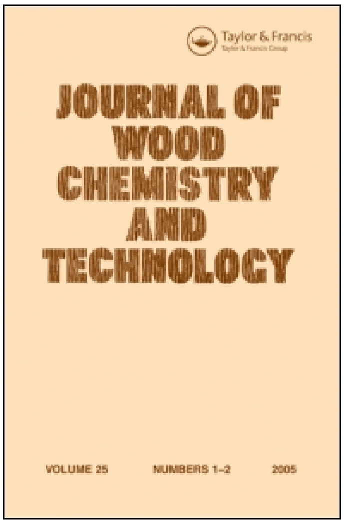
This article was downloaded by:
On: *25 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Wood Chemistry and Technology

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

Alkaline Treatment of Black Spruce Bark for the Manufacture of Binderless Fiberboard

Xinglian Geng[a]; S. Y. Zhang[a]; James Deng[a]
[a] Forintek Canada Corp., Québec, Canada

To cite this Article Geng, Xinglian , Zhang, S. Y. and Deng, James(2006) 'Alkaline Treatment of Black Spruce Bark for the Manufacture of Binderless Fiberboard', Journal of Wood Chemistry and Technology, 26: 4, 313 — 324

To link to this Article: DOI: 10.1080/02773810601076857

URL: http://dx.doi.org/10.1080/02773810601076857

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Journal of Wood Chemistry and Technology, 26: 313–324, 2006

ISSN 0277-3813 print/1532-2319 online
DOI: 10.1080/02773810601076857

Alkaline Treatment of Black Spruce Bark for the Manufacture of Binderless Fiberboard

Xinglian Geng, S. Y. Zhang, and James Deng
Forintek Canada Corp., Québec, Canada

Abstract: Black spruce bark from a lumber mill in eastern Canada was characterized for its chemical composition and suitability for the manufacture of fiberboard. The high holocellulose content and low lignin content indicated it contained a considerable amount of wood fibers. The bark was treated with 1% NaOH solution, pre-heated with steam, and subsequently steam-pressurized refined to produce fibers. The untreated bark was also pre-heated and refined for comparison purposes. The fiberboards made from alkaline-treated bark showed lighter color, higher internal bonding strength, higher modulus of rupture, and higher modulus of elasticity in comparison with the control panels. The thickness swelling of the panels made from treated and untreated bark was comparable. Pre-heating before refining was an important stage for the manufacture of binderless fiberboards from treated and untreated bark.

Keywords: Black spruce bark, alkaline treatment, pre-heating, refining, binderless, fiberboard

INTRODUCTION

Bark from some species contains an appreciable amount of fibers although the fibers are shorter and weaker than wood fibers. In addition, the bark produced from a commercial debarking operation often contains substantial amounts of

---

The Natural Sciences and Engineering Research Council of Canada (NSERC) is acknowledged for awarding an Industrial Research Fellowship to Xinglian Geng.

Address correspondence to James Deng, Forintek Canada Corp. 319, rue Franquet, Sainte-Foy, Québec G1P 4R4, Canada. E-mail: james.deng@qc.forintek.ca

wood, especially in winter.[1] Therefore, wood bark is a potential fiber resource. Bark has been used as wood furnish in the manufacture of particleboard and fiberboard but adding bark to the particleboard or fiberboard affects the appearance of the panels.[2–6] These bark-containing panels are often used as the core when surface appearance is important. Synthetic resins have been used in all the studies mentioned earlier. As a replacement for phenol in phenol-formaldehyde resin, tannin extracted from the barks of certain wood species has been commercially used for the production of wood adhesives since the 1970s.[7–9] The high content of tannins or phenolic components in bark provides it with excellent adhesion properties for the manufacture of binderless bark panels. Manufacturing bark panels without a synthetic resin has been investigated at low (below 210°C) or high (250 to 300°C) temperature by different research groups.[10–12] The studies indicate that, at temperatures from 180 to 400°C, chemical degradation and polymerization of bark components take place and the polymerization of phenolic components results in a very strong adhesion between bark particles.[13]

Softwood bark was selected for the present research for its self-bonding ability provided by its aromatic and lignin contents, which are higher than in hardwood barks.[14] There are four groups of eastern softwood in Canada, spruce, pine, fir, and cedar. Of these, spruce and balsam fir are the two most important pulpwood species. Spruce bark has a higher content of extractives than balsam fir bark[15] and black spruce bark has been selected for making particleboard because it is widely used for lumber and paper production in eastern Canada.[6] A number of physical properties and the chemical composition of black spruce bark in eastern Canada are known,[15] but these properties are representative of just the selected bark samples. Bark from the lumber industry also contains a certain amount of wood and has not been characterized for its chemical composition and suitability for the manufacture of binderless fiberboard.

Alkaline treatment of wood has been commercially used for producing chemimechanical pulp.[16,17] Alkaline treatment weakens the lignin bonds between the cellulosic fibers and softens the fibers, thus producing less damaged and more flexible fibers after refining. It is worthwhile to study the effect of the resulting fibers on the development of fiberboard strength. Tannin extracted from pine bark with 1% NaOH at 100°C for 30 min (bark:liquor ratio of 1 g/5 mL) produced strong bonds to wood at 175°C.[9] This result implies the possibility of using the alkaline bark extract as a wood adhesive.

Steaming of wheat straw during the refining process improved the mechanical properties of the resulting medium density fiberboard.[18] Steam-pressurized refining produced bulkier, longer, and coarser bark fibers. The resulting fiberboard had a smoother surface, and higher bending and tensile strengths, but lower internal bonding strength than the particleboards made from hammermilled bark.[4] The effect of pre-heating steam pressure in the refining process was also investigated in this work.

EXPERIMENTAL

Material

Black spruce bark was collected in summer from a lumber mill of Abitibi-Consolidated Inc. at Saint-Fulgence in Quebec, Canada. Sawdust and other contaminants were screened out, but the wood bundles were kept.

Chemical Analysis of the Bark

The bark was air-dried for two weeks and then ground in a Wiley mill fitted with a 35-mesh (0.5-mm) screen. The milled material was further screened with an 80-mesh sieve and the fraction retained on the 80-mesh sieve was collected. The collected material was stored in an airtight container to balance the moisture and used for chemical analysis.

TAPPI Test method T 264 cm-97[19] was used to prepare extractive-free samples for determination of ash, lignin, and holocellulose contents. The unextracted or original bark was used to determine 1% NaOH solubility and hot-water solubility. Ash content, Klason lignin content, 1% NaOH solubility, and hot-water solubility of the bark were determined according to TAPPI Test Methods T 211 om-93,[20] T 222 om-98,[21] T 212 om-98,[22] and T 207 cm-99,[23] respectively. The holocellulose content was analyzed according to TAPPI Useful Method 249.[24]

The pH value of the bark were determined with a procedure similar to that described in a previous report.[25] In brief, the bark sample (25 g, oven-dried) was refluxed in 250 mL of distilled water for 20 min and then filtered with Whatman no.1 filter paper. The residue was washed with about 100 mL of distilled water and the filtrate was diluted to 500 mL with distilled water. The resulting solution was tested for the pH.

Chemical Pretreatment of the Bark

The air-dried bark was hammermilled and then screened to remove particles smaller than 1.0 mm. The bark chips were soaked in 1% NaOH for 1 min, drained for 10 min, and then stored overnight at room temperature before refining.

Refining of the Bark

The treated and non-treated bark samples were pre-heated at 0.3 MPa or 0.75 MPa of steam pressure for 3 min in the cooking screw and then were pressure refined at a refiner speed of 2500 rpm and about 200–250 kWh/t of refining energy at the MDF pilot plant of Forintek Canada Corp. in Quebec City, Canada. The bark fibers were dried to a moisture content below 5% (oven-dry fiber basis).

FTIR Spectroscopy

Treated and untreated refined bark fibers obtained from the higher pre-heating pressure (0.75 MPa) were mixed with potassium bromide (KBr) (IR grade, Fisher Sci. Nepean, Ontario, Canada) and the mixture was formed into pellets with a Carver® Laboratory Press (Model 3912). FTIR (Fourier Transform Infrared) spectra were acquired on a Magna-IR 760 spectrometer (Nicolet Instrument Corp.). The OMNIC® software was used for data collection and analysis.

Characterization of Bark Fiber with Differential Scanning Calorimetry (DSC)

Calorimetric measurements were obtained on a DSC-2910 (TA Instruments, Inc, New Castle, DE). The DSC cell was pressurized to 4.1 MPa with nitrogen gas. The calorimeter was calibrated against indium (m.p. 156.6°C, $\Delta H = 28.45\ J/g$) at 10°C/min. The upper temperature limit was set at 250°C. The bark fiber samples (about 5 mg each) were weighed into a standard aluminum pan with a lid closure. An empty aluminum pan with the lid was used as a reference. Each sample was subjected to two measurements. For the first run, thermograms were recorded at a heating rate of 10°C/min between 40 to 250°C. For the second run, the sample at the end of the first run was cooled down to 40°C at an approximate rate of 6°C/min and the thermograms were recorded again at a heating rate of 10°C/min between 40 to 250°C. The Universal Analysis V2.6D software supplied by TA Instruments, Inc. (TA Instruments, Inc, New Castle, DE) was used to plot and analyze the thermal data. The DSC spectra have been normalized to represent 1 gram of sample. Only the bark fibers obtained from the higher pre-heating pressure (0.75 MPa) and refining process were analyzed.

Manufacture of Fiberboard Panels

Fiber mats were hand formed and pressed with a Diffenbacher press at 210°C for 6 min including de-gassing into 610 mm × 610 mm × 8.0 mm panels with a target density of $1200\ kg/m^3$. The closing time was controlled at about 60 s. Two panels under each condition were made.

Panel Property Evaluation

The panels were conditioned at 65 ± 1% relative humidity and 20 ± 3°C for two weeks. Two thickness swelling (TS) specimens (150 mm × 150 mm), 12 internal bonding (IB) specimens (50 mm × 50 mm) at the centers of panels, and 3 bending specimens (75 mm × 242 mm) at perpendicular positions for modulus of rupture (MOR) and modulus of elasticity (MOE) were cut from each panel and all properties were evaluated in accordance with ASTM D 1037-99.[26] The panel color was measured with a BYK-Gardner GmbH color-guide 45/0 colorimeter (Geretsried, Germany), where L* describes the lightness and a* and b* describe the chromatic coordinates on the green-red and blue-yellow axes, respectively.

RESULTS AND DISCUSSION

Characteristics of Black Spruce Bark

The ash content of the bark (see Table 1) was similar to that reported by Chang and Mitchell.[27] The lignin content of the bark, 31.6%, was much lower than reported by Harun and Labosky, which ranged from 40 to 55%.[28] The holocellulose content of the extractive-free bark, 50%, was high. In general, bark holocellulose contents range between 35 to 45%.[28] The hot water solubility of the unextracted bark was 26.8%; the 1% NaOH solubility was 57.1%. The bark produced in commercial debarking processes often contains substantial amounts of wood, which contains less lignin and extractives and more cellulose than the bark itself. The length and strength of wood fibers could contribute to the strength development of fiberboards, in particular, by positively influencing bending strength and stiffness. Hot water extractives of bark contain tannins, glycosides, and some carbohydrates. The 1% NaOH extractives also contain polyphenolic materials. These extractable components tend to change their structure during pre-heating, refining, and hot-pressing processes and, therefore, affect fiberboard properties.[29]

Table 1. Characteristics of the black spruce bark

Ash content of extractive-free bark, %	2.3
Klason lignin content of extractive-free bark, %	31.6
Holocellulose content of extractive-free bark, %	50.5
Hot water solubility of unextracted bark, %	26.8
1% NaOH solubility of unextracted bark, %	57.1
pH	4.99

Chemical Consequences of Alkaline Treatment

The moisture content of non-treated bark was 26%, and that of treated bark was 199%. That is to say, the bark absorbed 1.73 kg NaOH solution per kg of oven-dry bark after a 1 min-soaking treatment. Because this alkaline solution was 1% NaOH, treating 100 kg of bark should consume 1.74 kg of solid NaOH. The alkaline solution changed color to dark brown after the bark was soaked in it, but the amount of bark lost was not tested after the chemical treatment.

FTIR spectra of treated and untreated bark fibers are shown in Figure 1. Alkaline treatment resulted in a new shoulder at 947 cm^{-1} and this band may be assigned to the C-O stretching vibration in cellulose and hemicellulose.[30] A previous report indicated that alkaline treatment activates carboxylic acid groups of hemicellulose.[31] The band near 1288 cm^{-1}, which is assigned to C-O stretching vibration in phenolic ethers in lignin, decreased in intensity upon alkaline treatment. The band near 1625 cm^{-1} which is due to H-O-H deformation of adsorbed water and C-O stretching in lignin was also more apparent before alkaline treatment. The shoulder observed near 1747 cm^{-1} is primarily due to the C=O stretching vibration of the acetyl and carboxyl groups in hemicellulose and its intensity was decreased by the treatment. This observation is consistent with a previous

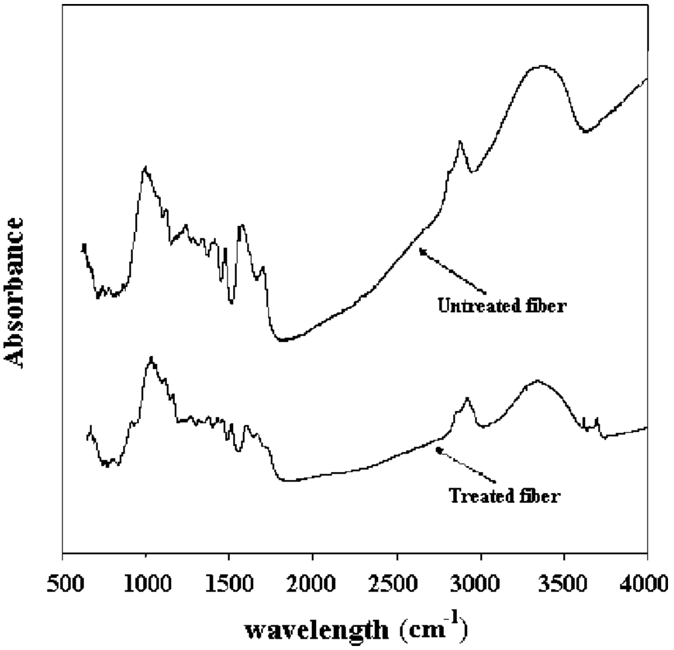


Figure 1. FTIR spectra of treated and untreated bark fibers.

report that deacetylation of wood is one of the main reactions during alkaline treatment.[17] Alkaline treatment greatly weakened the band intensity in the region of 3350 cm^{-1}, which is assigned to the stretching vibration of O-H groups involved in structures such as cellulose, hemicellulose, pectin, and lignin. New peaks, such as those at 3624 cm^{-1} and 3708 cm^{-1}, were observed after alkaline treatment.

As shown in Figures 2 and 3, big heat release peaks at about 186°C and 189°C were observed in DSC spectra of treated and untreated fibers, respectively. These results indicate that extensive exothermic reactions occurred at these temperatures. The peaks of the fiber samples disappeared when the samples were run a second time. Some of the bark components start to be degraded when temperatures are greater than 200°C. Chemical polymerization of phenolic extractives and degradation might occur simultaneously at high temperature.[11] The lack of peaks generated by the second DSC run suggests that the exothermic reaction observed in the first run was chemical bonding and that condensation was complete. The peak generated from untreated bark was slightly different from that of treated bark because the chemical nature of the bark had been changed by alkaline treatment.

Effect of Pre-heating Pressure on Fiber Properties

The treated and untreated bark samples were both pre-heated at lower (0.3 MPa) and higher (0.75 MPa) steam pressures, but they were refined at the same refiner speed and refining energy. The resultant fibers were hot-pressed at the same conditions to make fiberboards. The fibers from raw materials (both treated and non-treated bark) preheated at the lower steam pressure could not be effectively self-bonded and the resulting panels were too weak to test their properties. Obviously, at the same pre-heating time

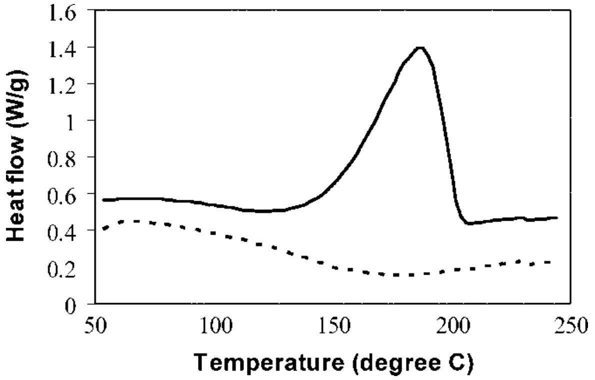


Figure 2. DSC spectra of untreated bark fibers (1st test: solid line, 2nd test: dotted line).

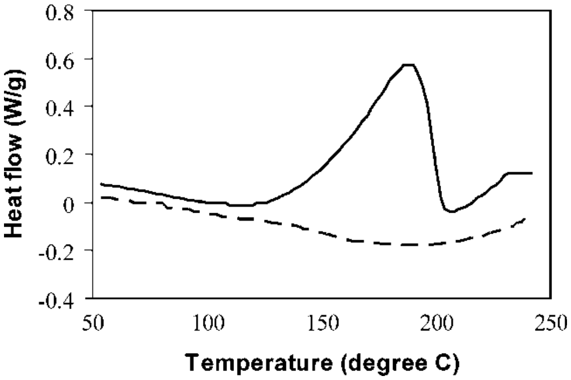


Figure 3. DSC spectra of alkaline treated bark fibers (1st test: solid line, 2nd test: dotted line).

(3 min), the treatment temperature significantly affected the fiber properties, and further affected the panel properties. Previous research found that steam treatment of *Pinus radiata* bark at 150–245°C for 3 min not only condensed tannins and formed less extractable polymers, but produced furfurals and hydroxymethyl furfural by hydrolysis of hemicellulose.[29] Similarly, in the present research, cooking black spruce bark for 3 min in the cooking screw should hydrolyze hemicellulose, release and condense extractives like tannins, and also modify fiber properties. The condensed polyphenolics and hydrolyzed hemicellulose remained during refining and then precipitated on the fiber after drying. These chemicals act as binders when the fiberboards are hot-pressed.[32] Furfural produced by partial hydrolysis of hemicellulose reacts in the hot-pressing process with phenolic substance from lignin to form condensed products similar to PF resins.[33] The higher the pre-heating pressure (higher temperature), the more severe these reactions, thus the stronger the resultant binding. For both treated and non-treated bark, higher pre-heating pressure chemically and physically modified the fibers and better fiberboards were produced. The pre-heating stage strongly influenced the fiberboard properties.

Effect of Alkaline Treatment on Fiberboard Mechanical Properties

Alkaline-treated bark was refined after 3-min pre-heating at 0.75 MPa of steam pressure and the resulting fiberboard had as high as 1.97 MPa of IB strength (Table 2). Untreated bark was pre-heated and refined at the same conditions, but the resulting fiberboard pressed at the same parameters had only 0.49 MPa of IB strength. Earlier reports indicated that bark particles can be formed into a board without the addition of synthetic resin at 200°C, but that a long pressing time (40–80 min) was required.[13] Bark particleboard could

Table 2. Properties of fiberboard made from treated and non-treated bark fibers

	Panel color			IB	MOR	MOE	TS
	L*	a*	b*	MPa	MPa	MPa	%
Untreated bark	29.72	6.63	12.20	0.49	10.8	1643	29.8
Treated bark	40.16	4.95	15.19	1.97	17.2	3255	28.6

be made in 5 to 10 min, but the press temperature had to be at 250 to 300°C.[11] In this work, fiberboards were manufactured from treated and untreated bark at 210°C and only 6 min of pressing. Bonding mechanisms of binderless fiberboard are hypothesized to be thermoplastic flow, physical consolidation, and chemical bonding. Studies on binderless larch bark board found that the polymerization of phenolic extractives in the bark played an important role in IB when the board was pressed for a short time at temperatures above 250°C.[12] There were more leached-out and condensed polyphenols and hydrolyzed hemicellulose on the surface of alkaline-treated bark than on that of untreated samples. On the other hand, alkali treatment of bark was directly related to the swelling level of fibers and more entire and flexible fibers were obtained from the swollen raw materials by subsequent refining.[17,34,35] The inter-fiber bonding area was increased by alkaline treatment.

Bark soaked in alkaline solution, pre-heated at 0.75 MPa of steam pressure and subsequently refined had a much higher panel MOR than did untreated bark (Table 2). Increased IB by alkaline treatment contributed to this bending strength. It has been demonstrated that alkaline treatment of hardwood strongly modifies fiber properties and improves fiber length and strength.[35] Alkaline treatment of bark followed by refining resulted in longer and stronger fibers and therefore significantly improved panel MOR.

Fiberboard made from untreated bark had a MOE of 1643 MPa, but the MOE of fiberboard made from alkaline-treated bark was 3255 MPa (Table 2). The elastic modulus of natural wood fiber is about 10 GPa, but elastic moduli of cellulose fibers obtained from wood fiber by chemical pulping processes are up to 40 GPa.[36] Alkaline treatment weakens the lignin bonds between the cellulosic fibers and partially hydrolyzed hemicellulose, so fibers are less damaged in subsequent refining processes. The treated fibers, which lower in hemicellulose content, had higher MOE and therefore resulted in higher MOE of fiberboards.

Effect of Alkaline Treatment on Fiberboard Thickness Swelling

Bark panels made from treated and untreated bark showed very similar TS values (Table 2), which were in the range of 28–30%. It has been demonstrated that deacetylation of wood and generation of carboxylic acid groups are the two principal chemical reactions during a mild alkaline treatment.[17,34,35] Both of these reactions result in an increase in hydroxyl groups. These hydroxyl groups might react with other chemicals, such as furfural from hydrolyzed hemicellulose, to develop the internal bonding. Compared to the negative effect on TS from hydroxyl groups, the positive effect from the increased IB might be stronger, so no significant difference in TS with and without alkaline treatment was observed.

Effect of Alkaline Treatment on Fiberboard Color

The panel color of treated bark was much lighter than that of untreated bark (Table 2). It was also observed that treated bark fiber had a lighter color than untreated bark fiber. The color is due to phenolic components, and condensation reactions between them led to color reduction.[29] Alkaline treatment brought more moisture to the bark and leached out more polyphenols at the same pre-heating condition. These components which leached out from bark started to polymerize during the refining process and this polymerization led to a color reduction of the fibers. Polymerization of polyphenols and lignin during the hot-pressing process further decreased the fiberboard color.

CONCLUSIONS

Black spruce bark residue from a lumber mill contained a certain amount of wood and was a suitable fiber resource for fiberboard. The high content of alkaline extractives of the bark itself provided high self-bonding ability. Pre-heating treatment of the bark at a higher steam pressure was required for development of both fiber properties and self-adhesion. Alkaline treatment of bark before pre-heating decreased the color of both the fibers and the resulting fiberboard and greatly improved fiberboard mechanical strength and stiffness, but did not have significant effects on dimensional stability. Additional experiments are necessary to optimize the alkaline treatment, preheating, refining, and hot-pressing conditions for the development of self-bonding performance.

REFERENCES

1. Laganière, B.; Hernández, R.E. Effects of radial force and tip path overlap on the ring debarking effciency of frozen balsam fir logs. Forest Products J. **2005**, *55* (3), 44–49.
2. Dost, W.A. Redwood bark fiber in particleboard. Forest Products J. **1971**, *21* (10), 38–43.

3. Chow, P. Phenol adhesive bonded medium-density fiberboard from Quercus rubral L. bark and sawdust. Wood and Fiber **1979**, *11* (2), 92–98.
4. Chow, P. Properties of medium-density, dry-formed fiberboard from seven hardwood residues and bark. Forest Products J. **1976**, *26* (5), 48–55.
5. Muszynski, Z.; McNatt, J.D. Investigations on the use of spruce bark in the manufacture of particleboard in Poland. Forest Products J. **1984**, *34* (1), 28–35.
6. Blanchet, P. Particleboard made from hammer milled black spruce bark residues. Wood Sci. Technol. **2000**, *34*, 11–19.
7. Pizzi, A.; Stephanou, A. Fast vs. slow-reacting non-modified tannin extracts for exterior particleboard adhesives. holz als Roh- und Werkstoff **1994**, *52*, 218–222.
8. Pizzi, A. Tannery row—The story of some natural and synthetic wood adhesives. Wood Sci. Technol. **2000**, *34* (4), 277–316.
9. Jorge, F.C.; Neto, C.P.; Irle, M.A.; Gil, M.H.; Jesus, J.P.D. Wood adhesives derived from alkaline extracts of maritime pine bark: preparation, physical characteristics and bonding efficacy. Holz als Roh- und Werkstoff **2002**, *60*, 303–310.
10. Wellons, J.D.; Krahmer, L. Self bonding in bark composites. Wood Science **1973**, *6* (2), 112–122.
11. Chow, S. Bark boards without synthetic resins. Forest Products J. **1975**, *25* (11), 32–37.
12. Matsumoto, A.; Nishikawa, K. Binderless boards from larch bark. Journal of Hokkaido Forest Products Research Institute **1982**, *365*, 1–7.
13. Chow, S.; Pickles, K.J. Thermal softening and degradation of wood and bark. Wood Fiber **1971**, *3* (3), 166–178.
14. Levitin, N. Chemical composition of the barks of white spruce, balsam fir and jack pine, R. *OPX194E, Eastern For. Prod. Lab*; Ottawa, Ontario, **1977**.
15. Isenberg, I.H. Pulpwoods of the United States and Canada. Vol. 1, Appleton, Wisconsin: The Institute of Pafer Chemistry, **1980**.
16. Ito, T.; Tsuchiya, H. Cold soda chemi-groundwood pulp and hot sulfite chemi-groundwood pulp in the newsprint mill: an empirical comparison. Pulp and Paper Canada **1976**, *77* (3), 37–43.
17. Zanuttini, M.; Citroni, M.; Martínez, M.J.; Marzocchi, V. Chemimechanical pulping of poplar wood. Alkaline wood pretreatment at low temperature. Holzforschung **1998**, *52* (4), 405–409.
18. Han, G.; Umemura, H.; Zhang, M.; Honda, T.; Kawai, S. Development of high-performance UF-bonded reed and wheat straw medium-density fiberboard. J. Wood Sci. **2001**, *47*, 350–355.
19. Tappi, Preparation of wood for chemical analysis. Tappi Test method T 264 cm-97, **1997**.
20. Tappi, Ash in wood, pulp, paper and paperboard: combustion at 525°C. Tappi Test Methods T 211 om-93, **1993**.
21. Tappi, Acid-insoluble lignin in wood and pulp. Tappi Test Methods T222 om-98, **1998**.
22. Tappi, One percent sodium hydroxide solubility of wood and pulp. Tappi Test Methods T212 om-98, **1998**.
23. Tappi, Water solubility of wood and pulp. Tappi Test Methods T207 cm-99, **1999**.
24. Tappi, Delignification of unbleached pulp (Chlorine gas method). Tappi Useful Method 249, **1976**.
25. Johns, W.E.; Niazi, K.A. Effect of pH buffering capacity of wood on the gelation time of urea-formaldehyde resin. Wood and Fiber **1980**, *12* (4), 255–263.
26. ASTM, Standard test methods for evaluating properties of wood-base fiber and particle panel materials. ASTM D 1037-99, **1999**.

27. Chang, Y.-P.; Mitchell, R.L. Chemical composition of common North American pulpwood barks. Tappi J. **1955**, *38* (5), 315–320.
28. Harun, J.; Labosky, J.P. Chemical constituents of five Northeastern barks. Wood and Fiber Sci. **1985**, *17* (2), 274–280.
29. Lomax, T.D.; Mackie, K.L.; Meder, R.; Croucher, M.; Burton, R.J. Steam explosion of Pinus radiata bark. J. Wood Chem. Tech. **1994**, *14* (4), 539–561.
30. Harrington, K.J.; Higgins, H.G.; Michell, A.J. Infrared spectra of Eucalyptus regnans F. Muell. and Pinus radiata D. Don. Holzforschung **1964**, *18* (4), 108–113.
31. Costanza, V.; Zanuttini, M.A. Optimal operation points in alkaline pulping. Latin American Applied Research **2004**, *34*, 155–164.
32. Velásquez, J.A.; Ferrando, F.; Farriol, X.; Salvadó, J. Binderless fiberboard from steam exploded Miscanthus sinensis. Wood Sci. Technol. **2003**, *37*, 269–278.
33. Mobarak, F.; Fahmy, Y.; Augustin, H. Binderless lignocellulose composite from bagasse and mechanism of self-bonding. Holzforschung **1982**, *36* (3), 131–135.
34. Zanuttini, M.; Marzocchi, V. Kinetics of alkaline deacetylation of poplar wood. Holzforschung **1997**, *51* (3), 251–256.
35. Zanuttini, M.; Marzocchi, V. Alkaline chemi-mechanical pulp from poplar. Relationship between chemical state, swelling and papermaking properties. Holzforschung **2003**, *57* (5), 489–495.
36. Bledzki, A.K.; Gassan, J. Composites reinforced with cellulose based fibres. Prog. Polym. Sci. **1999**, *24*, 221–274.