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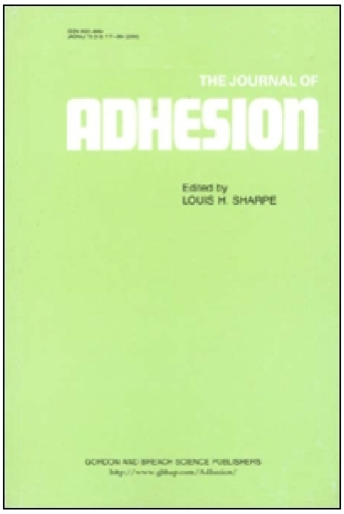

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The Mechanism of Adhesion of Phenol-Formaldehyde Resins to Cellulosic and Lignocellulosic Substrates

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Fiber Surface Modification—Part VIII[1]

The Mechanism of Adhesion of Phenol-Formaldehyde Resins to Cellulosic and Lignocellulosic Substrates.

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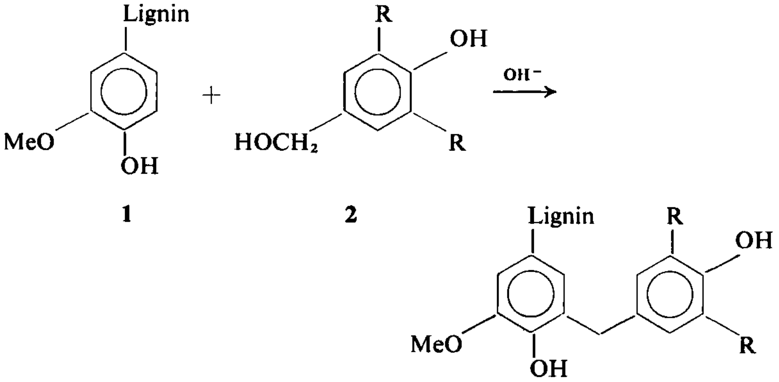
The mechanism of adhesion of phenolic resins to cellulosic and lignocellulosic fibers has been explored using a nonpolymerizable bromine-labelled benzyl alcohol as a model for the adhesive. Bromine analysis by neutron activation techniques is sufficiently sensitive to show that reaction occurs much more extensively with the lignified fibers. This is attributed to the formation of covalent linkages between the model adhesive and the guaiacyl units in the lignin. The excellent general performance of phenolic adhesives on cellulose and lignocellulosic substrates can therefore be in part ascribed to the existence of high enthalpy covalent chemical bonds between adherend and adhesive.

INTRODUCTION

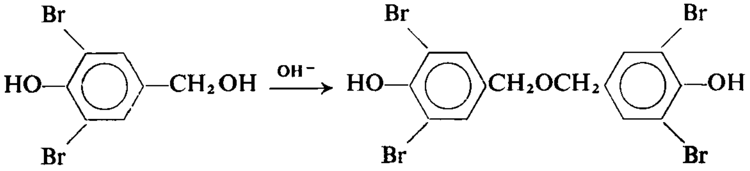
With the continuing development of high performance fiber composites[2–6] increasing attention has been directed toward the synthesis of rapid-curing materials[7] which will give a higher enthalpy bond between the fiber and the contiguous adhesive[8–12]. This is because fiber composites often fail under strain by the retraction of unbroken fibers from the enveloping binder mass[1,2,12]. However, before further attempting to invent new adhesives to satisfy the foregoing criteria it would be preferable to clarify the mechanism of adhesion of the best materials now being extensively used. Thus, it would be helpful to distinguish whether the strong adhesion of such binders is due only to van der Waals or London forces or if high energy chemical bonds between adherend and adhesive also play a decisive role. In the field of wood fiber composites the most widely used high performance resins are derived from acid- or base-catalyzed condensation polymerization of formaldehyde and phenol optionally supplemented with polyhydric phenols for more rapid curing cycles[7]. Attempts have therefore been made to determine the extent of reaction of such methylolated resins with either α-cellulose or cotton fibers but in all cases no unambiguous evidence for the extensive formation of chemical bonds has been unearthed[14-16]. On the other hand, similar efforts using lignocellulosic fibers have provided tentative indications of possible reactions with both phenol- and urea-formaldehyde resins[17,18]. Furthermore, changes in the chemical composition due to the aging of wood, which undoubtedly involve lignin[19], affect bonding[20]. The inhibition of a reaction forming covalent bonds between the lignin of the wood and the methylolated adhesive is thereby implied. Clearly, the presence of lignin with its guaiacyl units (1) offers a substantial opportunity for participation in condensations involving methylolated monomers or prepolymers (2), as outlined in Eq. (1), which is lacking in a purely cellulosic fiber. Nonetheless, direct and convincing evidence of such fiber-polymer condensations has not yet been secured because the anticipated extent of reaction, if any, would not be great and might therefore be difficult to measure by the conventional methods of analytical chemistry. However, these problems can be circumvented using neutron activation analysis and model compounds containing bromine as a molecular label. Based on this approach, unequivocal evidence is now presented for the formation of chemical bonds between cured phenol-formaldehyde resins and lignocellulosic, but not cellulosic, substrates.



(1)

RESULTS AND DISCUSSION

Any experiment which endeavors to demonstrate the reaction of polymer-forming compounds with a microporous substrate must effectively, from the outset, dispose of the potential criticism, which is valid for all of the previous research, that the combination is a consequence of physical entrapment of polymers within the infrastructure of the substrate[12]. In this work, 3,5-dibromo-4-hydroxybenzyl alcohol (**3**) was selected as a model for the constituents of the phenol-formaldehyde prepolymer because it contains an unhindered methylol group and is incapable of undergoing self-condensation beyond the formation of the dimer (**4**) because of the blocking effect of the bromine atoms ortho to the phenolic hydroxyl groups[21]. It cannot therefore be entrapped within the fiber by physical entanglement. The bromine atoms also act as labels for the model since they can readily be detected and measured[22] after conversion to ^{82}Br. Separate reactions of **3** with α-cellulose and a typical extractive-free lignocellulosic fiber were carried out under identical alkaline conditions. After exhaustive solvent extraction the treated fibers were analyzed. The irradiated α-cellulose gave 5.9 × 10^4 disintegrations/min g corresponding to a bromine content of 0.1 % while the irradiated lignocellulosic fiber gave 1.03 × 10^6 disintegrations/min g indicating a bromine content of 1.6 %. The possibility that adsorption might be responsible for the bromine content of the fibers was eliminated by substituting *o*-bromophenol for 3,5-dibromo-4-hydroxybenzyl alcohol in the reaction procedure. The bromine content of the lignocellulosic fibers was then found to be only 0.03 %.



3 **4**
(2)

These results indicate that any alkaline reaction of methylol compounds with α-cellulose occurs only very infrequently and is probably a consequence of the presence of adventitious functions or aldehydic end-groups[23] within the cellulose macromolecule. The latter possibility is favored by the magnitude of the bromine content of the modified α-cellulose fibers which is consistent with the combination of 1 mol of the 3,5-dibromo-4-hydroxybenzyl alcohol with each cellulose chain of DP $\simeq$ 1000[24].

In contrast, with lignin-containing fibers, there is a considerable amount of reaction which can only be attributed to the presence of this three-dimensional network macromolecule since the extractives have been removed and the hemicelluloses would be comparable in reactivity to α-cellulose. The combination of the alkaline 3,5-dibromo-4-hydroxybenzyl alcohol (and the corresponding phenol-formaldehyde adhesive) via its methylol group with a wood substrate presumably originates predominately in those phenylpropanoid units of lignin which possess both a free phenolic hydroxyl group and an associated unsubstituted ortho position. Although methinyl hydrogens alpha to a side chain carbonyl are also susceptible to methylolation, their role can be considered to be minor[21]. Furthermore, the distribution and location of hydroxymethyl groups in lignins which have been reacted with alkaline formaldehyde has been studied[25,26]. This lignin modification reaction is probably second order[21,24] and about 0.15 mol of such hydroxymethyl groups per methoxyl group can be introduced into spruce milled wood lignin. Since this particular lignin is comparable in composition to the lignin which constitutes about 30% of the fiber itself[24] the equivalent weight of the fiber to electrophilic attack can be calculated to be about 4600. The efficiency of the chemical combination of the phenolic adhesive, as represented by the model bromophenol is therefore approximately 46%. This substantial value reflects the accessibility of the acidic lignin-rich middle lamella of the original wood which now constitutes the periphery of the fiber and engenders the formation of high enthalpy covalent chemical bonds between the adherend and the adhesive.

EXPERIMENTAL

3,5-Dibromo-4-hydroxybenzyl alcohol

A solution of methyl 3,5-dibromo-4-hydroxybenzoate (10g, m.p. 123–124°)[25–27] in tetrahydrofuran (100 ml) was added dropwise to a stirred refluxing mixture of $LiAlH_4$ (6g) and tetrahydrofuran (250 ml) during 30 min and refluxing was continued for 2 hr. The cooled reaction mixture was treated sequentially with ethyl acetate (30 ml), 20% aqueous NaOH (20 ml) and conc. HCl (100 ml). Extraction with ether in the usual way afforded 3,5-dibromo-4-hydroxybenzyl alcohol (4.6g) which crystallized from chloroform-methanol as prismatic needles, m.p. 112–113°, eq. wt. 281 (reported [27]m.p. 116–117°, calc. eq. wt. 282.3.) and exhibited a NMR spectrum in CD_3COCD_3 containing singlets corresponding to phenolic and alcoholic hydroxyl, aromatic and benzylic protons in the ratio of 1:2:2:1 at respective displacements of 2.21, 6.33, 2.9 and 5.82τ relative to TMS.

Reaction of α-cellulose and lignocellulosic fibers with 3,5-dibromo-4-hydroxybenzyl alcohol (3)

The fibers (200 mg), pre-extracted with boiling acetone in a Soxhlet apparatus for 48 hr, were separately treated with water (3 ml) and a solution (5 ml) of the sodium salt of **3** (250 mg) and maintained at 80° for 12 hr in a nitrogen atmosphere. The fibers were then collected by filtration, washed with a 0.1N aqueous solution of hydrochloric acid (500 ml), extracted with acetone in a Soxhlet apparatus for 48 hr and dried at 60°.

Analytical methods

The bromine content of the fibers was determined by concurrent irradiation (10^{12} neutrons/cm^2 sec) of a sample (17 mg) and a standard (NH_4Br solution) for 15 min in the nuclear reactor facilities of the University of Washington. After appropriate cooling (6 hr) the samples were counted by integration of the 0.78 MeV photopeak of ^{82}Br using a 3″ × 3″ NaI (Tl) crystal and multichannel analyzer. The only significant gamma interference was that from the decay of ^{24}Na which was removed by spectrum stripping using a sodium standard.

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