Partitioning of Pine Bark Components to Obtain a Value-Added Product for Plywood Manufacture

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Abstract

Southern yellow pine (SYP) bark particles and bark extracts have been used only to a limited extent in wood-based composites due to poor performance relative to existing products and/or economic barriers. Our efforts to identify alternative applications for this biomass resource require the development of an improved understanding of the interrelationships between bark anatomy and chemistry. An intermediate level of processing, involving grinding and classification operations, was used to convert SYP bark into adhesive filler for plywood manufacture. This filler was lower in ash and extractives than another filler prepared by directly grinding the bark as received. Near-infrared spectroscopy was successfully coupled with multivariate analysis to develop a model to predict inner:outer bark ratios and thereby select preferred bark resources for this application.

Introduction

Southern yellow pine (SYP) bark collected by the forest products industry sector is usually burned in power boilers where it contributes significantly to demands for both electricity and heat. In some cases, such as at lumber mills and plywood plants, bark still presents a disposal issue. Efforts to obtain greater value from these bark resources have involved the development of applications for the extractives. For example, condensed tannins have been widely studied as a substitute for phenol in the production of phenol formaldehyde adhesive systems. Obstacles to the widespread industrial use of condensed tannins have been their high reactivity and natural variability (Pizzi, 1998). An alternative to using bark chemicals for wood composites has been consolidation of bark to make bark-based composites. Generally, the incorporation of bark in wood-based composites results in lower strength relative to that for composite structures made with wood alone (Blanchet

et al., 2000; Muszynski and McNatt, 1984). We are currently investigating applications for SYP bark requiring intermediate levels of processing. Limited availability of commonly-used plywood adhesive mix fillers (e.g., furfural residue, nutshell and alder bark flours) have led us to evaluate the utility of SYP bark fractions for this application.

One variable with respect to bark supplies is the relative amounts of inner (living phloem) and outer (rhytidome) bark; studies have demonstrated chemical differences between inner and outer bark tissues (Pearl and Buchanan, 1976; Hafizoglu et al., 1997). The outer bark of SYP can be further subdivided into the obliterated phloem tissue partitioned by periderms (Fig. 1). Differences in the chemistry between these two tissues are only now being addressed. Studies by others have shown that grinding and classification operations can afford bark fractions rich in different cell types, and thus, different levels of extractives (Ottone and Baldwin, 1981; Ross and Krahmer, 1971). In an analogous manner, we developed grinding and classification operations to produce a SYP bark fraction that could then be used to make a plywood adhesive mix filler with a lower extractives content than that prepared directly from the bark as received (Eberhardt and Reed, 2005; Eberhardt and Reed, 2007). This process also facilitated the removal of dirt present in the bark. To apply some degree of quality control over the variability of bark supplies targeted for this application, we also utilized NIR spectroscopy coupled with multivariate analyses as a means to identify SYP bark supplies better suited for this application (Eberhardt and So, 2005; So and Eberhardt, 2006).

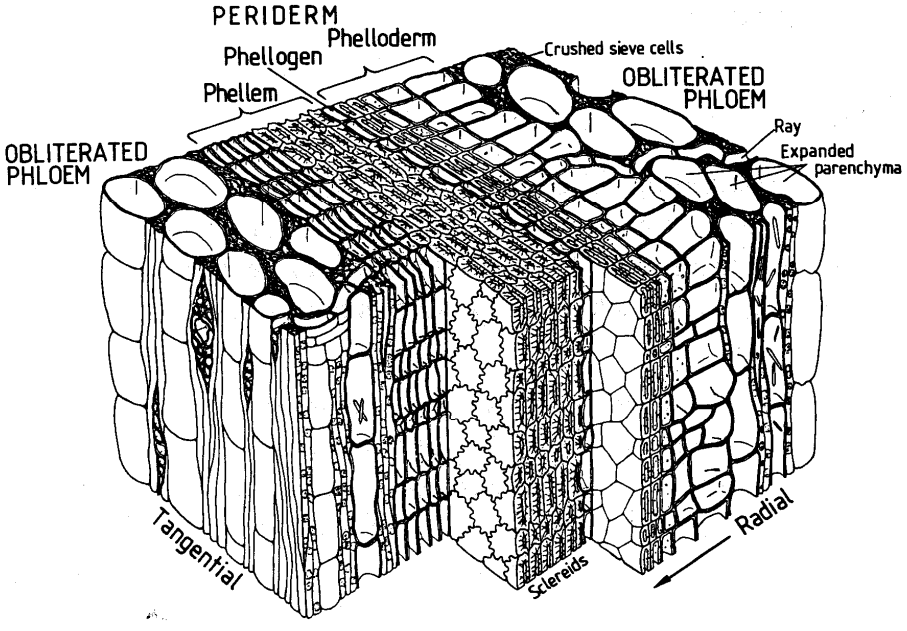

Fig. 1. Periderm and obliterated phloem tissues in SYP outer bark (Howard, 1971).

Materials and Methods

Bark preparation and analysis

SYP bark (essentially all *Pinus taeda* L.) samples were obtained from a local plywood plant and a local pulp mill. Whole bark samples were prepared by directly grinding the bark, as received, with an electric chipper shredder 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 as above. All bark samples were subsequently ground further in a Wiley mill equipped with a 2 mm mesh screen.

Preparation of fillers from bark

Samples of the whole bark meals were ground further in 100 g batches using a laboratory blender. Multiple batches were processed to collect enough material for use in the preparation of adhesive mixes. Each batch was ground at high speed for two 1-minute periods, between which, the canister was removed and briefly shaken by hand. Samples were classified for 30 minutes on a sieve shaker equipped with 20-, 35-, 80-, 100-, 140-, and 200-mesh sieves. Bark fractions passing through the 200-mesh sieve, which were rich in obliterated phloem tissue, were designated as filler A. Bark fractions retained on the 35 and 80-mesh sieves, which were rich in periderm tissue, were ground further in small batches (25g) using an ultra-centrifugal grinding mill (Retsch, Inc., Model ZM 200) equipped with a 12-tooth rotor and 0.12 mm (mesh) 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. Bark fractions were subjected to Soxhlet extraction with hexane and then 95% ethanol. Organic solvent extracts were dried *in vacuo*. Ash contents were determined using a muffle furnace set to 450ºC.

Adhesive mix preparation and plywood assembly

Adhesive mixes (Table 1) were prepared using the 3 bark-based fillers and a furfural residue control as previously reported (Eberhardt and Reed, 2007). Three-ply panels were immediately assembled from SYP wood veneers (305 mm × 305 mm × 3.175 mm) in sets of four to give 10, 20, 40, and 60 minute assembly times. Plywood panels were subsequently cut to afford specimens for testing by the standard method (NIST, 1996).

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	

Spectroscopy and model development

Near-infrared (NIR) spectra of milled bark samples were obtained with an ASD Field Spec Pro (Analytical Spectral Devices, Boulder, CO, USA) spectrometer at wavelengths between 350 and 2500 nm. Samples were transferred to a bottle cap, leveled, and rotated at 45 rpm to minimize specular interference and surface heterogeneity (So et al., 2004; So et al., 2004). Spectra were collected with a fiber optic probe oriented perpendicular to the sample surface while illuminated with a DC lamp oriented at 30 degrees above the surface.

Multivariate analysis of the data was performed using the Unscrambler (version 8.0) software (CAMO, Woodbridge, NJ, USA). Three NIR spectra were first averaged to one spectrum per sample. Partial least squares (PLS) regression was used to predict the amount of inner bark in the samples. Models were generated using full cross validation with the number of factors limited to only two due to the low number of samples. Multiplicative scatter correction (MSC) was also applied to the untreated spectra. The performance of the models was assessed using several common statistical measures. The correlation coefficient, R^2, is a measure of the strength of the fit to the data, and the root mean square error of calibration or prediction (RMSEC or RMSEP) is a measure of the calibration or prediction error in the fit, and is often expressed as a percentage of the mean value of interest (%RMSEC or %RMSEP of mean).

Results and Discussion

During preliminary experiments, whole bark meals were subjected to a variety of different grinding operations with a 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. Grinding as such resulted in a bimodal distribution of particle sizes with approximately 39% of the sample falling in the 35-80 mesh range and approximately 31% passing through the 200-mesh sieve into the sieve pan. Organic solvent extraction of these two bark fractions gave an extractives content for the 35-80 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 significantly lower extractives content.

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 et al., 1994). In some instances, a lack of success reflected the inability to obtain a material with a sufficiently fine particle size. 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.

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 from the vacuum/pressure testing of the test specimens are shown in Table 2. For the furfural residue, wood failures ranged from 57 to 92%. The best performance was obtained at an assembly time of 40 minutes; the performance of the furfural residue at the 20 and 60 minute assembly times were lower than the 85% 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% wood failure specification for the 20, 40, and 60 minute assembly times. Under the conditions employed, these results demonstrated the feasibility of producing usable filler from SYP bark as received. However, one limitation would be a high ash content (9.4%) relative to that for nutshell (1.1-1.5%) and alder bark (5.2%) flours (Sellers et al., 2005).

Table 2. Wood failures and shear strengths for plywood made with bark-based fillers and furfural residue.

	Filler Type [a]	Assembly Time (minutes)			
		10	20	40	60
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 (kPa)	Bark Filler A	1510	1440	1470	1270
	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.

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%. In contrast, the values for percent wood failure for bark filler A were all low in the range of 45 to 71%. Test specimens for bark filler A frequently showed signs of undercure which was attributed to interference from the higher extractives content. 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 significantly

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 better than furfural residue.

Bark supply differences

Samples of SYP bark were obtained from two different sources, a plywood plant and a paper mill. The bark from the plywood plant contained many small pieces of friable outer bark whereas the bark from the paper mill had many pieces of stringy inner bark with attached outer bark. Grab samples of the barks from the two sources were separated into inner and outer bark components for chemical characterization; significant differences in both the extractives and cell wall chemistries (Eberhardt and Reed, 2005) were observed. Compared to the bark sample from the plywood plant, that obtained from the pulp mill had a higher percentage of inner bark (Table 3). Given that the outer:inner bark ratio appears to be highly dependent upon the source, fractionation of bark samples would likely afford significantly different product yields. Specifically, when targeting periderm tissues for use in plywood adhesive mix fillers, the higher proportion of outer bark in the bark supply from the plywood plant would be preferred.

Table 3. Percentages of outer bark and inner bark in SYP bark samples from different sources.

Bark Source	Outer Bark	Inner Bark	Bark Rejects[a]	Outer:Inner Bark Ratio
Plywood Plant	77.4	13.5	9.1	5.8
Pulp Mill	57.8	38.7	3.5	1.5

[a]Bark rejects include stones, twigs, and other non-bark debris.

NIR spectroscopy and model development

Samples used for multivariate analysis were made to five predetermined compositions (0, 25, 50, and 100% inner bark) in triplicate, with another fifteen test samples of randomly generated composition. PLS modeling was performed on the NIR spectra to predict inner bark content. The spectral range used for modeling was between 500-2500 nm. The predetermined compositions were used for calibration with the (known) random compositions as the test set. An excellent correlation of $R_{calib}^2 = 0.99$ was obtained between the measured and NIR-predicted inner bark contents for the calibration samples (Table 4). The test samples, with their randomly generated compositions, can be seen to fit very well with the calibration in Fig. 2, with an $R_{test}^2 = 0.94$, and a low %RMSEP of mean of 11.5%. Thus, additional samples with unknown compositions can be estimated with a certain degree of confidence using this method.

Table 4. Regression statistics for prediction of inner bark content.

Wavelength Range	Sample Set	R^2	RMSEC/P [a]	%RMSEP of mean
500-2500 nm	Calibration	0.99	3.45	-
	Test	0.94	6.05	11.5
1100-2500 nm	Calibration	0.95	8.04	-
	Test	0.83	12.02	22.9
500-1100 nm	Calibration	0.99	3.95	-
	Test	0.96	4.99	9.5

[a]RMSEC/P is the root mean square error of calibration or prediction.

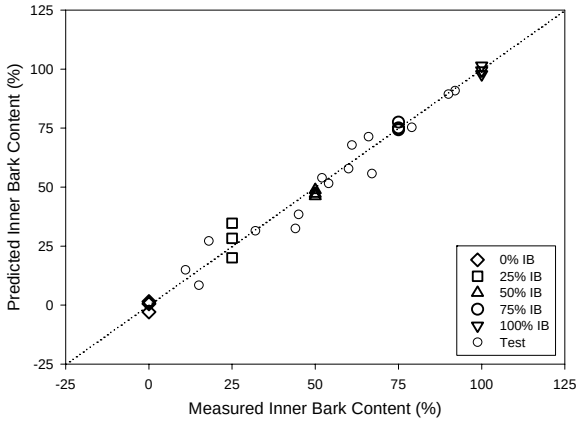

Fig. 2. Relationship between predicted and measured inner bark contents.

Additional models were produced using reduced wavelength ranges (500-1100 nm and 1100-2500 nm) for comparison (Table 4). While the higher NIR range (1100-2500 nm) gave excellent results ($R_{calib}^2 = 0.95$; $R_{test}^2 = 0.83$), the low visible-NIR range (500-1100 nm) gave even better results ($R_{calib}^2 = 0.99$; $R_{test}^2 = 0.96$). This allows the possibility of using lower cost, portable, shorter-wavelength spectrometers for field or process monitoring.

Conclusions

Grinding and classification operations, as outlined above, can significantly improve the performance of plywood adhesive mix fillers based on SYP bark from an industrial source. NIR spectroscopy coupled with multivariate analysis can be used to develop models to predict relative amounts of inner bark and outer bark in industrial bark samples. Since, the low visible-NIR range gave comparable results to the full wavelength range, the possibility of using lower cost, more portable shorter-wavelength spectrometers.

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