BONDING FIRE RETARDANTS TO WOOD. PART I. THERMAL BEHAVIOR OF CHEMICAL BONDING AGENTS[1]

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ABSTRACT

Bonding chemicals to wood can alleviate the problem of leachability, but the effects of such bonding on wood properties are not yet well researched. Propylene oxide, butylene oxide, acetic anhydride, and methyl isocyanate were bonded to southern pine, and the bonded wood's thermal properties were determined by thermogravimetric and evolved gas analysis. The initial decomposition temperature was significantly increased by epoxide bonding, slightly increased by acetyl bonding, and slightly reduced with isocyanate bonding as compared to nonbonded control. The amount of char generated during pyrolysis was nearly the same for the control, acetyl-, and isocyanate-bonded wood, and was reduced for epoxide-bonded wood. The volatile decomposition products from the epoxide-bonded wood had a higher heat of combustion than those of the control, whereas the heat of combustion of volatiles from acetyl- and isocyanate-bonded wood was almost the same as that of the control.

Keywords: Fire retardants, bonding agents, thermogravimetric analysis, thermal properties.

INTRODUCTION

Wood is a three-dimensional biopolymer composite composed primarily of cellulose, hemicellulose, and lignin. These polymers make up the cell wall and are responsible for most of the physical and chemical properties exhibited by wood. Wood is a preferred building/engineering material because it is economical, low in processing energy, renewable, strong, and aesthetically pleasing. It has, however, several disadvantageous properties such as combustibility, biodegradability, and changing dimensions with varying moisture contents. These properties of wood are all the result of chemical reactions involving degradative environmental agents. For example, wood burns primarily because the cellulose and hemicellulose polymers undergo pyrolytic and oxidative reactions with increasing temperature, giving off flammable gases. The lignin component, being more thermally
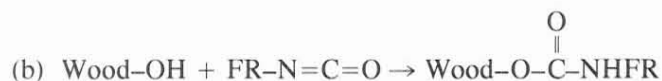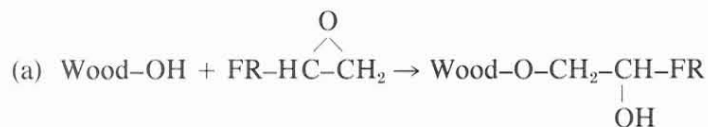
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stable, contributes more to char formation than does cellulose and hemicellulose. Increased char formation reduces flammable gas formation and helps insulate wood from further thermal degradation. The high molecular weight of cellulose is primarily responsible for wood strength, which decreases as cellulose degrades by pyrolytic mechanisms.

To improve the fire performance of wood, chemicals have been added to wood to reduce the amount of flammable gas and increase the amount of char. Fire-retardant chemicals have traditionally been inorganic salts, some of which are corrosive to metal fasteners and make the treated wood more hygroscopic. These water-soluble, impregnated chemicals are not bonded to the wood and are lost when wood is exposed to weathering elements. Inorganic salts are also acidic or basic in nature and may cause a reduction in wood strength through cellulose hydrolysis (Holmes 1977).

To overcome the problems of leachability, corrosivity, hygroscopicity, and strength reduction from traditional fire-retardant treatments, the Forest Products Laboratory has initiated a program to investigate bonding fire retardants to wood. This would require the synthesis of reactive fire-retardant chemicals that would bond to wood cell-wall polymer hydroxyl groups (Wood-B-FR): The types of bonding groups (B) that have been considered to bond the fire retardant (FR) to wood are epoxides (a), isocyanates (b), and anhydrides (c), which react with wood hydroxyl groups as follows:

$$\text{(a)} \quad \text{Wood–OH} + \text{FR–H}\overset{\overset{\displaystyle O}{\diagup\diagdown}}{C}\text{–CH}_2 \rightarrow \text{Wood–O–CH}_2\text{–}\underset{\underset{\displaystyle OH}{|}}{CH}\text{–FR}$$

$$\text{(b)} \quad \text{Wood–OH} + \text{FR–N=C=O} \rightarrow \text{Wood–O–}\overset{\overset{\displaystyle O}{\|}}{C}\text{–NHFR}$$

$$\text{(c)} \quad \text{Wood–OH} + \text{FR–}\overset{\overset{\displaystyle O}{\|}}{C}\text{–O–}\overset{\overset{\displaystyle O}{\|}}{C}\text{–FR} \rightarrow \text{Wood–O–}\overset{\overset{\displaystyle O}{\|}}{C}\text{–FR}$$

Each has been shown to form stable, leach-resistant chemical bonds with wood (Rowell and Gutzmer 1975; Rowell and Ellis 1981; Rowell 1982).

Several basic questions need to be answered in this approach to fire retardancy of wood: 1) Does the bonding agent add significantly to the generation of volatile products from the reacted wood under pyrolytic conditions? 2) What effect does the bonding agent have on the rate of volatile production and the amount of char formed during pyrolysis? 3) Does the bonding change the thermal stability of wood by changing the pyrolysis temperature? In summary, what effect does the bonding agent have on the pyrolysis of chemically bonded wood? The purpose of this research was to answer these questions using thermogravimetric analysis (TG) and evolved gas analysis (EGA).

<center>EXPERIMENTAL</center>

Southern pine oven-dried blocks (2 by 2 by 5 cm, radial by tangential by longitudinal) were reacted separately with either propylene oxide-triethylamine
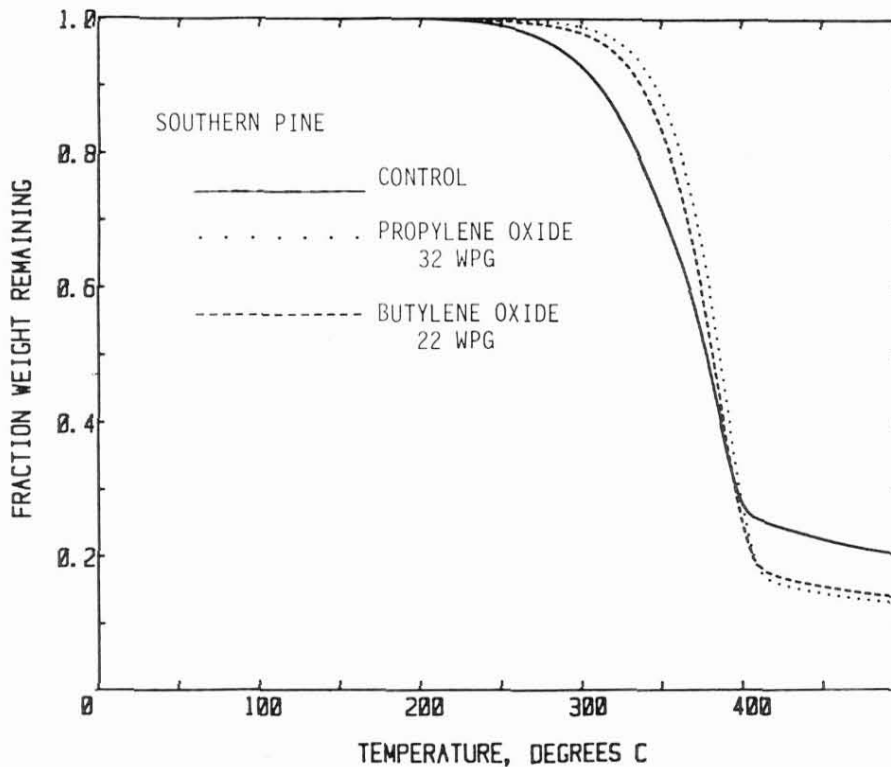
FIG. 1.   Thermogravimetric analysis of epoxide-modified wood.

(95/5 vol/vol), butylene oxide-triethylamine (95/5 vol/vol), methyl isocyanate alone or acetic anhydride-xylene (1/1 vol/vol) at 120 C, 150 lb per square inch as previously described (Rowell and Gutzmer 1975; Rowell and Ellis 1981; Rowell 1982). Specimens were prepared at 32 weight percent gain (WPG) for propylene oxide, 22 WPG for butylene oxide, 24 WPG for methyl isocyanate, and 24 WPG for acetic anhydride. Each specimen, along with an unreacted control, was ground to 40 mesh, extracted with benzene/ethanol (2/1 vol/vol) for 2 h, air-dried, and finally oven-dried at 105 C. Weight gains were calculated on an extracted, oven-dry basis.

Thermogravimetric analyses (TG) and derivative (DTG) analyses were performed on a Perkin-Elmer TGS-2 thermogravimetric system. A data acquisition system measured sample mass to 0.1 mg and run time to 0.004 s. Furnace temperature was programmed by the data system through a digital-to-analog converter. Samples of 5 ± 0.5 mg were charred at 20 C/min to a temperature of 500 C under nitrogen flowing at 200 ml/min.

Evolved gas analysis (EGA) was performed using the reaction coulometer combustible gas detection system by Susott (1980) and Susott et al. (1979). Samples of 2.0–2.5 mg were heated in a quartz furnace tube from room temperature to 500 C at 20 C/min under a 40 ml/min flow of high-purity nitrogen. A thermocouple attached to the bottom of the sample pan provided both the sample temperature
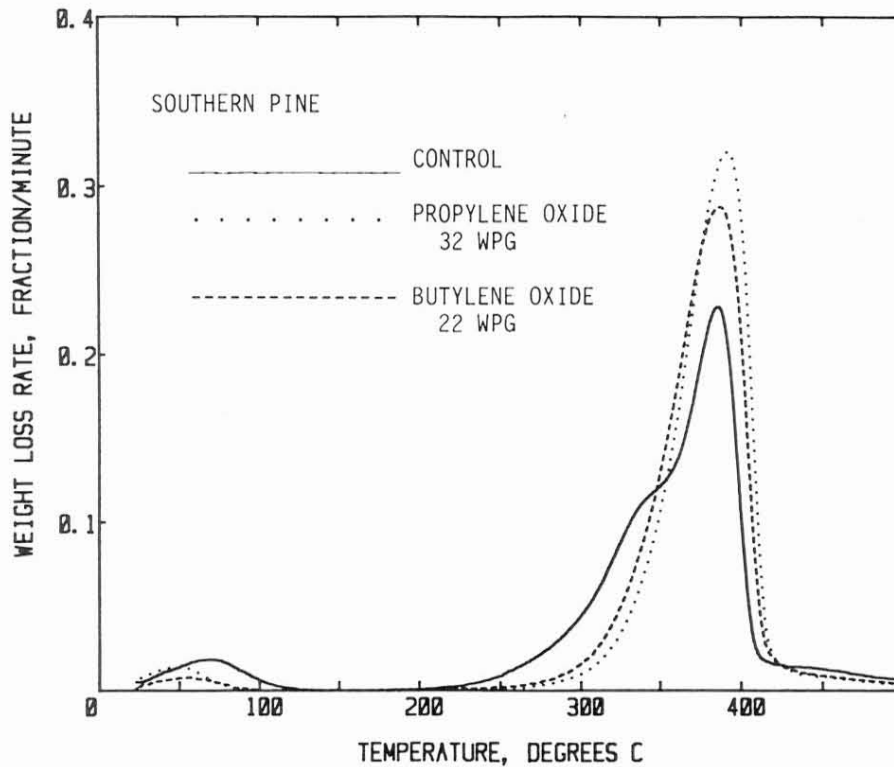
FIG. 2.   Derivative thermogravimetric analysis of epoxide-modified wood.

and feedback for temperature program control. The reaction coulometer detector was interfaced with a microcomputer that continuously monitored the sample temperature and detector output. Data analysis, including baseline correction and calculation of the integrated detector response, was performed using the micro-computer system. The heat of combustion of the volatile decomposition product mixture was determined on the basis of its proportionality with the quantity of oxygen used in combustion. Heats of combustion were calculated on the basis of the dry weight of the unpyrolyzed wood using a conversion value of 107 cal/mmole O_2. This has been demonstrated to be accurate to within 4% of values measured calorimetrically (Susott et al. 1979).

RESULTS AND DISCUSSION

Southern pine and ponderosa pine specimens were reacted with three different types of bonding agents: propylene and butylene oxides for epoxide bonding, methyl isocyanate for urethane bonding, and acetic anhydride for ester bonding.

Propylene oxide is a very flammable and explosive liquid. Bonding this chemical to wood might drastically change the burning characteristics. Although butylene oxide is much less flammable, it too, after bonding, might significantly alter the thermal properties of wood. Thermogravimetric analyses curves of a southern pine-propylene oxide specimen (32 WPG) and southern pine-butylene oxide specimen (22 WPG) show (Fig. 1) that epoxide-bonded wood starts to degrade ther-
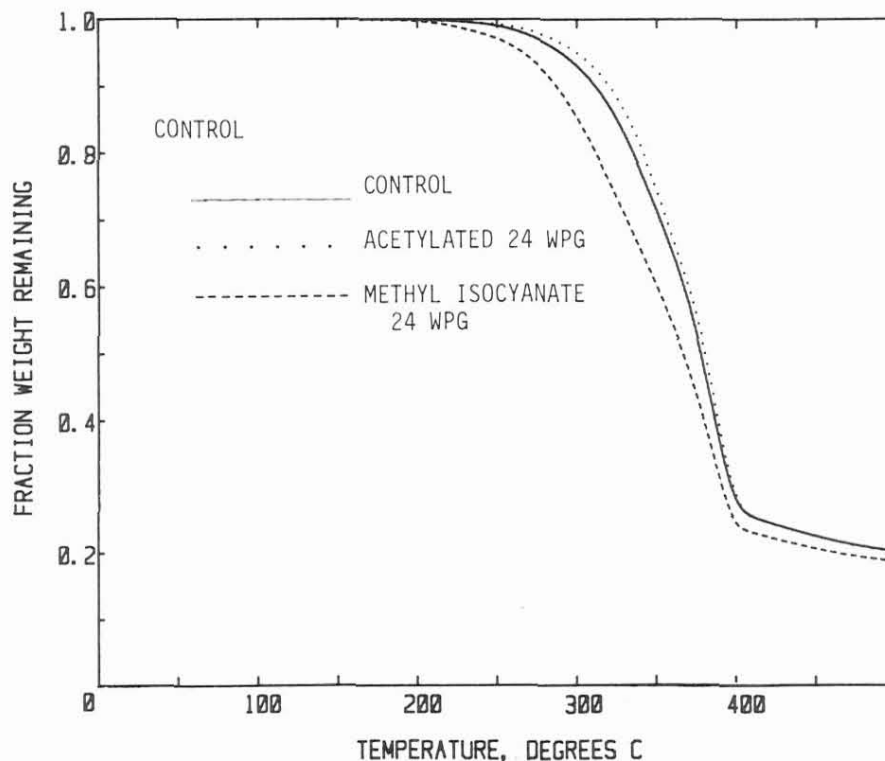
FIG. 3.   Thermogravimetric analysis of acetylated and isocyanate-modified wood.

mally at a slightly higher temperature than does nonbonded wood. Somewhat less char is formed with epoxide-modified wood than unmodified, indicating that the bonded chemical is lost with volatile products and does not contribute to char formation. Derivative thermogravimetric analyses curves (Fig. 2) show that the temperature of maximum rate of weight loss is the same for epoxide-bonded and nonbonded wood. However, the control specimens show a shoulder at 325 C prior to the weight loss maximum at 385 C. The low-temperature shoulder in the control is thought to be due to hemicellulose degradation. This shoulder was missing in the epoxide-bonded wood, which may mean that the stability of the hemicellulose polymers has been increased.

Thermal degradation of acetyl-bonded wood (24 WPG) is nearly identical to that of a nonbonded control specimen, whereas the isocyanate-bonded specimen (24 WPG) shows a lower initial decomposition temperature (Fig. 3). Both the acetyl- and isocyanate-bonded woods show similar amounts of char as compared to the control (Fig. 3).

Unlike epoxide-bonded wood, isocyanate- and acetyl-bonded wood show a shoulder before the peak in the weight loss plots (Fig. 4), as does the control. The low-temperature shoulder is broader in the isocyanate-bonded wood than in the control. This may mean the urethane degradation precedes the hemicellulose degradation, effectively broadening the low-temperature shoulder. In all cases the cellulose maximum remains at about 385 C.
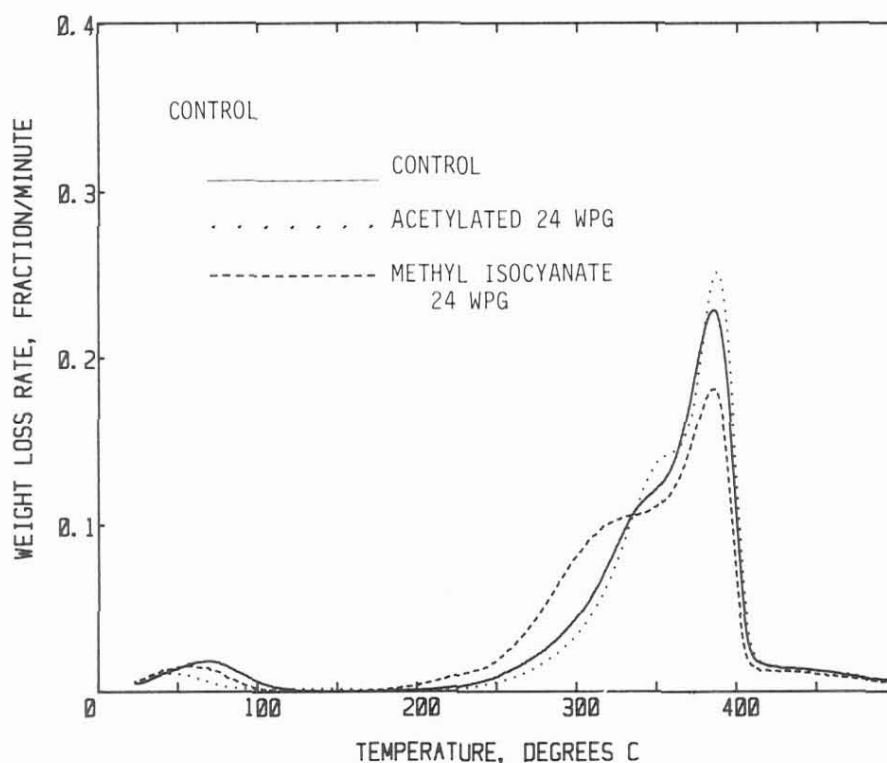
FIG. 4.   Derivative thermogravimetric acetylated and isocyanate-modified wood.

Because it is not possible to determine from TG and DTG analyses if the products from the combustion of bonded wood are more or less flammable than combustion products from nonbonded wood, EGA was done for southern pine control and southern pine bonded with propylene and butylene oxide reacted to 32 and 22 WPG, respectively (Fig. 5). As in the TG, the EGA control has a low-temperature shoulder at 325 C and a peak at 385 C, while the epoxide-bonded wood showed only one peak at 385 C. This again indicates an increase in the stability of the hemicellulose polymers after epoxide bonding.

The integrated EGA control specimen heated to 500 C shows a heat of combustion of the volatile products of 2.9 kcal/g based on the weight of the original dry fuel. For butylene oxide-bonded wood, the heat of combustion of the volatiles is 4.1 kcal/g, and for propylene oxide-bonded wood, it is 4.2 kcal/g. These results show that the volatiles coming from epoxide-bonded wood are significantly more flammable than volatiles from nonbonded wood. This is due to the higher heat of combustion of the epoxide added to the wood as compared to that of the decomposition products of the wood cell-wall polymers.

The EGA's for acetyl- and urethane-bonded southern pine specimens (Fig. 7) indicate that they decompose in approximately the same temperature range and at the same rate as the control.

The gaseous decomposition products from the acetyl- and urethane-bonded specimens have about the same heat of combustion as those of the control (Fig. 8). At equal weight gains of bonded chemical, the decomposition products of the
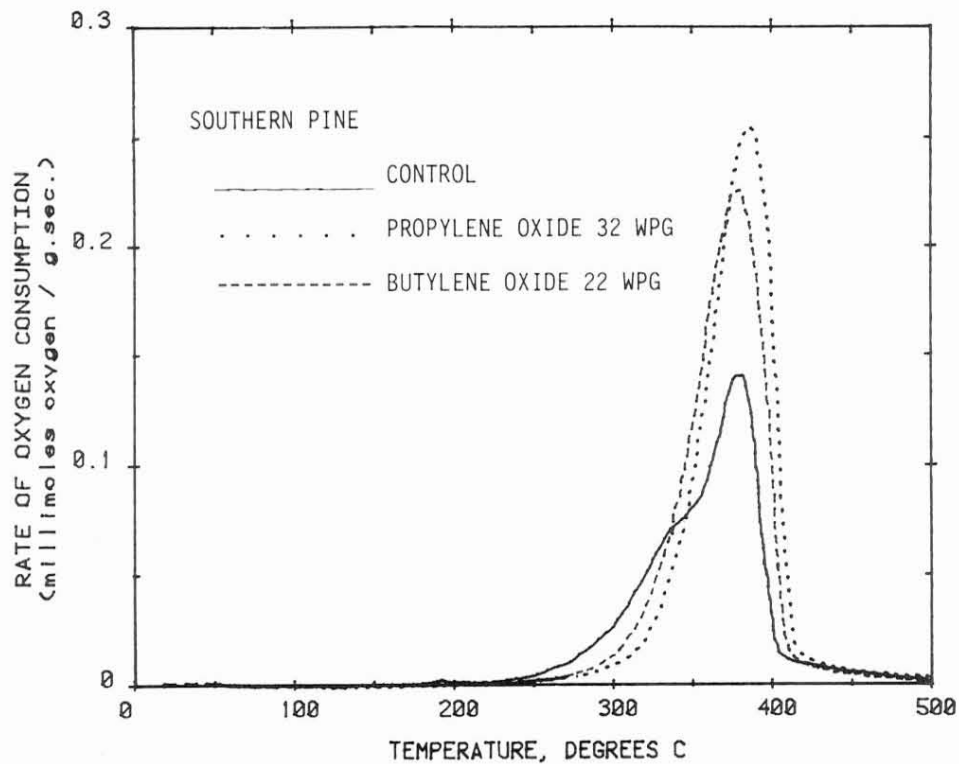
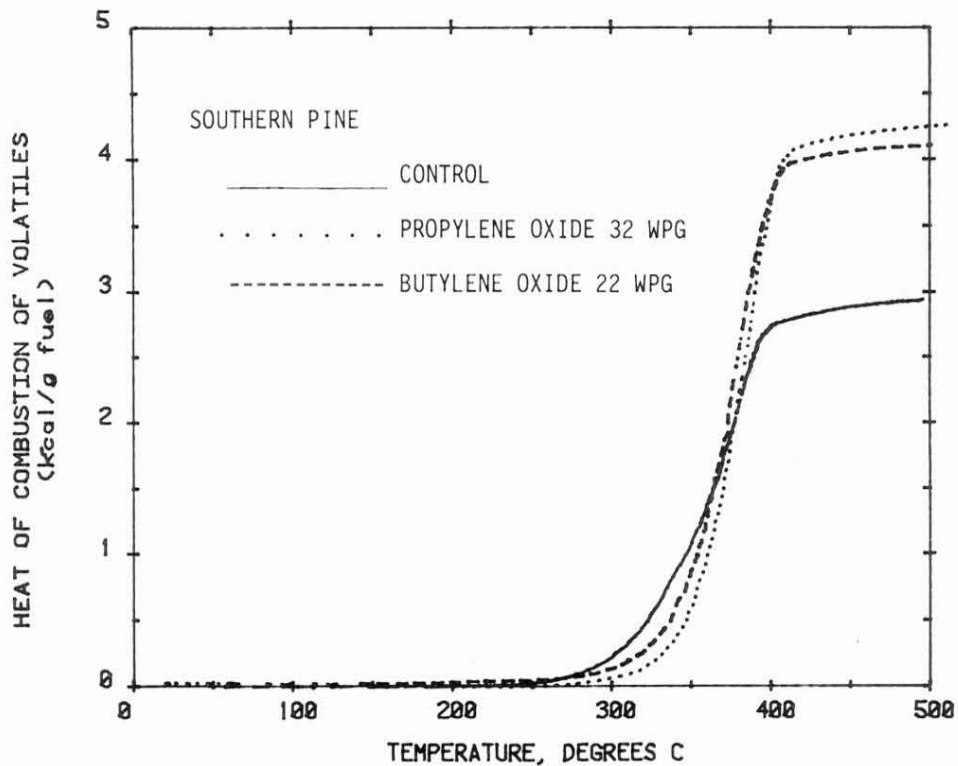FIG. 5. Evolved gas analysis of propylene and butylene oxide-modified wood.

FIG. 6. Heat of combustion of volatiles from propylene and butylene oxide-modified wood as determined from integrated evolved gas analysis.
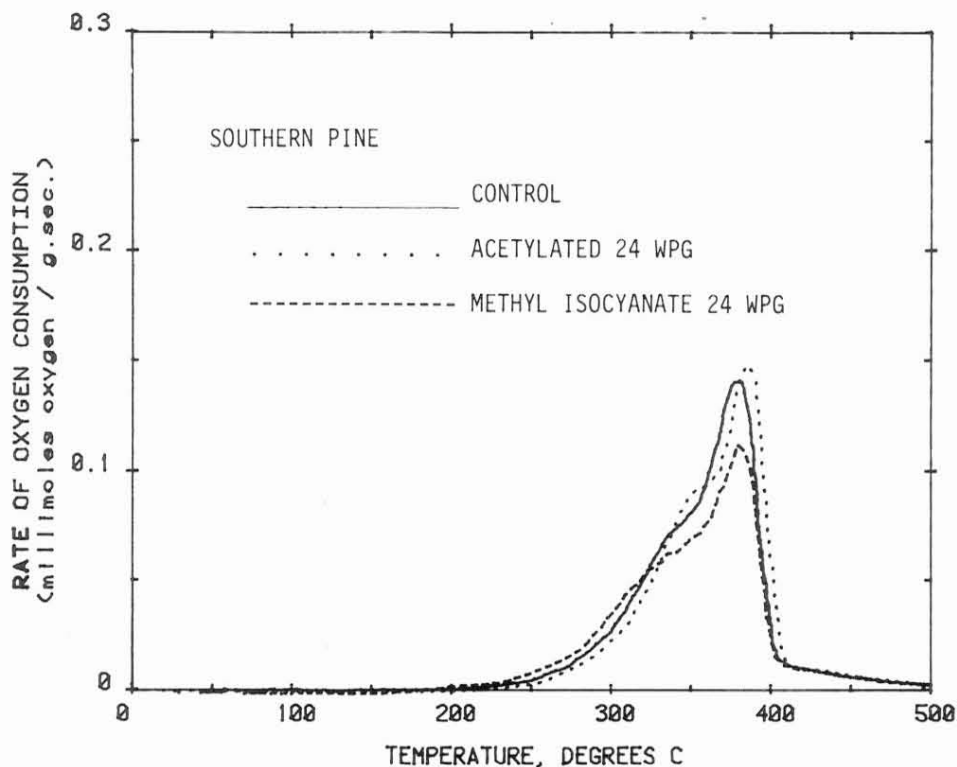
FIG. 7.   Evolved gas analysis of acetylated and isocyanate-modified wood.

acetyl specimen have a heat of combustion of 3.1 kcal/g and those of the urethane specimen have 2.7 kcal/g.

All of the above tests were also conducted on ponderosa pine with essentially the same results.

CONCLUSIONS

The thermal stability as shown by both TG and EGA decomposition temperatures was slightly increased by epoxides, was maintained with acetyl, and was slightly lowered by isocyanates, as compared to controls. The amount of char generated during pyrolysis was nearly the same for untreated wood, acetyl-, and isocyanate-bonded wood and reduced for epoxide-bonded wood. The epoxide bond seemed to stabilize the components that degraded at 325 C (hemicelluloses), and this component apparently gasified along with the cellulose component at 385 C. The ether linkage is more chemically stable and apparently more thermally stable than the acetyl linkage that bonds the polysaccharides. Thus, the bonded epoxide may still have been bonded to the carbohydrate at the temperature at which carbohydrate pyrolysis occurred.

Acetyl- and isocyanate-bonded chemicals did not stabilize the components degrading at 325 C but showed the same TG and EGA profiles as did the controls. Because ester and urethane bonds are not as stable to pyrolysis as ether linkages at high temperatures, there was a partial release of bonded chemical at low tem-
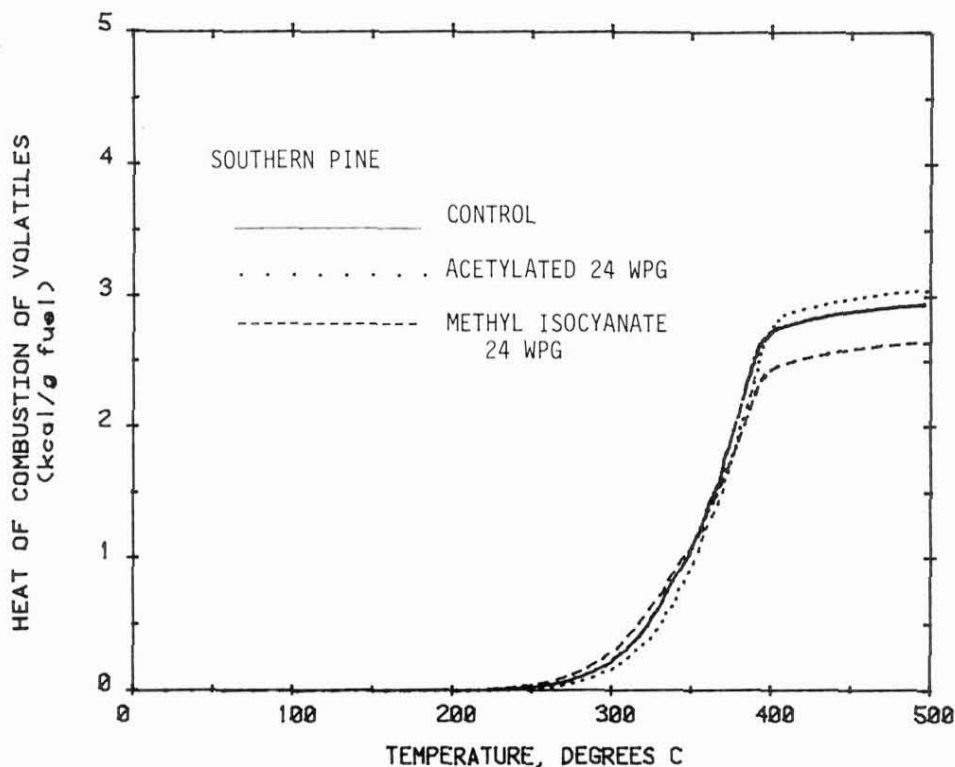
FIG. 8. Heat of combustion of volatiles from acetylated and isocyanate-modified wood as determined from integrated evolved gas analysis.

peratures. This may be a useful way to release a bonded chemical that would act as a gas phase flame suppressant.

Evolved gas analysis showed that the epoxide-bonded wood had a higher heat of combustion of volatiles than did the control. The heat of combustion of volatile products from acetyl- and methyl isocyanate-bonded wood was almost the same as that of the control. The high heat of combustion of volatiles observed for epoxide-bonded wood is due primarily to the hydrocarbon content attached to the bonding group. The epoxide bonding group $-CH_2-CH-$ accounts for

$$OH$$

part of the heat of combustion, but the $-CH_3$ and $-CH_2CH_3$ added by propylene and butylene oxides, respectively, also contribute. This extra hydrocarbon will be replaced with a fire retardant in future research.

The same is true for acetyl- and urethane-bonded wood. In the case of acetyl

$$O$$

bonding, only the $-C-$ bond will be present in the bonding of a fire retardant,

$$O$$

and in urethane bonding, the $-C-NH-$ bond will be present. Neither of these moieties should contribute significantly to the heat of combustion of the volatile products.

Fire retardants bonded to wood will be formulated in such a way that they either do not volatilize at the thermal decomposition temperature and catalyze the formation of char or volatilize simultaneously with the cell-wall polymers and act in the gas phase as a flame suppressant. The ultimate objective is to develop a leach-resistant, fire-retardant treatment.

Research is presently under way to synthesize halogen-, phosphorus-, and nitrogen-containing chemicals with reactive epoxide and isocyanate groups to be bonded to wood and tested for their fire-retardant properties.

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