Journal of Applied Polymer Science

Solution-state NMR analysis of hydroxymethylated resorcinol cured in the presence of crude milled-wood lignin from *Acer saccharum*

Daniel J. Yelle
U.S. Forest Service, Forest Products Laboratory, Madison, Wisconsin 53726
Correspondence to: D. J. Yelle (E-mail: dyelle@fs.fed.us)

ABSTRACT: Resorcinol-formaldehyde adhesives can reinforce stress fractures that appear from wood surface preparation. Researchers have found that applying the resorcinol-formaldehyde prepolymer, hydroxymethylated resorcinol, to the surface of wood improves the bond strength of epoxy and polyurethane adhesives to wood. Hydroxymethylated resorcinol is thought to plasticize lignin components and stabilize stress fractures through reactions with lignin subunits and hemicelluloses in wood. In this study, a dilute solution of hydroxymethylated resorcinol (HMR) is cured in the presence of a crude milled-wood lignin (cMWL) from *Acer saccharum* and subsequently dissolved in dimethylsulfoxide-d_6 to delineate reactivity with lignin and *O*-acetyl-(4-*O*-methylglucurono)xylan using solution-state NMR spectroscopy. ^{1}H–^{13}C single-bond correlation NMR experiments revealed that the HMR only formed 4,4′-diarylmethane structures with itself in the presence of the cMWL; the 2-methylols that formed remained free and did not crosslink with resorcinol. Cured HMR resin formed both 4,4′- and 2,4-diarylmethane structures, confirming that the presence of lignin and *O*-acetyl-(4-*O*-methylglucurono)xylan hinders crosslinking at the C-2 position. No evidence of reactivity between HMR and lignin subunits was found. New peaks consistent with ester linkages were observed in ^{13}C-NMR spectra of the cMWL sample treated with HMR that may be attributable to HMR moieties condensing with glucuronic acid substituents. © 2017 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2017**, *134*, 45398.

KEYWORDS: *Acer saccharum*; crude milled-wood lignin; hydroxymethylated resorcinol; *O*-acetyl-(4-*O*-methylglucurono)xylan; solution-state NMR spectroscopy

Received 6 April 2017; accepted 5 June 2017
DOI: 10.1002/app.45398

INTRODUCTION

Glued-laminated (glulam) beams remain an important wooden structural component in applications like bridges and piers that are exposed to the weather. The adhesive bonds under these harsh exterior conditions are tested to the point of delamination and any necessary repairs need to maintain the beam's structural integrity and strength. Hydroxymethylated resorcinol (HMR) has proven to be a highly effective primer in that it enhances the bonding and durability of epoxy, polyurethane, and glass-fiber reinforced polymers when bonded to wood.[1–5] However, the mechanism for which the HMR interacts with the wood cell wall and stabilizes wood polymer structure is not fully understood.

Several theories can be considered regarding how HMR may adhere and stabilize wood: (1) Interfacial adhesion, where HMR interacts only at the surface of the cell; (2) Lumen filling, where the HMR bulks the lumen and acts as a mechanical interlock; and (3) Cell wall permeation, where many different interactions become apparent including: (i) Micro/nanoscale mechanical interlock through void displacement, creating an interpermeating network; (ii) Secondary bond interactions where hydrogen bonding and van der Waal forces may play a significant role as the HMR closely interacts with cell wall polymers; and (iii) Primary bond reactions where the HMR may react with a wood polymer, or may create a crosslink between wood polymers. Interfacial adhesion is not a likely scenario since it has been shown that resorcinol formaldehyde (RF) can just as easily bond to acetylated wood as it can with non-acetylated wood.[6] Lumen filling and mechanical interlocking between the HMR that has penetrated the lumens and pits does not seem a likely scenario either since HMR is applied as dimers, trimers, and oligomers with low-molecular weight. Cell wall micro/nanoscale void displacement is believed to be the most influential of these theories due to the diverse amount of possibilities that can occur. Some researchers suggest microvoids within the wood cell wall may expand during the incorporation of a liquid chemical of low molecular weight in that immediate environment.[7–9] Son and Gardner,[10] using a Wilhelmy plate technique, showed that HMR improves the dimensional stability of maple veneer once exposed to liquid water, suggesting that low-molecular-weight HMR compounds are able to permeate the cell wall and, once cured, inhibit water absorption. If HMR has the capability of permeating the cell wall through microvoids,

there exists the possibility of secondary and primary bond interactions with wood polymer structures.

The original hypothesis of the HMR bonding mechanism was that secondary bond interactions (e.g., hydrogen) and primary bonds between HMR and wood, and between HMR and the applied adhesive were responsible.[1] Hydrogen bonding may play a role since the resorcinolic moiety, at any stage of polymerization, has two aromatic hydroxyls available for hydrogen bonding interactions. Primary bonds between HMR and wood have been suggested since HMR monomers/oligomers have been shown to noticeably stiffen the wood cell wall, allowing increased time and cooperativity of cell wall relaxations.[11] If cell wall polymers are indeed stabilized by the presence of HMR, it can then be assumed that the amorphous regions are most affected by HMR treatment. Son *et al.*[12] found that the glass transition temperature (T_g) of lignin decreased with increased HMR treatment time, while hemicelluloses displayed only a subtle shift in T_g. They also found that the calculated solubility parameter (via Hoy's method) for HMR (27.5 $J^{1/2}$ $cm^{3/2}$) was closer to lignin (31 $J^{1/2}$ $cm^{3/2}$) than hemicelluloses (36.3 $J^{1/2}$ $cm^{3/2}$). This suggests the HMR is more miscible with lignin than hemicelluloses and will tend to preferentially interact with lignin at the molecular level. Therefore, since lignin contains many more potential reactive sites than hemicelluloses, the reactivity between HMR and lignin to form new primary bonds is a reasonable hypothesis.[11]

Here, two-dimensional ^{1}H–^{13}C Heteronuclear Single-Quantum Coherence (HSQC) NMR experiments were performed to delineate whether lignin and *O*-acetyl-(4-*O*-methylglucurono)xylan from wood would react with HMR to form primary bonds. The most predominant linkage in HMR, once polymerized, is a methylene between the two resorcinolic units (i.e., a diarylmethane). The chemical shifts in NMR spectra of RF monomeric, oligomeric, and polymeric structures have been well studied.[13–16] However, what also may occur as HMR cures with wood is the formation of new linkages between lignin or xylan and an HMR moiety. Knowing whether or not linkages between HMR and amorphous polymers form will enhance the current understanding of its durability mechanism.

EXPERIMENTAL

Reagents

Resorcinol (99%, crystalline), formaldehyde (37% aq. sol., formalin), 1,4-dioxane (99%), and dimethylsulfoxide-d_6 (99.9% D) were from Sigma-Aldrich (Milwaukee, WI). Sodium hydroxide (pellets) required to make a 3 *M* solution was from Mallinckrodt Specialty Chemical Co. (Paris, KY).

Crude Milled-Wood Lignin Preparation

Wiley-milled (10 g, 40-mesh, extractive-free) sugar maple (*Acer saccharum*) wood was placed into an agate ball-milling vessel then ball-milled (18 h total with a 20 min interval and a 10 min pause time at 600 rpm) using a Retsch (Newtown, PA) PM100 planetary ball mill. To remove the ball-milled wood from the balls, a small shaker was used. The balls (coated with milled wood) were placed into three copper sieves, stacked on each other, and shook to displace the ball-milled wood into a copper pan below. The ball-milled wood was then transferred to a jar, weighed to obtain yield, and labeled.

The lignin preparation was followed by the procedures described by Björkman.[17] Briefly, about 10 g of the ball-milled sugar maple wood was weighed into a 500 mL flask. The flask was covered with foil and a stir-bar was added. Then, 96 mL of 1,4-dioxane with 4 mL of water was added to the flask, the flask was sealed, and the flask was purged with nitrogen and let stir for 24 h. The dioxane–water solution was then filtered through a sintered glass funnel to separate the soluble lignin fraction. The insoluble fraction was added to another 96:4 mL dioxane:-water mixture and stirred for another 24 h. The filtration was repeated as above. The extraction was repeated three times in total after which the crude milled-wood lignin (cMWL) was now fully isolated in the dioxane:water filtrate. The solvents were roto-evaporated to about 15 mL and the cMWL solution was freeze-dried to obtain a fine powder.

Preparing the HMR Solution and Curing with cMWL

The preparation of the HMR novolak solution followed the procedure outlined by Christiansen *et al.*[18] Briefly, for 100 g of the novolak-based HMR solution, 3.34 g of crystalline resorcinol was placed into a container with 90.43 g deionized water. Then, 2.44 g of a 3 *M* solution of sodium hydroxide was added, followed by 0.95 g of formalin to give a F/R molar ratio of 0.39. This solution was stirred well, capped and let sit for 24 h. From the HMR solution mixture, a 10 g aliquot was weighed onto an aluminum-weighing dish and 0.100 g of formalin was added and stirred to give a final F/R molar ratio of 1.54. This aliquot was let cure at 22 °C and 50% relative humidity (R.H.) for 24 h and placed into a vial labeled "HMR resin," To make the HMR–cMWL complex, 1.010 g of the HMR solution was placed into a Teflon cup followed by 0.010 g of formalin and stirred to give a final F/R molar ratio of 1.54. After 30 min, 0.099 g of cMWL was added and stirred with a Teflon stirring rod. This HMR–cMWL mixture was let cure at 22 °C and 50% R.H. for 24 h and placed into a vial labeled "HMR–cMWL complex." The final cured weight was 0.135 g with a HMR:cMWL ratio (wt/wt) of 0.26. After curing of the HMR resin and HMR–lignin complex, both materials were ground separately by hand using a mortar and pestle to break up any large chunks into fine powders. Each powdered sample (cMWL, HMR resin, and HMR–cMWL complex) was directly weighed (~75 mg) into 5-mm NMR tubes and 500 µL of dimethylsulfoxide-d_6 were added to each tube. The samples were sonicated at 30 °C for 1 h.

NMR Characterization of the HMR Resin, cMWL, and HMR–cMWL Complex

NMR spectra were acquired on a Bruker-Biospin (Rheinstetten, Germany) DRX 360 MHz spectrometer fitted with a 5-mm ^{1}H/broadband gradient probe with inverse geometry (^{1}H coils closest to the sample). HSQC spectra, where one-bond ^{1}H–^{13}C correlations are obtained, were acquired using the pulse sequence "invietgssi" and the following parameters: spectral width from 10 to 0 ppm (3592 Hz) in F2 (^{1}H) using 1400 data points for an acquisition time (AQ) of 195 ms, and interscan delay (D1) of 1.0 s, and from 172 to 0 ppm (14,490 Hz) in F1 (^{13}C) using 512 increments of 80 scans, for a total AQ of 16 h 50 min. The

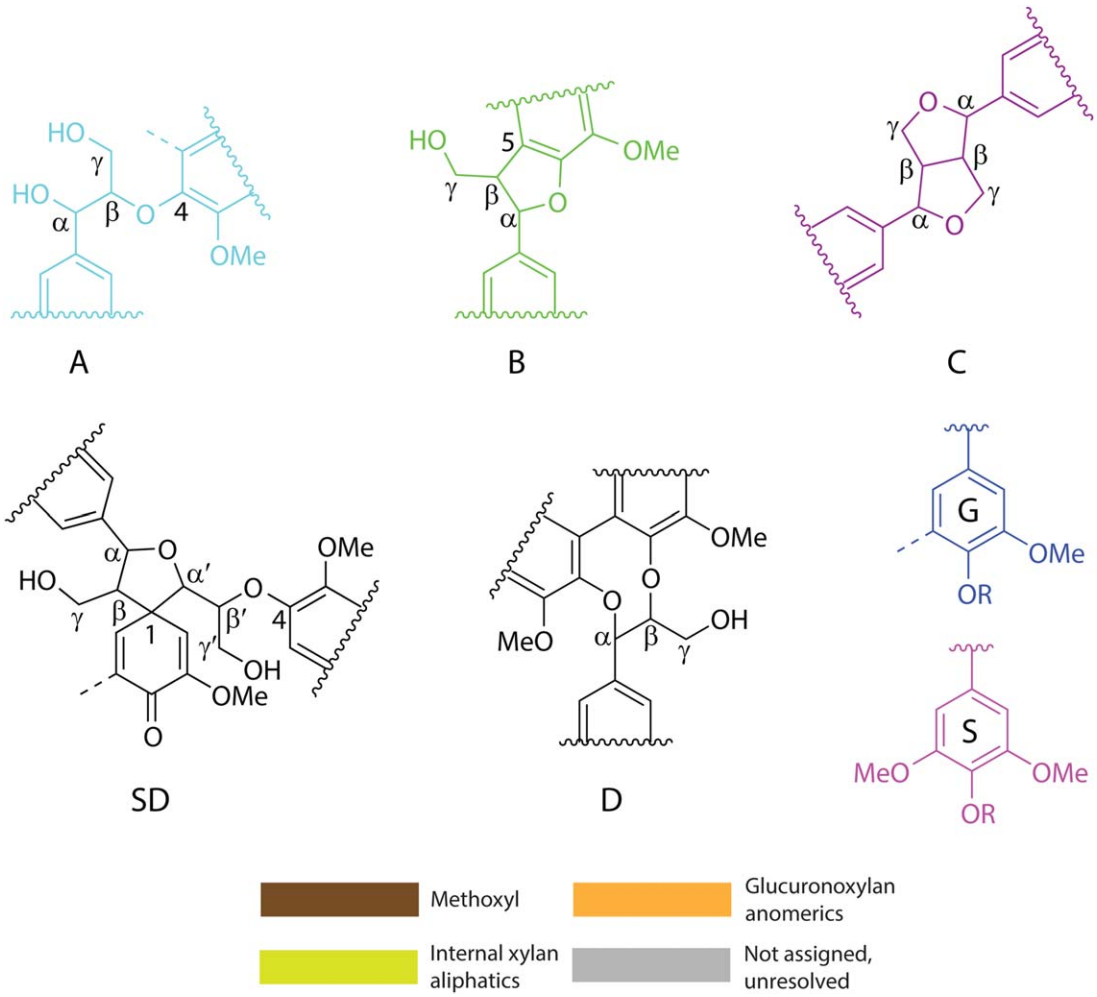

Figure 1. Key to the chemical structures for the lignin and *O*-acetyl-(4-*O*-methylglucurono)xylan in the cMWL found in the spectra in Figures 2 and 4. The structures are: (A) β-aryl ether in cyan, (B) phenylcoumaran in green, (C) resinol in purple, (SD) spirodienone/β-1, (D) dibenzodioxocin, (G) guaiacyl in blue, (S) syringyl in fuchsia. Other structures include: lignin methoxyl in brown, *O*-acetyl-(4-*O*-methylglucurono)xylan aliphatics in chartreuse, *O*-acetyl-(4-*O*-methylglucurono)xylan anomerics in orange, and structures currently not assigned or unresolved in gray. [Color figure can be viewed at wileyonlinelibrary.com]

$^{1}J_{CH}$ used was 145 Hz. Carbon spectra were acquired using the pulse program "zgpg70" with 64k data points, D1 of 0.500 s, AQ of 0.720 s (fast scanning), 99k scans, and a sweep width of 250 ppm (22,727 Hz) with a transmitter frequency offset of 105 ppm (9508 Hz). The central solvent peak of dimethylsulfoxide was used as an internal reference for all samples (δ_C 39.51, δ_H 2.49 ppm). Processing of the spectra and peak integrations were conducted using Bruker Biospin's TopSpin software (Mac, v. 3.0). Volume integration of the various contours was performed based on the lignin methoxyl contour as the lignin methoxyl group is believed to be the most stable functionality during curing of phenolics in the presence of alkali.[19] The processing used typical matched Gaussian apodization in the ^{13}C dimension. Prior to Fourier transformation, the data matrices were zero-filled to 1024 points in the ^{13}C dimension.

Chemical shift assignments of the lignin subunits were made using the NMR database of lignin and cell wall model compounds.[20] HMR and resocinolic moiety chemical shift assignments were made using ^{1}H, ^{13}C, and HSQC experiments, along with literature values.[13–16] *O*-acetyl-(4-*O*-methylglucurono)xylan chemical shift assignments were made using ^{1}H, ^{13}C, and HSQC experiments, along with literature values.[21,22] Figure 1 depicts the lignin and *O*-acetyl-(4-*O*-methylglucurono)xylan chemical structures found in the NMR spectra to follow.

RESULTS AND DISCUSSION

Sugar Maple cMWL

From the ^{1}H–^{13}C HSQC NMR spectrum of the cMWL (Figure 2), the sample has not just lignin structures, but also structures from *O*-acetyl-(4-*O*-methylglucurono)xylan. From the sidechain region of the spectrum, the lignin structures present are of the predominant linkages: β-aryl ethers (A), phenylcoumarans (B), resinols (C), and spirodienones (SD). The β-aryl ether is the principal linkage in lignin as seen by the strong Aα-contour peak (4.82/71.7 ppm) with an approximate proportion of 84% in sugar maple lignin. From visual inspection of the Aβ-

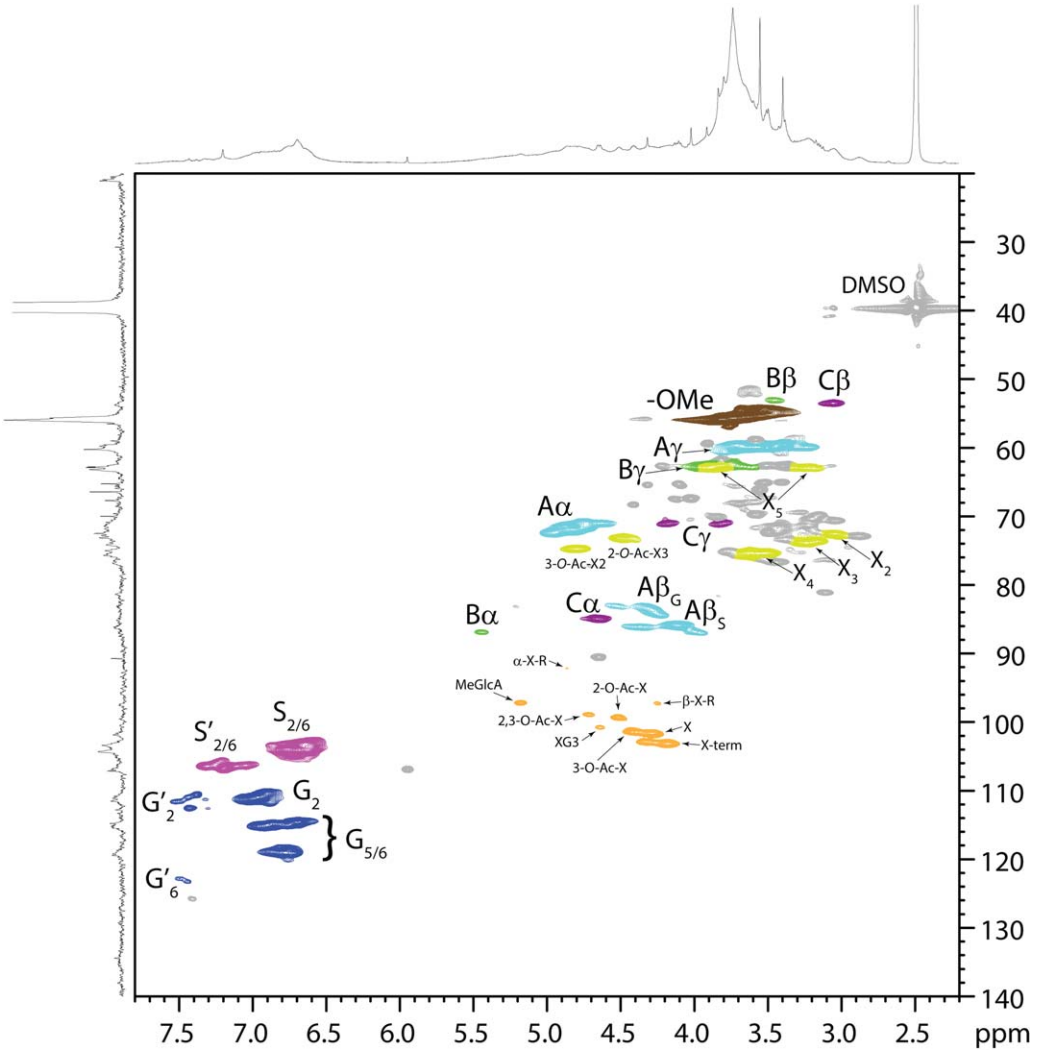

Figure 2. HSQC spectrum of cMWL from sugar maple (*Acer saccharum*). Note the spectrum shows the aliphatics, anomerics, and aromatics. All contour colors can be matched to their respective structures shown in Figure 1. [Color figure can be viewed at wileyonlinelibrary.com]

contours, the β-aryl ether linkage is more syringyl than guaiacyl in this particular species. This can be deduced by the stronger syringyl Aβ contour peak (centered around 4.12/85.9 ppm) compared to the guaiacyl Aβ contour peak (centered around 4.30/83.6 ppm). Resinol linkages are more abundant in angiosperm species, thus the more intense resinol Cα-contour peak (4.66/84.9 ppm) with an approximate proportion of 13% in sugar maple lignin. Phenylcoumaran linkages, with an approximate proportion of 3% in sugar maple lignin, have a less intense Bα-contour peak (5.44/86.8 ppm). Spirodienone/β-1 linkage correlations (not shown) were only detectable in the sidechain region at low contour intensity at 5.07/81.2 ppm, 2.75/59.8 ppm, and 4.11/79.4 ppm for SDα, SDβ, and SDβ′, respectively. Dibenzodioxocin linkage correlations (not shown) were also detectable in the sidechain region, but only seen at very low contour intensity at 4.82/83.2 ppm and 3.89/85.3 ppm for Dα and Dβ, respectively. The sidechain region also shows strong signals for internal β-D-xylan residues (X) with correlations for the 2-, 3-, 4-, and two 5-positions at 3.04/72.6 ppm, 3.24/73.8 ppm, 3.61/75.4 ppm, and (3.90 and 3.30)/62.9 ppm, respectively. The native acetates along the β-D-xylan backbone (2-*O*-Ac-X3 and 3-*O*-Ac-X2) are depicted at 4.50/73.1 ppm and 4.80/74.7 ppm, respectively. The relative ratio of 3-*O*-Ac-X:2-*O*-Ac-X was estimated from contour integration to be 1:0.9. In the aromatic region of the spectrum, the syringyl (S) and guaiacyl (G) units are shown along with their respective α-ketones (S′ and G′). An S:G ratio of 1.46 was calculated from the integration of $S_{2/6} + S'_{2/6}$ and $G_2 + G'_2$, with the $S_{2/6} + S'_{2/6}$ integral logically divided by two.

Analysis of the polysaccharide anomeric region showed that these H-1/C-1 correlations were fairly well resolved and included internal β-D-xylan (X) at 4.28/101.6 ppm, terminal β-D-xylan (X-term) at 4.18/103.1 ppm, along with naturally acetylated xylan (2-*O*-Ac-X, 3-*O*-Ac-X, and 2,3-*O*-Ac-X) at 4.51/99.3 ppm, 4.40/101.3 ppm, and 4.72/98.8 ppm, respectively. The 4-*O*-methyl-α-D-glucuronic acid (MeGlcA) was depicted at 5.18/97.2 ppm, along with MeGlcA 2-*O*-linked and 3-*O*-acetylated xylan (XG3) at 4.64/100.8 ppm. Reducing endgroups of

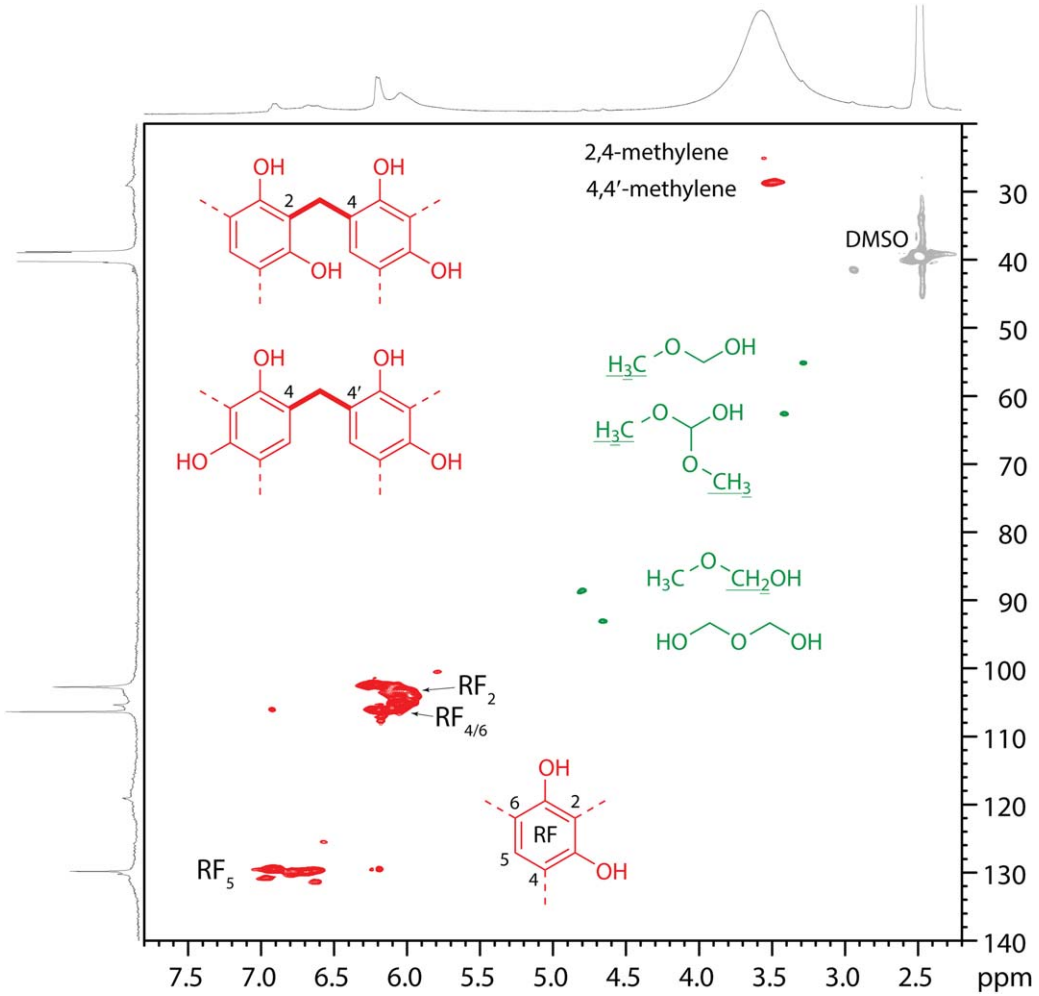

Figure 3. HSQC spectrum of cured HMR resin. Note the spectrum shows the aliphatics and aromatics. Contours and chemical structures for HMR are shown in red, while contours and chemical structures for formaldehyde-based moieties are shown in green. [Color figure can be viewed at wileyonlinelibrary.com]

xylan were also present at 4.86/92.1 ppm (α-X-R) and 4.24/97.3 ppm (β-X-R). The presence of these saccharides in the cMWL preparation demonstrate the ability of the dioxane–water mixture to extract certain hemicelluloses that may be in close proximity to lignin polymers or those saccharides that have similar miscibility with lignin.

HMR Resin After Curing

From the $^{1}H–^{13}C$ HSQC NMR spectrum of the cured HMR resin (Figure 3), the structures present include some early species, like methylene glycol and hemiformal groups from polyoxymethylene, as well as methylene bridges (diarylmethanes) between resorcinolic rings (i.e., 2,4- and 4,4′-methylene bridges).

The hemiformal (at 3.28/55.1 ppm and 3.42/62.6 ppm) and glycol (at 4.80/88.6 ppm and 4.66/93.1 ppm) groups present in the spectrum suggest that excess formaldehyde was in the cured resin. However, since no resorcinolic ring methylols were present, the excess formaldehyde was not able to further substitute resorcinol, even when some C-2- and C-6 positions were available. This might be due to some formaldehyde being entrapped in the HMR resin as it cured, keeping it unavailable for further reactions with the growing RF polymer.

In the aliphatic region, the 4,4′-methylene bridge (3.51/28.7 ppm) was the most dominant diarylmethane found, followed by the 2,4-methylene bridge (3.55/25.1 ppm). From volume integration of these contour peaks, the 4,4′-methylene bridges were approximately nine times more prevalent than the 2,4-methylene bridges. The C-2 position on the resorcinolic ring is well known to be the least reactive and, if present, the ^{13}C chemical shift of a 2,2′-methylene bridge would have resonated at approximately 18.5 ppm,[14] but no peaks were observed here.

The aromatic region showed evidence of unreacted C—H's on resorcinolic rings at the 2- and 4/6-positions (6.0–6.3/102–106 ppm). The C—H at the 5-position on resorcinolic rings is not expected to react, thus these peaks were present as well (6.6–7.0/129–132 ppm). No substituted methylols were present in the cured resin, meaning that all the methylols in the novolak were able to react to form methylene bridges.

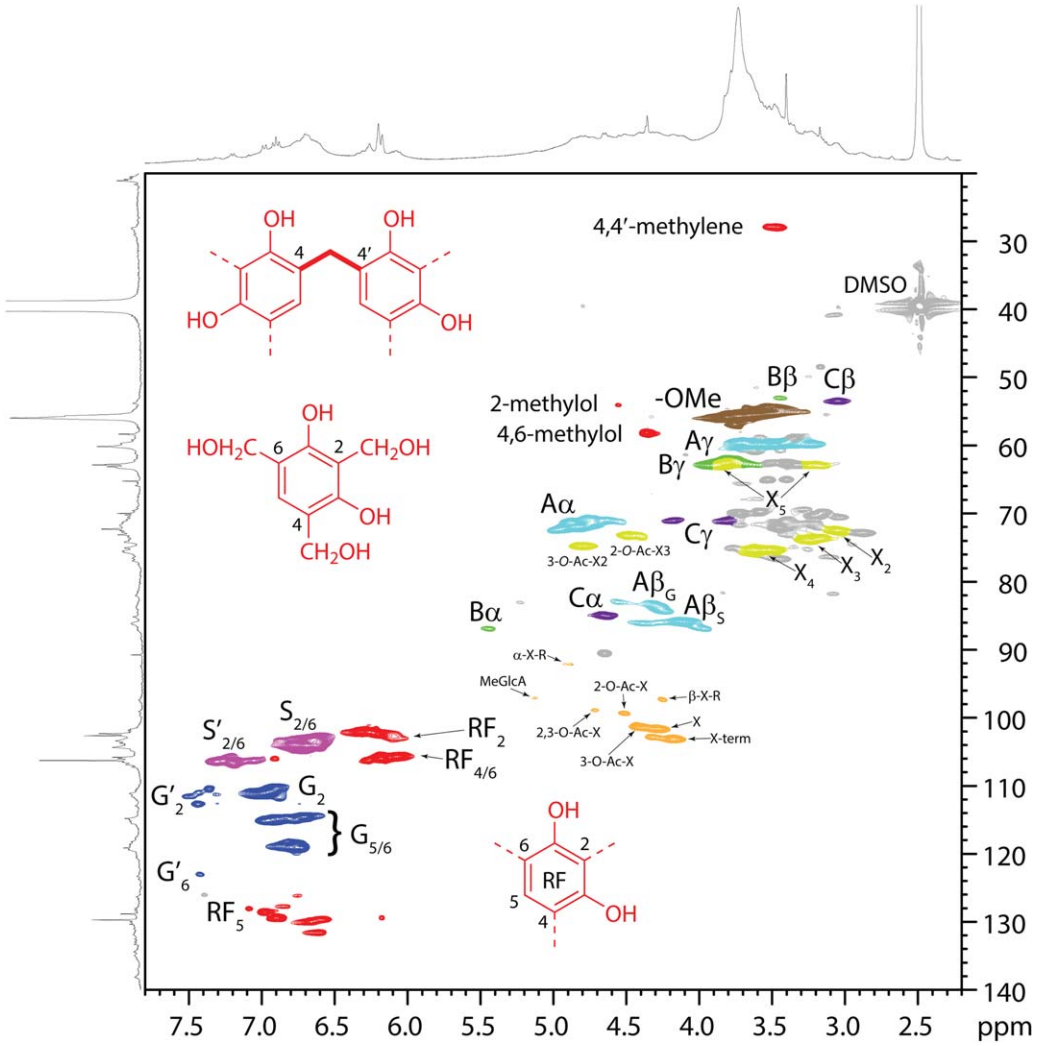

Figure 4. HSQC spectrum of HMR resin cured with cMWL from sugar maple (*Acer saccharum*). Note the spectrum shows the aliphatics, anomerics, and aromatics. HMR contours and chemical structures are shown in red. Contour colors for cMWL can be matched to their respective structures shown in Figure 1. [Color figure can be viewed at wileyonlinelibrary.com]

HMR–cMWL Complex

Native wood lignin has the capability to react with other phenolics in the presence of formaldehyde, but reactivity is normally seen under strongly alkaline or strongly acidic conditions. Under alkaline conditions and temperatures $\geq 100\,^{\circ}C$, free-phenolic lignin can undergo hydrolysis of the β-aryl ether and phenylcoumaran to give styryl ether[23–26] and stilbene structures.[25] Resorcinol has the capability to react with hydroxymethylated alkali lignin and lignin model compounds under acidic conditions to form methylenes between the C-2- or C-6 position on phenylpropanoids and the C-4- or C-6 position on resorcinol[27,28] or to form various condensation products at the benzylic position on phenylpropanoids.[29] However, since HMR is weakly basic (pH 8.5–9) and *Acer* spp. are weakly acidic (pH 5.3),[30] the conditions for HMR interacting with native amorphous wood polymers would be closer to neutral pH. To the author's knowledge, no research has been conducted to evaluate the reactivity of resorcinolic moieties with native amorphous polysaccharides from wood.

The ^{1}H–^{13}C HSQC NMR spectrum of the HMR–cMWL complex is shown in Figure 4. In the aliphatic region, only one large methylene contour peak at 3.47/28.0 ppm is seen. Comparing this methylene peak to the methylene peaks in the cured HMR resin (Figure 3), this peak is quite close to that of the 4,4′-methylene bridge, hence it is assigned as such. Further downfield in the aliphatic region the presence of methylols was evidenced by a contour peak at 4.36/58.1 ppm for the 4- and 6-methylols (a combined peak due to symmetry) and a smaller contour peak at 4.56/54.0 ppm for the 2-methylol. It was curious to see that the 2,4-methylene bridge was not formed in the HMR–cMWL complex, even with the availability of 2-methylols. This may be a result of steric hindrance and decreased HMR mobility with the bulky amorphous polymers around. The spectrum showed no evidence of polyoxymethylene from formaldehyde, so this suggests that all the formaldehyde had been converted to methylols. The lignin contour peaks show identical sidechain linkages to those seen in the native lignin HSQC (Figure 2), with β-aryl ethers (A),

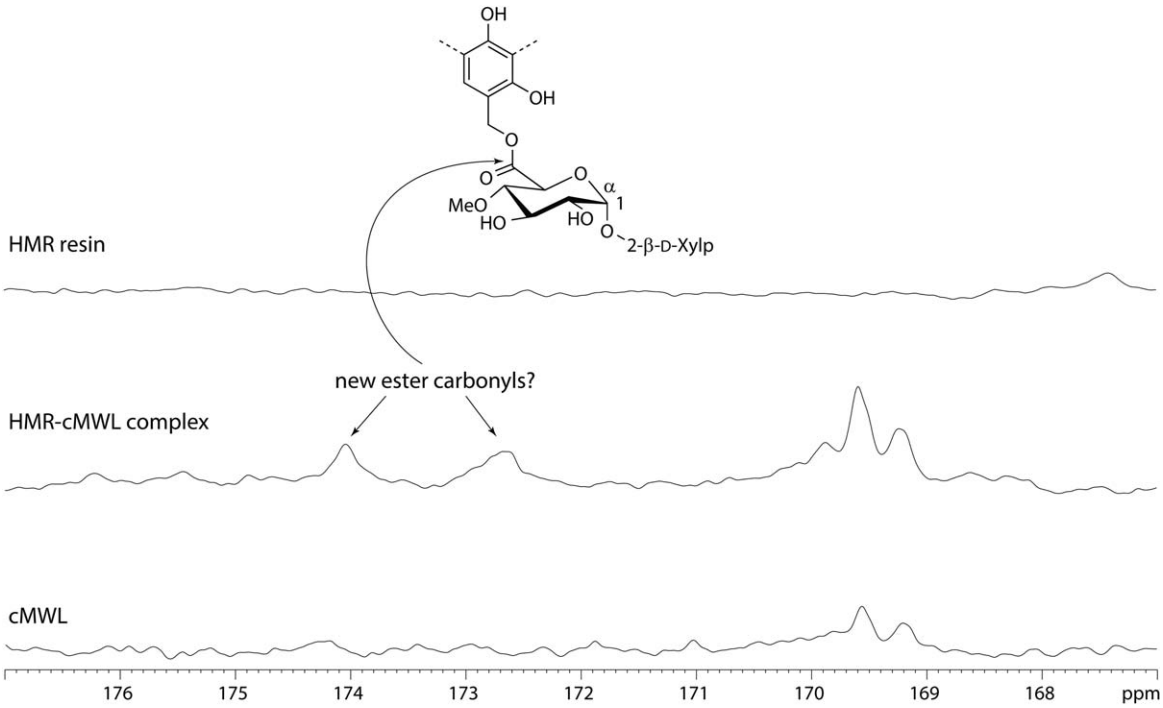

Figure 5. Stacked ^{13}C spectra of the cured HMR resin, HMR-cMWL complex, and cMWL showing the carbonyl region zoomed in. Note the tentative assignment for a new ester linkage between HMR and a glucuronic acid substituent.

phenylcoumarans (B), resinols (C), spirodienones (SD), and dibenzodioxocins (D).

In the aromatic region, the contour peaks from the unreacted (free) C—H's at the 2- and 4/6 positions on resorcinolic ring (6.0–6.3/102–106 ppm) were strikingly similar to those found in the spectrum of the cured HMR resin (Figure 3). The C—H at the 5-position on the resorcinolic ring (6.6–7.0/129–132 ppm) was present as well and displayed similar chemical shifts to those peaks in the cured HMR resin (Figure 3). From this spectrum, no other contour peaks were found to suggest reactivity of HMR with lignin. In previous work, NMR characterization of wood treated with alkaline phenol formaldehyde resin found new methylene bridges at the C-5 position of guaiacyl lignin aromatic units; new guaiacyl methylene bridges were confirmed via the characterization of new aromatic C—H contour peaks at the 6-position and new *ortho–ortho* methylene contour peaks.[26] Conversely, in this study no other new C—H contour peaks at the 6-position were detected in the aromatic region to suggest that a new methylene bridge has been formed between the C-5 position of guaiacyl lignin and a hydroxymethylated resorcinolic structure. An S:G ratio of 1.41 was calculated from the integration of $S_{2/6} + S'_{2/6}$ and $G_2 + G'_2$, which was quite close to that in the native lignin sample.

Modification of Native Lignin and Xylan Structures by HMR

To characterize and semi-quantify any changes to the native lignin polymer during HMR curing, volume integration of specific lignin contour peaks in the cMWL HSQC spectrum and the HMR–cMWL complex HSQC spectrum was conducted, relative to the lignin methoxyl group contour. Table I shows only the most abundant lignin linkages and their integrated α-contour peak: β-aryl ether (Aα), phenylcoumaran (Bα), and resinol (Cα), along with the syringyl ($S_{2/6}$) and guaiacyl (G_2) aromatic units. The minute differences between the integrals of the cMWL and the HMR–cMWL contour peaks suggest that native lignin was not modified by the HMR resin during curing. Integration of the sidechain *O*-Ac-β-D-Xyl*p* contour peaks in the cMWL and the HMR–cMWL complex showed only a slight decrease in native acetates. However, the 4-*O*-methyl-α-D-glucuronic acid contour peak in the anomeric region in the cMWL and the HMR–cMWL complex showed approximately two-third decrease in these substituents. This result hints that the carboxylic acid group may be participating in the HMR curing mechanism (i.e., acting as an electrophile for a hydroxymethylated resorcinolic moiety and condensing to form an ester linkage). If this is true, new ester carbonyl groups should be visible in the ^{13}C-NMR spectra of the HMR–cMWL complex. Figure 5 shows stacked ^{13}C-NMR spectra of the cMWL, HMR–cMWL complex, and HMR resin, with the carbonyl carbon region zoomed in. The ^{13}C-NMR spectra show the native xylan acetate carbonyl groups between 169.2 and 170.1 ppm. However, new ^{13}C peaks at 174.0 ppm and 172.6 ppm in the HMR–cMWL complex are present, which match closely to those of ester linkages found in the structure shown in Figure 5. Long-range heteronuclear multiple bond correlation (HMBC) experiments were attempted on the HMR–cMWL complex sample, but the fast relaxation (<80 ms) of the polymers in solution was disadvantageous toward acquiring meaningful data; long-range experiments require a

Table I. Volume integrals of Native Lignin and Xylan Substituent Contours in the HSQC Spectra of cMWL and the HMR–cMWL Complex Relative to the Lignin Methoxyl Contour

Contour	cMWL	HMR–cMWL
Aα	0.137	0.138
Bα	0.004	0.004
Cα	0.019	0.020
Lignin ($G_2 + G'_2$)	0.120	0.127
Lignin ($S_{2/6} + S'_{2/6}$)	0.176	0.179
OAc-Xylp	0.055	0.050
4-*O*-MeGlcA	0.005	0.002

minimum of 80 ms relaxation delay to capture long-range couplings. Nevertheless, it is plausible to interpret these new ester peaks as a product of 4-*O*-methyl-α-D-glucuronic acids condensing with excess HMR moieties in the cMWL and are tentatively assigned here as such. More investigative research is needed to confirm these structures.

Hypothesis of How HMR Interacts with Wood Cell Wall Polymers

Previously, Son *et al.* found that lignin in wood was plasticized by HMR as inferred from a decrease in T_g.[12] This is reasonable since this study found no chemical reactivity between HMR and native lignin structures.

Sun and Frazier found that wood was stiffened by HMR as inferred from the increased relaxation time and cooperativity, thereby suggesting primary bonds may be present between HMR and an amorphous wood polymer.[11] This is also reasonable since this study found that glucuronic acid substituents may react with HMR to form new ester linkages. These primary bonds may result in the stiffening effect postulated by Sun and Frazier.

From this study, and the previously aforementioned studies, HMR is hypothesized to interact intimately with native lignin structures, allowing for plasticization of lignin. However, this study postulates that HMR reactivity with itself is likely to predominate over any reaction with the guaiacyl C-5 position, possibly due to kinetics and steric hindrance issues. Glucuronic acid substituents may be a more likely candidate for HMR reactivity since the less hindered carboxylic acid group may interact more readily with the primary alcohol of the hydroxymethyl group.

CONCLUSIONS

HMR has proven to be an effective primer for wood bonded with various adhesives, like epoxy and polyurethane. Its bonding mechanism has been postulated to involve primary bond formation between HMR and amorphous wood polymers, such as lignin and hemicelluloses. In this study, a cMWL from sugar maple was treated with novolak-based HMR and cured. The resulting cMWL treated with HMR was characterized using solution-state NMR spectroscopy. Two-dimensional ^{1}H–^{13}C HSQC NMR experiments depicted all the lignin and *O*-acetyl-(4-*O*-methylglucurono)xylan structures in a native-state such that any reactivity between HMR and these amorphous wood polymers could be delineated. The NMR spectra did not show any evidence of HMR reactivity with lignin. However, ^{13}C NMR spectra of the cMWL treated with HMR showed tentative evidence of new ester linkages consistent with those potentially linking an HMR moiety to 4-*O*-methyl-α-D-glucuronic acid, a common xylan substituent typically found 1 in 10 xylose residues in hardwoods. This research gives new insights into HMR interactions with amorphous wood polymers and the ability of HMR to enhance bond durability upon moisture-induced swelling.

ACKNOWLEDGMENTS

Author gratefully acknowledges Prof. John Ralph for use of the 360 MHz Bruker NMR instrument at the U.S. Dairy Forage Research Center, Madison, WI.

REFERENCES

1. Vick, C. B.; Richter, K.; River, B. H.; Fried, A. R. *Wood Fiber Sci.* **1995**, *27*, 2.
2. Vick, C. B. *Adhes. Age* **1997**, *40*, 24.
3. Vick, C. B.; Okkonen, E. A. *Forest Prod. J.* **1997**, *47*, 71.
4. Vick, C. B.; Okkonen, E. A. *Forest Prod. J.* **2000**, *50*, 69.
5. Lopez-Anido, R.; Gardner, D. J.; Hensley, J. L. *Forest Prod. J.* **2000**, *50*, 43.
6. Frihart, C. R.; Brandon, R.; Ibach, R. E. In Proceedings of the 27th Annual Meeting of the Adhesion Society, Wilmington, NC, Feb 15–18, 2004; Chaudhury, M. K., Ed.; The Adhesion Society: Bethesda, MD, **2004**; p 329.
7. Torelli, N. *Les Ljubijana* **2000**, *52*, 141.
8. Hill, C.; Papadopoulos, A. N. *J. Inst. Wood Sci.* **2001**, *15*, 337.
9. Hill, C.; Papadopoulos, A. N.; Payne, D. *Wood Sci. Technol.* **2003**, *37*, 475.
10. Son, J.; Gardner, D. J. *Wood Fiber Sci.* **2004**, *36*, 98.
11. Sun, N.; Frazier, C. E. *Wood Fiber Sci.* **2005**, *37*, 673.
12. Son, J.; Tze, W. T. Y.; Gardner, D. J. *Wood Fiber Sci.* **2005**, *37*, 220.
13. Dankelman, W.; de Wit, J. *Die Angew. Makromol. Chem.* **1977**, *62*, 101.
14. Werstler, D. D. *Polymer* **1986**, *27*, 757.
15. Kim, M. G.; Amos, L. W.; Barnes, E. E. *J. Polym. Sci. Part A: Polym. Chem.* **1993**, *31*, 1871.
16. Christiansen, A. W. *J. Appl. Polym. Sci.* **2000**, *75*, 1760.
17. Björkman, A. *Svensk Papperstidning* **1956**, *59*, 477.
18. Christiansen, A. W.; Vick, C. B.; Okkonen, E. A. In Proceedings of Wood Adhesives 2000, South Lake Tahoe, Nevada, June 22–23, 2000; The Forest Products Society: Madison, WI, **2000**; p 245.
19. Gierer, J.; Lenz, B.; Norén, I.; Soderberg, S. *TAPPI* **1964**, *47*, 233.

20. Ralph, S. A.; Ralph, J.; Landucci, L. L. Available at: https://www.glbrc.org/databases_and_software/nmrdatabase/, **2004**. Accessed on June 19, 2017.

21. Teleman, A.; Lundqvist, J.; Tjerneld, F.; Stålbrand, Dahlman, O. *Carbohydr. Res.* **2000**, *329*, 807.

22. Yelle, D. J.; Ralph, J.; Frihart, C. R. *Magn. Reson. Chem.* **2008**, *46*, 508.

23. Freudenberg, K. *Chem. Ber.* **1947**, *80*, 149.

24. Ekman, K. H. *TAPPI* **1965**, *48*, 398.

25. Marton, J.; Marton, T.; Falkehag, S. I. In Lignin Structure and Reactions; Marton, J., Ed.; American Chemical Society: Washington, DC, **1966**; Vol. *59*, p 125.

26. Yelle, D. J.; Ralph, J. *Int. J. Adhes. Adhes.* **2016**, *70*, 26.

27. van Der Klashorst, G. H.; Jackson, S. A. *J. Wood Chem. Technol.* **1989**, *9*, 1.

28. van Der Klashorst, G. H.; Jackson, S. A. *J. Wood Chem. Technol.* **1989**, *9*, 17.

29. Nimz, H. *Holzforschung* **1969**, *23*, 84.

30. Sandermann, W.; Rothkamm, M. *Holz. Roh. Werkst.* **1959**, *17*, 433.