The effect of hemicellulose degradation on the mechanical properties of wood during brown rot decay

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The effect of hemicellulose degradation on the mechanical properties of wood during brown rot decay.

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Abstract

Incipient decay of wood by brown rot fungi causes measurable strength losses in wood before measurable weight loss occurs. Previous studies have shown that the high levels of strength loss that occur during incipient brown rot decay may be related to loss in hemicellulose. This paper investigates the effect of decay on hemicellulose composition and the relationship to the mechanical properties of the wood. An in vitro test method was used to allow progressive sampling of southern pine exposed to monocultures of a brown rot fungi. The wood was subsequently analysed by mechanical testing and chemical analysis. The results demonstrated a ratio of strength to weight loss of approximately 4:1. The chemical data indicated that early strength loss (up to 40%) was associated with loss of arabinan and galactan components. Subsequent strength loss (above 40%) was associated with the loss of the mannan and xylan components. Significant loss of glucan (representing cellulose) was only detected above 75% MOR loss.

Keywords: Brown rot decay, hemicellulose, bending strength

Introduction

During incipient decay of wood by brown rot fungi, changes in the chemical composition of wood results in measurable reductions in strength before measurable weight loss (Schmidt, 1978; Wilcox, 1978; Imamura, 1993; Kim et al, 1996). Brown rot causing fungi degrade the polysaccharide components (cellulose and hemicellulose) by depolymerisation without extensive loss of lignin. The loss of polysaccharides is first seen in the S2 layer of the secondary cell wall (Kuo et al, 1988; Blanchette et al, 1990). This layer has a comparatively lower lignin concentration than the S1 and S3 layers, possibly making the polysaccharides more accessible to degradation (Daniel, 1994). The hemicellulose components are degraded first and since the cellulose microfibril may be surrounded by a hemicellulose envelope, this may be a critical stage during fungal degradation (Illman and Highley, 1989; Green and Highley, 1997). Previous studies (Winandy and Morrell, 1993; Curling et al, 2000) have demonstrated a relationship between the degradation of hemicellulose components, such as arabinose and mannose, and wood strength losses. The significant reduction in strength observed during incipient decay is therefore likely to be due to hemicellulose decomposition.

In softwoods there are two principal hemicelluloses: galacto-glucomannan (70% mannan), which makes up approximately 60% of the total hemicellulose content, and arabino-4-O-methylglucuronoxylan (65% xylan), which constitutes the remaining 40%. Thus the amount of galactose/mannan and arabinan/xylan can be used to estimate the quantities of the major and minor, respectively, hemicellulose component of the wall (Timell, 1967; Highley, 1987).
The relationship between the chemical composition and mechanical properties of wood was investigated using an in vitro fungal exposure method (Curling et al, 2000) to follow changes in strength properties, weight loss and chemical composition over the course of fungal colonisation and the decay process.

**Method**

*Preparation of wood specimens*
Air-dried southern pine (Pinus spp.) sapwood test specimens (dimensions 250mm long x 25mm tangential x 10mm radial) were prepared, clear of knots, damage or defects. A 50mm section was removed from the end of each test specimen to determine moisture content and estimate initial dry weight.

The test specimens were sterilised using ionising gamma irradiation at a dose of 2.51Mrad. The specimens were sealed lying flat, and separate from each other, into a polyethylene envelope.

*Test organism*
Monocultures of the brown rot fungus - Gloeophyllum trabeum (Pers.:Fr) Murrill (Mad 617) were grown in liquid Baileys minimal media + 0.5% cellobiose cultures (Sigma chemicals St Louis, MO) at pH 4.5, 25°C and 70% relative humidity (Highley, 1973).

*Biological exposure*
One litre of vermiculite (horticultural grade) (Scotts, Marysville, Ohio, USA) was placed into a lidded aluminium pan (33 x 23 x 82.5mm) so that the bottom of the pan was covered. The vermiculite was then formed into a ridge, approximately 70mm wide, running the length of the long axis. Deionised water was added to adjust the moisture content of the vermiculite to 75% of its water holding capacity (determined from 6 random samples of the media using the method described in ASTM D2017-91 (ASTM 1994)). The pans were then autoclaved at 103.4 kPa and 121°C for 45 minutes.

*Fungal exposure*
The fungal inoculum was macerated for 30 seconds in a blender and 100ml of the resulting suspension was applied to the vermiculite 3 days before sample insertion. Sterile (uninoculated) controls were also prepared. The wood specimens were aseptically inserted into the pans with the middle section resting on the ridge of vermiculite, so that neither end touched the surface of the medium. An overlay of moist vermiculite was used to cover the middle third of the specimens (67mm) to a depth of approximately 10 mm to maintain an elevated moisture content in the specimens and to confine the majority of fungal activity to the central third of the specimens. The moisture content of the vermiculite was adjusted to 50% of its WHC and sterilized by autoclaving prior to addition.

The specimens were placed, 8 per tray, in 2 sets (A and B). At each sampling time 1 specimen was removed from each of 8 trays. Specimen removal alternated between sets i.e. set A was used at sampling points 1, 3, 5 etc and set B at sampling times 2, 4, 6 etc. This gave 8 replicates at
each sampling time. The cultures were incubated at 25°C (80°F) and 70% relative humidity for 10 weeks.

![Figure 1. Fungal exposure method (M = medium, S = specimen, VO = vermiculite overlay)](image)

**Assessment of test**
At each sampling time the specimens were removed from the pans, cleaned of any adhering mycelium and weighed. The specimens were placed in a drying cabinet at 60°C for an hour to lower the moisture content of the specimens. The specimens were then allowed to equilibrate to constant weight at 23°C (74°F) and 65% relative humidity prior to mechanical testing. A four point bending test with the load applied at the third points to a span of 175mm and a loading rate of 1.25mm/min (Winandy and Morrell, 1993) was used to determine Modulus of Rupture (MOR) Modulus of Elasticity (MOE) and work to maximum load (WML) values for the specimens (Work to Maximum Load is a measure of the combined strength and toughness of the wood under bending stress). The data of each test specimen were compared to that of unexposed controls to determine the reduction in MOR, MOE and WML of each specimen.

Following the mechanical testing, two 15mm by full cross section blocks were cut from each specimen from within the decay zone near the point of mechanical failure. One block was oven dried, weighed and the loss in dry weight determined, based on an estimated original dry weight (derived from the dry weight of the 50 mm section removed prior to the decay test). The second block was ground to pass a 30 mesh (547 µm) screen. The ground material from each replicate within a sampling time set was combined. Replicate samples of this material was then analysed for carbohydrates using high-pressure liquid chromatography (HPLC) (Pettersen and Schwandt, 1991).

**Results**

**Mechanical properties**
The mean weight loss, MOR loss and loss in MOE of the specimens are compared in Figure 2. Proportionally, it appeared, that MOR loss occurred at a greater rate than MOE loss.
Figure 2. Comparison of brown rot induced bending strength (MOR), stiffness (MOE) and weight loss in southern pine (\(=\) MOE \(=\) MOR).

The loss in MOR, loss in WML, loss in MOE and loss in dry weight over time are given in Figure 3. The data shows that WML and MOR are the first properties degraded followed by MOE and finally weight. The comparative average rates of loss also vary as shown in table 1.

**Table 1 Mean rate of property loss**

<table>
<thead>
<tr>
<th>Property</th>
<th>Approximate Rate of loss(^1) (% per day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WML</td>
<td>3.6</td>
</tr>
<tr>
<td>MOR</td>
<td>1.6</td>
</tr>
<tr>
<td>MOE</td>
<td>0.6</td>
</tr>
<tr>
<td>Weight</td>
<td>0.4</td>
</tr>
</tbody>
</table>

\(^1\)Rate of loss is calculated from linear portion of graph i.e. 0 to 21 days, 0 to 72 days for MOR, 0 to 56 days for MOE and 21 to 72 days for weight.
Chemical composition
The data on the percentage loss of the hemicellulose components in relation to strength loss are shown in Figure 4. The percentage loss of each component was determined in relation to the mean value of the undecayed specimens. The data showed that arabinan and galactan are degraded first. Substantive loss of xylan and mannan begins at approximately 40% loss in MOR whilst loss in glucan does not occur until approximately 75 - 90% loss in MOR.

Figure 3. Effect of decay on weight loss and mechanical properties. ( = WML, = MOR, = MOE, = Weight)
Discussion

Mechanical properties and weight
The strength/weight loss data (Figure 2) demonstrated that considerable bending strength loss occurs before significant weight loss, as has been reported previously (Schmidt et al, 1978; Wilcox, 1978; Imamura, 1993; Kim et al, 1996). The relationship appears very consistent as decay initiates and progresses. The MOE data is less linear but does show that loss in MOE is not as rapid as the loss in MOR. The data (Figure 3) shows the relationship between weight and bending strength loss is not only qualitative but may also be quantitative. At weight loss values of below 5% strength loss was approximately 40% and the loss in the work required to failure was reduced by 70-80%. This highlights the fact that if decay is microscopically detectable [5-10% weight loss (Wilcox, 1978)] then the mechanical and hence engineering properties of the timber have been reduced considerably. Our data show that once weight loss began (after approximately 40% strength loss) the ratio in the comparative loss in mechanical properties compared to weight loss was 9:1 for WML, 4:1 for MOR and 1.5:1 for MOE, for southern pine sapwood exposed to G.trabeum (Figure 3).

Chemical composition
The data on loss of hemicellulose and cellulose components showed that the arabinan and galactan components were degraded first followed by the mannann and xylan after 40-60% strength loss was achieved. The glucan components (primarily 90% representing cellulose) was not measurably degraded until 80-90% strength loss was achieved. At 90-100% MOR loss the galactan and mannann showed the highest percentage loss.
The data demonstrates a relationship between chemical changes, i.e. the sequential carbohydrate degradation and loss in bending strength during incipient stages of decay. Significant loss in arabinan and galactan began almost as soon as strength loss and appeared to proceed in a linear fashion. Some loss in xylan and mannan did occur with this earliest stage of decay, but it appeared that significant decay only occurred after about 40% strength loss. Significant loss in glucan only occurred after about 80% strength loss. Again, at 90% strength loss the greatest percentage loss was seen in the galactan and mannan components suggesting selective degradation of the galacto-glucomannan component, which has been previously reported (Highley, 1987). It is possible that the cellulose and main chain hemicellulose components may be undergoing depolymerisation without disassociation. This area is the focus of further research. In previous studies (Sweet and Winandy, 1999) of thermally degraded wood in which similar patterns of chemical changes and strength loss were observed, no evidence of hemicellulose or cellulose depolymerisation was found. The arabinan and galactan are side chain elements of the xylan and mannan main polymers (Timell, 1967) (Figure 5) and may be either more vulnerable to degradation or may have to be removed before the main chain of the polymer can be attacked.

---4- D-Glup-1-4- D-Manp-1-4- D-Manp-1---

| D-Galp |

\[O\text{-acetyl-galacto-glucomannan}\]

---4- D-Xylp-1-4- D-Xylp-1-4- D-Xylp-1---

| L-Arap |

\[\text{Arabin-4-O-methylglucurono-xylan}\]

Figure 5. Representative structures of the 2 main hemicellulose components. \((\text{Glu} = \text{glucose, Man} = \text{mannose, Gal} = \text{galactose, Xyl} = \text{xylose, Ara} = \text{arabinose})\)

As decay progressed to the stages involving significant weight loss, chemical composition also changed characteristically. The start of significant loss in the mannan and xylan components correlated with the start of significant weight loss - both at approximately 40% loss in MOR. Because mannan/xylan components make up approximately 18% of the wood compared to 8% for the galactan/arabinan components (Highley, 1987) it is understandable why significant weight loss does not occur until mannan and xylan degradation has begun. The development of substantial weight loss occurs once the cellulose (represented by glucan) is broken down significantly at a MOR loss of over 80%. It is also at this stage (80% loss in MOR) that loss in MOE increases rapidly suggesting that the stiffness of the wood is related to the cellulose rather than the hemicellulose composition. From the data, three stages of decay can be suggested (Table 2). It should be noted that these stages of decay refer to the process once decay has been initiated, a process which is heavily dependent on a number of factors in wood in-service. This test optimised conditions and the results, whilst indicative of the process, should not be used to determine likelihood of failure.
Table 2. The effect of progressive degradation of wood carbohydrates, due to decay, on wood mechanical properties.

<table>
<thead>
<tr>
<th>Level of decay</th>
<th>Component degraded</th>
<th>Loss in WML</th>
<th>Loss in MOR</th>
<th>Loss in MOE</th>
<th>Weight loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>Incipient</td>
<td>Minor hemicelluloses (Galactan and Arabinan)</td>
<td>0 – 80%</td>
<td>0 – 40%</td>
<td>0 – 20%</td>
<td>&lt; 5%</td>
</tr>
<tr>
<td>Moderate</td>
<td>All hemicellulose (Galactan, Arabinan, Mannan and Xylan)</td>
<td>80 – 95%</td>
<td>40 – 80%</td>
<td>20 – 35%</td>
<td>5 – 20%</td>
</tr>
<tr>
<td>Advanced</td>
<td>All hemicellulose and cellulose (Glucan)</td>
<td>&gt; 95%</td>
<td>75 – 100%</td>
<td>&gt; 35%</td>
<td>&gt; 20%</td>
</tr>
</tbody>
</table>

Conclusions

During the decay of southern pine sapwood by *G. trabeum*, it can be concluded that:-

Measurable weight loss began after an approximate 40% loss in MOR, and occurred in a relative ratio of 4:1 bending strength/weight loss.

Initial strength loss without measurable weight loss was corresponded to loss in the galactan and arabinan hemicellulose components.

The start of significant weight loss corresponded to the start of significant loss in the mannan and xylan components.

Major weight loss and loss in stiffness (MOE) corresponded to loss in the glucan component.

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