FREEZING OF WATER IN HARDBOARD: ABSENCE OF CHANGES IN MECHANICAL PROPERTIES[1]

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ABSTRACT

One-eighth-inch dry process and two species mixes of 7/16 in. wet process hardboard roofings plus 1/8 in. dry process and 7/16 in. wet process standard hardboards were examined using differential thermal analysis to ascertain the maximum moisture content that exterior hardboard could attain without exhibiting significant freezing. All samples with moisture contents greater than ≈20% exhibited high temperature freezing near −10 C. Additionally, dry process materials with moisture contents near or above 30% had a distinct low temperature freezing event near −35 C. Integration of the area under the freezing curves indicated that ≈3% of the water contained in these samples froze at low temperature. During thawing, this fraction of water melted above −10 C. This type of thermal hysteresis is characteristic of the freeze/thaw behavior expected for supercooled water. Mechanical strength tests performed on dry process (4.1 and 41.1% moisture content) and wet process (4.4 and 34.3% moisture content) standard hardboard exposed to freeze/thaw cycling to −50 C revealed no consistent changes in the modulus of elasticity, modulus of rupture, tensile strength parallel to surface, or internal bond strength.

Keywords: Hardboard, mechanical properties, moisture content, freezing.

The dimensional stability of wood and wood-based products such as hardboard in response to changing environmental conditions has been the focus of research for many years (Bodig and Jayne 1982; Myers and McNatt 1985). Most attention has been paid to sorption-based shrinking and swelling phenomena and their effect on the physical and mechanical properties of wood and wood-based products. However, the frequently overlooked and often coincident temperature-driven dimensional changes may also cause undesirable responses.

Schirp and Kubler (1968) described four mechanisms by which temperature-driven changes may occur in wood during cooling. These mechanisms have been reviewed by Skaar (1972). The first is the normal thermal contraction that occurs in dry wood. It is caused by a decrease in interatomic distances at low temperature. This factor contributes to the ob-

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servation that the transverse coefficients of thermal expansion in wood are much greater than those parallel to the grain. The second mechanism is the "cold-shrinkage" of wood near the fiber saturation point when it is exposed to freezing temperatures. This shrinkage is caused by the lower vapor pressure over ice in comparison to the vapor pressure of water over saturated wood cell walls. Formation of "frost cracks" in trees is believed to be associated with this mechanism (Kubler 1988; Phelps 1974), but may also be a direct consequence of ice formation itself (see the following). The volumetric expansion of water as it freezes (approximately 8%, Haymet 1987) in filled or nearly filled cell lumens or in small capillary pores is the third mechanism. This freezing would be expected to occur near 0 C in cell lumens, provided that an ice nucleus is available and that little solute is present in the water. Water in microcapillary pores would be expected to freeze at lower temperatures because of the curved surfaces that form between liquid water in the pores and vapor or ice above them (Everett 1961). Although it is often presumed that volumetric expansion during freezing is the primary cause of damage in heterogeneous porous materials, the growth of large ice crystals or "ice lenses" in such materials is usually of greater consequence (Everett 1961). Examples include frost heaving in soils (Everett 1961), spalling in masonry (Litvan 1978), and frost crack formation in wood (Kubler 1988). Large ice masses that cause separations in living tissues have also been observed in overwintering plants (Weigand 1906; Ashworth 1989). The final mechanism, the swelling of saturated wood between 0 and 4 C, is attributed to the thermal-expansion coefficient of water. While the physicochemical change identified with each of the four mechanisms is reversible, the external and/or internal change produced in a wood product from a temperature-drive contraction or expansion may not be reversible.

This study was designed (1) to ascertain the maximum moisture content that exterior hardboard samples could attain without exhibiting significant freezing as measured by differential thermal analysis (DTA), and (2) to determine if there are changes in the mechanical properties of hardboard that attend freeze/thaw cycles in which ice formation occurs. The hypothesis to be tested was that the expansion of absorbed water in lumens, cellwall pores, and intercellular spaces during freezing or that the growth of large ice crystals within the hardboard damages the hardboard sheet structure. The results should contribute to a better understanding of the performance of hardboard products under field freezing conditions.

MATERIALS AND METHODS

Materials

Three hardboard roofing substrates were provided by Masonite Corporation for analysis by DTA. These were ⅛ in. dry process experimental roofing and two species mixes of 7/16 in. wet process Woodruf®. Boards approximately 2 in. × 4 in. were preconditioned to four target equilibrium moisture contents (Table 1). Additionally, ⅛ in. dry process and 7/16 in. wet process standard hardboards at two target moisture contents were supplied for DTA and mechanical testing following freeze/thaw cycling. Samples from the latter two hardboard were sized according to ANSI/ASTM D 1037 (1978) directions for static bending, tensile strength parallel to surface (T_p), and internal bond (IB) tests. Five samples were used for each temperature treatment in static bending tests. A minimum of eight samples was used for each temperature treatment for T_p and IB tests.

DTA

Freezing or thawing of water in hardboard samples was monitored by DTA. Briefly, the DTA method involves cooling a sample and an inert reference at the same rate, but in separate chambers (Pope and Judd 1977). The test sample is enclosed in a small aluminum foil cup, attached to a temperature sensor and placed into one chamber. The reference is an empty foil cup attached to an identical temperature sensor and placed in the second

TABLE 1. *Properties of hardboards used for DTA and freeze/thaw (F/T) cycling studies.*

Peaks	Sample	Substrate	Moisture content (%)[1]		Exotherm	
			Target	Actual	High	Low
DTA tests	A	dry process	6–8	9.2	no	no
	B	experimental	12–14	21.2	yes	?
	C	roofing	18–20	29.9	yes	yes
	D		20–35	37.2	yes	yes
	E	Woodruf™	6–8	9.0	no	no
	F	(species mix 1)	12–14	14.1	no	no
	G		18–20	21.7	no	?
	H		20–35	33.5	yes	?
	I	Woodruf™	6–8	8.8	no	no
	J	(species mix 2)	12–14	14.7	no	no
	K		18–20	18.7	?	?
	L		20–35	31.5	yes	?
F/T cycle	M	1/8 in. standard	6–8	4.1	no	no
	N	hardboard	20–35	41.1	yes	yes
	O	7/16 in. standard	6–8	4.4	no	no
	P	hardboard	20–35	34.3	yes	no

[1] Moisture contents for samples M, N, O, and P are from samples prepared for freeze/thaw cycling. All values represent the average of three samples.

chamber. In samples with freezable water, ice formation causes a warming of the sample chamber due to the heat of fusion of water (≈80 cal/g at 0 C). The temperature difference between the reference chamber and the sample chamber is recorded as a freezing peak or exotherm. Thawing events result in heat absorption, causing a cooling of the sample chamber with respect to the reference chamber. This difference is recorded as a thawing peak or endotherm.

Differential thermal analyses were performed using two DTA systems described previously (George 1982; Roberts and George 1983). The first system utilizes YSI 423 thermistors, has three individual sample chambers, a reference chamber, and associated signal conditioning network. The second system is similar, but utilizes Rosemount Engineering 118MF platinum resistance sensors. The analog outputs from the DTAs are converted to digital format and stored on floppy disks using an Analog Devices AD363 data acquisition system interfaced with a Southwest Technical Products 6809 microcomputer. Data are plotted on a Houston Instruments 2000 X-Y plotter. Each DTA system can resolve freezing events that produce differential temperatures on the order of 0.001 C. Samples, ≈1/8 in. × 1/8 in., were weighed and wrapped in aluminum foil before being placed in the DTA chambers. Unless otherwise stated, the DTA cooling/thawing rate was 50 C/h. Following DTA, the samples were dried at 105 C for at least 24 hours and weighed. Moisture contents are expressed on the basis of percent dry weight.

Freeze/thaw cycling

These experiments were conducted in a Tenney Jr. High/Low temperature chamber equipped with a microprocessor-based temperature controller. Unless otherwise noted, separate hardboard specimens were exposed to one of the following freeze/thaw cycles: (1) +2 C (control); (2) five cycles from +5 C to −20 C; or (3) five cycles from +5 C to −50 C. The cooling/thawing rate was 5 C/h. Temperature was held for one hour at the high or low limit before cycling was resumed. Sample temperature was monitored with a 24 gauge copper-constantan thermocouple and recorded on a Honeywell Electronik 112 multipoint recorder. Test temperatures were within ±1 C of the setpoint. After cycling, samples were

conditioned in a controlled environment at 50 ± 5% RH and 22 ± 3 C prior to mechanical testing. Hardboard moisture contents at the time of freeze/cycling were determined from separate samples.

Mechanical property testing

Tests were conducted in accordance with ASTM D 1037 (1978), with minor exceptions as noted. All tests were performed on a Tinius-Olsen universal testing machine equipped with an X-Y strip chart recorder. Modulus of elasticity (MOE) and modulus of rupture (MOR) were determined from static bending tests. Deflection was calculated by multiplying the time required to reach the proportional limit (obtained from the strip chart) by testing machine head speed. Tensile strength parallel to surface tests were conducted using a modified serrated gripping surface 1 in. wide and 2 in. long. Internal bond tests were not modified.

An analysis of variance (ANOVA) was performed on the data collected for each strength property. Additionally, mean values for the strength properties were separated as a function of temperature by least squares analysis (LSMEANS). Separate analyses were performed for each moisture level (i.e., low and high) to avoid confounding influences of the known relationship between moisture content and strength properties of fiber based wood products (Bodig and Jayne 1982). Statistical analyses were performed using ANOVA and LSMEANS procedures from SAS (*S*tatistical *A*nalysis *S*ystem).

RESULTS AND DISCUSSION

Differential thermal analysis

Results of DTA on dry process experimental roofing and both species mixes of wet process Woodruf® indicate that samples with moisture contents greater than ≈20% contained freezable water (Table 1). High moisture samples of ⅛ in. and 7/16 in. standard hardboard also exhibited freezing. In general, when freezable water was present, all types of hardboard exhibited a high temperature exotherm near

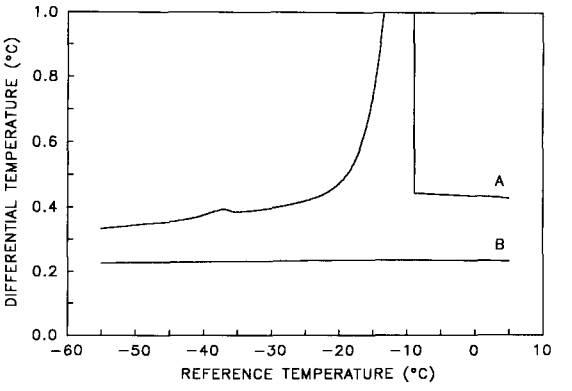

FIG. 1. Freezing curves determined by DTA for high moisture content (41.1%, A) and low moisture content (4.1%, B) ⅛ in. standard hardboard. See text for discussion.

−10 C. An additional low temperature exotherm was consistently observed near −35 C in 29.9 and 37.2% moisture content ⅛ in. experimental roofing and in high moisture ⅛ in. standard hardboard (Table 1, Fig. 1). This second exotherm remained in ⅛ in. standard hardboard when the cooling rate was reduced from 50 C/h to 5 C/h. Additionally, thawing analysis of ⅛ in. standard hardboard revealed that the water which crystallized near −35 C, melted above −10 C. Correcting for the decline in heat of fusion for water and then integrating exotherm peak areas for ⅛ in. standard hardboard indicated that ≈3% of total freezable water crystallized at low temperature.

The high temperature exotherm observed in high moisture hardboards is believed to be associated with the crystallization of bulk water in residual lumens and large intercellular or interfibrillar spaces. Similar exotherms have been observed in water-saturated heartwood of American sycamore (*Platanus occidentalis*) and paper birch (*Betula papyrifera*) (George 1983). The slight supercooling of this water was expected and could have been prevented by seeding the hardboard samples with ice just below 0 C. The freeze/thaw behavior of the fraction of water that crystallized at low temperature, however, is analogous to that exhibited by fractions of supercooled water in a variety of porous materials (Everett 1961; George

TABLE 2. *Least squares analyses of means for mechanical properties (sorted by moisture).*[1,2]

C, moisture	Static bending				Tension parallel		Internal bond	
	1/8 in.		7/16 in.					
	MOE	MOR	MOE	MOR	1/8 in.	7/16 in.	1/8 in.	7/16 in.
Control[3]	553,880a	6,540a	439,220a	4,980a	6,820a (4,940a)[4]	2,240a	385a (365a)[5]	116a
−20, low	602,180a	7,140a	434,920ab	4,760a	5,260b (4,840a)	2,400a	358a	113a
−50, low	556,040a	6,340a	408,700b	4,820a	4,680b (4,480a)	2,280a	239b (341a)	115a
Control	425,080a	5,440a	264,640a	3,640a	3,940a	1,940a	174a	46a
−20, high[6]	381,380b	4,640b	265,220a	3,600a	4,220a	1,620b	168a	45a
−50, high	394,000ab	5,100ab	242,020b	3,660a	4,400a	1,840a	174a	46a

[1] Means in a grouping (e.g. 1/8 in. : C : low : MOE; 1/8 in. : C : high : MOE; etc.) followed by the same letter are not significantly different at $P = 0.05$.
[2] All values in psi.
[3] Control samples are 2 C low or high moisture, respectively (see Table 1 for moisture contents).
[4] Repeat test (second set of low moisture samples).
[5] Repeat test (second set of low moisture samples; 2 C and −50 C).
[6] During freeze/thaw cycling to −20 C, 1/8 in. standard hardboard samples received an additional cycle to −12 C without hold2.

1983; Homeshaw 1981). A supercooled system is in a "metastable equilibrium" as defined by Glasstone (1946). Such a metastable system will undergo a spontaneous transition upon addition of the stable phase. Many investigators have shown that very pure water droplets can be supercooled to temperatures approaching −40 C (Bigg 1953; Fletcher 1970; Langham and Mason 1958; Rasmussen and MacKenzie 1972). In hardboard, the supercooled water may be located in the large spaces noted above. These spaces may presumably be interconnected by a complex system of water filled microcapillary pores. The melting point of water in the pores would be lowered due to surface chemical effects (i.e., due to the small radius of curvature of liquid/vapor or liquid/ice interfaces in the pores). Water in the large spaces may crystallize after an internal nucleation event or by ice growth through the pores at a sufficiently low temperature. If an internal nucleation event was responsible for ice formation, it was of a heterogeneous nature since the exotherm occurred above the homogeneous nucleation temperature expected for pure water.

Although large high temperature exotherms were observed in both species mixes of wet process Woodruf® and in 7/16 in. standard hardboard samples with the highest moisture contents, low temperature freezing events were either nonexistent or appeared to be smaller than those in dry process roofing or in 1/8 in. standard hardboard. When present, they occurred at higher temperatures. One might speculate that specimen density was related to low temperature freezing since the latter hardboard materials have a greater density and perhaps a larger number of small pores.

Mechanical properties tests

The LSMEANS for MOE, MOR, T_p, and IB as a function of temperature for 1/8 in. and 7/16 in. standard hardboard are given in Table 2. In the following discussion a significant effect derived from ANOVA indicates a probability of 0.05 or smaller for rejecting the stated effect.

Static bending

Analyses of variance of data from static bending tests on 1/8 in. and 7/16 in. standard hardboard showed an inconsistent response to temperature. A significant temperature effect was found between temperature and MOR for high moisture 1/8 in. samples. However, the LSMEANS for MOR revealed that the only significant difference was between control samples and those cycled to −20 C. Freezing, therefore, would not be a factor in this difference. Least squares analysis also revealed a similar difference between the mean MOE for high moisture control samples and that for samples cycled to −20 C. This difference was discounted on statistical grounds because of a lack of a significant temperature effect in the ANOVA on these data. Additionally, average

board thickness measured following cycling for high moisture controls, −20 C freeze/thaw cycle samples, and −50 C freeze/thaw cycle samples was 0.130 in. (specific gravity = 0.94), 0.139 in. (specific gravity = 0.90), and 0.135 in. (specific gravity = 0.91), respectively. The thickness difference between control and −20 C cycled samples was found to be significant (analysis not shown). When thickness was included as a linear covariant in an analysis of covariance, no significant temperature effect was found (analysis not shown). This result is consistent with the known influence of density on the strength characteristics of wood composites (Bodig and Jayne 1982); however, it should be noted that this influence is not linear. A more complex relationship between thickness and MOE or MOR would, therefore, need to be included in an analysis of covariance to adjust MOE and MOR accurately. Analysis of variance on 7/16 in. standard hardboard static bending data revealed a significant temperature effect on MOE for high moisture samples. No significant thickness versus temperature variation was present in 7/16 in. samples, and the statistical difference appears to be real. Least squares analysis also showed a significant difference between MOE means for high moisture controls and samples cycled to −20 C when compared to samples cycled to −50 C. A significant difference was also observed between the mean MOE for low moisture control samples and that for samples cycled to −50 C; however, a lack of a significant temperature effect in the ANOVA for these data discounted this difference.

The above analyses indicate that there was no consistent effect of freeze/thaw cycling on static bending properties for 1/8 in. and 7/16 in. standard hardboard. The difference between MOE means for high moisture 7/16 in. control and −20 C freeze/thaw cycle samples when compared to the −50 C freeze/thaw cycle samples appears to be statistically real, but its physical significance is unclear. Results of DTA indicate that little additional freezing takes place below −20 C in high moisture 7/16 in. substrata. A decline in strength properties in this region would, therefore, likely be due to a temperature-related change in constituents of the hardboard fiber itself. No data are available on any such low temperature change in hardboard products. To test the possibility that the resin utilized in the 7/16 in. hardboard manufacturing process might have unusual thermal properties, a resin sample was prepared and tested by DTA. It revealed no unusual low temperature thermal characteristics.

Tensile strength parallel to surface

A significant temperature effect on T_p was observed for low moisture samples. Least squares analysis revealed a difference in mean T_p values when low moisture control samples were compared to samples freeze/thaw cycled to −20 C or −50 C. Again, however, a nonrandom distribution of sample thicknesses with treatment appeared to be the cause of this difference and not any anomalous low temperature behavior in the low moisture samples. Average sample thickness for high moisture controls, −20 C freeze/thaw cycle samples, and −50 C freeze/thaw cycle samples was 0.123, 0.134, and 0.135 in., respectively. The thickness difference between the control samples and those cycled to low temperature was significant. An analysis of covariance analogous to that described above discounted the effect of freezing temperature on tensile stress (analysis not shown). A repeat T_p test was performed on a second set of low moisture samples to further investigate the influence of sample thickness. In this test, samples were randomized to reduce the likelihood that thickness differences would appear in the treatments. Statistical analyses performed on this data showed in influence of temperature on T_p. Analysis of variance on 7/16 in. test data showed a significant temperature effect on high moisture control samples. Freezing was apparently unrelated to this effect since least squares analysis showed a significant difference only between the mean T_p for samples cycled to −20 C and the other treatments. A nonrandom distribution of sample thicknesses was observed in low moisture 7/16 in. samples,

but did not greatly influence the statistical analyses.

Internal bond

Analysis of 1/8 in. and 7/16 in. hardboard test data indicated that the only significant temperature effect on IB strength was on 1/8 in. low moisture samples. Least squares analysis revealed a significant difference between mean IB for samples cycled to −50 C and the mean IB for the other treatments. A nonrandom distribution of thicknesses was observed in both 1/8 in. and 7/16 in. low moisture samples, but only in the former did it significantly alter the statistical analysis. Average sample thickness for 1/8 in. low moisture controls, −20 C freeze/thaw cycle samples, and −50 C freeze/thaw cycle samples was 0.132, 0.134, and 0.138 in., respectively. Analysis of covariance with thickness as a covariant (not shown) removed the statistical difference in the low moisture means. A repeat IB test was performed on 1/8 in. low moisture control samples and samples freeze/thaw cycled to −50 C. Samples were randomized so that thickness differences between treatments would be reduced. No temperature effect was observed in these data.

Although no statistical evaluation is shown here, the known moisture dependent decline in each of the strength properties evaluated above is apparent in the LSMEANS (Table 2).

CONCLUSIONS

The results of differential thermal analyses performed on dry process experimental roofing, two species mixes of wet process Woodruf®, and 1/8 in. and 7/16 in. standard hardboard revealed freezable water to be present above a moisture level of ≈20%. Two distinct freezing exotherms were observed. The first was present in all hardboards. It occurred above approximately −10 C and was believed to be associated with the freezing of bulk water in the samples. The second exotherm was observed to occur near −35 C in 1/8 in. experimental roofing and in 1/8 in. standard hardboard of high moisture content. It was attributed to the freezing of a supercooled fraction of water that may have been located in spaces isolated from bulk water by microcapillary pores. Mechanical strength tests performed on 1/8 in. and 7/16 in. standard hardboards exposed to freeze/thaw cycling to −50 C showed no consistent declines in the modulus of elasticity, modulus of rupture, tensile strength parallel to surface, or internal bond strength to be associated with either freezing exotherm. The results suggest that freeze/thaw cycling of exterior hardboard products composed of these or similar materials should not alter their performance beyond that associated with elevated moisture content.

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