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Section 4

Processes and properties

**Using X-ray scattering to elucidate the mechanisms behind the
moisture and fungal decay resistance of epoxybutene modified wood**

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Using X-ray scattering to elucidate the mechanisms behind the moisture and fungal decay resistance of epoxybutene modified wood

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ABSTRACT

Chemical modification of the hydroxyl groups of wood can improve the properties of wood by providing moisture and biological resistance, as well as dimensional stability. Southern pine solid wood was chemically modified to various weight percentage gains (WPG) with epoxybutene (EpB, 8%-38% WPG). After modification, specimens were extracted with a toluene: ethanol (2:1) solution for 2 hours or water leached for 2 weeks. The equilibrium moisture content (EMC) at 30%, 65% and 90% relative humidity (RH) and 27 °C was determined on all specimens. Laboratory soil block decay evaluations against the brown-rot fungus *Gloeophyllum trabeum* was performed and weight loss calculated by mass loss.

Biological efficacy was found, and the biological resistance correlated with the lowering of the equilibrium moisture content, suggesting that the mechanism of efficacy was due to moisture exclusion. To assist in understanding the mechanism of effectiveness, small angle x-ray scattering (SAXS) and wide-angle x-ray scattering (WAXS) were both performed. Preliminary WAXS results showed that the modification did not significantly change the cellulose crystalline lattice parameters. Preliminary SAXS results showed that epoxide addition led to an increased polydispersity in the microfibril alignment and broader microfibril angle distributions, thus, suggesting that modification may target regions outside the microfibrils. Further experimentation is underway to confirm these results.

Keywords: wood protection, durability, decay, moisture, wood modification, epoxides, WAXS, SAXS.

1. INTRODUCTION

Outdoor exposure of wood with naturally low durability often results in wood decay. The most common way to protect wood from fungal decay and thus, extend the lifetime of the product is with wood preservatives, such as oil-borne (creosote) and waterborne (chromated copper arsenate), and their mechanism of effectiveness is based on toxicity. Another approach to wood protection that is considered more environmentally friendly because of its lack of potential for toxic leaching is chemical modification of wood, which changes the wood cell wall components, namely, lignin, cellulose and hemicellulose and thus, improves the overall wood properties such as dimensional stability and biological resistance. (Rowell 2013).

Wood is decayed primarily by brown, white, or soft rot fungi. Brown rot fungi is of particularly interest because it can rapidly depolymerize all wood polymers leading to structural failure, especially in coniferous species commonly used in the construction market (Arantes and Goodell

2014). Four mechanisms for brown-rot fungal decay protection by chemical modification have been proposed and examined (Ringman et al. 2014a, 2014b): 1) fungal enzyme inefficiency because of non-recognition (Rowell, 2013); 2) fungal enzyme inefficiency because of lack of water at glycosidic bonds (Rowell 2013, Rowell and Ibach, 2018, Rowell et al. 2009); 3) reduced flow of low molecular weight fungal metabolites into the wood cell wall because of micropore blocking (Hill *et al.* 2005); and 4) inhibition of diffusion of fungal metabolites because of insufficient amounts of moisture in the wood cell wall (Papadopoulos and Hill 2002, Boonstra and Tjeerdsma 2006, Hunt et al. 2018). Though this is an area of active research, most evidence suggests that moisture-exclusion leads to the initial inhibition of brown rot degradation in chemically modified wood (Ringman et al. 2014a). Moreover, because serious decay occurs when the moisture content (MC) of wood is higher than the fiber saturation point, which is typically around 30%, effective chemical modification should aim to lower the cell wall MC below this level.

Chemically modifying the hydroxyls of lignocellulosic materials with epoxides can improve moisture and biological resistance (Hill 2006). The generalized reaction of epoxides with wood hydroxyl groups is:



After the initial reaction with a cell wall hydroxyl group to form an ether linkage, a new hydroxyl group originating from the epoxide is formed. In principle, this new hydroxyl group would enable subsequent chemical modifications to tailor the wood properties for specific applications (Rowell 2013).

Epoxides such as butylene oxide (BO) and propylene oxide (PO) have been used to modify forest products and improve their durability. Southern pine wood modified with over 20% weight percentage gain (WPG) of BO showed good resistance to brown and white-rot fungi, whereas similar levels of PO did not improve resistance to the brown-rot fungus, *G.trabeum* (Nilsson and Rowell 1982, Rowell and Ellis 1984a, and 1984b). Likewise, studies on southern pine solid wood modified with PO and BO, have shown that BO lowered the equilibrium moisture content (EMC) and was biologically effective, but PO was not effective in lowering the EMC nor in protecting the wood against *G.trabeum* (Ibach and Rowell 2000). This exception of PO is perhaps the key to understanding the mechanism of the resistance to attack by fungi by chemical modification. Interestingly, the EMC of PO modified wood was higher than the other modified wood, and this may be the reason for the lower biological resistance (Ibach et al. 2000).

This paper looks at the use of epoxybutene (EpB) to modify the hydroxyls of wood (Fig 1).

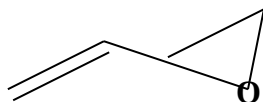


Figure 1. Chemical structure of Epoxybutene (EpB)

EpB was chosen as a new chemical modification system for wood. It is similar to BO, but imparts new chemistries because of the C=C double bond. Based on previous studies on wood modified with BO, it is expected that EpB may impart decay resistance by lowering the EMC of the wood cell wall, however, it is unclear how the modification will alter the wood cell wall structure (Ibach and Rowell 2000, Ibach et al. 2000). Given that neutron scattering studies have revealed that chemical modification meant to improve durability of wood must address moisture-induced nanostructural changes, particularly those at the cellulose elementary fibril level, it is vital to study

the effect of EpB modification in the wood nanostructure to learn about the mechanisms behind its efficacy (Plaza et al. 2016, Plaza 2017).

X-ray scattering methods such as wide-angle x-ray scattering (WAXS) and small-angle x-ray scattering (SAXS) are well-suited to provide insights on the effects of EpB modification on the wood cell wall nanostructure. Both WAXS and SAXS have been used extensively to study changes in nanostructure of lignocellulosic materials (Xu et al. 2013). WAXS has been used to measure changes in the cellulose crystalline lattice due to moisture uptake in wood (Zabler et al. 2010), and is routinely used to measure cellulose crystallinity and even the orientation of cellulose microfibrils (Xu et al. 2013, Donaldson 2008). While, SAXS has been used to study the distribution of microfibril angles in wood cell walls. (Reiterer et al. 1998, Lichtenegger et al. 2001, and Donaldson 2008).

This paper examines the correlation between EMC and biological resistance of southern pine solid wood chemically modified with different levels of epoxybutene (EpB). The overall aim of the research was to determine if EpB is a suitable new chemical modification system for wood, capable of providing fungal decay resistance. Furthermore, a combination of WAXS and SAXS studies was used to assess changes in the wood cell wall nanostructure as a function of EpB WPG, and gain insights on the mechanisms behind the efficacy of the treatment.

2. EXPERIMENTAL METHODS

Southern pine solid wood specimens were cut to the following dimensions: 2.54 radial x 2.54 tangential x 0.64 cm longitudinal. These dimensions are generally used in dimensional stability tests (Ellis and O'Dell 1999). Epoxybutene was from Eastman Chemical Company (Kingsport, TN). Triethylamine was from Sigma-Aldrich Chemical Company (Milwaukee, WI). The reactions were done in a stainless steel reaction vessel (Parr Instrument Company, Moline, IL).

2.1 Chemical Modification

The solid wood was oven dried at 105 °C for 24 hours in a forced draft oven and weighed prior to reaction with EpB. The vessel was loaded with the specimens, the epoxide (EpB), and the catalyst, triethylamine (TEA) (95:5 (vol:vol)). The vessel was flushed with dry nitrogen to remove air and moisture. The temperature was raised gradually to 120 °C and then the vessel was pressurized to 150 psi and held for various times (Rowell and Gutzmer 1975, Rowell and Ellis 1984b). The reaction times (up to 6 hours) were measured from the point of reaching the reaction temperature until the vessel was put in cold water to cool it and its contents. The treating solution was drained off. Specimens were air dried under a fume hood overnight prior to oven drying at 105 °C for 24 hours. The weight percent gains (WPG) were calculated from the dried weights.

2.2 Leaching and Extraction

Selected specimens were either water leached for 14 days (AWPA 1999) or extracted in a soxhlet extractor using toluene:ethanol (2:1, (vol:vol)) for 2 hours. WPG was calculated for unleached, water leached, and solvent extracted specimens.

2.3 Equilibrium Moisture Content (EMC)

EMC of unmodified control and modified wood specimens was determined by placing weighed, oven dried specimens in constant humidity rooms at 30%, 65%, or 90% relative humidity (RH) and 27 °C. After 14 days, specimens were reweighed until stable and the EMC was determined. Six replicates of each WPG level were run and averaged.

2.4 Biological Efficacy

The ASTM D 1413 standard soil block test was performed on the oven dried solid wood specimens (ASTM 1999). Five soil bottles each of unmodified controls and EpB modified specimens of southern pine solid wood specimens were exposed to the brown-rot fungus *Gloeophyllum trabeum*. Two soil bottles each with no fungus were run to monitor leaching of any chemicals. The solid wood specimens were removed from test following the standard 12 weeks. The extent of decay was determined as oven dry weight loss.

2.5 Sample preparation for WAXS and SAXS

One individual wood block from each level (Control, 5% EpB, 14% EpB and 30% EpB WPG) was soaked in water for an hour to ease cutting. Then, the blocks were cleaved perpendicular to the grain to reveal a longitudinal surface. Thin sections (300 micron thick) were then microtomed along these surfaces using a sledge microtome. The samples were held flat using glass slides and allowed to air dry for over 24 hours prior to data collection.

2.5.1 WAXS

Wide-angle x-ray diffraction data were collected in transmission mode using the Bruker (Billerica, MA, USA) D8 diffractometer at the Materials Science Center at the University of Wisconsin-Madison. A Cu-K α micro x-ray source ($\lambda = 1.5418 \text{ \AA}$) collimated with a 0.5 mm diameter aperture was used. The instrument is equipped with a VANTEC500 detector, with an array of 2048 by 2048 pixels, each with a size of 68 μm by 68 μm . The sample to detector distance used was 100 mm, and the exposure time for each measurement was 300 s. Silver behenate was used to calibrate the sample-detector distance. The relative humidity (RH) of the room was monitored during the measurements using a Sensirion (AG, Switzerland) SHT31 humidity sensor to ensure that all measurements were taken at the same RH. The 2D data was corrected for background contributions and then, anisotropically reduced using NIKA (Ilavsky 2012) to obtain the equatorial intensity profiles.

2.5.2 SAXS

Small angle x-ray scattering data were collected using a Rigaku (Auburn Hills, MI, USA) system with Cu-K α radiation source ($\lambda = 1.5418 \text{ \AA}$), and a 1mm x 1mm beam spot size. The sample to detector distance was 2 m, and the exposure time per measurement was 300 s. All measurements were taken at room temperature, and under vacuum to reduce air scattering contributions. First, silver behenate was used to calibrate the sample to detector distance. Then, the data was corrected for background contributions (i.e. parasitic scattering from the holder), and then azimuthally averaged in NIKA (Ilavsky 2012).

3. RESULTS AND DISCUSSION

3.1 Chemical Modification

Table 1 shows the conditions, time to reach reaction temperature, and reaction time for EpB modified solid wood. The reaction times of EpB were run up to a maximum of 6 hours.

3.2 Leaching and Extraction

Table 1 also shows the WPG before and after either water leaching or 2-hour toluene:ethanol extraction of the unmodified and EpB modified solid wood. There was weight loss from leaching and extraction with EpB. This indicates there may be unreacted epoxide left or soluble homopolymers were formed, especially during the heating period.

Table 1. Weight percent gain of EpB modified solid wood before and after water leaching and toluene:ethanol (2:1) extraction. Average values and standard deviations are reported in the table.

Epoxybutene					
	Time to reach reaction temp. To 120 °C [min.]	Reaction Time [hr.]	Unleached [WPG]	Water Leached [WPG]	Tol:Eth (2:1) Extracted [WPG]
Solid Wood	Control	0	0	-1.0 +/- 0.1	0.0 +/- 0.3
5 % TEA	13	1	10.0 +/- 1.4	5.7 +/- 0.8	7.3 +/- 1.7
150 psi	40	2	17.9 +/- 1.4	13.8 +/- 1.1	15.3 +/- 0.9
	40	6	38.5 +/- 2.8	32.3 +/- 2.6	29.7 +/- 1.9

3.3 EMC and Biological Efficacy

When analyzing biological efficacy with the soil block test, samples with <5% weight loss are considered a success. Weight losses in excess of 5% but less than 30% are considered a partial success and indicate a trend. Over 30% weight loss is a failure.

Table 2 shows the average EMC and weight loss of unmodified control and EpB modified solid wood. The EpB unleached solid wood shows marginal biological effectiveness (7.8+/-7.6% weight loss) with 18% WPG, but effectiveness at the highest WPG of 38% (2.9+/-0.3% weight loss). In the EpB leached and extracted solid wood, there is biological effectiveness (<3.9+/-2.2% weight loss) at the two highest levels (2 and 6 hour reaction times; leached 14 and 32 WPG, extracted 15 and 30 WPG). The biological resistance of EpB modified wood increased as the EMC decreased. This indicates that the mechanism of biological effectiveness is by moisture exclusion.

Table 2. Average EMC at 30, 65, and 90% relative humidity (RH) and weight loss (*G.trabeum*) of EpB chemically modified southern pine solid wood. Standard deviations of fungal weight loss are also shown.

Epoxybutene	Reaction time [hr]	WPG	30%RH	65%RH	90%RH	Wt. Loss [%]
UL C	0	0	5.7	10.6	16.3	64.6 +/- 3.2
UL	1	10	3.2	7.0	12.4	29.5 +/- 2.4
UL	2	18	2.5	5.9	10.9	7.8 +/- 7.6
UL	6	38	1.7	4.3	8.6	2.9 +/- 0.3
LC	0	-1.0	5.7	10.6	16.9	61.4 +/- 3.1
L	1	6	4.2	8.6	14.0	28.6 +/- 8.1
L	2	14	3.4	7.2	12.3	2.6 +/- 1.8
L	6	32	2.3	5.5	9.8	-0.4 +/- 0.0
EC	0	0	5.1	9.5	15.1	65.9 +/- 2.0
E	1	7	3.8	7.6	12.8	38.5 +/- 9.4
E	2	15	2.9	6.3	11.2	3.9 +/- 2.2
E	6	30	2.2	5.1	9.4	0.9 +/- 0.5

C = control, UL = unleached, L = water leached, E = toluene:ethanol (2:1) extracted

3.4 WAXS

Scattering from the crystalline cellulose in wood gives rise to the diffraction peaks typically observed in the 2D WAXS patterns from wood. A typical WAXS pattern showing the major diffraction peaks that were observable within the angular range available in this study is shown in Fig 2. The effects of modification on the reduced equatorial intensity profiles are shown in Fig 3.

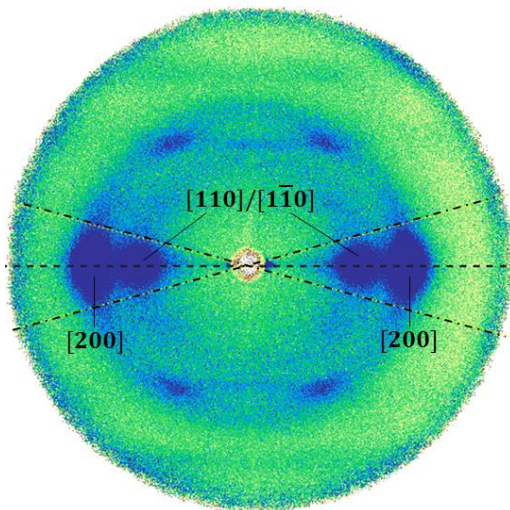


Figure 2. Typical diffraction pattern of unmodified wood. The major diffraction peaks from cellulose are indexed in the image.

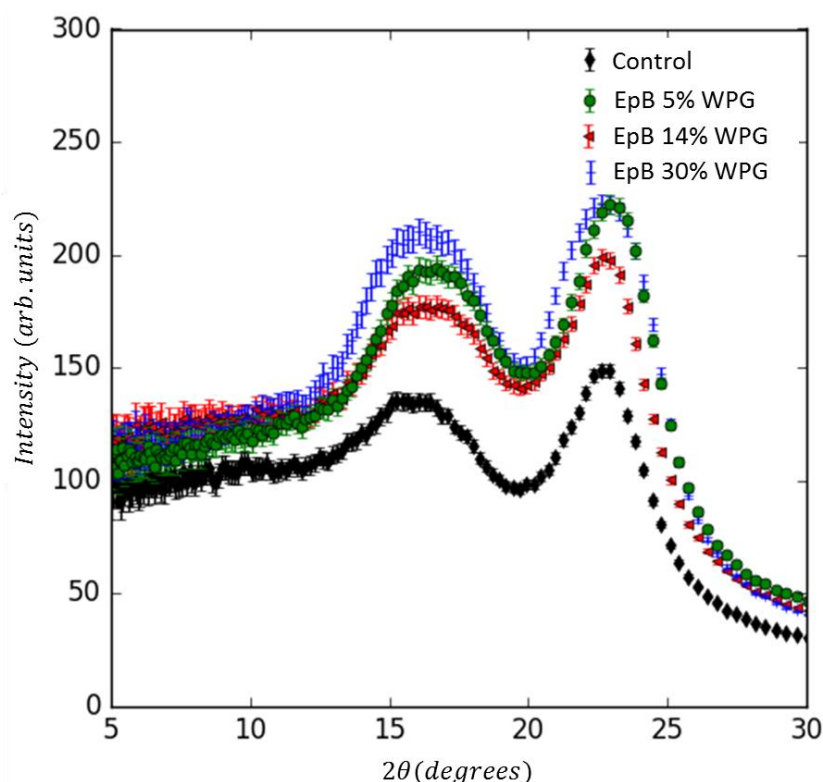


Figure 3. Equatorial intensity profiles obtained from WAXS of microtomed wood sections with different levels of epoxide modification.

To quantify any changes caused by the modification, each curve was fitted to a model that includes a cubic background (B), and three Pseudo-Voigt (PV) peaks (Eq 1).

$$I(2\theta) = B + PV_{110}(2\theta, A_1, \theta_{10}, \sigma_1,) + PV_{1\bar{1}0}(2\theta, A_2, \theta_{20}, \sigma_2,) + PV_{200}(2\theta, A_3, \theta_{30}, \sigma_3,) \quad (1)$$

Here, each PV peak function is a weighted sum of a Gaussian and Lorentzian distribution, (Eq 2) and is defined in terms of the following parameters: amplitude (A), peak position ($2\theta_{i0}$), width (σ_i) and a fraction (α) that controls the relative fraction of the Lorentzian and Gaussian components.

$$PV_i(2\theta, A_i, 2\theta_{i0}, \sigma_i, \alpha_i) = \frac{(1-\alpha_i)A_i}{\sigma_g\sqrt{2\pi}} e^{\left[-\frac{(2\theta-2\theta_{i0})^2}{2\sigma_g^2}\right]} + \frac{\alpha_i A_i}{\pi} \left[\frac{\sigma_i}{(2\theta-2\theta_{i0})^2 + \sigma_i^2} \right]; \text{ where } \sigma_g = \frac{\sigma_i}{\sqrt{2\ln 2}} \quad (2)$$

The data was fitted in Python using the numpy and lmfit (Newville et al. 2014) libraries. An example of the equatorial intensity profile and the fit are shown in Fig 4.

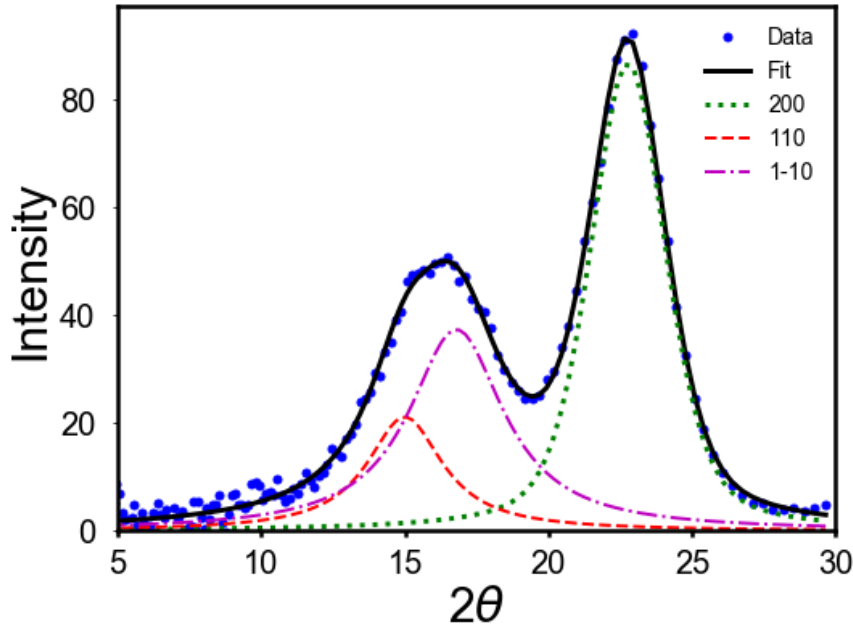


Figure 4. Intensity profile from unmodified wood showing the background subtracted data, fit and deconvolution of the peaks.

The measured peak positions were then used to calculate the Iβ cellulose monoclinic crystalline lattice parameters a , b and γ as outlined by Zabler and co-workers (Zabler et al. 2010). First, the peak positions were written in terms of their reciprocal space vector q according to Bragg's law (eq. 3):

$$q = \frac{4\pi \sin\theta}{\lambda} \quad (3)$$

Then, the following coupled non-linear equations were solved in a closed loop in Python using numpy to solve for all variables, namely, a , b and γ using the peak positions. Note that the peak position of the 200 peak was used to solve for the a -spacing (eq. 4), while the peak positions and spacing between the doublets (110) and ($1\bar{1}0$) were used to solve for the b -spacing and γ , respectively (eq. 5 - 6).

$$a = \frac{4\pi}{\sin\gamma \cdot q_{200}} \quad (4)$$

$$\frac{|q_{1\bar{1}0}| + |q_{110}|}{2} \approx \frac{2\pi\sqrt{a^2+b^2}}{ab\sin(\gamma)} \quad (5)$$

$$|q_{1\bar{1}0}| - |q_{110}| \approx -\frac{4\pi \cot(\gamma)}{\sqrt{a^2+b^2}} \quad (6)$$

The measured lattice parameters are listed in Table 3.

Table 3 Average cellulose crystalline lattice parameters obtained from fitting the WAXS equatorial intensity profiles. Standard deviation of the calculations is also shown.

Sample	a [nm]	b [nm]	γ [°]
Control	0.777 +/- 0.003	0.825 +/- 0.03	94.1 +/- 0.7
EpB 5% WPG	0.781 +/- 0.007	0.844 +/- 0.07	93.9 +/- 0.6
EpB 14% WPG	0.790 +/- 0.020	0.804 +/- 0.03	93.7 +/- 0.2
EpB 30% WPG	0.775 +/- 0.002	0.831 +/- 0.06	94.6 +/- 1.5

*WPG = weight gain percentage

3.4.1 WAXS Discussion

Preliminary results suggest that epoxide modification with EpB does not significantly affect the crystalline lattice parameters. The small changes measured in this study do not seem to be reproducible. This is an interesting result because previous studies have shown that moisture-uptake causes deformation of the cellulose crystallites likely due to some pressure being exerted by the swelling of the water-accessible wood polymers. (Zabler et al. 2010, Abe and Yamamoto 2006), Given that the EpB modification lowered the EMC of the wood samples one could have expected differences to arise in the swelling behaviour of the wood nanostructure, including the cellulose crystalline lattice. Thus, to minimize changes caused by variation in environment conditions, all measurements were performed at the same room conditions (20% RH, 20 °C). At this low humidity condition, differences between the moisture content of the samples should be minimal, and therefore, are not expected to affect our results. Nevertheless, future experiments where all the samples are conditioned to the same moisture content prior to the measurements would ensure that any changes measured are not caused by differences in moisture-content. Future studies where samples are measured after being conditioned to a high level of MC would be of particular interest to determine whether the overall deformation of the cellulose crystallites caused by moisture-uptake has been reduced due to the EpB modification. Additionally, since in this study only water leached samples were tested in order to avoid measuring changes in the patterns due to residues from the chemical modification, the effects of leaching will be explored in future studies by measuring both unleached samples and samples extracted with toluene.

3.5 SAXS

Scattering from the highly aligned cellulose microfibrils in the wood cell walls give rise to anisotropic scattering. A typical scattering pattern from unmodified wood is observed in Fig 5a. The effect of epoxide modification on the anisotropy of the scattering is shown in Fig 5b-c.

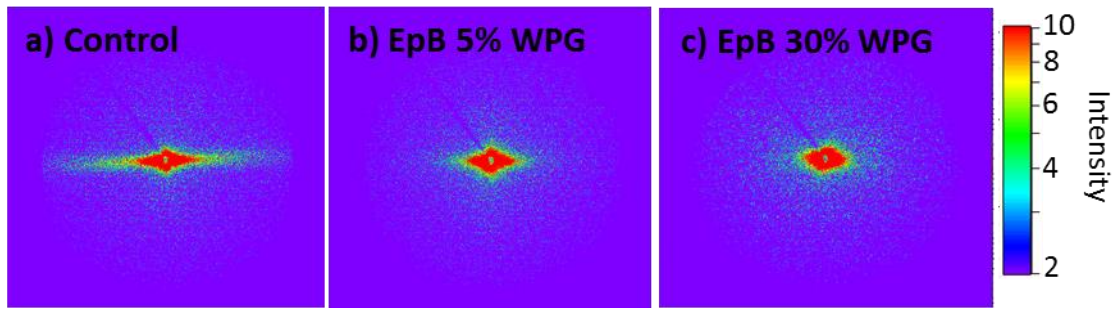


Figure 5. Effects of epoxide modification on the 2D SAXS anisotropic scattering patterns from wood. Patterns correspond to (a) unmodified wood, and wood modified with (b) EpB 5% WPG and (c) EpB 30%WPG.

These patterns were then reduced using the area shown in Fig 6 to obtain the azimuthal intensity profiles, and quantify changes in the microfibril angle distribution. The q -range of integration for all samples was from $0.0025 \text{ \AA}^{-1}$ to $0.023 \text{ \AA}^{-1}$. The azimuthal angle Φ range was 0° to 360° .

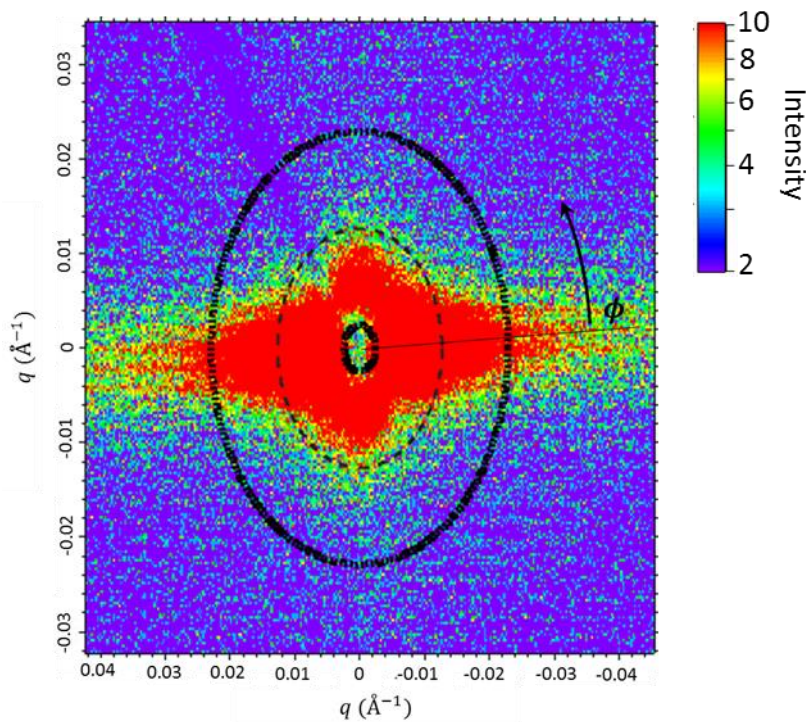


Figure 6. Typical area of integration used to obtain the azimuthal intensity profiles.

The effect of the epoxide modification on the azimuthal intensity profiles is shown in Fig 7.

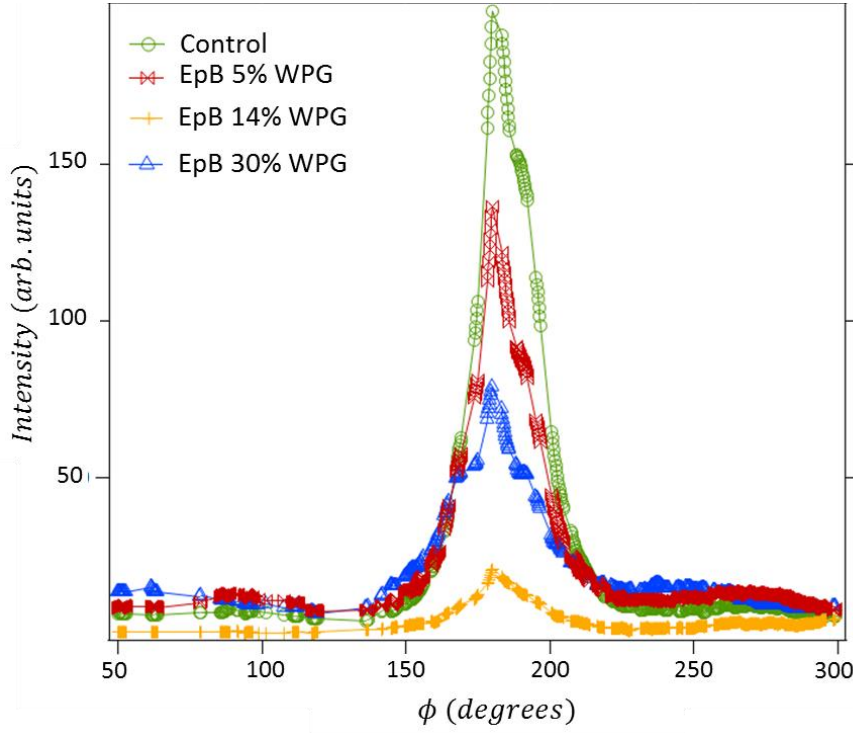


Figure 7. Effects of EpB modification on azimuthal intensity profiles.

3.5.1 Determination of the cellulose microfibril angle (MFA)

Since the data was collected on wood samples whose tracheid longitudinal axis was perpendicular to the incident beam, the orientation of the streak on the detector can be used to measure the microfibril angle (MFA). In this geometry, scattering from rectangular cells gives rise to three streaks: one oriented at $\phi = 0$ and two at $\phi = \pm MFA$.

Hence, to determine the MFA, the azimuthal intensity profiles were fitted to a model with a linear background and three Lorentzian peaks (Eq. 7) (Lichtenegger et al. 2001).

$$I(\phi) = B + L_1(\phi) + L_2(\phi) + L_3(\phi) \quad (7)$$

Each Lorentzian (L) is written in terms of its width (w), area (A) and peak position (ϕ_0) (Eq. 8).

$$L_i(\phi) = \left(2 * \frac{w}{\pi}\right) * \left(\frac{A}{4 * ((\phi - \phi_0)^2 + A^2)}\right) \quad (8)$$

A Lorentzian peak shape was selected because of its ability to fully capture the data with the least number of variables. All data were fitted using the Multi-peak fitting tool in IgorPro8 (Wavemetrics, Lake Oswego, OR, USA).

An example of the fitted profile is shown in Fig. 8. In this case, the central peak position occurs at $\phi = 180$ instead of $\phi = 0$, nevertheless, the other two peak positions occur at $\phi = \pm MFA$. The MFA reported is an average of these two peak positions.

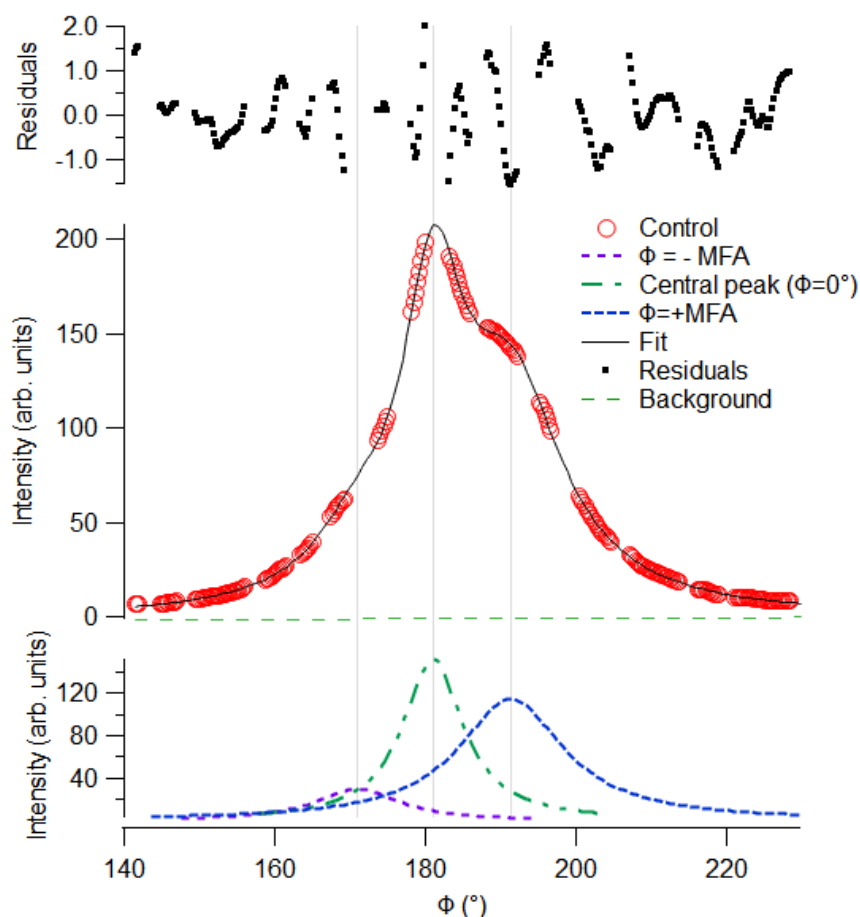


Figure 8. Example of fitting of the SAXS azimuthal profile, showing data, fit, deconvolution of the peaks, background and random residuals.

To quantify the broadening of the distribution the full width half maximum (FWHM) of the peaks were also calculated. Average MFA and FWHM values obtained are listed in Table 4.

Table 4. Results obtained from Lorentzian fitting of the SAXS azimuthal profiles. Average MFA and FWHM results as well as the standard deviation of the measurements are shown.

Sample	MFA (degrees)	FWHM (degrees)
Control	10.2 +/- 0.23	13.4 +/- 3.7
EpB 5% WPG	10.2 +/- 0.34	14.3 +/- 4.8
EpB 14% WPG	8.3 +/- 2.43	15.4 +/- 9.9
EpB 30% WPG	11.1 +/- 0.43	16.2 +/- 7.3

3.5.2 SAXS Discussion:

Preliminary SAXS 2D patterns revealed that epoxide modification decreased the overall alignment and anisotropic scattering from the samples. The anisotropic scattering extends farther in the q -range space compared to even low additions of epoxide, which would indicate that the epoxide modification is decreasing the long-range order of the microfibril alignment and/or the effective size of the microfibril. Interestingly, however, further analysis of the azimuthal intensity profiles showed that the average MFA did not change as a function of EpB WPG. While the increased peak broadening observed suggests that the polydispersity of the microfibril alignment increased with epoxide modification. The overall decrease in the intensity and sharpness of the anisotropic scattering features shown in figure 5, also supports that epoxide modification is broadening the

microfibril angle distribution. This would suggest that the modification targets regions outside the microfibrils. Increased number of replicates could further confirm these preliminary results. Further experimentation with thinner sections obtained from a single growth ring where we measure the microfibril angle before and after modification could further confirm the effect of epoxide modification on the microfibril angle distribution. Last but not least, the use of different integration areas in the analysis will also be explored. While we do not expect that varying the area of integration will affect the measurement of the MFA, here to improve statistics the azimuthal q-range of integration was held fixed for all samples, and perhaps increasing the range would reveal that the effect of modification in the broadening of the peaks is more drastic.

4. CONCLUSIONS

Chemical modification of solid wood with EpB showed a correlation between the EMC and fungal resistance which followed the moisture exclusion mechanism. Biological resistance increased with decreasing EMC, suggesting the mechanism of effectiveness is due to lowering of the cell wall moisture content. Biological effectiveness was found at both 18% and 38% WPG of EpB.

WAXS results revealed that epoxide modification did not significantly affect the cellulose crystalline structure, and as a result the cellulose crystalline lattice parameters remained unchanged as a function of epoxide modification. Whereas, SAXS results showed that epoxide modification led to increased polydispersity in the microfibril alignment, which indicated that the modification is likely targeting wood polymers outside the cellulose microfibrils. However, since the microfibril angle can change between growth rings further experimentation where the microfibril angle is measured before and after modification would confirm that the broadening observed is only caused by the modification.

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6. REFERENCES

- Abe, K. and Yamamoto, H. (2006) Change in mechanical interaction between cellulose microfibril and matrix substance in wood cell wall induced by hygrothermal treatment. *J. Wood Sci.* **52**, 107–110.
- ASTM. (1999) ASTM Standard Method of Testing Wood Preservatives by Laboratory Soil-Block Cultures. *American Society for Testing and Materials Des.* **D 1413**.
- Arantes, V. & Goodell, B. (2014) Current Understanding of Brown-Rot Fungal Biodegradation Mechanisms: A Review. *Deterior. Prot. Sustain. Biomater.* 3–21. doi:10.1021/bk-2014-1158.ch001
- AWPA. (1999) E11-97 Standard Method of Determining the Leachability of Wood Preservatives. *American Wood Preservers' Association Book of Standards*: 386-388.
- Boonstra, M.J., Tjeerdsma, B. (2006) Chemical analysis of heat treated softwoods. *Holz als Roh-Werkst.* **64**, 204–211.

- Donaldson, L. (2008) Microfibril angle: Measurement, variation and relationships - A review. *IAWA J.* **29**, 345–386.
- Ellis, W.D. and O'Dell, J.L. (1999) Wood-polymer composites made with acrylic monomers, isocyanate, and maleic anhydride. *Journal of Polymer Science.* **73**, 2493-2505.
- Hill, C. (2006) *Wood Modification: Chemical, Thermal and Other Processes*. Chapter 4: Chemical Modification of Wood (II): Reaction with Other Chemicals. pp. 77-97. West Sussex, England, John Wiley & Sons, Ltd.
- Hill, C.A.S., Forster, S.C., Farahani, M.R.M., Hale, M.D.C., Ormondroyd, G.A., Williams, G.R., (2005) An investigation of cell wall micropore blocking as a possible mechanism for the decay resistance of anhydride modified wood. *International Biodeterioration & Biodegradation.* **55**, 69-76.
- Hunt, C.G., Zelinka, S.L., Frihart, C.R., Lorenz, L., Yelle, D., Gleber, S-C., Vogt, S., Jakes, J.E. (2018) Acetylation increases relative humidity threshold for ion transport in wood cell walls – A means to understanding decay resistance. *International Biodeterioration & Biodegradation.* **133**, 230-237
- Ibach, R. E. and Rowell, R. M. (2000) Improvements in decay resistance based on moisture exclusion. *Molecular Crystals and Liquid Crystals.* **353**: 23-33.
- Ibach, R. E., Rowell, R. M. and Lee, B.-G. (2000) Decay Protection Based on Moisture Exclusion Resulting From Chemical Modification of Wood. *5th Pacific Rim Bio-Based Composites Symposium*, Canberra, Australia: 197-204.
- Ilavsky, J. (2012) Nika: Software for two-dimensional data reduction. *J. Appl. Crystallogr.* **45**, 324–328.
- Lichtenegger, H. C.; Reiterer, A.; Stanzl-Tschegg, S. E.; Fratzl, P. (2001) Comment about “ The measurement of the micro-fibril angle in soft-wood ” by K. M. Entwistle and N. J. Terrill. *J. Mater. Sci. Lett.* **20**, 2245–2247.
- Newville, M., Stensitzki, T., Allen, D. B., and Ingargiola, A. (2014) LMFIT: Non-Linear Least-Square Minimization and Curve-Fitting for Python. *Zenodo*. doi:10.5281/zenodo.11813
- Nilsson, T. and Rowell, R. M. (1982) Decay patterns observed in butylene oxide modified ponderosa pine after exposure in unsterile soil. *The International Journal of Wood Preservation.* **2**(3): 119-121.
- Plaza, N. Z., Pingali, S. V., Qian, S., Heller, W. T. & Jakes, J. E. (2016) Informing the improvement of forest products durability using small angle neutron scattering. *Cellulose* **23**, 1593–1607.
- Plaza, N. Z. (2017) Neutron Scattering Studies of Nano-Scale Wood-Water Interactions. (*Thesis*: University of Wisconsin-Madison, 2017).
- Papadopoulos, A.N., Hill, C.A.S. (2002) The biological effectiveness of wood modified with linear chain carboxylic acid anhydrides against *Coniophora puteana*. *Holz als Roh- Werkst.* **60**, 329–332
- Reiterer, A., Jakob, H. F., Stanzl-Tschegg, S. E. & Fratzl, P. (1998) Spiral angle of elementary cellulose fibrils in cell walls of *Picea abies* determined by small-angle x-ray scattering. *Wood Sci. Technol.* **32**, 335–345.
- Ringman, R., Pilgård, A., Alfredsen, G., Goodell, B., Richter, K. (2014a) Possible targets of wood modification in brown rot degradation. In International Research Group on Wood Protection 45th Annual Meeting IRG/WP 14-40676, pp. 1-13
- Ringman, R., Pilgård, A., Brischke, C., Richter, K. (2014b) Mode of action of brown rot decay resistance in modified wood: a review. *Holzforschung.* **68**, 239–246.
- Rowell, R. M. (2013) *Handbook of Wood Chemistry and Wood Composites* (Second Edition). Chapter 15: Chemical Modification of Wood. pp. 537-597. Boca Raton, FL, CRC Press, Taylor and Francis Group.

- Rowell, R. M. and Ellis, W. D (1984a) Effects of Moisture on the Chemical Modification of Wood with Epoxides and Isocyanates. *Wood and Fiber Science*. **16**(2): 257-267.
- Rowell, R. M. and Ellis, W. D. (1984b) Reaction of epoxides with wood. Madison, Wisconsin, *Forest Products Laboratory Report* 451.
- Rowell, R. M. and Gutzmer, D. I. (1975) Chemical Modification of Wood: Reactions of Alkylene Oxides with Southern Yellow Pine. *Wood Science* **7**(3): 240-246.
- Rowell, R.M., Ibach, R.E. (2018) Stable and durable wood products based on molecular modification. *Journal of Tropical Forest Science*, **30**(5), 488-495. <https://www.jstor.org/stable/26514440>.
- Rowell, R.M., Ibach, R.E., McSweeney, J., Nilsson, T. (2009) Understanding decay resistance, dimensional stability and strength changes in heat-treated and acetylated wood. *Wood Material Science & Engineering*. **4**, 14–22.
- Xu, F., Shi, Y.-C. & Wang, D. (2013) X-ray scattering studies of lignocellulosic biomass: A review. *Carbohydr. Polym.* **94**, 904–917.
- Zabler, S., Paris, O., Burgert, I. & Fratzl, P. (2010) Moisture changes in the plant cell wall force cellulose crystallites to deform. *J. Struct. Biol.* **171**, 133–141.