Eur. J. Wood Prod. (2014) 72:343–354
DOI 10.1007/s00107-014-0786-8

ORIGINAL

Improvement of tensile shear strength and wood failure percentage of 1C PUR bonded wooden joints at wet stage by means of DMF priming

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Received: 1 December 2013 / Published online: 25 February 2014

Abstract Tensile shear tests according to EN 302-1 for load-bearing timber structures were performed on European beech wood (*Fagus sylvatica* L.) and Douglas fir [*Pseudotsuga menziesii* (Mirb.) Franco] bonded by means of a one-component polyurethane adhesive (1C PUR). Results reveal a substantial loss of tensile shear strength (TSS) and wood failure percentage (WFP) at the wet stage compared to the dry stage. As can be seen from microscopic images, this is accompanied by a loss of adhesion at the boundary layer. Therefore, the aim of this work was to find a priming fluid that improves the load transmission between adhesive and adherend at the wet stage without introducing formaldehyde into the gluing process. A substantial improvement of TSS and WFP was achieved by means of the hygroscopic organic solvent *N,N*-dimethylformamide (DMF). In addition, contact angle measurements were carried out, revealing that DMF heavily enhances the wettability of the joining surface. Furthermore, it was attempted to integrate the outcomes into the swelling strain model stated by Frihart in 2009. By way of comparison a hydroxymethylated resorcinol coupling agent, a mixture of diphenylmethane-4,4′-diisocyanate isomers and water were also tested as priming fluids. The data confirm that TSS and WFP of 1C PUR bonded wooden joints do not correlate, whilst WFP is mostly not normally (at wet stage often bimodally) distributed.

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1 Introduction

Glued wooden joints for load bearing elements, such as glued laminated timber, have to sufficiently comply with the requirements of technical standards. For one-component polyurethane (1C PUR) bonded wooden joints the European standard EN 15425 (2008) sets thresholds for tensile shear strength (TSS) at the dry and wet stage, but not for wood failure percentage (WFP). Standards like CSA O112.9 (2004) or ASTM D 2559 (2004) are decisive for North America (NA). They comprise compression shear tests and set various thresholds for shear strength and WFP at the dry and wet stage. As a rule of thumb, they demand a WFP of at least 80 % (median) for hardwoods and 85 % for softwoods depending on conditioning and testing conditions. So far 1C PUR bonded joints have passed all the dry stage requirements, but they have problems overcoming the thresholds for WFP at the wet stage (Brandmair et al. 2012). Inter alia Uysal and Özçifçi (2006), Lopez-Suevos and Richter (2009) and Kläusler et al. (2013) confirmed a significant reduction of the performance of 1C PUR wood bondings at the wet stage compared to dry stage. Since the use of hardwoods for adhesively bonded structural elements is an issue of current interest (Schmidt et al. 2010a, 2010b, 2012; Strahm 2011; Flüshöh 2012), the delamination behavior of 1C PUR bonded beech wood elements has also been investigated. Schmidt et al. (2010b) concluded that the accordant demands of prEN 302-2 (2011) for type I and II adhesives can be met using a melamine–urea–formaldehyde polymer (MUF) with specifically prolonged closed assembly time.

The accordant 1C PUR bonded specimens however did not fulfill the delamination requirements of said standard. In the 1990s, Vick and Okkonen (1998) developed a hydroxymethylated resorcinol (HMR) coupling agent. This primer significantly improves the WFP of 1C PUR and MUF glued joints at the wet stage (Vick and Okkonen 2000) and also helps to reduce delamination (Lopez-Suevos and Richter 2009; Ohnesorge et al. 2010). However, it introduces formaldehyde into the gluing process and requires some laborious process steps (Eisenheld and Gardner 2005). The detailed mechanism where HMR takes effect is not yet completely understood, but several notable efforts have been made on this subject. Gardner and Tze (2001) investigated HMR treated wood by means of contact angle measurements. Their results indicate that the enhanced strength of HMR treated bonds is not caused by improved wetting of the adherends by the adhesive. The reaction mechanism between HMR and 1C PUR was investigated by Szczurek et al. (2010). They proposed that formation of urethane linkages takes place between methylol groups of the HMR on the one side and isocyanate groups of the 1C PUR on the other side. Son and Gardner (2004) and Christiansen (2005) studied the effect of HMR on the wood itself. Their findings indicate that HMR improves the bonding quality due to dimensional stabilization of the wooden substrate, leading to reduced stress between substrate and adhesive during climatic changes. Son et al. (2005) investigated the influence of HMR on maple veneer and postulated that this coupling agent also acts as a lignin plasticizer, generating an interphase which helps to reduce stresses caused by moisture changes. This finding contrasts with Sun and Frazier (2005) who reported that the highly reactive HMR rather stiffens the cell wall, which may be based on a crosslinking reaction between HMR and lignin. The current work aimed at finding a new basic approach for formaldehyde free priming of 1C PUR bonded wood. Therefore, the solvent *N,N*-dimethylformamide (DMF) was tested in comparison with three other priming fluids. The latter were water, a mixture of diphenylmethane-4,4′-diisocyanates isomers (pMDI) and the HMR primer. Water might be one of the simplest "primers" one can think of. The beneficial effect of water spray on the 1C PUR-gluing results is frequently mentioned in experience reports from industrial practice. According to Beaud et al. (2006) and Kägi et al. (2006), water spray is helpful when the ambient conditions are very dry, leading to fast superficial drying of the wooden adherends. Ashton (1973) proposed improving the adhesion of organic coatings on wood by means of a physico-chemical wood treatment. His basic approach was to swell wood in order to make more functional (OH−) groups available to the reagents. A polar fluid capable of swelling wood to an even higher degree than water is DMF. As Ashton (1973) and Mantanis et al. (1994a), (1994b) have summarized, it swells wood comparatively fast just by soaking at room temperature. This hygroscopic and high boiling solvent does not evaporate too quickly, thus giving some time for interactions with the wood and possibly also with the adhesive polymer. A quite different basic approach is priming by means of a mixture of pMDI. Such highly functional isocyanates promote bonding by reacting with polar groups of the wood (Lay and Cranley 2003). Under ideal conditions, pMDI is even capable of bonding covalently to the wood via formation of urethane linkages (Zouh and Frazier 2001). The hereby modified boundary layer would then represent additional linking points for the adhesive polymer. Gindl et al. (2004a) investigated the diffusion of pMDI into cell walls of spruce wood. They concluded that no pMDI diffuses into the cell walls on a microscopic level and added that this does not exclude a potential diffusion of pMDI compounds at nanometer scale.

2 Materials and methods

2.1 Wood

Based upon prEN 302-1 (2011) for tensile shear tests, boards of European beech wood (*Fagus sylvatica L.*) and Douglas fir [*Pseudotsuga menziesii* (Mirb.) Franco] were conditioned in the climate 20 °C/65 % relative humidity (RH) until equilibrium moisture content (EMC) was reached. Subsequently, the average raw densities of 679 kg/m^3 (beech) and 498 kg/m^3 (Douglas fir) were determined. The wood of each species was all derived from one section of the same log. Boards with flaws such as a very wavy direction of grain, knots or discolorations were sorted out. The material was then cut to size and planed conforming to the standard mentioned above. Prior to any testing, the boards were mixed in order to randomly scatter influences caused by the wood's inhomogeneity over the whole sampling.

2.2 Adhesive

All the bonding procedures were performed using the 1C PUR adhesive HB S 309 (Purbond® AG, Switzerland), approved for structural bonding of wood in Europe.

2.3 Priming liquids

For a concise overview of the used liquids see Table 1. The used DMF (C_3H_7NO, 73.09 g/mol) is a polar, high-boiling, toxic and hygroscopic solvent, produced by Sigma-Aldrich [puriss. p.a., ACS reagent, reag. Ph. Eur., ≥99.8 % (GC),

vapor pressure 2.7 mmHg (20 °C)]. The use of highly concentrated toxic DMF in practice might require further safety measures. Therefore, a solution of 5 % DMF was also tested. The pMDI Desmodur® VKS 20 (Bayer MaterialScience) is a solvent free mixture of diphenylmethane-4,4′-diisocyanates with isomers and homologues of high functionality (2.9). It contains about 31 % isocyanate and is preferably used as a hardener component in adhesive systems. The HMR priming fluid was prepared as described by Lopez-Suevos and Richter (2009).

2.4 Priming procedure

The adherends underwent the priming process within 30 min after planing. For the amounts applied per joining surface and the corresponding waiting times please refer to Table 1. The HMR priming fluid was applied onto the adherends by means of a paintbrush. For spraying of the deionized water, a standard hand-held water-spray bottle was used. Basically, additional moisture accelerates the 1C PUR reaction, but presence of a water film on the substrate leads to a very sudden reaction which impedes the proper formation of adhesion between adhesive and adherend. Therefore, 3 min were allowed for the water to penetrate and partly evaporate prior to 1C PUR application. DMF and pMDI were applied onto a metal sheet using a paintbrush, avoiding a spray mist. Subsequently, the bonding surfaces were covered with the sheets. This technique provides a more homogeneous liquid spread than direct brushing onto the wood.

2.5 Bonding process and sample manufacturing

After priming, 180 g/m^2 1C PUR were applied one-sided using a toothed spatula. Pressing was performed for 75 min at a specific pressure of 0.8 MPa in a calibrated press by means of a pressing jig. Consequently, the pressed parts were again stored in the climate 20 °C/65 % RH for at least 3 days in order to assure sufficient hardening of the adhesive before further processing. The climatized pressings were then cut to tensile shear test samples according to prEN 302-1 (2011).

2.6 Sample treatment, lots and testing procedure

Prior to testing, the specimens of each batch were mixed and afterwards divided into different lots ($n = 12$) for the treatments depicted in Table 2. Following the treatments, tensile shear tests according to the aforementioned standard were performed on a calibrated universal testing machine. Specimens were subjected to a constant testing speed of 0.9 mm/min and failed after 30–90 s in accordance with said standard. At the moment of testing, the average moisture contents of the beech specimens were 13.4 % (A1), 119.8 % (A2), 121.4 % (A4), and 14.7 % (A5). The evaluation of the WFP on the fracture surfaces was performed visually on the basis of ASTM D5266 (1999). Since moisture and temperature affect the performance of the glued joints (Schrödter and Niemz 2006; Clauß et al. 2010), a run of pre-tests was performed with treatments A1, A2 and A4 in order to be sure of the more decisive parameter. Whilst A1 functioned as the control batch, A2 and A4 mainly differed from each other regarding temperature sequence. Subsequently, the main test-runs followed comprising new control batches and primed specimens, supplemented by solid wood samples. The latter are suitable for an approximate assessment of the wood itself, but the measured values should be interpreted with caution. Such samples do not have a bondline and

Table 1 Priming fluids, applied amounts and waiting times

	Abbreviated designation	Applied amount (g/m^2)[a]	Waiting time
No primer application	Control	0	0
HMR	HMR	195	18 h
Water spray	Water	20	3 min
DMF, concentration 5 %	DMF 5	40	30 min
DMF, concentration 100 %	DMF 100	40	30 min
VKS 20, 30 min waiting time	pMDI 30	30	30 min
VKS 20, 1 day waiting time	pMDI 1d	30	1 day

[a] Average amount of primer applied per joining surface

Table 2 Sample treatment and threshold values

Technical standard	Sample treatments before testing		Threshold values Tensile shear strength (MPa)[b]
	Abbreviated designation	Description	
EN 15425 EN 302-1 Tensile shear test	A1	7 days storage at 20 °C/65 % RH[a]	10
	A2	4 days water storage at 20 °C	6
	A4	6 h storage in boiling water + 2 h submerged at 20 °C	6
	A5	A4 + reconditioning in 20 °C/65 % RH	8

[a] RH: Relative humidity of ambient air (%)

[b] Adhesive type I with 0.1 mm thickness of adhesive layer

consequently present a different stress distribution during testing. In addition, the divers arrangement of annual growth rings, wood rays, grain angles, etc. also influences the mechanical properties of the wood (Kollmann 1951; Niemz 1993; Burgert and Eckstein 2001) and accordingly of the bonded or un-bonded test specimen. Nonetheless, testing of bonded samples and solid wood samples appears to be the best feasible way for a comparative and approximate evaluation of the wooden adherend.

2.7 UV-light images

Frequently, it is difficult to separate shallow wood failure, adhesion failure and cohesion failure in the bondline from each other (definitions acc. to ASTM D907 2012), especially when adhesive and wood have almost the same colour. Fracture surfaces with just a few fiber layers on top of the adhesive layer, for example, can falsely look like adhesion failure instead of shallow wood failure. Particularly in such cases, the noted WFP of one and the same sample can vary quite a bit, depending on the person evaluating it. Advantageously, the used adhesive represents UV-fluorescent markers. Therefore, a combination of daylight-images and UV-light images of the fracture surfaces was used for the assessment of WFP.

2.8 ESEM-images

In order to support the findings obtained by UV-light and daylight photographs, further images of fractured specimens were prepared by means of an Environmental Scanning Electron Microscope (ESEM). To this end the fractured adherends were reassembled using a reflected light microscope and hereinafter embedded in epoxy resin. A series of about 15 adjacent ESEM pictures was taken from each of four representative specimens (two samples out of batch Control A4 and two out of lot DMF 100 A4). The consecutive images (4 × 15) were joined, thus displaying the complete fracture path (length 20 mm) of each sample. Additional pictures were taken using energy dispersive X-ray spectroscopy (EDX) to ensure a proper differentiation between epoxy resin and 1C PUR (images not depicted).

2.9 Contact angle measurements

As shown in previous works (Wellons 1980; River et al. 1991a; Dunky 2002; Hernandez and Cool 2008a, 2008b; Kläusler et al. 2013), sufficient wettability of the joining surface is an important precondition for good performance of the resulting joints. Therefore, the contact angle sequences of ten water droplets on four joining surfaces of freshly planed beech wood (half rift cut) were measured by means of the static sessile drop method. Two of the surfaces were DMF 100 primed, the other two remained unprimed. Beforehand, the wood was climatized in standard climate 20 °C/65 % RH until EMC was reached. Due to technical limitations, distilled water had to be used instead of the highly viscous 1C PUR. The measurements were carried out on a dataphysics contact angle system OCA supported by SCA 20 software. The droplet volume of 12 µl was applied 30 min after application of the DMF (in accordance with the waiting time depicted in Table 1), and the camera took pictures of the droplets' shapes with a frequency of 0.5 Hz (unprimed samples) and 25 Hz (DMF treated samples), respectively. The change in frequency was necessary due to the very high wettability of the primed surfaces compared to the non-primed ones. However, due to its porosity and inhomogeneity, wood is a non-ideal surface for contact angle measurements in principle (Gindl et al. 2004b; Santoni and Pizzo 2011). Therefore, the measured values should primarily be interpreted comparatively within the current study.

3 Results and discussion

The results of the pre-tests reveal that the impact of moisture is much more decisive for the performance of the 1C PUR bonded joints than the temperature of the water treatment (Fig. 1). Regarding TSS and WFP, no significant differences were detected between treatments A2 and A4. They both show substantial reduction of their values compared to the A1 treatment. Subsequently for the main test runs with primed samples, the A2 batches became obsolete and were replaced by A5 lots to investigate the bonding after re-drying.

3.1 Tensile shear strength of beech wood specimens

The results of TSS tests were firstly evaluated by Boxplots, giving an overview of data distribution, arithmetic means and medians (Fig. 2). A Shapiro–Wilk test on normal distribution (suitable for sample sizes $8 \leq n \leq 50$) was carried out for the beech wood data (Fig. 2) based on DIN ISO 5479 (2004) at the $\alpha = 0.05$ level. The result indicates that 88 % of these TSS batches comprise normally distributed data (Table 3). Therefore, confidence intervals were taken into consideration for the assessment of average mean value differences (Fig. 3). The TSS average values of the control samples (A1, A4, and A5) do not significantly differ from the accordant values of the solid wood samples. Hence, the 1C PUR bonded samples do not appear to be stronger or weaker than the solid wood itself. But all the batches (incl. solid wood) significantly lose strength from A1 to A4 and regain strength after re-drying (Figs. 2, 3). In

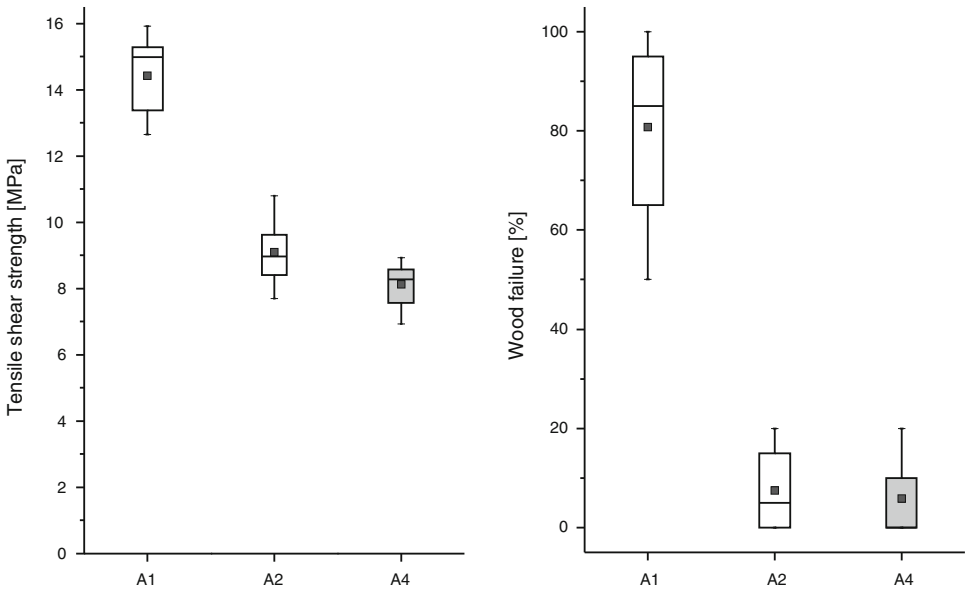

Fig. 1 Pre-tests (beech wood): tensile shear strength and wood failure percentage of beech wood specimens. *Whiskers* minimum and maximum values, *horizontal line* median, *square in box* arithmetic mean

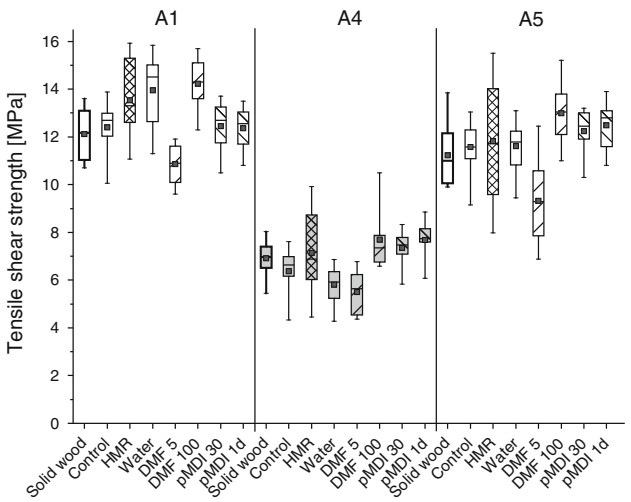

Fig. 2 Tensile shear strength of beech wood specimens. *Whiskers* minimum and maximum values, *horizontal line* median, *square in box* arithmetic mean

this respect it should be taken into account that also the wood itself loses strength when its moisture content rises up to fiber saturation (Kollmann 1951; Niemz 1993). According to River et al. (1991b), the loss of shear strength parallel to the grain between oven-dry and fiber saturation amounts to about 50 %, inter alia depending on the wood species. The fact that the bonded specimens lose strength at wet stage (A4 compared to A1) and regain strength due to re-drying (A5) points to the great importance of secondary bonds between the 1C PUR polymer on the one side and hydroxyl groups of the wood on the other side. Such bonds, in particular hydrogen bonds, are going to be ruptured due to the polar water molecules entering the interface (at the boundary layer) and the interphase (between bulk adhesive and bulk wood). The majority of these bonds is going to be re-established as soon as the water evaporates. In addition, swelling and shrinking of the composite material did obviously neither irreversibly damage the wood nor the adhesive polymer in the bondline. Otherwise such a regain of TSS (A5 compared to A1) would not be possible. The water and DMF 5 batches are the only ones revealing a significantly lower TSS after re-drying compared to A1. The HMR lots show increased scatter of individual values (Fig. 2), whilst their mean values do not significantly differ from the accordant values of the control batches (A1, A4, A5). When tested without any previous water contact (A1), the results of the water spray-batches reveal that this kind of treatment is capable of enhancing the TSS, thus confirming the industrial experience. However, this treatment is not helpful when the specimens are tested at the wet or re-dried stage (A4, A5). The A4 batch does not even meet the requirements of EN 15425 (2008) (Table 2). This also applies to the DMF 5 lots A4 and A5. On the contrary, the DMF 100 batches reveal significant improvements of TSS after A1 and A4 compared to the controls (Figs. 2, 3). Obviously, a sufficient concentration of fluid is needed for causing such an effect. Regarding priming with pMDI, neither a significant influence of waiting time nor of the primer itself on TSS was detected (A1, A4, A5 batches of pMDI 30 and pMDI 1d compared to accordant control batches).

3.2 Wood failure percentage of beech wood specimens

Some boxplots for WFP (Fig. 4) exhibit skewed distributions, like, e.g., DMF 100 (A4), showing an extreme range

Table 3 Shapiro-Wilk normality test

		Solid wood	Control	HMR	Water	DMF 5	DMF 100	pMDI 30	pMDI 1d
Tensile shear strength (MPa)	A1	x	x	x	x	x	x	x	
	A4	x		x	x	x		x	x
	A5	x	x	x	x	x	x	x	x
Wood failure (%)	A1	)(	x					x	x
	A4							x	
	A5		x		x	x		x	x

x: At the 0.05 level, this data was significantly drawn from a normally distributed population

)(: Excluded from normality test

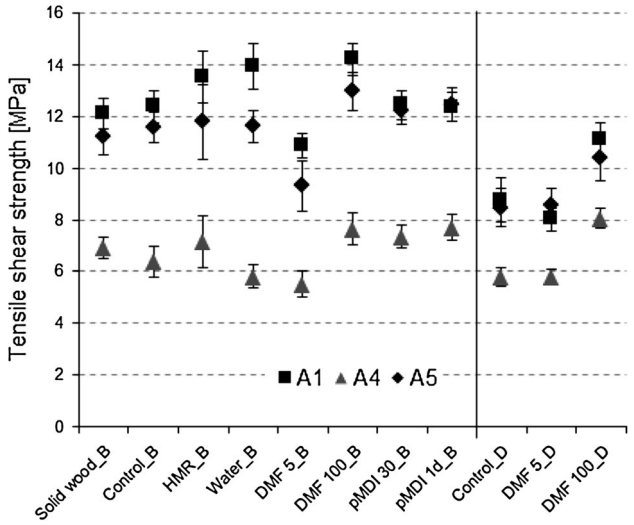

Fig. 3 Average values of tensile shear strength with confidence intervals at 95 % confidence level. Beech wood: _B, Douglas fir: _D

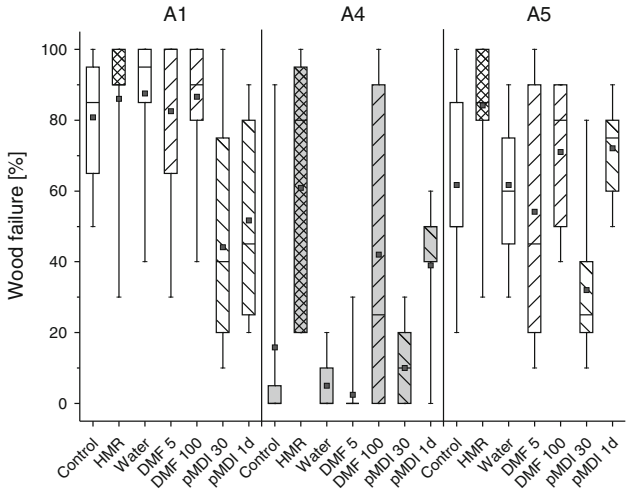

Fig. 4 Wood failure percentage of beech wood specimens. *Whiskers* minimum and maximum values, *Horizontal line in box* median, *square in box* arithmetic means value

($R = X\max - X\min = 100$ %) and a large inter-quartile range (IQR = Q.75−Q.25 = 90 %). Therefore, the Shapiro–Wilk test mentioned above was also carried out for the WFP data and demonstrated that only 43 % of the WFP batches reveal normal distribution (Table 3). The scatter plots (Fig. 5) support these observations, and histograms (not depicted) reveal bimodal distributions for the A4 batches Control, HMR and DMF 100. The accordant specimens reveal either very high or very low WFP on the same strength level. Not a single sample with medium WFP (30–70 %) was found within these A4 batches. These findings basically go in line with CSA O112.9 (2004), which explains that WFP is rarely found to be normally distributed. Hence regarding WFP results, medians should be given preference over average values. The control batches show high WFP after A1, low WFP when tested at wet stage (A4) and regained WFP after re-drying (Fig. 4). This applies to all the tested batches and goes in line with Kläusler et al. (2013). The HMR batches reveal high WFP after all the three treatments, notably the highest median values within the treatment groups A4 and A5 and basically in agreement with Vick and Okkonen (2000). In contrast, no improving effect of water spray or DMF 5 on WFP can be found after A4 and A5. But DMF 100 and pMDI 1d reveal a considerable improvement of WFP (medians compared to control median) after water contact (A4, A5). Both pMDI batches clearly show reduced WFP after A1 (compared to Control), but higher medians after A4 and A5. The given wood moisture content after A1 was certainly sufficient for the pMDI to react (He and Yan 2005). However, the results of the accordant A4 and A5 batches point to a strong influence of the waiting time on WFP after water treatment, which does not seem to be crucial after A1. In this regard, further experiments (e.g., with more graduations of waiting times) would help to get a clearer picture before further conclusion can be drawn regarding the influence of pMDI priming on WFP. In summary, HMR and DMF 100 turned out to be the only

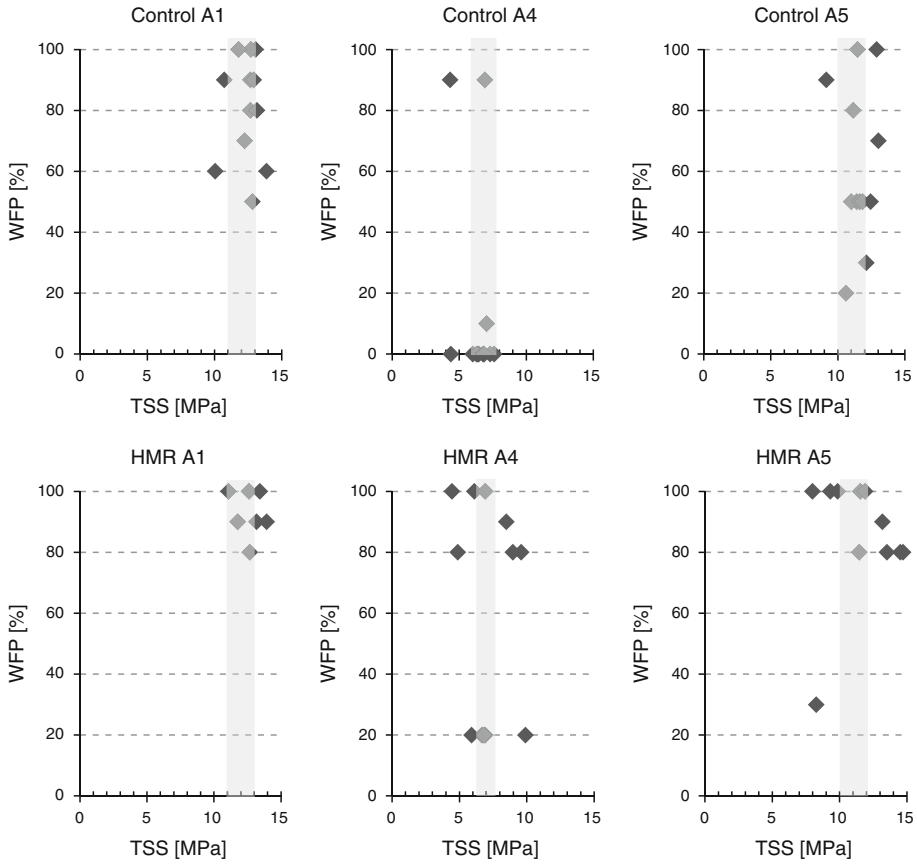

Fig. 5 Scatter plots. Gray rectangle in diagram: interquartile range of the TSS measured for the solid wood samples (beech wood). Values rounded according to EN 302-1

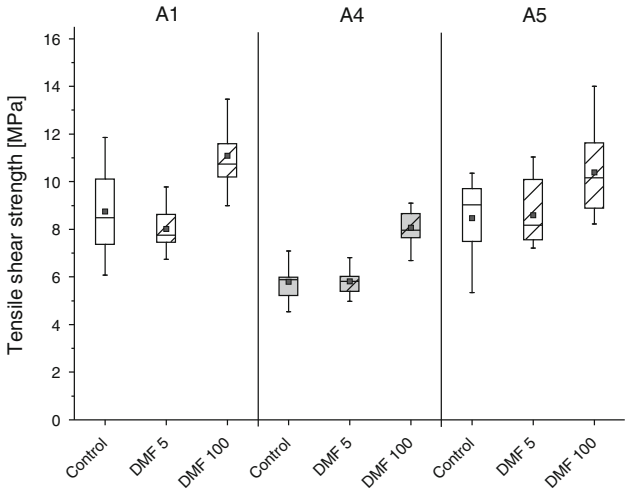

Fig. 6 Tensile shear strength of Douglas fir samples. *Whiskers* minimum and maximum values, *horizontal line* median, *square in box* arithmetic mean

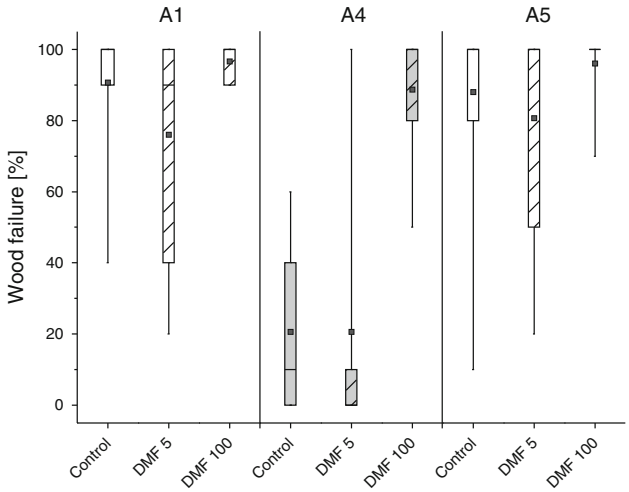

Fig. 7 Wood failure percentage of Douglas fir samples

priming liquids capable of enhancing WFP after all three treatments (A1, A4, A5), whereas HMR (median) is the only one reaching 80 % WFP after A4 and even 85 % after A5.

3.3 Tensile shear strength and WFP of the Douglas fir samples

The finding for the Douglas fir samples (Figs. 6, 7) basically go in line with those for the beech wood samples. Confidence intervals (Fig. 3) reveal a significant

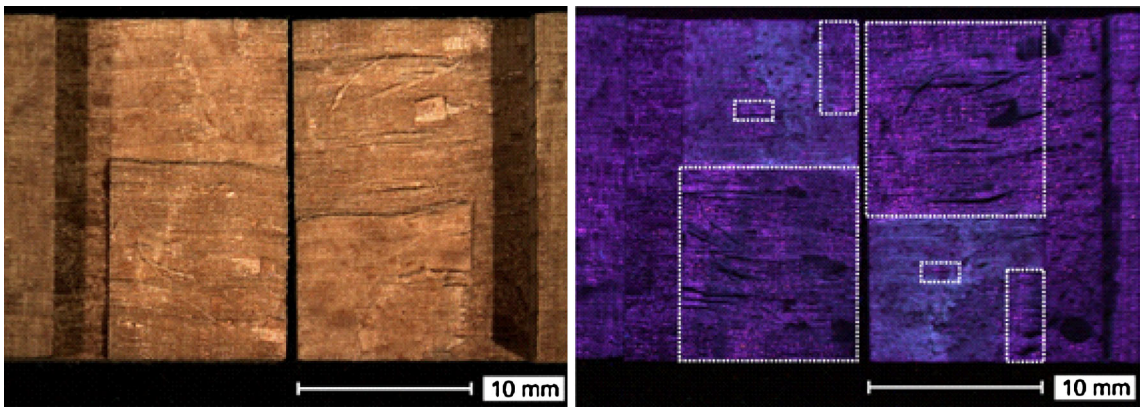

Fig. 8 Fracture surfaces of beech wood specimen with highest TSS (Control 13.0 MPa) after A5. *Left* artificial daylight, *Right* UV light, *dotted frames* encircle wood failure

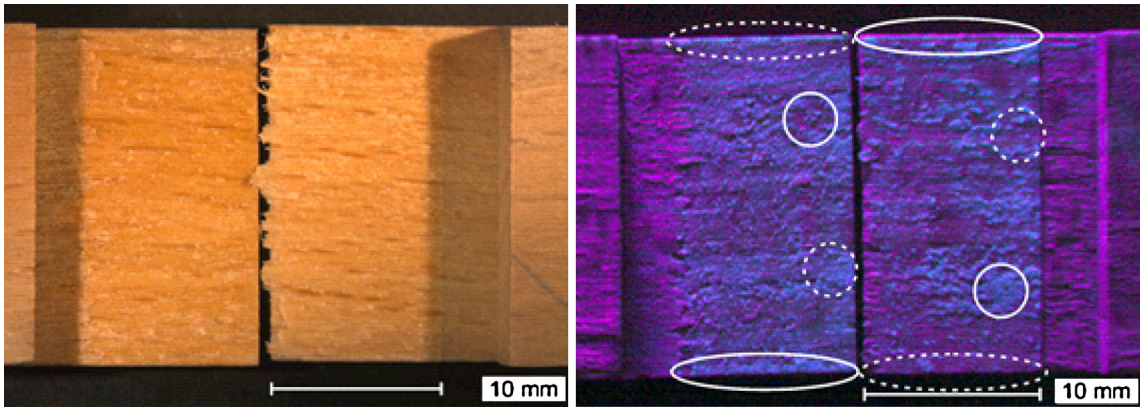

Fig. 9 Fracture surfaces of a beech wood specimen after A4 (Control). *Left* artificial daylight, 10 % WFP estimated due to "fibers" on the fracture surfaces. *Right* identical specimen under UV light: 0 % WFP detected. Matching shapes (oval–oval, circuit–circuit): Correspondent spots on the two surfaces, exemplarily disclosing selective loss of adhesion of the adhesive polymer

improvement of TSS after DMF 100 treatment compared to the accordant controls (A1, A4). After water contact (A4, A5) also WFP (Fig. 7) benefits from the DMF 100 treatment.

3.4 Correlation coefficients and scatter plots regarding beech wood specimens

Calculation of Spearman's rank correlation coefficient (r_{SP}) was used for evaluation of the correlation between TSS and WFP of the beech wood batches. This method is suitable for non-normally distributed lots and was exemplarily performed for the control batches. In summary, none of these lots revealed a significant correlation between the two parameters at $\alpha = 0.05$ level. It is fair to conclude that high (or low) WFP of 1C PUR bonded beech wood joints does not indicate high (or low) TSS of the 1C PUR bonded composite material (see also Fig. 5). But nonetheless the assessment of WFP of 1C PUR bonded joints is reasonable. Especially in case of extremely low strength a high WFP may point to low wood quality.

3.5 UV light photographs and ESEM images of beech wood specimens

For several specimens, the result of the WFP assessment varied quite a bit, dependent on the light source used. For example, the specimen depicted in Fig. 8 was rated as 100 % WFP at a first glance by means of daylight. Using UV-light in combination with a reflected light microscope, the value was corrected down to 70 % (66 % measured and rounded up acc. to prEN 302-1 2011). In summary, the combination of both light sources plus microscope proved effective. A closer look at the fracture surfaces of the A4 specimens (Fig. 9) revealed selective detachments of glue from the surfaces of the adherends. In total, nine samples of

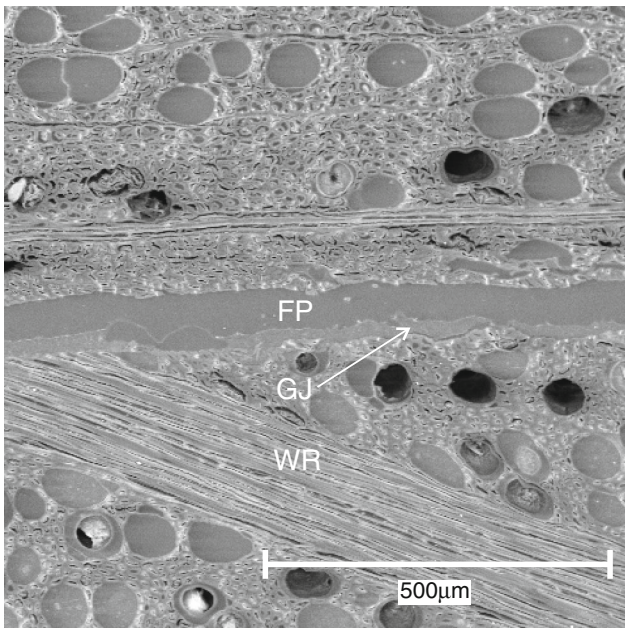

Fig. 10 ESEM image of beech wood specimen (Control) tested on TSS after A4. *FP* Fracture Path (filled with Epoxy resin for preparation), *GJ* Former Glued Joint (with residual 1C PUR) showing no wood failure but fracture between adhesive and adherend, *WR* Wood ray

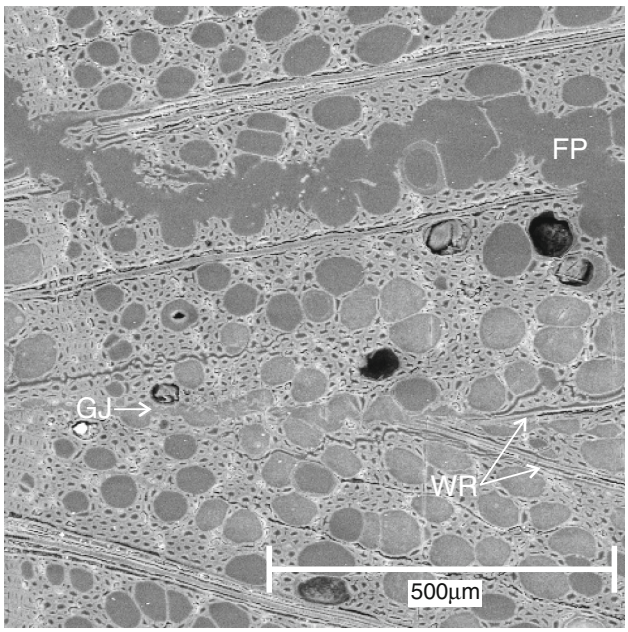

Fig. 11 ESEM image of beech wood specimen (DMF 100, A4) showing deep wood failure after TSS testing. *FP* Fracture Path (filled with Epoxy resin for preparation), *GJ* Glued Joint (filled with 1C PUR), *WR* Wood rays of the two adherends

Control batch A4 revealed 0 % WFP. Four of them were searched for selective loss of adhesion, which was found on each of them. Two depicted loss of adhesion on about 50 % of the fracture surface. On the contrary, after A1 or A5 loss of cohesion within the adhesive layer and wood failure were predominant.

Two more specimens of the Control A4 batch were investigated by means of ESEM images (Fig. 10). Results confirm the finding that fracture surfaces without wood failure of specimens tested at wet stage (A4) show loss of adhesion at the interface. In principal, it is difficult to draw general conclusions from a series of 15 ESEM pictures per specimen, representing one and the same plane within the sample. But nonetheless, the images taken from the fracture path after A4 (Fig. 10 exemplarily) depict a clear loss of adhesion over the whole width of the sample (20 mm). Another two specimens of batch DMF 100 were inspected after treatment A4 (Fig. 11 exemplarily). As the micrographs reveal, the DMF treated bondings are basically capable of creating deep wood failure (about 200–300 µm distance between fracture path and glued joint).

3.6 Contact angle measurements

Compared to the control samples, the DMF treatment heavily reduces the contact angle of the water on the adherends' surfaces (Fig. 12), measured 30 min after application of the DMF. It is more than likely that DMF changes the chemical composition of the boundary layer by influencing the wood extractives, thus affecting the wood's surface energy and glueability (Nussbaum 1999; Stehr et al. 2000; Gindl et al. 2004b).

3.7 Swelling strain model

In search of fundamental explanations for the behavior of adhesively bonded wood under changing moisture conditions, Frihart (2009) stated the swelling strain model. It focusses on the effect of swelling strain distribution on the failure behavior of glued wooden joints and recommends establishing the two groups of in situ polymerized adhesives (e.g., phenolic resins) and pre-polymerized adhesives (e.g., 1C PUR). According to the model, the penetration of in situ polymerized adhesives into the adherends' cell walls has a stabilizing effect by reducing the cell walls' swelling capacity. This promotes higher WFP at the wet stage, because the swelling strain occurs some cell rows away from the joint (Fig. 13, I) where less adhesive is present. Also the HMR treatment would basically fit into this group. On the contrary, pre-polymerized adhesives do not penetrate the cell walls (Fig. 13, II). Therefore, the swelling strain occurs at the interface, hereby advantaging a fracture path with low WFP. Based on the current results the model could be extended by a third variation. By using DMF as adhesion promoter for 1C PUR bonded wooden joints

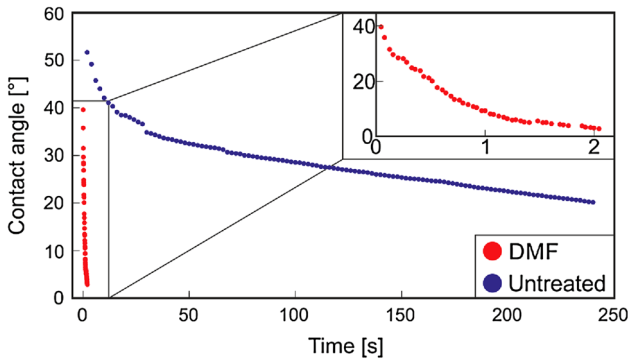

Fig. 12 Contact angle measurements on DMF 100 treated beech wood

(Fig. 13, III), a highly pre-swollen state of the adherends is created. It is likely that after pressing some of the high-boiling solvent slowly evaporates (especially at the edges of the specimens) and some of it remains in the wood, thus establishing a prolonged pre-swollen state. During A4 treatment this pre-swollen state might cause a shift of swelling strain away from the interface deeper into the bulk adherends where less DMF is present. According to the swelling strain model, such a shift promotes higher WFP at wet stage. In the current research, a period of about 2 weeks "evaporation time" elapsed between manufacturing of the pressings and A4 treatment. Obviously the prolonged high-grade pre-swelling by means of highly concentrated DMF has a different effect on WFP than the short-term pre-swelling by means of water spray or DMF 5 (very high water content). The water does not swell the wood to such a high extent and vaporizes until EMC of climate 20 °C/65 % RH (storage climate for re-drying) is reached. These observations basically go in line with the swelling strain model. However, further investigations and a more detailed knowledge of the penetration of pMDI into wooden cell walls are needed, before this kind of priming can clearly be classified in the model.

4 Conclusion

Within the present work, DMF 100 is the only adhesion promoter which significantly enhances the TSS of 1C PUR bonded beech wood joints after A1 and after A4. Regarding WFP the highly concentrated DMF improves the measured medians after all three treatments (A1, A4 and A5). The additional tests on Douglas fir confirm said results for TSS and WFP. No significant effect of pMDI priming on TSS was observed, and further experiments are needed to get a clear picture regarding the influence of this priming on WFP. Water spray improves TSS at dry stage (A1) but not after water contact (A4, A5). Furthermore, it does not improve the WFP of 1C PUR bonded joints. The HMR primer does not reveal a significant effect on TSS (A1, A4, and A5) but it substantially enhances WFP after all three treatments.

As UV-light micrographs and ESEM images depict, the loss of performance at the wet stage (Control A4 compared to A1) is accompanied by a loss of adhesion between adhesive polymer and the wooden adherends. The results after A5 for TSS indicate that this is a reversible effect, demonstrating the high importance of secondary bonds like hydrogen bonds for 1C PUR glued joints. Actually, the adhesion at wet stage was clearly improved by means of different priming liquids (HMR, DMF 100), resulting in a higher performance at wet stage (compared to Control). The UV tracers present in the quasi transparent adhesive turned out to be quite helpful for the assessment of WFP, which was carried out using a combination of UV-light and artificial daylight. Furthermore, the findings confirm that TSS and WFP of 1C PUR bonded joints do not correlate. The two parameters reveal very different distributions. Low WFP of 1C PUR bonded beech wood joints does not indicate low TSS of the bonded composite material and vice versa. It is reasonable to consider this aspect when it comes to the discussion, whether high WFP of 1C PUR bonded joints can serve as indicator for very high strength. The present work does not intend to recommend a specific

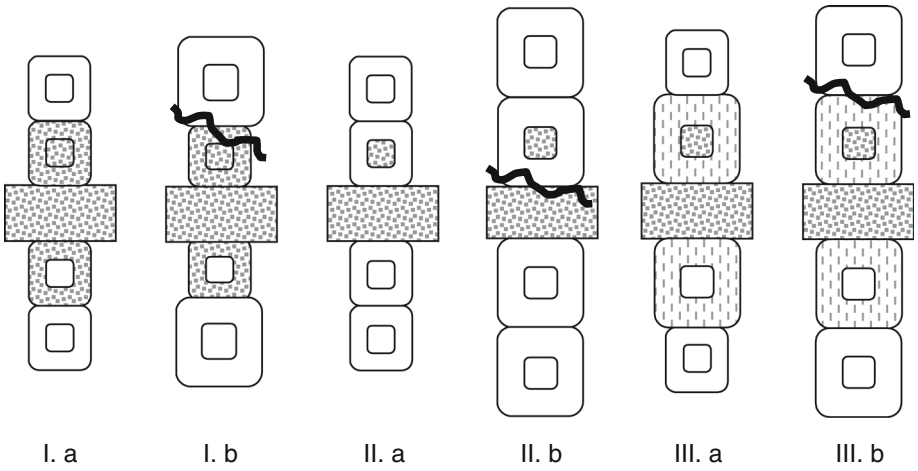

Fig. 13 Schematic drawing of glued joints. *I* Phenolic resin, *II* 1C PUR, *III* DMF + 1C PUR, *a* glued sample at dry stage, *b* glued sample at wet stage with fracture path (wavy black line) after tensile shear test; *cuboid in the center* bondline, *dotted areas* presence of adhesive polymer, *dashed areas* presence of DMF

fluid for priming in practice. Instead it is aimed to contribute to the fundamental understanding of the mechanisms of action of such adhesion promoters. Priority attention is being paid to the accordant effect of the solvent DMF. Sure enough, the results presented cannot exhaustively explain the measured effects of DMF on 1C PUR bonded wooden joints. It is likely that the reasons for the changes in TSS and WFP are a combination of different influencing factors, such as enhanced wettability of the bonding surface (likely contributing to the improved adhesion at wet stage), translocated swelling strain (see swelling strain model) and others. Therefore, a subsequent paper is in preparation dealing with the influence of DMF on the 1C PUR adhesive polymer on the one hand and the beech wood on the other hand. Further investigations should be carried out regarding possible alternative substances like the less toxic Dimethylacetamid (DMAC), but also regarding the influence of suitable solvents on the delamination behavior of 1C PUR bonded joints or the influence of such solvents on the bonding performance of wood species which so far are difficult to be bonded by means of 1C PUR (e.g., *Larix* spp.). In addition, the translocation of swelling strain mentioned above could be investigated using Digital Image Correlation or Speckle Interferometry (Valla et al. 2011; Keunecke et al. 2012).

Acknowledgments The authors would like to thank Dr. Christian Wamprecht (Bayer MaterialScience, Germany) for his valuable contribution and gratefully acknowledge the financial support of this research by the Commission for Technology and Innovation KTI/CTI (Bern, Switzerland) and the Purbond AG (Sempach-Station, Switzerland). Mrs. Gabriele Peschke (IfB, ETH Zürich) is cordially thanked for preparing the ESEM images.

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