DEVELOPMENT OF BONDING STRENGTH OF MODIFIED BIRCH VENEERS DURING ADHESIVE CURING

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ABSTRACT

This study investigated the bonding strength development of furfurylated, N-methylol melamine (NMM) modified and thermally treated birch veneers glued with hot curing phenol formaldehyde (PF) adhesive in different pressing (20, 160 s) and open assembly times (20 s, 10 min). For testing, the automated bonding evaluation system ABES was used with 2 N-mm⁻² applied pressure at 130°C. The bonding strength of both modified and unmodified samples increased significantly by prolongation of the pressing time from 20 to 160 s in all cases and for both open assembly times. A deviation was observed for the samples treated at 220°C and at 20 s open assembly time. With the exception of NMM modified veneers, bonding strength did not change significantly by increasing the assembly time in the case of 20 s pressing for both modified and unmodified samples. At 160 s pressing time, extension of the assembly time developed a better bonding for controls, NMM modified and thermally treated veneers at 180°C. The combination of 10 min assembly time and 160 s pressing time proved as the optimal bonding condition for controls, NMM modified and thermally treated veneers at 180°C while the highest bonding strength was noted in 20 assembly time and 160 s pressing time for furfurylated veneers. In most of the cases modification affected negatively the bonding performance of the veneers, in particular for furfurylated and NMM modified samples.
INTRODUCTION

Wood furniture and construction industries rely on effective bonding processes of wood upon cutting it into smaller pieces and rejoining these pieces together using different polymeric resins. Thus, desirable dimensions and quality of the final product can be achieved, and also the natural anisotropy of the wood can be reduced (Hass et al. 2012).

Mechanical interlocking, covalent bonding, and secondary interactions, such as Van der Waals forces and hydrogen bonding are known as involved mechanisms in adhesion between wood and adhesives while the bond formation is a dynamic process dependent on flow, transference, penetration, wetting and curing of adhesives (Marra 1992). The influencing factors on bond quality are mainly categorized in three groups: wood (e.g. species, cutting direction and free surface energy), adhesive (e.g. type, formulation, molecular weight and viscosity) and process related factors (e.g. assembly time, pressing time, pressure and temperature). These parameters have an interplay effect on each other, which also determines the final cost of production. For example, an optimized pressing or assembly time can reduce the production time and hence the production expenses (Kariž et al. 2009). Therefore, it is essential to study and optimize these parameters in order to optimise the production process and cost of glued wood products.

Several techniques have been successfully employed to study the curing of adhesives, as for example differential scanning calorimetry (Szesztay et al. 1993) and dielectrical analysis (Šernek and Kamke 2007). Evaluation of bonding strength is possible through thermomechanical analysis TMA (Soulard et al. 1999), dynamic mechanical analysis DMA (Umemura et al. 1996), torsional braid analysis TBA (Steiner and Warren 1981), integrated pressing and testing system IPATES (Heinemann 2004), and automated bonding evaluation system ABES (Humphrey 1990, 2006, Wescott et al. 2007, Jost and Šernek 2009). Among these methods, ABES provides useful information on both adhesive curing and the development of bonding strength, providing valuable data on the shear strength of the adhesive bond as a function of the pressing parameters and other conditions (Segerholm et al. 2010, Ferra et al. 2011, Rohumaa et al. 2014, Esteves et al. 2015). It should be noted that ABES is a destructive mechanical method providing only one data point per test, and thus it cannot be employed for continuous testing during the hot pressing of wood-based composites (Ferra et al. 2011).

During the last years, wood modification techniques showed a high potential to improve wood properties such as durability, weathering and UV resistance, dimensional stability, and hardness (Militz et al. 1997; Hill 2006). One of the challenges in this area is to effectively bond the different modified materials as their physical and chemical aspects are substantially altered by the passive, active (chemical), or thermal modifications in comparison to the unmodified wood (Boonstra and Tjeerdema 2006, Rowell 2006, Nguila Inari et al. 2007). To achieve this, a thorough understanding of the various factors affecting the interaction of the adhesives and the modified adherents is needed. This study investigated the development of bonding strength of furfurylated, melamine and thermally modified birch veneers during adhesive curing of phenol formaldehyde adhesive (PF) as a function of open assembly and pressing times by using ABES.
MATERIAL AND METHODS

Wood material and modifications

Silver birch (*Betula pendula* Roth) veneers with dimensions 150 × 150 × 0.8 mm (L × W × T) were provided from Southern Finland (Rusutjärvi) and used for the modifications. Thermal modification was performed at 180 and 220°C using a lab scale heating oven (UNOX S.p.A, Italy) through 9 gradual steps of heating by circulation of hot air and steam in the system, started at 60°C up to the maximum applied temperature (180 and 220°C) followed by a cooling down phase. The duration of the main heating phase (application of maximum temperature) was 3 h in each treatment. For melamine modification of the veneers, N-methylol melamine (NMM) resin Madurit MW840/75WA (Ineos Melamines GmbH, Frankfurt, Germany) was provided as an aqueous stock solution with a solid content of approx. 75 %. The solution of 20 % NMM solid content was used for impregnation of veneers in a steel vessel with 30 m vacuum (60 mbar) followed by soaking of the veneers in the treatment solution for 2 h, then pre-drying at room temperature (1 day), and finally gradual drying/curing phase at several temperatures of 40-120°C (1 day). Furfurylation was carried out by Skog og landskap (Ås, Norway) by using an industrially known FA70 mixture of furfuryl alcohol resulting to 75 % weight percent gain. Prior to testing, all veneers were stored in a climate chamber and conditioned at 20°C and 65 % RH.

Gluing and ABES testing

The hot-curing liquid phenol-formaldehyde (PF) adhesive used for this study was provided by Dynea Chemicals (Oy, Hamina, Finland) with the commercial name Prefere 14J021 (Tab. 1). It is made up of linear or branched oligomeric molecules in an aqueous solution, which creates a three-dimensionally crosslinking structure after curing (Laborie 2002, Dunky 2004). The adhesive was applied manually on a 5 × 20 mm area of the veneer samples with dimensions 20 × 117 mm by a micropipette (HandyStep electronic®, Wertheim, Germany).

An automated bond evaluation system ABES (Incorporated, Corvallis, OR, USA) was used for measuring bonding strength (Fig. 1).

![Fig. 1: Automated bond-evaluation system (ABES) used for the evaluation of bonding strength of veneers glued with PF adhesive.](image)

After application of the adhesive on each veneer surface, the two bonded veneers were mounted in-between the holding jaws of the device at a fixed open assembly time of 20 s and...
10 min (time interval between spreading the adhesive on the adherent and the completion of assembly process), and then the assembly was pressed at 2 N.mm⁻² and 130°C for the designated period of time. Finally, the two glued veneers of the assembly were separated by movement of the holding jaws and ABES provided the force, in N, necessary to break the glue line. The bonding strength was determined by the following formula:

\[ \text{Bonding strength} = \frac{\text{Force (N)}}{\text{Bonded area (mm}^2\text{)}} \quad (\text{N.mm}^{-2}) \]

Four combinations of open assembly (20 s, 10 min) and pressing (20, 160 s) times were used and can be seen in Tab. 2 together with all the other variables for ABES testing. In detail, the assembly time of 20 s reflects the initial wetting properties of the veneer surface (e.g. the ability of liquid glue to provide interfacial affinity for an adherent and to flow over its surface) and 10 min assembly time is close to the industrial process.

**Tab. 2: Testing parameters used to measure bonding shear strength with ABES.**

<table>
<thead>
<tr>
<th>Pressure (N.mm⁻²)</th>
<th>Amount of adhesive, (g.m⁻²)</th>
<th>Curing temperature</th>
<th>Bonded area (mm²)</th>
<th>Combination of open assembly and pressing times</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>100</td>
<td>130°C</td>
<td>4 x 20</td>
<td>20 s / 20 s</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>20 s / 160 s</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>10 min / 20 s</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>10 min / 160 s</td>
</tr>
</tbody>
</table>

Pressing time of 20 s refers to the condition under which the tack properties of the glue (e.g. the adhesive feature that allows formation of a bond of measurable strength instantly after adhesive and adherent contact under low pressure) can be evaluated, while 160 s pressing time is close to the industrial practice. Ten (10) replicates were used for each case, e.g. type of modification and combination of open assembly and pressing time. The total number of the tested assemblies was 200 (10 replicates × 5 treatments × 4 combinations of open assembly and pressing times).

**RESULTS AND DISCUSSION**

**Tab. 3: Bonding strength of control, N-methylolmelamine (NMM), furfurylated (FA) and thermally (TM) modified birch veneers glued with PF adhesive at 130°C by using different combinations of open assembly and pressing times.**

<table>
<thead>
<tr>
<th>Combination of open assembly and pressing times</th>
<th>Control</th>
<th>NMM</th>
<th>FA</th>
<th>TM 180°C</th>
<th>TM 220°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 s / 20 s</td>
<td>4.02±0.3 a</td>
<td>2.17±0.1 a</td>
<td>1.54±0.1 a</td>
<td>3.55±0.2 a</td>
<td>4.38±0.4 ab</td>
</tr>
<tr>
<td>20 s / 160 s</td>
<td>6.55±0.8 b</td>
<td>5.12±0.5 b</td>
<td>8.64±0.6 b</td>
<td>5.91±0.6 b</td>
<td>5.07±0.5 ab</td>
</tr>
<tr>
<td>10 min / 20 s</td>
<td>3.77±0.5 a</td>
<td>1.37±0.1 c</td>
<td>1.90±0.2 a</td>
<td>3.65±0.3 a</td>
<td>4.24±0.7 a</td>
</tr>
<tr>
<td>10 min / 160 s</td>
<td>9.12±1.3 c</td>
<td>6.22±0.7 d</td>
<td>7.56±0.8 c</td>
<td>8.25±0.9 c</td>
<td>5.85±0.8 b</td>
</tr>
<tr>
<td>F</td>
<td>60.408*</td>
<td>170.621*</td>
<td>349.820*</td>
<td>102.750*</td>
<td>9.475*</td>
</tr>
</tbody>
</table>

1 Mean values ± standard deviations
2 Values followed by a different letter within a column are statistically different (ANOVA and Tukey HSD test)
* Differences statistically significant at P = 5 %.
The shear strength bonding results with the relevant statistical analysis for differences according to ANOVA and Tukey HSD test for $P=5\%$ are presented in Tab. 3. For control samples, extending of the pressing time from 20 to 160 s significantly increased the shear strength values in both open assembly times. Jost and Šernek (2009) also reported a dependency between the curing of PF adhesive and pressing time when bonding beech veneers at 160°C. Open assembly time was found to affect bonding strength only for the high pressing time of 160 s as its prolongation from 20 s to 10 min provided a significant higher bonding strength. Actually, bonding strength achieved its peak for the higher assembly and pressing times (10 min and 160 s) and it was significantly different as compared to any other combination.

The various modifications followed more or less the trends of control samples in bonding strength development with changing open assembly and pressing times (Tab. 3). There was only one exception for the positive effect on bonding strength of the increased pressing time at each open assembly time, and it was noted in the case of thermal modification at 220°C. Although the bonding strength at 20 s open assembly time increased numerically with extending the pressing time from 20 to 160 s, the difference was not statistically significant. With the exception of the decreased bonding strength of FA modified veneers and also the thermal modification at 220°C for which open assembly time had no effect on the development of bonding strength for both pressing times, in other cases the increase in open assembly time from 20 s to 10 min at the high pressing time of 160 s produced significant higher bonding strength. Irrespective of NMM modified veneers, bonding strength remained unchanged at the low pressing time of 20 s with increasing the open assembly time in all other modifications as also noted for the controls. At this pressing time, the increase of open assembly time from 20 s to 10 min resulted to a significantly lower bonding strength of NMM modified veneers. Šernek et al. (1999) reported on little effect of extending open assembly time on penetration of urea-formaldehyde (UF) adhesive into beech. Another similarity of the different modified samples to controls was the significant highest bonding strength value for the combination of the prolonged open assembly and pressing times (10 min and 160 s). However, for thermally modified veneers at 220°C, this obtained value was only numerically (not statistically) higher than the rest of the cases while for the FA modified veneers the combination of 20 s open assembly time and 160 s pressing time gave the best performance. The curing behaviour of four synthesized UF resins was evaluated using ABES machine by considering the effect of pressing parameters (e.g. temperature, adhesive and hardener ratios) on shear strength during hot pressing. The results revealed a different bonding process for each type of the used resins with the best values of shear strength for the resin produced by alkaline–acid process at 100°C press temperature and 80 s press time (Ferra et al. 2011).

Changes in the hygroscopic behaviour and wetting properties of wood caused by various modifications can potentially affect and hinder proper curing of adhesives and hence the bonding performance (Boonstra et al. 1998, Petrišans et al. 2003, Šernek et al. 2008, Bastani et al. 2015a, b). As expected, for the majority of combinations of open assembly and pressing times the modifications had a negative effect on the bonding strength in comparison to controls, especially for furfurylation and NMM modification (Tab. 3). The bonding of these two types of modified veneers with such a hot curing PF adhesive is more dependent on pressing time than any other types of wood used in this study, as it was proved by their low bonding strength at 20 s pressing time in both assembly times, mainly due to poor initial wetting of the veneers surface after modification. The chemical combination of the surface of these modified materials can change by extending pressing time which resulted in an obviously much higher bonding strength values after 160 s of pressing. The bonding property of the same types of modified wood materials glued with three common cold-set wood adhesives together with details on the relationship between
bonding strength and bondline thickness, and adhesive penetration was investigated in previous studies (Bastani et al. 2015c, Bastani et al. 2016). It was found that the reduction in bonding strength of furfurylated and NMM modified wood with emulsion polymer isocyanate (EPI), polyvinyl acetate (PVAc) and polyurethane (PU) adhesives should be attributed mainly to the lower strength of the brittle modified wood and to the reduced internal surfaces for chemical bonding or mechanical of adhesives in the bulked modified wood. In the case of thermally modified Scots pine wood bonded with PU, it was found that the bondline was the weakest link compared to the wood itself. It was thus implied that the decreased adhesion should be attributed to the existence of less polar groups for bonding in thermally modified wood and to its poorer wettability hindering the proper curing of PU.

An overview on the obtained results of present study for each combination of pressing and assembly times indicated that in 20 s pressing and assembly times a decreased adhesion of about 62, 46 and 12 % was noted for FA, NMM and thermally modified veneers (180°C), respectively. Samples treated at 220°C showed 8 % higher bonding strength than controls for the above mentioned combination. In the case of 20 s assembly time and 160 s pressing, the bonding strength was also reduced for all types of modified wood, with the exception of 24 % higher bonding of FA modified veneers as compared to controls. For combination of 10 min assembly time and 20 s pressing, the bonding strength reduced after NMM modification (64%) and furfurylation (50%) while thermally treated veneers at 220°C represented the highest values among all cases, even 11 % higher than those of controls. The bonding strength was also reduced for all types of modified woods in the case of 10 min assembly time and 160 s pressing, 36 and 32 % for thermally treated (220°C) and NMM modified samples and 17 and 10 % for furfurylated and thermally treated samples at 180°C as compared to controls. The decreased adhesion properties of the modified veneers could be attributed to the poorer wettability of wood surface after modification as proved by contact angle and surface energy measurements on the same modified materials Bastani et al. (2015a). The reduction in shear strength after modification was also noted for samples bonded with different thermoplastic and thermosetting adhesives (Vick and Rowell 1990), with PF and UF (Šernek et al. 2007) and melamine-urea-formaldehyde adhesive (Šernek et al. 2008). A noticeable finding in this research was the highly improved bonding strength of furfurylated veneers by increasing pressing time in both assembly times, five and a half times higher in the case of 20 s assembly time and about four times higher in 10 min assembly time which illustrates the important role of temperature in effective bonding of FA modified veneers with hot curing PF adhesive. Furfuryl alcohol is known to react strongly with itself and starts to polymerize at presence of heat to build a cross-linked polymer, which might help to improve the bonding strength of furfurylated assemblies (Larsson-Brelid 2013). However, the curing chemistry of PF glue is a complex matter and dependent on several influencing factors (Laborie 2002, Dunky 2004).

**CONCLUSIONS**

Bonding strength of different types of modified birch veneers bonded with hot curing PF adhesive was examined in different pressing and open assembly times. The obtained results lead to the following conclusions:

- With the exception of modified veneers at 220°C and at 20 s open assembly time, extending of the pressing time from 20 to 160 s significantly improved the bonding strength in all cases for untreated and treated samples in both open assembly times.
With the exception of NMM modified veneers, for both modified and control samples, no significant change was seen in bonding strength by increasing the assembly time for the 20 pressing while at 160 s pressing, prolongation of assembly time improved bonding of controls, NMM modified and thermally treated veneers at 180°C.

The combination of 10 min assembly time and 160 s pressing time provided the highest bonding strength for controls, NMM modified and thermally treated veneers at 180°C while furfurylated samples gained the highest values in 20 assembly and 160 s pressing times.

In most of the cases, and especially in furfurylated and NMM modified samples, modification showed a negative effect on bonding strength. The bonding process of these two types of modified materials seemed to be highly dependent on pressing time. The obtained results of this study can be useful for effective bonding of various modified veneers with hot curing adhesives.

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