CAN MELAMINE-BASED WOOD PRIMERS HELP IN UNDERSTANDING BONDED WOOD DURABILITY?

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Introduction

Although wood has been bonded for thousands of years, truly durable bonds for exterior conditions have existed for only about 50 years. Despite the large volume of adhesives used in this market for production of laminated lumber and composites, factors that lead to durable bonds are still being explored. Understanding the factors that determine good versus poor bonds is not easy because of the chemical and structural complexities of wood. Heterogeneity abounds, from the macro-scale growth rings and cellular construction to the nano-scale domains of the three constituent polymers. Given the reduction in availability of large-diameter trees, the amount of laminated and composite wood products is increasing. Improved understanding of factors that lead to durable wood bonds is critical for making more cost-effective products.

Use of wood products in structural applications required more highly cross-linked adhesives to provide the necessary creep resistance. However, this results in the adhesive's inability to change dimensionally as the wood swells and shrinks in response to changes in moisture content. This differential expansion can lead to high stress gradients at the adhesive–wood interface. This interface is not as clearly defined for wood bonds as it is for bonds with most other materials because of the porosity of wood. Wood has the obvious porosity of lumens, but it also has the ability to absorb lower molecular weight chemicals into the cell wall structure.

Our prior research led to the hypothesis that adhesive failure can occur if the adhesive cannot withstand the stress as wood swells [1]. This concept is supported in the literature [2] and by more recent studies on how the hydroxyl-methyl resorcinol (HMR) primer functions [3]. The HMR primer has been found to be very effective in improving the exterior durability of many wood bonds [4]. Studies have provided much information on the interaction of the HMR primer with wood [5], but the chemical similarity of HMR to wood lignin components has limited these studies.

Melamine–formaldehyde adhesives form wood bonds with exterior durability, and the melamine is more easily studied because of its significant nitrogen content (compared with the lack of nitrogen in wood components). In addition, some melamine–formaldehyde chemicals reduce wood swelling [6], enter into wood cell walls [7], and strengthen them [8]. This information led to investigation on the use of melamine-based primers for improving the durability of epoxy-bonded wood.

Epoxies bond well to wood, providing good shear strength and high wood failures under dry conditions. However, under wet conditions, wood failure often drops to zero, with some reduction in shear strength. This limits the ability to use epoxies for wood bonding.

Epoxies are used where the substrates cannot be brought into close contact or clamping pressures are light; they are also used to repair delaminated or decayed wood beams. The lack of durability led to the development of the HMR primer [4]. In evaluating whether melamine-based primers can be used in the same manner as the HMR primer, the key piece of data is a high percentage wood failure after water soak using a standard wood bonding epoxy adhesive.

Experimental

A melamine adhesive (MF adhesive) was provided by Dynea Corporation (Springfield, Oregon), and hexamethylol melamine methyl ether (MME) was obtained from Structure Probe (Chester, Pennsylvania). A melamine–urea–formaldehyde (MUF) primer was prepared by reacting melamine (1.30 moles) with formaldehyde (2.95 moles) at pH 9 at 85–90ºC in water, then adjusting the pH to 9.6, followed by cooling to 35ºC and adding urea (0.18 moles).

The effects of the melamine-based primers were evaluated using compressive lap shear method ASTM D 905-99. Yellow-poplar (*Liriodendron tulipifera*) sapwood was cut into strips (6.4 mm thick, 31.8 mm wide, and 22.9 cm long). Some were not primed, and some were primed with MF adhesive, MUF primer, or MME. Primed samples were treated with a primer solution–catalyst matrix, using the typical spread rate of 0.15 kg/m^2 on each surface to be bonded, and allowed to dry one week. All were then bonded with an epoxy adhesive FPL 1-A [9] using a spread rate of 0.34 kg/m^2 per bondline; the assembled pieces were bonded overnight under light pressure and allowed to cure for at least 48 h prior to any testing. Block shear specimens with a 25.4- by 25.4-mm overlap area were cut from the bonded assemblies and randomly assigned for wet or dry shear test. The dry tests were performed as is, whereas the wet test was done after the blocks were placed underwater and treated for 30 min under vacuum at 635 mmHg, followed by 30 min of pressure ranging between 379 and 448 kPa. After shear testing, percentage wood failure was determined using ASTM D 5266-99.

Results and Discussion

Initial work was done using a commercial MF adhesive, which was diluted with deionized water to different concentrations, mixed with a *p*-phenol sulfonic acid–morpholine catalyst (1% and 10% wt.), and applied to each surface of the wood. After 1 week, the wood was bonded with the epoxy resin. For adhesive purposes, more concentrated solutions are needed to prevent starvation of the bondline due to overpenetration into the wood, but for priming purposes, high penetration is desired and is more likely with a dilute solution. As expected, the data in Table 1 show that more dilute solutions of the catalyzed MF adhesive gave improved wood failure. Interestingly, high concentrations gave low wood failure even under dry conditions, probably due to lack of adhesion to a surface coated with the MF adhesive. The 55% solids gave a thick coating on the wood that eliminated the surface roughness generally available for wood bonding.

Although the dilute MF adhesive showed some promise, the results were not equal to those that could be obtained with an HMR primer [4]. An important difference is that the HMR needs to be applied at low molecular weight in order to be a useful primer, while adhesives usually are of higher molecular weight to avoid overpenetration and to give a faster cure. Thus, the next stage was to make a MUF primer of low molecular weight by keeping the reaction time short. This primer of 47% solids was diluted to meet the desired percentage solids content and then mixed with a *p*-phenol sulfonic acid–morpholine catalyst prior to application. This catalyzed MUF primer again showed higher percentage wood failure under wet and dry conditions at the lowest primer levels, as shown in Table 2.

Having had some success using the catalyzed melamine–urea–formaldehyde primer, it seemed appropriate to try the catalyzed hexamethylol melamine methyl ether because other researchers had found an increase in bulk Brinell hardness and a decrease in swelling for MME-treated European beech sapwood [6]. MME is a monomeric blocked melamine–formaldehyde that has been used to cross-link hydroxyl-containing polymers. MME is catalyzed using *p*-toluene sulfonic acid catalyst. After priming each wood surface at 0.15 kg/m^2, the wood was heated for 48 h at 40°C and then 48 h at 60°C prior to bonding with the epoxy adhesive. This MME primer was very effective in improving the epoxy adhesion to wood after water soaking, as shown by data in Table 3.

Although these are preliminary experiments, the data from the various melamine-based primers showed consistent improvement in percentage wood failure using dilute primer solutions. The change in shear strengths was surprisingly small, considering the change in failure location under wet conditions from mostly along the bondline to mostly within the wood. This is consistent with prior data that showed the epoxy bonds were often strong under wet conditions but with much of the failure occurring within the bondline.

Table 1. Percentage wood failure after D 905 shear test for dry and wet samples using a catalyzed MF adhesive as a primer prior to epoxy bonding.

Percentage solids of MF adhesive	**Percentage wood failure**	
	Dry	**Wet**
55 (undiluted)	0	0
25	66	2
10	51	1
7	64	34
5	90	22
3	91	27

Table 2. Percentage wood failure after D 905 shear test for dry and wet samples using a catalyzed MUF primer.

Percentage solids of MUF primer	**Percentage wood failure**	
	Dry	**Wet**
(Unprimed)	85	3
5	99	15
4	92	6
3	100	93
2	98	100

Table 3. Percentage wood failure after D 905 shear test for dry and wet samples using a catalyzed MME primer.

Percentage solids of MME	**Percentage wood failure**	
	Dry	**Wet**
(Unprimed)	77	10
5	99	100
3	100	100
2	100	99

Conclusions

Epoxy-bonded wood has generally been shown to be surprisingly sensitive to wet conditions even though epoxies give durable bonds with many other substrates. This failure has been attributed to the inability of epoxies to adjust dimensionally to swelling of the wood under wet conditions [1]. Prior work conducted at the Forest Products Laboratory showed that priming the wood with low-molecular-weight hydroxymethyl resorcinol (HMR) prior to bonding with epoxies led to high wood failure even under wet conditions [4]. Originally this improvement was attributed to a coupling reaction of the primer between the wood and the epoxy, but more recently the model of reducing swelling at the wood surface has proven to more consistent with available data [5].

Although HMR primer has proven to be very effective in improving wood bonds under wet conditions, studying its role is hampered by the chemical similarity of HMR and lignin in wood. The durability of melamine–formaldehyde adhesives and other literature provided incentive to test whether melamine-based primers can provide the same performance as HMR primers. If so, then melamine primers, with their high nitrogen content, can allow the use of additional methods to study how these primers provide improved performance. This preliminary study showed that at least two melamine–formaldehyde compounds worked very well as primers to improve the durability of epoxy adhesive on yellow-poplar. These primers include a melamine–urea–formaldehyde resin and hexamethylol melamine methyl ether. Further studies should provide additional information about the mechanism of enhanced wood bond durability under wet conditions.

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