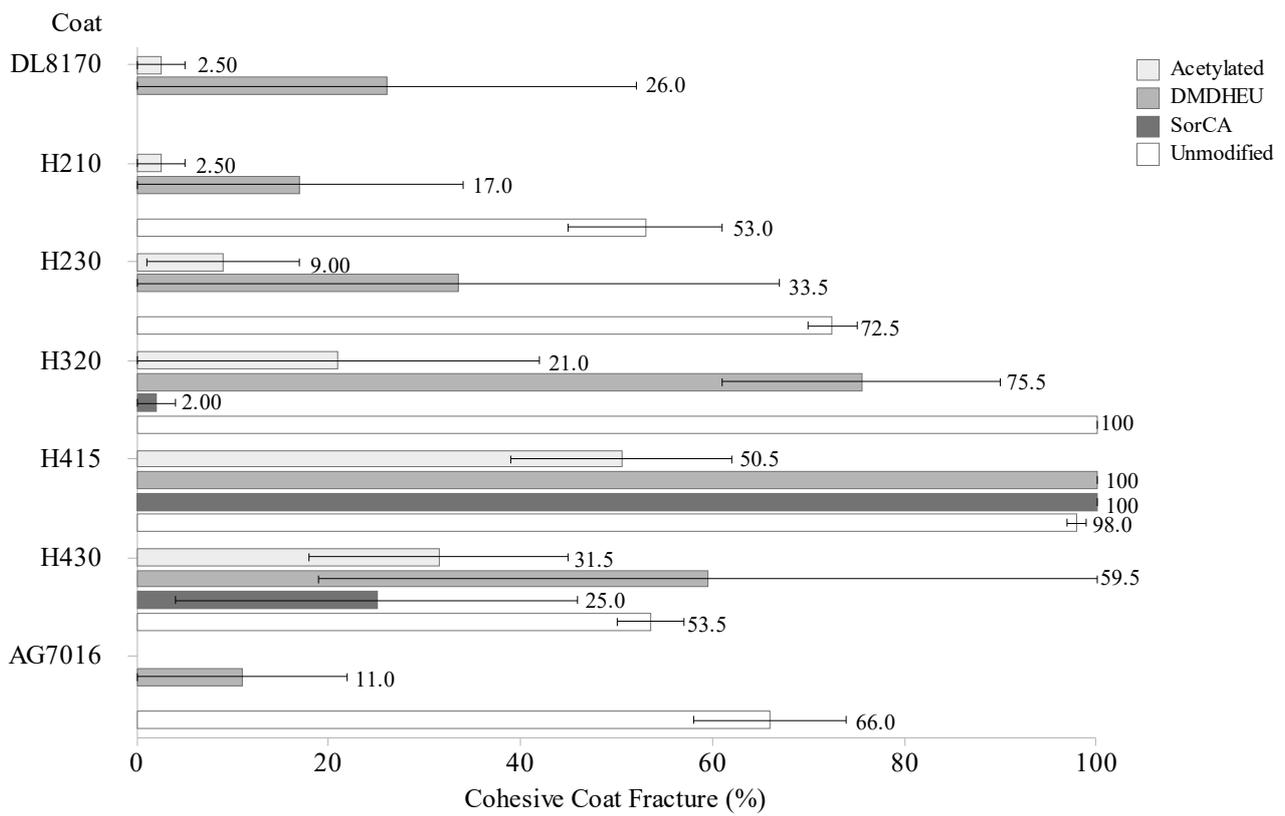
Unmodified wood is naturally hydrophilic, hence the humidity loadings at the interface between coatings and unmodified *P. sylvestris* wood observed in this study were seamless. In contrast, the evident anti-wetting effects of the wood modifications hindered wetness at the wood-coating interface. Consequently, up to 100% cohesive fractures within woods occurred in the coated modified *P. sylvestris* woods (Figure 4). The observed anti-wetting effect of wood modification was most dominant in SorCA-modified samples, followed by acetylated wood samples. Kurkowiak et al. [25,26] found that SorCA modification limits the water absorptivity of *P. sylvestris* wood, which is attributable to reduced voids owing to cell wall bulking and cross-linking. The anti-wetting effect of SorCA modification is also connected to its reactivity with the hydroxyl group [27] limiting the latter's availability. Likewise, the anti-wetting effect of acetylation is due to limited accessible hydroxyl [28–30] and reduced cell wall voids [28,31]. The DMDHEU-modified wood was relatively more wettable, which is attributable to more accessible hydroxyl resulting from DMDHEU modification [28,32]. The global average cohesive fracture within wood for the different wood types (80% for SorCA, 71% for acetylated, 43% for DMDHEU, and 9% for unmodified) is proportional to the observed anti-wetting effect and partly attributable to the lower strength perpendicular to wood grain direction. It is noteworthy that the global average wood fracture recorded for unmodified wood is also partly attributable to moisture re-equilibration during the humidity loading wait period, as observed in this study. Cohesive fractures within coatings ranged from 0 to 100% (Figure 5) for the different coatings on the *P. sylvestris* wood types. Based on wood type, the highest global average cohesive fracture within coatings occurred in coated unmodified woods (63.3%). This is indicative of deeper humidity load transfer from the unmodified woods to the coatings

which could facilitate swelling within the coatings and consequently cohesive fracture. For modified woods, the more wettable DMDHEU-modified wood recorded a 46.1% global average cohesive fracture within its coatings. Coatings on acetylated and SorCA-modified wood recorded global average cohesive fractures of 16.7% and 18.1%, respectively. Based on the recorded observations in this study, the wood–coating adhesion failure percentage is obtainable by subtracting the sum of the cohesive fractures within woods and coatings from 100%. Overall, the highest and lowest adhesion failures between woods and coatings, based on global averages, were recorded for coated unmodified (27.8%) and SorCA-modified (1.8%) *P. sylvestris* woods. Comparable adhesion failures between woods and coatings were obtained for coated acetylated (11.9%) and DMDHEU-modified (11.2%) woods despite their contrasting within-wood and within-coating cohesive fractures.



**Figure 4.** Cohesive fractures within woods during pull-off testing. Note: Data labels are mean values and bars are one standard error from the mean.

Based on factorial ANOVA, the *P. sylvestris* wood type–coat interaction effect was significant ( $p < 0.05$ ) on the pull-off strength of coatings (Table 6). The outcome of Tukey post hoc analysis based on individual (within) coat interactions with *P. sylvestris* wood types revealed that only the differences between the pull-off strengths of coat DL8170 on unmodified vs. acetylated, coat H210 on SorCA- vs. DMDHEU-modified, and coat AG7016 on unmodified vs. DMDHEU-modified wood samples were statistically significant ( $p_{adj} < 0.05$ ) (Table 6). All other mean pair comparisons for the pull-off strength of *P. sylvestris* wood type interaction with each coating yielded no significant differences ( $p_{adj} > 0.05$ ). Tukey post hoc results on the main effects of *P. sylvestris* wood types revealed that the pull-off strength of unmodified wood was significantly lower ( $p_{adj} < 0.05$ ) than that of modified woods (Table 6). The pairwise mean difference in pull-off strengths between all three modified wood types was not significant ( $p_{adj} > 0.05$ ).



**Figure 5.** Cohesive fractures within coatings during pull-off testing. Note: Data labels are mean values and bars are one standard error from the mean.

**Table 6.** Factorial ANOVA and Tukey post hoc results for pull-off strength of coatings on *P. sylvestris* L. wood types.

Factorial ANOVA					
Source of Variation	df	Sum of Squares	Mean Squares	F Value	Pr(>F)
<i>P. sylvestris</i> wood type	3	14.74	4.91	24.80	$8.77 \times 10^{-7}$ ***
Coat	6	22.52	3.75	18.95	$4.37 \times 10^{-7}$ ***
<i>P. sylvestris</i> wood type $\times$ Coat	16	9.71	0.61	3.07	0.01 *
Residuals	19	3.76	0.20		
Tukey Post Hoc Analysis <sup>1</sup>					
Group Comparison	Difference	Lower	Upper	<i>p</i> adj	
<i>P. sylvestris</i> wood type $\times$ within-coat interaction effect					
DL8170 * (Unmodified—Acetylated)	−2.60	−4.96	−0.24	0.019 *	
H210 * (SorCA—DMDHEU)	−2.39	−4.75	−0.03	0.044 *	
AG7016 * (Unmodified—DMDHEU)	−3.62	−5.97	−1.26	0.000 ***	
<i>P. sylvestris</i> wood type main effect					
Unmodified-Acetylated	−1.41	−1.90	−0.92	0.000 ***	
Unmodified-DMDHEU	−1.22	−1.77	−0.66	0.000 ***	
Unmodified-SorCA	−0.98	−1.49	−0.46	0.000 ***	

Significance codes: \*\*\*  $p < 0.001$ , \*  $p < 0.05$ . <sup>1</sup> Only group pairs with statistically significant differences are presented.

#### 4. Conclusions

The findings in this study established that:

- Coating adhesion on acetylated, DMDHEU- and SorCA-modified *P. sylvestris* woods exceeded that on unmodified wood, thus making the modified woods suitable substrates for the investigated coatings;
- Contrary to reported instances of adverse effects of thermal modification on coating adhesion, chemical modification is suited to integration with coatings for enhanced wood protection;
- Solvent-based coatings had better adhesion strengths on the acetylated, DMDHEU-modified and unmodified *P. sylvestris* woods than water-based coatings;
- Coating adhesion on SorCA-modified *P. sylvestris* wood was mostly better with water-based coatings compared to solvent-based coatings;
- Coatings on acetylated and DMDHEU-modified *P. sylvestris* woods exhibited wear-resistant hardness that is significantly better than on unmodified wood;
- The wear-resistant hardness of coatings on SorCA-modified wood is comparable to that of unmodified wood;
- Further studies on coating penetration into the modified woods and surface forces would facilitate deeper understanding of the mechanisms of coating adhesion to modified woods. Such deeper understanding could be further explored for a tailored improvement in coating adhesion on modified woods;
- The anti-wetting effect of wood modification combined with the water-repelling properties of coatings as observed in this study offer opportunity for synergistic improvements in wood hydrophobization. Such wood modification–coating synergy could be explored as a more sustainable wood hydrophobization alternative to developing superhydrophobic coatings with potentially harmful substances;
- The long-term behaviour of the coatings on the modified woods still needs to be evaluated through accelerated and outdoor exposure testing. Earlier studies offer hope that the higher dimensional stability of the modified woods leads to better long-term coating performance and fewer maintenance needs.
- Due to limitations concerning the starting material available for this study, the coated wood surfaces included radial and tangential surfaces, randomly distributed. The probable effect of the wood surface type could not be evidently assessed in this study. This can be explored in future studies.

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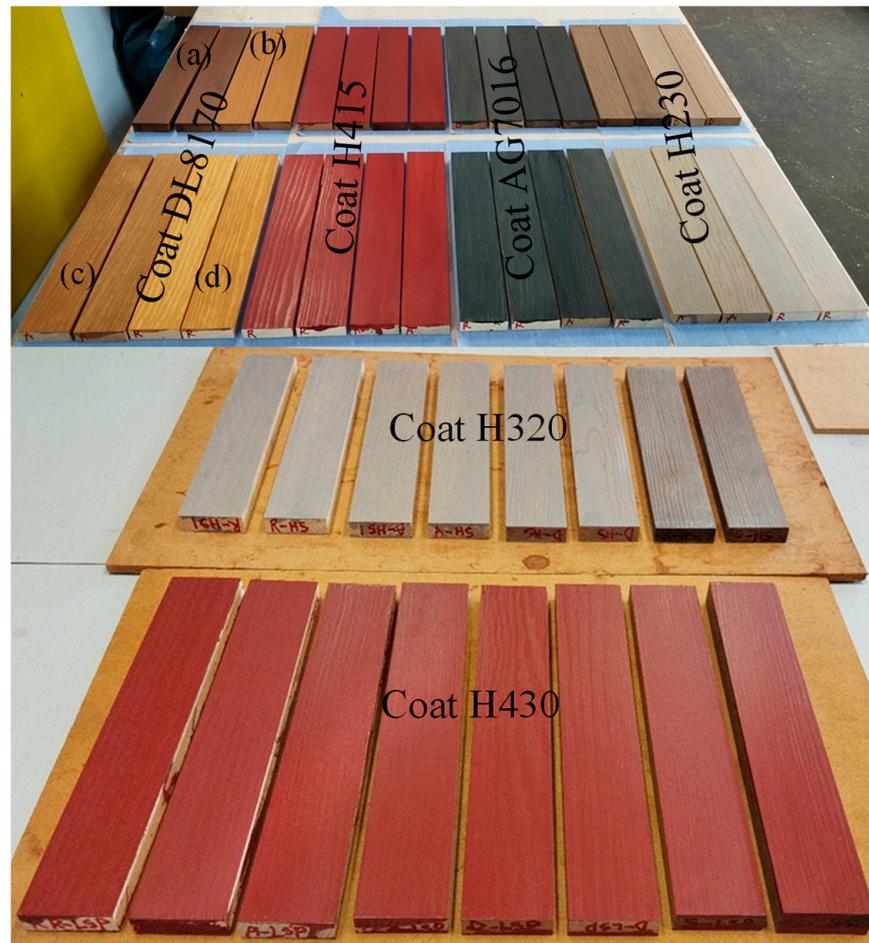
**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** Data are contained within the article.

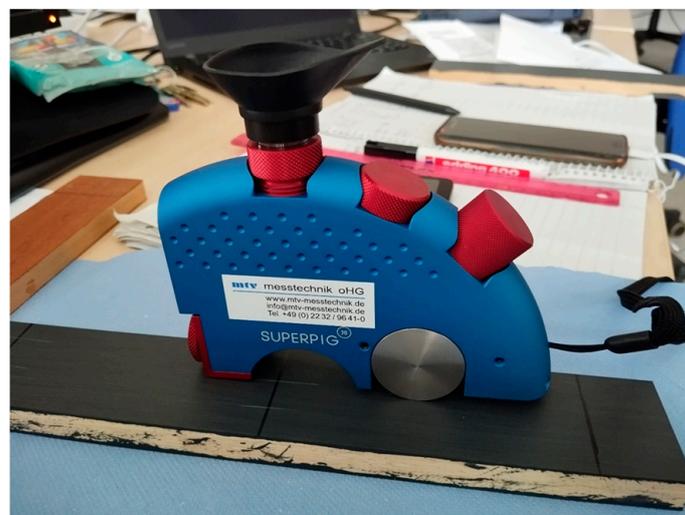
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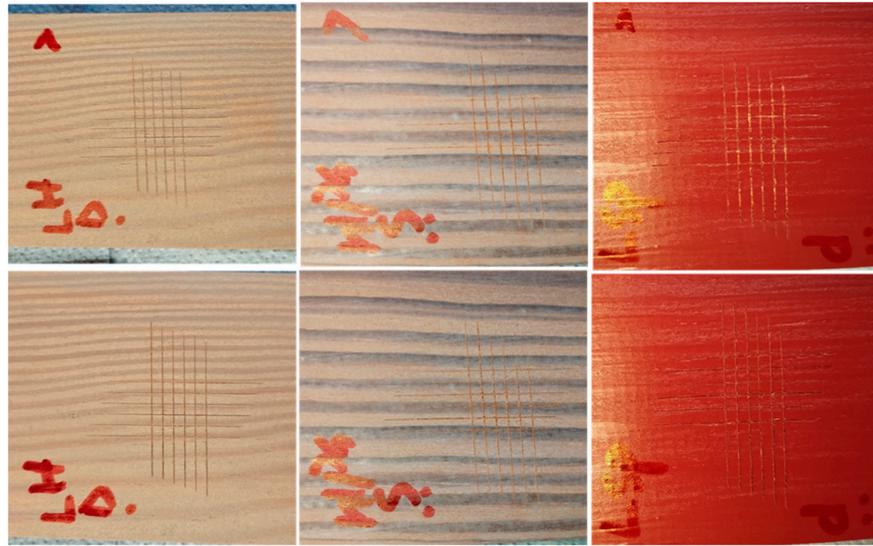
## Appendix A



**Figure A1.** Samples of modified and unmodified *P. sylvestris* L. wood coated with different coatings. E.g., Coat DL8170 on (a) SorCA-modified, (b) DMDHEU-modified, (c) acetylated, and (d) unmodified reference *P. sylvestris* wood.



**Figure A2.** Coating dry film thickness determination using SUPERPIG device.



**Figure A3.** Samples of coated modified *P. sylvestris* L. wood showing incisions before (**bottom**) and after (**top**) crosscut detachment testing.



**Figure A4.** Samples of coated modified and unmodified *P. sylvestris* L. wood with glued dollies before pull-off testing.



**Figure A5.** Samples of coated *P. sylvestris* L. wood showing different fracture patterns after pull-off testing. Note: Few instances of mixed fracture modes occurred in this study. However, due to the potential influence of the wetness gradient observed during the humidity loading, the categorization of fracture modes was conducted on an individual basis in terms of total cohesive fracture within woods, total cohesive fracture within coatings, and total adhesion failure between woods and coatings (i.e., where two or more fracture modes occurred on a tested surface, the fracture modes were categorized individually rather than lumped together as mixed mode).

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