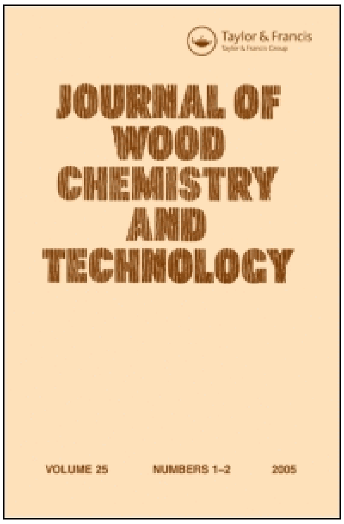

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BOND FORMATION BY WOOD SURFACE REACTIONS
PART IV ANALYSIS OF FURFURYL ALCOHOL, TANNIN AND MALEIC ACID BRIDGING AGENTS

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ABSTRACT

Solid wood panels (Acer saccharum Marsh.) were bonded with various bridging materials following nitric acid activation. These chemical bridging materials included tannin, furfuryl alcohol and mixtures of the two with and without maleic acid. High shear strengths were achieved with a tannin-furfuryl alcohol-maleic acid mixture (T-F-M) with or without the nitric acid activation.

The curing reactions of the bridging material were examined with differential scanning calorimetry (DSC). Furfuryl alcohol was found to be the most reactive component of the T-F-M. Results from both the bonding work and the DSC analysis showed little effect of open assembly time or pot-life. The furfuryl alcohol appeared to be nitrated by the nitric acid catalyst. The nitrated material apparently degraded at high temperature (180°C) in a violent reaction detected by DSC. While these reactions were not observed with the panels the possibility of violent reactions during pressing must be considered.

INTRODUCTION

The uncertainties in the supply and price of petroleum products have prompted research into new forms of wood adhesives. Recent research has focused on new systems that employ surface activation of wood with a strong oxidant along with conventional condensation adhesive components[1-3] or cross-linking agents such as diamines or diacids.[4,5]

One of the more successful processes involves pretreatment (activation) of wood with nitric acid which is followed by the addition of a diamine[4] or a furfuryl alcohol-lignin mixture.[1,6-8] Nitric acid is known to cause a number of different reactions with wood including oxidation, nitration and acid condensation.[9,10] Degradation of the wood substrate has also been observed with nitric acid treatment.[11]

The potential for bonding wood with nitric acid and furfuryl alcohol was first discussed in 1953 by Emerson.[12,13] After some refinement of Emerson's process a plant was opened by the Kroehler Manufacturing Company[14] for the production of bonded furniture panels. This plant produced a hardboard termed "culture wood" in which the fibers were activated with nitric acid before being mixed with furfural, ureas and tempering oils.

Since then furfuryl alcohol-lignin-maleic acid mixtures have been used as "gap-filling" mixtures for wood flakes that were pretreated with nitric acid.[1] The gap-filling mixture was found to have a long, but not infinite, pot-life. Particleboards prepared with this mixture had lower strength properties but better dimensional stability than phenolic controls. A mechanism for bond formation that involved both oxidation and acid-catalyzed condensation reactions was suggested.

The reactions of furfuryl alcohol have been previously investigated by thermal techniques such as differential scanning calorimetry (DSC). Miljkovic et al.[15] used differential scanning calorimetry (DSC) in conjunction with other techniques to look at the curing reactions of monomeric furfuryl alcohol and furfuryl alcohol resins. To eliminate problems with endothermic peaks due to evaporation of volatile compounds these researchers used hermetically sealed pans. They found three distinct exothermic peaks between 0 and 200°C. The location of these peaks was highly dependent on the amount of acid catalyst that was used. This observation is consistent with earlier data that showed the rate of cure to be dependent on both the pH and temperature of the system.[15,16]

The thermogram of a furfuryl alcohol resin with a moderate amount of catalyst showed two low-temperature exothermic peaks at 78° and 108°C, followed by a separate high-temperature peak that was not complete at 180°C. A rescan of the same mixture showed residual activity at temperatures above 160°C.[15] It was also noted that the resin had a hard and brittle appearance after the second peak at 108°C. Samples taken between the two low-temperature exothermic peaks showed the resin to resemble a hard rubber. Thus it was concluded that the first exotherm was the initial condensation reaction between methylol groups and 5-position hydrogens; while the second exothermic peak was thought to be due to several different reactions including the decomposition of methylene ether linkages, crosslinking between the 3 and 4 positions of the furan ring in the presence of free formaldehyde and ring-opening reactions.[15]

Formaldehyde, for crosslinking of the furfuryl alcohol polymer, is formed in situ from decomposition of methylol groups and methylene-ether bridges during the polymerization of the furfuryl alcohol.[15] Since this small amount of formaldehyde is readily consumed by the crosslinking reaction, very little, if any, formaldehyde evolution is expected from a cured furfuryl alcohol resin. This strongly contrasts with present formaldehyde release problems encountered with urea-formaldehyde (UF) resins. With the UF systems the formaldehyde is added and the unreacted compound migrates into the surrounding atmosphere.

Tannins were also included with furfuryl alcohol in the adhesive systems used in this investigation. Tannins are water-soluble polyphenolics that are commonly extracted from the bark of trees. Black wattle (Acacia mearnsii) is one commercial source of tannins that can be used for wood adhesives.[2] Most of these extracts can be represented by the flavan-3-ol, catechin (Figure 1). A typical reaction for catechin would be a condensation reaction through the phloroglucinol A ring. The reaction between the phloroglucinol A ring of catechin and formaldehyde proceeds at a rate comparable to that of phloroglucinol and formaldehyde, although slightly slower. This reduction in reactivity is probably due to steric hindrance by the rest of the tannin molecule connected to the A ring.[2] The catechol B ring in catechin is much less reactive toward formaldehyde than the A ring.

Furfural has also been shown to be reactive with tannins under acidic conditions. If the A ring on the tannin is modeled with resorcinol, its reactivity with furfural is much greater than if the A ring is represented by a phloroglucinol model. This difference in reactivity was present when only phlorogucinol and resorcinol were reacted with furfural and was not noted with other aldehydes. The major effect was thought to be steric hindrance by the third hydroxyl group present on phloroglucinol. In resorcinolic flavonoids the favored position of attack appears to be at the 6 position of the ring.[2] Resorcinol or resorcinolic materials such as tannins can react violently with furfuryl alcohol.

Previous investigators have also utilized tannins in adhesive formulations. Pizzi[2,17] combined maleic anhydride, tannin and formaldehyde to bond particleboard; while Boyette[18]

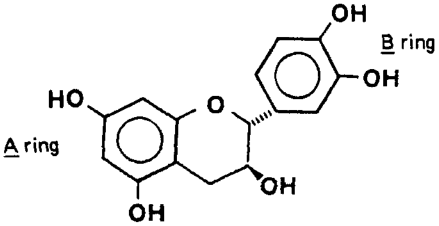

Figure 1. Structure of (+) catechin, a model compound representative of tannins.

bonded plywood with a similar mixture but without formaldehyde. Furfuryl alcohol/tannin mixtures have also been used to produce rigid foams.

A further anlaysis of bonding and reactions of furfuryl alcohol, tannin and lignin bridging agents in combination with nitric acid activation of wood is given in this paper.

Reagents

The components of the tannin-furfuryl alcohol-maleic acid (T-F-M) mixture were used at the following concentrations:

1. Tannin (28% aqueous solution)
2. Furfuryl alcohol (20% aqueous solution)
3. Maleic acid (28% aqueous solution)
4. Nitric acid (40% aqueous solution)

All of the reagents were purchased from commercial sources. For the T-F-M, these components were mixed at a (1.0:1.6:0.25) ratio of tannin-furfuryl alcohol-maleic acid. Variations from this recipe are noted in the text. The panels were all activated with 40 percent aqueous nitric acid.

Board Preparation

Shear strength values were obtained from a modified shear block test[19] from a parallel laminated sugar maple (*Acer* saccharum Marsh.). The panels were pressed at 170°C and 2 MPa pressure for 30 minutes. Nine modified shear blocks were cut from each panel. Each experiment was repeated to give a total of 18 shear blocks. Four randomly selected shear blocks, two from each board, were subjected to a vacuum pressure soak. Both the vacuum (1.013×10^5 dyne/cm^2 or 76 torr) and pressure (2.14×10^6 dyne/cm^2 or 1,615 torr) phases were held for 1/2 hour and the shear blocks were then tested wet. All of the shear samples were tested in an Ametek testing machine. The head speed was 0.038 centimeter per minute, as specified by ASTM Standard D-905.[20]

All the shear blocks for each condition were considered as a group and the average determined. The standard deviation and confidence intervals were calculated as described by Snedecor and Cochran.[21]

Instrumental Analysis

Infrared spectra were run on a Beckman TR-12 as KBr pellets or between KBr plates, depending on the sample. The differential scanning calorimeter (DSC) thermograms were run with sealed stainless steel large volume capsules (LVC) on a Perkin-Elmer DSC-2. The proton nuclear magnetic resonance spectra (NMR) were run on a Varian T-60 instrument with a deuterated dimethyl sulfoxide solvent. The ultraviolet spectra (UV) were run on a Beckman Acta III with a methanol solvent.

For DSC analysis, the different components were mixed in the specified proportions, the nitric acid catalyst was added and the solution stirred. After stirring, the solution was placed in a LVC and the capsule sealed. The capsule was then placed in the DSC sample holder and the scan started as quickly as possible. A LVC with a cured phenolic resin was used in the reference side of the DSC sample holder. The scanning rate was 10°C/min. and scanning range was from 0°C to 200°C. The IR spectra of the (T-F-M) mixture were of samples taken directly from the DSC capsules.

The material for the H^1-NMR and UV spectra was prepared by putting 10 ml of the T-F-M in a test tube. The test tube was placed in a preheated stainless steel bomb and sealed. The bomb was partly filled with oil to insure good heat transfer. The T-F-M mixture was heated for 20 minutes, cooled, and then extracted with tetrahydrofuran. The soluble portion was separated and the tetrahydrofuran evaporated under nitrogen. The residue was then redissolved in the appropriate solvent and the spectra were run.

RESULTS AND DISCUSSION

Bonding Results

The dry shear strengths of nitric acid activated panels bonded with furfuryl alcohol, tannin and furfuryl alcohol-tannin mixtures are shown in Figure 2. The dry and wet shear strength values and standard deviations are shown in Table 1. These results show that both tannin and furfuryl alcohol separately are capable of promoting a high strength wood bond. The tannin-furfuryl alcohol mixtures also gave high dry shear strength with the mixture containing the higher proportion of furfuryl alcohol giving the highest shear strengths. The wet shear strengths for all of the panels were about 45-50% of the dry shear strengths.

As mentioned earlier furfuryl alcohol is capable of forming a highly condensed polymer with the application of heat or by lowering the pH.[15] Tannins are also capable of undergoing condensation reactions with furfural[2] and other aldehydes; the latter may be produced as degradation products of the reaction of nitric acid with wood.[11,22] The tannin could either copolymerize with or act as a plasticizing agent for the furfuryl alcohol polymer.

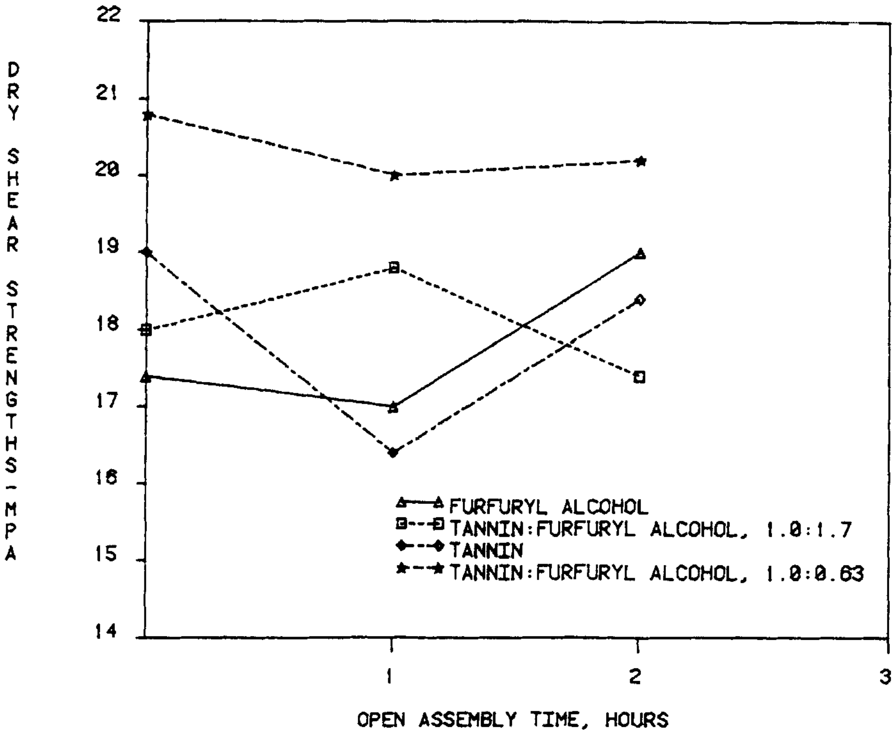

Figure 2. Dry shear strengths of sugar maple bonded with different bridging agents following nitric acid activation.

A tannin, furfuryl alcohol, maleic acid mixture (T-F-M) was also used to bond nitric acid activated panels. The maleic acid was added to see if changes in the viscosity of the bridging material would affect the shear strength. Maleic acid promotes the polymerization of furfuryl alcohol at room temperature, and thus; another variable, pot-life, was added to the experimental design.

As shown in Figure 3, neither the open assembly time or the pot-life had any consistent effect on the dry shear strength of the panels. The dry shear strengths were enhanced by the addition of the maleic acid, compared to the strengths

TABLE 1

Shear strength and confidence intervals for panels bonded with different bridging materials following nitric acid activation.

Chemical Bridging Agent	Open Assembly Time[a], hr	Dry Shear (DS), MPa	DS 95% Confidence Interval, MPa	Wet Shear (WS), MPa
Tannin	C[b]	10.94	1.40	2.03
	0	19.07	1.14	9.19
	1	16.49	1.05	8.64
	2	18.45	0.91	8.64
Furfuryl alcohol	C	5.17	0.94	0
	0	17.49	1.35	9.20
	1	16.90	1.05	10.43
	2	18.85	1.46	10.60
Tannin:Furfuryl alcohol I (1.0:1.7)	C	13.33	0.71	0
	0	20.76	0.46	8.51
	1	19.93	1.40	6.10
	2	20.02	0.97	9.78
Tannin:Furfuryl alcohol II (1.0:0.63)	C	11.75	1.03	0
	0	18.12	0.91	7.59
	1	18.71	0.56	6.84
	2	17.59	0.74	6.59

[a] Open assembly time is the length of time after the acid treatment and before the addition of the chemical bridging agent.

[b] C -- Control; the chemical bridging agent was added to a sample which had no acid pretreatment.

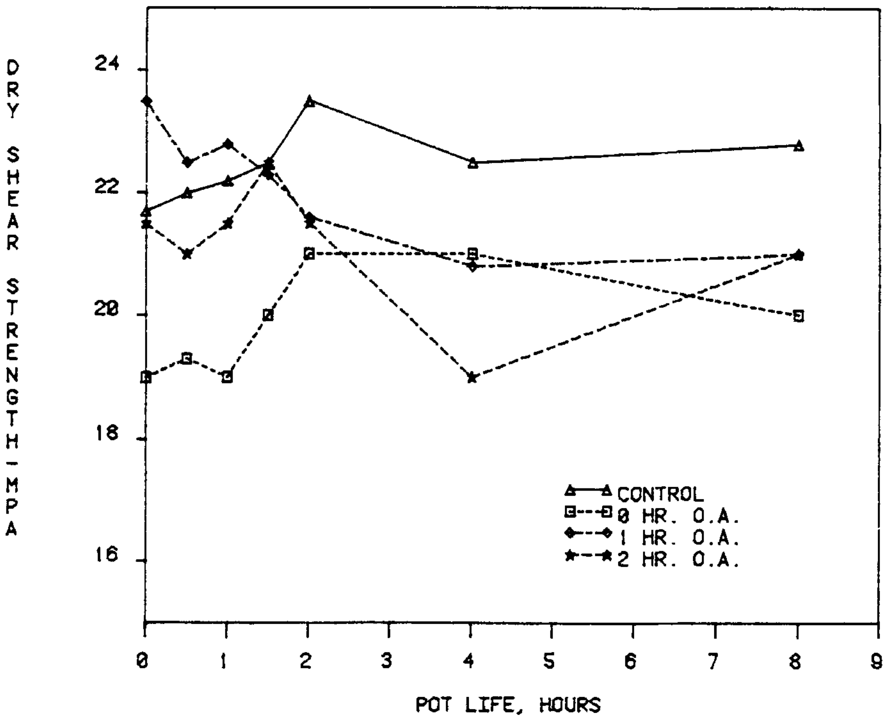

Figure 3. Dry shear strengths of sugar maple bonded for 30 minutes with T-F-M mixture.

of the tannin-furfuryl alcohol mixtures. The wet strength values after the vacuum-pressure soak were again about 45 percent of the dry shear strengths.

These strength values compare quite favorably with strength values for panels bonded with phenolic resins; although the wet shear strengths are slightly less than would be expected from well cured phenolic resins. The addition of maleic acid apparently lowers the pH of the T-F-M mixture enough to cure the mixture under the bonding conditions. A grainy precipitate formed after four hours reaction time, which was probably furfuryl alcohol oligomers. An attempt to confirm the nature of the precipitate with infrared spectroscopy was not successful because of the highly condensed and complex nature of the material.

It was also noted that the T-F-M mixture gave a high strength product without the nitric acid pretreatment. Although the acid activation clearly enhanced wood bonding with the tannin/furfuryl alcohol mixture (Table 1), the advantages of the pretreatment were much less with the T-F-M formulation. The additional costs of handling the strong acid in the plant and losses of long-term wood bond durability would probably preclude the use of the nitric acid activation with a T-F-M adhesive.

Due to the relative insensitivity of the shear strength to changes in the structure and reactions of the bridging material, other techniques were used to examine the T-F-M adhesive.

Thermal Analysis

Differential scanning calorimetry (DSC) was used to investigate the thermal characteristics of the (T-F-M) mixture with and without nitric acid. It was hoped that this technique would provide more information on the effects of increasing the pot-life of the T-F-M. This was accomplished by recording DSC thermograms of the T-F-M at various pot-life times. The thermograms for the T-F-M without nitric acid are shown in Figure 4. The thermogram at zero hours pot-life showed a broad exotherm at 100°C. A rescan of the mixture showed essentially no residual thermal activity. This indicates that the T-F-M had been cured into a unreactive polymer. As the pot-life was increased the broad exotherm at 110°C remained constant while a shoulder appeared at about 90°C.

After 8 hours the thermogram appeared to have flattened slightly while a low temperature exothermic shoulder appeared.

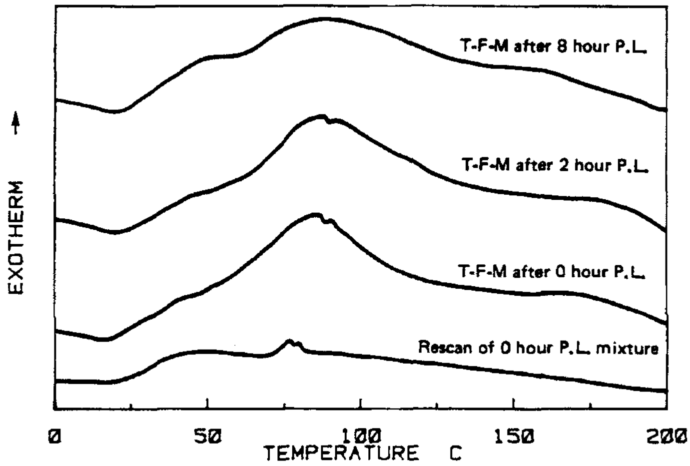

Figure 4. DSC thermograms of the T-F-M bridging material with different pot-lifes, without nitric acid.

Previous research has shown that both furan and phenolic polymers exhibit exothermic reactions in this region.[15,23] This behavior is generally interpreted as condensation reactions of the monomer and short chain oligomers. The flattening of the thermogram at 8 hours pot-life indicated that the magnitude of the condensation reaction had diminished.

The flattening of the DSC thermogram was probably due to maleic acid promoting condensation reactions, at a relatively slow rate, at room temperature. With the T-F-M partially condensed there would be a less intense reaction at elevated temperatures. The presence of a room temperature reaction was supported by the formation of a grainy precipitate in the T-F-M with long pot-life. The appearance of a shoulder at 90°C, with longer pot-life, could be due to reactions of the more highly condensed precipitate with the remainder of the T-F-M solution. The relatively minor changes in the thermograms support the results from the bonding studies that showed few changes in shear strength with increasing pot-life.

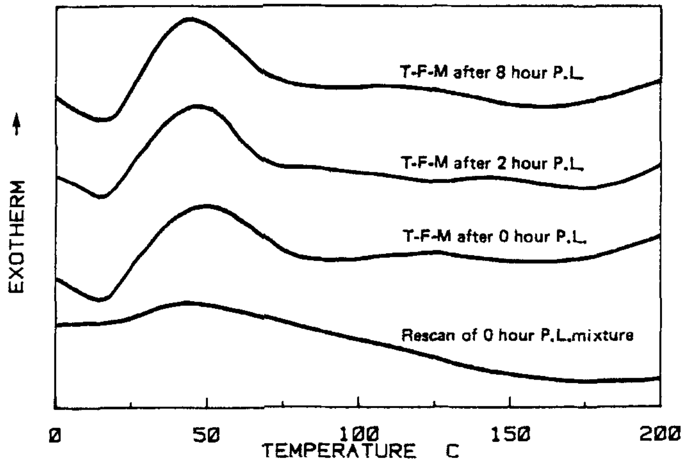

Figure 5. DSC thermograms of the T-F-M bridging material with different pot-lifes, with nitric acid added as a catalyst.

The addition of small amounts of nitric acid changed the appearance of the T-F-M thermogram (Figure 5). Small quantities of acid were used to simulate the residual free nitric acid present on the surface of the activated wood.[11] The exothermic peak was shifted to a lower temperature (60°C) and increased slightly in magnitude. Again, there was little change in the shape of the thermograms with increased pot-life. The shift of the exothermic peak to lower temperatures, with the addition of nitric acid, would be expected since the condensation reaction of furfuryl alcohol is known to be pH dependent.[16] The slight increase in the magnitude of the peak can also be explained by considering the reactions of furfuryl alcohol. With more catalyst and a lower pH, the reaction would be more sensitive to an increase in temperature and thus would react at a faster rate. Again, a rescan of the T-F-M showed no residual activity, which is typical of a cured furan resin.

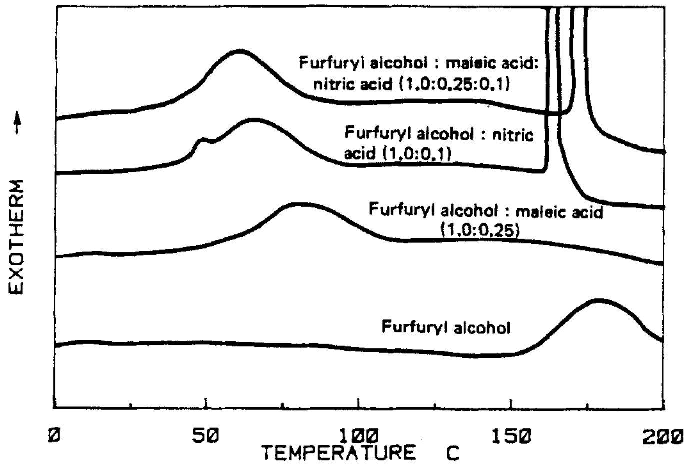

Figure 6. DSC thermograms of furfuryl alcohol, with and without acid catalysts.

Since the T-F-M mixture in the presence of nitric acid, had numerous possibilities for reactions and interactions between the various components, it was decided to analyze the components separately. The individual components were heated in sealed LVC and the resulting thermograms showed very little activity. Furfuryl alcohol showed an exothermic peak at 180°C while the other components showed minimal thermal activity.

The tannin mixed with furfuryl alcohol or either of the nitric or maleic acids gave only a very broad exotherm around 140-150°C. While some condensation of the tannin-acid mixtures may have taken place, there was no strong thermal behavior.

Furfuryl alcohol with the two acid catalysts was also examined with more striking results (Figure 6). While the polymerization exotherm was moved to a lower temperature (100°C) by the addition of maleic acid, it was the nitric acid-furfuryl alcohol combination that showed dramatic changes

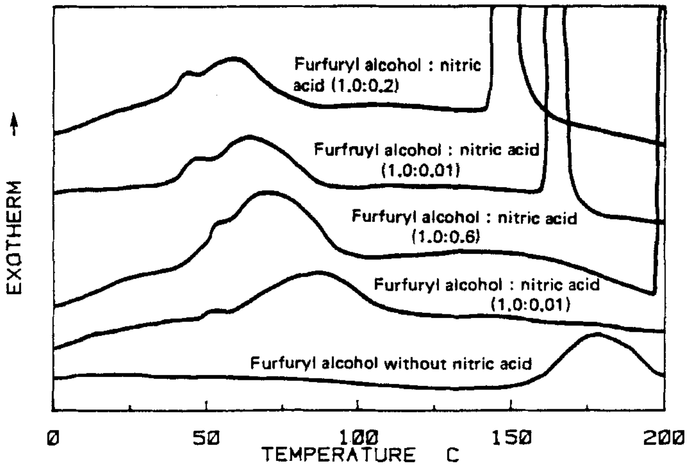

Figure 7. DSC thermograms of furfuryl alcohol containing different amounts of nitric acid.

in the thermogram. Nitric acid and furfuryl alcohol, either with or without maleic acid, seemed to be responsible for moving the broad exotherm to a lower temperature and for the appearance of the strong, sharp exothermic spike at 180°C.

The interaction of furfuryl alcohol with different amounts of nitric acid is shown in Figure 7. Both the exothermic peaks were shifted to lower temperatures with increasing amounts of nitric acid in the system. There are several possible reasons for the occurrence of the exothermic spike at the higher temperature (180°C); nitric acid can cause nitration and oxidation reactions as well as exhibiting acidic behavior.

The exothermic spike at 180°C could be due to degradation of nitro compounds that were formed by nitration of the furfuryl alcohol polymer. This would be expected to be a violent reaction since many nitrated organic molecules are known to be explosive. Furfuryl alcohol is aromatic in nature and would be expected to react as an aromatic compound. Nitration of substituted aromatic rings is known to occur under a wide variety of conditions. Nitration of furfuryl alcohol has also been previously reported although the reaction must be carried out under anhydrous conditions to obtain high yields.[16]

Oxidative degradation of the furan ring could also give an exothermic response. Ring opening occurs under certain acid conditions to give levulinic acid and other degradation products.[15] Furans can also participate in Diels-Alder reactions as either the nucleophile or the dienophile, depending on the reaction conditions and ring substituents.[16]

Furfuryl alcohol polymerization was also catalyzed with chromic acid to determine if the oxidizing ability of nitric acid was responsible for the exothermic spike at 180°C. While chromic acid gave an exothermic peak at 145°C, this peak was less than one-fourth of the intensity of the exothermic spike seen in the nitric acid-catalyzed sample. Based on these results it was tentatively concluded that the exothermic spike in the nitric acid-catalyzed furfuryl alcohol was not soley due to oxidation by the catalyst.

To investigate the effect of the open-assembly time on the curing of furfuryl alcohol, nitric acid treated wood was used to catalyze furfuryl alcohol reactions (Figure 8). The exothermic reactions that were noted in Figures 6 and 7 were present for the furfuryl alcohol catalyzed with nitric acid-treated wood. The thermogram of nitric acid-treated wood alone, showed a very broad exotherm at 160°C. Thus the reactions between the wood substrate and nitric acid did not substantially alter the other peaks in the thermogram. The nitric acid-treated wood-furfuryl alcohol thermograms only showed very minor changes when the furfuryl alcohol was reacted with wood with differing open assembly times.

It is likely that the wood contained absorbed nitric acid that was volatilized and promoted the condensation reactions

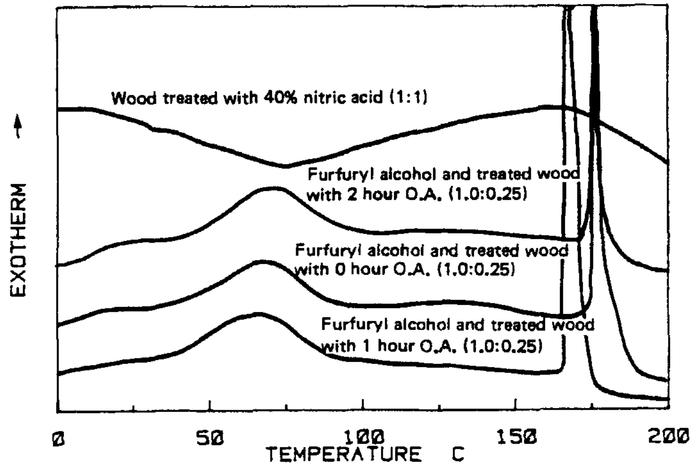

Figure 8. DSC thermogram of furfuryl alcohol with nitric acid-treated wood as a catalyst.

at a lower temperature as indicated by thermal analysis. These thermograms also support the results from the bonding study that showed the open assembly time had little effect on the dry shear strength. In the bonding work with T-F-M, the bonding temperature reached 140°C which was well above the temperature needed to induce condensation of the T-F-M. However, 140°C is well below the temperature of the sharp exothermic spike.

Infrared Spectroscopic Analysis

To examine the possible causes of the exothermic spike, the furfuryl alcohol-nitric acid mixture, sealed in an LVC, was heated to several different temperatures (25°, 60°, 110°, 160°, 190°C) in the DSC. The samples were removed at each temperature, the capsules were opened and infrared spectra of the resin obtained (Figures 9 and 10). The infrared spectra showed dramatic changes between the furfuryl alcohol monomer

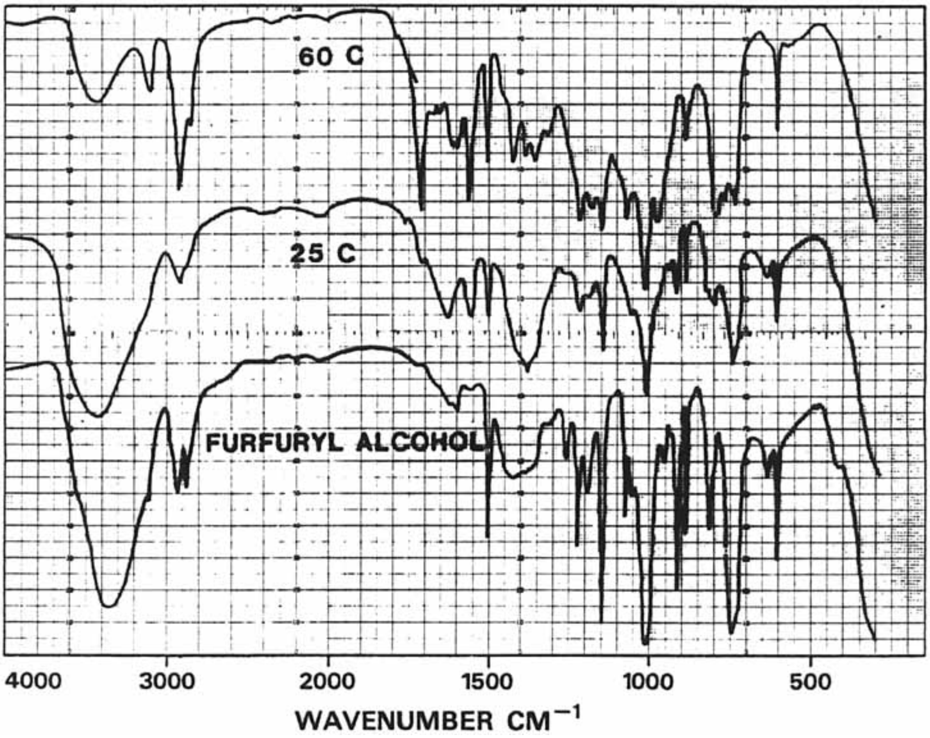

Figure 9. Infrared spectra of furfuryl alcohol and material extracted from furfuryl alcohol-nitric acid mixtures (1.6:0.1) heated to different temperatures (25-60 C).

and the polymer. The spectra became more diffuse after a period of heating, a phenomenon which is generally thought to be due to condensation. To quantify changes in the spectra the bands were normalized to that of the furan ring-stretching vibration band at 1600 cm^{-1}. The use of this band for an internal reference should be regarded with some caution, since earlier studies[15,24] have presented some evidence of furan

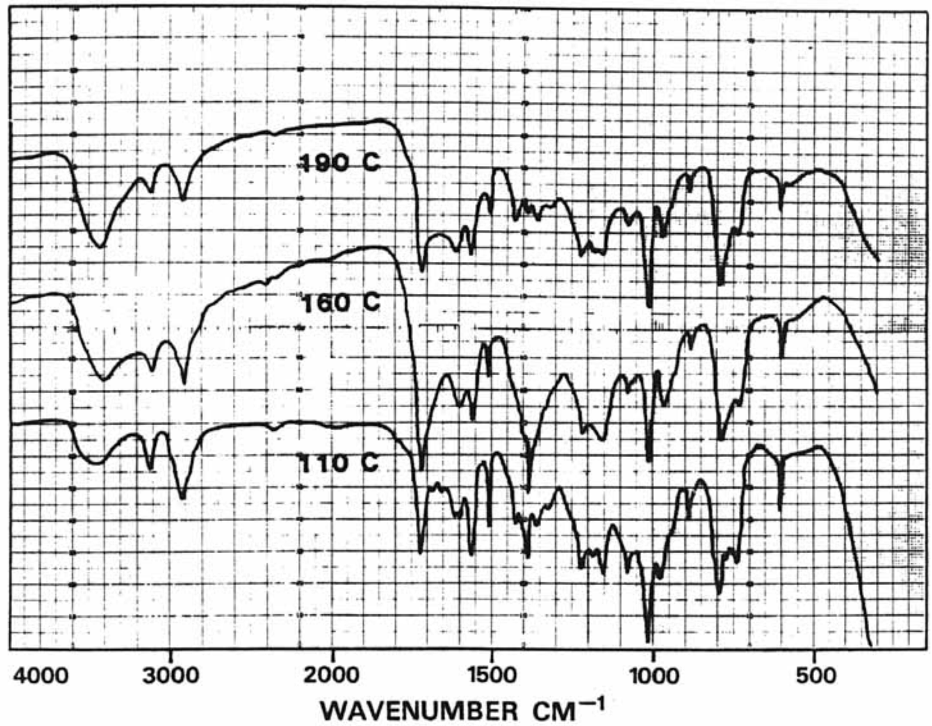

Figure 10. Infrared spectra of material extracted from furfuryl alcohol-nitric acid mixtures (1.6:0.1) heated to different temperatures (110-190 C).

ring opening, which would reduce the intensity of the band at 1600 cm^{-1}. The absorbance ratios for various bands are presented in Table 2. Band assignments (Table 3) were made after reviewing several articles on the polymerization of furfuryl alcohol resins.[15,24,25] Most of the trends shown in Table 2 correspond well with those found in a previous study.[15] The notable exception was the strong absorbance band at 1487 cm^{-1} which was assigned to the nitronium ion.[26]

Most of the changes seen in Table 2 can be explained by increased condensation of the furfuryl alcohol polymer. As the furan becomes more substituted the ring vibrations at 1560

TABLE 2
Relative absorbances of bands in the infrared spectra of furfuryl alcohol and furfuryl alcohol heated to different temperatures with a nitric acid catalyst.

	$A(\lambda)\ cm^{-1}/A\ 1600\ cm^{-1}$								
Sample	1710	1560	1510	1390	1148	1070	1020	790	730
Furfuryl alcohol (FA)	-	-	8.32	-	13.12	5.52	10.36	-	-
FA heated to 110°C	3.40	2.83	2.72	2.38	1.59	1.07	2.53	2.69	2.24
FA heated to 135°C	6.44	3.52	3.12	5.04	1.68	1.28	3.56	3.56	2.20
FA heated to 160°C	6.37	2.05	1.55	8.00	1.53	0.74	3.71	3.11	0.97
FA heated to 190°C	3.82	0.94	1.67	0.42	1.39	0.73	4.64	4.21	1.09

TABLE 3

Molecular motion of species associated with infrared absorbance of a specific wavelength.

1710 cm^{-1}	- Diketone and/or nitration of the furfuryl alcohol ring at the 5 position
1600 cm^{-1}	- Furan ring stretching
1560 cm^{-1}	- Furan ring stretching and/or nitration at the ring 5 position
1510 cm^{-1}	- Furan ring stretching
1390 cm^{-1}	- Nitronium ion
1148 cm^{-1}	- CH deformation
1070 cm^{-1}	- C-O-C stretching
1020 cm^{-1}	- C-O stretching and/or ring breathing
790 cm^{-1}	- Out-of-plane bending by 3 and 4 ring carbons
730 cm^{-1}	- Out-of-plane bending of C-H at the ring 5 position

and 1510 cm^{-1} decrease. The C-H and C-O-C stretching bands at 1148, 1070 and 1020 cm^{-1} remain fairly constant. Of particular interest are the bands that would be expected from nitration of the furan ring.

Nitration of furfural or furfuryl alcohol at the ring 5-position causes the formation of several new IR bands; the most prominent of which are at 1720, 1580, and 1350 cm^{-1}.[26] To determine if nitration of the furan ring had taken place, the IR spectra of the furfuryl alcohol-nitric acid mixtures heated to 110°, 135°, 160° and 190°C were examined. Analysis of the IR spectra was confounded by the absorbance peaks of the furfuryl alcohol polymer. All three of the bands that were strongly associated with 5-nitrofurfuryl alcohol and 5-nitrofurfural were also present in the spectra of the furfuryl alcohol polymer.

The relative intensity of the band at 1710 cm^{-1} (Table 2) decreased between 160°C and 190°C. In the furfuryl alcohol polymer this band (1720 cm^{-1}) was assigned to a diketone structure.[15] There is no simple mechanism that would explain the loss of the diketone structure between 160°C and 190°C. However, if nitration of furfuryl alcohol also contributed to this peak the loss of the nitro group would explain the observed reduction in intensity. There was a shoulder at 1350 cm^{-1} in the spectra of the resin heated to 110°C that could have been due to nitration. However, this area was overwhelmed by the nitronium ion absorbance at 1390 cm^{-1} in the spectra of the mixtures heated to 135°C and 160°C. The peak at 1580 cm^{-1} showed a significant loss between 160°C and 190°C but this behavior was also expected for the furfuryl alcohol polymer. However, the magnitude of the reduction is so large that there could also be a contribution due to loss of nitro groups.

Ultraviolet and Nuclear Magnetic Resonance Spectroscopic Analysis

Ultraviolet and proton nuclear magnetic resonance spectra of the mixtures were also obtained. The analysis of the results from the ultraviolet analysis was complicated because an accurate extinction coefficient for the low molecular weight mixture was not available. However, some qualitative deductions could be made. The spectra of the resin heated to 190°C showed an absorbance peak at 205 nm, while the absorptions for resins heated to 50°, 110°, and 160°C were shifted to longer wavelengths. This bathochromic shift is characteristic of furfural which has been nitrated. Nitration of furfural at the ring 5-position shifts the maximum from 271 nm to 309 nm.[26]

The proton nuclear magnetic resonance spectra were quite complex. In addition to the downfield protons associated with the furan ring, there were several very pronounced upfield peaks at 3.8 and 1.8 ppm that were most likely due to degradation products. Comparison of this part of the spectrum with known furfuryl alcohol degradation products did not yield any further information pertaining to the compound or compounds responsible for these peaks.

CONCLUSIONS

High shear strengths of bonded wood panels can be achieved with either tannin or furfuryl alcohol in conjunction with nitric acid activation. Even stronger bonds, comparable to phenolic controls, were obtained with a tannin-furfuryl alcohol-maleic acid formulation. The bonds realized with the T-F-M mixture were not strongly affected by nitric acid pretreatment, open assembly time or pot-life. A distinct advantage of the T-F-M system is minimal evolution of formaldehyde or other toxic chemicals from the bonded product.

This system may also be desired because it is based on renewable resources.

Through DSC studies, nitric acid was found to promote the condensation exotherm of the tannin-furfuryl alcohol-maleic acid mixture at a lower temperature than in the uncatalyzed sample. It appears that the furfuryl alcohol is the most reactive component of the bridging material. The furfuryl alcohol is apparently nitrated by the nitric acid and; at high temperatures (180°C), these nitro compounds degrade to give a very sharp exothermic spike in the DSC thermogram.

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