

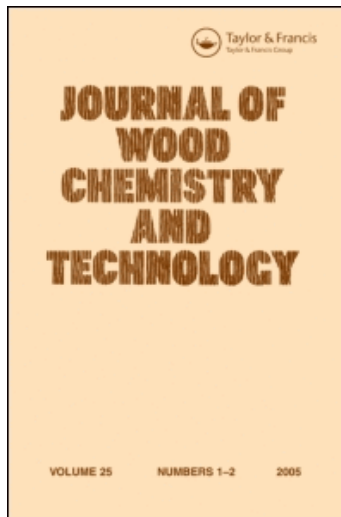
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Carbohydrate Modified Phenol-Formaldehyde Resins

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CARBOHYDRATE MODIFIED
PHENOL-FORMALDEHYDE RESINS

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ABSTRACT

For adhesive self-sufficiency, the wood industry needs new adhesive systems in which all or part of the petroleum-derived phenolic component is replaced by a renewable material without sacrificing high durability or ease of bonding. We tested the bonding of wood veneers, using phenolic resins in which part of the phenol-formaldehyde was replaced with carbohydrates. Our experiments show that the addition of non-reducing carbohydrates and various polyols to phenol-formaldehyde resol-resins does not adversely affect the dry- or wet-shear strength of 2-ply Douglas-fir panels bonded with the modified resins. Reducing carbohydrates, however, cannot be used as the modifier. In general, addition of about 0.6-1.0 mole of modifier per mole of phenol is optimal in the formulation of carbohydrate- or polyol-modified resin. Preliminary results show that part but not all of the modifier is chemically bound into the resin, apparently through an ether linkage. The water prehydrolysate of southern red oak wood, when reduced with sodium borohydride to convert the reducing sugars to alditols, can be used to modify phenol-formaldehyde resins. This use of wood prehydrolysates can be economically beneficial to processes producing alcohol and chemicals from wood as well as to the wood industry and consumers of bonded wood products.

INTRODUCTION

The most prominent wood adhesives over the last quarter of a century have been aminoplastic and polyphenolic types. Polyphenolic adhesives continue to be the most used for the production

of weather-resistant wood products. The energy crisis of the nineteen seventies, the high cost of phenol, and the inevitable decline in petroleum reserves have caused the wood industry to focus attention on obtaining adhesive self-sufficiency.² In practical terms this means that new adhesive systems are needed in which part, or perhaps all, of the petroleum-derived phenolic component is replaced by a readily available, renewable material without sacrificing high durability or ease of bonding.

In the literature of the last 50-60 years, various reports suggest that carbohydrates can be used to replace part of the phenolic component in phenol-formaldehyde adhesive resins. Wood is the world's most abundant renewable resource³ and about two-thirds of wood consists of carbohydrates (cellulose and hemicellulose). Large amounts of these carbohydrates are available in unused by-products of the pulp and paper and hardboard industries, or are potentially available from agricultural residues. In addition, carbohydrates would be made available as byproducts should recently proposed schemes be implemented to convert wood (especially hardwoods and hardwood residues) to alcohol or other chemicals. Thus, carbohydrates are a renewable resource potentially available to replace the phenolic component in phenol-formaldehyde adhesive resins used to bond wood.

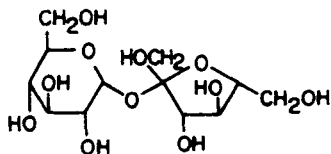
The Forest Products Laboratory (FPL), in cooperation with the Tennessee Valley Authority (TVA), has been studying a two-stage process for the production of alcohol or chemicals from wood.⁴ In the first stage (prehydrolysis), the hemicellulosic sugars are removed from wood by dilute sulfuric acid prehydrolysis at about 170°C.⁵ In the second stage (hydrolysis), the lignocellulosic residue from the first stage is hydrolyzed to glucose with dilute sulfuric acid at about 230°C. The lignin remains as a residue that is used to fuel the process. Prehydrolysis with dilute sulfuric acid can be replaced by a water prehydrolysis (autohydrolysis) process such as the Iotech steam explosion process⁶ or the Stake process.⁷ If sulfuric acid prehydrolysis is used, the hemicellulose is isolated primarily as free reducing sugars (mostly xylose from hardwoods). If water prehydrolysis is used, the hemicellulose is

isolated as a mixture predominantly of oligosaccharides and free reducing sugars.⁸ In either case, approximately equal amounts of glucose and hemicellulosic sugars are obtained from the two-stage process. For the FPL-TVA process and other similar processes to operate efficiently and economically, both the glucose and the hemicellulosic sugars must be utilized. Glucose is readily utilized by fermentation to alcohol or other chemicals. Hemicellulosic sugars have not so assured a use at the present time. Using them to replace part of the phenol-formaldehyde in wood adhesives would be economically beneficial to the proposed alcohol-producing processes. Equally important, it would benefit the wood industry, the wood adhesives industry, and ultimately the consumer of bonded wood products.

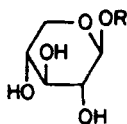
Early patents indicate that carbohydrates were first added to phenol-formaldehyde resol-resins for physical rather than chemical reasons.⁹ Indeed, glycerol and various polyglycols are added to current formulations apparently to improve their physical properties. Loetscher's patent¹⁰ seems to be the first covering a product formed from the reaction of all three constituents: phenol, formaldehyde, and a carbohydrate. Equal volumes of a 50% solution of sucrose, a 37-40% solution of formaldehyde and phenol were heated to homogeneity in the presence of 5% NaOH or KOH. The water-soluble resin was mixed with cellulose fillers and either molded or used for gluing wood.

Spahr and Lieb¹¹ also made resol-type resins for bonding wood by alkaline condensation of resorcinol, formaldehyde and water-soluble polyhydric alcohols, where glucose was defined as a polyhydric alcohol. However, Feigley¹² found that only about 4-7% reducing sugars could be added to molding and casting resins before the properties of the resin began to degrade.

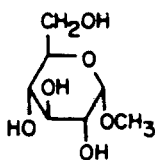
Chang and Kononenko¹³ showed that phenol-formaldehyde resins containing up to 33% sucrose (I) by weight could be used to bond Douglas-fir plywood. They found the wet-shear strengths of panels bonded with a sucrose-modified phenol-formaldehyde resin were higher than the dry-shear strengths of commercial Douglas-fir



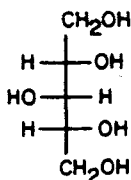
I Sucrose



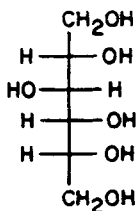
II a Xylose (R=H)

b Methyl xyloside (R=CH₃)

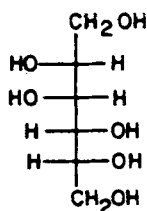
III Methyl glucoside



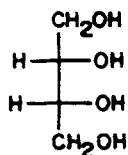
IV Xylitol



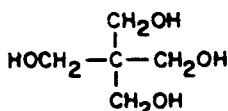
V Glucitol



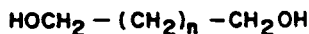
VI Mannitol



VII Erythritol



VIII Pentaerythritol



IX a 1,10-Decanediol (n=8)

b 1,3-Propanediol (n=1)

plywood. They claimed that sucrose replaced about 50% of the phenol used in a typical resin formulation. Because of the high water resistance of the set resin and the definite maximum in strength properties as a function of sucrose content, they concluded that sucrose was bound chemically into the resin.

In 1984, Hsu and Tassler¹⁴ obtained a patent for the production of hardboard using a modified phenol-formaldehyde resin. The resin was modified by replacing from 5-50% of the phenol by an equivalent amount of a concentrated aqueous complex of phenolic and

carbohydrate components obtained from the process water used for the steam digestion of wood chips. The examples in their patent indicate that, for the production of hardboards, the modified phenol-formaldehyde resins are equivalent to unmodified resins and have good shelf life.

Results are reported here of research, initiated in January 1983, to determine whether or not wood-derived carbohydrates, carbohydrate derivatives, and other polyhydric alcohols can be used to modify phenolic plywood adhesives by replacing part of the phenol-formaldehyde resin. Specifically, this research was to demonstrate that a water prehydrolysate of wood could be used to modify phenol-formaldehyde resol-resins. The dry- and wet-shear strength of two-ply Douglas-fir veneers bonded with various formulations were used to indicate resin adequacy. Preliminary research was also conducted to determine if the carbohydrate component is chemically incorporated into the final cured resin.

RESULTS AND DISCUSSION

Our research on modifying phenol-formaldehyde resins with carbohydrates built, in large part, on the work discussed above of Chang and Kononenko,¹³ who used sucrose as modifier. They found that the optimal ratio of sucrose/phenol/formaldehyde/NaOH was 0.3/1/2.3/0.5 on a mole basis. Figure 1 compares the dry- and wet-shear strengths of a commercial phenol-formaldehyde adhesive with those of an unmodified phenol-formaldehyde resin and a sucrose-modified phenol-formaldehyde resin prepared in our laboratory. These results show that sucrose can indeed be used to modify phenol-formaldehyde plywood adhesives. The results also serve as a standard against which to compare resins modified with other carbohydrates. Dry-shear strengths of about 7.6 ± 0.7 MPa (1100 ± 100 psi) and wet-shear strengths of about 5.2 ± 0.7 MPa (750 ± 100 psi) were obtained for 2-ply Douglas-fir veneer panels bonded with commercial, unmodified, and sucrose-modified resins. Further, these results can be compared to the average shear parallel to the grain for solid Douglas-fir wood,

which is about 7.8 ± 1.4 MPa to 10.4 ± 1.4 MPa (1130 ± 200 psi to 1515 ± 200 psi) as determined by ASTM D 2555, and to the true shear strength of dry Douglas-fir wood which is 6.0 ± 1.1 MPa (868 ± 159 psi) as determined by a new method.¹⁵

Resins Modified With Wood-Derived Carbohydrates

Ratio of Reactants. We used the optimal ratio of reactants determined by Chang and Kononenko as the basis for our investigations, assuming that they were generally applicable to a variety of carbohydrates. Sucrose (I) is a dimer of β -fructofuranose and α -glucopyranose. To give proportions of total carbohydrate similar to that of sucrose in a Chang and Kononenko modified resin, 0.6 moles of monomeric carbohydrate or carbohydrate derivative per mole of phenol were used in various modified phenolic resins.

Resins Modified with Wood Prehydrolysate. Hsu and Tassler¹⁴ used a formulation similar to that of Chang and Kononenko to make a modified phenolic hardboard adhesive using a phenolic/carbohydrate fraction obtained from steaming wood. The carbohydrate fraction (prehydrolysate) that would be obtained by water prehydrolysis of wood has approximately the same basic chemical composition as the fraction used by Hsu and Tassler. Our experiments with a water prehydrolysate obtained from southern red oak (Quercus falcata Michx.) indicated that it was not acceptable for direct modification of phenol-formaldehyde adhesives. For purposes of formulation, the freeze-dried prehydrolysate was considered to have a monomeric molecular weight equal to that of xylose. As illustrated in Figure 1, the dry-shear strength of the phenol-formaldehyde resin modified with 0.6 moles of prehydrolysate compared favorably to those of a commercial resin and an unmodified phenolic resin prepared in our laboratory. The wet-shear strength was unacceptable, indicating that the prehydrolysate could not be used directly for modification of phenol-formaldehyde resins for exterior grade plywood.

The difference between our results and those of Hsu and Tassler may result simply from differences in the performance requirements

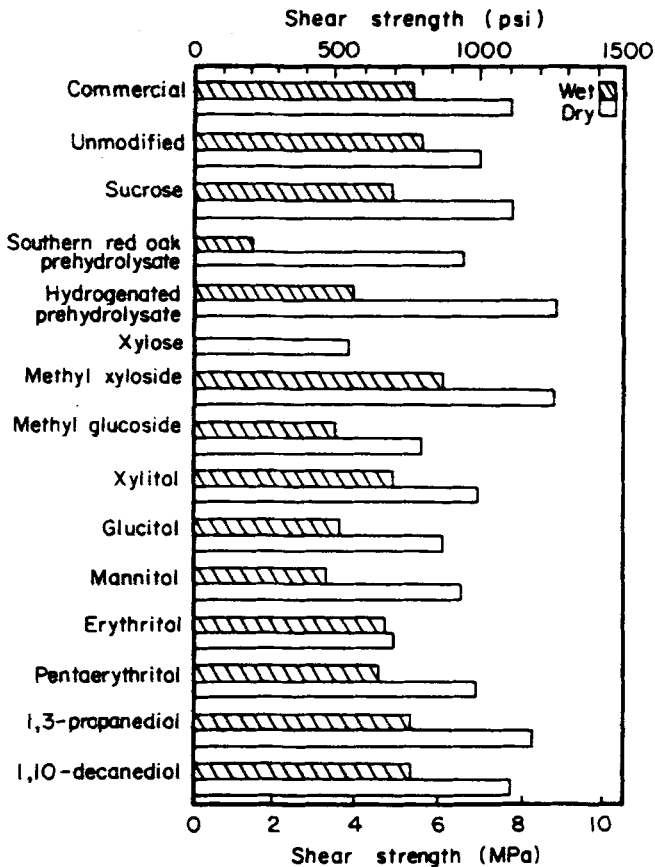


FIGURE 1. Comparison of wet- and dry-shear strengths of 2-ply Douglas-fir panels bonded with the following phenol-formaldehyde resins: Commercial, unmodified (prepared in the laboratory), and modified with sucrose, southern red oak prehydrolysate, reduced southern red oak prehydrolysate, or one of the specified carbohydrates or polyols. For the modified resins, the mole ratio of modifier/phenol/formaldehyde was 0.6/1/2.3 except that for sucrose the ratio was 0.3/1/2.3.

of the two systems being bonded, from the presence of higher amounts of total reducing sugars in our water prehydrolysate of southern red oak than in their steamed wood extract, or from the generally lower pressing temperatures used in our investigations. In any case, these differences indicate that further study is warranted on modifying phenol-formaldehyde resins with carbohydrates, especially for bonding wood veneer.

Because the southern red oak prehydrolysate did not give satisfactorily modified resins, carbohydrate components that were known either to be in the prehydrolysate or potentially derivable from components in the prehydrolysate were investigated for use in modifying resins. Through this approach we hoped to obtain a better understanding of the types of carbohydrate derivatives that could be used to modify phenolic resins.

Resins Modified with Xylose. Xylose (IIa) is the major hemicellulosic sugar in hardwoods. Thus, xylose and xylose oligosaccharides are major components in hardwood prehydrolysates. A phenol-formaldehyde resin modified with xylose (Fig. 1) gave unacceptable dry-shear strengths and no wet-shear strengths for bonded Douglas-fir veneers. Xylose, like other reducing sugars, rapidly undergoes β -elimination reactions in basic solution to form acidic components, especially saccharinic acids.¹⁶ These acidic reaction products can neutralize the base catalyst and are apparently detrimental to the formation and cure of the modified resin. The results obtained with xylose-modified resins confirm the fact that reducing sugars are detrimental to the final resin properties.

Oligosaccharides also undergo degradation reactions in basic solutions. These reactions proceed from the reducing end (i.e., the peeling reaction¹⁷) and lead to acidic degradation products. The formation of these degradation products prevents direct modification of phenol-formaldehyde resins with hardwood prehydrolysates.

Thus, although reducing sugars like xylose (IIa) contain an aldehydic functionality which one might expect to react into the phenolic resin system, this functionality is rapidly destroyed

under the conditions of resin formulation. In contrast, sucrose (I) is a non-reducing carbohydrate material; it has no free aldehydic functionality. This fact explains why sucrose can be used to modify phenolic resins, while reducing sugars cannot.

Resins Modified with Glycosides and Alditols. Problems in modifying phenolic resins with reducing sugars may be avoided by masking their aldehydic functionality to prevent its destruction. There are at least two methods for accomplishing this: 1) converting the carbohydrate to a glycoside, or 2) converting the aldehydic group to a primary alcohol (i.e., converting the free sugar to the corresponding alditol). Resins formulated with methyl xyloside (IIb; Fig. 1) gave excellent dry- and wet-shear strengths, confirming the rationale behind this general approach.

Resins formulated with the addition of methyl glucoside (III) were not as effective as those made with methyl xyloside. It has not yet been determined whether the difference arose from differences in the chemistry of the two resin systems or from pressing conditions not being optimal for the methyl glucoside-modified resins. Both systems gave results substantially better than those obtained with resins formulated with a free reducing sugar.

Alditols were also investigated for use in modifying resins (Fig. 1). Resins were formulated with xylitol (IV), glucitol (V), mannitol (VI), and erythritol (VII). The alditol formed from xylose (i.e., xylitol) gave the best results (Fig. 1). In all cases, the results indicated that resins modified with the alditol derivatives of carbohydrates were much better than resins modified with reducing sugars.

Resins Modified with Reduced Prehydrolysate. A sample of the water prehydrolysate obtained from southern red oak was reduced with sodium borohydride in methanol. About 60% of the original prehydrolysate consisted of sugars (primarily xylose and xylose oligosaccharides), the remainder being lignin-derived materials, furfural, and degradation products. After reduction, only about 2% of the prehydrolysate consisted of reducing sugars, showing that the aldehydic functionality of the free reducing sugars and

the reducing end groups of the oligosaccharides had been converted almost completely to primary alcohols. Modified resins made from the reduced prehydrolysate showed considerable improvement over those made with modified resins formulated from the original prehydrolysate (Fig. 1). The panels made from the resins modified with the reduced prehydrolysate had excellent dry-shear strengths and wet-shear strengths that approached those of the commercial resin, the unmodified resin prepared in the laboratory, and the Chang and Kononenko sucrose-modified-resin. The slightly lower wet-shear strengths probably resulted from the presence of other materials in the prehydrolysate. We have shown, for example, that prehydrolysis lignin can be used to modify phenol-formaldehyde resins;⁸ however, the resin thus modified must be cured at a higher temperature and for a longer time. Consequently, pressing conditions were not optimal for lignin components in the prehydrolysate. However, the results obtained with these panels further demonstrate that reducing sugars and reducing end-groups on oligosaccharides are detrimental to the modification of phenolic resins with carbohydrates under basic conditions. Further, they confirm that conversion of the aldehydic moiety to a non-reducing moiety tends to alleviate this detrimental effect.

Optimization. Except as described below, neither the optimal amount of a modifier needed to maximize shear strength nor the optimal pressing conditions were determined. Further, it should be stressed that the data on some of the modifiers are limited and the differences observed, for example, between different alditols, may have arisen from natural variations in wood strength. Overall the data indicate that wood-derived carbohydrates and carbohydrate derivatives can be used to modify phenol-formaldehyde adhesives. The modified resins can be used to bond wood veneers at conditions close to those used for the commercial production of plywood. Further studies on several of these systems are underway.

Resins Modified with Other Compounds

Modified resins were also formulated with pentaerythritol (VIII), 1,10-decanediol (IXa), and 1,3-propanediol (IXb). These

compounds contain only primary hydroxyl groups. In all three cases acceptable resins were formed (Fig. 1). The presence of primary hydroxyl groups alone in the modifier leads to acceptable resins. The proximity of the hydroxyl groups is unimportant as indicated by the results obtained with 1,3-propanediol- and 1,10-decanediol-modified resins. Presumably, if these compounds are incorporated into the resin, they react at two or more primary hydroxyls forming cross links. However, the results obtained with methyl xyloside, which has no primary hydroxyl groups, indicate that a modifier with secondary hydroxyls alone can also be used successfully to modify a phenol-formaldehyde resin. Thus, if cross-linking through the carbohydrate component is taking place, secondary as well as primary hydroxyls are apparently involved.

Variation of Shear Strength with Amount of Modifier

Resins modified with methyl xyloside (IIb), xylitol (IV), or 1,3-propanediol (IXb) were among the best modified resins. Resins modified with varying amounts of these components were studied to see how shear strength changed with changes in the amount of added modifier. Figure 2A shows that 0.3-1.0 mole of methyl xyloside per mole of phenol gave the best shear strengths. This corresponds to resins in which about 20 to 50% of the dry weight of the resin is carbohydrate. Xylitol-modified resins show a similar pattern (Fig. 2B). These data indicate that the optimal amount of xylitol to use in modifying phenolic resins is between about 0.3 and 1.0 mole per mole of phenol (about 20 to 50% of the dry weight of the resin). Resins modified with 1,3-propanediol (Fig. 2C) give panels whose dry- and wet-shear strengths continued to increase as the amount of modifier was increased. The data suggest that 1,3-propanediol in excess of one mole per mole of phenol (about 30% of the dry weight of the resin) can be used as a modifier.

Figures 2A-2C do not provide a direct comparison of modifiers in terms of their hydroxyl content as discussed above. But in Figure 3 the dry- and wet-shear strengths of two-ply Douglas-fir

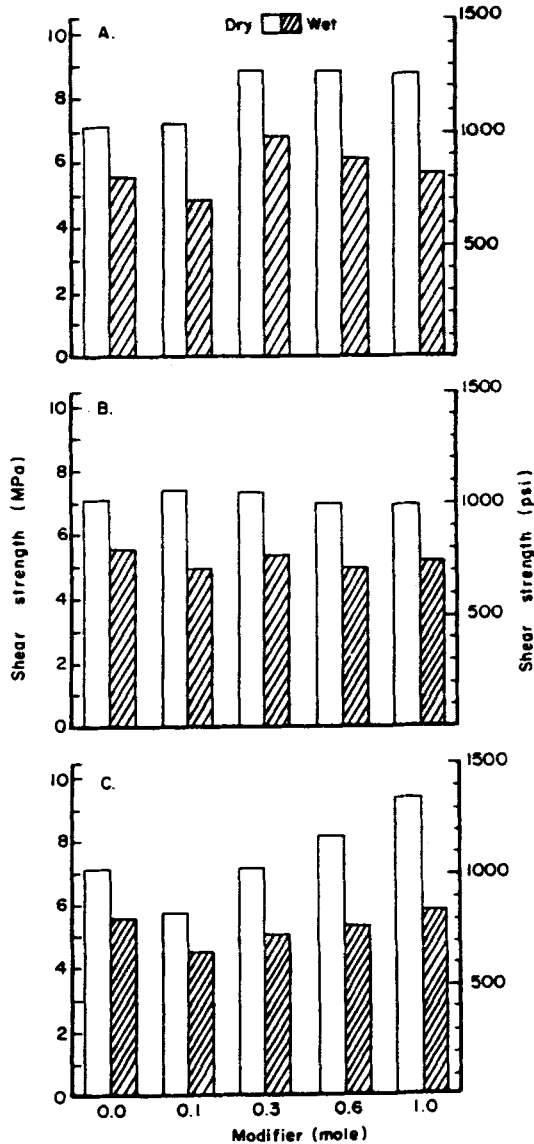


FIGURE 2. Variation of the dry- and wet-shear strengths of 2-ply Douglas-fir panels bonded with phenol-formaldehyde resins modified with methyl xyloside (A), xylitol (B), and 1,3-propanediol (C). Moles of modifier per mole of phenol were varied, as indicated. The mole ratio of phenol to formaldehyde was 1/2.3.

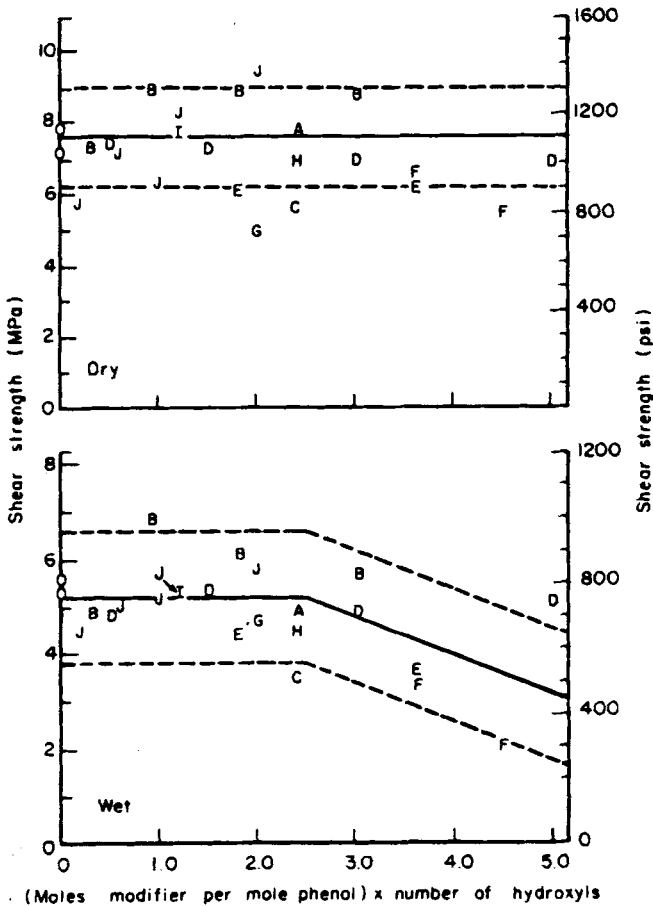


FIGURE 3. Variation of dry- and wet-shear strength of 2-ply Douglas-fir panels bonded with the following phenol-formaldehyde resins: Unmodified (O), modified with either sucrose (A), methyl xyloside (B), methyl glucoside (C), xylitol (D), glucitol (E), mannitol (F), erythritol (G), pentaerythritol (H), 1,10-decanediol (I), or 1,3-propanediol (J), as functions of hydroxyl content.

specimens are plotted as a function of "moles of hydroxyls", defined as moles of modifier per mole of phenol multiplied by the number of hydroxyls in the modifier. These plots allow direct comparison between resins modified with different modifiers, taking into account the hydroxyl content as an indication of the number of potential sites for chemical bonding.

In Figure 3 the solid lines represent the general trend in the plotted data and originate at the dry- and wet-shear strengths of the control resins [i.e. unmodified, commercial, and sucrose-modified phenol-formaldehyde resins (Figure 1)]. The dashed lines represent error limits of ± 1.4 MPa (± 200 psi) about the solid line. The bulk of the shear strength data for all the modified resins falls between these extremes. Variation of the data about the center line is probably caused by natural variation in the shear strength of the Douglas-fir veneer used to make the panels.

Figure 3 shows that dry-shear strength is unchanged by the addition of modifiers, even at the higher hydroxyl content studied and that wet-shear strength is unaffected by the addition of modifiers up to about 2.5 moles of hydroxyls, but is affected by the addition of modifiers at higher hydroxyl contents. This general trend correlates with the observation that some modifiers can be added to phenol-formaldehyde resins at higher molar ratios than other modifiers.

Phenolic resins can thus be successfully modified by additions of about 0.6-1.0 mole of non-reducing carbohydrates, carbohydrate derivatives, or polyols per mole of phenol, depending on the hydroxyl content of the modifier. These results are similar to those of Chang and Kononenko on modifying phenol-formaldehyde resins with sucrose. The modified resins can be used to bond wood veneers at conditions similar to those used in the plywood industry.

Incorporation of the Modifier into the Final Resin

Chang and Kononenko,¹³ observing the high water resistance of cured, sucrose-modified phenolic-resins and the occurrence of a

maximum in strength properties as a function of sucrose content, concluded that the sucrose was completely bound into the resin by chemical means. They did not, however, present any data to substantiate their view. It is important to understand the chemistry involved in modifying phenol-formaldehyde resol-resins with carbohydrates in order to establish how the resins are functioning. If the modifier is not reacted into the resin, then it plays the role of a filler rather than a modifier. In addition, knowledge about how carbohydrates are incorporated into the resin may possibly shed light on whether and how phenol resins bond to wood, since such bonding would, at least to some extent, involve reaction with carbohydrate components in the wood.

Chow¹⁸ has shown that phenol-formaldehyde resol-resins are highly accessible to water, even at room temperature. He prepared phenol-formaldehyde resins that contained potassium bromide. Because of the porous nature of the cured resin, almost complete extraction of the potassium bromide was possible with water at room temperature.

In our investigation various modified resins (Table 1) were cured, ground in a mortar and pestle, and extracted with water to determine whether the modifier was bound into the resin. The ground resins were first extracted with water at room temperature, and then with hot water in a Soxhlet apparatus. In all cases the bulk of any extractable material was removed by the water extraction at room temperature. Extraction results for resins modified with the following compounds are reported in Table 1: xylitol (IV); methyl xyloside (IIb); 1,3-propanediol (IXb); methyl glucoside (III); and sucrose (I). The amount of modifier extracted is the sum of the extracts made with room-temperature and hot water. The amount of modifier not extracted is assumed to be a measure of the amount of modifier that was chemically incorporated into the resin.

As the amount of modifier added to the resin is increased, the absolute amount of modifier reacted into the phenolic resin increases. When 0.1 mole of xylitol per mole of phenol is used as a modifier, about 0.075 mole (75%) is incorporated into the resin. When 1 mole

TABLE 1
Extractability of Phenol-Formaldehyde Resins.¹

Modifier added	Modifier extracted	Modifier reacted
- - Moles modifier/moles phenol \pm standard error - -		
XYLITOL		
0.1	0.025 \pm 0.005	0.075 \pm 0.005
0.3	0.15 \pm 0.05	0.15 \pm 0.05
0.6	0.35 \pm 0.05	0.25 \pm 0.05
1.0	0.7	0.3
METHYL XYLOSIDE		
0.6	0.35 \pm 0.005	0.25 \pm 0.05
1,3-PROPANEDIOL		
0.1	0.045 \pm 0.015	0.055 \pm 0.015
0.3	0.15 \pm 0.05	0.15 \pm 0.05
0.6	0.30 \pm 0.10	0.30 \pm 0.10
1.0	0.6	0.4
METHYL GLUCOSIDE		
0.6	0.4	0.2
SUCROSE		
0.3	0.1	0.2

¹Resins were cured as a thin film on aluminum foil at 140°C for 5-12 minutes.

of xylitol per mole of phenol is used, about 0.3 mole (30%) is incorporated into the resin. The results obtained with 1,3-propanediol- and methyl glucoside-modified resins are similar to those obtained with xylitol- and methyl xyloside-modified resins. On the basis of moles of monomeric carbohydrate, incorporation of sucrose (a dimer) into the modified resin is similar to, but toward the high end of, the range observed with the monomeric modifiers.

These results are rather surprising in light of the high wet-shear strengths generally observed for modified resins. They suggest that the modifiers react into the resin system to a limited extent but may also serve simply as filler. We do not know the nature of the chemical bonds formed nor whether the carbohydrates incorporated into the resin act as crosslinking agents or are added to the resin structure only as pendant side groups. Infrared (IR) studies of resins cured with and without the addition of modifiers show that the carbohydrates and polyols are incorporated into the resin as ethers. A weak but significant broad-absorption band at about 1080 cm^{-1} corresponding to the other linkage is observed in the IR spectrum of the cured, extracted xylitol-modified resin, but is not observed in the IR spectrum either of the cured, extracted unmodified resin or of xylitol. Further investigations are underway to elucidate whether the modifier is incorporated into the final cured resin.

CONCLUSIONS

From our results we conclude that:

1. Sucrose can be used to modify phenol-formaldehyde resins, confirming the report of Chang and Kononenko.¹³
2. Reducing sugars cannot be used successfully to modify phenol-formaldehyde resins, confirming a similar observation by Feigley.¹²
3. Non-reducing carbohydrate derivatives (e.g., alditols and methyl glycosides) can be used successfully to modify phenol-formaldehyde resins.
4. Other polyols (e.g., pentaerythritol) can be used successfully to modify phenol-formaldehyde resins.
5. Compounds with only primary alcoholic functionalities (e.g., 1,3-propanediol and 1,10-decanediol) can be used successfully to modify phenol-formaldehyde resins. The proximity of the alcoholic groups is thus unimportant.
6. The presence of primary alcoholic groups is not required for a compound to function as a modifier. For example, methyl

xyloside, which contains only secondary alcoholic groups, is an acceptable modifier. Secondary as well as primary alcohols are apparently involved if the modifier is reacted into the cured resin.

7. The prehydrolysate of southern red oak cannot be used directly to modify phenol-formaldehyde resins. Presumably, this is true of prehydrolysates obtainable from other species, because similar types of compounds are to be expected in the prehydrolysate of all species. Our observation contrasts with that made by Hsu and Tassler¹⁴ who used a similar fraction successfully to modify phenol-formaldehyde resins used to bond hardboard.

8. The reduced prehydrolysate of southern red oak can be used to modify phenol-formaldehyde resins. Resin so modified is superior to resin modified with the original prehydrolysate, further confirming that the addition of reducing sugars is detrimental to bonding. Panels bonded with this modified resin nevertheless had wet-shear strength somewhat lower than panels bonded with control resins. The lower wet-shear strengths are presumably caused by other components of the prehydrolysate.

9. In general, the addition of about 0.6-1.0 mole of monomeric modifier per mole of phenol is optimal for successful modification of phenol-formaldehyde resol-resins. This conclusion is in agreement with that of Chang and Kononenko¹³ who found that 0.3 mole of sucrose (a dimer) was optimal.

10. Phenol-formaldehyde resol-resins modified with non-reducing carbohydrate derivatives or polyols can be used at pressing temperatures and pressures similar to those now used commercially to make plywood.

11. Apparently, some part of the modifier is chemically incorporated into the final cured resin. The absolute amount of modifier incorporated increases with the amount initially added to the phenol-formaldehyde resin.

12. The modifier is apparently incorporated into the cured resin through ether linkages.

EXPERIMENTAL

Adhesive Formulation

Analytical grade reagents were combined in the following order:

- phenol (solid), 1.0 mole
- sodium hydroxide 0.5 mole plus 3.0 moles of water
- modifier, 0.3-1.0 mole
- paraformaldehyde, 2.3 moles.

The mixture was heated for 30 minutes at 85-90°C. The reaction was stopped by adding 2.6 moles of water and cooling the mixture rapidly. Methanol (5.5 moles) was then added to dilute the mixture to approximately 50% solids. The unmodified adhesive was formulated by the same procedure without addition of modifier.

Veneer

Rotary cut Douglas-fir veneer (3 mm thick) was conditioned to equilibrium moisture content at 27°C and 30% relative humidity. Pieces 150 x 150 mm² were cut and bonded into panels.

Bonding

Approximately 4-5 g of the phenol-formaldehyde adhesive was spread evenly on one piece of veneer, which was then dried by heating at 60°C for 1 hour. The coated piece of veneer was assembled into a two-ply panel with an uncoated piece of veneer, their grains running in parallel. The panel was placed into a heated press and pressed at 965 kPa (140 psi) for various times and temperatures.

Determination of Shear Strength

Each panel was conditioned at 27°C, 30% relative humidity for approximately 1 to 2 weeks before cutting into 14 2-ply lap shear specimens. Five specimens from each panel were tested for dry shear strength using a universal testing machine at a loading rate of 1 cm/min. Another five specimens from each panel were subjected

to a standard vacuum-pressure soak.¹⁹ A vacuum of 85 kPa (25 in. of mercury) was drawn on the specimens while in water and held for 30 minutes. The vacuum was broken and a pressure of 450 to 480 kPa (65-70 psi) was applied to the specimens still in water and held for 30 minutes. The shear strength was determined on the wet specimens. The remaining specimens were held in reserve.

Prehydrolysis of Southern Red Oak

Green southern red oak (Quercus falcata Michx.) wholewood chips (650 g, 150% moisture content) were prehydrolyzed with steam at 170°C for 30 minutes in the apparatus previously described.⁵ The prehydrolyzed chips were extracted successively with three 2 liter portions of hot water. The water extract was concentrated to dryness in vacuo to give a yellow-brown semisolid (120 g). The semisolid contained 22% total reducing sugars as measured by Nelson's colorimetric modification of the Somogyi method,²⁰ after hydrolysis to monomeric sugars as described in ASTM Method D 1915²¹ the reducing sugars content was 60%. High performance liquid chromatography analysis²² of the monomeric sugars showed they were composed of 80% xylose, 10% galactose, 4% glucose, and 6% other sugars.

Reduction of Southern Red Oak Prehydrolysate

Freeze-dried southern red oak prehydrolysate (10 g) was added to methanol (200 ml) with stirring. The prehydrolysate was not completely soluble. Sodium borohydride (3 g) was added in small portions over a 1-hour period so that the temperature of the mixture did not rise above 50°C. The mixture was stirred an additional hour after adding the sodium borohydride. Dowex 50W-X8 ion exchange resin was added slowly with mixing until the pH was reduced from 10 to 6. Water (100 ml) was added with stirring and the solution decanted from the resin. The resin was washed with water. The combined water/methanol solution was evaporated to dryness to give a solid residue. Methanol was added and evaporated

at reduced pressure to remove boric acid as volatile methyl borate. The resulting semisolid was resuspended in methanol and evaporated to dryness to give 9 g of reduced prehydrolysate. The reduced prehydrolysate contained 2% reducing sugars as measured by the Nelson colorimetric modification of the Somogyi method²⁰. The reduced prehydrolysate was further characterized by hydrolysis²¹ to monomeric sugars, after which the reducing sugars content was 39%.

Extraction of Cured Phenol-Formaldehyde Resins

A sample of the resin was spread as a thin coating onto a sheet of aluminum foil and cured in an oven at 140°C for 5 to 12 minutes. The cured resin was removed from the aluminum foil, weighed, and broken into small pieces that were placed in water (10-15 ml) for extraction at room temperature. After 1 to 2 hours the water was decanted from the solid resin. The resin was extracted in this manner an additional 3 or 4 times. The residue from the water extraction at room temperature was dried and ground in a mortar and pestle. The ground resin was extracted with hot water in a Soxhlet apparatus for 24 hours. The room temperature water extract and the hot water extract were neutralized with Dowex 50W-X8 ion exchange resin, concentrated, and diluted to a known volume for analysis. The quantity of modifier in the extract was determined by high performance liquid chromatography.²²

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