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The Impact of a CO₂ Laser on the Adhesion and Mold Resistance of a Synthetic Polymer Layer on a Wood Surface

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Abstract: In the wood industry, laser technologies are commonly applied for the sawing, engraving, or perforation of solid wood and wood composites, but less knowledge exists about their effect on the joining and painting of wood materials with synthetic polymer adhesives and coatings. In this work, a CO₂ laser with irradiation doses from 2.1 to 18.8 J·cm⁻² was used for the modification of European beech (*Fagus sylvatica* L.) and Norway spruce (*Picea abies* /L./ Karst) wood surfaces—either in the native state or after covering them with a layer of polyvinyl acetate (PVAc) or polyurethane (PUR) polymer. The adhesion strength of the phase interface “synthetic polymer—wood”, evaluated by the standard EN ISO 4624, decreased significantly and proportionately in all the laser modification modes, with higher irradiation doses leading to a more apparent degradation and carbonization of the wood adherent or the synthetic polymer layer. The mold resistance of the polymers, evaluated by the standard EN 15457, increased significantly for the less mold-resistant PVAc polymer after its irradiation on the wood adherent. However, the more mold-resistant PUR polymer was able to better resist the microscopic fungi *Aspergillus niger* Tiegh. and *Penicillium purpurogenum* Stoll. when irradiation doses of higher intensity acted firstly on the wood adherent.



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Keywords: wood; polyvinyl acetate; polyurethane; laser; damage; microscopy; adhesion; mold

1. Introduction

The intentional processing or modification of wood surfaces can be performed by various mechanical, physical, chemical, and biological methods. Their aim is to improve or optimize (1) the final characteristics of wood surfaces—e.g., their shape, roughness, hardness, color, gloss, and resistance (to water, sun, fire, fungi and other biological agents) [1–4]; (2) the inter-operational characteristics of wood surfaces—e.g., the wettability, free surface energy, and density—which are important before wood gluing/painting with natural and synthetic polymer adhesives/coatings [5–7]. A polymer layer of the adhesive/coating can also be processed or modified with the aim to achieve its general or specific optimum properties either for the final wood product (e.g., veneers on surface-treated wood furniture) [8] or for the further wood processing (e.g., the gluing of solid wood or wood particles in wood composites) [9].

Several physical methods can be used for the surface modification of wood in its native state as well as after its pretreatment with biocides, UV-absorbers, coatings, and other chemicals [2,10]. Today, the most perspective physical methods for wood surface modification are plasma methods [11–14] and laser methods [15–19]. Both these physical methods change the chemical structure of wood and other organic materials [2,17,20]. In this context, they should be able to change several characteristics of the wood surface and also of the adhesive or coating polymer layer applied on the wood surface—including the final adhesion strength and mold resistance.

Plasma changes the chemical composition of wood surfaces and also their wettability and some other properties [1,11,12,21]. Plasma in the presence of air in the lignin-polysaccharide matrix of wood specifically generates new hydroxyl, carbonyl, carboxyl,

peroxide or ether functional groups, and radicals, which are able to enter into further condensation reactions. Thereby, plasma on the wood surfaces forms a thin layer which is more wettable for polar liquids, with a consequent positive effect on the adhesion strength of polar and semi-polar coatings or adhesives to wood [12,13,22].

Laser technologies in the wood industry are commonly applied for the cutting, engraving, drilling/incising, surface treatment, or cleaning of solid wood and wood composites [23–30]. Laser beams change the chemical structure of irradiated wood surfaces [9,31]; their anatomy and morphology [23,25,32–34]; as well as their properties—e.g., their color, roughness, wettability, free surface energy, and resistance (to bacteria, molds, and other biological agents) [4,18,28,35,36]. The results of the X-ray photo-electron spectroscopy indicated an increased number of non-polar bonds such as C–C and C–H, with C–O bonds maintained without change [33]. The microscopic observations point out that treating wood surfaces with a laser beam may make the surface smoother because the cells melt down to a depth of several micrometers without their direct carbonization [33]. Dolan et al. [37] observed that cellulose fibrils coalesced and formed a bubble-like topology when exposed to the energy of a CO₂ laser. A laser is able to create similar changes also in other natural and synthetic polymer materials in connection with degradation, depolymerization, and carbonization processes in various types of organic macromolecules [38]. Lasers, unlike plasma, hydrophobize wood components and worsen the wettability of wood with water and other polar liquids—including polar synthetic polymer adhesives and coatings [6,12].

Adhesion processes play a significant role in contemporary material bonding and painting technologies. The final quality of bonded or painted wooden materials is conditioned by the interaction between the wood substrate and the liquid and following solid-cured adhesives or coatings. The formation of the “adhesive/coating–wood” phase interface is significantly determined mainly by two factors: (1) the surface properties of the wood adherent (e.g., density, porosity, roughness, wettability, free surface energy, pH value) and (2) the physical/chemical and application properties of the used adhesive or coating (e.g., polymer type, molecular weight, viscosity, surface tension, polarity, pH value, weight solid, density). However, some other factors can also affect the adhesion processes of wood bonding and painting—for example, the initial chemical, physical, or biological pretreatments of wood surfaces or the creation of internal stresses in the deposited polymer films or in the created “adhesive/coating–wood” interfaces. Surface pretreatment is one of the first and most important technological stages in the adhesive bonding process. Ülker [39] underlines that a particular pretreatment of wood for structural bonding will ideally produce a surface which is (1) free from contamination, (2) wettable by an adhesive, (3) optimally macro- and micro-rough, (4) mechanically stable, and (5) hydrolytically stable.

The biological resistance of bonded and painted wood against bacteria, molds, staining fungi, and decaying fungi is important mainly for products exposed to a moist environment [40,41]. Several natural adhesives and coatings—e.g., those based on sugar and protein macromolecules—are easily attacked and destroyed by biological agents. Such bio-degradations can then be quickly connected with the delamination of bonded wood products or the peeling of coatings from painted wood surfaces. Synthetic polymers have usually a higher resistance to biological attacks, and the most resistant to bacteria and molds are the polyurethane (PUR) polymers [42,43].

Assembly adhesives and coatings recommended for wooden products, such as solid wood panels, glulam, furniture parts, and sport or musical instruments, are manufactured from several synthetic polymers, including polyvinyl acetate (PVAc) and PUR polymers [44].

The PVAc polymer is the most widely used as a water emulsion. Its emulsion consistency is created by the polymerization of polar vinyl monomers, predominantly vinyl acetate, in water. From PVAc polymers, thermoplastic adhesives that are important for furniture manufacturing and carpentry are produced. The bonding principle of PVAc adhesives is based on the removal of water by penetration into the wood substrate or by the evaporation of water to the surrounding air. The forming of the bond also requires the

application of proper pressure. PVAc polymer systems show a long storage life and are easy to clean. However, the bond formed from them has a lower resistance to heat and is characterized by creep behavior. The biodeterioration of PVAc polymers occurs due to the enzymatic action of esterase created by filamentous fungi, whereas algae, yeasts, lichens, and bacteria can also degrade polyvinyl acetate macromolecules [45].

PUR polymers are synthesized by the reaction of various types of isocyanates with polyols, forming repeating polar urethane moiety units which have a good bonding ability to various surfaces. The biodeterioration of PUR polymers can occur through the enzymatic action of various hydrolases, such as ureases, proteases, and esterases, which are created by fungi (e.g., *Chaetomium globosum* Kunze ex Fr.) and bacteria (e.g., *Bacillus subtilis* Cohn) [46].

The aim of this work was to analyze the effect of a CO₂ laser on the adhesion strength and the resistance to molds of the PVAc and PUR polymers applied to the surfaces of beech and spruce woods.

2. Materials and Methods

2.1. Woods

The samples with dimensions of 250 × 130 × 10 mm (longitudinal × radial × tangential) were prepared from the boards of two wood species—European beech (*Fagus sylvatica* L.) and Norway spruce (*Picea abies* /L./Karst)—after their 2-year air seasoning under the roof. In total, 76 wood samples were collected for the experiment, including samples without knots, false heartwood, biological damage, growth defects, or inhomogeneity. Before performing the individual technological operations—(1) the application of the synthetic polymer layer directly on the top surface of the native wood or (2) the laser modification of the top surface of the native wood—the top surfaces of the native wood samples were sanded along the fibers with sandpapers of 80 grit and then 120 grit on the belt DREMEL[®]3000 grinder machine (Breda, The Netherlands). Following this, the wood samples were conditioned for 7 days at a temperature of 20 °C and a relative air humidity of 65%, achieving a moisture content from 11% to 13%.

2.2. Synthetic Polymers

The PVAc polymer was used in the form of a one-component water-dispersed adhesive TechnoBond D3 P (Agglu, Turčianske Teplice, Slovakia); see Table 1.

Table 1. Synthetic polymers in commercial adhesives and their processing conditions.

Synthetic Polymer	Polyvinyl Acetate PVAc	Polyurethane PUR
Adhesive	TechnoBond D3 P	Neopur 1791 and Adiflex 935
Density (kg·m ⁻³)	1080	1550
Weight solids (%)	51 ± 2	100
Colour after curing	transparent	light-white
pH value	3 ± 0.4	-
Spread rate (g·m ⁻²)	120–200	200–400
Open time (min)	15	90–130
Pressing time at 20 °C (h)	0.3	5

The PUR polymer was applied as two-component reactive adhesive Neopur 1791 mixed before the application of the hardener Adiflex 935 in a weight ratio of 100:20 (Neoflex Adhesives, Elche, Spain)—Table 1.

Both polymers in the form of adhesives were applied to the top surfaces of samples conditioned at a moisture content of 12 ± 1% by a hand toothed trowel in an amount (spread rate) of 200 g·m⁻² before or after the irradiation of the samples with a CO₂ laser. Following this, the samples were conditioned for 7 days without pressing at a temperature of 20 °C and a relative air humidity of 65%, achieving a moisture content from 11% to 13%.

2.3. Laser Irradiation of Surfaces

The commercial CO₂ laser LCS 100 device (Formetal Piesok, Piesok, Slovakia), working with a wavelength of 10.6 μm, was used for the irradiation of the top surfaces of the native wood samples as well as of the wood samples first covered with a layer of synthetic polymer. The effective power of the laser beam (45 W) was determined in continuous-wave mode using the equipment Coherent Radiation Model 201 (Coherent Inc., Santa Clara, CA, USA). The laser beam diameter (∅), used for the irradiation of the sample in one pass, was constantly 12 mm. The laser head moved perpendicularly to the top surface of sample at a determined scanning speed v from 18 to 2 cm·s⁻¹ (Table 2). With the aim to obtain an approximately uniform intensity of the irradiation dose H across the whole surface of the sample, with a width of 130 mm in the radial direction, the laser head moved in twenty-two passes parallel with the longitudinal direction of the sample, overlapping homogeneously with its surface (Figure 1).

Table 2. The laser irradiation doses (H) acting on the top surface of samples dependent on the scanning speed (v).

Sample	Ref.	A	B	C	D	E	F	G	H	I
Scanning speed v (cm·s ⁻¹)	-	18	16	14	12	10	8	6	4	2
Irradiation dose H (J·cm ⁻²)	0	2.1	2.3	2.7	3.1	3.8	4.7	6.3	9.4	18.8

Notes: Ref. represents reference samples (in total, 4 types of reference samples were used—i.e., from 2 wood species “beech or spruce” covered with 2 polymer types “PVAc or PUR”). Symbols A to I represent testing samples modified with 9 different irradiation doses (in total, 72 types of laser-irradiated samples—i.e., 9 irradiation doses “from A to I” × 2 wood species “beech or spruce” × 2 polymer types “PVAc or PUR” × 2 modes of polymer application “before or after irradiation of sample with a CO₂ laser”).

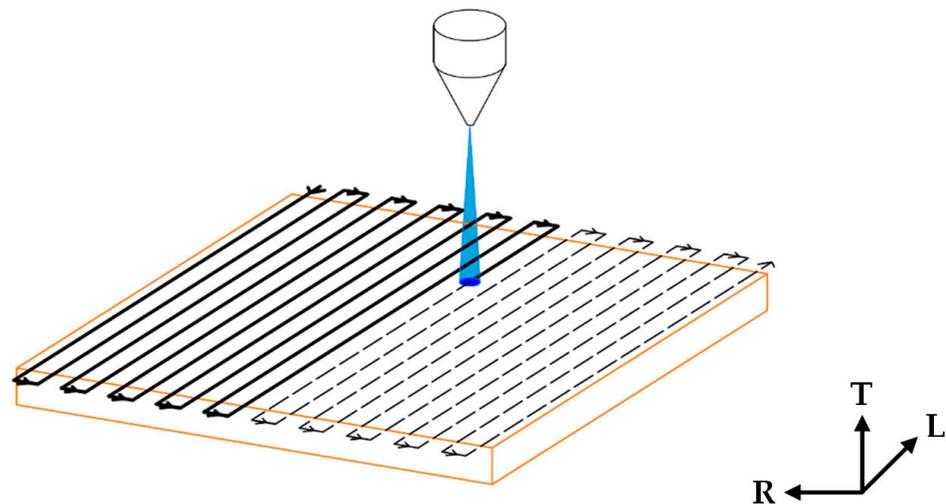


Figure 1. Scheme of the sample 250 × 130 × 10 mm (longitudinal × radial × tangential) irradiated with the beam of a CO₂ laser.

The irradiation doses H (J·cm⁻²) were calculated for the individual scanning speeds of the laser head v (cm·s⁻¹) and the other laser parameters in the modification process according to Equation (1):

$$H = (Pe \times \tau); S = (Pe \times L); (S \times v) \text{ (J·cm}^{-2}\text{)}, \quad (1)$$

where Pe (45 W) is the effective laser beam power acting on the top surface of the sample, τ (s) is the irradiation time of one pass (i.e., the ratio between the dimension of the wood sample in the direction of its irradiation L (25 cm) and the scanning speed of the laser head v (from 18 cm·s⁻¹ to 2 cm·s⁻¹)), and S ($\emptyset \times L = 1.2 \text{ cm} \times 25 \text{ cm} = 30 \text{ cm}^2$) is the area

irradiated during one pass (i.e., an area equal to the homogeneously irradiated area by the Gaussian distribution of the real laser intensity distribution for this area at three passes) (Figure 1).

2.4. Light Microscopy Analysis

The effects of a CO₂ laser on the structural changes in the top surfaces of wood samples covered with a layer of the synthetic polymers were assessed with the light microscope Olympus BX43F (Olympus Corporation, Tokyo, Japan) at a magnification of 10×.

2.5. Adhesion Strength of the “Synthetic Polymer—Wood” Interface

The adhesion strength (σ) of the synthetic polymer layer to the wood adherent was determined by the pull-off test for adhesion in accordance with the standard EN ISO 4624 [47], using the PosiTest AT-M Adhesion Tester instrument (DeFelsko, Ogdensburg, NY, USA). A bond connection of the steel-roller dolly ($\varnothing = 20$ mm) with the top surface of the sample (polymer layer present on wood adherent) was made by two-component epoxy resin (Repair Universal Epoxy Resin, Pattex, Henckel, Germany).

The pull-off test tensile strength method measures the tensile force perpendicular to the phase interface “adhesive/coating–wood” system required to tear off the steel-roller from the adhesive or coating present on the surface of the wood sample, at which the failures could occur either in the weakest interface “adhesive/coating–wood” or in the weakest component “adhesive/coating” or “wood”.

For each sample, the adhesion strength was determined in 4 places (Figure 2). In total, 304 adhesion tests were performed for 76 samples—i.e., for 4 reference samples and 72 samples modified with a CO₂ laser (i.e., 2 wood species: beech and spruce; 2 polymer types: PVAc and PUR; 2 modes of CO₂ laser modification: sample irradiated before or after covering with a layer of polymer; 9 laser irradiation doses. See Table 1).

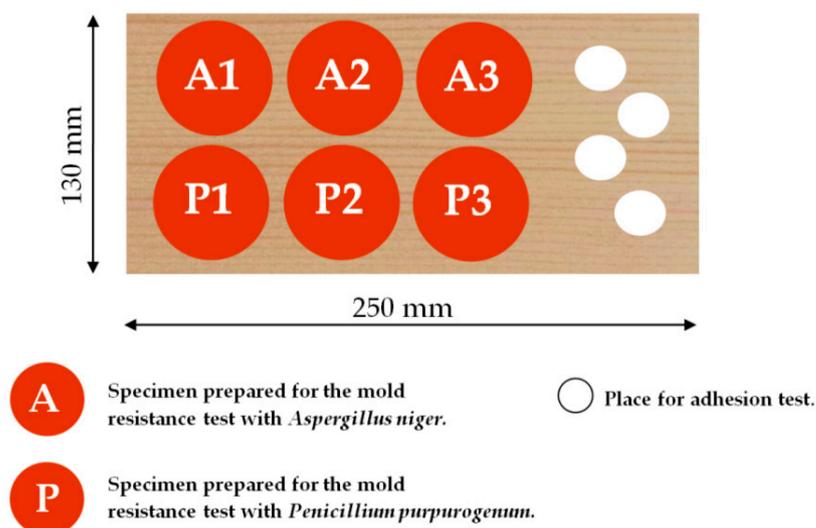


Figure 2. Scheme of sample with 4 places for the adhesion test and with 6 specimens prepared from it for the mold resistance test.

2.6. Mold Resistance of the Synthetic Polymer Layer on the Wood Adherent

For the mold growth activity (MGA) test, the top surfaces of circular specimens with a diameter of 54 mm (prepared from the relevant sample; see Figure 2) were exposed in accordance with the standard EN 15457 [48]. Sterilized specimens were placed into Petri dishes with a diameter of 120 mm on a 3 to 4 mm-thick layer of 4.9 wt.% Czapek–Dox agar medium (HiMedia Ltd., Mumbai, India) and inoculated with a spore suspension of the microscopic fungi *Aspergillus niger* Tiegh. (strain BAM 122; Bundesanstalt für Materialforschung und -prüfung, Berlin) and *Penicillium purpurogenum* Stoll. (strain BAM

24; Bundesanstalt für Materialforschung und -prüfung, Berlin), respectively. Both spore suspensions were prepared in sterile water in concentrations of 10^6 to 10^7 spores/mL. The incubation of the inoculated specimens lasted 21 days at a temperature of $24\text{ °C} \pm 2\text{ °C}$ and a relative air humidity of 90% to 95%. The mold resistance of the specimens was determined by the MGA values (from 0 to 4) using these criteria: 0, no mold growth on the top surface; 1, $\leq 10\%$; 2, $>10\%$ but $\leq 30\%$; 3, $>30\%$ but $\leq 50\%$; 4, $>50\%$.

2.7. Statistical Analysis

The measured data of the adhesion strength (σ) and the mold growth activity (MGA) were for individual groups of the reference and laser-modified samples evaluated on the basis of mean values and standard deviations. Using ANOVA, the effect of increased laser irradiation doses (H) from 2.1 to $18.8\text{ J}\cdot\text{cm}^{-2}$ on the adhesion strength and the mold resistance was analyzed by the linear correlations " $\sigma = a + b \cdot H$ " and " $MGA = a + b \cdot H$ ", together with the coefficients of determination, r^2 , and levels of significance, p .

3. Results and Discussion

3.1. Microscopy of Surfaces

The synthetic polymer layers present on the wood surfaces showed visible structural changes after irradiation with a CO_2 laser (Figures 3 and 4).

Due to the relatively smaller irradiation dose of $4.7\text{ J}\cdot\text{cm}^{-2}$, in the layers of PVAc and PUR polymers present on the wood surfaces air bubbles with diameters of 0.1 to 0.3 mm were created (Figure 3c,d and Figure 4c,d). The PVAc polymer obtained a yellow shade as well (Figure 3c,d). The bubbles in the synthetic polymer layers probably arose as a result of thermal decomposition reactions in their macromolecules, together with the creation of lower-molecular gasses which inflated a layer of thermoplastic PVAc polymer or a layer of the completely non-crosslinked PUR polymer. Similar bubbles in layers of synthetic polymers are intentionally created in intumescent types of fire retardants [49,50]. However, bubbles created due to CO_2 lasers could also be water molecules released from moist wood adherents (i.e., the water bonded in wood by hydrogen and other physical-chemical forces), as well as water and various small organic molecules created during the thermal destruction of the lignin-polysaccharide matrix of wood. A yellow shade in the laser-irradiated PVAc polymer could be explained by its lower thermal stability [51,52] in comparison to the PUR polymer [53,54].

By applying the highest irradiation dose of $18.8\text{ J}\cdot\text{cm}^{-2}$, the layers of PVAc and PUR polymers were evidently carbonized. They obtained brown shades until they were nearly a black color, at which the bubbles in the carbonized polymer layers had already burst in most cases (Figure 3e,f and Figure 4e,f).

The primary laser irradiation of the native wood surfaces also caused decomposition and carbonization processes—in this case, in the lignin-polysaccharide components of wood. The irradiation of wood surfaces with higher doses H was connected with their darkening—gradually from yellowing to browning and blackening—in accordance with other research works—e.g., [5,6,17–19,35].

3.2. Adhesion Strength

For the reference samples—i.e., samples unmodified with a CO_2 laser, a better adhesion strength between the layer of synthetic polymer and the wood adherent was determined for the PUR polymer (beech: $\sigma = 5.33\text{ MPa}$; spruce: $\sigma = 3.05\text{ MPa}$) than for the PVAc polymer (beech: $\sigma = 3.69\text{ MPa}$; spruce: $\sigma = 2.35\text{ MPa}$) (Tables 3 and 4).

The adhesion strength (σ) of the "synthetic polymer–wood" phase interface continuously decreased with the increase in the irradiation dose (H) of a CO_2 laser acting on the top surface of wood samples before or after covering them with a layer of synthetic polymer (Tables 3 and 4, Figures 5–7).

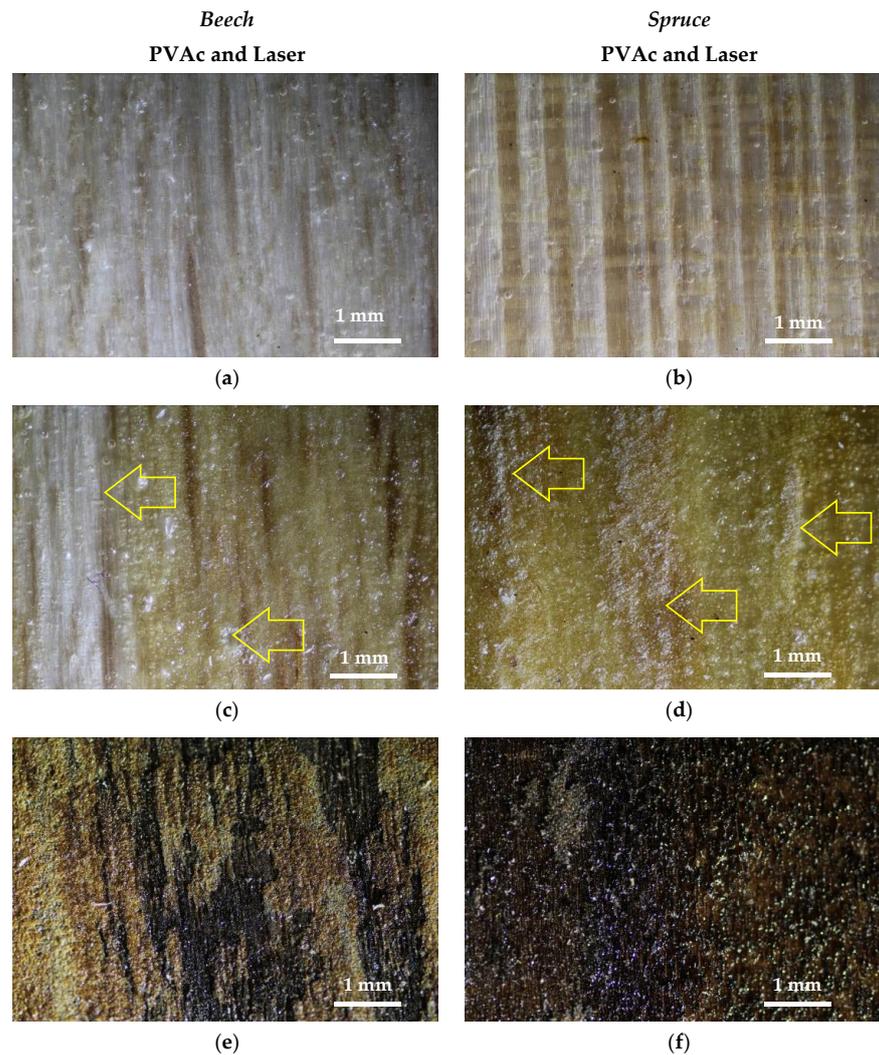


Figure 3. The microscopic image of the top surfaces of wood samples covered with a layer of PVAc polymer—reference (a,b: $H = 0.0 \text{ J}\cdot\text{cm}^{-2}$) and irradiated with a CO_2 laser with the mode “PVAc and Laser” when applying a medium irradiation dose (c,d: $H = 4.7 \text{ J}\cdot\text{cm}^{-2}$) with the irregular occurrence of air bubble zones in the heat-affected polymer layers, or a maximum irradiation dose (e,f: $H = 18.8 \text{ J}\cdot\text{cm}^{-2}$) with the intensive creation of air bubbles in the strongly carbonized polymer layers.

Table 3. The adhesion strength (σ) of the “synthetic polymer–wood” interface for the European beech wood samples irradiated with various doses of CO_2 laser (H) before or after application of the PVAc or PUR polymer layer.

Irradiation Dose H ($\text{J}\cdot\text{cm}^{-2}$)	Ref. 0	A 2.1	B 2.3	C 2.7	D 3.1	E 3.8	F 4.7	G 6.3	H 9.4	I 18.8
Beech										
Laser and PVAc	3.69 (0.73)	3.33 (0.46)	3.04 (0.39)	3.24 (0.29)	2.34 (0.36)	2.33 (0.41)	2.91 (0.71)	2.25 (0.45)	2.46 (0.62)	2.09 (0.27)
PVAc and Laser	3.69 (0.73)	3.01 (0.74)	3.18 (0.49)	2.84 (0.38)	2.45 (0.15)	2.32 (0.50)	2.77 (0.47)	2.49 (0.44)	2.35 (0.63)	1.95 (0.36)
Laser and PUR	5.33 (0.61)	3.52 (0.78)	2.77 (0.30)	2.79 (0.79)	3.08 (0.51)	2.19 (0.11)	2.25 (0.42)	2.73 (0.88)	2.00 (0.63)	1.59 (0.57)
PUR and Laser	5.33 (0.61)	4.69 (0.95)	4.57 (0.99)	3.89 (1.08)	3.84 (0.69)	2.90 (0.97)	2.87 (0.77)	3.17 (1.17)	2.87 (0.90)	2.03 (0.59)

Note: Mean value is from 4 measurements. Standard deviation is in parentheses.

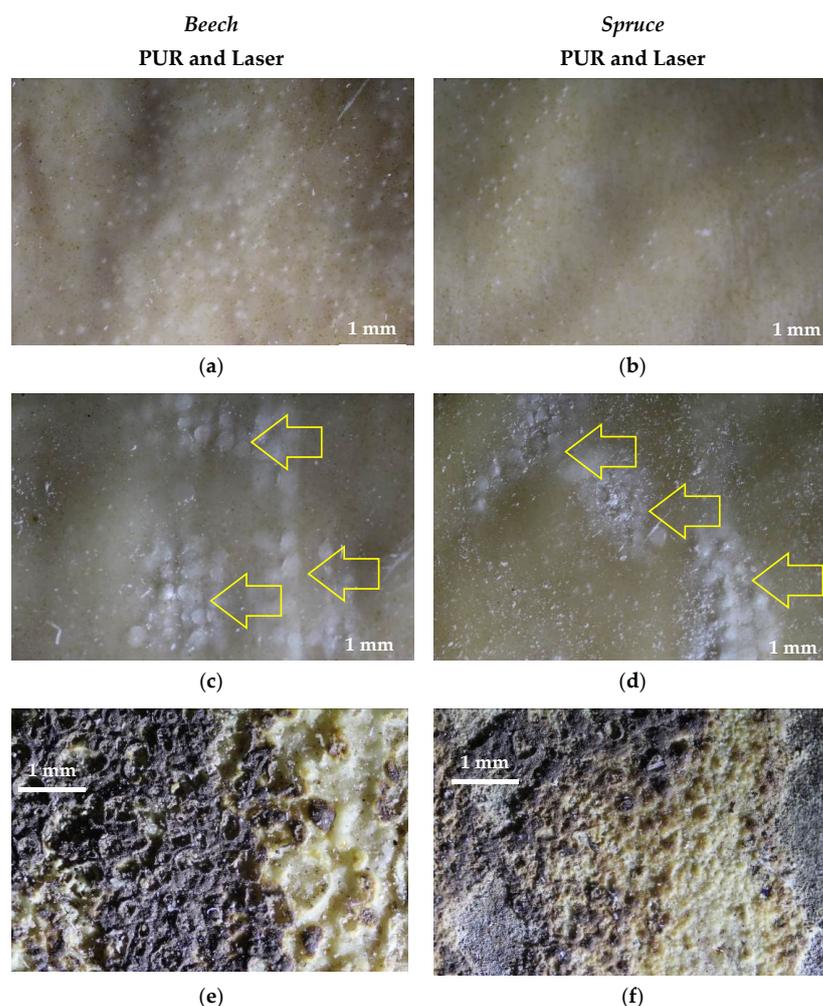


Figure 4. The microscopic image of the top surfaces of wood samples covered with a layer of PUR polymer—reference (a,b: $H = 0.0 \text{ J}\cdot\text{cm}^{-2}$) and irradiated with a CO_2 laser with the mode “PUR and Laser” when applying a medium irradiation dose (c,d: $H = 4.7 \text{ J}\cdot\text{cm}^{-2}$) with the irregular occurrence of air bubble zones in the heat-affected polymer layers, or a maximum irradiation dose (e,f: $H = 18.8 \text{ J}\cdot\text{cm}^{-2}$) with the intensive creation of air bubbles and their bursting in the strongly carbonized polymer layers.

Table 4. The adhesion strength (σ) of the “synthetic polymer–wood” interface for the Norway spruce wood samples irradiated with various doses of CO_2 laser (H) before or after the application of the PVAc or PUR polymer layer.

Irradiation Dose H ($\text{J}\cdot\text{cm}^{-2}$)	Ref. 0	A	B	C	D	E	F	G	H	I
		2.1	2.3	2.7	3.1	3.8	4.7	6.3	9.4	18.8
Spruce		Adhesion strength— σ (MPa)								
Laser and PVAc	2.35 (0.53)	2.27 (0.41)	2.20 (0.39)	1.97 (0.08)	2.08 (0.69)	1.93 (0.81)	1.78 (0.22)	1.78 (0.28)	1.18 (0.21)	1.22 (0.22)
PVAc and Laser	2.35 (0.53)	2.09 (0.26)	2.15 (0.42)	1.99 (0.12)	1.93 (0.40)	2.02 (0.29)	1.75 (0.34)	1.41 (0.25)	1.38 (0.12)	1.45 (0.26)
Laser and PUR	3.05 (0.38)	2.41 (0.41)	2.29 (0.58)	1.93 (0.37)	1.72 (0.51)	1.91 (0.24)	1.84 (0.25)	1.74 (0.52)	1.34 (0.40)	1.50 (0.25)
PUR and Laser	3.05 (0.38)	2.20 (0.50)	1.95 (0.57)	1.97 (0.50)	1.83 (0.76)	1.59 (0.30)	1.79 (0.28)	1.51 (0.23)	1.57 (0.33)	1.53 (0.21)

Note: Mean value is from 4 measurements. Standard deviation is in parentheses.

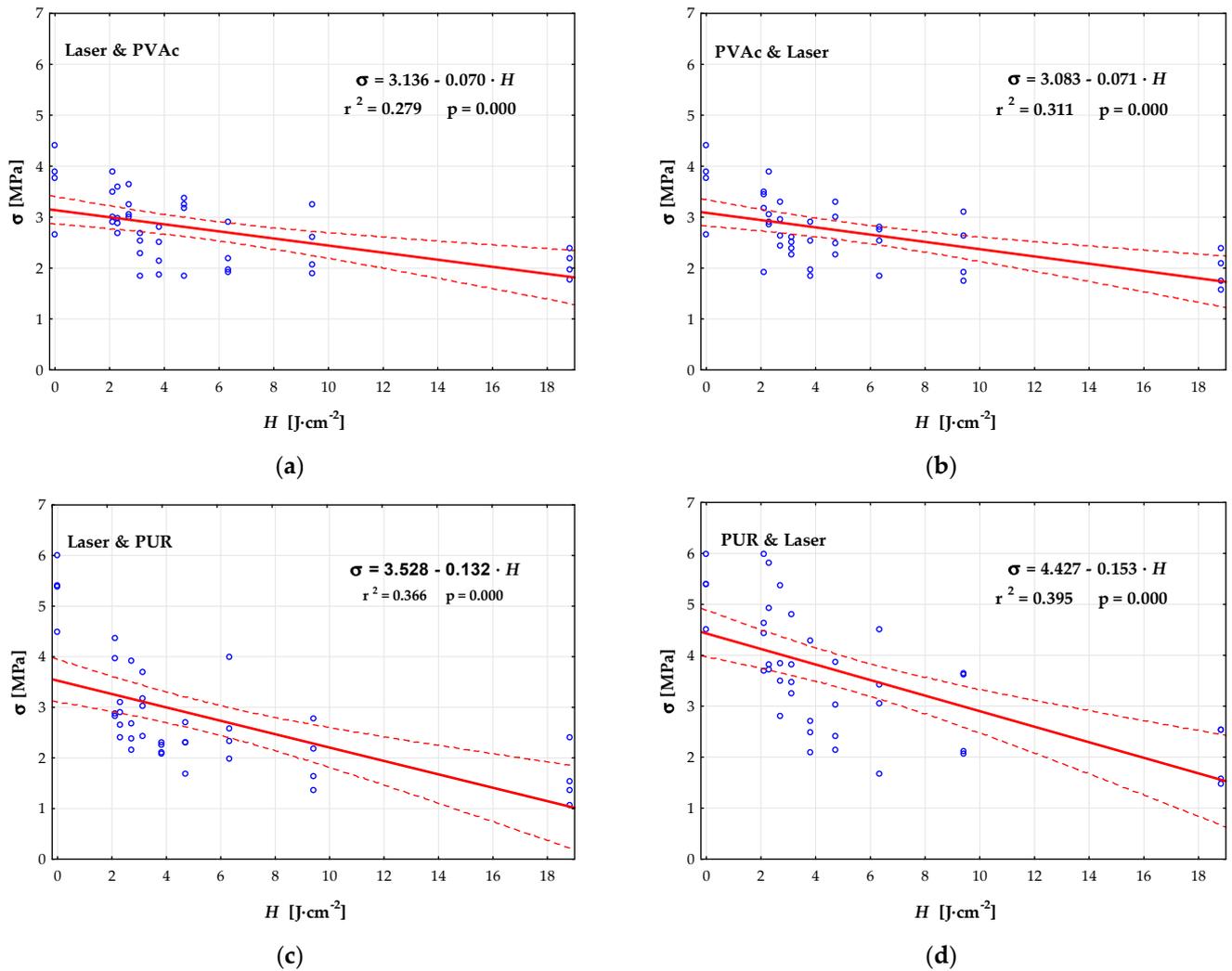


Figure 5. Linear correlations between the adhesion strengths (σ) and the irradiation doses of laser (H) acting on the top surface of the European beech wood samples when using the treatment mode: (a) “Laser and PVAc”, (b) “PVAc and Laser”, (c) “Laser and PUR”, and (d) “PUR and Laser”.

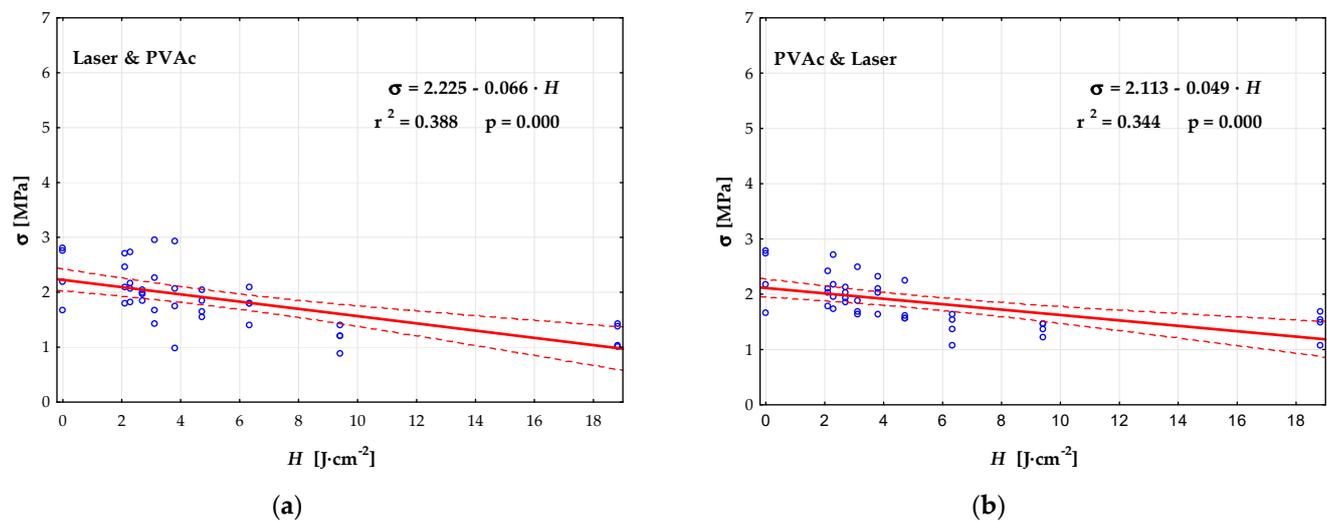


Figure 6. Cont.

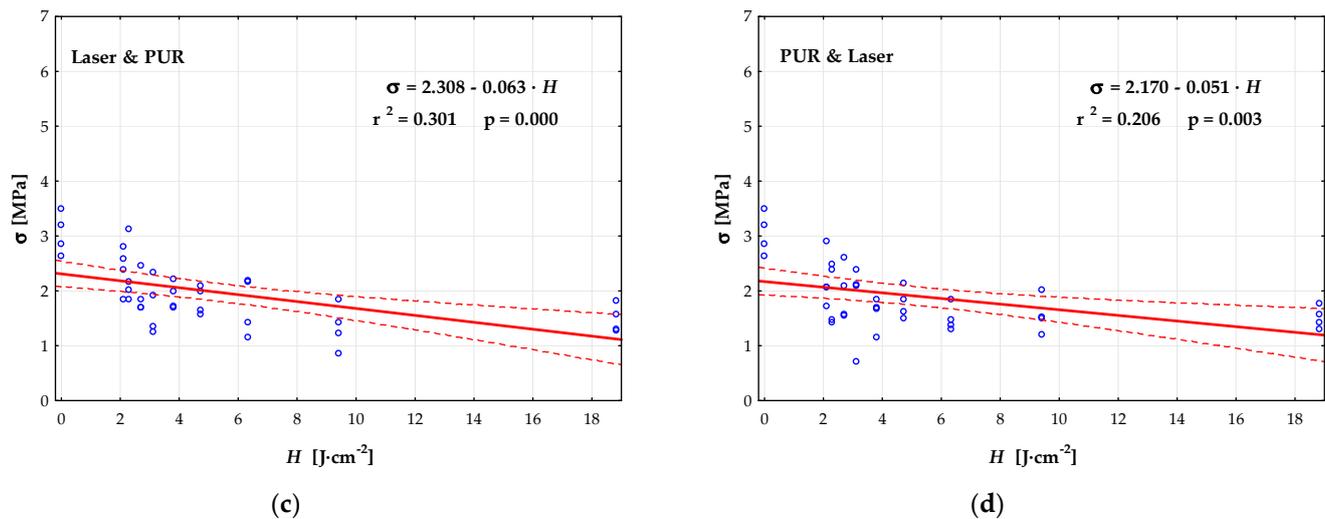


Figure 6. Linear correlations between the adhesion strengths (σ) and the irradiation doses of laser (H) acting on the top surface of the Norway spruce wood samples when using the treatment mode: (a) “Laser and PVAc”, (b) “PVAc and Laser”, (c) “Laser and PUR”, and (d) “PUR and Laser”.

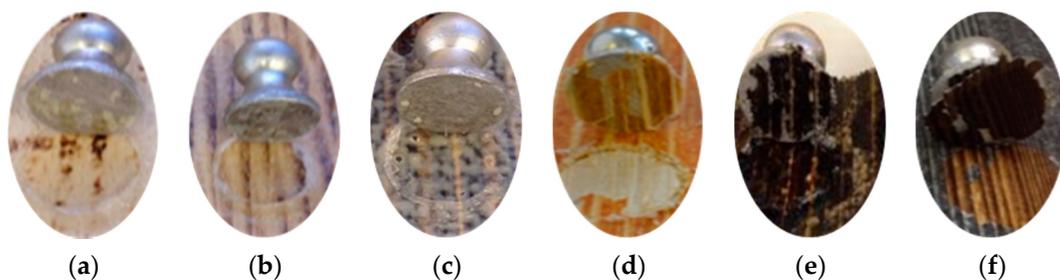


Figure 7. View of the “synthetic polymer–wood” phase interface damage created during the adhesion test of beech samples: (a) PVAc and Laser = $3.8 \text{ J}\cdot\text{cm}^{-2}$; (b) PVAc and Laser = $6.3 \text{ J}\cdot\text{cm}^{-2}$; (c) PVAc and Laser = $18.8 \text{ J}\cdot\text{cm}^{-2}$. Damage created during the adhesion test of spruce samples: (d) PVAc and Laser = $3.8 \text{ J}\cdot\text{cm}^{-2}$; (e) PUR and Laser = $18.8 \text{ J}\cdot\text{cm}^{-2}$; (f) Laser = $18.8 \text{ J}\cdot\text{cm}^{-2}$ and PUR. Note: In the adhesion tests, the weakest point for determining the joint was up to 70% of the phase boundary between the wood adherent and the synthetic polymer; the diameter of the steel-roller dolly is 20 mm—i.e., the test area is 3.14 cm^2 .

Due to the higher laser irradiation doses (H), in all cases—i.e., for two wood species, two synthetic polymer types, two modes of polymer layer application on the wood surface “before or after laser irradiation”—a significant decrease in the adhesion strength between the synthetic polymer layer and the wood adherent was found. For beech samples, the maximum decrease in the adhesion strength was determined using the highest irradiation dose H of $18.8 \text{ J}\cdot\text{cm}^{-2}$. When studying the effect of applying two different synthetic polymers to a beech wood adherent, a milder decrease in the adhesion strength due to an increase in the laser irradiation was found in the application of the PVAc layer (by 43.4% for the mode “Laser and Polymer” or by 47.2% for the mode “Polymer and Laser”) than in the application of the PUR layer (by 70.2% for the mode “Laser and Polymer” or by 61.9% for the mode “Polymer and Laser”) (Table 3). For spruce samples, the maximum decrease in the adhesion strength was in more cases determined for the application of the second highest irradiation dose H of $9.4 \text{ J}\cdot\text{cm}^{-2}$ (i.e., by 49.8% or 41.3% when using the PVAc layer, and by 56.1% or 48.5% when using PUR layer for the modes “Laser and Polymer” or “Polymer and Laser”) (Table 4).

The above knowledge related to the values of adhesion strength was confirmed by linear correlations ($\sigma = a + b \cdot H$), for which in the beech samples the coefficient of determination r^2 ranged from 0.279 to 0.395 with a level of significance of $p = 0.000$ (Figure 5), while in the spruce samples the r^2 ranged from 0.205 to 0.388 and the p from 0.000 to 0.003 (Figure 6). As mentioned above, for beech samples irradiated with a CO_2

laser, the “synthetic polymer–wood” phase interface weakened approximately 1.45 times more when using the PUR polymer layer (by 70.2% or 61.9%) than when using the PVAc one (by 43.4% or 47.2%); this tendency is also documented by the higher negative values of the parameter “b” in the linear correlations when using the PUR layer (Figure 5).

Summarizing the results of all the irradiation modes and doses of a CO₂ laser, the adhesion strength decreased more evidently (1) for the beech versus spruce wood adherent, (2) for the PUR versus PVAc polymer layer, and (3) for the laser beam focusing on the native wood versus synthetic polymer (Figures 5 and 6). This knowledge achieved for the beech wood adherent and the PUR polymer layer can be explained by the greater potential for adhesion strength drop due to the action of a CO₂ laser for such types of wood adherent or polymer layers, which in the initial reference state secured a higher adhesion strength for the “synthetic polymer–wood” phase interface.

3.3. Mold Resistance

The mold growth activity (MGA) of the microscopic fungi *Aspergillus niger* and *Penicillium purpurogenum* on the top surfaces of the native wood specimens (i.e., wood surfaces not covered with a layer of synthetic polymer and not modified with a CO₂ laser) was evident from a beginning of the mycological test, whereas on the final 21st day the molds covered more than 30% or 50% of the wood surfaces, with the MGA ranging from 3 to 4. This result confirmed the very low mold resistance of the natural/untreated beech [18,55,56] and spruce [57] woods.

The reference wood specimens, meaning specimens covered with a layer of synthetic polymer (i.e., wood surfaces covered with a layer of synthetic polymer but unmodified with a CO₂ laser), were more resistant to microscopic fungi, whereas the MGA values ranged from 2 to 3 for the layer with the PVAc polymer or from 0 to 1 for the layer with the PUR polymer (Tables 5 and 6; see Reference).

Table 5. The mold growth activity (MGA) evaluated after 21 days on the polymer layer present on the European beech wood adherent. Laser irradiation of specimens with doses (H) was performed before or after covering them with a layer of synthetic polymer.

Irradiation Dose H (J·cm ⁻²)	Ref. 0	A 2.1	B 2.3	C 2.7	D 3.1	E 3.8	F 4.7	G 6.3	H 9.4	I 18.8	MGA = $f(H)$ r^2 ; p -Value
Beech		<i>Aspergillus niger</i> —MGA (0–4)									
Laser and PVAc	2.67	2.67	2.67	2.33	2.33	2.00	1.67	1.67	2.00	2.33	$MGA = 2.334 - 0.019 \cdot H$ $r^2 = 0.070$; $p = 0.158$
PVAc and Laser	2.67	3.33	2.67	1.67	1.67	2.00	1.67	1.33	2.00	2.00	$MGA = 2.277 - 0.033 \cdot H$ $r^2 = 0.059$; $p = 0.196$
Laser and PUR	0.67	0.00	1.00	1.00	1.00	0.67	1.00	0.33	0.00	0.00	$MGA = 0.825 - 0.049 \cdot H$ $r^2 = 0.252$; $p = 0.005$
PUR and Laser	0.67	1.33	1.00	1.00	0.33	0.33	0.33	0.67	0.67	0.33	$MGA = 0.810 - 0.027 \cdot H$ $r^2 = 0.066$; $p = 0.170$
Beech		<i>Penicillium purpurogenum</i> —MGA (0–4)									
Laser and PVAc	2.33	2.33	2.67	2.33	2.33	2.00	1.33	1.67	1.67	2.00	$MGA = 2.224 - 0.030 \cdot H$ $r^2 = 0.030$; $p = 0.360$
PVAc and Laser	2.33	2.00	2.33	2.33	1.67	2.00	1.67	1.67	1.33	1.66	$MGA = 2.108 - 0.039 \cdot H$ $r^2 = 0.138$; $p = 0.043$
Laser and PUR	0.67	1.00	1.00	0.67	1.00	0.67	0.67	0.00	0.00	0.33	$MGA = 0.817 - 0.041 \cdot H$ $r^2 = 0.182$; $p = 0.019$
PUR and Laser	0.67	1.00	1.00	0.67	0.67	1.00	1.33	1.00	1.00	0.67	$MGA = 0.927 - 0.005 \cdot H$ $r^2 = 0.004$; $p = 0.733$

Note: Mean value is from 3 replicates. Relation $MGA = f(H)$ is determined from the individual values of 30 specimens. r^2 is the coefficient of determination. p is the level of significance.

Table 6. The mold growth activity (MGA) evaluated after 21 days on the polymer layer present on the Norway spruce wood adherent. Laser irradiation of specimens with doses (H) was performed before or after covering them with a layer of synthetic polymer.

Irradiation Dose H (J·cm ⁻²)	Ref. 0	A 2.1	B 2.3	C 2.7	D 3.1	E 3.8	F 4.7	G 6.3	H 9.4	I 18.8	MGA = f(H) r^2 ; p -Value
Spruce		<i>Aspergillus niger</i> —MGA (0–4)									
Laser and PVAc	2.33	2.00	2.67	2.33	2.33	2.00	1.67	1.33	1.67	1.67	MGA = 2.334 – 0.019 · H $r^2 = 0.157$; $p = 0.030$
PVAc and Laser	2.33	2.67	2.00	1.67	1.67	2.00	2.00	1.67	1.67	1.00	MGA = 2.167 – 0.063 · H $r^2 = 0.378$; $p = 0.000$
Laser and PUR	0.67	1.00	0.67	0.33	0.67	0.67	0.67	0.33	0.33	0.00	MGA = 0.754 – 0.042 · H $r^2 = 0.182$; $p = 0.019$
PUR and Laser	0.67	0.67	0.67	1.00	0.67	0.33	0.33	0.67	0.67	0.67	MGA = 0.637 – 0.001 · H $r^2 = 0.000$; $p = 0.973$
Spruce		<i>Penicillium purpurogenum</i> —MGA (0–4)									
Laser and PVAc	2.33	2.67	2.67	2.00	2.33	2.00	1.67	1.67	2.33	2.00	MGA = 2.277 – 0.021 · H $r^2 = 0.041$; $p = 0.281$
PVAc and Laser	2.33	2.33	2.00	2.00	2.00	2.33	1.67	2.00	2.00	1.67	MGA = 2.189 – 0.029 · H $r^2 = 0.135$; $p = 0.046$
Laser and PUR	0.33	0.67	1.00	1.00	0.33	1.00	1.00	0.33	0.67	0.67	MGA = 0.708 – 0.002 · H $r^2 = 0.000$; $p = 0.927$
PUR and Laser	0.67	0.67	0.67	0.67	0.33	0.33	0.33	1.00	0.67	1.00	MGA = 0.506 – 0.024 · H $r^2 = 0.065$; $p = 0.175$

Note: Mean value is from 3 replicates. Relation $MGA = f(H)$ is determined from the individual values of 30 specimens. r^2 is the coefficient of determination. p is the level of significance.

With an increase in the laser irradiation doses (H), the MGA values of the microscopic fungi determined on the top surfaces of the laser-modified specimens (i.e., the surfaces of specimens modified with a CO₂ laser before or after covering them with a layer of PVAc or PUR polymer) decreased significantly in comparison to the reference specimens only in some cases, as is documented by the results of the linear correlations $MGA = f(H)$ (Tables 5 and 6).

For the treatment mode “PVAc and Laser”, the MGA values decreased maximally to 1–2 from 2–3 determined for the reference “PVAc”. On the other hand, no significant change in the MGA occurred for the specimens treated with the mode “PUR and Laser”. This result can be explained by the evidently lower initial mold resistance of the PVAc polymer (Ref. PVAc: MGA = 2.33–2.67) in comparison to the very good initial mold resistance of the PUR polymer (Ref. PUR: MGA = 0.33–0.67) (Tables 5 and 6).

The MGA values usually reduced significantly ($p \leq 0.05$) due to the higher irradiation doses H only for specimens whose surfaces were modified with the following two modes: “PVAc and Laser” and “Laser and PUR” (Tables 5 and 6, Figures 8 and 9).

Using the “PVAc and Laser” mode—i.e., when specimens were firstly covered with a layer of PVAc polymer and subsequently irradiated with a CO₂ laser—the linear correlations ($MGA = a + b \cdot H$) for the beech specimens had the coefficient of determination r^2 0.059 (*Aspergillus niger*) or 0.138 (*Penicillium purpurogenum*) and the level of significance $p = 0.196$ (nonsignificant) or 0.043 (significant at the 95% level). The linear correlations for the spruce specimens were partly more representative, with the r^2 0.378 or 0.135 and the $p = 0.000$ (significant at the 99.9% level) or 0.046 (significant at the 95% level) (Tables 5 and 6, Figures 8 and 9).

Using the treatment mode “Laser and PUR”, a significant decrease in mold activity was found, with the MGA values of up to 0. In the linear correlations ($MGA = a + b \cdot H$) for beech specimens had the coefficient of determination r^2 0.252 (*Aspergillus niger*) or 0.182 (*Penicillium purpurogenum*) and the level of significance $p = 0.005$ or 0.019 (Table 4),

while spruce specimens had r^2 0.182 or 0.000 and $p = 0.019$ or 0.927 (Table 5). These tendencies toward the total stopping of mold activity on the PUR polymer layer present on the laser-irradiated wood adherent could be explained by the creation of mold-inhibitory substances during the laser modification of wood surface with their ability to penetrate through a liquid not-yet-hardened layer of PUR polymer before its curing on the top surface of specimen (i.e., on the top layer of the PUR polymer) exposed to the mycological test with molds. However, in the future this hypothesis has to be confirmed by physical and chemical analyses.

Beech

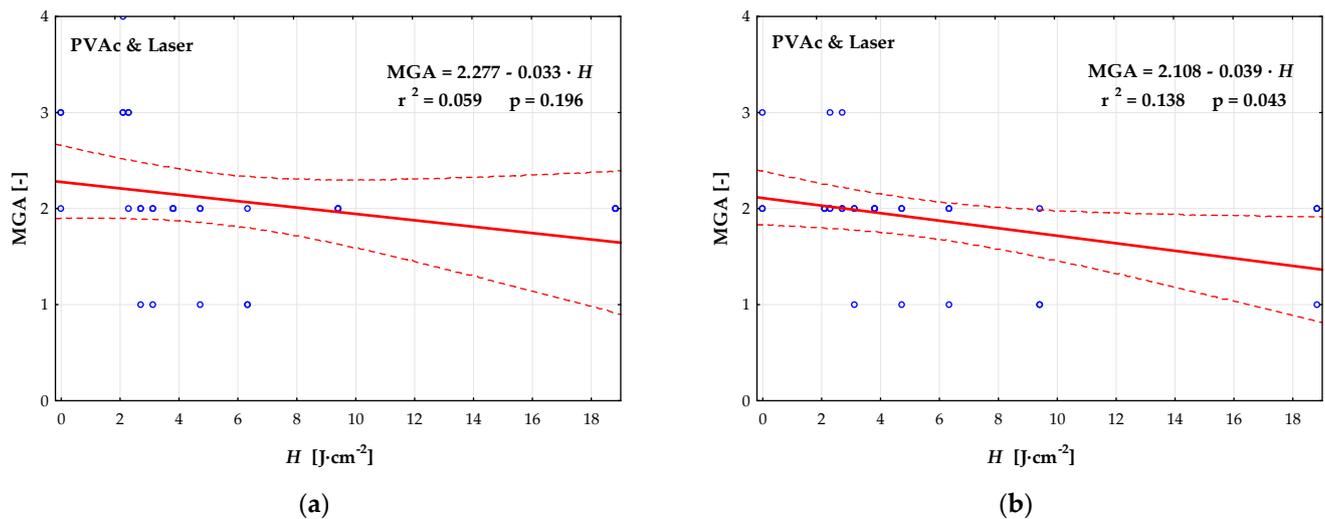


Figure 8. Linear correlations between the mold growth activities (MGA) of *Aspergillus niger* (a) or *Penicillium purpurogenum* (b) and the laser irradiation doses (H) acting on the top surface of the European beech wood samples when using the treatment mode “PVAc and Laser”.

Spruce

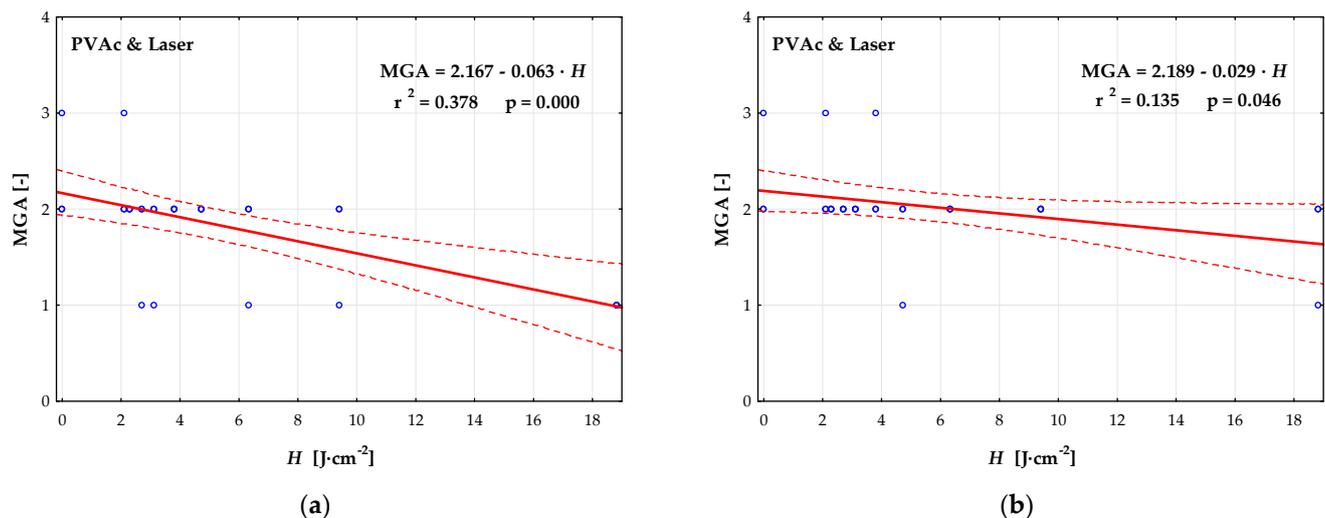


Figure 9. Linear correlations between the mold growth activities (MGA) of *Aspergillus niger* (a) or *Penicillium purpurogenum* (b) and the laser irradiation doses (H) acting on the top surface of the Norway spruce wood samples when using the treatment mode “PVAc and Laser”.

4. Conclusions

The increased doses H of CO₂ laser from 2.1 to 18.8 J·cm⁻² acting on the native beech and spruce wood surfaces or on the layers of synthetic PVAc and PUR polymers present on wood surfaces caused the decomposition and carbonization of wood components or synthetic polymers—visible by their darkening until blacking and the creation of air bubbles in synthetic polymers.

The adhesion strength between the synthetic polymer layer and the wood adherent decreased continuously in all cases with the increase in laser doses H from 2.1 J·cm⁻² until 18.8 J·cm⁻². The decrease in the adhesion strength when using H of 18.8 J·cm⁻² was from 41.3% (spruce: “PVAc and Laser”) up to 70.2% (beech: “Laser and PUR”). Due to the laser irradiation, the adhesion strength decreased more evidently for the beech wood versus the spruce wood adherent, for the PUR polymer versus the PVAc polymer layer, and for the laser beam focusing on the native wood versus the synthetic polymer.

The mold growth activities of the microscopic fungi *Aspergillus niger* and *Penicillium purpurogenum* on the surfaces of the tested specimens were evidently inhibited by the CO₂ laser only if the mode “PVAc and Laser” was used—i.e., if the wood specimens were firstly covered with a less mold-resistant PVAc polymer and subsequently irradiated with laser doses $H \geq 3.1$ J·cm⁻².

The achieved results indicated that the studied laser technological operations—(1) the laser pretreatment of wood surfaces before covering them with PVAc or PUR polymers, or (2) the laser treatment of PVAc or PUR layers present on the wood surface—are not best suited for practical use. In this light, laser-machined wood should not be directly bonded or painted with polymer adhesives or coatings and laser beams should not be focused on wood surfaces covered with synthetic polymer layers.

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