WOOD-CEMENT COMPOSITES: EFFECT OF MODEL COMPOUNDS ON HYDRATION CHARACTERISTICS AND TENSILE STRENGTH

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ABSTRACT

The development of wood-cement composite products is limited by cement's incompatibility with numerous wood species that inhibit cement setting and hardening. This study investigated the relative effects of specific model compounds commonly found in wood on the tensile splitting strength and hydration characteristics of Type I portland cement.

Model compounds representing classes of wood components were added to cement at concentrations of 0.01, 0.10, and 1.00%. Glucose decreased cement tensile strength by nearly 50%. Quercetin, xylan, and acetic acid lowered tensile strength by a lesser amount. Wood components added to cement in 0.10% concentrations had a greater effect on strength than on exothermic behavior. Little correlation was found between tensile splitting strength and exothermic hydration characteristics (maximum hydration temperature, time to maximum hydration temperature, and relative heat generation). The relative difference in heat generation between an additive-cement sample and a cement standard was best able to distinguish differences among wood component effects.

Keywords: Composites, tensile strength, hydration, exotherm, cellulose, lignin, hemicellulose, extractives.

INTRODUCTION

When particles of wood are mixed with portland cement paste and allowed to harden, a composite is formed that can be used as a structural material. These wood-cement composites have advantages over conventional wood building materials that include water, fire, and decay resistance. However, they have a high density, require long pressing cycles, and are restricted to specific wood species. The complex chemical and physical interactions that affect the bonding between wood and cement are poorly understood at present.

The nature and quantity of the wood component critically affect the cement hydration reactions and composite strength. Softwoods are generally more compatible with cement than hardwoods, although there are exceptions, such as west-

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ern larch (Miller et al. 1991). The exact cause(s) of cement inhibition by wood components is difficult to ascertain, since a number of complex chemical and physical processes are occurring. Classes of compounds that have been implicated as adversely affecting wood-cement hydration reactions include simple sugars (Biblis and Lo 1968; Previte 1971), sugar acids (Fischer et al. 1974; Sandermann et al. 1960; Massazza 1983), and hemicelluloses (Simatupang 1986).

The mechanism of inhibition of cement hydration and crystallization by wood components is poorly understood. Simple wood sugars may migrate to the wood surface during drying. Since these sugars contain hydroxyl and carboxylic acid functional groups, they may complex with calcium, aluminum, and iron cations in the cement to retard (Young 1970) and perhaps disrupt (Mariampol'skii et al. 1974) the crystallization reactions. These inhibitory reactions may take place at the wood-cement interface or in the surrounding cement matrix and weaken mechanical and chemical bonds between wood and cement.

Wood components may also be solubilized and/or degraded by calcium hydroxide (Whistler and BeMiller 1958), which is formed during cement hydration. Initial cement hydration produces calcium hydroxide, which results in an alkaline cement paste (pH = 12.5). Since hemicelluloses are noncrystalline and alkaline-soluble, they may dissolve in the cement paste and affect cement crystallization. For example, hemicelluloses could complex with metal ions in the cement through cis hydroxyls on mannose and galactose or through glucuronic acid groups. These reactions could decrease the crystallinity, strength, and/or hydration rate of cement. In addition, the hemicelluloses may undergo peeling reactions (Whistler and BeMiller 1958) in the alkaline cement to form inhibitory sugar acids (Fischer et al. 1974). The acetyl groups present in the hemicelluloses are probably cleaved by the alkali (Browning 1967; Goldstein 1984) to form potentially inhibitory metal acetate compounds. Since xylans are high in acetyl content and are the predominant hemicellulose in hardwoods, this alkaline hydrolysis may be a major reason why many hardwoods are incompatible with cement.

Nonpolar extractives such as the terpenes, resins, and fats may also migrate to the wood surface during drying. This hydrophobic surface layer may reduce hydrogen bonding between wood and cement and thus weaken interfacial bond strength. Phenolic compounds such as tannins also have a capacity to complex with metal ions in cement and potentially inhibit normal hydration reactions (Bash and Rakhimbaev 1973).

The objective of this project was to compare the relative effect of specific model compounds, representing classes of wood components, on the hydration and strength characteristics of Type I portland cement. Such information could be used to predict wood species compatibility with cement for product applications and also to begin to understand the mechanism and relative magnitude of inhibition.

METHODS AND PROCEDURES

Model compounds corresponding to common classes of wood components were added to Type I portland cement at several concentrations. Cellulose CP 11, a medium-length column chromatography cellulose powder, was used as a model cellulose compound. Indulin AT, a low-ash Westvaco kraft pine lignin, was used a a model lignin compound. A birch glucuronoxylan, isolated using an alkaline

extraction procedure (Miller 1987a), was used as a model hemicellulose compound. Acetic acid, glucose (simple sugar), quercetin dihydrate (tannin), alpha-pinene (terpene), oleic acid (fatty acid), abietic acid (resin acid) and beta-sitosterol (sterol) were used as model extractive compounds.

Samples for hydration and tensile strength tests were prepared by mixing 400 g of Type I portland cement with 0.01, 0.10, and 1.00% of each model compound. Deionized water (160 ml) was then added to the mixture at a ratio of 0.4 grams per gram of cement. Approximately one-half (250 grams) of this cement-additive-water mixture was placed in a plastic bag and a type J thermocouple was inserted into the center of the cement ball. The bag was then placed in an insulated Dewar flask in a constant temperature room. The temperature of the cement mixture was monitored and recorded over time using a portable computer (Miller 1987b). The hydration characteristics of maximum hydration temperature (TMAX) and the time to maximum hydration temperature (TTMAX) were recorded in order to compare the effects of specific model compounds on the intensity and rate of cement hydration.

In addition to TMAX and TTMAX, the relative amounts of heat generated were assessed in an attempt to develop an improved method for correlating strength with hydration properties. Heat generation was evaluated relative to each of two standards. As each temperature was recorded, calculations were made of the trapezoidal area bounded by the current and last temperatures for the sample mixture and room temperature or a neat cement standard. The sum of these areas during the first 48 hours of hydration were used as estimates of RAREA (heat generation area relative to room temperature) and NAREA (heat generation relative to a neat cement standard).

The other half of the cement/additive mixture was used to fill a 2-inch brass cube form to prepare samples for testing of tensile strength. After two days, the cement cubes were removed from the form and sealed in plastic. After a total of 28 days, the samples were loaded in compression across the cube diagonal (Miller 1987b) using an Instron testing machine to estimate the tensile splitting strength (ASTM 1983).

Three replications of each additive at each concentration were used in a randomized complete block design with blocking over time. Means were compared using Fisher's protected lsd test. The blocking by time was a significant source of variation for tensile splitting strength and NAREA. During the sample preparation and testing period, the ambient temperature fluctuated by as much as 10 degrees Celsius. This suggests that tensile strength was more sensitive to environmental temperature changes during mixing than all but one of the exothermic hydration characteristics.

RESULTS AND DISCUSSION

General hydration characteristics

Three time-temperature hydration curves for each model compound at each concentration were averaged to give a composite curve. Composite hydration curves for the samples containing model compounds which had the greatest effects at the 1.0% addition level are shown in Fig. 1. Xylan, glucose, and quercetin had a substantial inhibitory effect on cement exothermic behavior by decreasing the
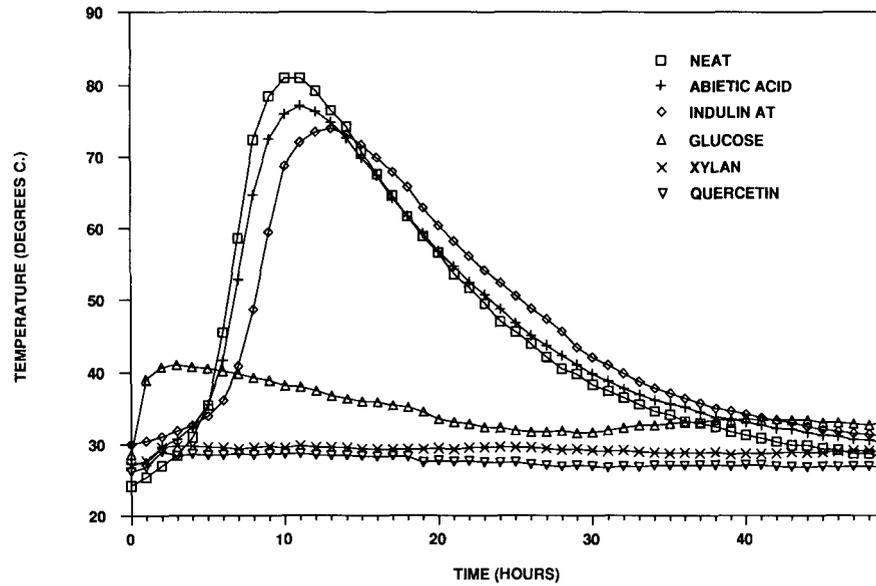
FIG. 1.   Time-temperature curves for samples containing the model wood compounds which had the greatest effect on cement exothermic behavior. Curves are averages of three replications of the 1.0% additive level samples.

intensity and amount of heat generation. In contrast, acetic acid, cellulose, alpha-pinene, oleic acid, and beta-sitosterol had little effect on exothermic behavior of cement. Abietic acid and Indulin AT caused an intermediate effect.

Maximum hydration temperature

The maximum hydration temperature (TMAX) is an estimate of the intensity of the exothermic hydration reactions. Although not statistically different from neat cement, half of the model compounds increased average exothermic intensity values (TMAX) as shown in Table 1. Only the glucose, quercetin dihydrate, and

TABLE 1.   *Statistical grouping of means of maximum hydration temperatures (TMAX) for cement-wood component mixtures (averages of 3 replications of 3 levels).*

Additive	Average TMAX (°C)	Grouping*
Alpha-pinene	85.2	A
Cellulose	84.6	AB
Acetic acid	84.2	ABC
Beta-sitosterol	82.9	ABC
Oleic acid	82.3	ABC
None (neat cement)	82.1	ABC**
Abietic acid	81.4	BC
Indulin AT	81.0	C
Glucose	68.2	D
Quercetin dihydrate	66.9	D
Birch xylan	63.3	E

* Additives with the same letter are not significantly different at the 5% significance level.
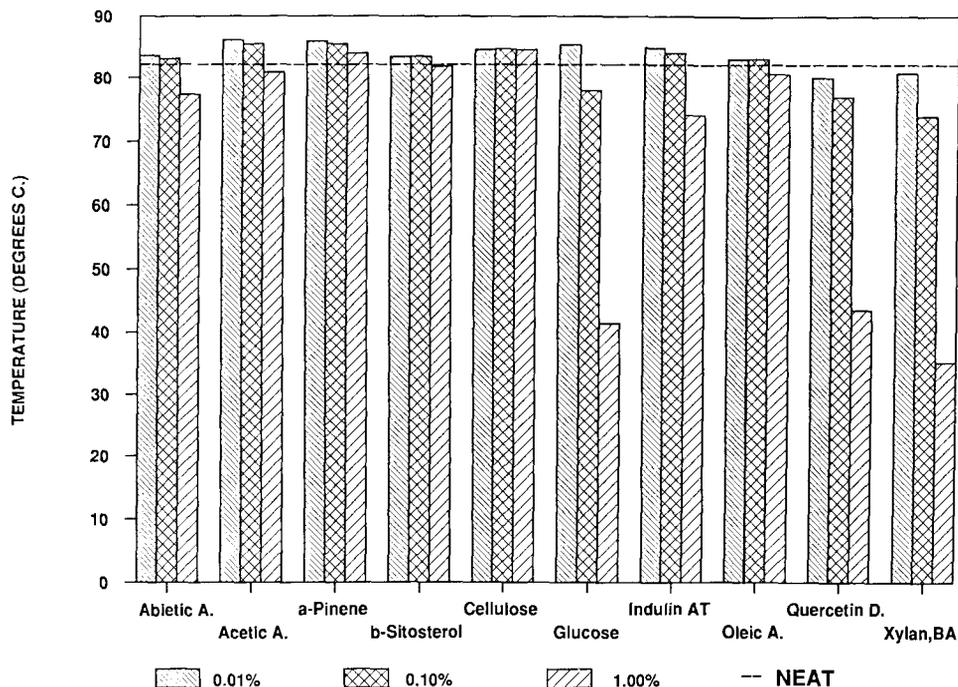** From orthogonal comparisons of additive-level means.

FIG. 2.   Mean maximum hydration temperatures of cement containing model compounds at 0.01%, 0.10%, and 1.00% concentrations. The maximum hydration temperature of neat cement (without additives) is indicated by the horizontal dotted line at 82.1 degrees Celsius.

birch xylan significantly decreased the intensity of the exothermic cement reactions. The greatest decrease in exothermic intensity of cement (23%) occurred with xylan additions. Oleic acid had the least average effect on exothermic intensity. This is in agreement with the results of Stein (1961), who found oleates to have little effect on the hydration of tricalcium silicate, the main compound in cement. Beta-sitosterol also had little effect on cement properties. The nonpolar characteristics and lack of interactive functional groups on oleic acid and beta-sitosterol probably minimize their interaction with the cement. These results suggest that woods such as southern pines having substantial amounts of fatty acids and sterols may be acceptable as furnish for wood-cement composites.

In many cases, the lower addition levels increased the average TMAX values above that of neat cement, as shown in Fig. 2. Additive concentrations of 0.01% increased intensity from neat cement for 8 of the 10 additives. Similar effects have been observed by Previte (1971), who found the maximum temperature of heat evolution to be increased with small additions of some compounds which also caused substantial decreases in maximum temperature with larger additions.

Time to maximum hydration temperature

Oleic acid, abietic acid, and cellulose appeared to have little effect on the delay of the exothermic cement reactions (TTMAX). Beta-sitosterol, acetic acid, and alpha-pinene additions shortened the average delay values. Only birch xylan and quercetin dihydrate significantly delayed the setting of cement, with xylan causing
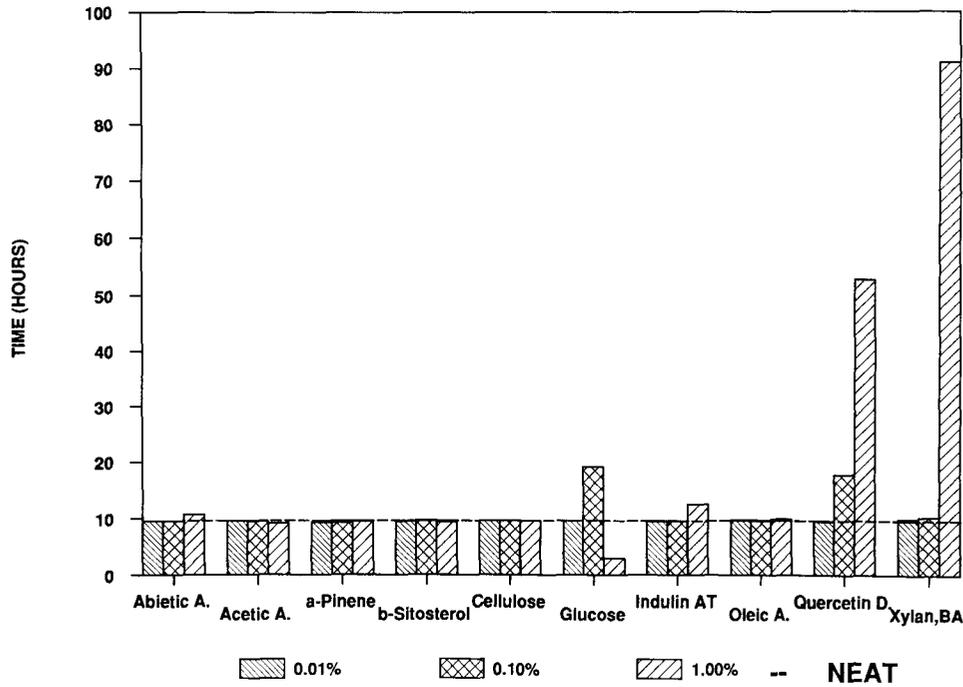
FIG. 3. Mean time to maximum hydration temperatures for cement containing model compounds at 0.01%, 0.10%, and 1.00% concentrations. The time to maximum hydration temperature of neat cement (without additives) is indicated as a horizontal dotted line at 9.9 hours.

the greatest delay (270%) (Table 2). Indulin AT and glucose also lengthened delay values, although not statistically longer than neat cement.

Averaged over all additives, the 1.0% additive level significantly increased TTMAX by 120%. If the trend of increased delay with increased additive levels continued through the 1.0% level of glucose as it had up to the 0.10% level (Fig. 3), TTMAX for 1.0% glucose-cement may have been longer than the 90 hours

TABLE 2. *Statistical grouping of means of times to maximum hydration temperature (TTMAX) for cement-wood component mixtures (averages of 3 replications of 3 levels).*

Additive	Average TTMAX (hours)	Grouping*
Alpha-pinene	9.3	A
Acetic acid	9.3	A
Beta-sitosterol	9.4	A
Cellulose	9.6	A
Oleic acid	9.8	A
None (neat cement)	9.9	A**
Abietic acid	9.9	A
Indulin AT	10.5	A
Glucose	10.5	A
Quercetin dihydrate	26.6	B
Birch xylan	36.9	C

* Additives with the same letter are not significantly different at the 5% significance level.
** From orthogonal comparisons of additive-level means.

TABLE 3.   *Statistical grouping of means of area differences of cement-wood component mixtures from neat cement (NAREA) (averages of 3 replications of 3 levels).*

Additive	NAREA (degree hours)	Grouping*
Acetic acid	26	A
Cellulose	2	AB
Beta-sitosterol	1	AB
None (neat cement)	0	AB**
Oleic acid	−0	AB
Alpha-pinene	−1	B
Indulin AT	−7	B
Abietic acid	−17	B
Glucose	−194	C
Birch xylan	−283	D
Quercetin dihydrate	−311	E

* Additives with the same letter are not significantly different at the 5% significance level.
** From orthogonal comparisons of additive-level means.

measured for xylan. However, the delay was not measured since it was longer than the time period over which exothermic activity was recorded. The recorded TTMAX for 1.0% glucose-cement (Fig. 1) was probably the peak of the delayed aluminate hydration instead of the silicate hydration peak measured for the other additives.

Heat generation differences

Another approach for comparing hydration characteristics of model compounds is to compare the relative amount of heat generated by a cement sample, as estimated by the area bounded by the hydration curve. Two methods of area comparisons were evaluated in this study. The first method was based on the heat generation (over the first 48 hours after mixing) of the additive-cement sample relative to room temperature (RAREA). Acetic acid, glucose, birch xylan, and quercetin dihydrate were the only compounds to significantly decrease RAREA, with the greatest decrease (−36%) exhibited by the xylan.

A second method that was used to compare heat generation was the area between an additive-cement sample hydration curve and a neat cement hydration curve (NAREA). Unlike RAREA, NAREA directly accounts for differences in cements. This advantage should make NAREA more useful for comparisons using data sampled under different conditions and with different types of cement.

NAREA was decreased the most by glucose, birch xylan, and quercetin dihydrate (Table 3), with the tannin having the greatest effect. This trend was also observed with RAREA. However, with NAREA values, glucose, birch xylan, and quercetin dihydrate not only significantly decreased the heat generation of cement, but were significantly different from each other. Based on this data, NAREA appears to be more capable of distinguishing and separating admixture effects than RAREA. This may be the result of temperature differences that affected cement response as mentioned earlier, since the blocks of replication were significantly different.

Tensile splitting strength

Indulin AT and oleic acid had the least effect on cement tensile splitting strength, as shown in Table 4. Similar effects of lignins on cement compressive strength
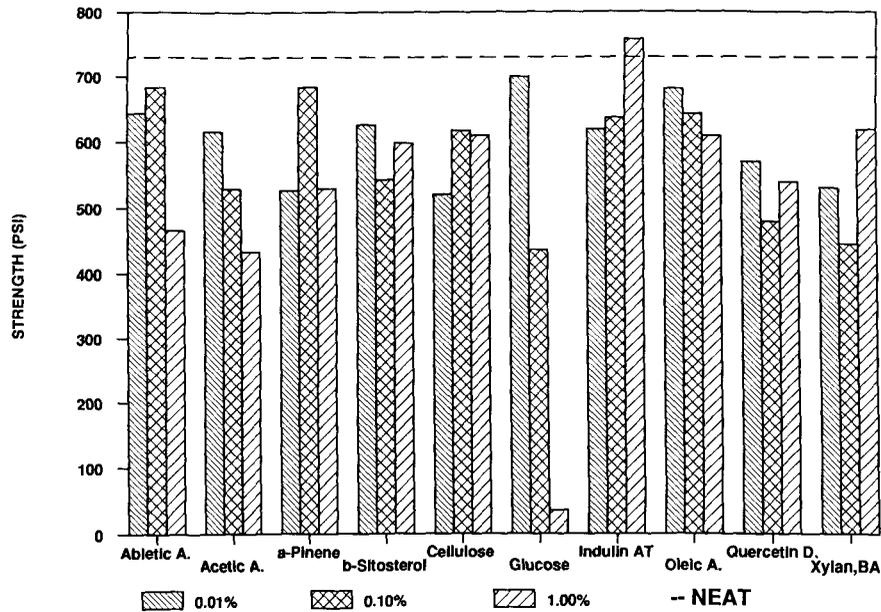
FIG. 4. Mean tensile splitting strength of cement containing model compounds at 0.01%, 0.10%, and 1.00% concentrations. The strength of neat cement (without additives) is indicated by the horizontal dotted line at 724 psi.

have been observed by other researchers (Clare and Sherwood 1954). The average strength value of the 1.0% Indulin-cement was greater than that of cement without additives (Fig. 4). This behavior may be due to inorganic contaminants left in the lignin preparation as residue from the kraft pulping process, since even minor compounds in portland cement may substantially affect strength development. Since Indulin AT is a degraded and impure lignin, this strength response may not be indicative of the effect of native lignin on cement. Indulin AT may warrant further investigation as an additive to improve low-strength wood-cement composites.

Abietic acid, beta-sitosterol, cellulose, and alpha-pinene were closely grouped in their effects on tensile strength, as shown in Table 4. Although not statistically different, cellulose decreased average tensile splitting strength values more than Indulin AT. Similar effects of cellulose on cement compressive strength have been observed by other researchers (Clare and Sherwood 1954).

Although all additives decreased the average tensile splitting strength of cement, the birch xylan, quercetin dihydrate, acetic acid, and glucose decreased strength a statistically significant amount (Table 4). The greatest decrease in tensile splitting strength of cement occurred with glucose, which lowered strength by over 40%.

The 27% decrease in cement strength with acetic acid suggests that hemicelluloses with high acetyl content, such as hardwood glucuronoxylans and softwood glucomannans, may be detrimental to tensile strength development. The acetyl ester linkages of these hemicelluloses are hydrolyzed by aqueous alkali (Browning 1967), as in a wet cement mixture, to liberate acetate such as that in acetic acid.

The 0.01% and 0.10% levels of addition had a much greater effect on strength

TABLE 4. *Statistical grouping of means of 28-day tensile splitting strength of cement-wood component mixtures (averages of 3 replications of 3 levels).*

Additive	Tensile splitting strength (psi)	Grouping*
None (neat cement)	724	A**
Indulin AT	671	A
Oleic acid	644	AB
Abietic acid	597	AB
Beta-sitosterol	589	AB
Cellulose	583	AB
Alpha-pinene	581	AB
Birch xylan	531	B
Quercetin dihydrate	529	B
Acetic acid	527	B
Glucose	390	C

* Additives with the same letter are not significantly different at the 5% significance level.
** From orthogonal comparisons of additive-level means.

than on maximum hydration temperature of cement. Even at low levels, tensile strength was affected by the model compounds, as shown in Fig. 4.

The third block or replication of samples was significantly weaker (15%) than the first two blocks. This difference in strength was probably the result of ambient temperature fluctuations that occurred during mixing and initial curing. The third replication was done during a period when the ambient temperature was cooler. Differences in the environmental temperature at time of placement are known to affect strength of concrete (Dodson and Rajagopalan 1979). The results from this study suggest that initial mixing of compounds at slightly higher temperatures could be used to increase the strength of wood-cement composites.

Correlations

The hydration characteristics (TMAX, TTMAX, RAREA, and NAREA) had low correlations with tensile splitting strength (TSS) as shown in Table 5. Although the lignin-cement was stronger than cellulose-cement (Table 4), the intensity of the exothermic reaction was significantly lower (Table 1). Acetic acid decreased the average tensile strength of cement, but had no detrimental effect on the intensity of the hydration reaction as estimated by TMAX. This suggests that the hydration characteristics and tensile strength measurements are probably estimating different features of the additive-cement system. The difference between strength and hydration characteristics is recognized in the cement industry, where it is commonly accepted that hydration is related to the rate of formation of the cement hydrates, and strength is related to the actual structure of the hydrated

TABLE 5. *Correlations of tensile splitting strength (TSS) and hydration characteristics for cement-wood component mixtures.*

	TMAX	TTMAX	RAREA	NAREA
TSS	0.36	0.10	0.25	0.22
TMAX	1.0	−0.61	0.92	0.93
TTMAX	—	1.0	−0.72	−0.73
RAREA	—	—	1.0	0.99

crystal matrix (Lea 1970). This study indicates that hydration characteristics of a wood-cement system do not appear to be accurate estimates of wood-cement compatibility when tensile strength is a concern.

SUMMARY AND CONCLUSIONS

Model compounds representing cellulose, lignin, fatty acid, resin acid, sterol, and terpene at concentrations of 1.0% or less did not significantly decrease tensile strength of cement. Glucose caused the greatest decrease in tensile strength (-40%), while the hemicellulose, tannin, and acetic acid decreased strength by a lesser amount. All hydration characteristics were substantially affected by sugar, tannin, and hemicellulose, with tannin and hemicellulose having the greatest effects.

Although the hydration characteristics had little correlation with tensile strength, the characteristic estimating the relative exothermic difference between the samples and neat cement (NAREA) appeared to be most sensitive to differences in additives. From the low correlations observed in this study, caution should be exercised in assessing compatibility based solely on hydration characteristics if tensile strength of the product is a primary concern.

This study suggests that wood species with substantial quantities of soluble tannins, sugars, hemicelluloses, or acids would decrease tensile strength of wood-cement composites.

ACKNOWLEDGMENT

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