The Role of Lignin in Surface-Activated Bonding of Lignocellulose—Characterized by Differential Scanning Calorimetryt

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The Role of Lignin in Surface-Activated Bonding of Lignocellulose—Characterized by Differential Scanning Calorimetry†

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The study of surface modification to prepare an optimum surface for bonding is of practical importance for the production of glued materials. Lignocellulosic materials contain many chemical groupings such as phenolic and alcoholic hydroxyls, carbonyl groups, etc., capable of being readily activated by physical or chemical methods. These active sites can then react under heat and pressure, either with active sites from another surface, or through a crosslinking agent to form a glued product.

This paper reports the role of lignin in the reactions between lignocellulosic materials and hydrogen peroxide studied by a differential scanning calorimetry method. The results showed that lignin is much more reactive toward hydrogen peroxide than is cellulose, and that the lignin-hydrogen peroxide reaction yields the highest enthalpy. Correlation between lignin and enthalpy, and enthalpy and bonding will also be discussed.

INTRODUCTION

The modification of surfaces by chemical, physical, or mechanical methods has been commonly employed to enhance surface reactivities and hence adhesion of low surface free-energy polymers. In fact, for very low surface energy polyolefins and fluorinated hydrocarbon polymers, the surfaces must be chemically modified in order to achieve satisfactory adhesion.[1–5]

Fortunately, polymeric wood components, namely cellulose, hemi-cellulose and lignin, contain many functional groupings such as alcoholic and phenolic hydroxyls, carbonyl groups, etc., and are, therefore, more reactive than hydrocarbon polymers. Energetically wood surface is several times higher than these polymers.[6,7] However, wood surfaces, like many other dry solids which lack smoothness, cleanliness and deformability, are not capable of reacting with each other.

Researchers involved in wood bonding without conventional type adhesives during the last decade have used chemical modification to develop a new bonding technique, the so-called surface activated bonding, for wood and derived lignocellulosic materials. Promising preliminary results have been reported.[8-13] The system involves the surface treatment with specific activators to create active sites on wood surface. These active sites can then react under pressure and temperature, either directly with the active sites on the other surface or through a crosslinking agent to produce bonded composite wood products. One of the activators which has produced bonded products with good mechanical and physical properties is hydrogen peroxide, H_2O_2.

Thermal analysis is a group of techniques in which a physical property of a substance and/or its reaction products is measured as a function of temperature while the substance is subjected to a controlled temperature program.[14] The applications of these techniques to lignocellulosic materials have been recently reviewed by Nguyen et al.[15,16] One of the commonly used methods to characterize chemical reaction is differential scanning calorimetry (DSC), which yields curves that are unique for a particular chemical composition or configuration changes associated with changes in enthalpy.

This paper reports the effects of lignin on the characteristics of reaction between cellulose and hydrogen peroxide studied by high pressure differential scanning calorimetry. The relationship between these characteristics and the bonding strength of the glued product is developed.

EXPERIMENTAL METHODS

Materials

Hydrogen peroxide solution used was ACS reagent grade of 50 weight percent concentration ("Perone 50", DuPont de Nemours and Co.). Microcrystalline cellulose (Sigma cell Type 38, Sigma Chemical Company) was used as the cellulose, and finely ground lignin was obtained from brown cubical rot heartwood of Libocedrus decurrens Torr. (produced by Polyporus amarus). This lignin contains about 10–15% carbohydrates in a Klason lignin (lignin isolated by Klason using H_2SO_4 acid) determination. The DSC characteristics of this lignin did not differ from Björkman (lignin isolated by Björkman using

vibrated milling and extraction with solvent) and Klason lignins, compared on the basis of their H_2O_2 oxidation reactions. Lignin was extracted for 12 h in 95% ethanol and 12 h in boiling water to remove polar extractives. The extracted lignin was immersed overnight in 5% ethylenediamine tetraacetic acid disodium salt (EDTA) solution to remove catalytically active metal ions either pre-existing or resulting from machining and grinding (metal ions are known to catalyze the H_2O_2 decomposition). The EDTA-treated lignin was washed with distilled water. All lignin and cellulose materials were vacuum dried at 75°C and stored in a desiccator until use.

Sample preparation

Lignin and cellulose mixtures of 5:95, 25:75, 50:50 and 75:25 weight ratios were oven-dried and mixed with 50 weight percent H_2O_2. One part of 50% H_2O_2 was mixed with two parts of lignocellulosic material (oven-dry weight) in a Pyrex weighing container and stored under closed conditions for eight hours to prevent evaporation and to obtain thorough penetration of the aqueous H_2O_2 into lignocellulose particles. Unless otherwise stated, other sample preparation procedures used in this work have been described elsewhere.[17]

Thermal analysis

Due to the volatility of aqueous hydrogen peroxide and its sensitivity to the nature of the specimen container, a DSC technique was developed earlier to study the reaction between hydrogen peroxide and lignocellulose.[17-19] It was found that, at ambient pressure and in a pinhole-vented deactivated aluminum pan (pan treated with H_2O_2-HNO_3 solutions), the DSC curves of the H_2O_2-treated lignocellulose showed an H_2O_2 evaporation endotherm followed by a lignocellulose-H_2O_2 reaction exotherm, and that these two reaction processes overlapped each other. At 975 psi pressure and under the same sample pan conditions, the evaporation endotherm was delayed considerably while the temperature of the reaction exotherm was unchanged. These two peaks were separated and clearly seen on the DSC curves. These conditions were found optimal for studying the reaction between lignocellulose and hydrogen peroxide and were used for this study. Accordingly, a DuPont 910 high pressure DSC operating at 975 psi N_2 pressure connected directly to the DuPont 990 Thermal Analyzer, and H_2O_2-HNO_3 deactivated aluminum pans, each with a pinhole vent on top, were used. A sample of 1.42 mg and a heating rate of 20°C/min were used. Unless otherwise stated, other experimental details as well as operating procedures of the high pressure DSC were as described in a previous paper.[18]

RESULTS AND DISCUSSION

Influence of lignin on thermal behavior of the reaction between cellulose and H_2O_2

The DSC curves of the H_2O_2-treated lignin/cellulose mixtures are shown in Figure 1. From this figure, it is evident that hydrogen peroxide-treated cellulose and cellulose/lignin mixtures undergo two exothermic reactions (T_1 and T_2) which are different in extent and temperatures, while DSC of H_2O_2-treated lignin exhibits only one exotherm peaking at 152°C. The first exotherm (150–180°C) is due to two simultaneous reactions, H_2O_2 decomposition and reaction between H_2O_2 and lignocellulose, and the second exotherm (210–
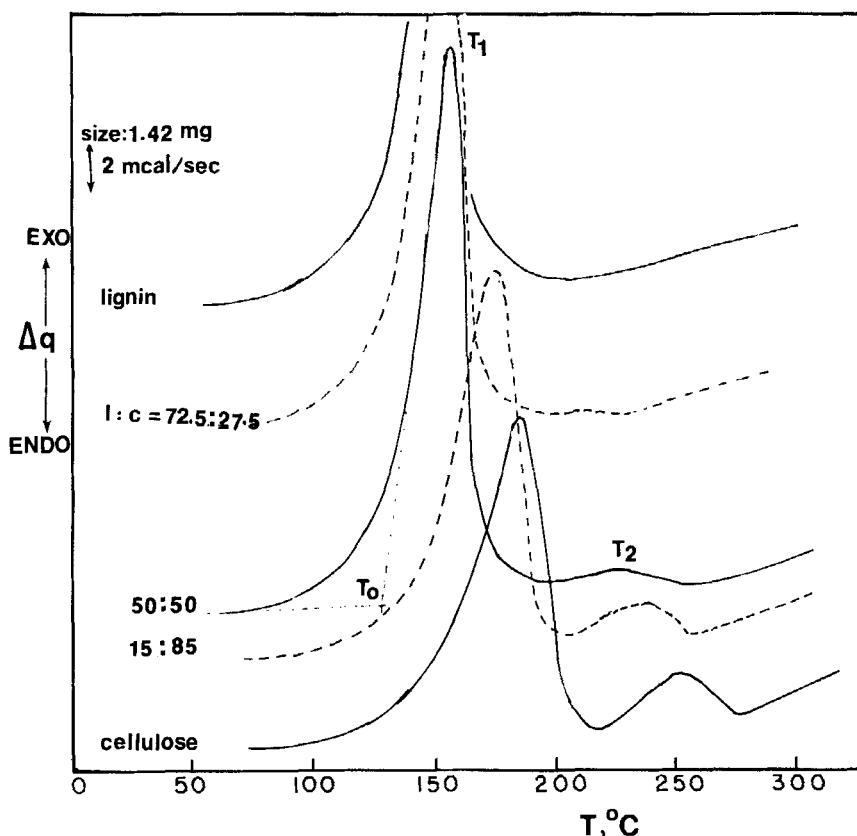
FIGURE 1   DSC curves of H_2O_2 treated lignin-cellulose mixtures in an HNO_3–H_2O_2 treated aluminum pan with a pinhole at 975 psi N_2 pressure. Heating rate: 20°C min^{-1}; sample size: 1.42 mg.

250°C) in the case of cellulose and cellulose lignin mixtures is due to the thermal oxidation and degradation of carbohydrate under pressure by oxygen which was trapped in the sample pan and released from the first exotherm reaction.[18,20]

The onset temperature (intersection between the leading edge and the baseline), T_0, and maximum peak temperature (intersection between peak leading and receding edges), T_1, of the first exotherm, and maximum peak temperature, T_2, of the second exotherm, as functions of lignin concentration, are shown in Figure 2. As evidenced from Figures 1 and 2, both the onset and maximum temperatures of the first exotherm decreased as lignin content increased from 0 to 50%. They change very little thereafter. When T_0 and T_1 were plotted against natural logarithm (ln) of lignin concentration $[L]$ (weight percent), straight lines fitted by Eqs (1) and (2) were obtained:

$$\ln [L] = -0.1363T_0 + 21.52, \quad r_0^2 = 0.974 \tag{1}$$

$$\ln [L] = -0.0977T_1 + 19.66, \quad r_1^2 = 0.980 \tag{2}$$

where T_0 (°C) and T_1 (°C) are the onset and peak temperatures of the first exotherm, respectively, and r^2 is the square of the correlation coefficient. These mathematical expressions can be used to approximate the concentration of lignin in any particular lignin-cellulose mixture. This can be achieved by treating the mixture with H_2O_2, then using DSC at high pressure in a pinhole vented aluminum pan. Figure 1 also shows that as the lignin concentration increased, both the peak height and peak sharpness increased. In other words, when the lignin-cellulose ratio increased, both the reactivity and the rate of the reaction between H_2O_2 and lignocellulose increased.

For the second exothermic reaction, as the lignin concentration increased, both peak temperature (T_2) and peak area (area under the curve) decreased. The second exotherm completely disappeared finally when only lignin was present, indicating that this exothermic reaction is associated with the carbohydrate only. When the second exothermic peak temperature, T_2, was plotted against the concentration of lignin $[L]$ (Figure 2), a straight line fitted by Eq. (3) was derived:

$$[L] = -2.0206T_2 + 501.13, \quad r_2^2 = 0.98 \tag{3}$$

Again this equation could be used to estimate the concentration of lignin in cellulose. It should be noted that Eqs (1) and (2) were derived for physical mixtures of lignin and cellulose. For lignocellulose complexes such as wood or other plant cell walls, the equations may not be applicable. For example, assuming white fir contains 28% lignin[21], T_1 calculated from Eq. (2) is 167°C, which is 14°C lower than the peak temperatures of the first exotherm obtained from reference 18 for H_2O_2-treated white fir. However, a value of 234°C for T_2
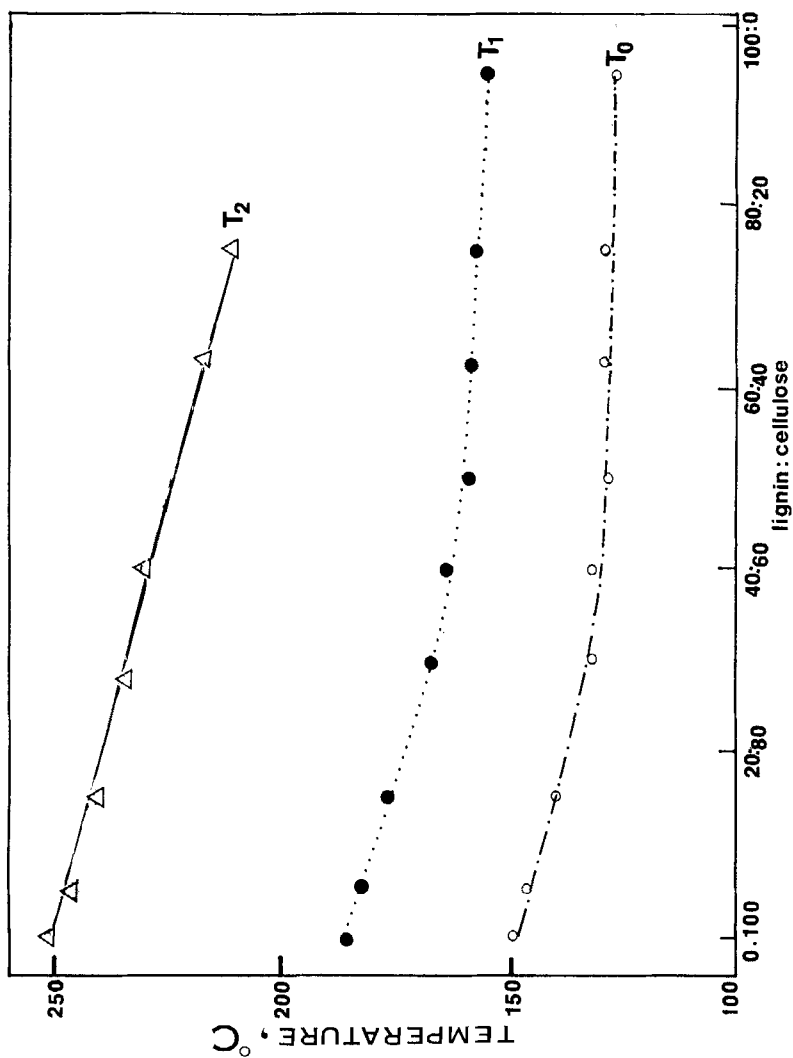
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FIGURE 2   Relationship between lignin concentration and exothermic peak temperatures.

calculated from Eq. (3) agrees very well with the 236°C obtained for the second exothermic peak of the same DSC curve.

Influence of lignin on heat of reaction between cellulose and H_2O_2

The determination of ΔH, the reaction enthalpy, from the DSC or DTA data has been widely practiced, based on the relationship of direct proportion between peak area and the change in enthalpy as expressed in the following equation:

$$\Delta H = \frac{A}{M} \cdot k \tag{4}$$

where ΔH is the change in enthalpy, A is the peak area, M is the sample mass, and k is the calibration factor. For a DuPont DSC, ΔH could be calculated using the following expression:[22]

$$\Delta H = \frac{A}{M} \cdot \frac{B\Delta qE}{6.452} \tag{5}$$

where B = time base setting (sec/cm)

$\quad E$ = cell calibration coefficient (dimensionless)

$\quad \Delta q$ = calorimetric sensitivity (mcal/sec/cm)

$\quad \Delta H$ = mcal/g if A and M are in cm^2 and gram, respectively.

Since B and Δq are the instrument settings, E is the dependent variable which must be calibrated for the experimental conditions under study.

As seen earlier, the DSC curves of H_2O_2-treated lignin/cellulose mixtures in a pinhole vented aluminum pan at 975 psi N_2 pressure yielded two exothermic peaks at 150–180°C and at 210–250°C, respectively, depending on lignin/cellulose ratios. To calculate the enthalpy of these reactions, E must be calibrated as a function of pressure and temperature utilizing known standard materials.

Such calibration (Figure 3), as well as the derivation of E at elevated pressure as a function of heat of fusion and melting point at atmospheric pressure, were presented elsewhere.[23]

Substituting E values obtained from Figure 3 at 975 psi pressure and temperatures corresponding to the first and second exothermic peaks into Eq. (5), the enthalpies of these reactions for cellulose, wood and lignin were calculated and are presented in Table I.

As indicated earlier, the first exotherm, which results from the oxidation reaction between lignocellulose and H_2O_2, involves the formation of reactive
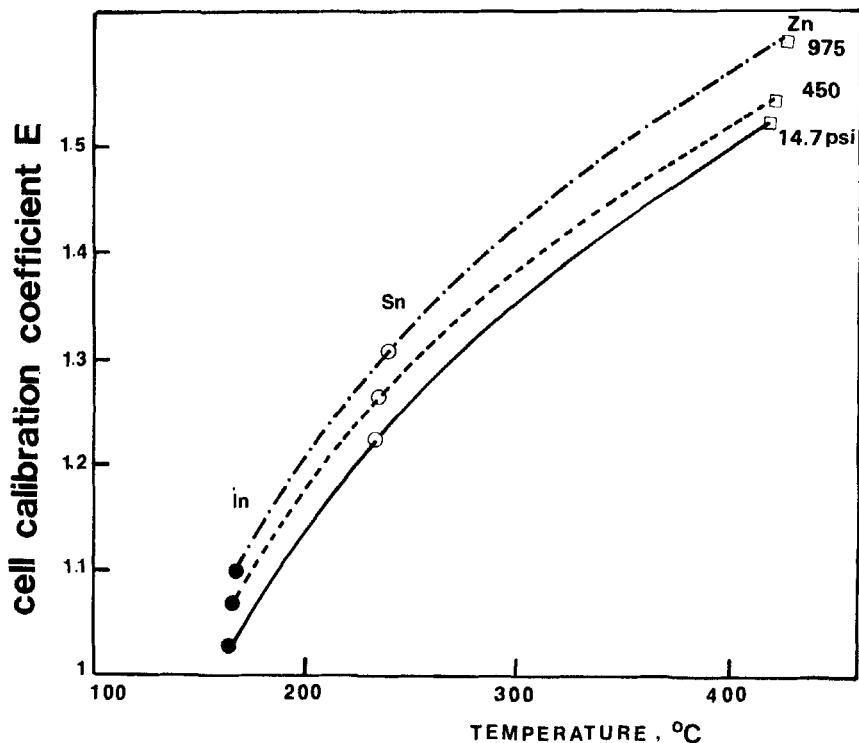
FIGURE 3 Dependence of cell calibration coefficient, E, on temperature determination for In, Sn and Zn at different pressures.

species. It is therefore assumed to be related to bonding properties of the composite product. The second exotherm only involves thermal degradation of carbohydrate. For that reason the following discussions will center on the first exotherm.

These results (Table I) indicate that among the materials studied, lignin-H_2O_2 reaction under N_2 yielded the highest enthalpy, while enthalpy of cellulose-H_2O_2 reaction is slightly lower than that of wood but considerably lower than lignin. More extensive enthalpy data on lignocellulosic materials and model compounds under N_2 and O_2 are given elsewhere.[20,23]

The heats of reactions between H_2O_2 and lignocellulose as a function of lignin content are shown in Figure 4. The first exothermic heat of reaction increases sharply with the increase in lignin content from 0 to 50%, and more gradually thereafter, while the second exothermic enthalpy reverses the trend with a slight reduction between 0 and 15% lignin concentration and a drastic decrease thereafter.

TABLE I

Heat of reactions between H_2O_2 and lignocellulosic materials

| Materials | Enthalpy, ΔH | |
	1st exotherm ΔH_1, cal/g H_2O_2	2nd exotherm ΔH_2, cal/g carbohydrate
Cellulose (crystalline)	1840	128
Lignin (brown rot)	2500	0
Wood (white fir flour)	1940[1]	170[1,2]

[1] Area data obtained from Ref. 18.
[2] Assume alcohol and water extracted white fir contains 72% carbohydrate (approximate based on Ref. 21).

The first exothermic heat of reaction of H_2O_2-treated white fir fits quite well in the relationship between lignin/cellulose ratio and ΔH_1 presented in Figure 4. For example, assuming alcohol and water extracted white fir contains 17% hemicellulose (arabinoxylan, $\Delta H_1 = 1930$[23]), 28% lignin and 55% cellulose,[21] the calculated ΔH is 2040 cal/g H_2O_2, as compared to 1940 cal/g H_2O_2 for wood. The difference could be due to the presence of carbohydrates other than xylan in hemicellulose. But it could also be due to the complex structure of wood in which lignin and other carbohydrates are not simply mixed, but rather follow a complex arrangement with the possibility of the lignin molecules being interspersed with carbohydrates. Furthermore, the chemical composition of a wood surface is not necessarily identical with the composition of the wood as a whole. The investigation of the heat of reaction between a simple mixture of lignin model compounds such as lignan and cellulose and of lignin model compound adsorbed into cellulose could help to elucidate this problem.

In a study of autoadhesion of wood, Stofko[12] found that the bonding strength (internal bond) of a composite lignocellulose product made using hydrogen peroxide as an oxidizer was a function of lignin concentration, and that lignin was primarily responsible for the bonding. Stofko proposed that oxidative coupling of lignin was the main contributor to the bonding strength observed, although acid catalyzed condensation may have also occurred.

When the heat of reaction of the 1st exotherm (ΔH_1) obtained in this study was plotted against the natural logarithm of tensile strength (S) values obtained by Stofko at the same lignin concentration, a linear relationship expressed by Eq. (6) was obtained and is shown in Figure 5:

$$\ln S = 0.00128\, \Delta H_1 + 3.798, \quad r^2 = 0.95 \tag{6}$$

This correlation could be of some practical importance by showing a way to predict the bonding strength of the composite product using hydrogen
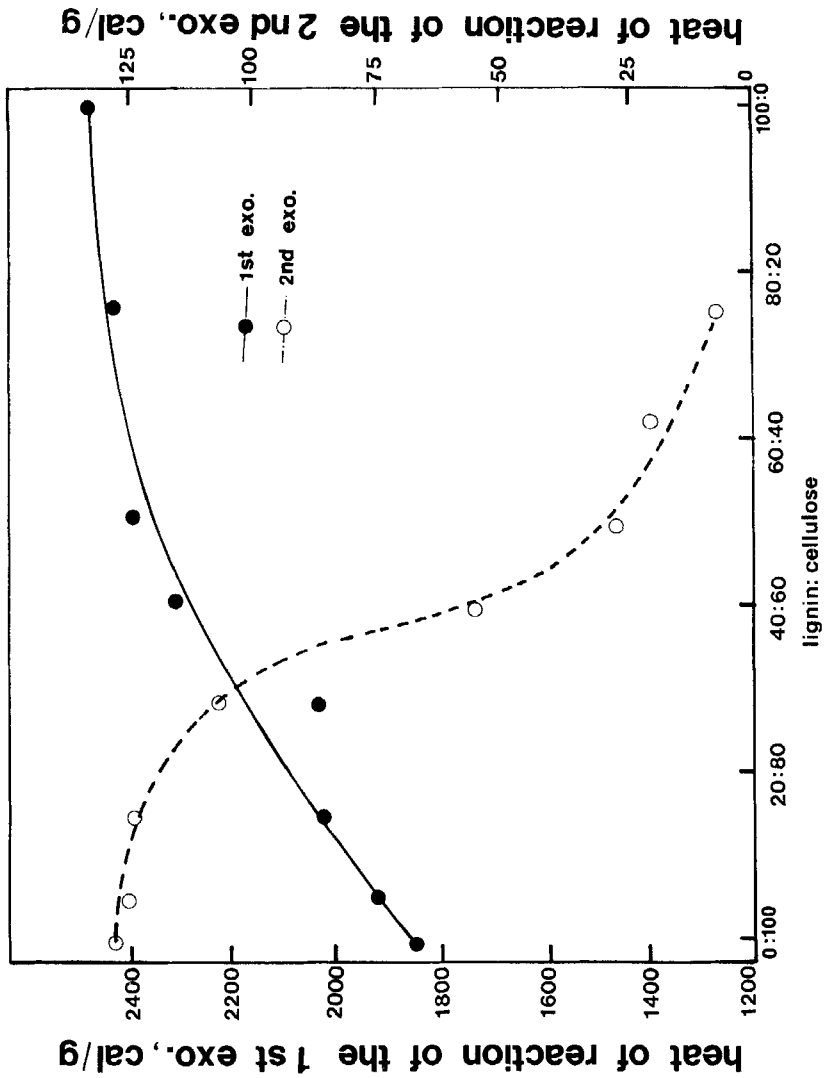
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FIGURE 4 Effects of lignin concentration on the heats of the reaction between H_2O_2 and cellulose.
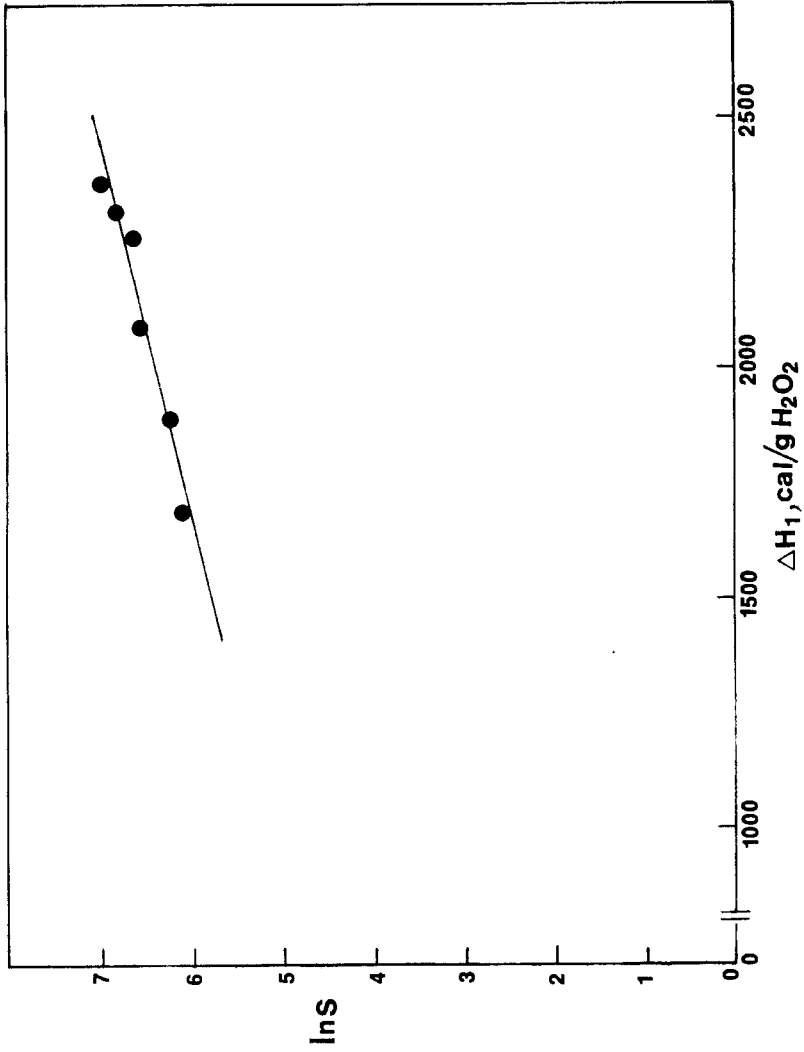
FIGURE 5   Correlation between H_2O_2-lignocellulose heat of reaction and bonding strength of compositeboard.

peroxide as a surface activator. While the correlation between the bonding strength and heat of reaction has been found for hydrogen peroxide, similar relationships may be expected with other oxidizers.

CONCLUSIONS

Using differential scanning calorimetry at high pressure for reactions in a pinhole vented deactivated aluminum pan, the effects of lignin on the reaction between hydrogen peroxide, a surface activator, and lignocellulose were characterized. Lignin was found to be more reactive than cellulose. Both reaction temperatures and enthalpies were found to be functions of the lignin content in cellulose. A correlation indicated that the bonding quality was a function of the exothermic heat of reactions between the hydrogen peroxide and lignocellulosic materials.

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