Chemical modification of Norway spruce (Picea abies (L) Karst) wood with melamine formaldehyde resin

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Impregnation of Norway spruce soft wood with melamine formaldehyde (MF) resin under vacuum-pressure process showed promising potential to improve number of properties, such as, dimensional stability and surface hardness. In this study, MF resin impregnated wood was evaluated at different levels of weight percent gain (WPG) compared to untreated one, mainly for dimensional stability and surface hardness. The modified wood, at 22.9 level of WPG possessed increase in dimensional stability in terms of anti-swelling efficiency and surface hardness by 17.5% and 124% over untreated, control. Chemical adherence and/or reaction takes place onto wood cell wall components other than cell lumens, which was proved by vertical density profile (VDP), UV microscopic and scanning electron microscopic (SEM) studies.

Keywords: Norway spruce soft wood, Melamine formaldehyde resin, Picea abies, Dimensional stability, Surface hardness, Impregnated wood

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Natural solid wood is being widely used as one of the versatile materials for many applications like building, construction or furniture which is due to a range of positive characteristics of wood as it provides favourable mass/strength ratio, is of low thermal conductance, is biodegradable, and last but not the least; it has neutral carbon dioxide balance. However, there are some inherent drawbacks such as dimensional instability with change in moisture content, low resistance against fungi and insect’s attack, low durability of many species, expressed photo-yellowing and unsatisfying mechanical strength properties of wood that are often perceived as negative by the end users. A promising way to remove these limitations is controlled chemical modification to have value added materials for different constructions that still possess all the natural inherent properties of solid wood. Attempts have been made to modify wood1-9 by using a number of chemical substances like esterifying and esterifying agents, acetals, alkylene oxides, alkoxyxilane coupling agents and silylating agents and some have shown improvement in dimensional stability and/or durability through improved decay resistance of wood to biotic and abiotic agents10-13. But, chemical modifications have not proved to be satisfactory, regarding mechanical strength properties, as modification processes have often shown either insignificant and or slightly negative effect10,14-15.

Melamine (1,3,5–triamino–2,4,6 triazine) formaldehyde is an important class of thermosetting polymeric material17 used in decorative laminates, moulding compounds, adhesives, coatings and other products. So far, solid wood, MF resins have not been widely applied industrially because of its higher cost in comparison to other polymerizable monomers and prepolymers. Nevertheless, a number of investigators have treated solid wood with melamine, considering its potential to improve properties of solid wood. Recently, in one of our experimental results, it was found that MF resin treated wood, preserved increased hardness and natural colour even after long term simulated weathering18.
As a part of larger study, the purpose of the present work was to determine whether, the modification process can result in dimensionally stable wood with improved surface hardness at a time at different levels of WPG of the chemical. Chemical modification takes place in the cell wall level which was determined with the help of vertical density profile (VDP), UV microscopic and scanning electron microscopic (SEM) studies.

**Experimental Procedure**

**Raw materials**

Thirty four rectangular samples of size 75×10×60 mm (Radial×Tangential×Longitudinal) were cut out from a single air dried log of Norway spruce (Picea abies L, Karst) heart wood to ensure homogeneity. The samples were then conditioned in a climate chamber (20°C and 65% RH) for constant weight, prior to resin impregnation.

**MF resin**

Melamine formaldehyde (1:3) resin (Pre MER, AMI, Linz, Austria) of following characteristic properties was used for impregnating wood (manufacturer instruction):
- Polydispersity, $M_w/M_n$ (weight/number average molar mass) $\approx 1000/750$;
- Methanol (solids content based) $\approx 27$%;
- Formaldehyde (solids content based) $\approx 36$%;
- $pH \approx 9$

**Impregnation scheme**

The climatically conditioned wood samples were impregnated in a stainless steel reactor, using vacuum-pressure cycle as an industrially relevant process. For this purpose, a factorial design with four factors at two levels was adopted to have different levels of WPG of chemical onto wood. This included treatment pressure during pressure phases (1000 and 5000 mbar), temperature (20 and 60°C), duration of phases (10 and 30 min) and repetition of cycles (2 and 6 cycles). Thus, thirty two samples out of thirty four were impregnated in 16 different impregnation conditions, with two parallel samples for each condition. The remaining two samples were used as reference (controlled) for comparative study. Immediately after treatment, the samples were cured at 150°C for 10 min in a heated press after removing the adsorbed chemicals on the surface, to have smooth surface. Then, the samples were conditioned in the climate chamber (20°C and 65% RH) for subsequent evaluation of different properties after subjecting the treated and untreated samples from oven-dry to water soaked and then from water soaked to oven-dry state.

**Evaluation of properties**

**Determination of weight percent gain (WPG)**

The WPG or chemical loading (in percentage, %) on to treated sample was calculated using relation,

$$WPG = \frac{(W_a - W_b)}{W_b} \quad ... \quad (1)$$

where $W_a$ and $W_b$ are oven dry weight after and before treatment of the samples respectively.

**Determination of dimensional stability**

The dimensional stability (in percentage, %) of treated wood was calculated using following relations:

$$S = \frac{(V_2 - V_1)}{V_1} \quad \ldots \quad (2)$$

where $S$ is volumetric swelling coefficient, $V_1$ is oven dried volume before humidity conditioning and $V_2$ is volume after humidity conditioning of wood samples.

$$ASE = \frac{(S_1 - S_2)}{S_1} \quad \ldots \quad (3)$$

where $ASE$ is anti swelling efficiency due to impregnation and $S_2$ and $S_1$ are volumetric swelling coefficient of treated and untreated samples respectively.

**Scanning electron microscopy (SEM)**

For taking scanning electron micrographs (SEMs), cubical blocks of size 2×2×2mm were cut out from corners of treated and untreated wood samples. The samples were then made gold sputter coated at 1 kV and 20 mA and images were acquired in the Scanning Electron Microscope (Philips, XL30E SEM) at 10 and 15 kV in transverse direction.

**Determination of vertical density profile (VDP)**

For determination of VDP, treated and untreated samples were cut in to size of 50×10×50 mm (Radial×Tangential×Longitudinal). The VDP was measured in Grecon DA-X, a laboratory density profile measuring instrument with direct scanning gamma-ray densitometry system across the thickness of the sample at an incremental step of 0.02 mm. Thus, 490-505 density points resulted from this process across the thickness of 10 mm.
UV microscopic study

For quantitative measurement of melamine in the cell wall, UV microscopic study was carried out. For taking UV microscopic spectra, match-stick like specimens of 5 mm length in longitudinal direction were cut out from treated and untreated samples and dehydrated in pure ethanol and acetone, before they were embedded in Spurr’s resin. Then, transverse sections of 1 µm thickness were cut out in Leica Ultracut ultramicrotome equipped with Diamond Histo diamond knife. The sections were subsequently picked-up from the trough and placed on to quartz glass slide by means of a platinum wire loop. After adding a drop of water, the sections were covered with quartz slips for immediate observation and quantitative measurement in Zeiss MPM800 micro spectrophotometer microscope. The microscope was equipped with UV light source, a mono-chromator, and a PbS detector enabling determination of spectra at wave length ranging from 235 to 350 nm at a magnification of 1000x with a circular measuring spot of 1 µm in diameter. With this small measuring spot, the quantitative measurement of melamine in late wood cell wall was carried out. The thin walled early cells were unconsidered because of biasing edge effects that are likely to occur at cell wall thickness less than 2 µm.

Quantitative evaluation was achieved through UV spectra, normalised against the absorbance of untreated cell wall at wavelength 290 nm (A290). This wavelength was chosen for normalization because it is close to maximum absorbance of lignin at around 280 nm where, slight absorbance of MF resin is observed.

The actual MF resin content in wood cell wall after treatment was determined using the relation,

\[ MF \text{ resin content} \ (v/v) = \frac{(TA_{245} - UTA_{245})}{MFA_{245}} \cdot D \] … (4)

where \( TA_{245} \) and \( UTA_{245} \) are UV light absorbance of cell wall at 245 nm for treated and untreated samples respectively, \( MFA_{245} \) is absorbance of pure MF resin in the cell lumen and \( D \) is density of MF resin.

Determination of surface hardness

Surface hardness of treated and untreated samples was determined using universal testing machine (UPM 10kN, Zwick, Ulm, Germany) with steel ball indenter (Brinell) of 10 mm diameter. The standard maximum force of the test was 1000N with standard speed of 4 mm per min of the movable steel ball with total test time of 25 s. The hardness was calculated according to European Standard (EN 1534)²⁰ using following relation as an average of ten measurements (five each from both surfaces) from each sample.

\[ HB = \frac{2F}{\pi D (D - \sqrt{D^2 - d^2})} \] … (5)

where \( HB \) is hardness in N.mm², \( F \) is maximum force in N, \( D \) is diameter of steel ball indenter in mm and \( d \) is the diameter of indented mark in mm.

Results and Discussion

From the experimental results, it is apparent that the dimensional stability in terms of ASE was increased with increased levels of WPG of MF resin on to wood (Table 1). The highest ASE value of 17.5% was achieved at 22.9 level of WPG. Cellulose, being the chief constituent of wood with its reactive OH groups, absorbs atmospheric moisture that causes swelling of wood. This process is reversible, because on drying the wood shrinks again, and this ultimately results in dimensional changes⁴. The highest value of dimensional stability (17.5%) at 22.9 level of WPG achieved in the present studies might be due to blocking of water assessable OH groups of wood components with MF resin, which was perceived even

<table>
<thead>
<tr>
<th>Reagents</th>
<th>WPG</th>
<th>S (%)</th>
<th>ASE (%)</th>
<th>Hardness (N.mm²)</th>
<th>MF content in cell wall (v/v)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>0.0</td>
<td>17.0</td>
<td>-</td>
<td>17.6</td>
<td>0.0</td>
</tr>
<tr>
<td>MF resin treated</td>
<td>7.3</td>
<td>15.6</td>
<td>8.6</td>
<td>27.6 (57)</td>
<td>na</td>
</tr>
<tr>
<td></td>
<td>13.2</td>
<td>14.3</td>
<td>16.1</td>
<td>29.8 (69)</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td>22.9</td>
<td>14.1</td>
<td>17.5</td>
<td>39.4 (124)</td>
<td>0.10</td>
</tr>
</tbody>
</table>

(Values in parentheses are percent increase in hardness of treated samples over untreated one; na – not analysed)
after repeated wetting and drying of wood. Since, the MF resin in the experiment caused volumetric swelling of wood, it could be inferred that the resin could easily penetrate the wood substrate to reach OH groups of cell wall components for dimensional stability. The fact that the resin can easily penetrate wood substrate due to impregnation can be well explained with the help of Fig. 1b, in which some wood lumens were filled with MF resin. Even a higher ASE could be achieved by full resin penetration. Rowell and Ellis reported that WPG of isocyanate, epoxide and methyl-isocyanate reacted wood up to about 25 to 30 caused increase in ASE that starts decreasing at higher WPG due to rupture of cell wall. The increase in ASE of MF resin treated wood in the present studies up to WPG 22.9 (Table 1) is well supported by their findings.

The results of surface hardness measurements are summarised in Table 1. It is apparent from experimental results that MF resin treatment caused significant increase in surface hardness with increased levels of WPG. The highest value of hardness of 39.4 N.mm⁻² (124% increase of hardness over untreated one) was achieved at 22.9 level of WPG (Table 1). The increase of surface hardness of wood might be due to MF resin adherence and/or reaction with cell wall components in micro-level up to 1 mm of depth in transverse direction. The penetration and adherence and/or reaction of resin with wood cell wall components up to 1 mm of depth took place due to vacuum-pressure impregnation process of wood which was also clearly revealed from the results of density profile studies (Fig. 2). A significant increase in density of treated wood for both the surfaces was due to adherence and/or reaction of resin with the wood cell wall components (Fig. 2). The higher value of density of surfaces of treated wood at 22.9 level of WPG in comparison to others might be due to deposition of some portions of resin in cell lumens too (Fig. 1b). Thus, from the experimental findings, it can be inferred that resin’s adherence and/or reaction on the surfaces of treated wood caused increase in surface hardness considerably. The persistence of surface hardness even after long term exposure to artificial weathering of MF resin impregnated wood under vacuum-pressure-process was also recorded in earlier finding. It has also been reported by many workers that the melamine treatment increases the hardness of wood. But, in the present investigation, the significant enhancement of surface hardness could be achieved by an industrially relevant vacuum-pressure impregnation process, which was not possible in an earlier study.

Improvement of dimensional stability and surface hardness of MF resin impregnated wood under vacuum-pressure process takes place due to adherence and/or reaction of resin with cell wall components and
it can well be justified with the help of UV micro spectrophotometric study. With the help of this study, quantitative measurement of resin in cell wall of treated wood was determined. Fig. 3 displays typical spectra of pure MF resin and MF resin treated cell wall at different levels of WPG. Untreated cell wall (at 0.0 WPG) had their maximum UV light absorbance at 235 nm, which steadily decreased from this wavelength onward reaching a local minimum at 255-260 nm, followed by an uprising towards a local maximum at around 280 nm. Pure MF resin spectra exhibited an absorbance peak at around 245 nm, with a steep decline onwards, reaching nearly zero absorbance at around 295 nm. On the other hand, absorbances of MF treated cell wall were significantly higher than untreated one, at a wavelength range of 235-262 nm. The higher is the WPG, the higher is the MF concentration in the cell wall, which in turn showed higher absorbances at wavelengths less than 240 nm (Table 1 and Fig. 3). This clearly reveals the adherence and/or reaction of MF resin in cellular level of wood, which in turn helps in dimensional stability and increase in surface hardness of treated wood.

Conclusion

From the present study, it can be concluded that the treatment of solid wood with MF resin in an industrially relevant vacuum-pressure process has a promising potential to improve performance properties like dimensional stability and surface hardness at a time. However, the authors recommend taking up detailed pilot-plan study for commercial feasibility of the present findings.

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