



Hydroxymethylated resorcinol (HMR) primer to improve the performance of wood-adhesive bonds – A review

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ABSTRACT

A hydroxymethylated resorcinol (HMR) primer was developed in the 1990s to improve the performance of epoxy-bonded wood lamellas for use in moist conditions. Its chemical composition resembles a strongly diluted resorcinol-formaldehyde adhesive, which is applied before the actual adhesive. The effectiveness of HMR priming is proven for different wood species and adhesive types based on delamination tests and shear strength measurements. However, the primer is not used in the industrial mass production of glued laminated timber. The reason can be found in additional process steps, therefore costs, and the fact that certain combinations of currently broadly available wood species and adhesives yield proper bonds without the additional use of a primer.

Nevertheless, due to ongoing changes in the availability of wood species, it becomes increasingly important to consider the use of currently less-used wood species, including the corresponding adaptations in the production process. Since it is known that the HMR primer improves the bond performance, but is not used due to necessary process changes, it would be interesting to integrate the primer's functionality into existing adhesive systems.

This review summarizes and structures the available information on the HMR primer from previous research. Furthermore, that information is critically discussed and a model of functionality is introduced. Finally, it is evaluated if the existing knowledge about the HMR primer is sufficient to transfer its mode of action into existing adhesive systems or which questions need to be addressed to do so.

1. Introduction

Adhesive bonding is essential in many production processes in today's wood industry including load-bearing glued laminated timber (GLT). It is necessary that the bondings show sufficient adhesion and cohesion, as well as remain durable during their entire service time.

The production of GLT in Europe is regulated in the EN 14080:2013 [1]. Actually, 15 of the 16 permitted wood species are softwoods while poplar is the only hardwood. A survey among German, Austrian and Swiss GLT producers in 2009 revealed that above 96% of all GLT is produced from spruce and fir [2]. This highlights the focus on only very few wood species in GLT production.

The adhesive systems commonly used for the production of GLT include melamine-formaldehyde (MF), melamine-urea-formaldehyde (MUF), phenol-resorcinol-formaldehyde (PRF), one-component polyurethane (1C-PUR), and emulsion-polymer isocyanate (EPI). In Europe, the requirements for these different types of adhesives are described in the standards EN 302 [3] (phenolic and aminoplastic), EN 15425 [4]

(1C-PUR) and EN 16254 [5] (EPI), whereas the testing procedures are described in EN 302-1 to -8 [6–13]. In Canada and the USA, the requirements for the bondings are described by the CSA O112.9 [14] or the ASTM D2559 [15]. Since spruce and fir were predominant for decades, the existing adhesives and processes have been optimized for those wood species.

When considering the production of GLT from wood species besides the predominant ones, industrial-scale bonding can be challenging. To name two challenges, there are species i) with high amounts of extractives that can diminish the bond quality, e.g., larch [16], yellow-cedar [17] or ii) with strong shrinkage and swelling behavior that induce high stresses into the bondline, e.g., beech [18].

Considering ongoing changes in silviculture, e.g., due to climate adaptation or enhanced biodiversity, the availability of wood species will change in the future [19]. Therefore, it is mandatory to introduce new species into the production of GLT based on their availability. Also, some species offer additional advantages compared to spruce and fir, e.g., i) larch and yellow cedar show higher durability [20] or ii) beech

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shows higher mechanical properties [21], which allow smaller cross-sections of GLT. However, regardless of the used wood species, the final products must meet the existing standards while allowing an economically competitive production.

To overcome the insufficient performance of the bonding, the use of a primer can be considered. The ASTM D907 – 08b [22] defines a primer as ‘a coating applied to a surface, prior to the application of an adhesive, to improve the performance of the bond’. A subgroup of primers are coupling agents, which include ‘a substance having functional groups that are capable of reacting with the surfaces of two different substances, thereby chemically bridging them’ [22]. However, the use of a primer adds a further process step into the GLT production including all related costs, as well as a possible source for extra problems. Therefore, it is easy to comprehend that primers are not widely spread in the production of GLT, especially when it is redundant using spruce and fir.

In general, the concept of improving the bond quality of difficult-to-bond wood species with chemical pretreatment is not new. Descriptions of primers for wood can already be found in the 1920s. Truax [23] described increases in shear strength and wood failure by treating the wood with aqueous solutions of 10% “caustic soda” (sodium hydroxide, NaOH) or 10% “milk of lime” (calcium hydroxide, Ca(OH)₂). Interest in industrial-scale applications of primers for wood was first found in patents of the late 1960s and early 1970s. A patent of Rhône Poulenc S. A. (Paris, France) from 1968 described a primer based on isocyanate and organoalkoxysilanes, which improved the adhesion of silicone elastomers to different materials, including wood [24]. In 1972, the Weyerhaeuser Company (Tacoma WA, USA) patented a polyethylenimine (PEI) based primer for wood [25]. A year later, the Monsanto Company (St. Louis MO, USA) patented the use of “materials obtained from the reaction product of ethylene oxide with a multi-functional active hydrogen compound”, which was applied to green wood before drying. Presented examples of materials successfully used to increase the wood failure were “tris-polyethylene oxide sorbitan monooleate” (Polysorbate 80), as well as two formulations of resoles diluted in water [26]. In the early 1990s, it was observed that epoxy (EP) adhesives showed poor bond quality for wood under wet conditions, as well as in combination with chemically treated wood [27]. Inspired by the positive reports of Weyerhaeuser’s PEI primer, research at the USDA Forest Products Laboratory readopted the wood primer idea [28]. In 1996, a patent of the newly developed hydroxymethylated resorcinol (HMR) primer was approved [27]. In 2005, Huntsman Polyurethanes (West Deptford NJ, USA) patented for a 1C-PUR adhesive the optional use of a primer. The described primer consists of waterborne solutions of urea, polyvinyl alcohol, salts of dodecylbenzene sulfonic acid or copolymers of ethylene and vinyl acetate [29]. A primer in an aqueous solution based on polyamine, preferably a polyethylenimine with a pH ≥ 11.5 was patented in 2012 by the Commonwealth Scientific and Industrial Research Organization [30]. Also in 2012, Adamopoulos et al. [31] experimented with an aqueous phenol-formaldehyde primer, which had negative effects on the bond quality. In 2014, dimethylformamide (DMF) was assessed as a primer at the ETH Zürich. Even though a positive effect was observed, the authors concluded that due to its hazards it is not suitable as an industrially used primer [32–34]. In 2015, the Henkel AG & Co. KGaA (Düsseldorf, Germany) received a patent for a primer based on Polysorbate 20 to be used with their 1C-PUR adhesives [35]. The commercial name of the primer is LOCTITE® PR 3105 PURBOND for which some publications are available [35–40]. A second patent was approved in 2020 that describes a glycol-based primer specially designed for wood with high extractive contents, e.g., larch [41]. The commercial name of this primer is LOCTITE® PR 7010 PURBOND [42]. Henkel’s waterborne primers both have a viscosity of 500 mPa·s or below and must be applied by spraying [40,42].

To benefit from the primer, but avoiding the separate application step required, we will evaluate if it is possible to integrate its functionality into already existing adhesive systems. The basic condition for that is to understand the primer’s mode(s) of action. In the past, the most

extensive research was done on the functionality of the HMR primer. Moreover, many studies show the effectiveness of the HMR primer to improve the quality of wood bonds. Therefore, we select the HMR primer as a conceptual model.

This contribution will review in the following chapters the existing literature on the HMR primer. Starting with chapters on the primer’s effectiveness in standardized testing, followed by the primer’s application as well as the mechanisms that occur during curing. The main chapter discusses previous research on the primer’s functionality, followed by a chapter combining the state of the art to a model of functionality. The last chapter, the conclusion, will refer back to the questions that will be accompanying the reader during the entire review: i) What are the primer’s mechanisms that lead to improved bonding performance? ii) Is the existing knowledge sufficient to purposely transfer the primer’s mode of action into existing adhesive systems? and iii) What open questions need to be addressed in the future?

2. Effectiveness

This chapter presents the comparison of the bond quality assessments with and without HMR-treatment, intending to visualize the primer’s effectiveness and to give an overview of wood species, wood treatments and the adhesive chemistries the HMR primer has been tested on.

Shear strength (SS) results and the corresponding wood failure percentages (WFP) from various authors [17,27,34,43–59] are visualized in Fig. 1. The shape of the markers allows quick identification of whether the measurement was conducted in dry conditions (round marker) or wet conditions (diamond marker). Additionally, a detailed table listing information for each result, i.e., adhesive type, wood species, test method, pretreatment and, if necessary, further details are available in the electronic supplementary (Table ES-1).

The following observations can be seen when comparing the results of unprimed and HMR-primed wood:

- i) Most comparisons used EP (28) and 1C-PUR (30) adhesives, the WFP often strongly improves, while the SS-values often increase moderate to strong.
- ii) Limited comparisons are available for poly(vinyl acetate) (PVAc) (5) and MF (6) adhesives, therefore, only tendencies can be assumed. The primer seems to have a positive effect on the SS, while mixed influences on the WFP can be observed.
- iii) For the three comparisons with EPI adhesive, the changes in the WFP are negligible or very small. The SS-values from two of three measurements remain unchanged by the HMR-treatment, while the third reduces about 20%.
- iv) Few comparisons are available for MUF (4) and PRF (3) adhesives, the SS-values remain almost completely unchanged after HMR-treatment. Four out of seven measurements show an improvement of the WFP, while one remains unchanged at 100% and two reduce 5%-points while remaining high above 85%.

Another method for the evaluation of the bond quality is the delamination test, which is complementary to the shear strength experiments. An overview of delamination results from various authors [17,27,43,44,48,51,55–57,60–62] is presented in Fig. 2, with detailed information in the electronic supplementary (Table ES-2).

By exposing the specimens to harsh changes of their moisture content during the measurement, the corresponding swelling and shrinking induce high stresses into the wood and the bondline. The HMR-priming improved the delamination behavior for 40 out of 41 measurements with different adhesives and wood species. The only exception was when using EPI adhesive and eucalyptus, however, the corresponding publication does not explain this unique result [51]. Another observation is that, for PRF bonds, the delamination of unprimed wood is comparably low.

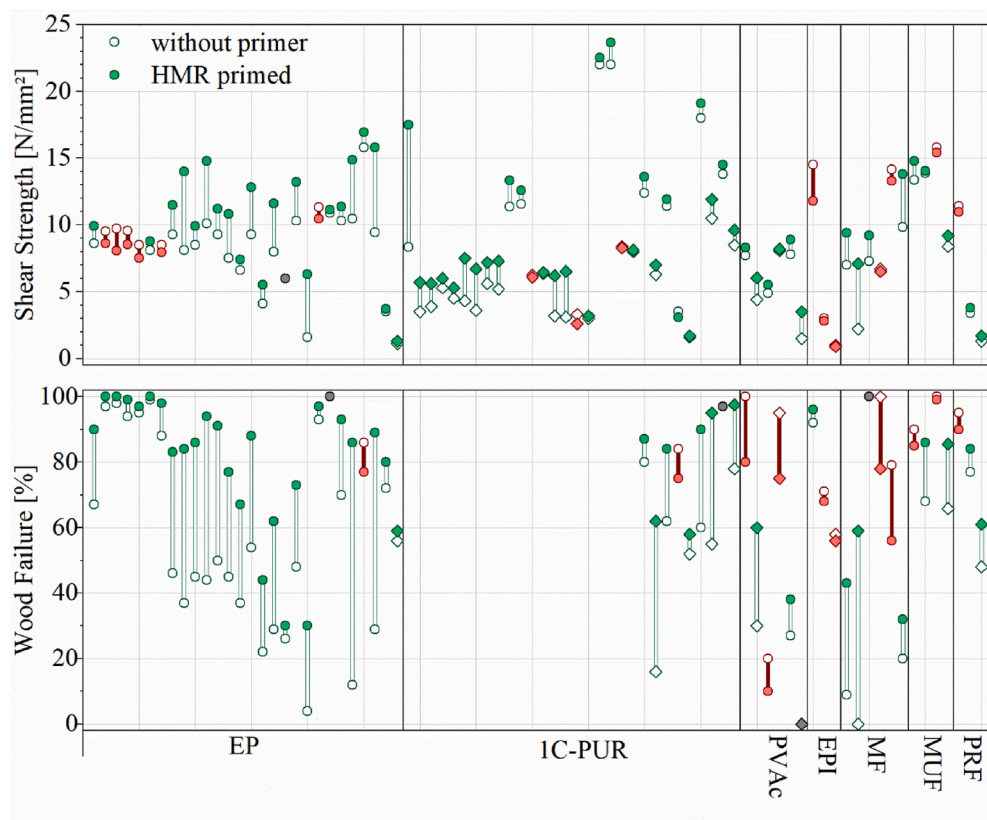


Fig. 1. Effect of HMR priming, evaluated by shear strength and wood failure. The bar between the pair of data points (empty symbols and filled symbols correspond to unprimed and HMR-primed wood, respectively) indicates if the HMR priming improved (green, unfilled) or impaired (red, filled) the result. When the filled symbols are above the empty counterpart, it indicates that the HMR-treatment improved the system studied. Round and diamond markers indicate measurements conducted in the dry and wet states, respectively. A detailed list of the results can be found in the electronic supplementary. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

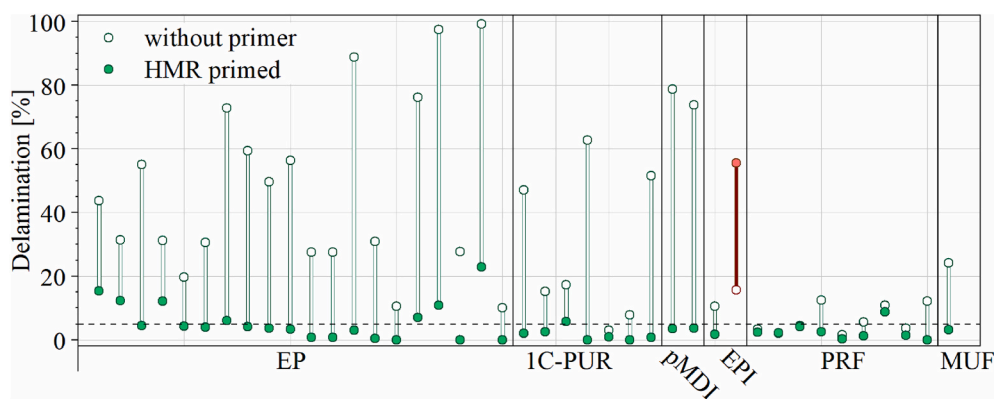


Fig. 2. Delamination percentage for bonded wood with and without HMR-priming. The bar between the pair of data points (empty symbols and filled symbols correspond to unprimed and HMR-primed wood, respectively) indicates if the HMR-priming improved (green, unfilled) or impaired (red, filled) the result. When the filled symbols are below the empty counterpart, it indicates that the HMR-treatment improved the system studied. The dashed line indicates the 5% threshold required to pass ASTM D 2559 [15] and EN 391 [63]. A detailed list of the results can be found in the electronic supplementary. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

HMR-primed wood also showed positive effects not only for applications for GLT but also when used for oriented strand boards (OSB) [64] or when bonding wood to other materials, e.g., glass- or carbon-fiber reinforced polymers [65–68]. Therefore, in summary, it has been shown that by using the HMR primer the bond quality predominantly improves as indicated by the increased SS-values, WFP and resistance to delamination.

3. Application

The HMR primer is prepared by reacting its components (Table 1), i. e., formaldehyde and resorcinol, under mildly alkaline conditions (pH = 8.5–9.0). The molar ratio of formaldehyde to resorcinol (F/R) is 1.54, similar to the conditions for resoles preparation, where the excess of formaldehyde generates several reactive methylol (hydroxymethyl) groups on the linked aromatic units susceptible to condensation. Before

Table 1
Formulation of HMR and n-HMR primers.

Components	Parts by Weight (%)	
	HMR	n-HMR
Water, deionized	90.43	90.43
Resorcinol, crystalline	3.34	3.34
Sodium hydroxide, 3 M	2.44	2.44
Formaldehyde, 37% in methanol and water	3.79	–
(for storable A-stage)	–	0.95
(for applicable B-stage)	–	2.84
Sodium dodecyl sulfate ^a	0.50	0.50
Total	100.5	100.5

^a Added before the application of the primer to improve the wetting of the wood.

its application, the originally developed HMR primer has to react for 4 h at room temperature [28] until the window with molecules of a favorable size opens. At the end of the preparation process, sodium dodecyl sulfate (SDS) - a surfactant - may be added to assist the wetting of the wood [44]. The reported amount of SDS (0.5% by weight) results in a concentration of approximately 18 mM, which is above the critical micelle concentration (CMC) of 8 mM [69]. It can be assumed that a reduction of the SDS concentration below the CMC would not have negative consequences on the performance of the HMR primer.

Due to the inconvenience of waiting 4 h between starting the reaction and the application of the primer, the “novolak-HMR” primer (n-HMR) was developed [70]. For the name given, the term “novolak” is deduced from RF adhesives and refers to the multi-stage characteristic of the n-HMR primer, rather than the other characteristics: the F/R ratio and the pH-value [71,72]. The preparation of n-HMR requires the same total amount of the components as for the HMR primer. However, the formaldehyde is added in two separate steps (Table 1). The first portion of the formaldehyde creates the A-stage of the primer with an F/R-ratio lower than 1, similar to the conditions for novolak preparation. Therefore, the storage life of the A-stage is extended due to the low reactivity caused by the absence of free methylol groups. The second portion of formaldehyde activates the n-HMR directly before its application [70, 73] reaching the B-stage with an F/R-ratio higher than 1 preparing the condition for crosslinking.

Even though it is not mentioned explicitly, certainly a given time, e. g., ‘overnight’, should pass between adding both portions of formaldehyde. Christiansen [74] described the maximum storage life of the A-stage from a theoretical perspective as ‘indefinitely’. However, no experimental data for a maximum storage life were given.

On the laboratory scale, commonly 150 g/m² of the original HMR, or the n-HMR’s B-stage, are applied by brushing on a freshly prepared wood surface. Lower spread rates have been used in a few studies, e.g., 85 g/m² [53] or 75 g/m² [55]. A comparison of the spread rates 150 g/m² and 75 g/m² showed comparable delamination behavior, as well as shear strengths [55].

Before the adhesive can be applied onto the HMR-treated wood surface, the solvent (water) has to be removed by evaporation. To take this into account, the drying time between primer and adhesive application in most studies goes from 12 h to 24 h. However, Vick [57] compared different drying times of HMR-treated wood from 1 h to 24 h on CCA-treated (chromated copper arsenate) Southern pine lamella subsequently bonded with two PRF adhesives observing that the delamination rate was not affected by the drying time. Eisenheld et al. [75] accelerated the drying time of n-HMR on hard maple (*Acer saccharum*) by using infrared (IR) heaters for 10 min before bonding it with EP adhesive. The influence of the IR-drying was assessed by compression shear force, where no negative influence of the accelerated drying was observed.

The working life of the original HMR was evaluated by Vick et al. [76], who applied the primer at different time intervals after its preparation onto Douglas fir boards. After drying, the boards were bonded with an EP adhesive and evaluated in a delamination test according to ASTM D2559 - 92 [77]. The delamination value with untreated wood was 49.5% [70]. When the original HMR was applied 4–8 h after its preparation, the delamination was below the 5% maximum threshold, as seen in Fig. 3a. In parallel, differential scanning calorimetry (DSC) experiments were performed to analyze the reactivity of the HMR primer. The DSC thermograms showed that the reaction continued during the working life and finally stopped after approximately 24 h. The same experiments were conducted by Christiansen et al. [70] for the B-stage of n-HMR. A delamination rate below 5% was obtained for reaction times between 0 h and 7 h. Even though the reactivity of n-HMR is slightly lower compared to the original HMR primer, it shows a comparable loss in reactivity, represented in the declining values of enthalpy as a function of time (Fig. 3b).

To summarize the presented information, there are two attempts for

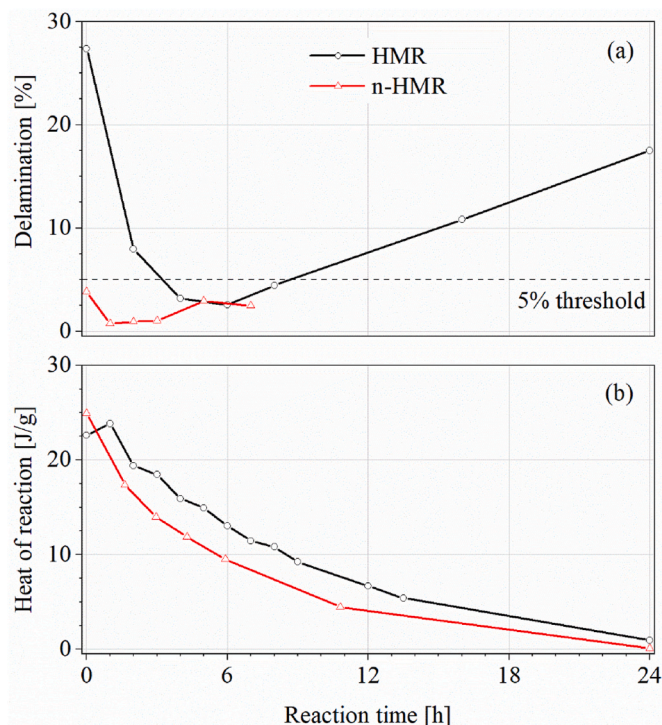


Fig. 3. Effect of HMR and n-HMR primers as a function of the reaction time and working life on (a) delamination of EP bonded Douglas fir, delamination without HMR is 49.5% (b) reactivity measured by DSC. Data from Refs. [70,76].

the production of resorcinol-formaldehyde (RF) primers i) the original, reactive HMR primer (resole-like) and ii) the stable n-HMR primer (novolak-like), which is activated after adding further formaldehyde and allowing to crosslink.

The advantage of the stable n-HMR is, on the one hand, its easy production while maintaining its positive effects. On the other hand, the lower reactivity which increases the storage life of its A-stage and, therefore, when compared to the original HMR primer makes it more attractive for industrial uses.

4. Curing

As previously mentioned, the wood yields the best delamination results when the original HMR primer is applied between 4 and 8 h after its preparation. For a better understanding of this behavior, Vick et al. [76] investigated the chemical reaction of the original HMR using gel permeation chromatography (GPC) within this period. They observed the formation of different size-distributions of polymers, which include different formaldehyde-resorcinol methylene-linked oligomers and polymers. After 8 h, about 58% of the formaldehyde had reacted with the resorcinol molecules to form reactive hydroxymethyl groups. The remaining 42% of the total formaldehyde had formed methylene bridges between the resorcinol rings [76].

Christiansen [78] used ¹³C nuclear magnetic resonance (¹³C NMR) spectroscopy to further analyze the evolution of the original HMR during the reaction. The ¹³C NMR measurements started approximately 10 min after adding the formaldehyde. It was observed that 95% of the initial formaldehyde had reacted 2 h after preparation. In Fig. 4a, an overview of HMR’s different formaldehyde derivatives is plotted against the reaction time. It can be observed for the original HMR primer that this reaction occurs approximately six times more likely on the resorcinol ring’s 4-/6-position than at the 2-position. This is in line with reports by Durairaj [79] for chemically similar RF adhesives. Also, a drop in the pH-value from initially 9.2 to 8.7 after 2.2 h was observed [78]. Christiansen et al. [73] repeated the ¹³C NMR measurements for the

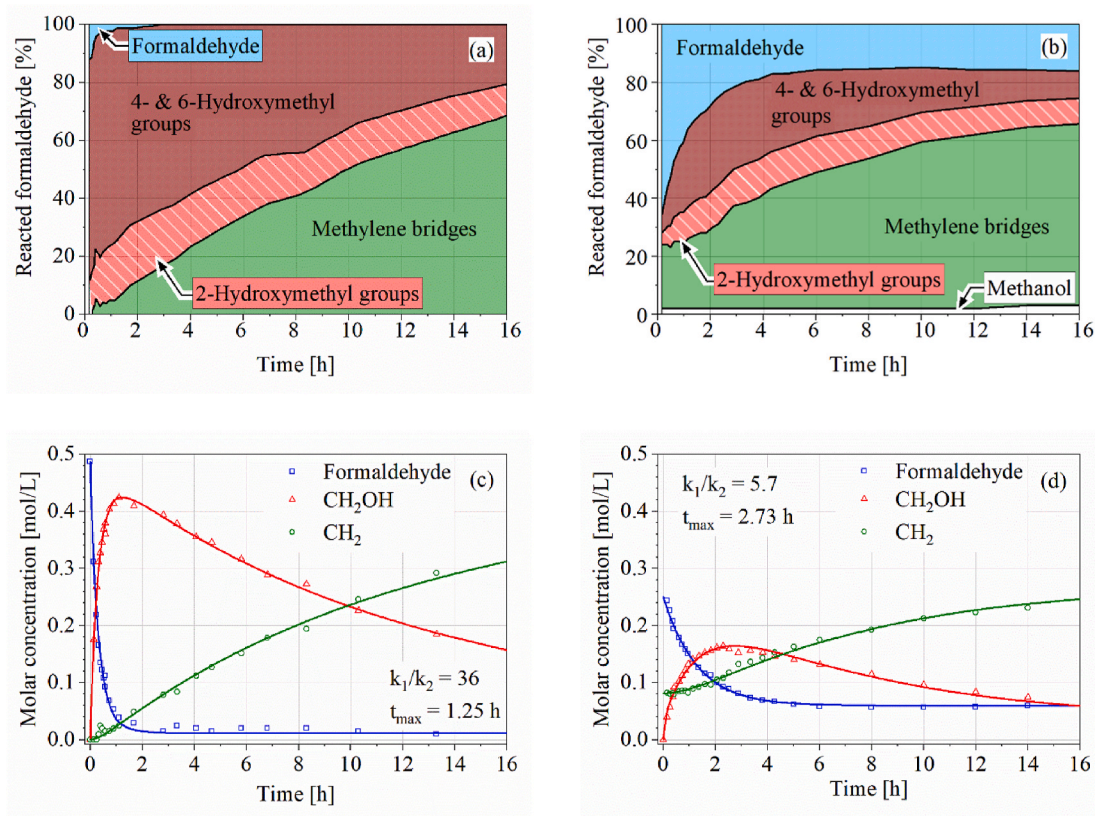


Fig. 4. Changes in the distribution of formaldehyde-containing compounds and derivatives over the reaction time in (a) the original HMR-primer, data from Ref. [78] and (b) the n-HMR primer, where the A-stage is activated to the B-stage by addition of formaldehyde at 0 h, data from Ref. [73]. The 10 min delay of each measurement results from the time between starting the reaction and the measurement. Based on the data of [73,78], the kinetics for the formation of hydroxymethyl groups (CH₂OH) and methylene bridges (CH₂) are shown in (c) for the original HMR primer and (d) the n-HMR primer, respectively.

n-HMR, as shown in Fig. 4b. Therefore, to the already completely reacted A-stage, with 98% methylene bridges and 2% methanol, the formaldehyde needed for reaching the B-stage was added. At the beginning of the ¹³C NMR measurements, 22% of methylene bridges were detected. Since the ratio of formaldehyde added for the A-stage and B-stage is 1 to 3, this 22% will primarily be the reacted formaldehyde from the A-stage. From Fig. 4b, it is easily notable that about 15% of the added formaldehyde did not react as hydroxymethyl groups or methylene bridges. This leads to the questions: i) Why does this formaldehyde fraction remain unreacted? and, ii) What happens with this remaining

formaldehyde of the n-HMR's B-stage, which the original HMR doesn't contain?

When preparing the original HMR primer, two reactions occur irreversibly and consecutively as can be seen in Fig. 4c. In the first reaction step, the formaldehyde (F/R > 1) reacts with the resorcinol forming the corresponding hydroxymethyl groups on the aromatic ring within the first 2 h controlled by a kinetic constant k_1 . Once enough hydroxymethyl groups are formed, the second reaction step takes place which is controlled by a kinetic constant k_2 . The ratio between k_1 and k_2 is 36. This means, that the formation of hydroxymethyl groups is faster than

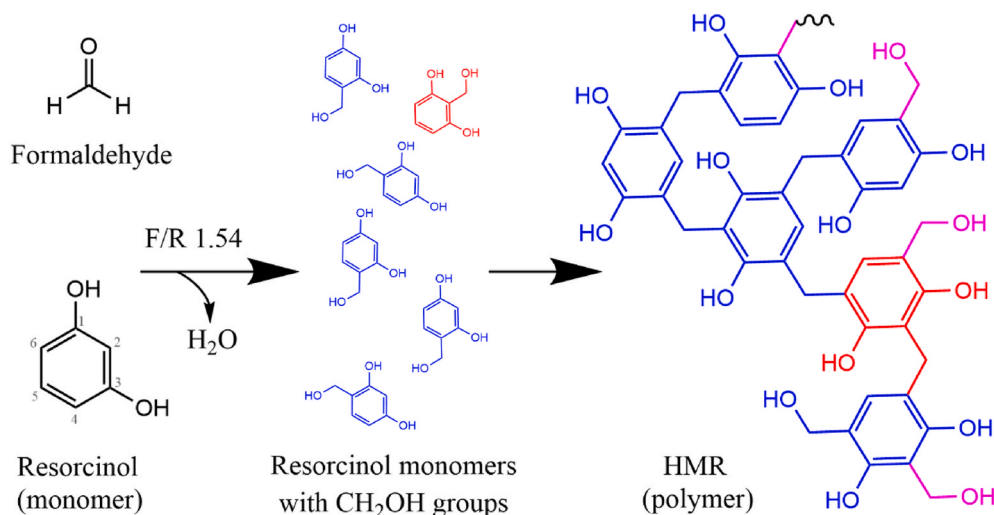


Fig. 5. Condensation process of the original HMR primer. In the first reaction step, a formaldehyde molecule attaches to the resorcinol monomer. In the second reaction step, the hydroxymethylated intermediates form among each other methylene bridges (CH₂) and, thereby, polymers (polymerization, branching and crosslinking) with additional hydroxymethyl reactive groups (pink) attached. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

their consumption towards methylene bridge formation. Therefore, there is a detectable accumulation of the former until no more hydroxymethyl groups are formed and, consequently, they react to connect resorcinol rings. The hydroxymethylated resorcinol monomers react and form methylene bridges with the corresponding formation of polymers by chain-extension, branching and crosslinking (Fig. 5). The F/R ratio of 1.54 is above the theoretical perfect stoichiometric ratio of 1.5. The almost complete consumption of formaldehyde allows the conjecture that 100% of the 2-, 4- and 6-positions of the resorcinol aromatic rings are reacted. Hence, it can be assumed that an almost perfect and dense RF network is created, with no or only little reactive hydroxymethyl reactive groups left.

In contrast to the original HMR primer, the n-HMR is prepared in two stages where the first stage (A-stage) is prepared with a shortage of formaldehyde ($F/R < 1$). The F/R ratio of 0.39 leads mainly to the formation of short oligomers, mostly dimers with no available hydroxymethyl groups (Fig. 6). It can be speculated, that the resorcinol rings are connected predominantly at the 4-4'-position, and in less proportion at the 2-4' position. Fig. 4b shows the ^{13}C NMR result after adding formaldehyde to the n-HMR's A-stage to start the reaction of the B-stage. It first appears, that the previously mentioned ratio of occupied 2- and 4-/6-ring positions is not followed. However, it has to be kept in mind that the occupied reaction sites from the A-stage are already included in the methylene bridges. In Fig. 4d, it can be observed that the first reaction step (k_1), consisting of attaching a formaldehyde molecule to a resorcinol ring, occurs much slower compared to the original HMR primer. This is because the aromatic ring belongs to a dimer structure with less access and slower mobility. Due to the lower availability of the hydroxymethyl groups, the second reaction step (k_2), dealing with the formation of methylene bridges, also occurs more slowly. The ratio between k_1 and k_2 for the n-HMR primer is 5.7 and, therefore, four times lower compared to the original HMR primer. The chance of forming longer chains increases from the oligomers at the A-stage (Fig. 7), compared to the situation for the original HMR primer, however, based on the remaining formaldehyde it can be concluded that the resorcinol rings are not densely crosslinked causing the formation of a less dense macromolecular network.

To prove that the crosslinking of HMR is necessary for its positive effects, Christiansen [80] replaced different amounts of resorcinol in n-HMR with 2-methylresorcinol. Both molecules are similar in structure. However, the 2-methylresorcinol has only two functional groups that are available for crosslinking, while resorcinol has three. Therefore, the 2-methylresorcinol can only form linear polymer chains, while the

resorcinol can form networks. The different formulations were compared by delamination according to ASTM D2559 - 97a [81] of EP bonded Southern yellow pine (*Pinus* spp.). Christiansen [80] observed higher delamination values when increasing the proportion of 2-methylresorcinol.

It can be considered that the original HMR and the n-HMR's B-stage react with the wood's polymers. The most likely bonds include methylene bridges and hydrogen bonds [44]. Sun et al. [82] proposed that reactions could likely occur with the wood's lignin, since for the chemically similar phenol-formaldehyde adhesives, such a reaction was already shown by various authors [83–86]. Due to the similar structures of phenol and resorcinol, it would be expected to find a similar result for the HMR's resorcinol. Yelle [87] investigated whether chemical bonds between HMR and lignin from sugar maple (*Acer saccharum*) were present using NMR. While no reaction between HMR and lignin was observed, a reaction with xylan (a polysaccharide belonging to the hemicelluloses) was detected. Even though Yelle [87] found no proof for a reaction of the HMR with the crude milled-wood lignin, in theory, abundant hydroxyl groups should be available for reaction. To visualize the reaction between HMR and the wood's polymers, possible interactions between HMR and lignin, as well as HMR and polysaccharides are depicted in Fig. 8 and Fig. 9, respectively.

Based on the information presented in this chapter related to the curing process of the original HMR and the n-HMR primers, the following can be summarized:

- i) The original HMR primer formulation consumes formaldehyde much faster than the n-HMR primer.
- ii) In the n-HMR's two-stage process, around 15% of the formaldehyde remains unreacted. This results in a lower degree of polymerization, compared to the HMR primer, where all formaldehyde is consumed during the curing.
- iii) It became apparent, that crosslinking of the primer is necessary for its positive effects on the bond performance, or the presence of reactive sides (methylol groups) that can couple with the wood's polymers.
- iv) It was shown that the HMR primer and the wood's polymers have the possibility to form bonds, during the primer's application window.

5. Functionality

This chapter will present how the understanding of the primer's

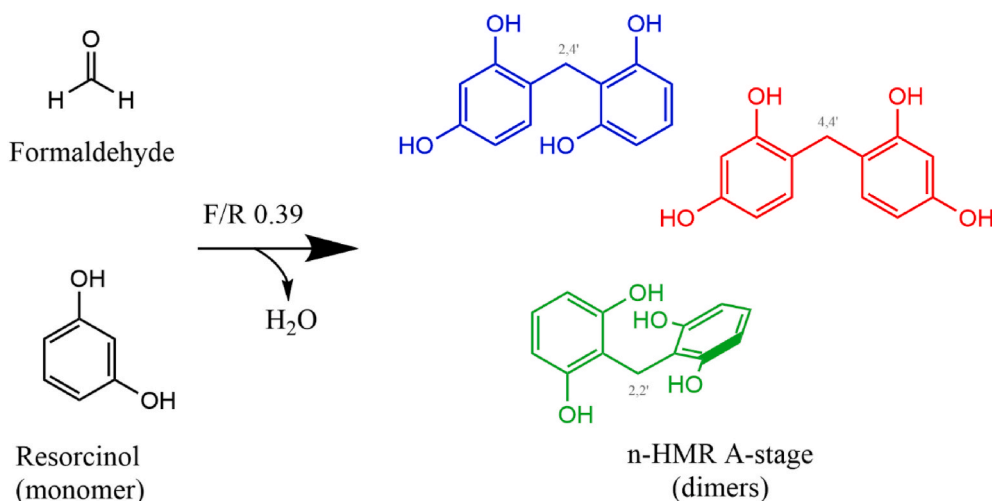


Fig. 6. Condensation process of the n-HMR primer's A-stage. Formation of methylene bridges (CH_2) primarily between two resorcinol molecules to form different oligomers (mainly dimers). Presented here are three different examples of dimers, where the 4,4' dimer is formed predominantly, followed by the less likely 2,4' dimer and the least likely 2,2' dimer.

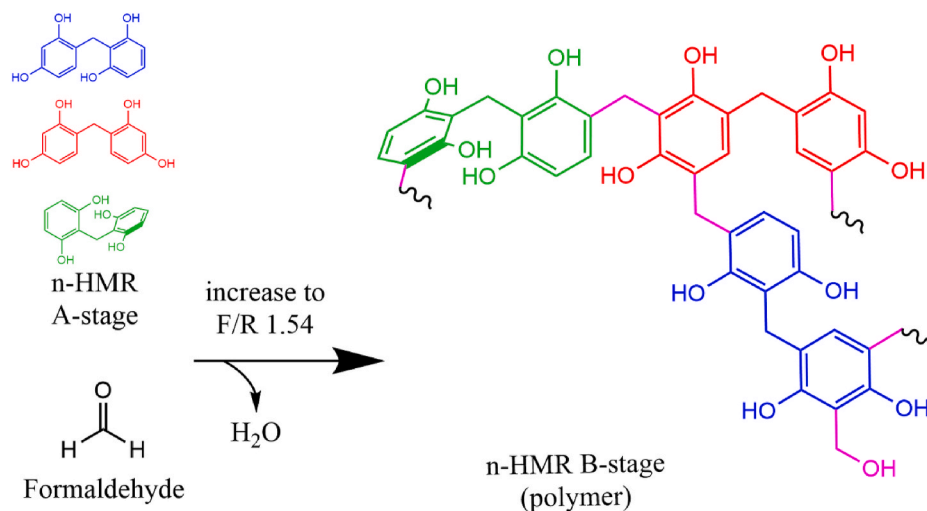


Fig. 7. Condensation process of the n-HMR primer's B-stage. Formation of new methylene bridges (CH₂) towards the extension of the degree of polymerization, branching and crosslinking as well as formation of new hydroxymethyl groups (pink). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

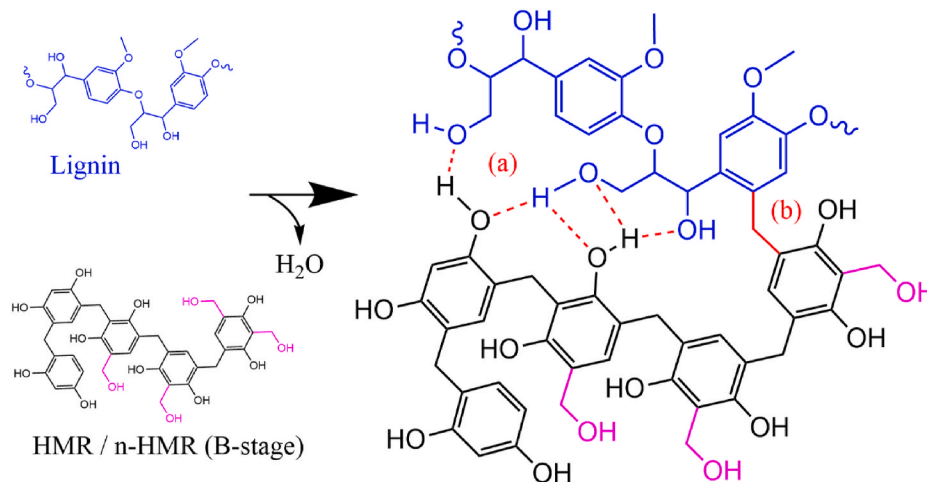


Fig. 8. Suggested interactions between the HMR and lignin, examples of (a) hydrogen bonds, (b) methylene bridges.

functionality changed over the years and discuss critically the current state of the art. When the HMR primer was first introduced in the 1990s, it was assumed that its positive effect came from the covalent and non-covalent bonds - i.e., van der Waals interactions, dipole-dipole interactions, hydrogen bonding, and π - π interactions [28] - formed by a coupling mechanism between wood and EP adhesives. Similar bonding enhancement was observed with 1C-PUR adhesives [60]. Szczurek et al. [88] have shown by ¹³C NMR measurements the formation of carbamate groups (urethanes) connecting the HMR primer and the isocyanates from the 1C-PUR adhesive. By linking their results to Pizzi et al. [89], it was deduced by Szczurek et al. [88] that the 1C-PUR forms carbamate groups with either the hydroxymethyl or the aromatic hydroxyl groups of the resorcinol ring, the latter being less reactive than the former due to its low nucleophilicity. Examples of the described reaction of the HMR primer with 1C-PUR and EP adhesives are shown in Fig. 10. Due to its ability to connect to the wood's polymers and also the 1C-PUR and EP, up to now, the HMR primer is sometimes also referred to as a coupling agent. However, when comparing the available reaction sites for the 1C-PUR and EP adhesive at the dried HMR (Fig. 10) and the wood's polymers (Figs. 8 and 9), it can be noticed that both offer the same reactive sites (OH-groups). Therefore, even though a coupling by the HMR primer between 1C-PUR and EP appears possible, at the same time

it is not compulsively necessary.

In 2005, Gardner et al. [90], as well as Christiansen [80], questioned that the previously described coupling effects are primarily responsible for the positive effects of the HMR primer. Gardner et al. [90] concluded based on adhesion theory and observed changes in mechanical and physical properties of HMR-primed wood, that those changed properties in this interphase play a major role in the positive effects of HMR treatment, rather than a coupling effect. Gardner et al. [90] refer to results from different studies, which are included later in this chapter.

Christiansen [80] conducted experiments aiming to show that the primary positive effect of the HMR primer does not originate from a coupling. After applying the n-HMR primer to boards of loblolly pine (*Pinus taeda* L.), Christiansen et al. [91] stored those boards for 1, 2, 4, 8 and 16 days before applying EP adhesive. The 5% delamination limit of ASTM D2559 - 97a [81] was fulfilled regardless of the time between primer and adhesive application. Based on this, Christiansen [80] examined further drying times and temperatures of n-HMR-treated Southern yellow pine (*Pinus* spp.) before bonding it with EP adhesive. The treated wood was stored for 12 h at room temperature (RT), three months at RT, four days at 50 °C, and 12 h at 70 °C. After bonding all storage variants resulted in comparable delamination values below 5%, Christiansen [80] suggests that the initially available hydroxymethyl

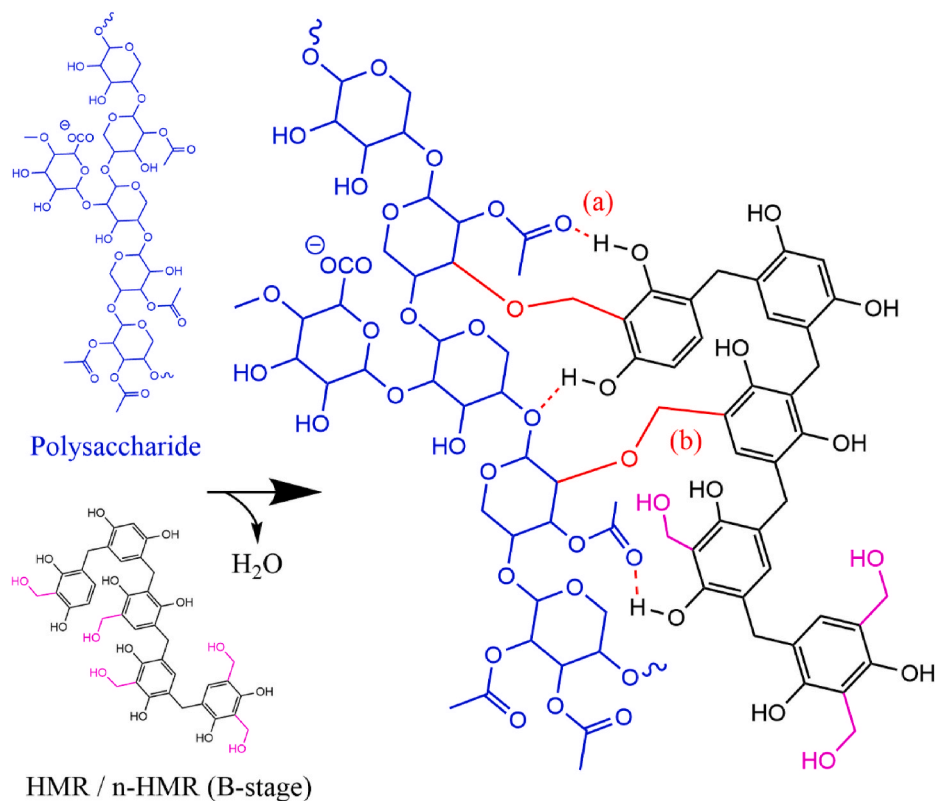


Fig. 9. Suggested interactions between HMR and polysaccharides (hemicelluloses and surface/amorphous cellulose) on the example of hardwood's xylan, showing (a) hydrogen bonds, and (b) methylene bridges.

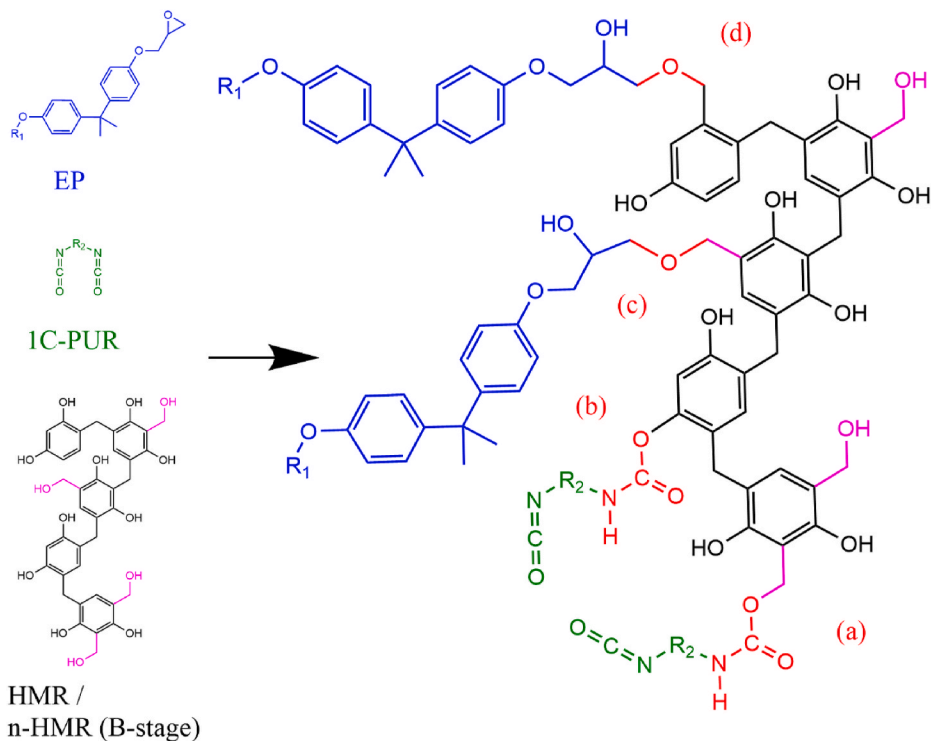


Fig. 10. Reaction between the HMR/n-HMR (B-stage) primer and 1C-PUR adhesives (a) carbamate linkage formed when reacting with a hydroxymethyl group, (b) carbamate linkage formed when reacting with an aromatic hydroxyl group at the resorcinol moiety - and an EP adhesives - (c) ether link formed when reacting with a hydroxymethyl group, (d) carbamate linkage formed when reacting with an aromatic hydroxyl group at the resorcinol moiety.

groups would have been consumed and not be available for further reaction. Another conjecture could be that the HMR treatment prevented the migration of extractives to the surface, which are described to be one of the major causes of difficulties to bond aged wood surfaces [92]. However, if the OH-groups would have been unavailable, it can also be assumed that this would have had a negative impact on the adhesive's adhesion to the RF-/wood-surface. Therefore, the delamination rate should have increased, instead of remaining at comparable levels. Due to the absence of convincing counter experiments, unfortunately, only speculations are possible for the reason why no changes in the delamination results were observed.

In addition to the experiments, Christiansen [80] introduced a theoretical approach to why HMR would not couple with EP. Therefore, Christiansen [80] pointed to Streitwieser et al. [93] that EP usually forms ether bridges under acidic conditions, but HMR is slightly alkaline and, according to Bolger [94] (p.70), EP would not react with alcohols at room temperature. Both statements would contradict the assumption that EP adhesives can react with the alcohols (OH-groups) of the HMR primer. However, those statements appear to be made in different contexts and, therefore, not transferable to the given situation. Streitwieser et al. [93] refer to commercial EP adhesives preferentially using an acidic catalyst for the ring-opening (curing) mechanism where an acidic milieu is created by mixing the adhesive's two components. The statement of Bolger [94] is made in the context of modifications of heat curing PUR adhesives with epoxy-groups, without presenting evidence for it. Contradictory to that, the (generalized) statement of Bolger [94], in the bonding of metals, it is the state of the art to use room temperature for curing two-component EP adhesives, which are known to react with the OH-groups of the substrate's surface [95]. Therefore, it can still be considered, that EP adhesives are capable of reacting with the available OH-groups on the surface of the HMR-treated wood. Moreover, the considerations by Christiansen [80] did not address the adhesion between 1C-PUR and HMR-treated wood described by Szczurek et al. [88]. Gardner et al. [90] allow us to conclude that other mechanisms are likely to contribute more to the HMR primer's positive effects than a coupling effect.

To gain information on how the HMR treatment influences the interaction with liquids, different authors conducted contact angle (Θ) measurements and calculated the surface energy (γ). A material's γ is often seen as the first indicator of a material's bondability. For a cured PRF adhesive - which is chemically similar to the cured HMR - γ is according to Kinloch [96] 52 mJ/m². This is in the same range as a fresh wood surface (40–55 mJ/m²) [97] and clearly above the often considered minimum for bondability of 28 mJ/m². On HMR-treated and untreated Southern pine, the Θ -value was measured with water as a test liquid by Sernek et al. [98], as well as Gardner et al. [99]. Even though different test methods were used in both studies, Θ reduced by the HMR treatment. Gardner et al. [99] also observed a reduction of Θ on Douglas fir, when measured with water. On the other hand, Lu et al. [51] observed an increase of Θ measured with water as a test liquid on Eucalyptus. Since it is known that Θ measured with water and adhesives do not necessarily behave comparably, Sernek et al. [98], as well as Gardner et al. [99], used PF adhesives as a test liquid on HMR-treated and untreated Southern pine and Douglas fir. Both studies observed a slight increase in the Θ -values compared to untreated wood. Also for pMDI adhesive as a test liquid, Gardner et al. [99] reported a slight increase of Θ by HMR treatment. Schirle et al. [52] measured Θ with 1C-PUR adhesives on differently prepared surfaces of Douglas fir, spruce and larch wood. No differences between untreated and HMR-treated wood could be observed. A possible explanation for not observing any differences might be found in the high viscosity of 1C-PUR adhesives – above 5'000 mPa s -, which hindered flow on the wood. Due to the limited studies and information available, the only conclusion that can be drawn with certainty is that, based on the observation of changed Θ , the HMR treatment changes the wood's surface energetic state.

In addition to the already mentioned measurements, Gardner et al.

[99] determined Θ on Southern pine and Douglas fir with methylene iodide, ethylene glycol and formamide. These experiments allowed calculation of the γ -value together with its dispersive (γ_d) and polar (γ_p) components. For untreated and HMR-treated samples, the γ -values changed from 51 mJ/m² (γ_d : 44, γ_p : 7) to 44 mJ/m² (γ_d : 33, γ_p : 11), and from 50 mJ/m² (γ_d : 38, γ_p : 12) to 44 mJ/m² (γ_d : 31, γ_p : 19), respectively. The increase of γ_p on the HMR-treated wood supports a possible increase of hydroxymethyl groups on the wood surface which might ease the formation of secondary interactions and the formation of covalent bonds during the curing of the adhesives. The findings of Gardner et al. [99] were later linked to X-ray photoelectron spectroscopy (XPS) results on hard maple veneers by Tze et al. [100]. The spectroscopic experiments showed an increase in the C/O-ratio from 0.44 to 0.53 after the HMR-treatment. The C₁-peak associated with C–C and C–H bonds increased from 0.57 to 0.69 after HMR-treatment, while respectively the C₂-peak associated with C–O bonds decreased from 0.33 to 0.23. For the C₃-peak associated with C=O and O–C–O bonds, the HMR-treatment decreased the population of such bonds slightly from 0.10 to 0.08. Tze et al. [100] stated that the increase of non-oxidized carbons on the wood surface could explain the increased Θ of apolar liquids. The results for the HMR-treated wood align to pure RF polymer (C/O-ratio 0.56, C₁ 0.73, C₂ 0.18, C₃ 0.10).

The results of the XPS measurements indicate the existence of an RF layer on the wood's surface. Since the HMR primer will penetrate the subsurface of the wood through the interconnected cells, it can be assumed that such a surface does not only form on the wood's surface, but also on levels inside the wood, e.g., on the interface of the cell wall and lumen. How could such an RF layer on the wood's subsurface be involved in the primer's positive effects on bonding? One assumption is by changing the flow of adhesive, e.g., when pressing the two wood substrates together during the bonding process, or water.

Due to the high water content (approx. 95%) and very low viscosity, the HMR primer has an efficient penetration. According to Gardner et al. [90], a sufficient amount of HMR molecules with a molecular weight below 1'000 Da were present during the application window from 4 to 8 h, which could penetrate the cell walls of the wood. The source for the threshold of 1'000 Da is not apparent, but assumable from Sellers [101] who referred to Tarkow et al. [102] and Stamm [103,104]. Our own simulation on the molar mass (compare electronic [supplementary Figure ES-1](#)) confirms the presence of molecules below 1'000 Da during the primer's window of effectiveness. Even though the argumentation for cell wall penetration appears conclusive, we want to discuss it critically to allow for a wider understanding. As mentioned above, a time window of 4–8 h after the HMR's preparation is required for the HMR's positive effects. On the other hand, the B-stage of the n-HMR can be used immediately after adding the second portion of formaldehyde. This indicates that the RF molecules require a certain degree of polymerization - the size of the polymer -, for their positive effect. On the other hand, with progressing polymerization the reactivity of the HMR primer, including its ability to react with the wood's polymers, reduces. If the penetration into the wood cell walls would be exclusively the only important factor, the positive effect of the HMR primer would appear directly after its application. But the waiting time of 4 h with the HMR and the formation of oligomers during the A-stage of the n-HMR shows, that a certain molecular size is required. Tarkow et al. [102] and Stamm [103,104] observed the ability of poly(ethylene glycol) (PEG) - a non-reactive substance - of different molecular size to prevent the swelling of the cells walls. Wood cells treated with PEGs with a molar mass below 1'000 Da [104] or 3'000 Da [102] did not absorb water. On the other hand, PEGs with higher molecular size did not prevent the absorption of water. Therefore, it was interpreted that the penetration limit or cut-off of the cell wall is at 1'000 Da or 3'000 Da. However, the HMR primer is a reactive mixture of chemicals carried in water (approx. 95%) with also a very different molecular geometry. Due to the different properties of PEG and HMR, it appears rather difficult to transfer this threshold from one substance to the other. However, experimental data

still indicates cell wall penetration of the HMR molecules, e.g., by a modified stress relaxation [82] or changes in T_g [105], which will be discussed later in detail. Still, the experiments of Tarkow et al. [102] and Stamm [103,104] have shown that by swelling cell walls with PEG, further swelling by water can be prevented. The observation that small, non-reactive PEG molecules prevent the cell wall swelling allows some questions about the HMR: Why do the HMR molecules require a waiting time – bigger molecular size – for the positive effect? Is it possible that not a small molecule but a bigger still reactive one is more favorable? Is a mixture of different size molecules (polydisperse distribution) favorable? Would adding less formaldehyde prevent the molecules exceeding the favorable size? For this question, it is worth recalling Carother's equation, which says that already small variations out of the stoichiometry lead to a strong reduction of the final degree of polymerization. If the molecular size is the important factor, regardless of reactivity, why is adding more reactive formaldehyde to the A-stage of the n-HMR necessary? Assumedly, the dimmers could act as a plasticizer in the wood, but no crosslinking is possible. When studying the application window of n-HMR (compare Fig. 3), the tests stopped 7 h after adding the formaldehyde to the A-stage. However, after 7 h a big improvement to the untreated specimens was still present. What happens after this 7 h, does the positive effect of the n-HMR remain? The simulated molar mass in supplementary Figure ES-1 indicates that the n-HMR's molar mass would increase exponentially until reaching its gel point after approximately 12.4 h. This allows the assumption that the n-HMR primer loses its effectiveness between the experimentally proven 7 h and the simulated gel time at ca. 12.4 h.

What generally can be assumed is, that when the HMR's small molecules - together with the water molecules - intend to diffuse into the wood cell walls, two scenarios are plausible for the still reactive RF molecules: i) they diffuse together with the water molecules and have the possibility to react with the available reactive groups in the cell wall, and/or ii) they accumulate on the interface of the cell wall and the lumen.

Follrich et al. [58] tried to identify remains of HMR inside and outside of the cell wall on HMR-treated spruce (*Picea abies* Karst.) by UV spectroscopy. However, no resorcinol was detected within the observed 1 μm thick microsection. They suspected the reason was the low concentration of resorcinol, which could not be detected with the applied method. Another possible explanation for not observing the presence of resorcinol, especially in the form of cured RF polymer, could be the brittleness of RF polymers, therefore, it might have splintered off during the preparation of the microsections.

Sun et al. [82] compared stress relaxation at different temperatures (25 °C, 65 °C & 115 °C) in a single cantilever bending setup at 0.03% static strain. Therefore, yellow poplar (*Liriodendron tulipifera*) specimens ($40 \times 10 \times 4 \text{ mm}^3$) were systematically relaxed and later compared with and without HMR treatment or a treatment with a solution of phenol in water. The solution of phenol can penetrate easily into the cell walls, but compared to HMR no crosslinking can be expected due to its non-reactivity. Fig. 11 shows, based on data extracted from Fig. 2 of Sun et al. [82], the normalized stress relaxation curves of HMR-treated wood and the control measurement at 25 °C. To optimize the fitting to the extracted data in Fig. 11, a double stretched exponential function (Eq. (1), $n = 2$) - the Maxwell-Wiechert stress relaxation model -, was used instead of a single stretched exponential function (Eq. (1), $n = 1$) as the one used in Sun et al. [82].

$$\frac{\sigma(t)}{\sigma_0} = \frac{\sigma_\infty}{\sigma_0} + \sum_{i=1}^n \frac{\sigma_i}{\sigma_0} e^{-\left(\frac{t-t_0}{\tau_i}\right)^{\beta_i}} \quad (\text{Eq. 1})$$

This double exponential decay function was implemented based on the idea of having different relaxation processes for a viscoelastic semicrystalline material with at least two different polydisperse distributions of amorphous components, i.e., hemicelluloses and lignin, which have different mechanical behavior. The results obtained show the same

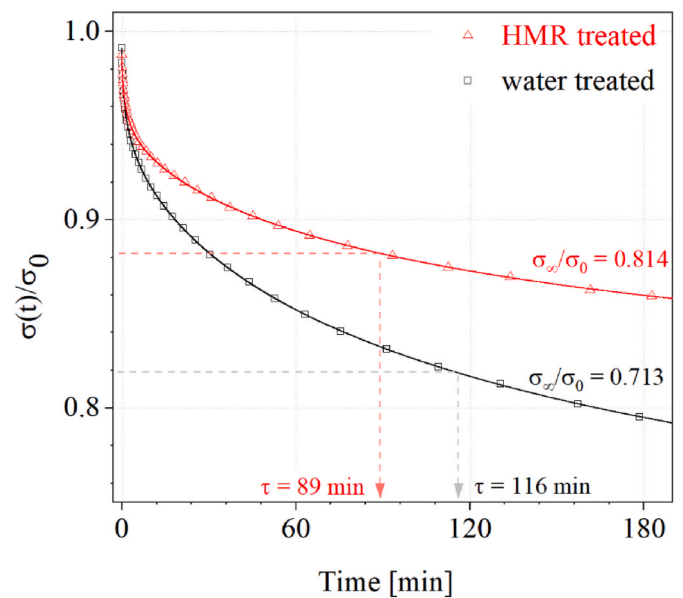


Fig. 11. Stress relaxation behavior of HMR-treated and water-treated yellow poplar at 25 °C when exposed to 0.03% static strain. Data extracted from Ref. [82] and fitted using a double stretched exponential decay function to calculate the characteristic relaxation time (τ) of each sample, as well as the asymptotic stress value $\sigma(t)/\sigma_\infty$. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

tendency as can be observed from the characteristic relaxation time (τ): 89 min and 116 min for the HMR- and the water-treated wood, respectively. These results indicate that the HMR molecules either reduce the viscosity or increase the elastic modulus of the wood biopolymers that they interact with ($\tau = \eta/E$). Therefore, the HMR-treatment clearly modifies the mechanical properties of wood. Sun et al. [82] assume a chemical interaction of the HMR within the cell wall, rather than a simple bulking of the HMR. While Sun et al. [82] exclusively present relative data points, further interpretations of the results, in particular, the stresses caused by the 0.03% strain, are not possible. Therefore, while Sun et al. [82] describe that “HMR treatment significantly stiffens the wood against stress relaxation” the authors of this review see the need for additional research to confirm or revise this statement based on absolute values.

Son et al. [105] used dynamic mechanical analysis (DMTA) and DSC to assess the influence of different HMR-treatment intensities and drying times. Therefore, small maple (*Acer saccharum*) specimens ($0.6 \times 6 \times 34 \text{ mm}^3$) were, first, oven-dried before being soaked for 1, 15 or 30 min in water or the original HMR primer, and then dried for 1, 12 or 24 h. The DMTA experiments were performed using three-point bending (0.01% dynamic strain at 1 Hz) between -40 and 150 °C at a heat ramp of 5 K/min. The storage modulus (G') after HMR treatment increased when compared to the corresponding counterparts with water treatment, but also a significantly lower MC. This makes it difficult to assess if the increased G' is a result of the presence of the HMR components or due to a lower MC. However, it raises the interesting question, does the HMR treatment influence the dynamics to incorporate and emit water while establishing the equilibrium MC (EMC)? After using a mathematical model to compare all results at 12% MC, Son et al. [105] consolidate that no significant differences appear to be present. Independent from their DMTA measurements, Son et al. [105] observed a lowered glass transition temperature (T_g) of the lignin from the HMR treatment by means of DSC. They deduced that a softening of the material, which was assumed to be caused by a plasticization effect of the HMR molecules in the lignin domains with the corresponding shift of glass transition towards lower temperatures. Chowdhury [106] discussed these results critically, referring to Back et al. [107], that the T_g of

lignin should be significantly higher, and suspects that the observed phenomena would not be caused by a change in the lignin's T_g . However, it is important to note, that Son et al. [105] conducted their DSC measurements not on kiln-dried specimens but at an MC of 4–5%. Different studies show a strong reduction of T_g by the specimens MC already at small changes [108–110]. Therefore it appears that the concerns of Chowdhury [106] can be refuted.

Moon et al. [111] investigated the modulus of elasticity (MoE) as well as the dimensional stability and EMC, on early wood and late wood of loblolly pine (*Pinus taeda* L.) once before and after treating it with n-HMR or a control treatment, respectively. Small specimens ($30 \times 1.1 \times 1.1 \text{ mm}^3$) were first dried for reference measurement and then conditioned at $24^\circ\text{C}/65\% \text{ RH}$ and $27^\circ\text{C}/90\% \text{ RH}$. At those climates, the weight was measured and the dimension at the specimen's center was measured by caliper (scale interval 0.01 mm). Following, the elastic modulus in three-point bending was determined by step measurements of 0.1 N from 0 to 0.6 N, where each step was followed by 10 s pauses for relaxation. For the EMC and MoE, Moon et al. [111] observed no significant differences between untreated and HMR-treated wood. Moon et al. [111] discuss critically their experimental approach for the measurements of dimensional stability and recognize that the chosen approach made it difficult to identify differences caused by the HMR treatment.

Swelling experiments on veneer samples ($34 \times 6 \times 0.6 \text{ mm}^3$) of maple (*Acer saccharum*) with and without HMR primer were performed by Son et al. [112]. Before and after being soaked in water for 24 h, the samples' perimeter was determined by the Wilhelmy plate method in octane as well as complementary by caliper. HMR treatment showed with the Wilhelmy plate method indicated a reduced swelling from 7.8 to 1.6%, as well as similar results by caliper measurements. Additionally, the water uptake after soaking the samples for 30 min in water was determined, showing that untreated wood incorporated approximately three times the amount of water than HMR-treated wood.

So far, when discussing the influence of the HMR primer on the swelling of wood it is noted how HMR-treated wood behaves when exposed to water. However, it was not yet addressed how the HMR-treatment itself causes swelling. Specific questions raised here: i) How much does treatment with HMR swell the wood compared to pure water as a swelling medium? ii) How reversible is the swelling process of HMR-treated wood when returning to an EMC? iii) How does such a pre-swelling contribute to the positive effects of the HMR-treatment before causing swelling by the adhesive application and/or testing procedure?

In this section, the state of the art about the functionality of the HMR primer was presented:

- i) During the curing process of HMR, an RF polymer layer is created on the surface of the wood, altering the surface properties.
 - a. On the cured RF polymer layer, thermoset adhesives, e.g., EP or 1C-PUR adhesives, can establish covalent and non-covalent bonds. Even though by definition, the created RF polymer layer is able to couple wood and the adhesive, it is still questionable whether it is necessary and, therefore, a major functionality of the primer.
 - b. Wettability and surface tension of the surface layer, which later will be brought in contact with the liquid adhesive, is modified.
- ii) It is likely that the HMR primer penetrates into cell walls and initiates swelling while still reactive and is able to react with the wood's polymers.
- iii) The HMR-treatment increased the relaxation behavior of the treated wood. However, no clear change in the MoE was observed.
- iv) A softening of the wood's lignin is indicated due to the plasticizer behavior of RF molecules with the lignin domains.

- v) The swelling (dimensional change) from absorbing liquid water by HMR-treated wood is strongly reduced. For exposure to different MCs, no reliable data is available.
- vi) The EMC of wood appears not or only a little affected by the HMR treatment. However, at the same time, the soaking by liquid water seems to be retarded and/or reduced.

6. Model of functionality

The previous chapters have described the effectiveness and the application of the HMR primer together with further insight into the mechanisms during the curing process and the primer's functionality. In Fig. 12, the findings from the previous chapters are visualized and merged into a comprehensive model, which will be described in the following paragraphs.

- (a) The first step for the HMR treatment consists of applying the aqueous HMR solution to the wood's surface. Commonly, a spread rate of 150 g/m^2 is applied, which is equivalent to a 0.15 mm water column on the wood's surface.
- (b) The main amount of the HMR primer enters the wood structures, while only water and volatile formaldehyde-based compounds can evaporate into the surrounding air. This is not possible for the resorcinol and resorcinol derivatives due to their low vapor pressure.
- (c) When penetrating the wood, water causes swelling of the wood cell walls. It is already known that compared to pure water, alkaline aqueous solutions increase the swelling of wood, which also applies to the HMR (pH-value: 8.5 to 9.0). While small reactive components can penetrate the cell walls, bigger molecules formed during the curing process of the HMR primer remain on the outer surface or are deposited on the interface of lumen and cell walls in the subsurface layer.
- (d) After reaching advanced reaction progress between the HMR molecules with themselves or the lignocellulosic wood's polymers, and the wood has dried back to its EMC, several modifications of the wood can be presumed:
 - ① Molecules with a high molar mass do not penetrate the cell walls, but form by intermolecular reaction a thin RF polymer layer connected to the wood's surface. This highly crosslinked and hydrophobic RF polymer layer could influence the flow of liquids, e.g., the liquid adhesive (potentially leading to deeper penetration), as well as water and speculatively also extractives.
 - ② In the interphase wood layer (see ④ in Fig. 12), HMR molecules with a high molar mass are deposited in the interface between the lumen and cell wall where it can form a thin RF polymer layer similar to the one described in the previous point. It also can be supposed that this polymer layer influences the liquid transport processes.
 - ③ HMR molecules with a medium-to-low molar mass penetrate the cell wall where they react and crosslink with the wood's polymers. Assumedly, due to the hydrophobicity of the RF polymers and the consumption of water-binding sites in the cell wall regions near the lumen, i.e., hydroxyl groups, further moisture diffusion and swelling of those cell walls is reduced.
 - ④ As a result of the penetration and diffusion of the HMR molecules into the wood structure, a gradient of the reacted primer is present from the wood's surface and, therefore, all effects due to the presence of such reacted HMR molecules decrease along with the depth.
 - ⑤ Below the interphase affected by the HMR-treatment, the wood remains unaffected.

It becomes visible, that the HMR introduces several changes to the wood and, thereby, offers the possibility for a mixture of functionalities.

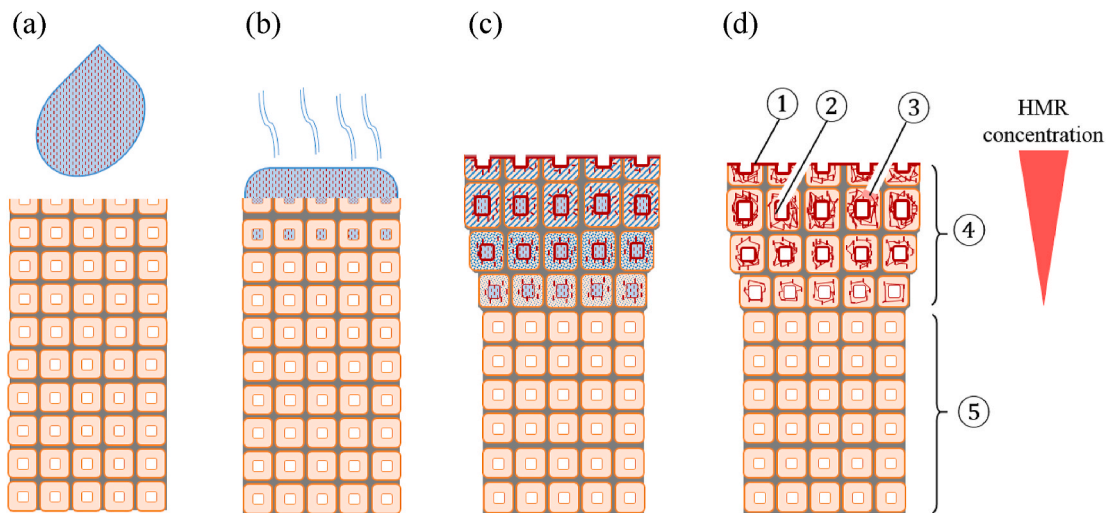


Fig. 12. Illustration of changes in the wood's first cell layers caused by HMR treatment. (a) HMR primer application, (b) wetting through the wood's surface and water evaporation, (c) cell wall diffusion and cell swelling, and (d) final state after the EMC is reestablished: ① HMR polymer layer on wood's surface, ② thin HMR layer on the lumen-cell wall interface, ③ RF-rich regions inside the cell wall, ④ HMR modified wood region, and ⑤ below the HMR boundary remains an unaltered wood region.

However, the described modifications of the wood do not yet include a bonding with a second adhered. In order to understand the HMR's functionality in bonded specimens, some theoretical considerations might be taken into account. The HMR's positive effects can be observed when conducting SS tests in dry and wet conditions where both, the SS and the WFP, improve. It can be speculated that the increasing SS is a result of the increased WFP. In delamination experiments, the positive effect of the HMR treatment becomes even more pronounced. The harsh MC changes introduce high internal stresses into the wood and, thereby, also deformations. The HMR treatment seems to relieve the bondline from those damaging effects.

How could the HMR treatment prevent failures in the bondline, or, in other words, how could it increase the WFP? The obvious answer is that the failure should occur in the wood instead of the bondline. Therefore, the HMR treatment seems to positively manipulate the formation of stress peaks in the bondline and the wood regions nearby (Fig. 13a). In the chain-link model, Marra [113] describes different areas in the region

of a wood-adhesive bond (Fig. 13b). It is pointed out that the 'adherent subsurface' (links 6 & 7) consists of the wood regions damaged by mechanical surface preparation and is one of the weakest links in the model. The HMR treatment is applied onto this weak wood region, affecting this region as well as the 'proper wood' region below.

It can be speculated that the HMR reduces the creation and/or the transfer of stresses in the wood-HMR interphase. In order to reduce the creation of moisture-induced stresses, one measure could be to prevent moisture changes from reaching the cell walls, e.g., by acting as a hydrophobic agent. Another measure could be to swell the cell walls during the HMR application, while it is not restrained by the adhesive, and blocking possible reaction sites with other molecules. This would cause a permanent 'pre-swelling' that later would prevent the creation of stresses by changing MCs, where the adhesive would hinder swelling and hence causing local stress peaks.

To reduce or retard the transfer of moisture-induced stresses to the bondline a plasticization (decreased MoE) of the wood-HMR interphase

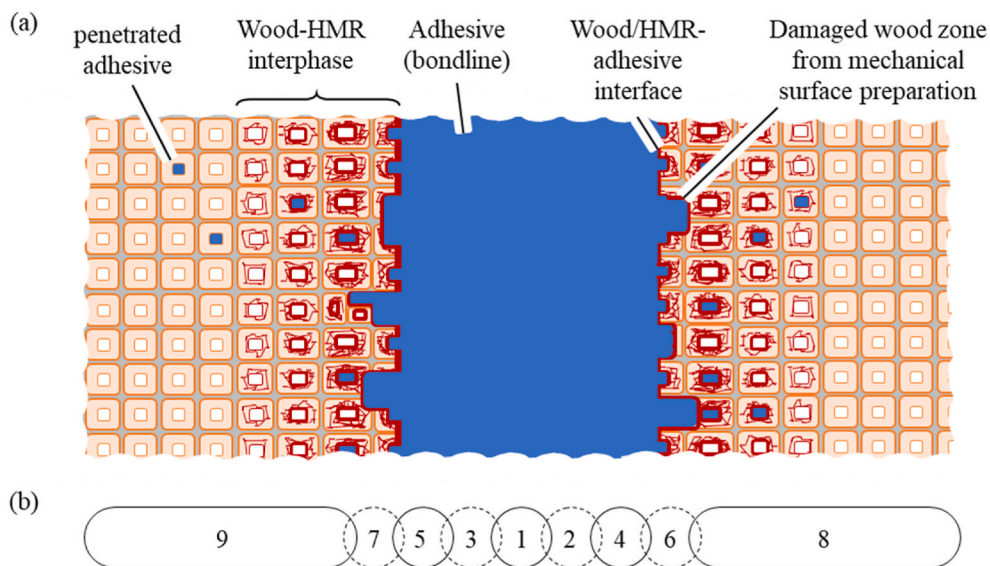


Fig. 13. (a) Visualisation of two HMR-treated wood surfaces bonded together. (b) The chain-link model from Marra [113]: (1) the adhesive film, (2) and (3) intraadhesive boundary layer, (4) and (5) adhesive-adherent interface, (6) and (7) adherend subsurface, (8) and (9) the adherend proper. Marra points out that the 'dashed links are most vulnerable to malformation'.

is a possible explanation. It can be speculated that a reduction of the MoE in the wood-HMR interphase could compensate moisture-induced stresses by deformation before transferring it towards the bondline. Moreover, for stresses-induced during SS-tests - in dry and wet stages -, a plasticization of the HMR-treated wood could ease local deformation and, thereby, reduce the creation of stress peaks in the bondline region.

On the other hand, it can be speculated that a stiffening (increased MoE) appears less likely to be the cause of the HMR's positive effects. While it could be argued for moisture-induced stresses that the 'adherent subsurface' would be reinforced and thereby a failure in that region prevented, this hypothesis seems to have difficulties explaining the improvements observed in the SS tests. If the HMR-treated wood would be stiffer, the deformation in the SS test, and thereby the likeliness to be the starting point of failure, would be reduced in the HMR-treated region. The logical consequence would be that the deformation increases elsewhere, namely in the bondline or the unaltered wood. However, the bondline and nearby parts of the wood are already the regions deforming the most in SS experiments. Here, those stresses would be transformed into additional deformation especially with viscoelastic adhesives such as EP and 1C-PUR. It was shown by Serrano et al. [114], using digital image correlation (DIC), that the highest deformation with EP and 1C-PUR adhesives occurs in the bondline and are higher compared to the bondline of a rather stiff PRF adhesive. The DIC measurements also revealed local deformation peaks for EP and 1C-PUR adhesives in the bondline and one adherent, however, the peak was not transferred to the other adherent. Therefore, it could be expected that more stress would be added to the unaltered wood below the HMR-treated surface and to the bondline due to increased stiffness of the HMR-treated wood. Hence, an increased MoE would lead to an earlier failure in the bondline and therefore a reduced WFP or delamination, respectively.

However, while one study observed a reduction in the T_g of lignin in HMR-treated wood, which would indicate a plasticization, other studies observed no significant change in the MoE. Therefore, the critical question on how the HMR-treatment influences the stress transfer in the bondline region cannot be answered with certainty and requires further investigation.

7. Conclusions

When comparing the bonding quality in standardized testing with and without the application of HMR primer, the effectiveness of the primer is given with different combinations of wood species and adhesive types.

Nevertheless, even though indications about the possible involved mechanisms exist, it is safe to say that up to now, a clear understanding of the HMR's mechanisms has not yet been accomplished. Important questions on the functionality cannot be answered with certainty, due to the lack of information as well as complementary or seemingly contradictory findings. Also, it became clear that the HMR treatment creates several modifications of the wood in parallel, allowing more than one function to be responsible for the positive effects of the HMR primer.

Referring to the three leading questions of this review, a clear answer on the mechanisms leading to the improved bond performance by the HMR treatment is currently not yet possible. Therefore, with the current state of knowledge, it is not feasible to point to one prime mechanism in particular and to propose research efforts to include this mechanism in an adhesive formulation.

Based on the presented review and discussion, and the hypotheses involved in the proposed model of functionality, we identify the following research questions.

Where does the HMR remain in the wood? It is not known how deep the HMR primer penetrates the wood tissue and therefore how thick the modified wood region is. Moreover, the quantity distribution over the wood's cross-section is unknown. While it is broadly assumed that the HMR penetrates the wood tissue, it is not yet shown how deep it

penetrates into the individual wood cells and the middle lamella, or if some of the HMR remains in the interface between the cell wall and the lumen. Moreover, the quantity of HMR on the wood's surface remains unknown. To answer those open points, different methods combining microscopy with spectroscopy could be applied. It appears possible to chemically attach a marker to the HMR-molecules, which would ease the identification of the primer's location.

How does the HMR treatment modify the hygroscopic behavior of wood, as well as the interactions with water, extractives and adhesives?

The determination of water vapor sorption would give information on how the HMR influences the EMC. Transmission properties will help to understand if water/moisture and extractives are transported differently through HMR-primed wood. Also, measurements on how the HMR causes a 'pre-swelling' when applied onto wood and if those are reversible would answer whether the HMR treatment reduces the creation of stresses.

How does the HMR primer influence stress formation and stress transfer near the bondline? This can be inspected by digital image correlation (DIC) experiments, where stresses can be implemented by changing MCs or by applying (quasi) static loads, on HMR-treated bulk wood, as well as on bonded specimens.

How does HMR interact with the wood's polymers on a chemical level? Performing nanoindentation atomic force microscopy (AFM) experiments coupled with Raman spectroscopy would allow for answering which chemical reaction/composition, e.g., crosslinking with short or long molecules, is responsible for a certain mechanical response.

How do bonds with HMR-treated wood perform under dynamic loads? Therefore, dynamic test setups, e.g., DMTA for small specimens or dynamic universal test machine for bigger specimens, can be used at defined MCs. During fatigue experiments, e.g., Wöhler curves, on bulk wood and bonded specimens, the durability of HMR-treated and untreated wood can be compared. Results would reveal if the durability changes by the HMR-treatment or the mode of failure, i.e., adhesion, cohesion or wood failure.

Declaration of competing interest

The reported research is financed by the Bavarian State Institute of Forestry (Germany). No conflict of interest exists.

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Appendix A. Supplementary data

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