

## Article

# Tensile and Impact Bending Properties of Chemically Modified Scots Pine

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**Abstract:** This study deals with the influence of chemical modification on elasto-mechanical properties of Scots pine (*Pinus sylvestris* L.). The elasto-mechanical properties examined were impact bending strength, determined by impact bending test; tensile strength; and work to maximum load in traction, determined by tensile tests. The modification agents used were one melamine-formaldehyde resin (MF), one low molecular weight phenol-formaldehyde resin, one higher molecular weight phenol-formaldehyde resin, and a dimethylol dihydroxyethyleneurea (DMDHEU). Special attention was paid to the influence of the solution concentration (0.5%, 5%, and 20%). With an increase in the concentration of each modification agent, the elasto-mechanical properties decreased as compared to the control specimens. Especially impact bending strength decreased greatly by modifications with the 0.5% solutions of each agent (by 37% to 47%). Modification with DMDHEU resulted in the highest overall reduction of the elasto-mechanical properties examined (up to 81% in work to maximum load in traction at 20% solution concentration). The results indicate that embrittlement is not primarily related to the degree of modification depended on used solution concentration. It is therefore assumed that molecular size and the resulting ability to penetrate into the cell wall could be crucial. The results show that, in the application of chemically modified wood, impact and tensile loads should be avoided even after treatment with low concentrations.

**Keywords:** wood modification; melamine-formaldehyde resin; phenol-formaldehyde resin; DMDHEU; impact bending strength; tensile strength

## 1. Introduction

Among others the main objectives of chemical modifications of wood are to improve dimensional stability and resistance against wood-decaying fungi in order to offer an alternative to tropical hardwoods. The modification may, however, also cause undesirable changes of other wood characteristics, mainly elasto-mechanical properties. The reasons why chemical modification systems influence biological and physical properties of wood have been the subject of numerous studies [1–4]. There is still a lack of knowledge about the mode of action of the resins. However, mechanisms via which impregnation modifications work according to Hill [5] are: (1) permanent swelling by incorporating the resin in the cell wall structure (bulking); (2) moisture content is reduced; (3) cell wall pores with a size of 2–4 nm are blocked and it is assumed that a chemical reactions between modification agents and cell wall polymers (cross-linking) occurs.

Impregnation modifications based on reactive resins have been shown to result in embrittlement of wood [6–8]. The embrittlement is most evident in a decrease of tensile properties and dynamic strength properties like impact bending strength [9,10].

Studies have shown that a treatment with melamine-formaldehyde (MF) resin, besides providing decay resistance and dimensional stability, increases compressive strength and hardness, while decreasing tensile and impact bending strength compared to untreated wood [11–13].

As early as the 1930s, Stamm and Seborg [7] modified wood with phenol-formaldehyde (PF) resins and thereby enhanced the dimensional stability as well as the durability of the wood. Bicke et al. [9] found bending strength and modulus of elasticity in bending of plywood increased after modification with a PF-resin. At the same time, the impact bending strength decreases. Alike modification with MF-resins, tensile strength of wood modified with PF-resins also exhibits a lower tensile strength [14]. Furuno, Imamura, and Kajita [15] as well as [16] examined the influence of the molecular weight of the PF-resin on its ability to penetrate the wooden cell wall using microscopy. They stated that, with an increase of the molecular weight, a higher share of the resins remained in the cell wall lumen.

It has been shown that wood modification with dimethylol dihydroxyethyleneurea (DMDHEU) increases resistance against wood decaying fungi, dimensional stability, compressive strength, and hardness while reducing tensile and impact bending strength [6,17–19]. Bollmus [20] showed that wood modification with DMDHEU causes a large reduction of the impact bending strength already at a very low concentration of 0.5%.

In this study, the influence of modifications with curing resins on the most susceptible elasto-mechanical properties was examined. In addition to tensile strength and impact bending strength, work to maximum load in traction of modified wood was investigated in order to be able to compare tensile and dynamic bending properties. Four different modification systems were applied in three different concentrations to Scots pine sapwood.

The main objectives of this study were to investigate the impact of (1) the concentration of the modification solution and (2) the modification agent itself on impact bending strength, tensile strength and work to maximum load in traction.

## 2. Materials and Methods

### 2.1. Specimens and Modification Agents

The specimens were made from sapwood of Scots pine (*Pinus sylvestris* L.). The modification was conducted on specimens of the dimensions  $28 \times 28 \times 470 \text{ mm}^3$  (radial  $\times$  tangential  $\times$  axial) for tensile tests and  $10 \times 10 \times 150 \text{ mm}^3$  for impact bending tests. The agents for modification were a methyl-etherified melamine formaldehyde resin (MF), a low molecular weight phenol-formaldehyde resin (Phenol1), a higher molecular weight phenol-formaldehyde resin (Phenol2) as well as dimethylol dihydroxyethyleneurea (DMDHEU, Table 1). Each of these modification agents was applied at concentrations (mass-%) of 0.5%, 5%, and 20%. Untreated specimens functioned as controls.

**Table 1.** Properties of stock resins according to manufacturer specifications.

Resin	pH-Value	Solid Content (%)	Molar Weight (g/mol)	Solvent	Catalyst	Additive
MF	10–11	73.5	840	Water		Triethanolamin, 1% *
Phenol1	9.2	43.5	159	Water		
Phenol2	8–10	54.9	452	20% Ethanol Water mixture		
DMDHEU	5–6	71.8		Water	Magnesium Nitrate, 2% *	

\* Concentration based on resin.

### 2.2. Oven-Dry Density

Specimens were sorted according to their oven-dry density before modification in order to minimize the influence of the density on the examined elasto-mechanical properties. Specimens for the tensile test showed a maximum deviation from the median oven-dry density of  $\pm 15\%$ . Specimens for the impact bending test showed a maximum deviation from the median oven-dry density of  $\pm 5\%$ .

### 2.3. Equilibrium Moisture Content (EMC)

Specimens were conditioned at 20 °C and 65% relative humidity (RH) in order to minimize the influence of the moisture content on the examined elasto-mechanical properties. The EMC of control specimens was calculated as

$$EMC = \frac{(m_1 - m_0)}{m_0} \times 100 (\%) \quad (1)$$

where  $EMC$  = equilibrium moisture content, %;  $m_1$  = mass of untreated, conditioned specimen, g;  $m_0$  = mass of untreated, oven-dry specimen, g.

There are two possible reference values to calculate EMC of modified wood. Material moisture content  $MC$  is defined as the proportion of moisture of wood based on the dry mass of the modified wood. Reduced equilibrium moisture content  $EMC_R$  is defined as the proportion of moisture in wood based on the oven-dry mass of the untreated wood, thus eliminating the influence of the weight added by the resin.

$$MC = \frac{(m_3 - m_2)}{m_2} \times 100 (\%) \quad (2)$$

$$EMC_R = \frac{(m_3 - m_2)}{m_0} \times 100 (\%) \quad (3)$$

where  $MC$  = material moisture content, %;  $m_3$  = mass of modified, conditioned specimen, g;  $m_2$  = mass of modified, dry specimen, g;  $EMC_R$  = reduced equilibrium moisture content, %;  $m_0$  = mass of untreated, oven-dry specimen, g.

$EMC_R$  of treated and EMC of untreated specimens were reached if the mass has not changed more than 0.1% within an interval of 24 h after storage at 20 °C and 65% RH.

### 2.4. Modification

The modification was performed identically for all modification agents. The first modification step, the impregnation, was conducted in a vacuum pressure impregnation plant. The three phases of the impregnation were (a) vacuum (−0.096 Mpa, 1 h), (b) pressure (1.2 Mpa, 2 h), and (c) diffusion (no pressure, 1 h). The second modification step, the curing, was conducted by slowly increasing the temperature up to 120 °C in a drying oven using the following drying scheme (Table 2).

Table 2. Drying scheme for modification.

Temperature (°C)	Climate Chamber/Drying Oven	Time (h)
20	climate chamber	168
40	drying oven	4
80	drying oven	4
103	drying oven	4
120	drying oven	36

Specimens for tensile testing were further processed into a bone-like shape only after modification in order to achieve a high manufacturing accuracy.

### 2.5. Weight Percent Gain (WPG)

The deposition of the modification agent in the wood caused a permanent weight percent gain. This is an indicator of the degree of modification. The WPG was examined in each specimen after the curing and calculated as

$$WPG = \frac{(m_2 - m_0)}{m_0} \times 100 (\%) \quad (4)$$

where  $WPG$  = weight percent gain, %;  $m_2$  = mass of modified, dry specimen, g;  $m_0$  = mass of untreated, dry specimen, g.

## 2.6. Elasto-Mechanical Testing

Specimens that were warped or showed cracks after modification were excluded, which lead to different numbers of specimens. All specimens were conditioned at 20 °C and 65% RH before testing.

### 2.6.1. Impact Bending Strength

Impact bending strength  $\omega$  was tested with the hammer method (load of XXXJ) in tangential direction following DIN 52 189-1 [21] by means of dynamic impact bending tests. The specimen dimensions were deviant from the standard  $10 \times 10 \times 150 \text{ mm}^3$ . The tests were performed using the Resil Impactor (CEAST) with a supporting width of 115 mm. Numbers of specimens varied between 23 and 37 (Table 3).

$$\omega = \frac{1000 \times W}{a \times b} \text{ (kJ/ m}^2\text{)} \quad (5)$$

where  $\omega$  = impact bending strength, kJ/ m<sup>2</sup>;  $W$  = work necessary to break the specimen, J;  $a$  = height of conditioned specimen, mm;  $b$  = width of conditioned specimen, mm.

**Table 3.** Number of specimens depending on the modification agent and concentration.

Treatment	Number of Specimens							
	Impact Bending Specimens				Tensile Test Specimens			
	Control	0.5%	5%	20%	Control	0.5%	5%	20%
Control	23				35			
MF		37	37	37		33	33	33
Phenol1		36	37	37		33	31	33
Phenol2		37	37	36		33	33	33
DMDHEU		37	37	36		33	33	32

### 2.6.2. Tensile Strength Parallel to Grain and Work to Maximum Load in Traction

Tensile strength  $\beta_Z$  was tested parallel to grain following DIN 52 188 [22]. The tests were performed using a Zmart.Pro with a 100 kN load cell (ZWICK ROELL, Ulm, Germany). Specimens were of 470 mm length. The clamping surface was  $50 \times 50 \text{ mm}^2$  with a height of 15 mm. The tapered part of the specimens showed a height  $a$  (tangential) of 6 mm and a width  $b$  (radial) of 20 mm in the area of the smallest cross-section (numbers of specimens varied between 31 and 35) (Table 3).

The software TestExpert II (ZWICK ROELL, Ulm, Germany) calculated the tensile strength  $\beta_Z$  according to the formula

$$\beta_Z = \frac{F_{max}}{a \times b} \text{ (N/mm}^2\text{)} \quad (6)$$

where  $\beta_Z$  = tensile strength, N/mm<sup>2</sup>;  $F_{max}$  = maximum force necessary to tear the specimen, N;  $a$  = height of conditioned specimen in the area of the smallest cross-section, mm;  $b$  = width of conditioned specimen in the area of the smallest cross-section, mm.

Strain to failure (mm) was measured by the VideoExtens camera system (ZWICK ROELL, Ulm, Germany). Work to maximum load in traction (kJ/m<sup>2</sup>) was calculated by TestExpert II (ZWICK ROELL, Ulm, Germany) as the integral of the stress–strain curve from the origin to the maximum force  $F_{max}$ .

## 2.7. Statistical Analysis

Each group of modified specimens was tested for significant difference in contrast to the control group using ANOVA and Tukey HSD tests at an error level of  $\alpha = 0.05$ . Both ANOVA and Tukey HSD are parametric hypothesis tests and as such are based on the assumptions of normal distribution and of homogeneity of variances. Most groups fulfilled the criterion of normal distribution, some did not fulfill the criterion of homogeneity of variances. However, homogeneity of variance is considered less important for balanced samples. As the numbers of specimens were balanced (Table 3) and due to the

higher power of parametric tests, it was decided to apply parametric hypothesis test (i.e., ANOVA and Tukey HSD).

### 3. Results and Discussion

#### 3.1. Density and Moisture Content

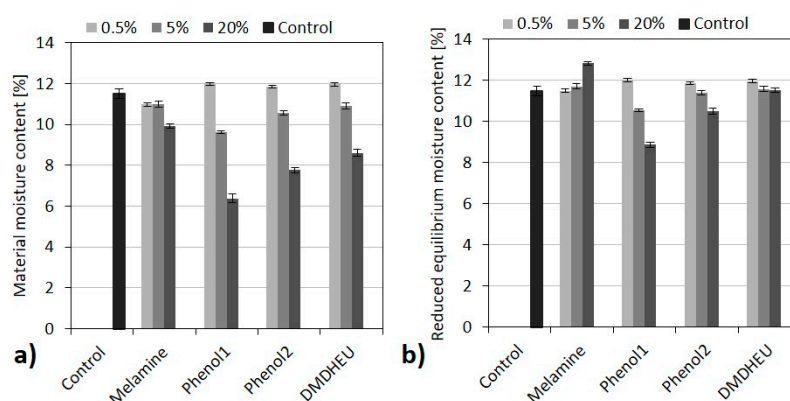
Density and moisture content (below fiber saturation) of native wooden specimens have a strong influence on their elasto-mechanical properties [23]. In this study, density and moisture content were examined based on the impact bending specimens.

Table 4 shows the oven-dry density of the specimens. Since the specimens were sorted according to their oven-dry density before modification, the maximum deviation from the mean oven-dry density within each group was only  $\pm 15\%$  for tensile specimens and  $\pm 5\%$  for impact bending specimens.

**Table 4.** Native and modified oven-dry density ( $\text{g/cm}^3$ ) of impact bending specimens depending on the modification agent and the concentration (mean).

Treatment	Native Oven-Dry Density ( $\text{kg/m}^3$ )				Modified Oven-Dry Density ( $\text{kg/m}^3$ )		
	Control	0.5%	5%	20%	0.5%	5%	20%
Control	471.76						
Melamine		476.23	471.74	474.74	490.43	493.78	598.35
Phenol1		475.11	470.06	470.48	470.38	490.58	595.31
Phenol2		469.33	471.25	478.82	465.50	489.91	601.02
DMDHEU		472.92	475.77	470.89	467.56	488.44	578.68

Material moisture content (MC) decreased with increasing intensity of the modification (Figure 1a). This was to be expected as the additional weight due to the modification changed the basis on which the MC is calculated. Reduced equilibrium moisture content  $EMC_R$ , however, avoids this effect by calculating the moisture content on the basis of the dry weight before modification [5,17]). In contrast to MC,  $EMC_R$  decreased only after modification with either one of the phenol-resins (Figure 1b). Since  $EMC_R$  values varied between 8.9% and 12.8%, an influence of the moisture content on the examined elasto-mechanical properties cannot be eliminated.



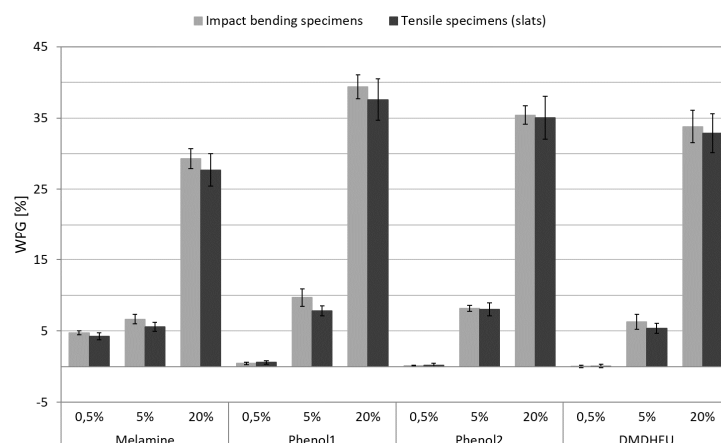
**Figure 1.** (a) Material moisture content MC (%) and (b) reduced equilibrium moisture content  $EMC_R$  (%) at 20 °C and 65% RH of impact bending specimens depending on the modification agent (mean and SD).

Hosseinpourpia et al. [24] stated that modification with a phenol-resin (molecular weight of 191 g/mol) decreased  $EMC_R$  stronger than modification with MF. It is therefore assumed that the molecular weight and therefore the cell wall penetration, irrespective of the resin, has a great influence on the

penetration and thus on wood properties. Xie [25] reported a slightly increased  $EMC_R$  also after modification with DMDHEU.

### 3.2. Weight Percent Gain (WPG)

Figure 2 shows an increasing WPG with increasing concentration for each modification agent tested. Modifications with 0.5% solutions of both phenol-resins and DMDHEU led to negligible WPG values of less than 0.6%. The highest WPG (ca. 39%) was caused by the lower molecular weight Phenol1 at a concentration of 20%. There was no clear difference in the WPG between smaller impact bending specimens and larger tensile specimens (slats) which demonstrates good penetration into wood species.



**Figure 2.** Weight Percent Gain (%) of impact bending and tensile specimens depending on modification agent and concentration (mean and SD).

### 3.3. Elasto-Mechanical Properties

#### 3.3.1. Impact Bending Testing

The impact bending strength of defect-free control specimens (Table 5) was rather low. Wagenführ [26] states values of 15 ... 40 ... 130 kJ/m<sup>2</sup> for Scots pine. An explanation for the low values might lie in the smaller specimen dimensions and shorter supporting width of the testing device than stated in DIN 25 189-1 [21]. According to Krech [27] impact bending strength increases with increasing specimen dimensions and increasing supporting width.

**Table 5.** Impact bending strength (kJ/m<sup>2</sup>) and change compared to control (%) depending on the modification agent and the concentration (mean ± SD).

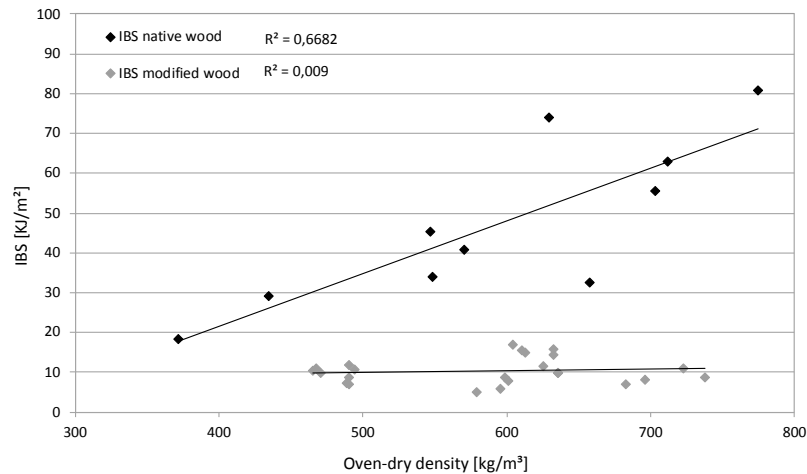
Treatment	Impact Bending Strength					
	Control	0.5%		5%		20%
	(kJ/m <sup>2</sup> )	(kJ/m <sup>2</sup> )	(%)	(kJ/m <sup>2</sup> )	(%)	(kJ/m <sup>2</sup> )
Control	18.8 ± 3.3					
MF		11.9 ± 2.0	−37 <sup>1</sup>	10.8 ± 2.5	−43 <sup>1</sup>	8.8 ± 3.0
Phenol1		9.9 ± 2.1	−47 <sup>1</sup>	7.1 ± 2.0	−62 <sup>1</sup>	5.8 ± 1.2
Phenol2		10.4 ± 1.9	−44 <sup>1</sup>	8.6 ± 2.3	−54 <sup>1</sup>	7.7 ± 2.4
DMDHEU		10.9 ± 3.1	−42 <sup>1</sup>	7.3 ± 2.2	−61 <sup>1</sup>	5.0 ± 1.8

<sup>1</sup> indicates that the value is significantly different from control at  $\alpha = 0.05$ .

Modified specimens exhibited significantly lower impact bending strength values than control specimens (Table 4). The values decreased with increasing concentrations of the agent for each

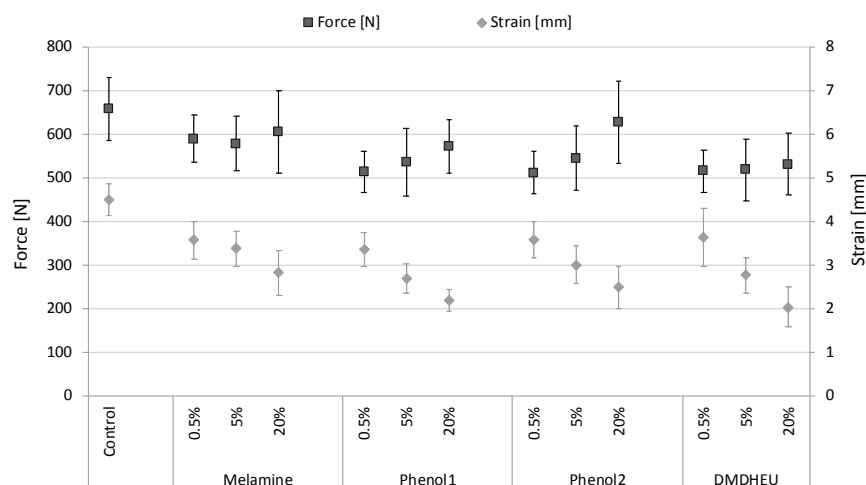
modification. Specimens modified with 0.5% solutions already showed a decrease in the impact bending strength of up to 47% (Phenol1). Other authors also found the impact bending strength of chemically modified wood to be reduced [8,19]

Modification caused an increase of density due to deposition of the resin (Table 3). Results from the impact bending test indicate, that this increase in density did not have the same effect on elasto-mechanical properties as higher density in native wood (Figure 3).



**Figure 3.** Relationship between impact bending strength (IBS) ( $\text{kJ/m}^2$ ) and oven-dry density ( $\text{kg/m}^3$ ) of native wood species (data from Brischke [28]) and differently modified wood with varying WPG.

Impact bending strength depends on the force applied as well as the deflection the specimen performs before breaking. Modified specimen absorbed similar amounts of force as control specimens (Figure 4). The deflection of modified specimens at  $F_{max}$  showed a decreasing tendency with increasing solution concentrations for each modification agent. This shows that the reduction of impact bending strength is mainly caused by the reduction of resiliency as the modification increases the stiffness of the specimens [8].



**Figure 4.** Maximum force (N) and deflection (mm) in impact bending depending on modification agent and concentration (mean and SD).

### 3.3.2. Tensile Testing Parallel to Grain

Tensile strength parallel to grain of control specimens was within the range [26] stated for Scots pine ( $35 \dots 104 \dots 196 \text{ N/mm}^2$ ). Modified specimens showed lower tensile strength values than control



specimens (Table 6). The values decreased with increasing concentrations of the agents. The strongest decrease was observed in the specimens modified with DMDHEU (51%). Other authors also found the tensile strength of chemically modified wood to be reduced [9,13,29].

**Table 6.** Tensile strength (N/mm<sup>2</sup>) and change compared to control (%) depending on the modification agent and the concentration (mean  $\pm$  SD).

Treatment	Tensile Strength						
	Control (N/mm <sup>2</sup> )	0.5% (N/mm <sup>2</sup> )	(%)	5% (N/mm <sup>2</sup> )	(%)	20% (N/mm <sup>2</sup> )	(%)
Control	93.9 $\pm$ 25.1						
MF		79.3 $\pm$ 22.2	−16 <sup>0</sup>	75.6 $\pm$ 23.7	−19 <sup>1</sup>	69.1 $\pm$ 18.8	−26 <sup>1</sup>
Phenol1		75.7 $\pm$ 22.9	−19 <sup>1</sup>	72.1 $\pm$ 17.9	−23 <sup>1</sup>	59.0 $\pm$ 13.2	−37 <sup>1</sup>
Phenol2		85.8 $\pm$ 22.4	−9 <sup>0</sup>	70.6 $\pm$ 18.1	−25 <sup>1</sup>	70.7 $\pm$ 13.7	−25 <sup>1</sup>
DMDHEU		84.7 $\pm$ 21.3	−10 <sup>0</sup>	60.6 $\pm$ 18.6	−35 <sup>1</sup>	45.6 $\pm$ 11.4	−51 <sup>1</sup>

<sup>1</sup> indicates that the value is significantly different from control at  $\alpha = 0.05$ , <sup>0</sup> indicates that the value is not significantly different from control at  $\alpha = 0.05$ .

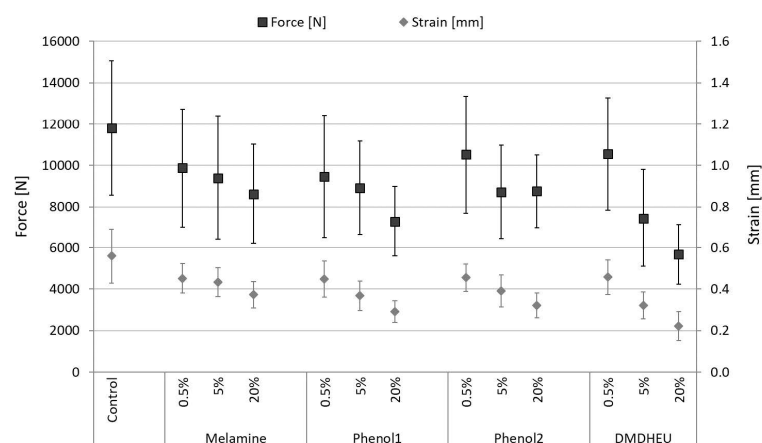
Modified specimens exhibited significantly lower values of work to maximum load in traction than control specimens (Table 7). For each modification, values decreased with increasing concentrations of the modification agents. Similar to impact bending strength, specimens modified with 0.5% solutions already showed a significant decrease in the work to maximum load in traction of up to 36% (Phenol1). Again, the strongest decrease over-all was observed in the specimens modified with DMDHEU (81%).

**Table 7.** Work to maximum load in traction (kJ/m<sup>2</sup>) and change compared to control (%) depending on the modification agent and the concentration (mean  $\pm$  SD).

Treatment	Work to Maximum Load in Traction (kJ/m <sup>2</sup> )						
	Control (kJ/m <sup>2</sup> )	0.5% (kJ/m <sup>2</sup> )	(%)	5% (kJ/m <sup>2</sup> )	(%)	20% (kJ/m <sup>2</sup> )	(%)
Control	28.2 $\pm$ 9.6						
MF		19.3 $\pm$ 7.2	−32 <sup>1</sup>	17.0 $\pm$ 6.9	−40 <sup>1</sup>	13.5 $\pm$ 4.3	−52 <sup>1</sup>
Phenol1		17.9 $\pm$ 7.0	−36 <sup>1</sup>	13.7 $\pm$ 4.7	−51 <sup>1</sup>	8.8 $\pm$ 2.4	−69 <sup>1</sup>
Phenol2		20.4 $\pm$ 7.3	−27 <sup>1</sup>	14.4 $\pm$ 4.5	−49 <sup>1</sup>	11.7 $\pm$ 3.2	−58 <sup>1</sup>
DMDHEU		21.0 $\pm$ 8.4	−25 <sup>1</sup>	10.2 $\pm$ 4.6	−64 <sup>1</sup>	5.4 $\pm$ 2.3	−81 <sup>1</sup>

<sup>1</sup> indicates that the value is significantly different from control at  $\alpha = 0.05$ .

In contrast to results from impact bending tests, both  $F_{max}$  and maximum strain in traction were reduced with increasing concentrations of each agent (Figure 5).



**Figure 5.** Maximum force (N) and strain (mm) in traction depending on modification agent and concentration (mean and SD).



Tensile properties are mainly determined by the properties of the single cellulose fiber [23,30]. Tests among others by [19] suggest that chemical modification reduces tensile properties of the fibers by embrittlement as a result of deposition of the agent in the fiber cell walls.

### 3.4. Influence of (Low) Concentration

The influence of the solution concentration was evident in all examined elasto-mechanical properties and for each modification agent. The higher the concentration, the stronger was the reduction. As stated by Bollmus [20] for DMDHEU, this study affirmed the strong influence of chemical modifications, especially on impact bending strength, and work to maximum load in traction already at a concentrations as low as 0.5%.

As the curing temperature was the same regardless of the modification concentration, it thus might be a possible explanation for the strong influence of the low concentration modification on the elasto-mechanical properties. Fengel and Wegener [31] as well as Nicholas and Williams [32] state that under certain circumstances (duration, pressure, moisture content) temperatures above 100 °C might lead to mass losses and reduced elasto-mechanical properties. Thus, it was assumed that the curing temperature of 120 °C, applied for 24 h, could have caused slight decreases in elasto-mechanical properties. However, it is highly unlikely that this curing process caused a decrease of up to 47% of impact bending strength (Table 3). Further investigations should be conducted on the strong influence of very low modification concentrations on elasto-mechanical properties of wood.

### 3.5. Influence of Modification Agents

Reasons for reduced elasto-mechanical properties of chemically modified wood have been discussed widely [23,33,34]. In which manner, a modification agent affects the elasto-mechanical properties of wood is determined by various factors. The most important factors are: penetration in to the cell wall, cross-linking, pH value, and formaldehyde content. To assess the influence of each factor separately is very difficult, and as the factors might inter- or counteract, the topic is very complex.

One reason for the strong influence of Phenol1 on the elasto-mechanical properties already at a low concentration could be its low molecular weight compared to Phenol2 and MF. This enables the resin to penetrate into the cell wall through nano-pores, whereas only a fraction of those modification systems with a higher molecular weight was able to enter the cell wall [15,16,20,35,36]. However, at a concentration of 0.5%, even if the modification system penetrated the cell wall completely, a reduction as strong as measured in this study was probably not solely due to the modification agent.

Penetration of the cell wall is a requirement for the modification agent to be able to affect  $EMC_R$  of wood. Lower  $EMC_R$  of specimens modified with phenol-formaldehyde resins, especially Phenol1 at 20%, could have had a positive influence on elasto-mechanical properties [20,23]. However, the results of this study did not show a positive effect of a lower  $EMC_R$  on elasto-mechanical properties as specimens modified with Phenol1 exhibited strong reductions of properties just like specimens modified with other modification agents.

During curing, the molecules of the modification agent build a network. If reactions between the modification agent and wood cell wall polymers take place, this is called cross-linking. Cross-linking restricts the flexibility of the wood and thus decreases the ability to relieve mechanic stress through strain [10,32,37]. It has been discussed whether the modification agents applied in this study are able to cross-link with the cell wall [6,38–40]. However, it is rather unlikely that cross-linking occurs at a concentration as low as 0.5%. Even if no cross-linking takes place, the rigid structure of the cured resin itself stiffens the wood to some extent [5]. Since embrittlement of chemically modified wood is one of the biggest drawbacks, further investigations regarding cross-linking are necessary.

The pH-values of the modification agents at initial composition varied (Table 1). The pH-values at the concentrations used for modification were not measured, but it was assumed that they varied between the modifications agents as well. Depending on the pH-value in combination with temperature, different chemical reactions take place [1]. Which milieu occurred during the modification

and how it affected the elasto-mechanical properties [10,28] should be subject to further investigations. As DMDHEU was the only modification agent with an acidic pH value, this could be a reason for the fact that it caused the strongest reductions of all elasto-mechanical properties examined. It is known that treatment with high or low pH values has an effect on wood properties.

All of the modification systems applied in this study contained formaldehyde (methanal, CH<sub>2</sub>O) at different concentrations. Formaldehyde tends to form networks as it is bifunctional [41]. According to Burmester [42] as well as Rowell [43], treatment of wood with formaldehyde alone leads to a considerable embrittlement of the wood. Reasons for this are cross-linking and hydrolysis of cellulose. A higher formaldehyde content of DMDHEU compared to the other modification agents could be a reason for the strong reduction of elasto-mechanical properties of wood modified with DMDHEU. Research in the past focused on formaldehyde containing resins, which have the advantage of faster and more complete curing. However, more recent developments show [44] that even without formaldehyde, some resins do show good potential for wood modification.

#### 4. Conclusions

This study investigated the influence of four chemical modification agents (MF, Phenol1, Phenol2, DMDHEU) in three concentrations (0.5%, 5%, 20%) on impact bending strength, tensile strength, and work to maximum load in traction of Scots pine. The main findings were:

1. Influence of the concentration of the modification solution. A clear concentration-dependent reduction was evident in impact bending strength, tensile strength and work to maximum load in traction of the modified specimens of each modification agent. The significant reduction in impact bending strength and work to maximum load in traction already after modifications with 0.5% solutions of each agent was remarkable.
2. Influence of the modification agent. There was a difference in the intensity of the influence, but inherently each modification caused a reduction of the examined elasto-mechanical properties. In fact, the modification agents showed similar influences regardless of differences in molecular weight or pH-value. Each modification agent caused a striking reduction of elasto-mechanical properties already at a very low concentration of 0.5%. Presumably, the strongest influence of the modifications on the elasto-mechanical properties was through embrittlement, which restricts mechanical stress relief through strain.

The results show that in the application of chemically modified wood, impact and tensile loads should be avoided even after treatment with low concentrations.

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