Surface properties of coated MDF pre-treated with atmospheric plasma and the influence of artificial weathering

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HIGHLIGHTS

• Enhanced wettability of MDF substrate with coating achieved with air discharge.
• Introduction of standard and non-standard surface evaluation methods.
• Plasma treatment reduced surfaces color and gloss changes during weathering.
• No influence of plasma treatment on mechanical properties of surface system.

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ABSTRACT

A non-thermal plasma treatment generated in air at atmospheric pressure was used for surface modification of medium density fiberboard (MDF) substrate. Untreated and plasma-treated substrates were coated with a waterborne acrylic coating and exposed to accelerated artificial weathering (AAW) in interior mode. Plasma treatment increased the surface free energy of MDF by about 50%, which positively influenced on the wettability of the MDF with the coating. Weathering of the coated MDF caused a decrease in surface gloss and color changes, which were less pronounced for plasma-treated samples. Attenuated total reflection Fourier transform infrared spectra and microscopic analysis revealed degradation of the acrylic resin on the coated MDF due to light irradiation during weathering. After 250 h of weathering, the surface roughness of the coated MDF increased by about 3 μm. The coated MDF surfaces started to lose their hydrophobic character after 50 h of weathering. Finally, the determination of mechanical properties showed that coated MDF became more resistant to scratching during AAW, while the adhesion of the coating film to the MDF substrate was not affected in a significant trend with time of AAW. In both cases, no influence of plasma treatment was detected.

1. Introduction

Medium density fiberboard (MDF) is a widely used wood-based engineered composite material for construction and furniture [1,2]. Physical and mechanical properties, easy workability, and ready availability make MDF favorable for the production of interior fittings, office furniture, or kitchen cabinets [3,4]. The smoothness, non-porosity, and homogeneity of the MDF surface also enables application of different types of coating materials [5–7].

Apart from providing a specific visual characteristics of all wood-based materials, protection against degradation due to the weathering process, including physical and chemical influences, is the main objective of surface treatments with coatings. With the application of varnishes, stains and paints it is also possible to improve the appearance and extend service life of MDF [6,8]. Waterborne coating systems represent a promising alternative for the surface treatment of MDF [9]. The selection of a particular coating depends on the environmental conditions [10]. Coatings for interior use have to withstand different degradation factors due to the daily activities in our living spaces. The response of the coated product to light irradiation, climatic variations, mechanical damage (scratching, abrasion, impacts) and chemical damage [2,8] are of prime importance in indoor areas [8,11,12]. Polyacrylates and polyurethanes are considered the most important binders in the formulation of transparent, waterborne coating materials for...
wood-based products in indoor applications [12,13]. However, a prerequisite for adequate surface protection of wood-based substrates with coatings is good wettability of surfaces with a liquid coating [14]. Wettability can be evaluated by a contact angle (CA) measured between a horizontal surface of a solid and the surface of a coating droplet. A lower coating CA indicates better and more desirable wettability [15]. From the perspective of the substrate, besides the higher polar character of the surface free energy (SFE), better wettability is associated with higher surface roughness [15,16].

It is common practice to machine wooden surfaces before applying coatings. Alternatively, the wettability and other surface properties of any wood-based material can be modified by the use of plasmas in air or other gasses, which can be done at atmospheric or reduced pressures [17]. In particular, as reported in the literature, dielectric barrier discharge (DBD) plasmas are most commonly used for the treatment of MDF. For instance, Volkenhauer and co-workers [18] reported increased hydrophilicity of plasma-treated (PT) MDF. This was the reason for enhanced adhesion performance of PT MDF with waterborne polyvinyl acetate adhesive. In a recent study, Hazir and co-workers [19] reported up to 22% improvement in adhesion strength of coating system containing of waterborne coatings on plasma pre-treated MDF. Applications of other types of plasmas on MDF were also investigated. The main process parameters when using a plasma torch to modify MDF surfaces were investigated by Perisse and co-authors [20]. De Cademartori and co-workers [21] reported an increased oxygen content on MDF surfaces and their improved wettability after helium-DBD treatment. In another study, improved adhesion of acrylic coating was found when argon was used as a working gas [22]. MDF was also used as a substrate for the deposition of a macroscopic coating layer of polyester with a plasma jet [23].

Exposure of uncoated or coated wood-based materials to weathering, including light irradiation, elevated relative humidity (RH), and temperature [24], results in various changes in the properties of the bulk material [1] or its surface [25–27]. Long-term natural weathering can be substituted with accelerated artificial weathering (AAW [28]). Through the exposure of a particular material to AAW, the performance of the material can be evaluated much more quickly. In an AAW chamber, environmental conditions are controlled according to defined test protocols. Irradiation of natural sunlight to tested material can be imitated with a xenon-arc lamp [29]. Combinations of structural and chemical changes in the irradiated material are reflected in changes in surface wettability, roughness, color, and gloss [30,31]. Considering only coated surfaces, weathering affects the mechanical properties of the coating, such as adhesion and hardness [32–35].

The physical and mechanical properties of coated materials are influenced by the roles of the coating film, underlying substrate, and the interface, which together form the surface system [36]. External influences on coated materials are reflected in damage at different levels. Deformation responses of the coating film or the entire surface system can be analyzed on a microscopic level [37].

The present study aims to quantify the possible influence of plasma pre-treatment on the properties of MDF coated with a waterborne coating and on the performance during a subsequent exposure to AAW. Pre-treatment of the MDF substrate was performed using a recently developed DBD plasma in a floating electrode configuration generated in air at atmospheric pressure. The influence of PT was first investigated in terms of surface morphology and wettability of MDF with water and coating. The performance of the coated MDF samples, both untreated and PT, was evaluated during 250 h of AAW in interior mode in terms of color, gloss, chemical properties, wettability with water, microstructure, and morphology. Finally, the influences of PT and AAW on the mechanical properties of the coated MDF were determined by analyzing the response of the surfaces to scratching and by measuring the peel force of the coating films.

2. Materials and methods

2.1. Materials

From 3 mm thick MDF boards, specimens with dimensions of 300 mm × 75 mm were divided in untreated (UT) and plasma-treated (PTd) series. Prior to experiments, the material was stored in a chamber with a temperature of 20 °C and RH of 65%. Under these conditions, the MDF reached a density of (802 ± 10) kg/m³ and an equilibrium moisture content of 10.4%, as determined gravimetrically.

As a coating material, a pigmented commercial acrylic waterborne coating (Belinka Interier, Belinka Belles, d.o.o., Ljubljana, Slovenia) with a solid content of 37.8% was used.

Fig. 1. The sketch of the plasma setup and photos of generated different plasma discharges: (a) without substrate, (b) treatment of beech wood substrate, (c) treatment of MDF substrate. The photos were taken by Nikon D5600 photo camera (f/6.3, 0.1 s, ISO 1600).
2.2. Plasma treatment process

MDF samples were treated with non-thermal DBD plasma in floating electrode configuration (FE-DBD) in air at atmospheric pressure. The details of the setup are described in previous studies [38,39]. Alternating high voltage (frequency 5 kHz, 15 kV peak voltage) was supplied by high voltage power source into two parallel brass electrodes, each insulated by an alumina ceramic dielectric. The distance between the insulated electrodes was set to 5 mm, and the distance between the dielectrics and the surface of the workpiece was 1 mm. Fig. 1 shows the sketch of the plasma setup and example photos of the plasma discharges. The MDF, or any other lignocellulosic substrate (e.g. wood), represents the workpiece. A high voltage power source of 10 kV peak voltage was supplied to create the plasma discharges.

2.3. Surface roughness measurements

The influence of PT on the surface morphology of MDF was examined with a LEXT OLS5000 confocal laser scanning microscope (CLSM, Olympus, Tokyo, Japan). Morphology analysis was performed on 5 spots of MDF surfaces before and after PT (PTd-2 and PTd-3, 3 samples each), as well as during AAW (c.f. Section 2.6), and for analyzing the scratching traces (c.f. Section 2.11). To ensure repeatability, the measurements were recorded at different spots on each individual sample at 5-fold magnification with the scanned area of 2560 μm × 2560 μm. Non-contact 3-dimensional (3D) laser microscopy was performed using a laser light source with a wavelength of 405 nm, with a maximum lateral resolution of 0.12 μm. The OLS50-S-AA software (Olympus, Tokyo, Japan) was used to calculate the average absolute deviation of the roughness irregularities from the mean sample surface over the sampling area Sn [40].

2.4. Determination of surface free energy (SFE) and wettability with coating

Surface wetting properties and surface free energies on UT and PTd MDF were determined on the basis of contact angle (CA) measurements of three liquids: deionized water (surface tension: polar part \( \gamma_p = 51.0 \) mN/m, dispersive part \( \gamma_d = 21.9 \) mN/m), diiodomethane (\( \gamma_p = 0.0 \) mN/m, \( \gamma_d = 50.8 \) mN/m) and formamide (\( \gamma_p = 39.0 \) mN/m, \( \gamma_d = 19.0 \) mN/m) [34]. Twelve 5 μL droplets of each liquid were applied to 3 (100 mm × 75 mm) samples of the UT series and each PTd series with Theta optical goniometer (Biolin Scientific Oy, Espoo, Finland). The corresponding goniometer software was used to measure the CA between the surface of the substrates and the tangent line fitting the shape of droplet. The SFE was calculated using the Lifshitz-van der Waals acid-base method [41-44]. The same procedure was used to measure the CA of the coating on 3 MDF samples per series, where the volume of the applied droplets was 10 μL. After 24 h, the top-view photos of cured coating droplets were taken using photo camera (f/5.6, 0.02 s, ISO 1250) and the areas of the droplets were measured using Fiji software (ImageJ 1.46d, Madison, WI, USA).

2.5. Coating film formation

The UT and PTd MDF samples (5 per series) with the initial dimensions were manually coated using a quadruple coating applicator. At the rate of applicator movement of approximately 30 mm/s, coating films with a wet film thickness of 240 μm (approximately 130 g/m²) were created. The determination of the dry film thickness is explained in Section 2.10. Before further analyses, the samples were stored for 21 days in a dark room at a temperature of 20 °C and a RH of 35%.

2.6. Accelerated artificial weathering (AAW) process

The coated MDF samples, either UT, PTd-2 or PTd-3, were cut in two halves and exposed to AAW in the Atlas SUNTEST XXL+ chamber (Atlas Material Testing Technology, Mount Prospect, IL, USA) according to the EN ISO 11341 [45] standard in the interior mode. The xenon-arc lamp behind a 3 mm glass filter produced a light spectrum equivalent to sunlight entering through the window glass [28,46]. Settings of the AAW device established the following conditions in the chamber: a light irradiance of 340 nm, irradiation power of 0.35 W m⁻², a RH of 65%, a chamber temperature of 35 °C and the temperature at the black panel sensor of 55 °C. The samples were exposed to weathering for 10 h, 50 h, 100 h, and 250 h. As reported in the literature, the selected durations of irradiation to xenon-arc light lead to detectable changes in various properties of materials similar to those used in this study [28,30,47]. After completion of each weathering interval, three samples from each series were taken out of the chamber for further work and analyses.

2.7. Determination of visual properties

The changes in visual properties, gloss, and color of the surfaces of the samples were monitored during the AAW intervals in 10 measurements of each property on each sample. Gloss, as a property related to the intensity of light reflected in the specular direction [8], was measured with a gloss meter AcuGloss TRI (X-Rite, Grand Rapids, MI, USA) at the angle between the light source and the observed plane of 60°. CIELAB color space components (\( L^* \), \( a^* \) and \( b^* \)) were measured using the spectrophotometer SP62 (X-Rite) with the D65 light type. Color changes of the sample surfaces (\( \Delta E^* \)) were calculated according to equation (1):

\[
\Delta E^* = \sqrt{\left(\Delta L^*\right)^2 + \left(\Delta a^*\right)^2 + \left(\Delta b^*\right)^2},
\]

where the parameters \( \Delta L^* \), \( \Delta a^* \) and \( \Delta b^* \) represent the changes between the initial value of \( L^* \), \( a^* \) and \( b^* \) at the end of each AAW interval.

2.8. Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy

Forsthuber and Grüll [45] reported the usability of ATR-FTIR to quantify the photo oxidation rates of coatings due to the exposure to xenon-arc light. In this study, ATR-FTIR was used to evaluate the changes in chemical bonds in the coating films due to photochemical degradation during AAW. The spectra were recorded using the PerkinElmer Spectrum Two (PerkinElmer Inc., Waltham, MA, USA) ATR-FTIR spectrometer, with a LiTaO₃ detector type in the transmittance mode. Spectra were corrected for background and measured in 3 spots (16 scans per spot) on individual sample, in a wavelength region from 600 cm⁻¹ to 4000 cm⁻¹ at a resolution of 0.5 cm⁻¹. Relevant absorption bands were then interpreted using the corresponding software (Spectrum V.10.5.3, PerkinElmer Inc.).

2.9. Wettability of coated samples with water during AAW

In order to detect the influence of AAW on the in hydrophobic characteristics of the coating film, the CA of deionized water was measured after each weathering period. Optical goniometer Theta was used to measure the angle of 105 μL water droplets deposited on the surface of each sample of coated MDF. The lower the CA was, the lower the ability of a coating film to protect the surface from water [48].

2.10. Scanning electron microscopy (SEM) analysis

SEM was used to analyze the microscopic changes on the sample surfaces due to AAW. The spots of interest were observed with a
scanning electron microscope FEI Quanta 250 (FEI, Hillsboro, OR, USA). Prior to observations, samples were coated with a gold conductive layer. Images were acquired with the backscatter detector at 1000 \times magnification in high vacuum (0.085 Pa) with an electron source voltage of 5.0 kV, at a working distance of 10 mm, and a spot size of 3.0 nm. During the acquisition of each image, the time of beam passage through the sample was 60 \mu s. SEM was also used to determine the dry coating film thickness and to analyze the scratch traces (Section 2.11).

2.11. Determination of response to scratching

The response of the coated surfaces to scratching was determined during AAW according to the modified circular method described in EN 15186 [49] with a scratch hardness tester (model 413, Erichsen GmbH & Co. KG, Hemer, Germany) as presented in Fig. 2. The specimen of 100 mm \times 100 mm in size was clamped on a turntable. The 90° angled diamond test tip with the radius at the tip of 90 \mu m was attached to a load arm, which applied the test load to the specimen. After one full rotation of the specimen (30°/s), circular traces with diameters of 45 mm (applied force 5 N) or 55 mm (applied force 7 N) were induced on the specimen surface (Fig. 2a). Morphological studies of the residual patterns were performed by CLSM on 5 sections of the individual scratch to obtain representative results of the response to scratching on the wider surface. Generalized 3D scratch maps were created (Fig. 2b), in an attempt to model material contact behavior. Similarly to what was reported by Barletta and co-authors [11], the 3D reconstruction of the scratch patterns using the profiler enabled the analysis of the deformation response. As shown in Fig. 2c, the surface area of the scratch and the average depth of the scratch were determined. An example of the height profile (mean of 5 profiles measured per length of individual scratch
The volume of the caused scratch trace was evaluated as follows:

\[ V = \frac{A \times l \times d}{2} \]

where \( V \) is the volume of the scratch [\( \mu m^3 \)], \( A \) is the measured area of the scratch [\( \mu m^2 \)], \( l \) is the length of the analyzed scratch [1275 \( \mu m \)], and \( d \) is the average depth of the scratch [\( \mu m \)].

The top views and cross sections of the scratch traces and their surroundings were analyzed with SEM. Images were acquired with the large field detector at 300 \( \times \) and 1000 \( \times \) magnification in low vacuum (50 Pa) with an electron source voltage of 5.0 kV, at a working distance of 10 mm, and a spot size of 3.0 nm. During the acquisition of the image, the time of beam passage through the sample was 60 \( \mu s \).

### 2.12. Determination of coating peeling force

The peeling force test was applied to determine the adhesion of the coating to UT and PTd MDF samples with respect to time of AAW. The 200 mm \( \times \) 20 mm cotton tissue strips were glued on the coated MDF samples with a 2-component epoxy glue (UHU plus endfest, UHU, Bühl, Germany). After 24 h, the boundaries of the glued strips were carefully cut down to the substrate to prevent propagation of defects outside of the test area. The bonded cotton strips were peeled using a Z100 tensile testing machine (Zwick GmbH & Co. KG, Ulm, Germany) as presented in Fig. 3. The strips were pulled at a peel angle of 15° at a testing machine crosshead speed of 100 mm/min. The recording of the peeling force started when it firstly exceeded 10 N. From this point on, the force was recorded every 0.01 s of measurement. After the test, the share of the coating adhesion failure was visually estimated. The reported peeling force and percentage of adhesion failure represent the average of 3 measurements for each type of a sample.

### 3. Results and discussion

#### 3.1. Surface free energy

PT of MDF caused an increase of both the non-polar dispersive Lifshitz-van der Waals (\( \gamma^{LW} \)) and polar acid-base (\( \gamma^{AB} \)) components of SFE, as shown in Table 1. Compared with UT MDF, the \( \gamma^{AB} \) of PTd MDF was found to be about 1.2-times higher for both PTd-2 and PTd-3. However, PT of MDF significantly increased \( \gamma^{LW} \) 30.3-times for PTd-2 and 24.3-times for PTd-3, compared to the \( \gamma^{LW} \) values of UT MDF. It was also shown that PT decreased the electron-donating part of \( \gamma^{AB} \) (\( \gamma^- \)) but greatly increased the \( \gamma^{AB} \) electron-accepting (\( \gamma^+ \)) part. Finally, as calculated according to Lifshitz-van der Waals acid-base method, the total SFE (\( \gamma^{tot} \)) of MDF was the lowest on UT samples (32.5 mJ/m²), higher on PTd-3 samples (49.3 mJ/m²), and the highest on PTd-2 samples (53.2 mJ/m²). These results indicate that MDF was likely oxidized and thus activated and was significantly more hydrophilic after PT. The lower feed speed of the MDF workpiece through the plasma discharge increased the SFE of MDF more than higher feed speed.

The improvement of hydrophilicity of MDF by PT is most likely influenced by the dielectric properties of MDF. Higher moisture content in the treated substrate makes MDF more electrically conductive, which also affects the effect of PT to enhanced hydrophilicity [4]. However, this assumption was not part of this study.

#### 3.2. Coating CAs

Fig. 4 shows the evolution of the coating CAs on UT, PTd-2, and PTd-3 MDF substrates as well as the areas of the cured coating droplets 24 h after deposition. The initial CAs decreased rapidly on all three samples in the first 10 s after droplet deposition due to penetration of the liquid into the substrate and due to the spreading of the liquid over the surface of the solid [30, 51]. The increase in SFE of MDF after PT contributed to improved surface wettability of MDF with a waterborne acrylic coating. As presented in Fig. 4, the formed CAs of coating droplets were significantly lower when applied to PTd MDF than to UT MDF. However, the difference in coating CAs observed on PTd-2 and PTd-3 samples after 60 s of measurement of 39.6° and 40.1°, respectively, is only minor and does not reflect the larger difference in SFE between PTd-2 and PTd-3.

Perisse and co-authors [19] found that the longer PT applies more energy to the MDF surface and therefore a greater decrease in CAs is achieved than with a faster treatment. The reason for this is due to surface oxidation, including the formation of C–O, C=C–O and O–C=O bonds.

The lower CAs of the coating are reflected in a larger area of MDF covered by the droplets. 24 h after deposition, the droplets on UT samples covered in average 16.9 mm² of MDF, on PTd-2 samples 23.9 mm², and on PTd-3 samples 21.5 mm².

#### 3.3. Changes of color and gloss

According to the measured gloss values, detected at 60° angle of incidence, the analyzed surfaces were denoted as matt glossy [52]. A reduction of gloss with time of AAW was related to the degradation of the coating during weathering [27, 53] and the associated increased surface roughness of a coating [54, 55]. Similar to what was reported by
Custódio and Eusébio [27], the largest changes in gloss of wood coated with waterborne acrylic coating and exposed to AAW were detected at the beginning of weathering (Fig. 5). The highest initial gloss was detected on PTd-2 samples (16.2), followed by PTd-3 samples (14.5), and on UT samples (12.0). The initial gloss values indicated that PT contributed to the increase in gloss. This could be related to enhanced wettability of the MDF by the coating, but definitely with the reduced roughness of the coating film surface. With the exposure of samples to AAW the gloss decreased. The greatest decrease in gloss was detected after the first 10 h of weathering and was very similar for all three sample types. With further weathering, the gloss decreased at a slower rate. After 250 h of weathering, the gloss of PTd samples remained higher than that of UT samples. The gloss of PTd-2 samples decreased to 15.2 (−6.5%), of PTd-3 samples to 13.6 (−6.2%) and of UT samples to 11.1 (−7.1%). In conclusion, PT seems to reduce the influence of AAW on the gloss changes.

Fig. 5. Changes of gloss of UT, PTd-2 and PTd-3 coated MDF during the time of AAW.

3.4. ATR-FTIR spectra

ATR-FTIR experiments were performed in order to study the chemical degradation of the coating acrylic systems caused by the AAW. As shown in Fig. 7, the only and constantly noticeable spectral changes were detected in a broad band between 2800 cm\(^{-1}\) and 3000 cm\(^{-1}\), in the alkyl region [57–60], with the bands at 2850 cm\(^{-1}\) and 2920 cm\(^{-1}\) denoting stretching in methyl and methylene groups, including hydrocarbon (C–H) chains [30,61]. The transmittance signal of these bands became remarkably larger after 50 h of AAW, indicating the formation of hydroxyl bonds during the degradation of the acrylic resin [45,46]. However, no additional changes were detected in the spectra during further weathering process. Regardless of the feed speed, the PT had no effect on the detected spectra throughout the spectral entire wavelength span, which dataset is provided in the supplementary material (Fig. S1).

Chemical degradation of the polymer matrix involves the formation of species that are readily ablated from the surface, leading to loss of gloss, increase in hardness, and rougher morphology [52].

3.5. Wettability of coated MDF

The behavior of water droplets deposited on coated MDF over the time of AAW was a good indicator of the ability of the coating film to protect the substrate from water ingress. During the first 50 h of weathering, the initial low wetting character of the coating film seemed to be unaffected. Additional 50 h of AAW caused a slight decrease in the formed CAs of water droplets. After 250 h of weathering, the wettability of the coating film with water increased significantly (Fig. 8). With further AAW, an additional loss of coating film wettability would be expected [62]. However, the influence of PT on coating films wettability character was not detected during the entire period of AAW.

Fig. 6. Color changes of UT, PTd-2 and PTd-3 coated MDF during the time of AAW (left) and the pictures of the samples during the time of AAW (right). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)
3.6. Changes in coating films microstructure and surface morphology

When comparing coated MDF before AAW and after AAW, weathering caused changes in the microstructure of the coating film (Fig. 9). Such structural changes were detected on both UT and PTd samples. Apparently, the surface microstructure of the unexposed sample was relatively homogenous. After 250 h of weathering, semi-circular deformations appeared in the coating film, which were attributed to the photo-degradation of the coating polymer induced by light transmission [63]. These physical changes are most likely consistent with chemical changes detected with ATR-FTIR analysis [51]. However, no blistering or cracking was detected, which would possibly occur after prolonged weathering [64].

The roughness of MDF depended on many variables, such as the type of raw material, the type and amount of resin used, the moisture content of the boards, the sanding process during manufacture, etc. [65]. Treatment of the MDF substrate with plasma caused a reduction of surface roughness. On average, the arithmetic mean surface roughness ($S_a$) of PTd-2 MDF decreased by 0.17 ($\pm$ 0.06) $\mu$m, while $S_a$ of PTd-3 MDF decreased by 0.13 ($\pm$ 0.03) $\mu$m. This reduced surface roughness of MDF after PT could be the consequence of surface cleaning [39], but not surface etching, as often reported when the PT process was carried out with other types of setups and by different treatment parameters [66].

The relative changes of $S_a$ of the coated MDF with respect to the pre-
treatment method and time of AAW are presented in Fig. 10. The results showed an increase in surface roughness with weathering. This behavior had a relevant influence on the decrease of gloss and consequently on the appearance of the polymer coating [67]. Scalarone and co-workers [68] reported that the most relevant morphological changes, which occur with time to waterborne acrylic coatings, are primarily related to the exudation of surfactants. In addition, the photo degradation of coating during weathering was accompanied by oxidation, hydrolysis and scissions of the polymer chains. This lead to the removal of low molecular weight compounds, thus generating micro-cavities and micro-holes on the surface [58]. Pre-treatment of MDF with plasma did not seem to have any effect on the changes in surface roughness of the coating film for the examined time of AAW. The images of the coated UT and PTd MDF before AAW and after 250 h of AAW, showing the surface morphology detected by CLSM, can be found in the supplementary material (Fig. S2).

3.7. Response of surfaces to scratching

Exemplary SEM images of the samples’ surfaces after scratching with a tip loaded with a force of 5 N are shown in Fig. 11. The advancing tip caused deformations in the entire surface system, i.e. in the coating film and underlying MDF substrate, regardless of the load applied to the tip. The ploughing phenomenon of flat surfaces caused the appearance of fractures in the form of pile-ups at the scratch pattern surface [69]. The pile-up formations were the result of the deformation induced in the material by the compressive and tensile stress fields that develop in front of and behind the advancing tip during the progressive scratching load [70]. For the sample cross section shown in Fig. 11a, the scratch was approximately 170.8 μm wide and 46.2 μm deep. The thickness of the coating dry film was measured at different spots of the micrographs as shown in Fig. 11b, and was estimated to be 37.7 ± 5 μm. No obvious differences in the coating film thickness were detected on UT MDF and PTd MDF. Top-view SEM analysis of the scratches revealed the differences in the deformations caused on the non-weathered sample (Fig. 11c) and on the sample exposed to AAW for 250 h (Fig. 11d). For the non-weathered sample, the longer deformations of the coating film and larger pile-up formations in the scratch surroundings indicated a higher elasticity of the coating film. Exposure of coated material to AAW with light irradiation (including ultra-violet light) and elevated temperature, appeared to make the coating film harder [2] or more resistant to scratching [71]. This is assumed to be due to the shorter deformations of the coating film and smaller pile-up formations in the scratch surroundings. As supported by the findings of ATR-FTIR analysis, the coating polymer became more crosslinked, but more brittle [36,72]. Determination of the mechanical properties (e.g. tensile strength) of non-weathered and weathered free film of the coating might additionally support this assumption [12,13].

The representative 2D cross sectional profiles of the scratch patterns and their surroundings, as obtained by the CLSM investigation and extracted by 3D morphology, are shown in Fig. 12. The width and depth of the scratch profile depended on the force applied to the scratch tip. The larger the force, the wider and deeper the scratch becomes. Morphological 3D images of coated and scratched UT and PTd MDF before AAW and after 250 h of AAW, are provided in the supplementary material (Fig. S3).

From the scratch and morphological data, including scratch area and average depth of each scratch, the volume of the material scratched out was calculated (Fig. 13). As expected, and with a similar trend for the 2D cross sectional profiles of the scratch patterns, the volume scratched out was greater when the surfaces were scratched with greater (7 N) than lower (5 N) force. A large dissipation of the calculated volumes indicates large differences in the areas and depths of the analyzed scratching traces at the selected spots. Although the error bars partially overlap between the filled or hatched columns, the trend of decreasing volume with time of AAW was visible. Again, the reason for this behavior can be found in the increasing crosslinking of the coating polymer with time and the increased resistance of the coating to mechanical damage [61]. However, an influence of the pre-treatment method of the MDF substrate was again not found.

3.8. Coating peeling force

The scratch resistance of polymer films is generally related to the adhesion strength of the films to the substrate [65,66,73]. The results of the coating peeling force measurements did not show a continuous trend
with time of AAW, neither with the pre-treatment method of the MDF before coating application (Table 2). For the time of AAW used in this study, the adhesion force of the coating films showed no trend of change, neither negative nor positive. Pre-treatment of the MDF substrate with plasma did not increase the adhesion of the waterborne coating to the substrate, as could be expected from the reports in the literature (e.g. ref. [18]). Although the PT increased the SFE of the MDF surface, this positive influence did not reflect in the increased coating adhesion strength determined with peeling force measurements. The reason for this could be due to the method used. A different result could be obtained by using a different method for determination of coating adhesion strength (e.g. by determination of coating pull-off adhesion strength) or by performing the measurements on more sample replicates. However, the influence of weathering or pre-treatment of MDF with plasma on coating adherence to the substrate could be more pronounced with longer exposure to weathering than used in this study.

4. Conclusions

A non-thermal DBD plasma in a floating electrode configuration (FEDBD) was shown to be a viable technique for modifying the surface of medium density fiberboards (MDF). The treatment with plasma increased the surface free energy (SFE) of MDF, which had a positive
effect on the wettability of MDF with a waterborne commercial acrylic coating. Both the increased SFE and improved wettability could be related to the reduced surface roughness and surface oxidation after treatment with plasma. Exposure of the coated MDF to an accelerated artificial weathering (AAW) process resulted in changes in the visual and mechanical properties of the coating films. Surface gloss decreased with AAW, but, higher overall gloss values were found on plasma-treated samples. Plasma treatment (PT) also reduced the color changes of the surfaces that occurred during the whole period of AAW. The recorded ATR-FTIR spectra revealed the formation of hydroxyl bonds in the coating films during AAW, indicating the degradation of the acrylic resin by the light irradiation. The coated MDF started to lose its hydrophobic character after 50 h of AAW. PT of MDF had no influence on the chemical changes in the coating films nor on the hydrophobic behavior before, during, or after AAW. As shown by the microscopic analyses, irradiation of the samples with xenon-arc led to the formation of semi-circular deformations in the coating film. The changes in the microstructure of the coating film reflected also in the increasing surface roughness with the time of AAW. Finally, the determination of mechanical properties showed that the coated MDF became more resistant to scratching during AAW, while the adhesion of the coating film to the MDF substrate was not significantly affected over the time of AAW. In both cases, no influence of PT was detected.

We can conclude that the pre-treatment of MDF with atmospheric FE-DBD plasma enhanced the ability of MDF to interact with the waterborne acrylic coating. During AAW, the positive effect of PT was confirmed in reduced changes in gloss and color. However, the mechanical properties of the surfaces of the coated MDF were not improved by the plasma pre-treatment.

### Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.matchemphys.2021.124358.

### References


EN ISO 11341, Paints and Varnishes


