WATER SOLUBLE LARCH EXTRACTIVE: IMPACT ON 1P-PUR WOOD BONDS

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Abstract

Timber of larch has become increasingly important as construction material for weather exposed applications. Craftsman occasionally report an abnormal delamination when adhesive bonded laminations of the larch wood were used in utility class 3. Previous research has shown that bonding problems are enhanced when one part polyurethane adhesive (1P-PUR) is used. Our own studies and literature review suggest that a larch specific water soluble extractive may be associated with the reported failure mechanism.

In order to simulate the effects of the wood extractive Arabinogalactan (AG) which is specific for larch, specified amounts of synthetically produced AG were applied with a brush on spruce and fir wood samples. Shear strength of the AG treated, 1PPUR bonded spruce (*Picea abies*) and fir wood (*Abies alba*) as well as on larch wood samples (*Larix decidua*, *Larix sibirica*) was determined after two aging treatments according to EN 302-1.

The obtained results indicate that high contents of AG (20 w.% and more) combined with a high moisture significantly reduce the 1P-PUR bonding capacity. AG seems to accumulate as a barrier layer which occludes the lumen of tracheids and prevents a deeper adhesive penetration. Additionally AG is able to undergo chemical reactions with the free isocyanategroups of the pMDI-units (1P-PUR) and subsequently hampers the curing process by absorbing free water.

Keywords: larch extractive, arabinogalactan, 1P-PUR, adhesive, shear strength, delamination

INTRODUCTION

Wood of larch has become increasingly important as construction material for weather exposed utility classes. The slightly better durability of larch heartwood, compared to spruce and fir, allows the use of wood in non-ground contact structures without treatment with wood preservatives. For many structural applications and products with a high demand for dimensional stability, glued laminated sections are increasingly used as an alternative to solid larch wood. Craftsman occasionally report delamination when adhesive bonded laminations of larch wood are used in utility class 3, although production conditions during the gluing process are perfectly controlled. Previous research has shown that there is an increase of bonding problems when a one part polyurethane adhesive (1P-PUR) was used. Own research has elucidated specific wet bonding problems of 1PPUR bonded larch under laboratory conditions (SCHIRLE *et al.* 2002). The latter problem impairs the general application of structural 1P-PUR adhesives and the reliability of bonded larch elements, thus reducing the technical and ecological potentials of larch wood for non-ground contact constructions. Own studies and literature review indicate that the larch specific water soluble extractive Arabinogalactan (AG) might be associated with the experienced failure mechanism. In a study on particleboards made of larch heartwood (Dix & ROFFAEL 1994) postulated that extractives might negatively interact during curing of a binder based on diisocyanate (pMDI). (FIRZLAFF 2000) speculated on the possible role of AG in larch bonding with 1PPUR without providing experimental evidence.

The purpose of our study was to examine and to improve the understanding of the role of AG in larch bonding and to identify solutions to improve the reliability of glued larch products, especially when bonded with 1P-PUR adhesive.

MATERIAL AND METHODS

A complete overview of treated samples is provided in Table 1.

Boards of spruce and fir were painted with commercially extracted larch AG in specific amounts (10 w.%, 20 w.%, 30 w.%, 40 w.%, 50 w.% and 100 w.% in relation to the dry mass of the wood volume corresponding to the surface area multiplied with a thickness of 50 μm). The crystalline AG was solved in distilled water. The samples were painted with the solution and than stored for 4 hours in a dry climate (20°/35% RH) before bonding.

Natural European and Siberian larch wood specimens were also tested. In order to correlate the results of the mechanical tests with the amount of AG on the surface, the concentration of AG on the surface within a reference zone was determined analytically according to (COTÉ *et al.* 1966, COTÉ *et al.* 1967). The surface of 80 larch wood specimens were treated with HMR-Primer (VICK *et al.* 1995) before bonding. After HMR-Primer treatment samples were stored for 4 hours in a standard climate (20°/65% RH) before bonding as recommended by (VICK & OKKONEN 2000).

Wood Structure and Properties ´06
edited by S. Kurjatko, J. Kúdela & R. Lagaňa, pp. 71–76

ISBN 80–968869–4–3

Table 1 Number of 1P-PUR bonded specimens for tensile tests

	untreated	AG treatment						Resin 4 %	HMR Primer	distilled Water
		10 %	20 %	30 %	40 %	50 %	100 %			
Fir	70	60	30	30	30	30	–	30	–	–
Spruce	30	30	–	–	–	–	30	–	–	–
European Larch	86	–	–	–	–	–	–	–	50	76
Siberian Larch	40	–	–	–	–	–	–	–	30	40

Table 2 Type and duration of treatment prior to tensile shear tests

	No treatment Standard atmosphere	**Treatment I** Climatic cyclic storage	**Treatment II** Immersion in cold water
Standard	EN 302-1	EN 302-3	EN 302-1
Treatment	A1 (7 days, 20°/65% RH)	Chapter 6.5 (24 h at 50 ± 2°/87.5 ± 2.5 % RH 8 h at 10 ± 2°/87.5 ± 2.5 % RH 16 h at 50 ±2°/≤20 % RH conditioning at20°/65 % RH, dry testing)	A3(4 days immersion in coldwater at (20 ± 5)°C,conditioning at 20°/65% RH, dry testing)

Additionally, to reduce the effect of natural AG and thereby to improve the adhesion quality, 116 larch wood specimens were washed under running distilled water for approx. 10 seconds. The washed specimens were conditioned for a minimum of 5 hours in dry climate (20°/35% RH) before bonding.

All specimens were bonded with a commercially available 1P-PUR wood adhesive used for structural applications and classified as type II adhesive according to EN 301. The bonding was performed according to the manufacturer recommendations.

METHODS

Analysis of chemical bonds

For the assessment of the formation of chemical bonds between AG and the adhesive Fourier Transform Infrared Spectroscopy (FTIR) was applied. This method allows the identification of chemical bonds in a molecule by producing an infrared absorption spectrum.

Tensile shear testing

The shear strength of lap joint test specimens with thin bond line was determined according to EN 302-1 using a Zwick/Roell Z 100 universal testing machine, with an adjusted cross speed of 1.5–2.5 kN/min. Prior to the tensile tests the subsets of the specimens were subjected to aging treatments specified in Table 2.

In addition to the numerical shear strength values expressed in N/mm^2 the number of wood failures on the ruptured surface was estimated and graded in 10 % steps. Selected bond lines were examined with transmitted and/or incident light microscopy.

RESULTS

The IR-spectra of the reference substances and the hardened compound are shown in Figure 1 and 2.

The IR-spectrum of the AG/1P-PUR-compound shows an absorbance intensity, which is between the absorbance intensity of pure AG and the hardened adhesive (Fig. 1).

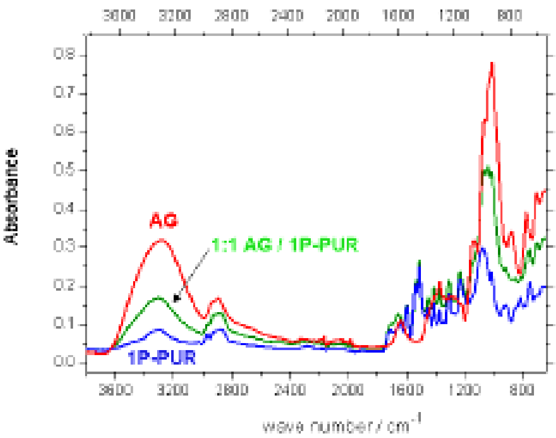

Figure 1 IR-spectra of the hardened AG / 1P-PUR compound compared to AG and 1P-PUR

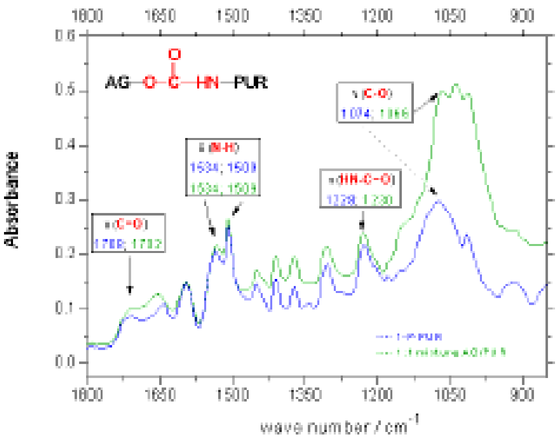

Figure 2 IR-spectra of the hardened AG / 1P-PUR compound compared to 1P-PUR at the characteristic vibration bands of urethane

Table 3 Shear strength and wood failure of 1P-PUR bonded spruce and fir wood specimens

Test Series	**AG content [w.%]**	**Mean Shear strength [N/mm²]**			**Wood failure [%]**			**Density* [kg/m³]**
		Standard climate	Treatment I	Treatment II	Standard climate	Treatment I	Treatment II	
1 (spruce)	0	9.17 (1.13)	10.27 (0.87)	9.16 (1.24)	100 (0.0)			408 (11.8)
1 (spruce)	10	8.87 (0.70)	8.70 (0.40)	**5.81** (0.45)	97 (4.8)	87 (9.5)	**19** (13.7)	
1 (spruce)	100	**8.18** (0.69)	**6.70** (0.95)	**3.44** (1.32)	**62** (16.2)	**59** (19.1)	**5** (7.1)	
2 (fir)	0	8.71 (1.20)	8.55 (0.53)	8.55 (0.37)	100 (0.0)			472 (20.1)
2 (fir)	10	8.51 (0.93)	9.16 (0.62)	**4.97** (0.78)	93 (9.5)	67 (15.7)	**4** (7.0)	
3 (fir)	0	6.08 (0.38)	6.23 (0.43)	5.72 (0.36)	100 (0.0)			408 (18.5)
3 (fir)	10	6.96 (0.69)	6.54 (0.78)	**5.32** (1.01)	94 (8.4)	97 (6.7)	**19** (14.5)	
3 (fir)	20	6.43 (0.74)	6.46 (0.63)	**2.41** (0.32)	98 (4.4)	93 (10.0)	**0** (0.0)	
3 (fir)	30	6.38 (0.77)	6.08 (0.86)	**2.94** (0.43)	96 (7.0)	96 (5.2)	**0** (0.0)	
3 (fir)	40	6.12 (0.50)	6.28 (0.51)	**1.56** (0.31)	95 (5.3)	94 (7.0)	**0** (0.0)	
3 (fir)	50	5.28 (0.80)	5.77 (0.28)	**1.54** (0.84)	97 (6.7)	99 (3.2)	**0** (0.0)	

Standard deviation in brackets
* 12 % moisture content

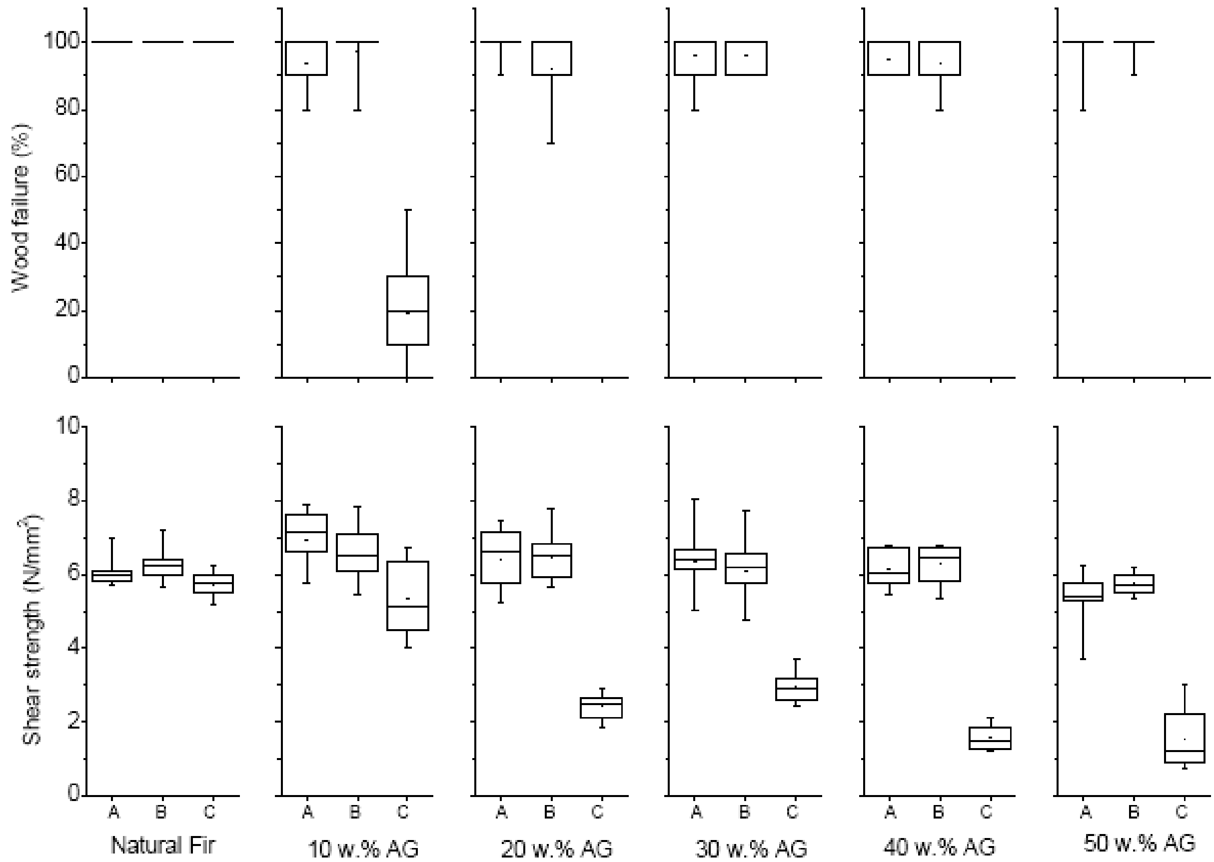

Figure 3 Wood failure and shear strength of AG treated and 1P-PUR bonded fir sample subsets after conditioning at 20°/65 % RH and the two aging treatments; only data test series 3 (A Standard climate, B Treatment I, C Treatment II)

A lower vibration intensity of the hydroxyl groups (vibration range between 3288 cm^{-1} and 3296 cm^{-1}) of the AG/1P-PUR-compound compared to pure AG indicates that urethane bonds are generated between OH-functionalities of AG and isocyanate groups of the adhesive. According to the same reaction there is a higher vibration intensity of the hydroxyl groups of the AG/PUR-compound when compared with the hardened 1P-PUR.

The formation of additional urethane bonds results in a displacement of the absorbance intensity of the AG/1PPUR-compound when compared to 1P-PUR at the vibration range from 1066 cm^{-1} to 1702 cm^{-1}. It is evident that the absorbance intensity at the characteristic vibration bands of urethane bonds increased for the compound when compared with the hardened 1P-PUR (Fig. 2).

The shear strength values and the wood failure rates for all tested 1P-PUR bonded spruce and fir wood specimens are provided in Table 3. Due to the different wood densities the results are presented separately for the three test series.

Natural spruce and fir wood samples (AG content 0 w.%) did not show significant differences ($p<0.05$ T-Test) neither for shear strength tests nor for wood failure after the ageing treatments (see Table 3). The mean longitudinal tensile shear strength for natural spruce wood was approx. 9.5 N/mm^2. The mean longitudinal tensile shear strength for natural fir was 8.6 N/mm^2 for specimens in test series 2 and 6.0 N/mm^2 for specimens in test series 3. The wood failure was estimated as 100 % (see Figure 3).

Treatment I did not affect the nominal strength values of spruce/fir treated with 10 w.% to 50 w.% AG, but in some cases the induced shrinkage and swelling movement caused a slight reduction in mean wood failure rate. Spruce/fir wood specimens treated with 10 w.% AG showed significant ($p < 0.05$ T-Test) reduction in shear strength after treatment II (–28 % on average compared with untreated spruce/fir wood specimens after treatment II), while wood failure rate increased dramatically to 18 % on average (Fig. 3).

The shear strength and the wood failure of fir samples treated with 20 w.% to 50 w.% remained unaffected by AG after storing at standard climate as well as after treatment I. After treatment II the shear strength was reduced dramatically from 5.72 N/mm^2 for untreated fir wood specimens to 1.54 N/mm^2 for fir wood specimens with 50 w.% AG (−73 % on average) (Fig. 3).

A further increase in AG quantity to 100 w.% on the surfaces of the spruce wood specimens of test series 1 reduced shear strength accordingly when moisture and shrinkage effects were induced by the ageing treatments (Table 3). Both reductions in strength from 8.2 N/mm^2 to 6.7 N/mm^2 after treatment I and to 3.4 N/mm^2 after treatment II were significant at the 0.05% level. Even the shear strength after storage at a standard climate was reduced significantly (from 9.2 N/mm^2 to 8.2 N/mm^2 on average) if the surface was treated with 100 w.% AG. The wood failure rate decreased to 62 % after conditioning at a standard climate and 59 % after treatment I and was reduced to 5 % after treatment II.

Microscopic analyses of the tested specimens confirmed the results of the mechanical tests. Figure 4 shows the characteristic wood failure of specimens with a high adhesion quality. Figure 5 illustrates frequently observed cohesive adhesive failure of 1P-PUR bonded spruce with a high content of AG after treatment II.

In general the 1P-PUR bonded fir wood showed a deep adhesive penetration and a intact and fine bond line (Figure 6). In comparison the fir wood specimen treated with 10 w.% AG, bonded with 1P-PUR and stored in cold water before tensile testing showed partly a poor adhesive penetration and a thicker bond line. A distinct delamination at the interface between adhesive and wood is illustrated in Figure 7. This characteristic delamination feature has been found frequently in fir and spruce wood specimen with 10 w.% AG after treatment I and II and consistently in fir and spruce wood specimens with more than 20 w.% AG.

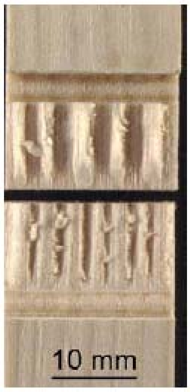

Figure 4 Shear zone of untreated spruce with characteristic wood failure

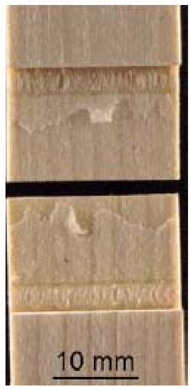

Figure 5 Shear zone of spruce treated with 100 w.% AG; after aging treatment II

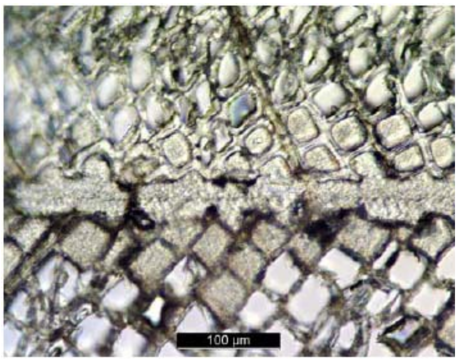

Figure 6 Transverse section of 1P-PUR bonded fir after aging treatment II showing an intact bond line

The analysed contents of AG in the tested larch wood specimens are provided in Figure 8. They range in average between 9 w.% and 10 w.% in heartwood. Only at the boundary between heart- and sapwood higher amounts of AG were analysed. These concentrations are rather low when compared with former findings

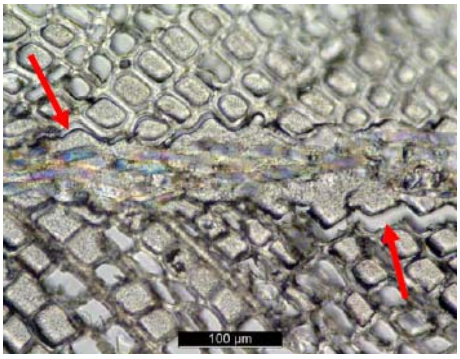

Figure 7 Transverse section of a 1P-PUR bond line in fir after aging treatment II; wood were treated with 10 w.% AG before bonding

(Coté *et al.* 1966). Thus, in general larch wood contains appreciable amounts of AG, usually within a wide range of 5–30 w.%.

Shear tests on bonded larch specimens revealed no apparent gluing problems. The mean shear strength of the bonded specimens after storage at standard climate conditions as well as after treatment I and II are at the same level as the shear strength of untreated larch wood. Nevertheless there is a slight reduction in wood failure rate with increased aging stress. The adhesion failures were predominantly located in latewood zones. Obviously the effective AG contents (in average < 10 w.%) of the tested larch specimens were too low to impair the adhesion quality significantly.

The process of washing larch boards under running distilled cold water before bonding, revealed surprising results. In contrast to the presumption the adhesion quality after the two aging treatments decreased significantly (see Figure 9). Microscopic analyses showed that bond lines are often separated from the watered wood surface already before tensile testing (Figure 10). In comparison to the untreated larch wood thicker bond lines with a poor adhesive penetration were detected on the watered larch wood specimens.

The other strategy to improve the adhesion quality of 1P-PUR bonded larch was a surface treatment with HMRPrimer. The HMR primed larch specimens showed higher mean shear strength values compared to the untreated specimens and a higher value of wood failure rates (Figure 11). Obviously the effect of the HMR-Primer resulted in an improved adhesion quality after the two aging treatments even though the penetration depth of the adhesive into the wood structure did not appear to be improved (Figure 12).

DISCUSSION

The results show that when AG is applied artificially the wood surface characteristics are altered, which obviously influences the gluing behaviour. The AG treated fir and spruce wood specimens as well as the watered larch specimens bonded with 1P-PUR showed unpredictable adhesion qualities in the presence of humidity or liquid moisture. The results

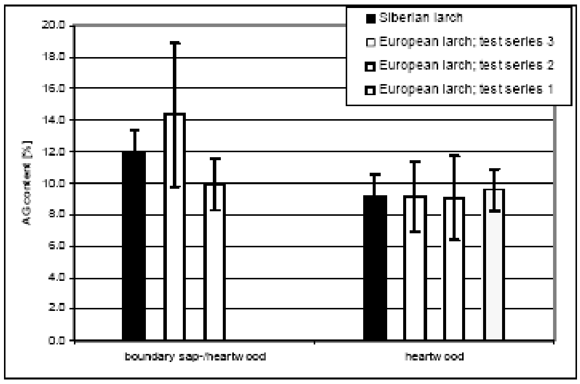

Figure 8 AG content analysed in wood of Sib. and Euro. larch

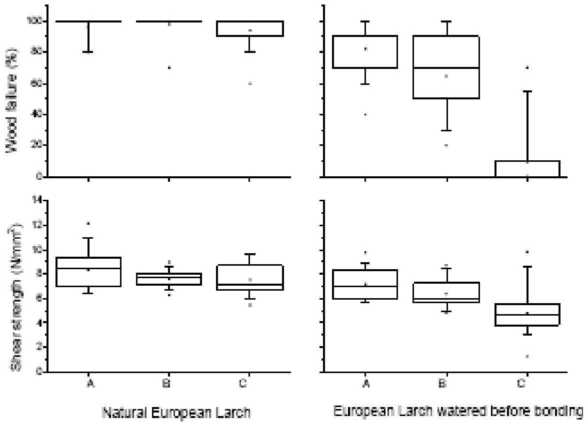

Figure 9 Wood failure and shear strength of watered 1P-PUR bonded European larch wood samples (A Standard climate, B Treatment I, C Treatment II)

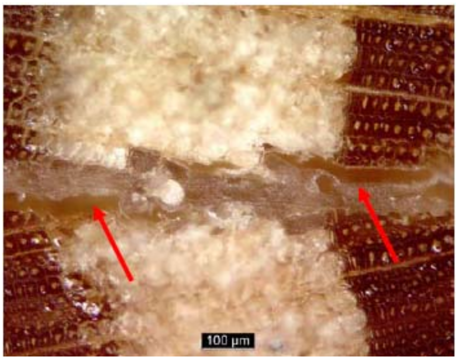

Figure 10 Transverse section of a 1P-PUR bond line in European larch after treatment II; N.B. wood surface was treated with water before bonding

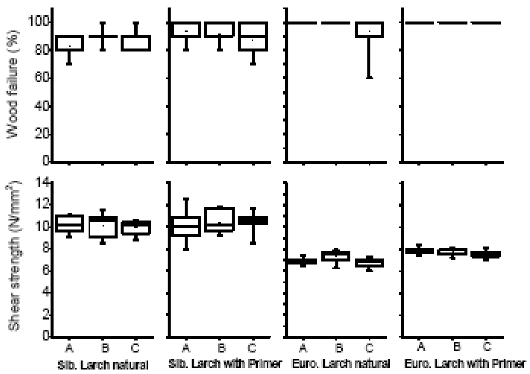

Figure 11 Wood failure and shear strength of HMR primed, 1P-PUR bonded Siberian and European larch wood samples (A Standard climate, B Treatment I, C Treatment II)

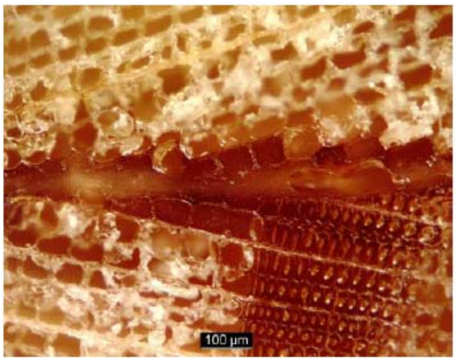

Figure 12 Transverse section of a 1P-PUR bond line in European larch; wood surface was HMR primed before bonding

indicate that an AG content of more than 20 w.% induces bond line defects in 1P-PUR wood bonds when humidity acts as stressor. However, below a concentration of 10 w.% the effect of AG on the bond strength appears to be moderate.

Hypotheses to explain the detected characteristic failures are firstly that a high concentration of AG forms a barrier layer which occludes the lumen of the surface tracheids and prevents a sufficient adhesive penetration and hence reduces mechanical linkage. Contact angle measurements performed with water on natural fir and fir wood specimens treated with different amounts of AG confirmed the latter hypothesis. On the one hand AG abets a well and fast spreading of water based liquids on the surface, on the other hand AG prevents a penetration of water based liquids into the wood.

Secondly IR spectroscopy shows that there is a possibility of chemical reactions between AG and 1P-PUR. Primary hydroxyl groups (AG) react with free isocyanate groups (pMDI units of polyurethane) to form urethane bonds. When physical strain caused by wood shrinkage or swelling acts on the delicate, less entangled adhesive network, the inherent strength is insufficient and results in cohesive failure. If additional moisture dissolves the AG this effect seems to be intensified.

Finally, crystalline AG has a high affinity to absorb water which can hamper the curing process of an adhesive at the interface between adhesive and wood cells.

Two strategies to improve the adhesion quality of 1P-PUR bonded larch specimen were tested. The first method, washing the surface with cold water before bonding, failed and resulted in considerable gluing problems. Watering the surface of larch wood might affect the transport of AG from inside the wood towards the surface resulting in a more homogeneous distribution of AG at the surface and/or a change of the AG consistency. The second method, painting the surface with HMR-Primer before bonding, resulted in a superior adhesion quality. The penetration of HMR-Primer into the interface zone counteracts moisture uptake and thus reduces shrinkage and swelling. Microscopic analyses of the bond lines combined with the results of the tensile tests suggest that HMR-Primer does not improve the mechanical interlinking between the adhesive and wood but increases the strength of the chemical bonds between 1P-PUR and larch wood.

To date affects of an increased concentration of AG can only be simulated on artificially treated spruce and fir wood specimens. It would be desirable to investigate larch wood samples with AG contents > 15 w.% on average, in order to provide further evidence for our hypotheses.

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