

# Polycondensation and Autocondensation Networks in Polyflavonoid Tannins. I. Final Networks

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**ABSTRACT:** A thermomechanical analysis (TMA) study, directly on a bonded joint during the process of adhesive hardening, on the synergy and interference between polycondensation and autocondensation on procyanidin, and profisetinidin–prorobinetinidin-type polyflavonoid tannins network formation and hardening, confirmed that also at the higher curing temperatures characteristic of the hardening of tannin-based wood adhesives, hardening by polycondensation can be coupled with simultaneous hardening of tannins by autocondensation. Some coreactants appear to depress the tannin autocondensation while still leaving a small contribution of this reaction to the formation of the final crosslinked network. Other coreactants instead appear to enhance formation of the final network by synergy between the 2 condensation mechanisms, while still others do not show any interference between the 2 types of reaction. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 1083–1091, 1998

**Key words:** tannins; polyflavonoids; polymer networks; polycondensation; autocondensation; adhesives; thermomechanical analysis

## INTRODUCTION

Polyflavonoid tannins are natural polyphenolic materials that can be hardened by reaction with formaldehyde.<sup>1</sup> They have now been used for over 20 years as industrial thermosetting tannin–formaldehyde adhesives for wood products.<sup>1</sup> Industrial polyflavonoid tannin extracts are mostly composed of flavan-3-ols repeating units, smaller fractions of polysaccharides, and simple sugars. Two types of phenolic rings having different reactivities with formaldehyde are present on each flavan-3-ol repeating unit, namely, A-rings and B-rings (Scheme 1).

Recently, the radical mechanisms of the reaction of autocondensation and networking to hardened

resins of polyflavonoid tannins induced by bases and by weak Lewis acids has been described.<sup>2–8</sup> The application of such a reaction for the application to wood adhesives of tannins hardened without the use of an aldehyde has also been examined.<sup>9</sup> The results of this latter investigation revealed that, notwithstanding the differences in structure and behavior of different polyflavonoid tannins, effective wood particleboard bonding could be obtained based just on the autocondensation reaction of tannins. The results showed, however, that tannins hardened in this manner only yielded bonds of interior-grade quality,<sup>9</sup> while the reaction of tannins as phenolic materials with formaldehyde has always traditionally yielded weather- and boil-proof networks, hence, exterior-grade bonds.<sup>1</sup> The reasons for such a behaviour has mainly been ascribed to the low crosslinking density of tannin networks obtained exclusively through their reaction of autocondensation.<sup>9,10</sup>

The autocondensation reaction of tannins to yield resins, however, still holds great interest as

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plys, each 0.6 mm thick, bonded with each system for total sample dimensions of  $21 \times 6 \times 1.4$  mm, were tested in nonisothermic mode between 40 and 220°C at a heating rate of 10°C/min with a Mettler 40 TMA apparatus in 3 points bending on a span of 18 mm, exercising a force cycle of 0.1/0.5N on the specimens with each force cycle of 12 s (6s/6s). The classical mechanics relation between force and deflection  $E = [L^3/(4bh^3)][\Delta F/(\Delta f)]$  allows the calculation of the Young's modulus  $E$  for each case tested. As the deflections  $\Delta f$  obtained were proven to be constant and reproducible,<sup>12,13</sup> the values of  $m$  for the resins were calculated.

## DISCUSSION

The results in Tables I and II, showing both the values of minimal deflection after complete curing of the resin in the joint as well as the minimum value of degrees of freedom  $m$  for the completely crosslinked networks yield some interesting conclusions. In the case of tannin alone, the favoring of the reaction of autocondensation by addition of silica yields a more crosslinked network, as shown by the lower values of  $f$  and  $m$ , at both pHs tested for quebracho tannin, which should then considerably benefit as regards hardened strength once silica is added, as already shown by other, applied means.<sup>9</sup> In the case of pine tannin, the improvement is instead very small at the low pH value (pH = 4.5), while addition of silica appears to worsen performance at the higher pH tested (pH = 9.5), with this effect also having been already proven by applied means directly on wood panel products.<sup>9</sup> In the case of the faster tannin, the deduction derived from previous applied work<sup>9</sup> that with fast tannins, the autocondensation reactivity is so high that the hardened network is less crosslinked because it is immobilized earlier on in the reaction, hence, at larger values of  $m$ , appears to be confirmed. Addition of hexamethylenetetramine (hexamine) does not improve the effect of silica on the tannin as the trend is the same as for tannin alone + silica in the case of pine tannin, but it appears to improve the extent of crosslinking in the case of quebracho tannin. Addition of only hexamine to the tannin appears to give only slightly improved results on just tannin autocondensation; but at high pH, it improves considerably the level of crosslinking of the hardened network, an improvement already noticed by applied means<sup>20</sup> by an increase in

hardened network strength. This effect is even more noticeable for quebracho tannin, indicating that slowing down hexamine decomposition by increasing the pH<sup>30</sup> equal to maximizing the charged, unstable methylene bases,<sup>22,31</sup> stability, and increasing the intensity as a nucleophilic of the tannin equals better crosslinking density of the hardened network (within limits).

Paraformaldehyde yields much better hardened networks than hexamine for quebracho tannin, while it yields only slightly improved results for pine tannin (hence, for pine tannin, there is hardly any difference when using hexamine or paraformaldehyde). The improvement when silica is also added are noticeable for pine tannin, indicating that in the case of pine tannin + paraformaldehyde + silica, silica also contributes to final networking. This does not appear to occur in the case of quebracho tannin.

The addition of the paraformaldehyde–urea hardening system yields better results in all cases than paraformaldehyde alone and hexamine alone, indicating that urea participates in the crosslinking mechanism. This would be expected as urea can react with formaldehyde at both the 2 pHs tried, although by a different mechanism, and when added to tannins in moderate amounts, it has long been proven to improve the strength of hardened tannin networks.<sup>10,20</sup> Addition of silica does not improve at all, or very little, the crosslinking density when the paraformaldehyde–urea hardener is used.

In the case of diisocyanate, crosslinking with the tannin, although present, is at a low level, and the good results obtained are mainly due to the reaction of the diisocyanate with water to form crosslinked polyureas and biurets.<sup>10</sup> Addition of silica in this case improves network crosslinking, particularly in the case of the slower reacting quebracho tannin. The diisocyanate + paraformaldehyde hardening system, already used commercially for several years for pine tannin,<sup>10,32</sup> presents different behaviors for the 2 tannins: in pine, unexpectedly, a more flexible hardened network appears to be formed, as a consequence of a majority of crosslinks being urethane bridges formed by reaction of the isocyanate with the methylol groups introduced on the tannin by its reaction with formaldehyde.<sup>10,32</sup> This is an indication that the level of crosslinking of the hardened network, as represented by the value of  $m$ , cannot always be taken as a direct measure of the strength of a bonded joint when an important proportion of a bridge modifying the inherent ri-

**Table I** Deflection  $f$  and Number of Degrees of Freedom  $m$  for Pine Tannin Bonded Joints Hardened Under Different Conditions and with Different Hardening Systems. Degree of Conversion  $p$  on Final Network Formation (on a Total, Possible Final Degree of Conversion  $p = 2^{12}$ ) Starting from Dimer and from Linear Natural Polymer at its Typical  $DPn^{34}$  is Also Reported

Hardening System	pH	$f(\mu\text{m})$		$m$ for Dimer		$m$ for Prepolymer		$p^a$	%	$p^a$	%
		Alone	+SiO <sub>2</sub>	Alone	+SiO <sub>2</sub>	Alone	+SiO <sub>2</sub>				
Pine tannin alone	4.5	23.6	22.2	10.3	9.6	3.06	2.85	1.65	82.5	1.70	85
	9.5	20.3	28.7	8.7	12.6	2.56	3.85	1.78	89	1.52	76
Pine tannin + hexamine	4.5	23.0	22.8	10.0	9.9	2.97	2.94	1.67	83.5	1.68	84
	9.5	18.9	23.6	8.1	10.3	2.34	3.06	1.85	92.5	1.65	82.5
Pine tannin + furfuryl alcohol	2.2	23.3	—	10.1	—	3.02	—	1.66	83	—	—
	4.5	21.0	16.2	9.1	6.9	2.66	1.92	1.75	87.5	2.04	100+
	9.5	19.2	23.2	8.2	10.0	2.39	3.00	1.84	92	1.67	83.5
Pine tannin + paraformaldehyde	4.5	22.7	20.1	9.9	8.7	2.93	2.52	1.68	84	1.79	89.5
	7.2	15.5	16.7	6.5	7.1	1.81	2.00	2.11	100+	2.00	100
Pine tannin + paraformaldehyde + urea	4.5	20.8	18.4	9.0	7.9	2.63	2.26	1.76	88	1.89	94.5
	7.2	14.5	18.9	6.1	8.1	1.66	2.34	2.20	110	1.85	92.5
Pine tannin + MDI	4.5	20.1	21.4	8.7	9.3	2.52	2.73	1.79	89.5	1.73	86.5
	9.5	15.6	17.5	6.6	7.5	1.83	2.12	2.09	100	1.94	97
Pine tannin + MDI + paraformaldehyde	4.5	21.3	19.5	9.2	8.4	2.64	2.43	1.44	72	1.82	91
	7.2	14.4	17.9	6.0	7.6	1.63	2.18	1.40	70	1.92	96
Phloroglucinol monomer-paraformaldehyde	4.5	20.3	—	8.7	—	—	—	—	—	—	—
Control ( $m$ reported is for monomer)				14.0							
Catechol monomer-paraformaldehyde	4.5	47.7	—	—	—	—	—	—	—	—	—
Control ( $m$ reported is for monomer)				—							

<sup>a</sup> When expressed in  $m$ , the degree of conversion  $p$  is expressed on the basis of 2.

**Table II** Deflection  $f$  and Number of Degrees of Freedom  $m$  for Quebracho Tannin Bonded Joints Hardened Under Different Conditions and with Different Hardening Systems. Degree of Conversion  $p$  on Final Network Formation (on a Total, Possible Final Degree of Conversion  $p = 2^{12}$ ) Starting from Dimer and from Linear Natural Polymer at its Typical  $DP_n^{34}$  is Also Reported

Hardening System	pH	$f(\mu\text{m})$		$m$ for Dimer		$m$ for Prepolymer		$p$	$\%$	$p$	$\%$
		Alone	+SiO <sub>2</sub>	Alone	+SiO <sub>2</sub>	Alone	+SiO <sub>2</sub>				
Modified quebracho tannin alone	7.3	25.8	19.1	11.3	8.2	2.93	2.02	1.68	84	1.99	100
	10.3	22.4	17.0	9.7	7.2	2.47	1.73	1.81	91	2.16	100+
Modified quebracho tannin + hexamine	7.3	43.8	20.0	19.5	8.6	5.38	2.14	1.37	69	1.93	97
	10.3	25.6	16.5	11.2	7.0	2.90	1.67	1.69	85	2.20	100+
Modified quebracho tannin + furfuryl alcohol	7.3	22.6	19.9	9.8	8.6	2.49	2.13	1.80	90	1.94	97
	10.3	23.1	18.3	10.0	7.8	2.56	1.91	1.78	89	2.05	100+
Modified quebracho tannin + paraformaldehyde	7.3	18.3	19.2	7.8	8.2	1.91	2.03	2.05	100+	1.99	100
Modified quebracho tannin + paraformaldehyde + urea	7.3	16.6	15.7	7.0	6.6	1.68	1.56	2.19	100+	2.28	100+
Modified quebracho tannin + MDI	7.3	18.3	16.2	7.8	6.9	1.91	1.62	2.05	100+	2.23	100+
	10.3	18.9	14.1	8.1	5.9	1.99	1.34	2.01	100	2.49	100+
Modified quebracho tannin + MDI + paraformaldehyde	7.3	15.9	20.8	6.7	9.0	1.58	2.25	2.27	100+	1.89	95
Phloroglucinol monomer/paraformaldehyde <sup>a</sup>	4.5	20.3		8.7							
Resorcinol monomer/paraformaldehyde <sup>a</sup>	4.5	20.5		8.8							
Catechol monomer/paraformaldehyde <sup>a</sup>	4.5	47.7		14.0							
Pyrogallol monomer/paraformaldehyde <sup>a</sup>	4.5	19.8		17.6							

<sup>a</sup> Controls ( $m$  reported is for monomer).

**Table III Order of Tightness and Descending Strength of Final Crosslinked Networks Measured Through the Value of  $m$  for Different Pine Tannin and Quebracho Tannin Cured with Different Hardeners**


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$m$ Value Achieved for Pine Tannin Alone (for polymer):					
Paraf.~MDI~paraf./urea~MDI~paraf. <hexamine~furfuryl alc. > <i>tannin alone</i> ≤ SiO <sub>2</sub>					
← ————— strong ionic hardening <—//—> pure autocondensation <sup>a</sup>					
$m$ Value achieved for pine tannin + silica (for polymer):					
furfuryl alc.~paraf.~MDI~paraf./MDI~paraf./urea<< <i>tannin alone</i>					
yes <sup>b</sup>	a little	no	yes	no	no
$m$ Value achieved for quebracho tannin alone (for polymer):					
paraf./MDI~paraf./urea~SiO <sub>2</sub> <paraf.~MDI<< <i>tannin alone</i> ~furfuryl alc.<hexamine					
$m$ Value achieved for quebracho tannin + silica (for polymer):					
MDI<paraf./urea~hexamine~ <i>tannin alone</i> ≤furfuryl alc.~paraf.<paraf./MDI					

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<sup>a</sup> paraf. indicates paraformaldehyde.

<sup>b</sup> Yes/no indicates the SiO<sub>2</sub> contribution.

gidity of the network, such as a urethane, is introduced. This will yield a much more flexible network, hence, a greater deflection in bending and a higher value of  $m$ , but, also, a greater strength of the network due to viscoelastic dissipation of energy<sup>33</sup> a fact already noticed from applied results on panel products bonded with this system.<sup>10,32</sup> In quebracho tannin instead, due to its inherently much lower reactivity with formaldehyde, the proportion of methylol groups formed in time to react with isocyanate groups is lower, and, consequently, a lower proportion of urethane bridges is formed, with the adhesive system reverting to the formation of a greater proportion of methylene bridges and, hence, to a more rigid network. Addition of silica does not improve noticeably the crosslinking level and the rigidity of the network either in the more flexible pine tannin based system and also does not improve it (it actually makes it worse) in the already more rigid networks like those obtained with quebracho tannin.

The relative order of the effect of the different hardening systems is the same if one considers the values of  $m$  for the tannin dimer or for the polymer (of typical  $DP_n$ <sup>34</sup>), but their differences are more or less marked in the 2 cases. Thus, in Table III, from the results shown in Tables I and II, one obtains a series of scales of the minimum value of  $m$  obtained as a function of the different formulations used.

The scales in Table III mean that in the case of pine tannin, SiO<sub>2</sub> functions mainly as an accelerator, a catalyst of tannin autocondensation, but which, when all cases are taken into account, does not give higher ultimate strength than the tannin autocondensed without silica. The more evident

change of position in the 2 scales above when adding silica are observed for the paraf./MDI case and the furfuryl alcohol case. In the case of quebracho tannin, it is evident that the presence of silica is a great leveller of the performance of the different hardeners, and that in the absence of silica, the paraf./MDI system yielding the most crosslinked network indicates not only a lower proportion of urethane crosslinks is formed but also that paraformaldehyde appears to react with the —NH— groups of the urethane bridges and with the —NH— groups of the polyureas formed. The order in the scale of quebracho tannin appears to fit well with the applied cured strength results obtained for wood joints bonded with hardened quebracho adhesives,<sup>10,20</sup> in these, paraformaldehyde hardener has always shown to yield much greater strength than hexamine hardener. It is then a balance of the rate of curing in the case of hexamine: too high or equally too low a rate of hardening the worse the strength results and the level of crosslinking of hexamine-hardened quebracho networks are.

In the case of MDI, it is possible to deduce that other crosslinking reactions are superimposed on the system studied by observing that the value of  $p_{gel}$  is higher than 1 (an absurd result otherwise). This is also noticeable in the paraformaldehyde-urea case, confirming what is discussed above for such a hardening system, and in the furfuryl alcohol + SiO<sub>2</sub> case.

In Table IV the gel and start of vitrification temperatures of all the different systems are reported. Two temperatures, namely,  $T_1$  and  $T_2$ , are reported as the curves of the joints elastic modulus increase are always divided into 2 well-defined steps. The  $T_1$  temperature is taken here

**Table IV Gelling ( $T_1$ ) and Vitrification ( $T_2$ ) Temperatures for Different Pine and Quebracho Tannin Hardening Systems**

	Pine Tannin					Modified Quebracho Tannin		
	pH	Alone		+ SiO <sub>2</sub>		pH	Alone $T_1$ (°C)	+ SiO <sub>2</sub> $T_1$ (°C)
		$T_1$ (°C)	$T_2$ (°C)	$T_1$ (°C)	$T_2$ (°C)			
Tannin alone	4.5	95.4	120.1	95.6	132.1	7.3	114.2	96.2
	9.5	81.1	130.1	54.5	122.0	10.3	104.4	61.4
Tannin + hexamine	4.5	67.2	107.8	94.3	181.1	7.3	103.3	122.8
	9.5	99.5	157.2	55.9	128.5	10.3	102.8	62.3
Tannin + furfuryl alcohol	2.2	152.2	190.2	—	—	—	—	—
	4.5	83.4	160.9	111.5	—	7.3	118.3	121.0
	9.5	96.1	152.9	53.6	111.2	10.3	116.0	57.2
Tannin + paraformaldehyde	4.5	95.2	144.8	83.8	104.5	—	—	—
	7.2	72.8	168.4	75.3	128.3	7.3	120.8	104.8
Tannin + paraformaldehyde + urea	4.5	105.9	132.4	100.9	115.8	—	—	—
	7.2	86.8	133.2	75.4	152.4	7.3	121.8	132.6
Tannin + MDI	4.5	99.9	134.2	84.1	143.8	7.3	120.4	105.8
	9.5	104.2	104.2	60.6	115.6	10.3	110.5	60.5
Tannin + MDI + paraformaldehyde	4.5	82.6	—	84.7	139.8	—	—	—
	7.2	72.2	115.1	72.3	121.8	7.3	125.1	109.1

as the flex point of the first step of the modulus curve, hence, of its first derivative first peak. Later work<sup>15,35</sup> has shown that this is not the case, with the gel point corresponding to the first inverse peak of the first derivative curve, thus to the start of the second step of the modulus increase curve. While a good part of the temperature results in Table IV are indicative of what is likely to occur and correspond to what expected from previous applied results, there is considerable variability in the results obtained, indicating that complex, nonpure systems (a mix of flavonoid types) are at play. In general, but not always,  $T_1$  (gel temperature) is higher than  $T_1$  silica at low pHs, where SiO<sub>2</sub> has difficulty in dissolving and might thus retard the reaction, while SiO<sub>2</sub> tends to accelerate (but not always) the systems at the higher pH values tested. The same trends are observed for  $T_2$  (start of vitrification temperature). It is also clear that while the main trends outlined are, in general, respected, there are some other important parameters that have a bearing and that interfere on the results obtained. In general, for the more reactive tannin system (pine), lower gel and hardening temperatures occur. However, a system being faster gelling does not always mean that it yields a strong, more crosslinked network, and vice versa. The predominant observation that

can be made from Table III is that the variability of gel and hardening temperatures observed is due to the different flavonoid species present in each tannin and to the different rates at which they react with each different hardening system. In general, the trends noticed are what would be expected and are consistent with the results in Tables I and II, with some notable exceptions: namely, for pine tannin, the gel temperature  $T_1$  of the hexamine and furfuryl alcohol systems at the higher pH and without SiO<sub>2</sub>, the hardening temperature  $T_2$  for paraformaldehyde at pH 7.2, and the  $T_2$  of all the paraf.-urea and MDI alone cases in presence of SiO<sub>2</sub>. This reflects the fact that these systems are a complex mix of a variety of reactions, which is, indeed, known to be the case. The results for the quebracho tannin appear to be much more regular and the trends are what expected.

In Table V the temperatures at which the minimum value of  $m$  is obtained are shown. In general, the value of  $T_1$  silica is higher than the value of  $T_1$  alone, indicating that in the former case, 2 separate and independent reactions are at play: namely, the ionic hardening polycondensation reaction, and the SiO<sub>2</sub>-induced tannin autocondensation, both radical and ionic. All the data are consistent with what would be

**Table V** Temperatures at Which  $m_{\min}$  is Observed

	Pine Tannin			Modified Quebracho Tannin		
	pH	Alone (°C)	+ SiO <sub>2</sub> (°C)	PH	Alone (°C)	+ SiO <sub>2</sub> (°C)
Tannin alone	4.5	147.0	159.7	7.3	134.8	151.3
	9.5	156.2	169.3	10.3	144.7	121.6
Tannin + hexamine	4.5	151.7	182.1	7.3	110.2	154.5
	9.5	126.7	156.0	10.3	152.3	164.4
Tannin + furfuryl alcohol	2.2	207.4	—	—	—	—
	4.5	177.7	158.2	7.3	144.7	148.8
	9.5	156.9	154.3	10.3	157.1	157.5
Tannin + paraformaldehyde	4.5	125.1	114.1	—	—	—
	7.2	143.0	131.7	7.3	167.4	152.7
Tannin + paraformaldehyde + urea	4.5	149.9	158.4	—	—	—
	7.2	146.2	173.9	7.3	182.0	163.8
Tannin + MDI	4.5	147.7	166.4	7.3	156.2	158.6
	9.5	152.8	154.5	10.3	161.7	154.5
Tannin + MDI + paraformaldehyde	4.5	107.5	173.9	—	—	—
	7.2	89.6	165.8	7.3	159.6	169.3

expected from the reactions involved, from what is already known about them, and with the results in Tables I and II.

## CONCLUSION

In conclusion, all the above confirmed also that at the higher curing temperatures characteristic of the hardening of tannin-based wood adhesives hardening by polycondensation can be coupled with simultaneous hardening of tannins by autocondensation. Some coreactants, such as paraformaldehyde, appear to depress tannin autocondensation while still leaving a small contribution of this reaction to the formation of the final crosslinked network. Other coreactants, such as hexamine, instead appear to enhance formation of the final network by synergy between the 2 condensation mechanisms for the slower reacting tannins, while still others, again, such as hexamine, do not show any interference between the 2 types of reaction for the faster reacting procyanidin tannins.

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