RELATIONSHIPS BETWEEN MECHANICAL PROPERTIES, WEIGHT LOSS, AND CHEMICAL COMPOSITION OF WOOD DURING INCIPIENT 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 duringmay he related to loss in hemicellulose. This study investigates the effect of decay on hemicellulose composition and the relationship of decay 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 brown-rot fungi. The wood was subsequently analyzed by mechanical testing and chemical analysis. The results demonstrated a ratio of strength tu weight loss of approximately 4: I. The chemical data indicated that early strength loss (up to 40%) was associated with loss of arabinan and galactan components. Subsequent strength loss (greater than 40%) was associated with the loss of the mannan and xylan components. Significant loss of glucan (representing cellulose) was only detected at greater than 75 percent modulus of rupture loss.

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 (9,10,13,14,17), Brown-rot-causing fungi degrade the polysaccharide components (cellulose and hemicellulose) by depolymerization without extensive loss of lignin. The loss of polysaccharides is first seen in the S2 layer of the secondary cell wall (2,11). This layer has a comparatively lower lignin concentration than the S1 and S3 layers, possibly making the polysaccharides more accessible to degradation (4). The hemicellulose components are degraded first. and since the cellulose microfibril may he surrounded by a hemicellulose envelope. this may be a critical stage during fungal degradation (5,8). Previous studies (3,18) have demonstrated arelationship 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 he caused by hemicellulose decomposition.

In softwoods, there are two principal hemicelluloses: galacto-glucomannan (70% mannan), which makes up approximately 60 percent of the total hemicellulose content, and arabino-4-0-methylglucuronoxylan (65% xylan), which constitutes the remaining 40 percent. 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 (7,16).

The relationship between the chemical composition and mechanical properties of wood was investigated using an *in vitro* fungal exposure method (3) to follow changes in strength properties.

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Forest Prod. J. 52(7/8):34-39.

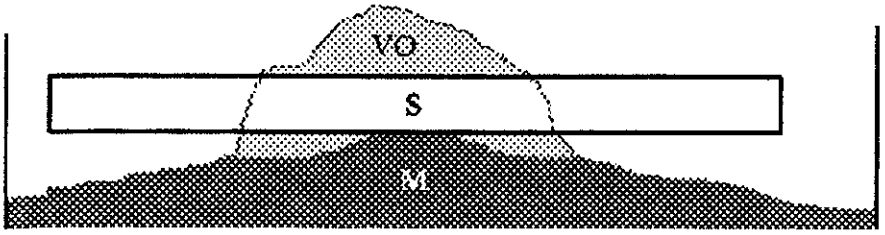

Figure 1 .—Fungal exposure method; M =medium: S =specimen; VO = vermiculite overlay.

weight loss, and chemical composition during the course of fungal colonization and the decay process.

METHODS

A preliminary study with wood specimens exposed to monocultures of two different brown-rot fungi for 12 weeks on three different types of media was carried out to generate differing levels of decay so that the relationship between strength loss. weight loss, and changes in chemical composition could be assessed.

The main study involved following the progression of decay. using one fungal species. from inoculation to advanced decay.

PRELIMINARY EXPERIMENT

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

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

Test organisms. — Monocultures of two brown-rot fungi, *Gloeophyllum trabeum* (Pers.:Fr) Murrill (Mad 617) and *Postia placenta* (Fr.) Cooke and Eriksson (Mad 698), were grown in liquid Baileys minimal media + 0.5 percent cellobiose cultures (Sigma Chemicals, St. Louis, Missouri) at pH 4.5, 25°C, and 70 percent relative humidity (RH) (6).

Biological exposure. — Three different substrates were used: soil (a silty loam topsoil), vermiculite (horticultural grade) (Scotts, Marysville, Ohio), and 70:30 vermiculite/soil mixture.

One liter of the substrate was placed into a lidded aluminium pan (33 by 23 by 82.5 mm) so that the bottom of the pan was covered. The medium was then formed into a ridge. approximately 70 mm wide, running the length of the long axis. Deionized water was added to adjust the moisture content (MC) of the medium to 100 percent of its water-holding capacity (WHC) (determined from six random samples of the medium using the method described in ASTM D 2017-94 (1)). 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 100 mL of the resulting suspension was applied to the substrate 3 days before sample insertion. Sterile (uninoculated) controls were also prepared. The wood specimens were aseptically inserted into the pans (eight per pan. two pans per medium-fungus-time point combination) with the middle section resting on the ridge of medium. so that neither end touched the medium surface (Fig. 1). An overlay of moist vermiculite was used to cover the middle third of the specimens (67 mm) to a depth of approximately 10 mm to maintain an elevated MC in the specimens and to confine the majority of fungal activity to the central third of the specimens. The MC of the vermiculite overlay was adjusted to 50 percent of its WHC and sterilized by autoclaving prior to addition. The cultures were incubated at 25°C and 70 percent RH for 6 and 12 weeks.

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 MC of the specimens, The specimens were then allowed to equilibrate to constant weight at 23°C and 65 percent RH prior to mechanical testing. A four-point bending test with the load applied at the third points to a span of 175 mm and a loading rate of 1.25 mm/min. (18) was used to determine modulus of rupture (MOR), modulus of elasticity (MOE). and work to maximum load (WML) values for the specimens (WML is a measure of the energy absorption or toughness of the wood under bending stress). Metal platens were placed beneath the load heads to spread the load and prevent compression. If compression did occur at the load points or if the sample broke outside of the central section (the expected zone of maximum bending moment), then the sample was discarded. The data of each test specimen were compared with that of unexposed controls to determine the reduction in MOR. MOE, and WML of each specimen.

Following the mechanical testing, two 15-mm 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 and weighed. and the loss in dry weight was 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 undried 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 were then analyzed for carbohydrates using high-pressure liquid chromatography (HPLC) (12).

PROGRESSIVE EFFECTS OF DECAY ON STRENGTH, WEIGHT, AND CHEMICAL COMPOSITION

The main study followed the progression of decay with time. The method used was the same as in the preliminary experiment except for the following points.

Only vermiculite, adjusted to 75 percent of its WHC, was used as the medium. *Gloeophyllum trabeum* was the only brown-rot fungus used. The wood specimens were aseptically inserted into the pans with the middle section resting on the ridge of media, so that neither end touched the surface of the medium. Sixteen trays were used, containing eight specimens per tray, in two sets (A and B). At each sampling time, one speci-

men was removed from each of the eight trays. Specimen removal alternated between sets, that is. set A was used at sampling times 1, 3, 5, etc., and set B at sampling times 2, 4, 6, etc. This gave eight replicates at each sampling time. The cultures were incubated at 25°C and 70 percent RH for a maximum period of 10 weeks with sampling twice per week for the first 6 weeks and once at week 8 and week 10.

RESULTS

PRELIMINARY EXPERIMENT

Decay progressed at different rates on the different media resulting in the wood being decayed to varying extents at the sampling times. Combining the data for the different media and time points gave results that could be used to examine the progression of decay. The mean weight loss of the specimens is compared with MOR loss and MOE loss in **Figures 2a** and **2b.** respectively. The data show that the relationship between weight loss and loss in MOR and MOE was approximately the same for both fungi tested. Proportionally, it appeared that MOR loss occurred at a greater rate than MOE loss. No strength (MOR) losses less than 40 percent for *G. trabeum* and 22 percent for *P. placenta* were obtained.

The percentage loss of the chemical constituent in relation to the percentage loss in MOR is shown in **Figures 3a** and **3b** for each fungus species. For both fungi. significant levels (greater than 5%) of arabinan and galactan were degraded at lower levels of MOR loss compared with xylan and mannan. where 5 percent loss occurred after approximately 40 percent MOR loss, and glucan, where 5 percent loss occurred after MOR loss above 75 percent.

PROGRESSIVE EFFECTS OF DECAY ON STRENGTH, WEIGHT, AND CHEMICAL COMPOSITION

The losses in MOR, WML, MOE, and dry weight are given in **Figure 4.** The data showed that the comparative average rates of loss vary between properties **(Table 1)** and that there is a lag between the start in loss of WML. MOR, and MOE and start in weight loss.

Figure 5 shows the percentage loss of the hemicellulose components in relation to strength loss (MOR). 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

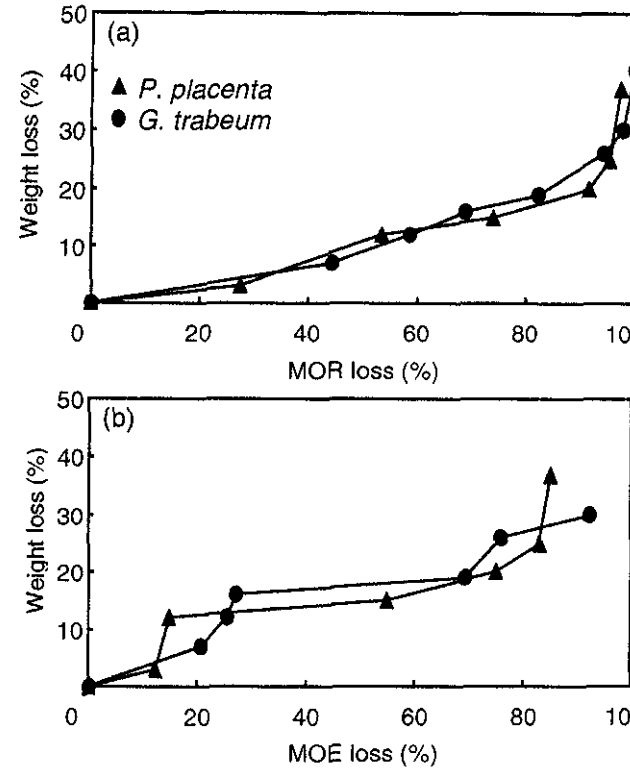

Figure 2. — Brown-rot-induced (a) bending strength (MOR) loss and (b) stiffness (MOE) loss compared with weight loss in southern pine.

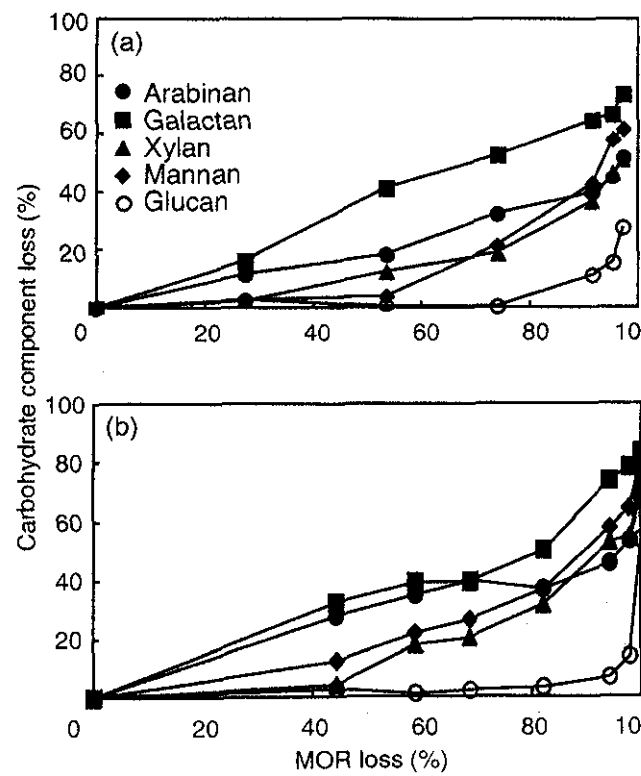

Figure 3. —Comparison of loss of carbohydrate components with loss in bending strength (MOR), caused by (a) *P. placenta* and (b) *G. trabeum.*

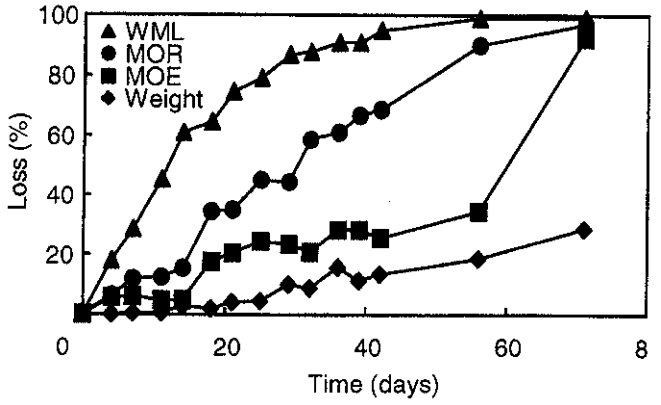

Figure 4.-Effect of decay on weight loss and mechanical properties

TABLE 1. —Mean rate of property loss.[a]

Property	Approximate rate of loss[b] (% per day)
WML	3.6
MOR	1.6
MOE	0.6
	0.4

[a] WML = work to maximum load: MOR = modulus of rupture: MOE = modulus of elasticity.

[b] Rate of loss is calculated from linear portion of Figure 4. that is, 0 to 2 I days for WML; 0 to 72 days for MOR; 0 to 56 days for MOE; and 21 to 72 days for weight.

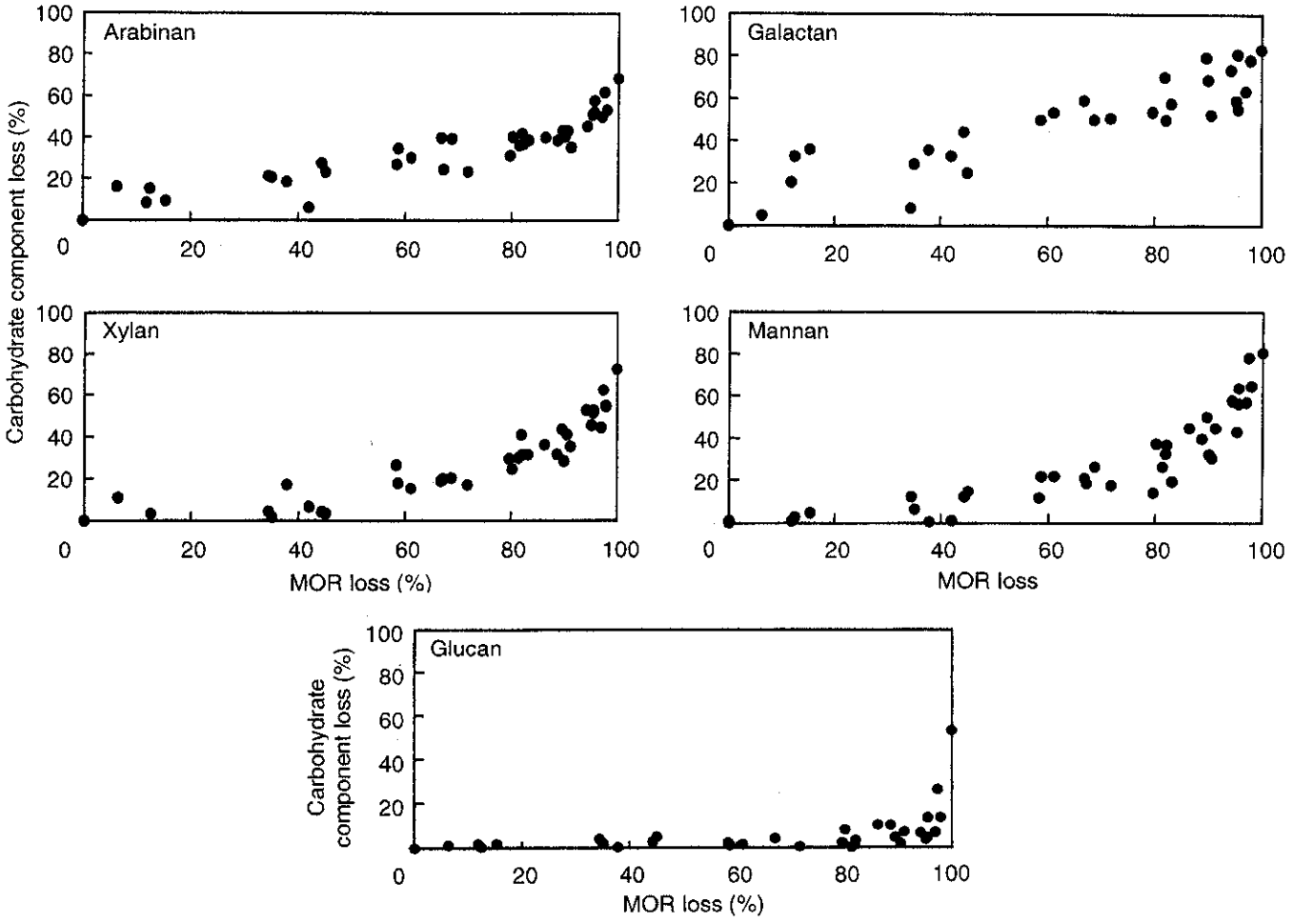

Figure 5. — Progressive loss of carbohydrate components in relation to bending strength loss caused by *G. trabeum.*

degraded first. Substantive loss of xylan and mannan begins at approximately 40 percent loss in MOR while loss in glucan does not occur until approximately 75 to 90 percent loss in MOR.

DISCUSSION

MECHANICAL PROPERTIES AND WEIGHT

The strength/weight loss data from the preliminary experiment **(Fig. 1)** demonstrated that considerable bending strength loss occurs before significant weight loss, as has been reponed previously (9,10,13,14,17). The relationship appears very consistent as decay initi-

TABLE 2. — The effect of progressive degradation of wood carbohydrates, due to decay, on wood mechanical properties[a]

Component degraded	Loss in WML	Loss in MOR	Loss in MOE	Weight loss
	(%)			
Minor hemicellulose (galactan and arabinan)	0 to 80	0 to 40	0 to 20	< 5
All hemicellulose (galactan, arabinan, mannan, and xylan)	80 to 95	40 to 80	20 to 35	5 to 20
All hemicellulose and cellulose (glucan)	> 95	75 to 100	> 35	> 20

[a] WML = work to maximum load: MOR = modulus of rupture; MOE = modulus of elasticity.

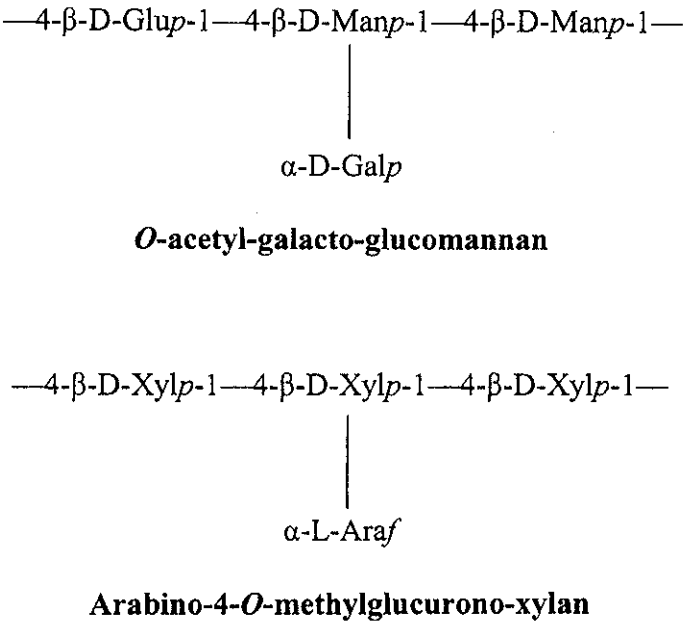

Figure 6. — Representative Structures of the two main hemi-cellulose components: Glu = glucose; Man = mannose; Gal = galactose; Xyl = xylose; and Ara = arabinose.

ates and progresses. It also appears to he consistent for both fungi tested. The MOE data are less consistent between the two fungi, but these data show that loss in MOE is not as rapid as the loss in MOR. The data from the main study **(Fig. 4)** also showed that the relationship between weight and bending strength loss is not only qualitative but may also he quantitative. At weight loss values below 5 percent, strength loss was approximately 40 percent and the work required to produce failure was reduced by 70 to 80 percent. This highlights the fact that if decay is microscopically detectable (5% to 10% weight loss [17]), then the mechanical and hence engineering properties of the timber have been reduced considerably. Our data showed that, for southern pine sapwood exposed to *G. trabeum* **(Fig. 4),** once weight loss began (after approximately 40% strengh loss), the ratio in the comparative loss in mechanical properties compared with weight loss was 9:l for WML. 4:1 for MOR, and 1.5:1 for MOE.

CHEMICAL COMPOSITION

The data from the preliminary experiment on loss of hemicellulose and cellulose components showed a similar trend for both fungi. The arabinan and galactan components were degraded first, followed by the mannan and xylan after 40 to 60 percent strength loss. The glucan components (primarily 90% representing cellulose) were not measurably degraded until 80 to 90 percent strength loss was achieved. At 90 to 100 percent MOR loss, the galactan and mannan showed the highest percentage loss.

The data from the main study demonstrated a relationship between chemical changes, that is, 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 degradation of these carbohydrates only occurred after about 40 percent strength loss. Significant loss in glucan only occurred after about 80 percent strength loss. Again, at 90 percent 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 (7). The cellulose and main chain hemicellulose components may possibly be undergoing depolymerization (without disassociation). Loss of crystallinity of the cellulose may also influence strength loss. This area is the focus of further research. In a previous study (15) of thermally degraded wood in which similar patterns of chemical changes and strength loss were observed. no evidence of hemicellulose or cellulose depolymerization was found. The arabinan and galactan are side chain elements of the xylan and mannan main polymers (16) and may be either more vulnerable to degradation or may have to be removed before the main chain of the polymer can be attacked. Figure 6 shows the representative structures of the two main hemi-cellulose components.

As decay progressed to the stages involving significant weight loss. chemcal composition also changed characteristically. The start of significant loss in the mannan and xylan components correlated with the start of significant weight loss: both occurred at approximately 40 percent loss in MOR. Because mannan-xylan components make up approximately 18 percent of the wood compared with 8 percent for the galactan-arabinan components (7). 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 an MOR loss of more than 80 percent. 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, as shown in **Table 2.**

CONCLUSIONS

From the data for the decay of southern pine sapwood by *G. trabeum,* supported by the data for *P. placenta,* it can be concluded that 1) measurable weight loss began after approximately 40 percent loss in MOR and occurred in a relative ratio of 4:1 bending strength loss/weight loss; 2) initial strength loss without measurable weight loss corresponded to loss in the galactan and arabinan hemicellulose components; 3) the start of significant weight loss corresponded with the start of significant loss in the mannan and xylan components; and 4) major weight loss and loss in stiffness (MOE) corresponded to loss in the glucan component.

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