THERMAL CHARACTERISTICS OF DOUGLAS-FIR BARK FIBER—25 C TO 250 C[1]

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ABSTRACT

To determine if extractives control the thermal properties of Douglas-fir [*Pseudotsuga menziesii* (Mirb.) Franco] bark fiber at lower temperatures and limit its utility for reinforcing plastic, fiber and its extractives were subjected to differential scanning calorimetry and thermogravimetric analyses. In addition, the amount and composition of volatiles were measured as a function of temperature and fiber recovery process.

Heating bark fiber to 250 C yielded water and carbon dioxide as the major volatiles, the amounts increasing disproportionately as the extractive content of the fiber increased. Because the extractives were thermally less stable than the fiber wall, recovering bark fiber of low extractive content by pressurized refining reduced volatilization more than fiber recovery by atmospheric refining or alkali extraction.

Keywords: Differential scanning calorimetry, differential thermal analysis, thermogravimetric analysis, Douglas-fir, bark fiber, disc-refining, extractives.

The wood industry of the Pacific Northwest annually generates more than 1.5 million tons of bark from Douglas-fir, *Pseudotsuga menziesii* (Mirb.) Franco (Hall 1971). Although much of this residue is used as fuel, including bark fractions in composite products would yield a greater financial return.

Cells in the fiber (sclereid) fraction of Douglas-fir bark are spear-shaped, lignified, thick-walled, and approximately 1 mm long and 50 μm in diameter (Miller et al. 1974). Their chemical components resemble those in the fiber walls of wood (Chen 1973; Zerrudo 1972; and Laver et al. 1974), but 13–18% of the bark fibers may be extractives.

Phenolic and polypropylene moldings have been strengthened by including bark fibers but not to the extent expected (Miller et al. 1974; Miller and Wellons 1978). For the bark fiber to reinforce plastics, it must bond to the plastic. This requires that the bark fiber not volatilize excessively at processing temperatures. Such volatiles not only interfere with bonding, but also bubble the molded plastic, weakening it and disturbing its surface texture.
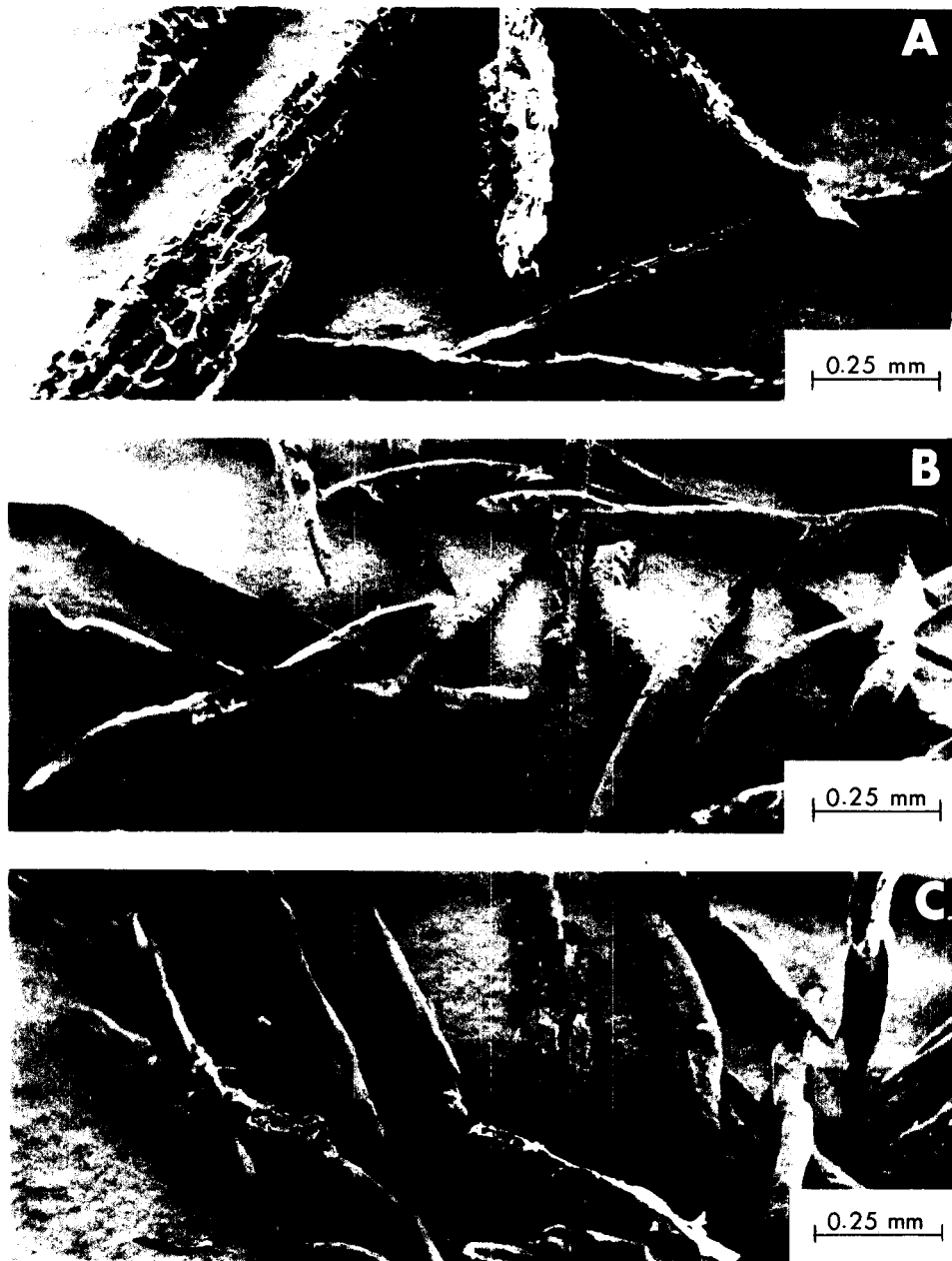

FIG. 1.   Scanning electron micrographs of Douglas-fir bark fiber. (A) Atmospheric disc-refined, (B) pressurized disc-refined, and (C) alkali extracted (Miller et al. 1974).

We tested the hypotheses that the thermal properties of Douglas-fir bark fiber at lower temperatures limit its utility as a reinforcing fiber and that extractive components control those thermal properties. Because most extractives are associated with a sheath on the fiber surface (Kiefer and Kurth 1953), any process

TABLE 1. *Extractive content of bark fibers from sequential extraction.*

Extracting solvent and temperature	% Extractives[a]		
	Fiber A, atmospheric-refined	Fiber B, pressure-refined	Fiber C, alkali-extracted
Benzene (60 C)	4.4	0.6	1.4
Diethyl ether (25 C)	0.8	Trace	Trace
Ethanol (60 C)	7.1	2.1	1.5
Water (60 C)	1.0	0.8	5.0
Total	13.3	3.5	7.9

[a] Percent based on ovendry weight of unextracted fiber.

that efficiently removes the sheath should not only reduce the amount of extractives and any related volatilization by the fiber, but it should also improve bonding to the fiber surface. Therefore, if our hypotheses are true, the thermal properties of bark fiber can be modified as needed by varying the fiber recovery process.

MATERIALS AND PROCEDURES

Bark fractionation and fiber characterization

Three types of fiber were prepared from Douglas-fir bark (Fig. 1). Atmospheric disc-refining of dry bark yielded a relatively "crude" fiber, A, that was isolated by a combination of electrical and mechanical screening (Short et al. 1973). Fiber B was obtained from whole bark that had been pressurized, disc-refined at 25 psi of steam pressure, and isolated by flotation in cold water and wet screening (Miller and Wellons 1978). Weyerhaeuser Company supplied the third type, C, that was obtained by mechanically grinding and screening whole bark, extracting the fibers with kraft white liquor at 100 C, washing them with clean water, and rod-milling the extracted fibers.

The proportion of nonfibrous material was determined by photographing random samples of the fiber fractions, projecting the photograph onto a dot grid, and counting the dots on fiber and other particles. The extractables in the three fibers were isolated by continuously dripping heated solvent (2.4 ℓ) at a rate of 0.1 ℓ per hour from a separatory funnel through a fiber sample (50 g) in a Soxhlet thimble. The solvent and extractables were collected in a cold flask, reducing the possibility of decompassing the extractives during isolation. The sequence of solvents and extraction temperatures was: benzene (60 C), diethyl ether (25 C), ethanol (60 C), and water (60 C). Extractives were recovered on a rotary evaporator. All fiber types and their extractives were conditioned under vacuum over Drierite, and residual water was determined by Karl Fischer titration (Browning 1967).

Differential scanning calorimetry (DSC)

Duplicate 10-mg samples of the fibers and their extractives were analyzed with a Perkin-Elmer Differential Scanning Calorimeter, model DSC-1B, using nitrogen as the carrier gas (37 cc/minute). Samples were packed in uncovered aluminum pans and heated to 250 C at 10 C/minute with a calorimeter sensitivity of 16 mcal/second. Simultaneously, a thermal conductivity detector analyzed effluent.
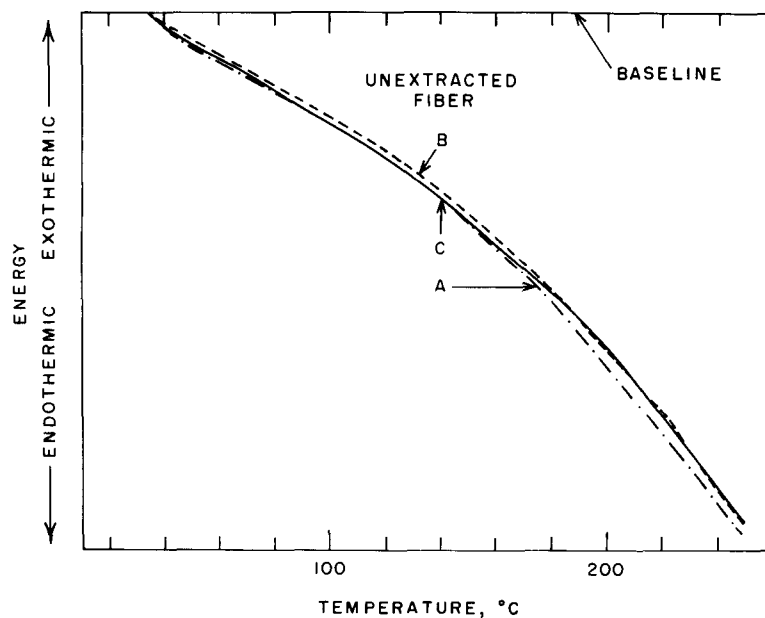
FIG. 2. Differential scanning calorigrams of fibers from Douglas-fir bark. Curves were almost identical before and after extraction.

Thermogravimetric analyses (TGA)

A Perkin-Elmer model TGS-1 Thermobalance determined weight loss of the duplicate samples (1–3 mg) and their extractives when heated to 250 C at 10 C/minute in uncovered platinum pans. Nitrogen gas carried the volatiles through a series of liquid-nitrogen cold traps, then most of the nitrogen was stripped from the condensed volatiles by evacuating the cold traps for 24 seconds. The condensed sample in the cold traps was warmed to room temperature and analyzed with a Varian Mat CH7 Mass Spectrometer.

In addition, we placed duplicate 1–3 mg samples of fiber in a platinum TGA
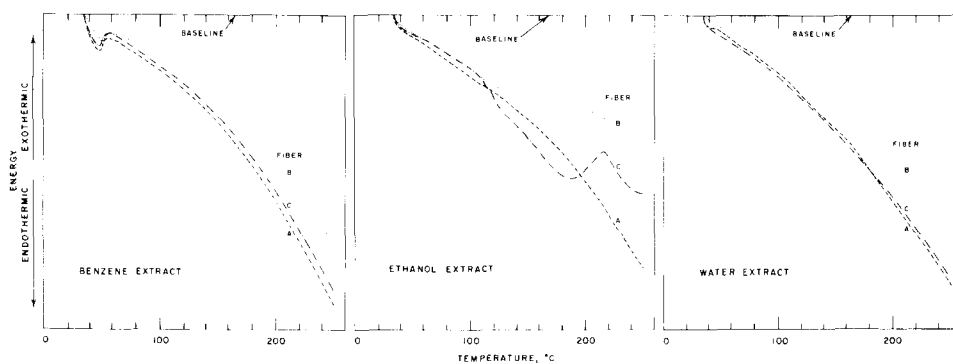

FIG. 3. Differential scanning calorigrams of extractives from fiber of Douglas-fir bark.
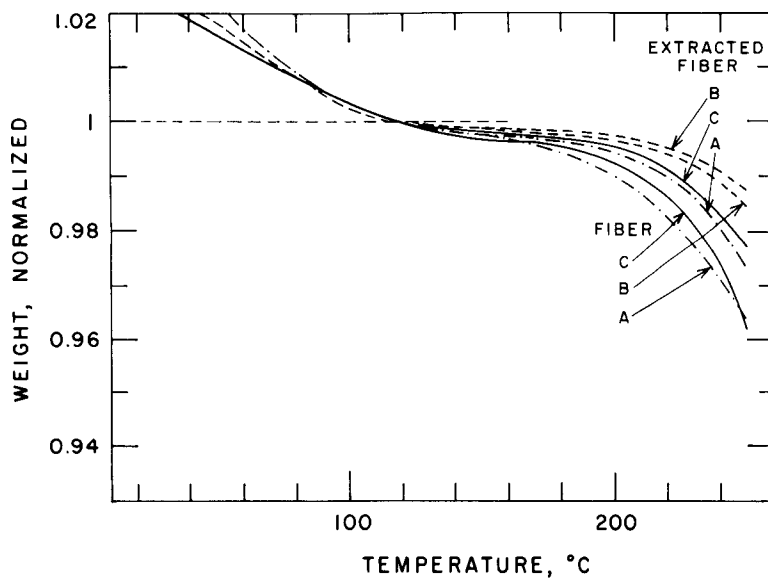
FIG. 4.   Thermogravimetric analyses of fibers from Douglas-fir bark.

sample pan suspended in the TGA furnace, which was evacuated to approximately 5×10^{-3} torr, then heated to 250 C at a rate of 10 C/minute. The increased pressure (± 0.07 torr) was recorded with an oil manometer.

THERMAL ANALYSES OF FIBERS

Fiber properties

Fibers B and C, the pressure-refined and alkali-extracted fibers, contained no cork or other nonfibrous fragments. Fiber A, the atmospheric-refined fiber, was 10% cork (volume basis), an impurity that should increase the amount of extractives because cork is 40% extractives, whereas fiber is 14% (Hergert and Kurth 1952; and Kiefer and Kurth 1953).

Electron micrographs of fiber A (Fig. 1) showed single and bundled fibers

TABLE 2.   *Thermogravimetric analyses and quantities of volatiles generated by heating bark fibers.*

Sample	% of original weight lost when heated at:		ml gas/g fiber at STP[a]	
	35 to 120 C	120 to 250 C	35 to 120 C	120 to 250 C
Unextracted fiber				
A	2.6	3.6	34	35
B	2.2	1.6	40	24
C	2.1	3.7	31	37
Extracted fiber				
A	2.9	2.7	37	32
B	2.4	1.2	41	23
C	2.0	2.2	34	30

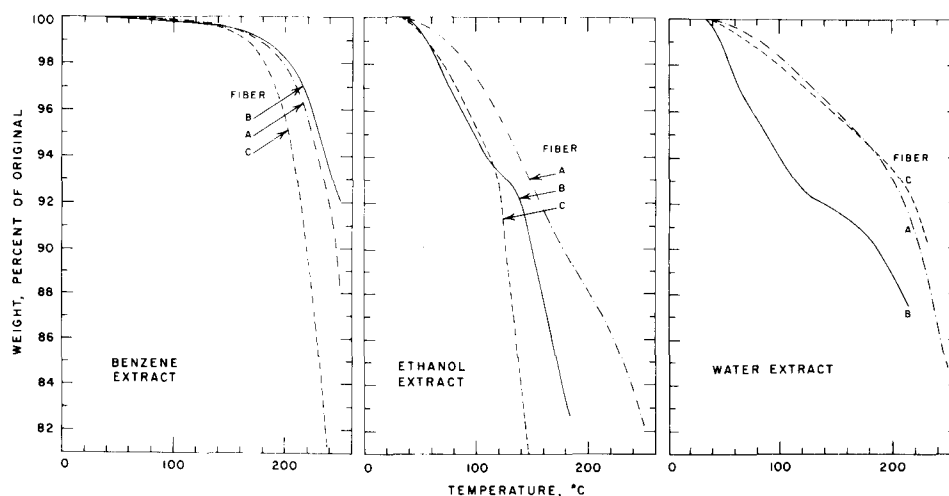[a] Standard temperature and pressure are 0 C and 760 torr.

FIG. 5. Thermogravimetric analyses of extractives from fibers of Douglas-fir bark.

completely encased by a matrix of torn parenchyma cells, conforming to the general shape of the fibers. Kiefer and Kurth (1953) thought this was a phenolic sheath because the parenchyma cells of bark contain a large amount of phenolic material. Fiber A had the most extractives, 13.3% (Table 1). Removing these extractives did not cleave fibers from the bundles, similar to results reported by Hergert and Kurth (1952) and Kiefer and Kurth (1953).

Fiber C had less sheathing than fiber A, and only a few fibers were in bundles, reflecting the effect of the alkali extraction and the subsequent rod milling. Although we expected fiber C to have the least extractives, it had the greatest percentage of water-soluble extractives and was intermediate in total content of extractives. Apparently, during manufacturing, either the alkali degraded the fiber and increased its solubility, or washing was insufficient to remove extractives.

Fiber B was the "cleanest," single fibers with no surrounding sheath. The pressure refining may have removed the sheath by separating the fiber from adjacent cells at the middle lamella (Wellons and Miller 1972). The flotation and wet screening used to purify fiber B effectively removed broken fibers and extraneous materials. Because of the cold-water recovery process, fiber B should contain less water solubles than fiber A. However, the low total content of extractives, 3.6%, was surprising. Apparently, most of the alcohol solubles were in the fiber sheath which was effectively removed by the pressurized refining process.

Differential scanning calorimetry

DSC scans before and after extraction were nearly identical for all three fiber types (Fig. 2). As temperature increased, scans were increasingly endothermic with no obvious transition temperatures or exotherms. This endothermic response was the sum of increasing heat capacity, vapor loss, and endothermic decomposition. Thus, other thermal responses masked any differences in the amount of thermally induced volatilization.

The effluent detector showed substantial differences in either amount or com-

position of gas volatilized from fiber types and substantially less volatilization after extraction.

Because the DSC responses were so similar (Fig. 2) but the effluent detector indicated that the amount or composition of volatiles varied in proportion to the extractives, the various extractives were analyzed by DSC (Fig. 3). The ether-soluble extractives were only trace components of all three fiber types, so their thermal responses are not reported.

In general, as temperature increased from 35 to 250 C, the benzene-, ethanol-, and water-soluble extractives were increasingly endothermic (especially for fibers A and C) and produced few distinct endotherms or exotherms (Fig. 3). However, the benzene-soluble extractives for all three fibers melted near 48 C as previously reported by Kurth (1967), producing an endothermic peak. The ethanol solubles of fibers B and C melted near 115 C, producing no endothermic peak. Instead, they produced an increasingly endothermic DSC response with distinct and unexplainable exotherms at 180 C and 215 C, respectively. The DSC scans of the ethanol solubles of fiber A were similar to those of the unextracted fibers.

Thermogravimetric analysis

Because the DSC scans were not definitive, we used TGA to confirm the effluent analyses. Unextracted fiber B lost the least weight, 3.8%, when heated from ambient to 250 C; fiber C lost 5.8% of its initial weight; and fiber A, with a 6.2% weight loss, was the least thermally stable (Table 2). Duplicate analyses were indistinguishable.

Superimposing the thermograms of the fibers at 120 C (Fig. 4) removes differences in initial moisture and represents the behavior of the different "dried" fibers. The weight loss from ambient to 120 C agreed with the moisture contents determined by Fischer titration. Fiber B had few extractives, lost the least weight when heated from 120 C to 250 C, and changed little when extractives were removed. Fibers A and C had many more extractives and lost more weight when heated, although extraction reduced that weight loss. Extraction neither removed the sheath surrounding fiber A nor completely cleaned the surface of fiber C, leaving surface encrustations (Fig. 1) and residual extractives that seemed to cause the differences between the TGA scans of the extracted fibers.

The extractives were considerably less thermally stable than the extracted fibers (Fig. 5). The benzene solubles were thermally the most stable of the extractives; they did not lose substantial weight until heated in the range of 165 C to 180 C. At temperatures greater than 165 C, the rate of weight loss was considerably greater for benzene solubles from fiber C, possibly due to the alkali used to isolate this fiber. However, the greater quantity of benzene solubles in fiber A likely made this extractive an important contributor to the thermal outgassing of fiber A.

The ethanol-soluble extractives were thermally the least stable. For fiber A, these extractives lost substantial weight at 75 C and continued to lose weight as temperature increased. The ethanol solubles from fiber B lost substantial weight at 60 C; the rate of weight loss decreased between 110 C and 130 C, but increased at 130 C. Weight loss by ethanol solubles from fiber C was essentially identical to that of fiber B up to about 120 C but then further increased greatly. Apparently, the steam used to recover fiber B and the alkali used to recover fiber C affected

TABLE 3. *Composition of volatiles generated from heated bark fibers and their extractives.*[a]

| | Temperature range | | | |
| | 25 to 170 C | | 170 to 250 C | |
Sample	% H$_2$O	% CO$_2$	% H$_2$O	% CO$_2$
Fiber A	94	0	92	0
Benzene solubles[b]	98			2
Ethanol solubles[b]	65			1
Water solubles[b]	79			17
Fiber B	97	2	88	4
Benzene solubles[b]	92			8
Ethanol solubles	81	0	38	8
Water solubles[b]	83			11
Fiber C	95	3	91	2
Benzene solubles[b]	94[c]			3
Ethanol solubles	93	3	65	16
Water solubles	96	4	80[b]	16

[a] The peaks at mass numbers 18 and 44 are assumed totally due to water and carbon dioxide.
[b] Due to insufficient sample, only one analysis was made for the entire range, 25 C to 250 C.
[c] Approximately 3% O$_2$ was introduced by an air leak.

thermal stability. However, the slightly greater thermal stability of the ethanol solubles from fiber A likely was offset by the greater quantity of these extractives in fiber A.

The water-soluble extractives of fibers A and C responded similarly to increasing temperature—weight loss gradually increased from 40 C to 250 C. The larger amount of water solubles in fiber C should have caused significant volatilization when fiber C was heated. The water-soluble extractives of fiber B responded quite differently, losing substantial weight when the fiber with its higher moisture content was heated from 50 C to near 120 C. We do not know why the water solubles from fiber B were more hygroscopic than those from A or C. The effluent detector indicated that fiber B also volatilized considerably near 180 C, accompanying the increased rate of weight loss at temperatures above 180 C, an increase which also occurred for fibers A and C.

Quantitative and qualitative gas analyses

The volumes of gas produced as a result of the thermally-induced weight losses (Table 2) substantiate the TGA scans, reaffirm the superiority of fiber B as an additive to molding compounds, and confirm the effect of extractive components. The volume of gas produced by heating from 120 C to 250 C was greater per gram of fibers before than after extraction. This difference was greatest for the alkali-extracted fiber C and least for the pressure-refined fiber B. Half the gas generated by all three fiber types can be eliminated by initially heating the fibers to 120 C (Table 2).

Generally more than 90% of the volatiles from these fibers was water, with the balance mostly carbon dioxide (Table 3). Because both methane and carbon monoxide would have partly evaporated when excess nitrogen was swept from the cold traps, we suspect the experimental error of this analysis was about 3%. The gas composition was nearly the same at temperatures above and below 170 C,

but the percent of water decreased slightly at the higher temperatures and was replaced by other degradation products.

Partly because of adsorbed solvent, the gases evolved from the extractives were more heterogeneous than those from the fibers, but the extractives decomposed mostly to water and carbon dioxide.

The volatiles from ethanol-soluble extractives contained significantly less water, especially from 170 C to 250 C, than the volatiles from the benzene- or water-soluble extractives. Although as much as half of the nonaqueous volatiles from the ethanol solubles could be attributed to adsorbed ethanol, the remainder was a complex mixture with several unidentified fragments of larger molecules, especially at mass numbers 57 and 86.

The water solubles of the three fiber types generated volatiles containing approximately 80% water and 15% carbon dioxide. These extractives had the highest initial moisture content, inflating the percentage of water, so the true percentage of carbon dioxide probably was higher than reported.

The amount of volatilization tolerable from bark fiber in a plastic molding is unknown, but possibly can be estimated from Hendricksen and McCain (1971) who used fiber C, after drying, in thermoplastic moldings heated to 210 C. At this temperature, fiber C lost approximately 1% of its weight in the TGA. Using 1% weight loss as a criterion, our results suggest that fiber A could not be used at temperatures above 199 C, whereas fiber B could be used at temperatures up to 237 C.

CONCLUSIONS

1. High extractive content disproportionately increases thermal volatilization of Douglas-fir bark fiber at temperatures below 250 C.
2. The volatiles generated by heating the bark fiber to 250 C consist mostly of water and some carbon dioxide.
3. The amount of thermal volatilization as bark fiber is heated from ambient to 250 C can be controlled partly by the fiber recovery process. Pressurized, disc-refined fiber contains fewer extractives and is more stable thermally than fiber extracted with alkali or isolated by atmospheric disc-refining of whole bark.

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