Induced Accelerated Autocondensation of Polyflavonoid Tannins for Phenolic Polycondensates. II. Cellulose Effect and Application

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SYNOPSIS

Polyflavonoid tannin autocondensation was found to be facilitated by the reaction occurring on cellulose and lignocellulosic substrates. Although the mechanism of polyflavonoid autocondensation induced by cellulose differs from that induced by the action of Lewis acids, the subsequent reaction of autocondensation appears to be similar. The determining step of tannin rearrangement pathways under alkaline conditions in cellulose-induced higher-temperature autocondensation is the favoring of the heterocycle pyran ring opening over the normal interflavonoid bond cleavage and catechinic acid rearrangement. This is caused by relevant bond weakening and easier cleavage induced by strong attractive forces between flavonoid and cellulosic substrate. Applied bonding of cellulosic substrates by polyflavonoid tannin autocondensation reactions appears to be feasible and to occur as predicted from theoretical predictions. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The autocondensation of polyflavonoid tannins induced by Lewis acids as described in the preceding article[1] opens up the possibility for new applications of polymeric tannins as adhesives. Foremost could be the use of tannins as wood adhesives without the use of any formaldehyde, or any other aldehydes, leading to an environmentally friendly, no formaldehyde emission, natural binder.

Recently, the acceleration induced by a cellulose substrate on the polycondensation and hardening of synthetic phenol–formaldehyde resins was reported.[2] By the nature of this catalytic activation, a similar effect by a cellulose substrate could occur also in the type of autocondensation described in the preceding articles.[1,2] This aspect needs to be investigated before application of the tannin autocondensation reaction to wood adhesives. This article deals, then, with the catalytic activation, autocondensation, and hardening of polyflavonoid tannins

induced by a lignocellulosic substrate, its comparison with Lewis acid-induced autocondensations, and with the applied results obtained by both in one type of relevant application.

EXPERIMENTAL

Differential Scanning Calorimetry (DSC)

The samples were tested by placing in crucibles a small amount of pine tannin 40% solution at pH 12, pine tannin 40% solution + 4% SiO_2 (Areosyl) at pH 12, and pine tannin 40% solution at pH 12 on filter paper for the mass proportion of tannin to paper of 1 : 1. The sample crucibles were then heated at different heating rates, namely, 5, 10, 15, 20, 25, and 30 K per min to a maximum of 573 K. The activation energies of the different exotherms for pine tannin alone, for pine tannin + 4% SiO_2, and for pine tannin + cellulose were 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[3] equation.

Table I   (a) Energies of Interaction of a Monoflavonoid and a Biflavonoid with a Crystalline Cellulose I Model and (b) Energy Contributions to Flavonoid Model Interaction with Crystalline Cellulose I

	E Interaction (k cal/mol)
(+)-Catechin/crystalline cellulose I	-31.28[a]
cis-Fisetinidol-4,6-cis-fisetinidol/crystalline cellulose I	-13.59[b]

	Minimum-energy Conformations (in k cal/mol)				
Energy	A (+)-Catechin	B Cellulose I Crystallite	C 4,6-Linked Biflavonoid	D (+)-Catechin/Cellulose	E Biflavonoid/$_n$ Cellulose
Compression	0.7692	16.9740	1.5981	17.6381	18.6866
Bending	3.8208	53.8121	6.5956	58.4353	60.8961
Stretch bend	-0.0566	5.4888	-0.0188	5.5008	5.5486
van der Waals	8.3591	108.0160	20.2757	116.3548	128.2007
Other	-12.3440	-17.7579	-32.3617	-62.9322	-64.3285
Torsional	-14.7146	44.2106	-26.5962	30.1347	17.6850
Charge dipole	0.0000	0.0000	0.0000	0.0000	0.0000
Dipole	0.0152	0.1693	0.1821	0.3489	0.2968
Final steric energy	-14.1509	210.9130	-30.3252	165.4803	166.9851

[a] $= D - (A + B)$.
[b] $= E - (B + C)$.

Molecular Mechanics

An unconstrained force-field program, MM2-87 (Ref. 4) was used for the calculation of the minimum internal energies of (+)-catechin monomer, of cis,trans(+)-fisetinidol-4,6-cis,trans(+)-fisetinidol dimer, and the energies of interaction of the conformations of minimum energy of the interaction of monomer and dimer with an elementary crystallite of cellulose I. The conformation of the cellulose crystallite was maintained fixed and the coordinates used were those of Pizzi and Eaton[5] refined from X-ray diffraction results of Chu and Jeffrey[6] and Ham and Williams.[7] The interaction work was conducted according to methodologies already reported.[8] The results were checked also with a constrained force-field program already reported[5,8] and found to be consistent with that reported in Table I. The MM2-87 program capacity had to be increased to work on structures of more than 350 atoms, by small

Table II   Dry IB Strength Results of Interior-Grade Particleboard Prepared Using Tannin Autocondensation Binders

	pH	SiO$_2$ (%)	Pecan Tannin		Mimosa Tannin		Pine Tannin	
			Density (g/cm^3)	IB strength (MPa)	Density (g/cm^3)	IB Strength (MPa)	Density (g/cm^3)	IB Strength (MPa)
On wood alone	5.8	0	0.685	0.15	0.688	0.05	0.680	0.12
	8.2	0	0.706	0.23	0.693	0.03	0.696	0.21
	10.2	0	0.705	0.70	0.699	0.16	0.685	0.46
	12.4	0	0.701	0.69	0.700	0.27	0.703	0.58
	13.5	0	0.715	0.75	—	—	0.699	0.74
With SiO$_2$	10.2	0	0.705	0.70	0.699	0.16	0.701	0.46
	10.2	3	0.713	0.32	0.698	0.48	0.705	0.29
	10.2	6	0.692	0.30	0.699	0.45	0.702	0.26
	10.2	9	0.693	0.30	0.701	0.39	0.695	0.23

programming changes in almost all the subroutines.[8] Changes were also made to the parameter files and these included the incorporation of a variety of dielectric constants and the addition of a line to the torsional parameters that is suitable for π-conjugated systems.[8]

Applied Tests

Duplicate laboratory wood particleboards of dimensions $400 \times 400 \times 12$ mm were prepared by applying 40% (pine, pecan, and mimosa) tannin aqueous solutions with and without SiO_2 at the pH indicated in Table II to industrial pine wood particles to obtain 10% tannin extract solids on solid dry wood. Moisture content of the resinated chips was 21–25%. The boards were prepared by hot pressing at 200°C for 25 s/mm final thickness and for a total pressing time of 7.5 min, with a cycle of 2 min at 25 kg/cm² pressure, 2.5 min at 12 kg/cm², and 3 min at 3–5 kg/cm². The boards were tested, for internal bond (IB) strength dry, board density, and formaldehyde emission, according to the specifications of relevant international standards specifications.[9] Formaldehyde emission results were all zero. IB strength and density results are reported in Table II.

DISCUSSION

The energies of activation, calculated by the Kissinger equation,[3] of the SiO_2-catalyzed and cellulose substrate-catalyzed reactions of tannin autocondensation are shown in Table III. The exotherm peaks reported for pine tannin alone indicate that a variety of reactions occur as the temperature increases. As $Si(OH)_4$ is added to the tannin, certain of these reactions acquire a preponderant importance to the detriment of others. Thus, two of the reactions, those with the lower energy of activation, do not appear to occur anymore, whereas the SiO_2 influence has rendered more favorable the remaining reactions. It is of some importance that some less favored reactions become the most favored by addition of SiO_2 to the detriment of the more commonly occurring reactions that do not appear to occur anymore. The presence of $Si(OH)_4$ has then redirected the pathways of tannin rearrangement in an alkaline environment and at higher temperatures.

Such results appear to confirm that the reaction of the heterocycle pyran ring opening, which can occur in procyanidin (pine) tannins but which is not usually favored in relation to the interflavonoid link cleavage, has, instead, become the most favored one of the two. It also confirms the reduction or total absence of catechinic acid and the phlobatannin rearrangements already observed by other techniques.[1] The known sequence of events[1,10,11] in heterocycle ring opening and interflavonoid link cleavage allows at least a tentative deduction of what reaction steps the exotherms in Table III represent. In pine tannin alone, the first exotherm is likely to belong to the interflavonoid link cleavage reaction (10.4 k cal/mol); the third, to the reaction of interchain autocondensation (202 kcal/mol) that is known to be difficult in procyanidin[1,10,11]; and the fourth, to the easier to occur final step of the catechinic acid rearrangement (13 k cal/mol).[10,12] The second exotherm (ring opening) does not occur anymore on cellulose, indicating that such a reaction has become highly unfavorable. The fifth exotherm, probably the final networking reaction of the resin, has become even more favorable, confirming the preponderance of autocondensation of the tannin

Table III   Maximum Peak Temperatures of DSC Exotherms and Relative Energies of Activation Calculated by Kissinger Equation

	Peak Temperatures (°C)				
Pine tannin alone	94°	107–110.3°	112.6–114.6°	115–117°	143.7–165°
Pine tannin ± 4% SiO_2	—	105–100°	109–112°	—	139–150°
Pine tannin + cellulose	—	—	122°	—	139–150°

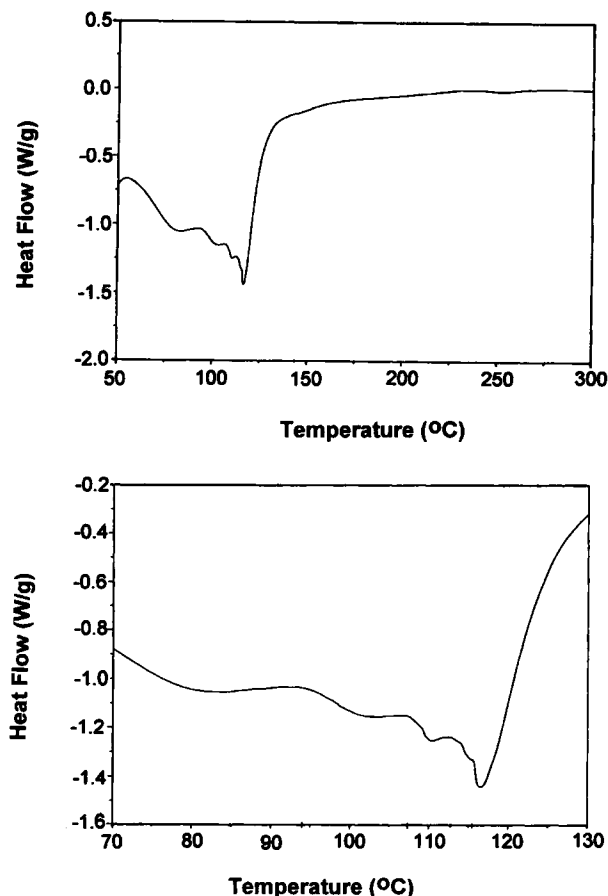|	Activation Energy (kcal/mol)				
Pine tannin alone	10.4	58.4	202.8	13.3	26.2
Pine tannin ± 4% SiO_2	—	36.8	67.1	—	20.2
Pine tannin + cellulose	—	—	8.5	—	3.5
Most likely = reaction	Interflavonoid cleavage	Ring opening	Autocondensation	Catechinic acid rearrangement	—

Figure 1 DSC trace and exotherms of the autocondensation reaction of pine tannin extract on cellulose (pine tannin extract to cellulose ratio = 1 : 1).

under the reaction conditions used. On the basis of the mechanisms already deduced by other techniques, it is possible to confirm the shift in relative importance of the reactions at play. In pine tannin alone, at pH 8 or higher, interflavonoid link cleavage and catechinic acid rearrangements are the reactions occurring with ease and to the greatest extent. As SiO_2 is introduced, heterocycle ring opening becomes favored and the formation of a great proportion of highly reactive C2 sites on the flavonoid units renders much more favorable C2–C8/C2–C6 interchain autocondensations, as already determined by other techniques.[1] The question of $Si(OH)_4$ being, or not being, involved in interchain autocondensation is answered by these results: It needs to be involved as the "pegging" of the reactive C2 sites by —O—$Si(OH)_4$ would cause the complete absence of the catechinic acid rearrangement, as indeed observed from the DSC data and from ^{13}C-NMR results already presented.[1] With the data available, it is not possible to deduce what reaction the fifth exo-

therm represents. The extent of the shifted emphasis in rearrangement pathways induced by $Si(OH)_4$ is shown in Figures 1 and 2.

The catalytic activation and acceleration induced by a cellulose substrate on phenol–formaldehyde polycondensations has been shown[2] to depend on the weakening and consequent easier cleavage of the relevant bonds in phenolic oligomers induced by the sum of secondary forces binding the phenolic molecule to the substrate.[2,8] In tannin autocondensation, the mechanism of the reactions involved indicates that cellulose-induced catalytic activation also occurs: The DSC results in Table III confirm this.

The effect noticeable from the DSC results in Table III is very marked in relation to the acceleration induced by 4% SiO_2. This would be expected as the pine tannin extract-to-cellulose mass ratio that was used was 1 : 1. Thus, the effect of SiO_2 on mass parity is more intense than that of cellulose. The 1 : 1 tannin:cellulose ratio mixed was, however, of importance, as this is approximately the ratio present in a glue line at the adhesive/substrate in-
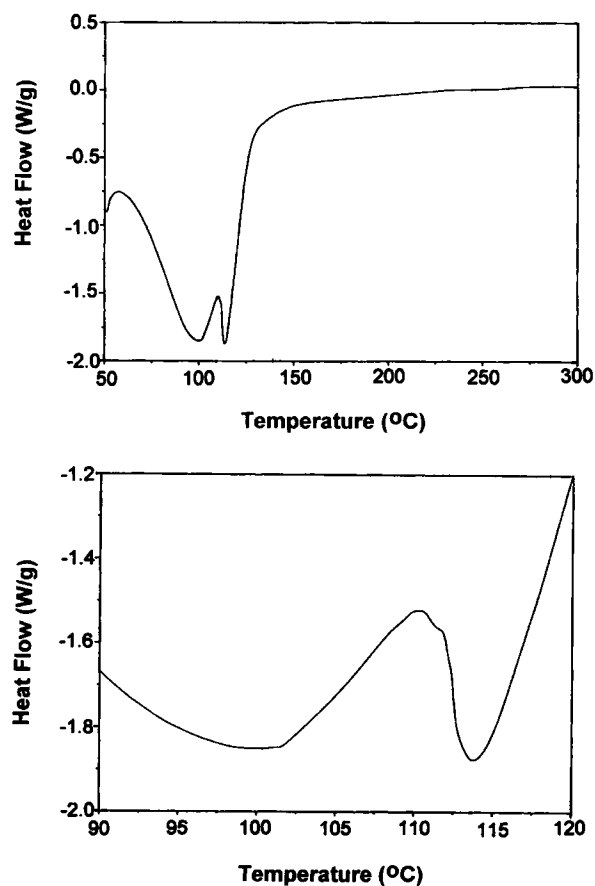

Figure 2 DSC trace and exotherms of the silica-induced autocondensation reaction of pine tannin extract (4% silica on solid pine tannin extract).

terface for wood adhesives. In Table I, the maximum values of the energies of interaction calculated by molecular mechanics[13] between (+)-catechin, a flavonoid monomer, and cis,trans(+)-fisetinidol-4,6-cis,trans(+)-fisetinidol, a flavonoid dimer, on an elementary cellulose I crystallite are reported.[13] The first model is representative of the repeating unit of procyanidin tannins (such as pine), and the second, of a dimer of profisetinidin tannins (such as quebracho and mimosa). In both cases, a significant attractive interaction develops between the flavonoid and cellulose substrate. This indicates that weakening of the relative bonds that need to cleave for the autocondensation to proceed is not only just likely to occur, but that the effect should be quite marked, as indeed observed experimentally.[1] Of particular interest is that the (+)-catechin/cellulose interaction is markedly stronger than that in the case of the fisetinidol dimer. It infers that the cellulose effect on tannin autocondensation is more marked in procyanidin/prodelphinidin tannins, such as pine and pecan tannins, than in profisetinidin/prorobinetinidin ones such as mimosa and quebracho, as also observed experimentally (Table II). This again confirms that in the presence of cellulose under alkaline conditions the polyflavonoid rearrangement pathway is markedly shifted in favor of the pyran ring opening on procyanidin tannins. It is more so than in profisetinidin tannin where the pyran ring opening is, anyway, the more favored reaction even in the absence of cellulose.[11,14] Autocondensation induced by cellulose will then be considerably more evident in procyanidins/prodelphinidins than in profisetinidins/prorobinetinidins, as indeed is the case observed from the dry internal bond (IB) strengths obtained for wood particleboard shown in Table II; the pecan and pine tannin autocondensation binders giving much stronger IBs than does the mimosa tannin binder, when only cellulose-induced activation is used (Table II, results on wood alone).

Of interest in Table II also are the results obtained when both cellulose- and SiO_2-induced activations are used. Boards of excellent IB strength, satisfying the requirements of international standards,[9] are obtained by self-condensation induced just by the cellulose substrate, when using pecan and pine tannins (but not with mimosa tannin), at pHs of 10.2 and higher (Table II). For mimosa, both mechanisms are instead needed. The slower-reacting mimosa benefits, up to a certain level, by the presence of both activation mechanisms: The faster-reacting pecan and pine do not, and the presence of both mechanisms becomes deleterious as seen from

decreasing values of IB strength with increasing SiO_2 percentages.

The acceleration is so intense in this case that progressive precuring of the binder during preparation of the board occurs; hence, the decreasing results observed. The results in Table II represent maximum strengths obtained under the conditions indicated, and, hence, were obtained at long board hot-pressing times: IB strengths are lower at the faster press times significant for industrial application.

In conclusion, the catalytic activation of the autocondensation of polyflavonoid tannins, induced by a cellulose substrate or by any chemical presenting a Lewis acid behavior, such as $Si(OH)_4$, affords the possibility to prepare interior-grade wood binders that do not contain any aldehyde. These are completely naturally derived wood adhesives, presenting no formaldehyde emission, environmentally friendly, and of no toxicity, with the potential to deliver the same performance as currently used interior-grade synthetic wood adhesives.

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