Strategies for improving the performance of plywood adhesive mix fillers from southern yellow pine bark

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Abstract

Southern yellow pine bark was obtained from an industrial source and subjected to grinding and classification operations to ultimately afford finely ground bark fractions for evaluation as plywood adhesive mix fillers. Specifically, by grinding in a laboratory blender, we were able to generate a bark fraction rich in periderm tissue with its interlocking spiculate stone cells (sclereids). Another significant bark fraction was comprised of cellular debris from the obliterated phloem tissues in bark that are partitioned by the periderms. Through the grinding and classification operations employed in this study, the filler rich in periderm tissue had superior performance (≥ 90% wood failures) over both the filler rich in obliterated phloem tissue and that prepared directly from the bark as received. This appears to be related to the removal of extractive-rich bark components that likely promote resin undercure. The periderm-rich filler had the added benefit of an ash content (2.5%) that was significantly lower than that for the whole bark filler (9.4%).

Harvested trees are commonly transported to the processing site as bark-covered logs. For southern yellow pine (SYP), approximately 18 percent of the transported load is comprised of bark (Hemingway 1997). Most SYP bark, especially that available at pulpmills, is burned in power boilers where it contributes significantly to the energy demands of this industry sector. In some cases, bark still presents a disposal issue at lumber mills and plywood plants.

Efforts to obtain greater value from such bark resources have generally involved the development of applications for the extractives. For example, condensed tannins from SYP bark have been used to make thermosetting adhesives for wood composite manufacture. While adhesives based on wattle (*Acacia mearnsii* De Wild.) condensed tannins have been commercialized, efforts with SYP condensed tannins have fallen short because of difficulties in competing with entrenched phenolic adhesive systems on the basis of both price and performance (Kreibich 1989). Promising results were obtained with SYP tannin sulfonates as partial substitutes in phenol-resorcinol-formaldehyde adhesives (Kreibich and Hemingway 1989); however, again, commercialization has not been forthcoming. An alternative to using bark as a source of chemicals has been the pressing of bark fragments together to make bark-based composites (Chow 1975). The incorporation of bark along with wood in particleboards has also been studied. Generally, as bark usage increases, particleboard strength decreases (Muszynski and McNatt 1984, Blanchet et al. 2000).

We are currently investigating applications for SYP bark requiring intermediate levels of processing that fall between the isolation of chemical constituents and the fabrication of bark-based composites. One option under evaluation is the use of SYP bark in plywood adhesive mix fillers. For plywood manufacturing, fillers are added to the adhesive mix to improve its workability. Specifically, these finely ground organic and/or inorganic materials promote bonding by holding the adhesive on the veneer surface where it is needed (Sellers 1985). Aside from performance, desirable filler features include low cost, consistent quality, and sufficient supplies. Commonly used plywood adhesive mix fillers include furfural residue, alder bark, and nutshell flours. Elimination of do-

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mestic supplies of furfural residue, and the demand for nutshell flours by other industry sectors, has created interest in finding alternatives.

A few reports describe the use of SYP bark to make plywood adhesive mix fillers (Sellers 1994). For our study, one concern was that the high extractives content of SYP bark could interfere with the resin cure. Studies on bark anatomy and chemistry have shown that grinding and classification operations can afford bark fractions rich in different cell types, and thus, different levels of extractives (Ross and Krahmer 1971, Ottone and Baldwin 1981). Our objective was to determine if we could apply similar grinding and classification operations to produce a SYP bark fraction that could then be used to make a plywood adhesive mix filler with improved performance over a filler prepared directly from the bark as received. The high level of dirt in an industrial bark supply presented another concern since plywood adhesive mix fillers with high ash contents can greatly increase tool wear during cutting operations (Sellers 1989, Sellers and Gardner 1989, Sellers et al. 2005). Therefore, it was also of interest to determine whether our grinding and classification operations would facilitate the removal of dirt present in our bark supply.

Materials and methods

Bark preparation and analysis

SYP bark (essentially all *Pinus taeda* L.) was collected near the debarking station at a local plywood plant. Whole bark samples were prepared by directly grinding the bark, as received, with an electric chipper shredder (Echo, Inc., Model SH-5000) and drying under ambient conditions. Additional samples of bark were carefully peeled by hand to separate the inner bark (phloem) from the outer bark (rhytidome) prior to grinding and drying. All bark samples were subsequently ground further in a Wiley mill equipped with a 10-mesh screen and the resultant bark meals were sealed in plastic bags and stored in a freezer until needed.

Samples of the whole bark and outer bark meals (< 10 mesh) were ground further in 100-g batches using a laboratory blender (Waring Laboratory, Model 36BL23). Each batch was ground at high speed for two 1-minute periods, between which the canister was removed and briefly shaken by hand. Samples of the bark meals and batches of the blender-ground bark were individually classified for 30 minutes on a sieve shaker (W.S. Tyler, Ro-Tap, Model RX-29) equipped with 20-, 35-, 80-, 100-, 140-, and 200-mesh sieves. Fractions retained on each sieve and in the bottom pan were collected from repeated operations to obtain enough material in each particle size range to determine fraction weight and ash distributions. All ash contents were determined using a muffle furnace set to 450°C. Extractive contents of the whole bark fractions with the 35- to 80- and < 200-mesh particle sizes were of particular interest and thus subjected to Soxhlet extractions with hexane and then ethanol to determine the extractives contents of each. To determine the resistance of the coarser bark particles to further size reduction in the blender, sets of whole bark fractions retained on the 20-, 35-, 80-, and 100-mesh sieves were combined into one batch, ground again in the blender, and then classified to determine fraction weight and ash distributions.

Bark-based fillers

All bark-based fillers were prepared from the whole bark meal. Multiple batches were processed to collect enough material for use in the preparation of adhesive mixes. After processing in the blender and sieve shaker as before, whole bark fractions passing through the 200-mesh sieve, which were rich in obliterated phloem tissue, were designated as filler A. The whole bark fractions retained on the 35- and 80-mesh sieves, which were rich in periderm tissue were ground further in small batches (25 g) using an ultra-centrifugal grinding mill (Retsch, Inc., Model ZM 200) equipped with a 12-tooth rotor and 0.12-mm ring sieve. The finely ground material was then classified as before. Most of the material passed through the 200-mesh sieve and was designated as filler B. Finally, a sample of whole bark meal was directly ground in the ultra-centrifugal grinding mill and classified; again, most of the material passed through the 200-mesh sieve. This material was designated as filler C.

Table 1.—Adhesive mix for bonding SYP plywood.

	Adhesive mix	Mix solids
	(%)	
Filler	6.7	15.0
Extender	7.4	16.6
Sodium hydroxide solids	1.6	3.6
Resin solids	28.9	64.8
Total mix solids	44.6	100.0
Total mix water	55.4	
Total mix	100.0	

Adhesive mix preparation

Adhesive mixes were prepared as shown in **Table 1** using the three bark-based fillers and a furfural residue control (FuraTex, Bates & Co., Inc.). The filler was mixed with the added water followed by the addition of a hard wheat extender (HW-200, Bates & Co., Inc.). For a typical 2,000-g batch of adhesive mix, up to 200 g liquid resin (6500B, Borden Chemical, 45 percent solids) was added to obtain a suitable consistency for working the extender gluten. Additional resin was then added to adjust the mix viscosity; the total amount of resin added before the addition of the caustic (50% NaOH) was between 350 to 400 g. After the caustic addition and mixing (15 min), the remainder of the resin was added to obtain the final adhesive mix. Further mixing (5 min) was followed by the determination of the adhesive mix viscosity (Brookfield).

Plywood assembly and testing

SYP wood veneers (305 mm by 305 mm by 3.175 mm) were sorted to remove those that had unacceptable defects (e.g., rough veneer, staining). The average veneer moisture content was 5.1 percent (dry weight basis) as determined by ovendrying selected veneers at 103° ± 2°C. A roll spreader (Black Bros. Inc.) was used to apply the adhesive mix to core veneers at a rate of 366 g/m^2, double glueline basis. Three-ply panels were immediately assembled in sets of four to give 10-, 20-, 40-, and 60-minute assembly times. After 5 minutes into the assembly process, all panels were prepressed (690 kP, 5 min) with an air pod press (Tyler Manufacturing Co.). The panels with a 10-minute assembly time were transferred as quickly as possible to the hot-press (Williams-White Co.) for pressing (157°C, 1240 kP, 3 min). Finished panels were stored in a hot box overnight. For each experiment, panels were prepared in duplicate for each filler and assembly time.

Plywood panels were subsequently cut to afford 10 test specimens each for testing with the lathe checks in the closed and open configurations. Samples were tested using the standard shear test following the standard vacuum/pressure pretreatment (NIST 1996). After drying in an oven (75°C), values for percent wood failure were determined.

Results and discussion

SYP bark from a plywood plant was used for this study since it represented a currently available industrial bark resource. Bark fragments varied considerably in size with the larger fragments having both outer bark (rhytidome) and inner bark (phloem) components; smaller fragments were mostly outer bark. In the living tree, as new phloem is formed, the older phloem undergoes anatomical changes and becomes obliterated phloem as it is sealed off by developing periderms (Howard 1971). Thus, the outer bark of SYP, which is mostly nonliving, is comprised of both obliterated phloem and periderm tissues. In this study, grinding and classification operations were employed to separate the bark into its components in an effort to produce a bark fraction lower in extractives and ash. It was hypothesized that a plywood adhesive mix filler prepared from this fraction would have improved performance over a filler obtained by directly grinding the bark as received.

Table 2.—Fraction weight and ash distributions for whole bark sample.

	Grinding operations					
	Wiley mill alone			Wiley mill and blender		
Particle size range	Fraction weight	Fraction ash content	Ash distribution[a]	Fraction weight	Fraction ash content	Ash distribution[a]
(mesh)	(%)					
> 20	11.8	1.8	2.3	0.3	ND[b]	ND
20 to 35	35.3	3.1	12.1	11.3	1.4	2.0
35 to 80	31.5	7.0	23.8	39.4	4.1	20.3
80 to 100	2.6	14.5	4.1	3.8	7.6	3.7
100 to 140	4.6	25.3	12.5	6.1	13.2	10.2
140 to 200	3.8	30.2	12.6	7.7	16.1	15.6
< 200	10.4	28.7	32.6	31.4	12.1	48.2
Total	100.0		100.0	100.0		100.0

[a]Calculated as a percentage of the sum of the ash present in all fractions.
[b]ND = not determined.

Partitioning of bark components

During preliminary experiments, whole bark meals were subjected to a variety of different grinding operations with the blender to determine whether the action of the rotating blade would preferentially grind the seemingly delicate phloem and obliterated phloem tissues more than the harder periderms with their interlocking spiculate stone cells (sclereids). Observations by light microscopy showed that the bark fractions with the larger particle sizes had a higher proportion of periderm tissue. In the case of the bark fractions with the smaller particle sizes, observations showed cellular debris with cell wall thicknesses consistent with those expected for phloem and obliterated phloem tissues. These observations validated our speculation that the periderm tissue would show greater resistance to grinding under the conditions employed.

Classification of the whole bark meals gave more than 75 percent of the material as coarser than 80 mesh (**Table 2**). After the additional grinding step with the blender, roughly 50 percent of the material was coarser than 80 mesh. This resulted in a bimodal distribution of particle sizes with approximately 39 percent of the sample falling in the 35- to 80-mesh range and approximately 31 percent passing through the 200-mesh sieve into the sieve pan. Organic solvent extraction of these two bark fractions gave an extractives content for the 35- to 80-mesh fraction (3.6%) that was one half that obtained for the material passing through the 200-mesh sieve (7.1%). Accordingly, the grinding and classification process employed was effective in producing a bark fraction with a considerably lower extractives content.

Ash in whole bark fractions

Ash determinations for the whole bark fractions are also shown in **Table 2**. Since only a small amount of material was retained on the 20-mesh sieve for the bark subjected to grinding in the blender, the ash content for this fraction was not determined. Results show that the ash content increases with decreasing particle size. The lower ash contents for the blender-ground bark samples reflect the transfer of low-ash material from the larger particle sizes to the bark fractions with the smaller particle sizes. Using the fraction weight and ash content values for each bark fraction, the distribution of ash among all of the fractions was calculated. Through grinding in the blender, the amount of ash in the fractions coarser than 80 mesh was reduced from about 38 percent to about 22 percent. Accordingly, in addition to the partitioning at the cellular level, these results show an added benefit of ash removal from the periderm tissue targeted for further grinding to obtain a suitable plywood adhesive mix filler.

Repeat of blender grinding operation

Sets of bark fractions retained on the 20-, 35-, 80-, and 100-mesh sieves were combined into one batch, ground again in the blender, and classified as before. The results in **Table 3** show that more than 80 percent of the material remained coarser than 80 mesh. This further demonstrated that the periderm particles are resistant to disintegration by the rotating blade of the laboratory blender. Accompanying the small loss of material at the larger particle sizes was a further reduction in the ash content. Since the majority of the sample remained in the 35- to 80-mesh fraction, the distribution of ash was skewed toward this fraction.

Ash in outer bark fractions

Reported ash contents for *P. taeda* whole bark are slightly less than 1 percent (McGinnis and Parikh 1975, Labosky 1979). In addition to this ash, an appreciable amount of dirt typically accompanies industrial supplies of bark and thereby contributes considerably to the value for ash content. Determination of the ash contents for inner and outer bark meals showed that the values for the inner bark (3.8%) were twice that obtained for the outer bark (1.6%). Grinding and classification of the outer bark gave fraction weight distributions (**Table 4**) that were analogous to those obtained with the whole bark (**Table 2**). Thus, these data suggest that an opera-

Table 3.—Fraction weight and ash distributions for combined whole bark fractions (>20–100 mesh) ground a second time with blender.

Particle size range	Combined fractions	Combined fractions after grinding a second time		
	Fraction weight	Fraction weight	Fraction ash content	Ash distribution[a]
(mesh)	----------	(%)	----------	
> 20	0.2	0.0	ND[b]	ND
20 to 35	16.7	9.0	1.0	2.7
35 to 80	75.6	74.0	2.9	63.9
80 to 100	7.5	6.1	9.3	17.2
100 to 140	0	4.5	5.6	7.7
140 to 200	0	2.0	4.2	2.6
< 200	0	4.4	4.4	5.9
Total	100.0	100.0		100.0

[a]Calculated as a percentage of the sum of the ash present in all fractions.
[b]ND = not determined.

Table 4.—Fraction weight and ash distributions for outer bark sample.

Particle size range	Grinding operations					
	Wiley mill alone			Wiley mill and blender		
	Fraction weight	Fraction ash content	Ash distribution[a]	Fraction weight	Fraction ash content	Ash distribution[a]
(mesh)	----------		(%)	----------		
> 20	7.4	0.6	2.6	0.0	ND[b]	ND
20 to 35	34.5	0.6	12.1	11.3	0.3	1.8
35 to 80	35.5	1.3	28.9	41.3	0.8	17.4
80 to 100	3.2	2.5	4.9	6.9	2.0	7.3
100 to 140	4.6	3.7	10.5	2.5	2.5	3.4
140 to 200	3.8	3.8	9.6	5.4	3.0	8.7
< 200	11.0	11.0	31.4	32.6	3.5	61.4
Total	100.0		100.0	100.0		100.0

[a]Calculated as a percentage of the sum of the ash present in all fractions.
[b]ND = not determined.

Table 5.—Wood failures and shear strengths for plywood made with bark-based fillers and furfural residue.

		Assembly time			
	Filler type[a]	10 min	20 min	40 min	60 min
Wood failure (%)	Bark filler A	45	66	61	71
	Bark filler B	90	91	91	93
	Bark filler C	80	86	88	91
	Furfural residue	57	77	92	77
Shear strength	Bark filler A	1510	1440	1470	1270
(kPa)	Bark filler B	1610	1740	1450	1630
	Bark filler C	1790	1570	1490	1460
	Furfural residue	1690	1500	1480	1520

[a]Bark-based fillers were prepared from bark fractions rich in either obliterated phloem (filler A) or periderm (filler B) tissues; a filler was also prepared from whole bark (filler C) as received.

tion focused on only outer bark provides only a slight benefit in the yield of the desired bark fractions rich in periderm tissue. As expected, the lower ash contents reflect that much of the grit accompanying the bark was lost during the process of separating the inner bark from the outer bark.

Filler preparation

Prior research has shown some success with the use of finely ground SYP bark as an adhesive mix filler for plywood manufacturing (Sellers 1994). In some instances, a lack of success reflected the inability to obtain a material that was sufficiently ground. Unlike reports on other alternative fillers (Oh et al. 1997, Oh and Sellers 1999), our attempts to obtain sufficiently ground material with a Wiley mill were unsuccessful, even with new knives and close knife tolerances. Acceptable products were subsequently obtained using an ultra-centrifugal mill, albeit in small batches (25 g). Bark fractions retained on 35- and 80-mesh sieves were combined and ground in the ultra-centrifugal mill. The resultant finely ground material was then classified to afford bark filler B as the material passing through the 200-mesh sieve. Although this added another, and perhaps unnecessary, classification step, it provided a sample more suitable for comparison to bark filler A, which was the material that passed through the 200-mesh sieve after the grinding operation with the blender.

Adhesive mix preparation

Plywood adhesive mixes were prepared with the bark fillers and the furfural residue control the day prior to use. The viscosities for the adhesive mixes containing bark fillers A, B, and C were 11,660, 14,190, and 12,310 mPa·s, respectively, when measured after preparation. Values increased to between 17,000 to 19,500 mPa·s after 24 hours and 17,300 to 20,500 mPa·s after 48 hours of standing at room temperature. For the furfural residue, the viscosity was initially lower at 8,250 mPa·s. A more pronounced increase in viscosity over time was observed with values of 18,640 and 28,100 mPa·s after 24 and 48 hours, respectively. Although the viscosities of the adhesive mixes with the bark-based fillers were initially higher than that for the furfural residue, the bark-based fillers afforded adhesive mixes with greater stability in viscosity for a longer period of time.

Plywood assembly and testing

Three-ply plywood panels were then manufactured using four assembly times to assess the performance of the bark-based fillers. Values for percent wood failure and shear strength are shown in **Table 5**. For the furfural residue, wood failures ranged from 57 to 92 percent. The best performance was obtained at an assembly time of 40 minutes; the performances of the furfural residue at the 20- and 60-minute assembly times were lower than the 85 percent wood failure specification. Thus, the adhesive mix may not have been optimized for this filler. However, this does not detract from the direct comparison to the bark-based fillers under investigation. In the case of bark filler C, the performance was in a tighter range, with panels meeting the 85 percent wood failure

specification for the 20-, 40-, and 60-minute assembly times. Under the conditions employed, these results demonstrated the feasibility of producing a usable filler from SYP bark as received. However, one limitation would be a high ash content (9.4%) relative to that for nutshell (1.1% to 1.5%) and alder bark (5.2%) flours (Sellers et al. 2005).

It is especially interesting to note that the values for percent wood failure for bark filler C were intermediate to those obtained for the fillers prepared from the bark fractions rich in either periderm (filler B) or obliterated phloem (filler A) tissues. For all assembly times, the values for percent wood failure for bark filler B were high with a very tight range of 90 to 93 percent. In contrast, the values for percent wood failure for bark filler A were all low, in the range of 45 to 71 percent. Test specimens for bark filler A frequently showed signs of undercure, which was attributed to interference from the higher extractives content. During preliminary experiments, the occurrence of undercure for this filler was reduced when the veneers were overdried (Eberhardt and Reed 2005). It was also observed that the prepress tack with bark filler A was not acceptable as evidenced by occurrences of ply separation not observed with the furfural residue or the other bark-based fillers. Despite the problems encountered with bark filler A, the values for shear strength were not indicative of poor performance. As expected, the ash content of bark filler B (2.5%) was considerably lower than that obtained for bark filler A (12.2%). Thus, through the grinding and classification processes employed, we were able to produce a plywood adhesive mix filler with improved performance and lower ash than that which could be obtained by directly grinding the SYP bark as received. Moreover, under the conditions employed, a filler based on SYP bark can be produced that can perform as well as furfural residue.

Conclusions

Grinding and classification operations, as just outlined, can considerably improve the performance of plywood adhesive mix fillers based on SYP bark from an industrial source. Fillers based on SYP bark can be prepared that perform as well as long established fillers such as furfural residue. An added benefit of the grinding and classification operations employed is a considerable reduction in ash contents attributed to the high levels of dirt found in industrial bark supplies.

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