

Wood-Induced Catalytic Activation of PF Adhesives Autopolymerization vs. PF/Wood Covalent Bonding

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SYNOPSIS

The reaction of polycondensation of phenol-formaldehyde (PF) resins in the presence of wood was confirmed to have a lower energy of activation than of the PF resin alone. Under the low temperature and short curing times characteristic of the application of PF resins as thermosetting wood adhesives DSC, TGA, chemical kinetics, and IR of PF resins and relevant model compounds were carried out. These indicated that two effects appear to be present when a PF resin cures on a wood surface, both induced by the polymeric constituents of the substrate, namely carbohydrates and lignin. These appear to be (1) the catalytic activation of the resin self-condensation induced particularly by carbohydrates such as crystalline and amorphous cellulose and hemicelluloses and (2) the formation of resin/substrate covalent bonding, particularly in the case of lignin. The first appears to be, by far, the major cause of the lowering of the activation energy of PF resins curing. The contribution of the second has been found to be very small and often negligible under the conditions pertaining to thermosetting wood adhesives applications. Molecular mechanics results appear to indicate that the marked catalytic activation of PF resins autocondensation and curing appears to be induced by the strong set of PF adhesive/substrate secondary forces interactions which appear to weaken bonds which, by cleavage, lead to PF resins autocondensation. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

A complete understanding of the phenomenon of adhesion of a phenol-formaldehyde (PF) resin, or any other resin, to a lignocellulosic substrate is fundamental to the evaluation of bond strength and bond strength development in wood products. The influence the substrate exercises on the kinetic and curing behavior of the resin, and the reasons for such an influence, are not immediately obvious. It has been repeatedly established, for instance, that the energy of activation of the reaction of polycondensation of PF resins, and also of UF and MF resins, is markedly influenced by the presence of wood.¹⁻⁷ In the presence of wood, the energy of activation of the polycondensation reaction of these resins is considerably lowered.¹⁻⁷ This infers that

resin polymerization and cross-linking proceed at a much faster rate when the resin is in molecular contact with one or more of the main polymeric wood constituents. This phenomenon has, since its initial discovery, been ascribed to the formation of covalent bonds between synthetic resin and the main constituents of the wood matrix. While there is no doubt that covalent bonds can be formed⁸ linking PF resols (resins carrying hydroxybenzyl alcohol groups) adhesives, and UF and MF resins, to lignin and wood carbohydrate, it is also important to consider the conditions under which they are formed. Prolonged heating and high temperatures are conducive to resin-substrate covalent bonds being formed,⁸ as demonstrated by certain applications of these resins to natural textiles.⁸ What needs to be addressed then is to what extent are resin-substrate covalent bonds formed under the standard application conditions for thermosetting wood adhesives. The maximum temperature in the strength-determining center of the core of a particleboard for example, only reaches

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a maximum of 100–105°C at the pressing times and temperatures characteristic of such a wood-bonding process.⁹ Pressing times are fast, varying between 7 and 15 s per mm thickness of the panel. Thus, temperatures are not extreme, while times for curing are very short.

A variety of investigations has been conducted to demonstrate the concept of resin to wood substrate covalent bonding. The majority of these have been by Differential Scanning Calorimetry (DSC) or Thermogravimetric Analysis (TGA).^{1–3,10} Infrared (IR) and ultraviolet (UV) spectrophotometry have also been used.^{6,11} The DSC and TGA investigations conducted are subjected to time and temperature limitations: for instance, scans of 10–20°C/min to a maximum of 250–300°C. Even considering the main curing exotherm of a PF resin as occurring approximately at 130–150°C (which it does), this will be reached in not less than 5–10 min after heating has started. A particleboard core, instead, remains at a maximum of 100–105°C for only 20 to 60 s, and reaches this maximum temperature in 80–120 s. Some indications that covalent bonds do not form or form to a very small extent even in conditions much more drastic than these has also been reported.^{12–14} The IR and UV investigations used even more extreme conditions: 14 h at 190°C for the IR^{11,15} and 2 h at 120°C for the UV investigations.⁶ As a consequence, formation of covalent bonds was demonstrated, but the extreme conditions used also implied that the situation might be very different at the much lower temperatures and shorter times characteristic of wood adhesives applications.

A controversial but acute review¹⁵ of the subject concluded that the evidence presented clearly indicates that no covalent bonds are formed under the conditions characteristic of thermosetting wood adhesives applications. This might also be too extreme. Molecular mechanics studies^{17–21} have given a grounding to the theory that strong wood adhesive bonding can be equally well, and completely explained by the sum of a multitude of resin/substrate secondary forces interactions, without any need for interfacial resin to substrate covalent bonds. In this, the molecular mechanics conclusions are in agreement with the most accepted theories of adhesion in fields other than wood adhesives.²² The undeniable experimental fact remains, however, that a lignocellulosic substrate facilitates PF and other resins curing by lowering the apparent energy of activation of the polycondensation.

This article is aimed at investigating the relative merits of covalent bonding vs. secondary forces bonding in the thermosetting wood adhesives field.

EXPERIMENTAL

Phenol-Formaldehyde Resin

Phenol (94. g, 1 mol) was mixed with 32 g water and 8 g methanol. The mixture was maintained at 40°C for 30 min under mechanical stirring during which two amounts of 5 g each of 33% NaOH were added. Paraformaldehyde (55 g, 1.8 mol) was added and the temperature of the reaction mixture was increased to reflux over a period of 30 min, during which another two aliquots of 5 g each of 33% NaOH were added. The reaction was maintained at reflux for 1 h and then cooled and stored. The resin obtained had a solids content of 59%.

Preparation of Samples

Diluted Phenol-Formaldehyde Resin (PF) and Wood Flour

PF resin (2.725 g) was diluted in water (6.652 g) affording a 2 : 5 resin to water solution. The diluted resin was then absorbed onto wood flour (1.584 g) (Pinus radiata dry sapwood ground to a flour of 200 mesh).

Phenol-Formaldehyde (PF) Resin and Wood Flour

PF resin (5.370 g) was absorbed onto wood flour (0.88 g).

Saligenin on Filter Paper

Saligenin (*o*-hydroxybenzylalcohol) (0.558 g) was dissolved in water (5.050 g) and a 30% sodium hydroxide solution (0.667 g) to give a solution of pH = 12.8. The saligenin solution was then absorbed onto filter paper (Whatman number 1 Chromatography paper) and allowed to dry in a desiccator. The concentration of saligenin on filter paper was 0.890 *M*.

p-Hydroxybenzylalcohol on Filter Paper

p-Saligenin (para-hydroxybenzylalcohol) (0.510 g) was dissolved in water (5.221 g) and a 30% sodium hydroxide (0.877 g) solution added to afford a solution of pH = 13.8.

The *p*-saligenin was then absorbed onto filter paper and allowed to dry in a desiccator. The concentration of *p*-saligenin on filter paper was 0.787 *M*.

Saligenin and Kraft Lignin

Saligenin (undissolved) was crushed with either bagasse or kraft lignin using a pestle and mortar. A ratio of 50 : 50 saligenin to lignin was used.

Saligenin and Wood Flour

A 50 : 50 mixture by mass of saligenin (undissolved) and wood flour was crushed using a pestle and mortar.

Saligenin and *p*-Hydroxybenzylalcohol and Cotton Wool

A 50 : 50 mixture by mass of saligenin and cotton wool were crushed in a pestle and mortar.

***p*-Hydroxybenzylalcohol and Kraft Lignin**

p-Saligenin (undissolved) was crushed with either bagasse lignin or kraft lignin using a pestle and mortar. A ratio of 50 : 50 *p*-saligenin to lignin was used.

***p*-Hydroxybenzylalcohol and Wood Flour**

A mixture of 50% *p*-saligenin and 50% wood flour were crushed together in a pestle and mortar.

***p*-Hydroxybenzylalcohol and Cotton Wool**

A 50 : 50 mixture by mass of *p*-saligenin and cotton wool were crushed in a pestle and mortar.

Testing of Samples

The samples were tested by placing a small amount into a sample crucible. The sample crucibles were then heated at different heating rates, namely 5°K, 10°K, 15°K, 20°K, 25°K, and 30°K per minute until a maximum of 573°K. In the case of the model compounds above, further heating rates were also used, namely 7°K, 8°K, 18°K, 18.5°K, 19°K, 19.5°K, for a total of 12 different heating rates.

The activation energy of the curing reaction of the PF resin alone, of the PF resin on different substrates, and of *o*-hydroxybenzylalcohol (saligenin) and *p*-hydroxybenzylalcohol both alone and on different substrates was calculated on the basis of the variation of the temperature of the maximum of each exotherm (T_{\max}) of the DSC scan as a function of the temperature rate increase of the DSC scan, using the Kissinger equation.²³ Thus, the $\ln(\text{rate of temperature increase} / T_{\max}^2)$ was graphed in function of $1/T_{\max}$ and from the Kissinger equation. The energy of activation corresponding to each identified exotherm was obtained. Also, onset and final temperature of each exotherm were recorded.

The identical reactions were repeated and followed by Thermogravimetric Analysis (TGA) at the identical temperature increment rates as for the

DSC scans. TGA traces and first derivative traces were obtained, as an initial step to distinguish which exotherms in the DSC scans corresponded to any type of polycondensation. Furthermore, DSC and TGA scans of all the substrates alone were obtained for the same purpose.

All the scans were conducted in nitrogen atmosphere. Each DSC and TGA scan was repeated with a Mettler DSC 20 of lower precision to control the position of the main exotherm of the reactions.

Model Compound Kinetics

Phenol (1 mol) in 77 mL H₂O, 3.5 mL NaOH 30% water solution at pH 10.5 was heated at 94°C and 33.3 g paraformaldehyde added. At periodic intervals of 5 min in the first 15 min of reaction and afterwards at 10-min intervals, aliquots of the reaction mixture were withdrawn and analyzed for free formaldehyde concentration by the hydroxylamine hydrochloride method. The same reactions were repeated using 1 mol of guaiacol (1-hydroxy-2-methoxybenzene), veratrol (1,2-dimethoxybenzene), and glucose. The reactions were found to obey a second-order kinetic law. The apparent rate constants were determined.

FT-IR Analysis

The same reactions followed by DSC and TGA were followed by reflectance FT-IR spectrophotometry, at a temperature of 60°C, using a JASCO 3000 FT-IR spectrophotometer. The IR spectra are shown in Figures 5 and 6 (Basic spectra at the beginning of the reaction with change of more indicative bands). Gum arabic was used as a model of an amorphous polymeric carbohydrate such as hemicelluloses.

DISCUSSION

As in a PF resin polycondensation, water is released at each condensation step; a DSC analysis to have any meaning must always be coupled with a TGA analysis. This, to confirm which DSC exotherms correspond to distinct TGA first derivative loss of mass by water evaporation and, thus, likely to belong to a condensation. DSC or TGA, if used in isolation, are techniques that are recognized to give results that are, at best, difficult to interpret.^{24,25} In this investigation only DSC exotherms that could be clearly identified by TGA to belong to any polycondensation were considered.

The model compounds DSC scans yielded a series

of several, discreet exotherms: an expected result if it is considered that a monohydroxybenzylalcohol must self-condense to dimers first and then to ever higher oligomers in a series of steps, which are definable in the early stages of the reaction. The PF resin, instead, already a mixture of a variety of higher oligomers, gave only a series of three exotherms. In Figures 1, 2, and 3, DSC scans with their corresponding TGA and TGAs first derivative traces are shown for the PF resin alone, for ortho-hydroxybenzylalcohol (saligenin) and para-hydroxybenzylalcohol. The final energies of activation for each exotherm for the two model compounds and for a PF resin are reported in Tables I, II, and III. The temperature maxima and range of the PF resin show correspondence with those of the model compounds. The first PF exotherm with the first exotherm of the *p*-hydroxybenzylalcohol model compounds. The second PF exotherm with the sum of the second and third exotherm of the *p*-hydroxybenzylalcohol model compound, or possibly the third only, and the first of saligenin. The third exotherm appears to be a wider example of the fourth exotherm of the *p*-hydroxybenzylalcohol model compound. The main exothermic peak for PF and *p*-hydroxybenzylalcohol model compound appears clearly to be the same with a maximum at 135–140°C at the lower temperatures (up to 160°C) of the scan, and saligenin at a slightly lower temperature. From Tables I, II, and III it appears that all the main constituents of the wood substrate, at some stages of the reaction, contribute to the decrease of the energy of activation of the whole polycondensation, or of important steps in it. The data in Tables I to III cannot, of course, tell directly if the decrease in energy of activation is due to covalent coreaction between resin and substrate,

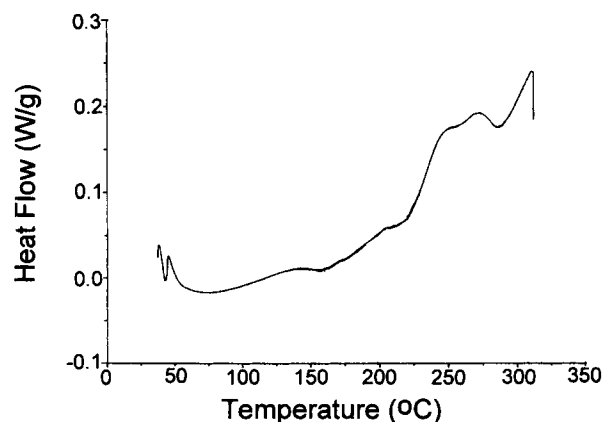


Figure 1 DSC scan at 15°C/min of *p*-hydroxybenzylalcohol.

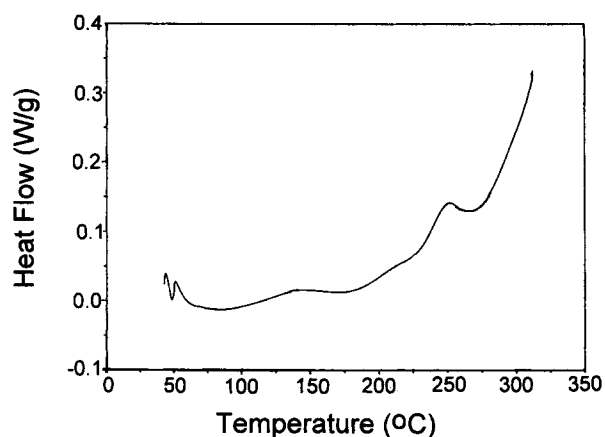


Figure 2 DSC scan at 15°C/min of *o*-hydroxybenzylalcohol.

or to a catalytic activation of the resin self-condensation induced by the wood constituents. An interesting aspect is, however, noticeable, and some conclusions can be drawn: any real exotherm that is not present in the self-condensation of the model compound alone is very likely due to reactions between model compound oligomers and the substrate. This is so because any reaction between model and substrate will be a different condensation reaction than the self-condensation of the model alone: it will give a differently positioned exotherm specific to, and characteristic of, that particular reaction. In this respect, Tables I and II render evident that covalent bonds between resin and lignin appear to form, and at a variety of stages in the polycondensation. That some covalent bonds between model compounds (and model resin) and cellulose form at the higher temperatures is also evident. What is also evident, however, is that the energy of activation of the self-

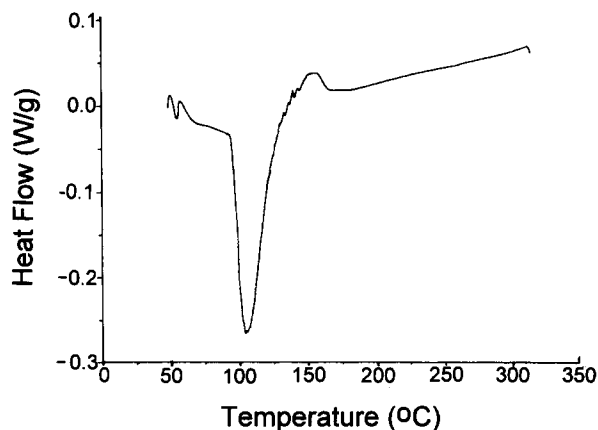


Figure 3 DSC scan at 15 s/min of PF resin.

Table I Activation Energies of Exotherms of *p*-Hydroxybenzylalcohol Polycondensation and Curing Obtained by DSC and Kissinger Equation, Corresponding to TGA Mass Losses

	Activation Energy (kcal/mol)						
<i>p</i> -Hydroxybenzylalcohol alone	—	24.58	31.18	—	—	26.83	—
<i>p</i> -Hydroxybenzylalcohol + lignin	25.24	72.06	25.89	30.14	20.09	12.62	—
<i>p</i> -Hydroxybenzylalcohol + cellulose	—	—	12.67	—	21.56	23.39	36.71
<i>p</i> -Hydroxybenzylalcohol + wood flour	29.75	60.56	30.48	—	—	21.31	15.01
Average peak temperature (°C)	98.4	110.7	139.7	149.9	194	247.6	267.2
Peak temperature range (°C)	93.1–103	107.6–115.7	127–155.9	145.8–152	180.6–210.3	231.7–261	256.5–280
Main exotherm peak	—	—	Main	—	—	—	—
			*				

condensation exotherms of the model compounds on some substrates, particularly cellulose at the lower temperatures, also strongly decrease. This cannot be ascribed to resin/substrate covalent bonds being formed, because they are characteristic self-condensation exotherms exclusively specific to the models alone. This implies that the substrate catalytically activates the self-condensation of the model and model resin. At the lower temperatures, of greater interest to wood adhesives applications, both lignin and particularly cellulose, and crystalline cellulose at that, appear to activate PF self-condensation and curing. It is important to note the differences between *p*-hydroxybenzylalcohol and the ortho-isomeride (saligenin). While for the *p*-hydroxybenzylalcohol close correlation with the PF resin trends can be observed, this is more difficult to observe in the case of saligenin. This is so because the number and type of higher molecular weight isomerides that can be formed by progressive self-condensation of saligenin is significantly higher than for *p*-hydroxybenzylalcohol. This causes a multitude of smaller exothermic peaks that smooth the curve at the more important lower temperature range,

rendering more difficult or impossible the calculation of the energy of activation of saligenin self-condensations. Deductions become as a consequence incomplete and more fragmentary.

The questions that remain are, then: (1) to what extent is wood bonding dependent, respectively, from resin/substrate covalent bonding or from resin/substrate secondary forces, and (2) what is the cause of the resin-accelerated self-condensation. The extent and intensities of the exotherms, or better, the areas enclosed under the exotherm peaks, give an indication of the answer to the first question. Thus, the main exotherm of the PF resin self-condensation (139°C max, Table III, Fig. 1) encloses well over 95% of the total area enclosed under all the lower temperature exotherms. The situation is similar but not as extreme for the two hydroxybenzylalcohol models.²⁵ An indication that in a precondensed PF resin lower mobility and diffusion problems due to lower substrate wettability, limit even further the possibility of covalent bonding.

In conclusion, the DSC part of this study indicates that the proportion of exotherms due to resin to substrate covalent bonding is small in relation to

Table II Activation Energies of Exotherms of *o*-Hydroxybenzylalcohol Polycondensation and Curing Obtained by DSC and Kissinger Equation, Corresponding to TGA Mass Losses

	Activation Energy (kcal/mol)				
<i>o</i> -Saligenin alone	*	*	20.64	16.97	—
<i>o</i> -Saligenin + wood flour	28.52	—	—	18.23	20.29
<i>o</i> -Saligenin + lignin	12.2	14.74	25.97	—	—
<i>o</i> -Saligenin + cellulose (paper)	11.83	—	29.82	17.77	—
Average peak temperature (°C)	115.5	161.2	203.9	232.6	269
Peak temperature range (°C)	111.8–151	156.6–165.7	184.5–218	207.5–264	259.7–

* A multitude of small peaks that is impossible to define in DSC. In TGA, a single very wide step.

Table III Activation Energies of Exotherms of a PF Resin Polycondensation and Curing Obtained by DSC and Kissinger Equation, Corresponding to TGA Mass Losses

	Activation Energy (kcal/mol)		
PF resin alone	55.61	23.85	29.15
PF resin + lignin	—	15.82	21.37
PF resin + cellulose*	6.91	16.73	20.84
PF resin + cellulose†	20.34	20.21	26.29
PF resin + wood flour	14.53	12.04	8.44
Average peak temperature (°C)	90.1°	135.4°	161.7°
Peak temperature range (°C)	65–104	102.8–159	147.9–179.9
Main exothermic peak		Main	

* Cotton wool.

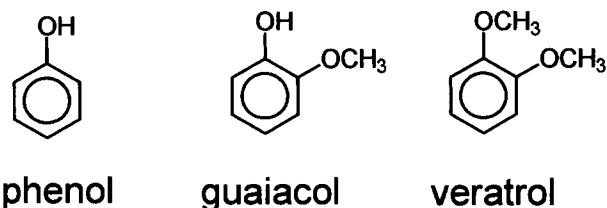
† Filter paper.

the surface-activated self-condensation exotherms of the resin. TGA traces, furthermore, indicate that mass loss is small in the endotherms corresponding to a preceding resin/substrate covalent bonding exotherm; it is, instead, considerable for the endotherms following self-condensation of the resin.

Unusual results also occur. For example, the first exotherm of the PF resin proper in Table III, indicate no exothermic peak in the PF plus lignin case; indicative that in the PF resin used, any reaction with lignin in that particular temperature range occurs to an extent too small to give a visible, detectable exotherm. In this context, lignin appears to retard the reaction, this apparent result being most probably due to a diffusion problem. Cellulose, instead, appears to again activate the reaction, and the value of the results for wood flour confirm this in relation to the proportion of cellulose and crystalline cellulose contained in the filter paper, cotton wool, and wood flour used. In this respect, it appears that crystalline cellulose activates the self-condensation of the phenolic resin more than amorphous cellulose. This because in all the PF resin exotherms (Table III) the activation energy of the condensation is decreased more markedly by cotton wool cellulose which is more than 90% crystalline,²⁹ than by filter paper cellulose which is 50% crystalline or less. The study used softwood wood flour (*Pinus radiata*) the guaiacyl character of the lignin of which is typically between 85% and 95%.²⁷ In hardwoods, and in latewood, in which syringyl moieties (of lower nucleophilicity and with more blocked sites) are generally in higher proportion,²⁷ the occurrence of resin to substrate covalent bonding should become more remote. It is also interesting to note that in DSC scans at low temperature increments (5°C/min) precision and reproducibility of the multitude of single step peaks in which the main PF exotherm is resolved

remain constant and are excellent. An example is shown in Figure 4.

Model compounds kinetics of the reactions of phenol, guaiacol, veratrol, and glucose with formaldehyde were also used to confirm and supplement the DSC/TGA findings. Phenol was used as a model of the reaction of a PF resin methylol group with other available resin nuclei; guaiacol, veratrol, and glucose as models of the reaction of the PF resin methylol groups with, respectively, the free phenolic hydroxyl guaiacyl units of lignin, no phenolic hydroxyls guaiacyl units of lignin, and with cellulose and hemicelluloses.



These model compound kinetics at 95°C, in the pH range 2 to 11, indicate by the rate constants

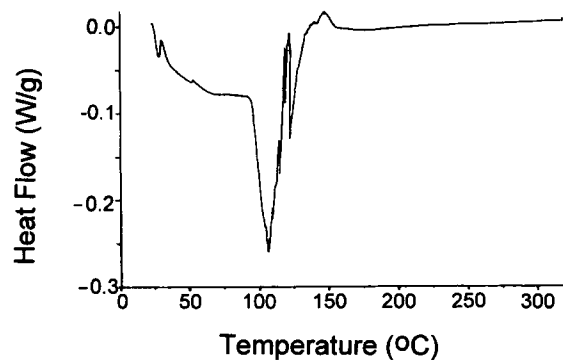
**Figure 4** DSC scan at 5 s/min of PF resin.

Table IV Rate Constants for the Reaction of Different Phenols with Formaldehyde

	k in liter/(moles × second)		
	pH 11	pH 8	pH 2
Reaction temperature (centigrade)	95°C	95°C	95°C
Reactants			
Phenol : formaldehyde	3.24×10^{-2}	4.01×10^{-3}	2.71×10^{-4}
Guaiacol : formaldehyde	2.89×10^{-2}	4.38×10^{-4}	1.49×10^{-4}
Veratrol : formaldehyde	1.38×10^{-4}	—	—
Glucose : formaldehyde	5.80×10^{-5}	—	—

obtained (Table IV), that the reaction of formaldehyde and PF methylols with phenol is the most favored. This is followed fairly closely by the reaction of formaldehyde with guaiacol which, at 95°C, pH 11 (Table IV), is $\pm 15\%$ slower than the former. The reaction of veratrol and glucose with formaldehyde present rate constants, respectively, 230 and 550 times smaller than the phenol-formaldehyde reaction (Table IV). Covalent bonding between resin and substrate can then readily occur on guaiacyl lignin nuclei presenting a free phenolic hydroxy group, barred problems of diffusion. The resin/substrate covalent bonding reaction is definitely too slow to occur on lignin guaiacyl nuclei in which a phenolic hydroxyl is not present (i.e., veratrol). The typical number of free phenolic hydroxyls in guaiacyl lignins is reported to be of 0.16 mol per 100 g lignin.³⁰ The reaction leading to covalent bonding between resin and wood carbohydrates appears to be even less favorable, considering the rate constant of the glucose/formaldehyde reaction (Table IV). The latter is a clear indication of the preponderance of the catalytic activation effect of some carbohydrates on PF resins self-condensation. The former is an indication that the proportion of covalent bonds that can form between resin and substrate has to be small under any reaction conditions, and very small, indeed, under the standard conditions prevalent in thermosetting wood adhesives application.

Reflectance FT-IR on PF resins and the two hydroxybenzylalcohol models also confirmed certain aspects of the DSC/TGA and chemical kinetics findings. Only a very small proportion of covalent bonds could be detected in reaction times of up to 6 h. The variation of the PF resin spectra indicate that the PF alone spectrum after 6 h of reaction is identical to that observed for PF on gum arabic after 60 min, confirming existence of catalytic activation also by amorphous carbohydrates (Fig. 5). That it is catalytic activation rather than coreaction is sustained by the fact that in equimolar homogeneous

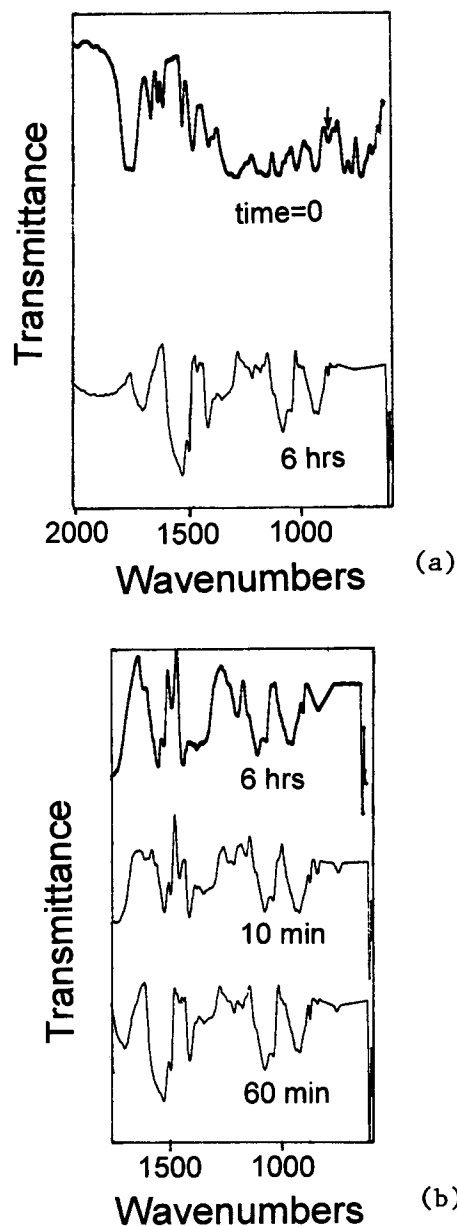


Figure 5 FT-IR of (a) PF resin alone and (b) PF + gum arabic after, respectively, 6 h and 60 min.

reactions the PF-CH₂OH group bands at 3200 cm⁻¹ decrease markedly and disappear at 10 and 60 min of reaction, while after 60 min the gum arabic hydroxy groups bands intensities are unaltered. Furthermore, the band at 750 cm⁻¹ of para-disubstituted benzenic nuclei shows the same rate of disappearance in 2 h for PF on gum arabic as it does in 6 h for PF resin alone. As regards the models (Fig. 6) the band at 1550 cm⁻¹ characteristic of *p*-hydroxybenzylalcohol, in the presence of a polymeric carbohydrate such as gum arabic, decreases rapidly after 10 min heating and has almost disappeared after 60 min of heating. In the case of *p*-hydroxybenzylalcohol in the presence of lignin, the same band only disappears after 6 h heating. The reaction on carbohydrates is, hence, considerably faster than on lignin: considering the model kinetics studies already presented, this can only be if the reaction is of a different nature on the two different substrates: activation of phenolic resin self-condensation on the polymeric carbohydrates and possibly this and covalent bonding as regards lignin. Also, on cellulose, the disappearance of the 1550 cm⁻¹ band is faster than on lignin, having disappeared well before 6 h. In the case of *p*-hydroxybenzylalcohol on kraft lignin, the disubstituted aromatic ring band at 840 cm⁻¹ disappears within 10 min of heating, indicating that some rapid reaction to form covalent bond with lignin does, indeed, occur.

The reasons for the existence of catalytic activation of the self-condensation of the adhesive resin induced by the substrate must be considered. Molecular mechanics studies have indicated that the sum of secondary forces binding a resin to a substrate is quite considerable.¹⁷⁻²¹ Table V gives values for a variety of PF oligomers.¹⁷⁻¹⁹ Similar values have been obtained also for UF resins.^{20,21} These secondary forces involve charge and dipolar interactions: they involve, hence, partial displacement of bonds and other electrons in the structure. Thus, the strong forces of attraction to the substrate cause variations in the strength of bonds and intensity of reactive sites within the PF oligomers considered. This is a well-known effect in heterogeneous catalysis.²⁸ Bond cleavage and bond formation within a molecule or between molecules are greatly facilitated by chemisorption on to a catalyst surface. In the case of a PF resin on cellulose, the strong secondary interactions are likely to influence the reaction of self-condensation of the resin. From the values in Table V, in the case of a hydroxybenzylalcohol, the bonds that are most likely to be weakened as a consequence of the sum of the compound/substrate secondary forces are, first, the C—O bond of the hydroxybenzylalcohol group, inducing a stronger positive charge

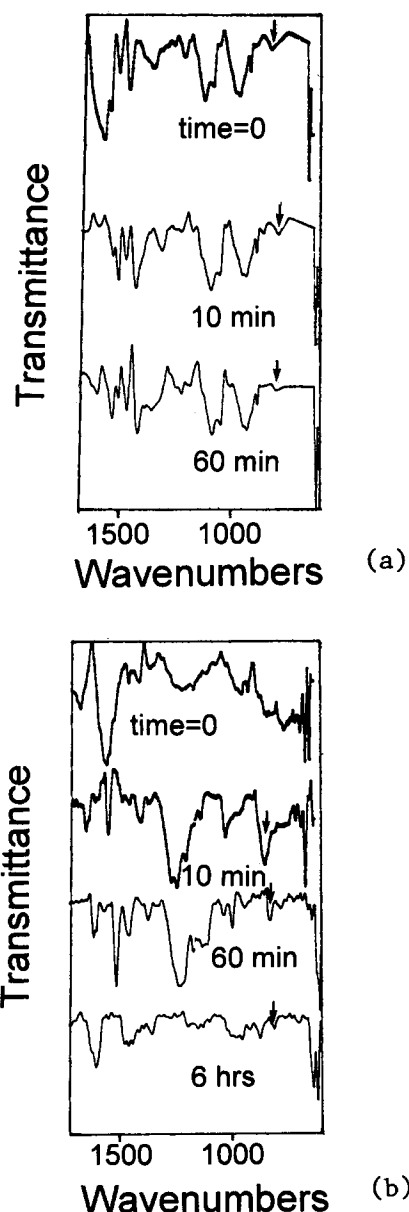
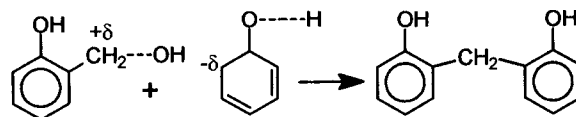


Figure 6 FT-IR of *p*-hydroxybenzylalcohol with (a) gum arabic, (b) kraft lignin at times 0, 10 min, 60 min, and 6 h of reaction.

on the carbon atom, possibly even a carbocation.



Thus, at the usual sites driving a phenol-formaldehyde polycondensation.

Conversely, the further weakening of the phenolic O—H bond is likely to lead to a stronger negative charge delocalized on the ortho and para portions

Table V Molecular Mechanics Calculated Sum of Secondary Forces Binding PF Oligomers to Surface of an Elementary Crystal of Cellulose I [18, 19] (in kcal/mole)

PF Species	Interaction Energy (kcal/mol)	
	Average	Minimum
Trihydroxybenzyl alcohol	-35.9	-50.0
<i>o,o</i> -Dihydroxy diphenyl methane	-14.5	-20.8
<i>o,p</i> -Dihydroxy diphenyl methane	-14.2	-17.9
<i>o</i> -Hydroxy benzyl alcohol	-12.2	-19.7
<i>p,p</i> -Dihydroxy diphenyl methane	-11.8	-14.7
<i>o,p</i> -Dihydroxybenzyl alcohol	-10.5	-15.0
<i>p</i> -Hydroxybenzyl alcohol	-10.6	-13.3
<i>o,o</i> -Dihydroxybenzyl alcohol	-5.3	-9.3

of the aromatic ring. The PF self-condensation reaction, a bimolecular reaction, is then more rapid as a consequence of the substrate-induced activation of the only two types of reactive sites of phenolic oligomers. In the case of ortho- and para-hydroxybenzylalcohol, the maximum energy of interaction with the surface of crystalline cellulose are, respectively, of 19.7 and 13.3 kcal/mol. Such secondary forces attraction between synthetic oligomer and substrate if mostly concentrated on a single bond such as the C—O of the hydroxybenzylalcohol group would weaken it by up to 25%. In theory, the reaction of two PF oligomers molecules activated to such an extent would yield a condensation of a rate up to 600 times faster than the same condensation when in the absence of the substrate. This means, for example, that a PF condensation of rate constant $3.3 \times 10^{-2} \ell \times \text{mol}^{-1} \times \text{s}^{-1}$ (Table IV) at 95°C could with surface activation have a rate constant of up to 1.98×10 under identical reaction conditions. Calculation of the decrease in energy of activation, at parity of collisional factor (which is not likely), yields a decrease in energy of activation from 23.85 kcal/mol (Table III) down to a value of 19.1 kcal/mol: approximately the same order of magnitude observed in Table III for cellulose surface activation of the main curing exotherm. Expected variations of the collisional factor and diffusion considerations can account for the remaining difference (Table III).

An interesting concept that could also be advanced is that some of the resin/substrate covalent bonds, if formed on the carbohydrates (not on lignin), could be the initial step to catalytic activation of the resin self-condensation. The concept of initial molecule-catalyst covalent bond formation in het-

erogeneous catalysis is also well recognized in other chemical systems.²⁸ If this is the case or not, it is not possible to ascertain with the present data, although such a concept could also explain the low proportion of resin/substrate covalent bonds found at any time, these being then only part of an intermediate transient state.

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