

# Polycondensation and Autocondensation Networks in Polyflavonoid Tannins. II. Polycondensation Versus Autocondensation

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**ABSTRACT:** The curves of increase of modulus as a function of temperature obtained by thermomechanical analysis (TMA) of joints bonded with different polyflavonoid tannins–hardener systems show a succession of different plateaus. Equally, the increase of modulus first-derivate curves show a succession of several peaks. Both the position and extent of the plateaus of the modulus curve as well as the peaks of its first derivate curve show considerable apparent variability in relative intensity and sometime in relative position on the thermogram. This variability appears to be due to the superimposition of the series of polycondensation reactions of the different phenolic nuclei, which constitute the flavonoid repeating unit of each tannin with each different hardener on the pattern of plateaus peaks induced by the noncrosslinked entanglement networks formed by the linear increase of the polymer in the early stages of the polycondensation. This succession of stages in the thermograms is described not only for a procyanidin type and for a profisetinidin prorobinetinidin type tannin, but also on the basis of the TMA results of the polycondensation of simple phenolic model compounds of the tannin nuclei as well as of linear, noncrosslinkable model polymers for the entanglement networks case. The effect of different polycondensation hardeners on the extent of tannin autocondensation indicates that the more marked the polycondensation, the earlier entanglement networks appear, and the lower the temperature at which they appear. Autocondensation is always shown to participate to the formation of the final, hardened tannin network, more or much less markedly, according to the hardener used. The proportion of the network due to polycondensation appears to be related to the extent of water resistance of the final network, while the contribution of tannin autocondensation appears to be only limited to the dry strength of the network. It is also shown that the traditionally accepted “comfortable” correspondence of gel point and start of vitrification with features of the TMA-obtained modulus increase curves loses its significance in complex systems such as flavonoid tannins, in which phenolic sites of greatly different reactivities coexist on the same molecule. A progression of formation and successive tightenings of a network by different mechanisms induced by sites of different reactivity describes better the reality of the situation. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 1093–1109, 1998

**Key words:** tannins; polymer networks; polycondensation; autocondensation; phenols; thermomechanical analysis; entanglement; gel point; rearrangements; polyflavonoids; hardeners; complex systems

## INTRODUCTION AND BACKGROUND

The underlying and immediately evident characteristic of the modulus curves and of the mod-

ulus first derivate curves in most of the experiments reported is the inherent and sometime quite extreme variability in the curves shape. In short, replicate modulus, but particularly, first derivate curves belonging to the same tannin + hardener system, as well as curves belonging to similar cases, often have a very different shape and appearance. Replicate first-derivate curves often present the same relevant

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peaks, at the same temperature, but of completely different relative height. Equally, some peak might disappear, or reduce to a lesser one, or to a shoulder, from being the dominant first derivate peak in another replicate of the same experiment for the same resin + hardener system. Thus, the first overall impression is that no regularity of results exists, that is, no regularity in the progression of modulus increase of the bonded joint. However, replicate curves of the same case, as well as curves belonging to similar cases of clearly identical and/or similar shapes often occur. This indicates that the apparent irregularity in replicate patterns is likely to be due to the overlapping of a number of different effects that exist as a consequence of the complexity of the systems studied.

It was only realized at the end of the total experiments what this superposition of patterns was and what caused the very evident apparent variability. An overview of this has to be presented first, as otherwise discussion and understanding of what occurs becomes too complex to present in just one article. There are 2 main patterns of increase of the joints modulus when tannins are reacted with a hardener, namely, the increase in modulus due to the following:

1. The progress of the polycondensation reaction between tannin and hardener (and in the case of tannin alone, the progress of the autocondensation, which involves the same phenolic nuclei). This pattern is already rather complex as between 2 and 4 phenolic nuclei capable of reacting with the hardener exist in each type of tannin. Thus, in the pine tannin repeating unit, a very reactive A-ring based on the structure of phloroglucinol, and a less reactive B-ring, based on catechol, both occur on each tannin repeating unit. These will react at a different temperature and will then give rise to a number of different plateaus and flex points on the modulus curve (and a series of peaks on the first derivate curve). In the case of quebracho tannin, 2 types of A-ring structure exist, mostly resorcinol, but also phloroglucinol structures, and 2 types of B-ring structure exist namely, pyrogallol and catechol structures. These all have different reactivity and the progression of reactions of each of these with a hardener, from the most to the least reactive as the temperature of the total system increases, causes a progression of plateaus

in the curve of the modulus (and of peaks on the first derivate curve), which are at least dissimilar to the pattern observed for pine tannin.

2. The initial progress of the polycondensation (and autocondensation too) at the lower temperatures leads initially to linear polymers. As the average length of these linear polymers increases to a critical value, depending on temperature and concentration, entanglement networks form, which also give some modulus plateaus and some first derivate peaks. This second pattern is superimposed on the pattern described under pattern (1), above. Furthermore, this pattern is not completely independent but is influenced by the polycondensation in pattern in (1), and vice versa. The temperature of appearance of the entanglement network plateau varies. It depends on the different capability of the different polymers to hang onto the water and to the extent of the polycondensation as regards the reaching of the critical length at which detectable entanglement can occur (it is a balance between the temperature at which entanglement can occur as a function of the length of the polymer chains; the higher the temperature, then the drier the material, and, hence, the shorter the chains that are needed; the lower the temperature, the longer the critical length of the chains needed, and, thus, the greater the level of polycondensation needed to reach the critical length). This is, hence, a pattern of plateaus and peaks that is rather variable.

The first plateau (which sometimes appears as a modulus peak) is generally only due to the entanglement of linear polymers, and the modulus decrease that follows it is generally, but not only, due to the increase mobility as a consequence of the increasing temperature. As polycondensation networking becomes strong enough to overcome this effect, then the value of the modulus increases again to a higher plateau.

Thus, for instance, if pine tannin A-rings react rapidly and linearly to show a modulus curve plateau due to an entanglement network, this is due to the reaction being rapid and the polymer being linear until that point. The increase in modulus which follows, due to the polycondensation crosslinking stage, might then be relatively small (a smaller percentage of the final modulus) in

relation to the preceding increase in modulus. Due to the variety and number of reactive sites and the complex structure of the tannin, the initial linear increase in length due to polycondensation might be lower; namely, tridimensional crosslinking might, for any reason, start to occur earlier in the reaction. The entanglement plateau will then occur at a different, lower temperature or might not even occur at all, depending on what the critical entanglement length of the polymer is at that lower temperature and at that concentration. In this case, as a consequence, a smaller increase in the modulus will or might be observed, followed by a much more evident increase in modulus due to the crosslinking reaction.

Thus, for the first resin + hardener system case, the first modulus increase is as great or greater than the second one, while, in the second case, the first increase in modulus will be much smaller than the second one. Very different first derivate curve patterns will correspond to these two cases: in the first example, 2 peaks of comparable height might appear, while in the second example, the first peak might be much smaller or even be a shoulder of the second, now a much more pronounced peak. The crosslinking level of the final network is, however, the same (hence, very similar final  $m$ ), within the limits of experimental error. It is also clear from the 2 examples that as regards the appearance of the curve of modulus increase, and even more in the case of its first derivate, (1) influences (2) and, vice versa, that (2) also influences (1).

It is the superposition of these 2 basic patterns, and their relative shifting in relation to one another as outlined in the 2 examples above, which gives their inherent appearance of variability to the curves obtained. If the complexity of the reactions due to the different phenolic nuclei of a tannin is added to this basic mechanism, the patterns obtained can become very complex indeed to elucidate.

It is accepted wisdom in TMA experiments on resins that, respectively, the start of the uprise and the flex point in the increase of the modulus curve as a function of temperature, hence, the temperature of its first derivate peak, represent, respectively, the gel point and the start of vitrification of the resin.<sup>1-3</sup> These concepts lose significance in the systems at hand. Where is the real start of vitrification? Is it at the flex point of the increase in modulus caused by the polymer reaching a critical, temperature- and concentration-dependent length sufficient to yield an entanglement network? Or, rather, at the flex point of the

increase in modulus caused by the onset of tridimensional covalent crosslinking, especially when this might depend from the occurrence of the former? The increase in synthetic resins modulus curves is generally smoothed to yield a single flex point,<sup>1-3</sup> which is then the start of vitrification point. This approach is technically acceptable, although conceptually open to debate, in cases in which the initial increase in modulus due to entanglement is small (as in the slow reacting synthetic phenol-formaldehyde resins). Its use, however, does not solve the situation at hand in which the initial entanglement-due modulus increase is often important due to the several different types of very fast reacting phenolic nuclei present. In this case then, all the modulus increases were, and had to be taken into consideration.

## EXPERIMENTAL

### Tannin Extracts Solutions and Control Phenols

Two types of commercial flavonoid tannin extracts were used, namely pine (*Pinus radiata*) bark tannin extract (a procyanidin tannin), from Chile, and quebracho (*Schinopsis balansae*) wood tannin extract (a profisetinidin/prorobinetinidin tannin), from Argentina, the latter modified for use in wood adhesives according to procedures already reported.<sup>4</sup> Tannin extracts water solutions of 40% concentration were prepared by dissolving spray-dried powder of each tannin extract in water and adjusting pH with 33% solution sodium hydroxyde. To these solutions were added 10% of each hardener system on weight of dry tannin extract. Control reactions of the phenolic monomers of different reactivity as model compounds of the different tannin phenolic nuclei, namely, phloroglucinol (1,3,5-trihydroxy benzene), resorcinol (1,3-dihydroxy benzene), pyrogallol (1,2,3-trihydroxybenzene), and catechol (1,2-dihydroxy benzene) with formaldehyde (paraformaldehyde fine powder 96% was used) in the molar ratio of phenol-to-formaldehyde of 1 : 2 and with the phenol prepared at 40% concentration in water. They were finally used for the same purpose as water solutions of a linear vinyl polymer, of carboxymethyl cellulose, and starch, also at 40% concentration in water.

### Thermomechanical Analysis Determination of Average Number of Degrees Freedom of Cured Networks

Recently, work on the formation of polymer networks by photopolymerizable and polyester sur-

face finishes on wood and of polycondensation resins used as wood adhesives has yielded a mathematical relationship<sup>5-7</sup> between the energy of interaction ( $E$ ) at the synthetic polymer-wood interface calculated by molecular mechanics (work of adhesion), the number of degrees of freedom ( $m$ ) of the segment of the synthetic polymer between 2 crosslinking nodes, the coefficient of branching  $\alpha$ , hence, the functionality of the starting monomer, and the relative deflection ( $f$ ) obtained by thermomechanical analysis (TMA) of wood specimens coated or bonded with the adhesive through the expression  $f = km/\alpha E$ , where  $k$  is a constant.<sup>5-7</sup> Regression equations<sup>6</sup> directly correlating  $m$  with  $E$  and  $m$  with  $f$  have been derived for hardened phenol-formaldehyde (PF), resorcinol-formaldehyde (RF), melamine-formaldehyde (MF) and tannin-formaldehyde (TF) resins. These relationships will then be used to correlate the number-average degree of polymerization ( $DP_n$ ) and  $p_{gel}$  with  $m$  for the tannin resins alone and in the presence of the different hardeners used (with and without silica).

To this purpose, the resins above were tested dynamically by TMA on a Mettler apparatus. Samples of beech wood alone, and of 2 beech wood plies of 0.6 mm each bonded with each system for total sample dimension of  $21 \times 6 \times 1.4$  mm were tested in nonisothermal mode between 40 and 220°C at a heating rate of 10°C/min with a Mettler 40 TMA apparatus in three 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 (6 s/6 s). 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>6,7</sup> the values of  $m$  for the resins were calculated.

## DISCUSSION

In Tables I and II are reported the results of the TMA of noncrosslinkable, linear polymers to describe the entanglement effect. By doing the TMAs of noncrosslinkable polymers (Fig. 1) and of the timber alone (Fig. 2), it is clear that the end part (descending) of all the modulus curves is exclusively due to timber degradation and  $T_g$  variation; thus, the increase in  $E$  after 90°C all take place against the lowering of  $E$  of the timber alone; hence, the modulus plateaus and the first derivate peaks appear to be less important than

what they really are (they are more important than what it appears). Starch, for instance, has only 1  $E$  plateau, at 118–123°C, with the rest of the plateaus being exclusively and only timber-related. Furthermore, any plateaus occurring before 90°C are also due to the timber alone, but it is still important to find out the values of  $m$  (or of the moduli) to evaluate the relative contribution to the total modulus of the 2 opposite effects (that of the timber and that of the hardening, or drying in linear polymers, adhesive). As regards entanglement networks of noncrosslinkable linear polymers, only 1 modulus plateau occurs, as well as only a clear well-defined first derivate peak. The temperature at which such a clear first derivate peak appears varies from polymer to polymer. This is so because the level at which the water proportion needs to decrease in order that the length of the polymer can be considered critical for the formation of an entanglement network differs from polymer to polymer. From Tables I and II, it is clear that the temperature of the main, and only clean first-derivate peak depends exclusively on how tight the polymer holds onto the water. For instance CMC, which is known to hold strongly onto water, gives the final entanglement (drying) peak at much higher temperature than the other linear polymers. Thus, the peaks of the tannin alone cases in the tables could be autocondensation plateaus, just entanglement (drying) plateaus, or, most likely, both; or better, 1 plateau will be the entanglement plateau (the first one), and the other ones that follow are likely to be the autocondensation ones.

The patterns of relative modulus curves plateaus shown in Table I correspond well to the patterns of the position of modulus curves flex points defined by the series of first-derivate peaks, as shown in Table III. While the latter often show more peaks than what visible from the former, the former, being simpler, are also somewhat easier to interpret. Thus, from Table I, it is clear that the autocondensation plateaus are at 110 and at 136°C, indicating that the autocondensation plateaus are often very near to be superimposed in the different cases to the first and second reaction characteristic of phloroglucinol with electrophiles. This again confirms that in pine tannin, at the pHs used, the ionic autocondensation route is the most important one,<sup>8,9</sup> also clearly indicating that the reaction functions as the condensation of the carbocation formed by heterocycle opening at C2 with a reactive site on the phloroglucinol A-ring of another flavonoid. The relative percentage values of the modulus (in

**Table I** Temperatures (in °C) of Start of Plateaus for Pine Tannin Modulus Increase Curves, for Simple Phenol Model Compound Controls, for Control Noncrosslinkable Linear Polymer Entanglement Networks, and for the Wood Substrate Alone

System	Relative Modulus	Modulus (GPa)
Tannin alone, pH 4.5	110(80)	136(100)
Tannin alone, pH 9.5	112(86)	123(90)
+Paraformaldehyde, pH 4.5	106(86)	127(100)
+Paraformaldehyde, pH 7.2	98(75)	149(100)
+Hexamine, pH 4.5	107(60)	144(92)
+Hexamine, pH 9.5	100(85)	148(100)
+Furfuryl alcohol, pH 2.2	111(30)	147(100)
+Furfuryl alcohol, pH 4.5	103(80)	137(91) 160(94)
+Furfuryl alcohol, pH 9.5	94(56)	146(63)
+Paraform.-urea, pH 4.5	101(65)	132(40)
+Paraform.-urea, pH 7.2	80(33)	133(93)
+MDI, pH 4.5	86(56)	144(100)
+MDI, pH 9.5	73(32)	[ ↓ 129(89) ]
+MDI-paraform., pH 4.5	107(73)	144(98)
+MDI-paraform., pH 7.2	102(59)	146(100)
Phloroglucinol-form.	103(21)	140(86)
Resorcinol-form.	107(22)	190(100)
Pyrogallol-form.	60(14)	148(100)
Catechol-form.	97(54)	148(97)
Linear vinylic		158(95)
Linear CMC		153(98)
Starch		171(98)
Wood (substrate alone)	25(100)	183(91)
	72(72)	177(100)
		204(100)
		179(95)
		>200
		164(100)
		175(92)
		163
		2.45
		1.17
		1.76
		1.17
		1.51
		2.27
		1.11
		1.67
		1.64
		2.46
		1.75
		1.16 <sup>a</sup>
		1.73
		1.15 <sup>a</sup>
		1.19 <sup>a</sup>
		1.79
		0.49 <sup>a</sup>
		219(86)
		0.74
		0.53 <sup>b</sup>
		0.80
		1.26 <sup>b</sup>
		1.89
		0.45 <sup>b</sup>
		0.68
		0.33
		0.50

The percentages of the final value of the relative modulus for each system reached at each plateau are reported in parenthesis.

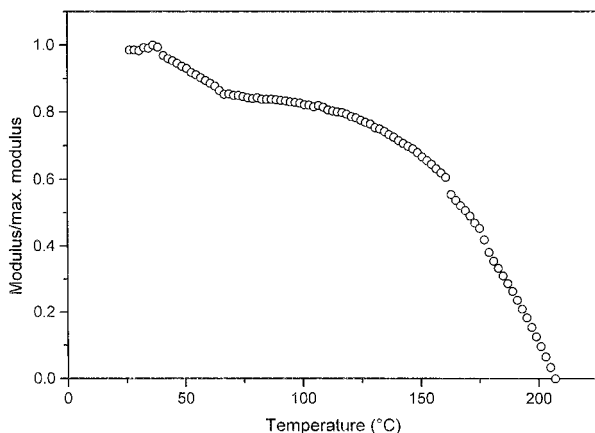
<sup>a</sup> Phloroglucinol-form:  $\alpha = 0.5$ ;  $f = 20.3 \mu\text{m}$ ;  $m = 8.7$ . Resorcinol-form:  $\alpha = 0.5$ ;  $f = 20.5 \mu\text{m}$ ;  $m = 8.8$ . Pyrogallol-form:  $\alpha = 1$ ;  $f = 19.8 \mu\text{m}$ ;  $m = 17.6$ . Catechol-form.  $\alpha = 0.3$ ;  $f = 47.7 \mu\text{m}$ ;  $m = 14.0$ .

<sup>b</sup> Linear vinylic:  $\alpha = 1$ ;  $f = 44.6 \mu\text{m}$ ;  $m = 40.4$ . Starch:  $\alpha = 1$ ;  $f = 52.4 \mu\text{m}$ ;  $m = 47.6$ . Linear CMC:  $\alpha = 1$ ;  $f = 18.7 \mu\text{m}$ ;  $m = 16.6$ .

**Table II** Temperatures (in °C) of Start of Plateaus for Quebracho Tannin Modulus Increase Curves, for Simple Phenol Model Compound Controls, for Control Noncrosslinkable Linear Polymers Entanglement Networks, and for the Wood Substrate Alone.

System	Relative Modulus	Modulus (GPa)
Tannin alone, pH 7.3	128(95)	148(60)
Tannin alone, pH 10.3	118(89)	149(100)
+Paraformaldehyde, pH 7.3	110(39)	145(99)
+Hexamine, pH 7.3	120(100)	159(71)
+Hexamine, pH 10.3	112(62)	152-172(100)
+Furfuryl alcohol, pH 7.3	127(85)	145(99)
+Furfuryl alcohol, pH 10.3	125(89)	145(97)
+Paraform./urea, pH 7.3	114(28)	145(92)
+MDI, pH 7.3	107(39)	158(100)
+MDI, pH 10.3	111(64)	158(100)
+MDI-paraform., pH 7.3	109(46)	160(100)
Phloroglucinol-form.	118(88)	150(97)
Resorcinol-form.	114(60)	171(98)
Pyrogallol-form.	102(59)	183(91)
Catechol-form.	103(21)	177(100)
Linear vinylic	107(22)	204(100)
Linear CMC	60(14)	159(97)
Starch	97(54)	173(100)
Wood (substrate alone)	25(100)	163(91)
	72(72)	150(100)
	90(82)	148(89)
		160(84)
		206(91)
		219(86)
		0.53
		1.26
		0.45
		0.33
		0.50

The percentages of the final value of the relative modulus for each system reached at each plateau are reported in parenthesis.



**Figure 1** Curve of the variation of the ratio modulus-max modulus as a function of temperature of the wood substrate alone.

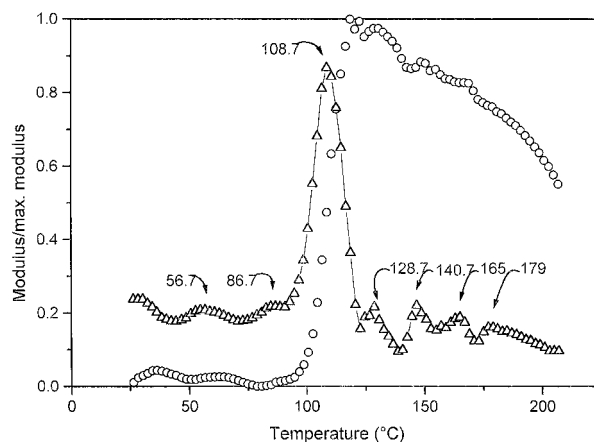
parentheses) also give a very clear indication of the contribution of the different reactions to the total modulus and allow, in combination with the minimum values of  $m$  shown in Table I, the evaluation also of their contribution to the network strength while the network is forming. An interesting point is that the plateaus due to reaction with formaldehyde-type compounds near the autocondensation plateaus occur at a lower temperature, indicating that the polycondensation is always a more effective route to form a network than the autocondensation.

In Tables I, II, and III is given the possible interpretation of the first derivate peak pattern by the reaction of 4 simple phenol models with formaldehyde (Fig. 3). The modulus curves give, in general, 2 noticeable plateaus, one at 100–125°C, and one at 140–175°C. The first one should then be indicative of the gel point, and the second one of the hardening and vitrification of the systems. However, according to accepted wisdom, the flex point in a relative modulus curve, corresponding to a first-derivate peak of the same curve, should correspond to the start of vitrification of the system, and the plateau reached should be the networking and/or vitrification plateau. As a consequence, in the pine tannin modulus curve, the immediate impression is that there are 2 gel points and 2 vitrification plateaus, and these do not belong to the 2 highly reactive phloroglucinol and resorcinol A-rings because only phloroglucinol-type A-rings exist in pine tannin. It would imply that phloroglucinol is present in the tannin in 2 different forms, but this cannot be in the case of the pure phloroglucinol, in which the same effect is also noticed. In the case of the

pure phloroglucinol and/or formaldehyde reaction, and for the pine tannin too, there often are up to 4 first-derivate peaks and 4 modulus curve plateaus.

As a consequence of the behavior of linear non-crosslinkable polymers, and of the behavior of the pure phenols during polycondensation (Tables I and II) under the same conditions, it is interesting to question why the reaction of pure phloroglucinol with formaldehyde, and of pine tannin with a hardener, presents up to 4 first-derivate peaks and why its modulus curve presents up to 4 plateaus in the ascending part of the modulus curve. This is unacceptable on the basis that the start of each uprise corresponds to a gel point, that the flex point of each uprise (corresponding to a first derivate peak) is the start of vitrification, and that the plateaus that follow are the final vitrification (4 gel points + 4 vitrification cannot be the case). The scheme proposed is shown in Scheme 1.

This scheme is valid not only for  $\Phi\text{—CH}_2\text{—OCH}_2\text{—}\Phi$  bridges but also for  $\Phi\text{—CH}_2\text{NHCH}_2\text{—}\Phi$  bridges with the reorganization of the latter type to  $\Phi\text{—CH}_2\text{—}\Phi$  being slower (see hexamine, pH 9.5, peak at 137°C). Also apparent from the table is that the faster the reaction, the higher the proportion of  $\text{—CH}_2\text{OCH}_2\text{—}$  bridges. The final lowering of the modulus is due to the start of wood degeneration<sup>5</sup> (hemicelluloses and lignin) rather than hardened adhesive degradation, and it always start at approximately 175–185°C. All this is schematically shown in Figure 4. In the case of pine tannin, the first derivate peak of the reaction of the low reactivity catechol B-ring is generally



**Figure 2** Curve of the variation of the ratio modulus-max modulus (○) as a function of temperature and curve of its first derivate (△) of joints bonded with a linear noncrosslinked polymer (starch).

**Table III** Temperatures in °C of Clear Peaks for Pine Tannin Modulus Increase First-Derivate Curves, for Simple Phenols Model Compounds Controls and for Control Noncrosslinkable Linear Polymers Entanglement Networks

Tannin alone, pH 4.5	56(5)	—	74(13)	[81(17)]	95(25) <sup>a</sup>	107(18) <sup>a</sup>	121(10)	128(6)	[140]
Tannin alone, pH 9.5	55(9)	—	74(18) <sup>a</sup>	82(18)	95(16)	107(19)	119(11)	131(—)	140(—)
+Parafomaldehyde, pH 4.5	55(5)	66(11)	—	86(21)	95(23) <sup>a</sup>	103(18)	122(12)	—	140(4)
+Parafomaldehyde, pH 7.2	—	69(25)	79(25) <sup>a</sup>	—	93(21) <sup>a</sup>	109(18) <sup>a</sup>	123(16) <sup>a</sup>	131(—)	[142(—)]
+Hexamine, pH 4.5	56(4)	66(7)	71(10)	88(17) <sup>a</sup>	99(16)	—	125(1) <sup>a</sup>	135(8)	147(3)
+Hexamine, pH 9.5	56(5)	66(8)	[77(28)]	86(28) <sup>a</sup>	—	102(4)[↓ 110]	118(5)	132(6)	[147(4)]
+Furfuryl alcohol, pH 2.2	59(—)	—	74(3)	87(6)	—	107(12) <sup>a</sup>	125(18) <sup>a</sup>	137(14)	149(7)
+Furfuryl alcohol, pH 4.5	51(7)	[67(20)]	75(27) <sup>a</sup>	—	90(26) <sup>a</sup>	102(2)	116(9)	140(2)	—
+Furfuryl alcohol, pH 9.5	54(6)	64(11)	80(22)	89(22)	97(26) <sup>a</sup>	109(23) <sup>a</sup>	124(9)	139(5)	150(5)
+Paraform.-urea, pH 4.5	56(3)	—	—	82(8)	—	104(49) <sup>a</sup>	—	138(7)	—
+Paraform.-urea, pH 7.2	52(3)	—	78(34) <sup>a</sup>	89(28)	—	109(26) <sup>a</sup>	125(15) <sup>a</sup>	—	—
+MDI, pH 4.5	57(7)	[65(1)]	73(16)	—	91(19)102(27)	106(27) <sup>a</sup>	120(11)	134(9)	148(2)
+MDI, pH 9.5	51(6)	66(15)	77(18)	—	96(23)	106(26) <sup>a</sup>	123(17)	131(12)	147(3)
+MDI-paraform., pH 4.5	56(7)	—	75(20)	81(28) <sup>a</sup>	98(25) <sup>a</sup> [↓ 99]	—	—	—	—
+MDI-paraform., pH 7.2	[51(15)]	[60(65)]	74(58) <sup>a</sup>	[88(38)]	[↓ 95]	—	119(15)	129(10)	145(2)
+SiO <sub>2</sub> , pH 4.5	54(7)	63(9)	77(17)	—	92(21) <sup>a</sup>	103(23)[110(19)]	124(7)	—	142(5)
+SiO <sub>2</sub> , pH 9.5	51(12)	63(13)	[75(7)]	—	93(4)	104(9)	115(12) <sup>a</sup>	125(12) <sup>a</sup>	138(5)
Phloroglucinol/form.	—	—	76(8)	—	93(34) <sup>b</sup>	104(32) <sup>b</sup>	121(4)	—	144(13)
Resorcinol/form.	—	—	—	—	96(18) <sup>a</sup>	109(40) <sup>b</sup>	122(9)	—	139(—)
Pyrogallol/form.	—	—	—	—	—	102(18) <sup>a</sup>	116(38) <sup>b</sup>	—	141(14)
Catechol/form.	—	—	—	—	—	—	115(5)	—	141(50) <sup>b</sup>
Linear vnylic	—	—	—	89(10) <sup>a</sup>	—	105(11) <sup>a</sup>	116(8) <sup>a</sup>	—	—
Linear CMC	50(1)	63(2)	—	82(6)	92(7)	—	112(35)	122(33)	130(28) <sup>a</sup>
Starch	57(1)	—	—	87(1)	—	109(31) <sup>a</sup>	—	129(1)	141(3)
									165/179

The relative intensities of each first-derivate peak for each system are reported in parenthesis and are normalized to render possible comparison between different systems.

<sup>a</sup> Major first-derivate peaks corresponding to major variations of modulus.

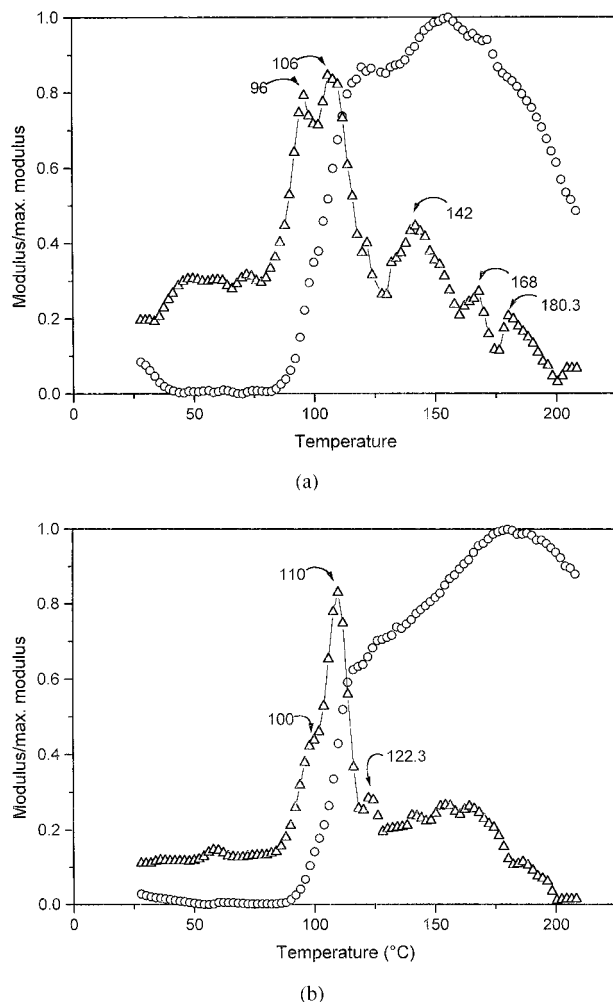
<sup>b</sup> Only for the simple phenols controls: the most intense first-derivate peak.

( ) Relative peak intensity.

[ ] Important first-derivate peaks or shoulders that do not appear in each of the 3 replicate of each experiment.

↓ Important, sudden descending (negative) peak.





**Figure 3** Curve of the variation of the ratio modulus-max modulus (O) as a function of temperature and curve of its first derivate ( $\Delta$ ) of joints bonded with (a) phloroglucinol monomer-paraformaldehyde at pH 4.5 and (b) resorcinol monomer-paraformaldehyde at pH 4.5.

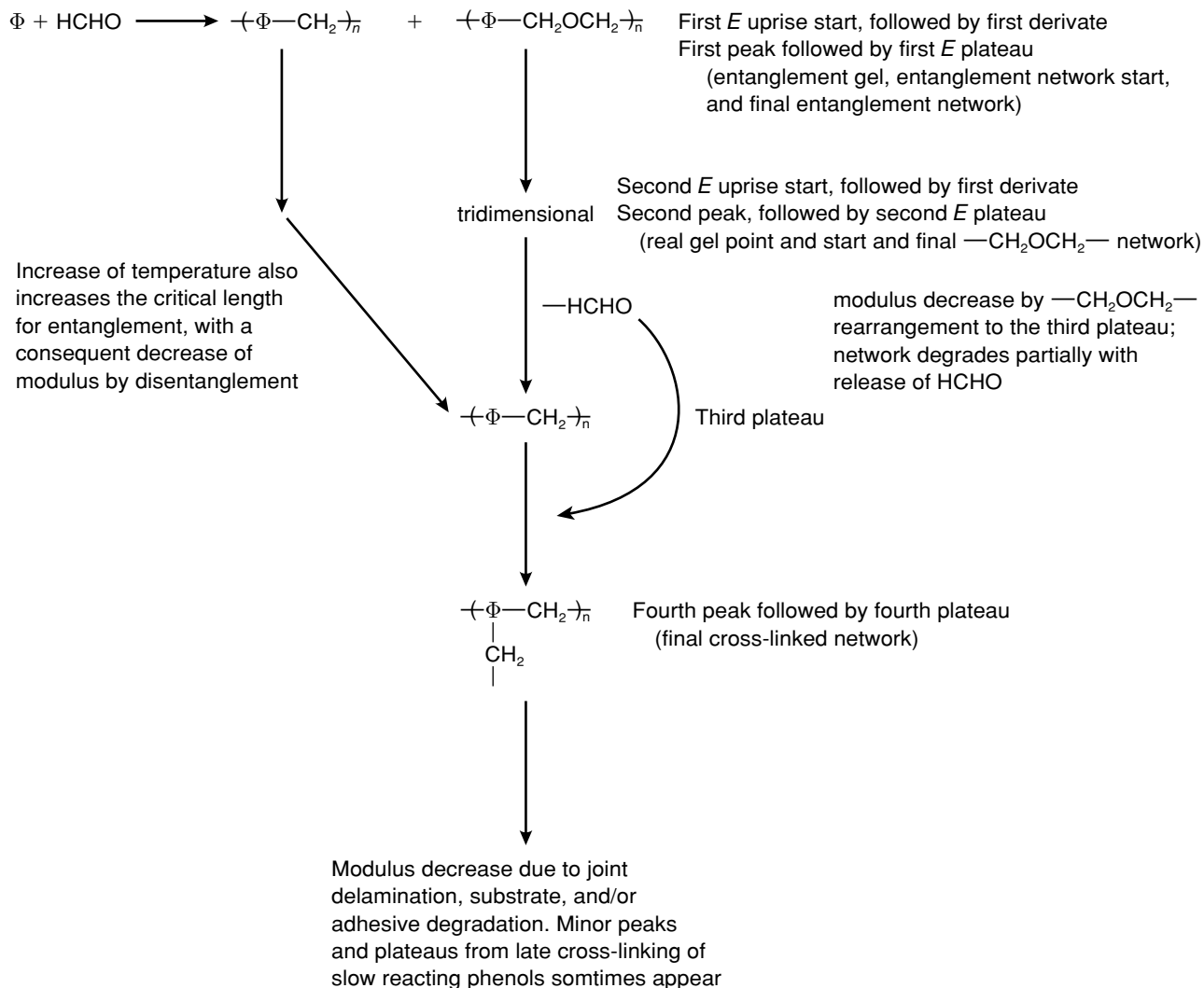
clearly observable at the same temperature as for pure catechol at approximately 140–145°C; thus, it appears as a small peak in the already descending part of the curve, where degradation of the joint substrate is already the most important process.

To evaluate the effect of each hardener under the different conditions of pH used, each single pine tannin + hardener case in the tables must then be discussed in light of the above.

In Tables I, III, IV, and V, the absolute and relative modulus values as a function of the temperature at each step of the curve for pine tannin alone (Table I) and for pine tannin + silica (Table IV) are respectively reported numerically, and the peaks of their respective first derivatives (Table III

for the modulus values in Table I; Table V for the values in Table IV). Also in the tables are the control values obtained for the reaction of paraformaldehyde with the 4 types of constituent phenolic nuclei present in flavonoid tannins, namely, phloroglucinol, resorcinol, pyrogallol, and catechol. This was done to identify which nuclei and what reactions are involved during gelling and curing of pine tannin when using different hardening systems and under different conditions. The first deduction that can be made is that, in general, for both autocondensation (tannin alone case), as well as for tannins hardened by ionic coreactants, the type of nuclei involved appear to be, in general, the same. It is worthwhile to examine the case of paraformaldehyde first because this is the most common hardener used in tannin adhesives. Comparing the case of tannin alone and tannin + paraformaldehyde, both in the absence of silica, 2 points become immediately evident: (1) the intensity of the relative modulus values are different at different stages of the reaction, and, as a consequence, the first-derivate peaks are of different intensities in the 2 cases; and (2) in the reaction with paraformaldehyde, 2 first-derivate peaks, which exist for pure tannin autocondensation, disappear (74 and 128°C), and 1 peak, which was not present before, does appear (at 66–69.3°C). Thus, the peak at 66–69°C is somehow characteristic of the reaction of pine tannin with paraformaldehyde, and also characteristic of this reaction is the increase in intensity of the first derivate peaks at 108 and 153°C. The 66–69°C peak is of lower intensity at pH 4.5 than at pH 7.2 due to the reaction of the tannin with formaldehyde being much slower at the lower pH. It is, however, too unreliable to draw any conclusions from the lower temperature region ( $t < 90^\circ\text{C}$ ) because this is the region dominated by moisture and/or wood substrate effects (Table I). The peak at 108–109°C is generally the peak (shoulder in the case of the modulus curve), which could be smoothed in normal thermal analysis (Fig. 1), but which cannot be in the tannin case due to the different types of reactive phenolic nuclei present in the tannin. Generally, the peak at 130–133°C should be the last to be considered because, afterwards, all the peaks appear to be internal rearrangement peaks.

Thus, comparing the modulus values at pH 4.5 of the tannin alone and of pine tannin + paraformaldehyde, these are in the ratio 1 : 1.04 (Table I), hence, just about identical; and it is then clear that, at least in appearance, the reaction of formaldehyde with the tannin does contribute very

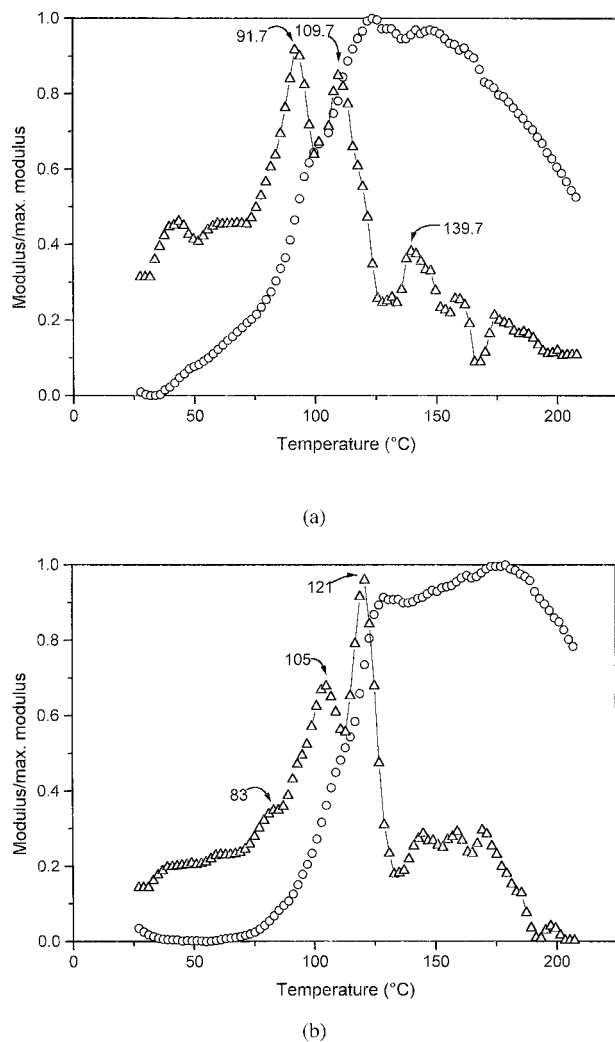


Scheme 1

little, because it is too slow possibly, to the formation and crosslinking of the network, with the exception of the reaction of the 66°C peak, the nature of which is unknown. However, when comparing the same 2 cases at pHs 9.5 and 7.2, respectively, the relative modulus ratio becomes of 1.31, meaning that improving the value of *m* (dimer) from 8.5 to 6.5 (Table I) should improve the strength of the hardened network of at least  $\geq 30\%$ . In reality, this does not mean that formaldehyde contributes only 30% more to the strength of the network. From the results at low pH, approximately half the strength of the network is due to the presence of the reaction between tannin and paraformaldehyde and half to the tannin autocondensation reaction, but the total strength of the network is only  $\pm 30\%$  higher than in the case of the tannin alone, in which only

autocondensation occurs. The conclusion then is that the presence of paraformaldehyde depresses the reaction of tannin autocondensation; hence, the polycondensation reaction depresses the autocondensation reaction simply because they have the same speed and they are in competition for the same reactive sites. At higher pH, the polycondensation predominates, but it is also evident that under normal tannin adhesives hardening conditions, in which paraformaldehyde is the hardener, the autocondensation is still present and contributes a nonnegligible percentage of the total adhesive strength. Thus, autocondensation is depressed by the presence of paraformaldehyde, but it always participates anyway to the hardened tannin adhesive strength.

It is next worthwhile to consider on the same basis the case of hexamine as the hardener of pine



**Figure 4** Curve of the variation of the ratio modulus-max modulus (O) as a function of temperature and curve of its first derivative ( $\Delta$ ) of joints bonded with (a) pine tannin-paraformaldehyde at pH 4.5 and (b) modified quebracho tannin-paraformaldehyde at pH 7.3.

tannin. At pH 4.5, the reaction of decomposition of hexamine is at its fastest,<sup>10</sup> but at this pH, the tannin is very near to its minimum reactivity with an electrophile (and not only with formaldehyde). The sum of these 2 effects leads to the reaction of hexamine with the tannin being slower than the tannin autocondensation, and this is shown by the relative values of  $m$  (previous article,<sup>11</sup> Table I) and by the sum of the first-derivate peaks intensities being lower (Table III). At pH 9.5 instead, comparing the cases of pine tannin alone with the pine tannin + hexamine, it is noticeable that the intensity of the hexamine peaks is greater, indicating a much greater proportion of polycondensation-based crosslinking.

Direct comparison between the paraformaldehyde and hexamine cases, even from Table III, clearly indicate that the hexamine hardened network is less crosslinked than the paraformaldehyde hardened one, but only to a small extent. An interesting point is that the 66°C first-derivate peak is present but is also much less intense in the hexamine case than in the paraformaldehyde case. As the mechanism of hexamine hardening of the tannin is only in small part similar to that of paraformaldehyde, this indicates that the 66–69°C peak corresponds to the formation of reactive hydroxybenzyl alcohol (methylol) groups on the tannin phenolic nuclei, which would considerably increase entanglement and secondary forces of interactions. This would explain why such new peak does not correspond to any peak observed with the simple phenolic model compounds.

As regards the reaction of furfuryl alcohol with pine tannin, a few observations of interest can also be made. The first-derivate traces yield much more distinct and well separated peaks when furfuryl alcohol is present, a clear sign of the lack of interference between the 2 systems. There appear to be no, or erratic, synergy between the silica-based hardening and the furfuryl alcohol-based polycondensation (Tables III and IV). Even more strange is that while it is evident that some of the peaks only belong to the reaction of furfuryl alcohol by itself because they do not appear in any of the other systems, the value of  $m$  decreases<sup>11</sup>; hence, a better crosslinked network is produced, the higher the pH. Thus, 3 pH were tried in this case, namely, pHs 2.2, 4.5, and 9.5, because it is well known that furfuryl alcohol self-condensation occurs mostly at acid pHs.<sup>12</sup> It is then clear that at the more acid pH furfuryl alcohol favors self-condensation and that little or no reaction between tannin and furfuryl alcohol occurs; as the pH increases and furfuryl alcohol self-condensation becomes less favorable, even disappearing altogether at pH 9.5, then the reaction between tannin and furfuryl alcohol starts to occur, and the network produced is then better-crosslinked.

A very clear and distinct first-derivate peak pattern emerges for all the pine tannin + MDI alone cases, indicating a two-reaction system in which the reaction of the isocyanate group with water is the main, dominant component, and in which hardly any reaction of MDI with the tannin is noticeable. The situation becomes quite different in the pine tannin + MDI + paraformaldehyde case, in which superimposed onto a small intensity, almost insignificant tannin + MDI and

**Table IV** Temperatures (in °C) of the Start of Plateaus for Pine Tannin + SiO<sub>2</sub> Modulus Increase Curves, for Simple Phenol Model Compound Controls (Without SiO<sub>2</sub>) and for Noncrosslinkable Linear Polymer Entanglement Networks

										Relative Modulus	Modulus (GPa)
Tannin alone, pH 4.5			103(67)							1.00	1.60
Tannin alone, pH 9.5	75(58)	82(65)		108(67)		125(85)	146(100)			0.77	1.23
+Paraformaldehyde, pH 4.5		81(48)		111(98)	118(100)	126(77)	136(89)	154(99)		1.10	1.76
+Paraformaldehyde, pH 7.2		—		112(86)		127(96)	142(92)			1.33	2.13
+Hexamine, pH 4.5						123(84)	150(99)	163(96)	178(92)	0.97	1.55
+Hexamine, pH 9.5		85(59)				123(87)	142(84)	162(95)	182(100)	0.94	1.50
+Furfuryl alcohol, pH 4.5		92(39)		[108(58)]		126(92)	148(100)	154(100)	175(94)	1.37	2.19
+Furfuryl alcohol, pH 9.5		83(58)		[108(77)]		[128(94)]	147(97)			0.96	1.54
+Paraform.-urea, pH 4.5		99(7)		109(75)		126(87)	148(98)			1.21	1.94
+Paraform.-urea, pH 7.2		94(68)		114(74)		130(88)	141(84)	156(94)	176(96)	1.17	1.87
+MDI, pH 4.5		86(56)				126(80)	140(86)	190(100)		1.04	1.66
+MDI, pH 9.5			105(72)			125(92)	148(100)			1.27	2.03
+MDI-Paraform., pH 4.5	73(32)			108(83)		123(91)	148(97)	158(95)	176(100)	1.14	1.82
+MDI-Paraform., pH 7.2				107(73)		130(91)	150(97)	153(98)		1.24	1.98
Phloroglucinol/form.			102(59)		118(88)			171(98)		1.09	1.75
Resorcinol/form.			103(21)		114(60)			183(91)	204(100)	1.08	1.73
Pyrogallol/form.			107(22)			128(135)		177(100)		1.12	1.79
Catechol/form.						124(68)		173(100)	206(91)	0.46	0.74
Linear vnylic	60(14)	97(54)				124(92)	137(100)	159(97)		0.50	0.80
Linear CMC						127(71)	132(87)	150(100)		1.18	1.89
Starch					118-123(100)	128(99)	148(89)	160(84)		0.43	0.68

The percentages of the final value of the relative modulus for each system reached at each plateau are reported in parenthesis.

**Table V** Temperatures (in °C) of Clear Peaks for Pine Tannin + SiO<sub>2</sub> Modulus Increase First-Derivate Curves, for Simple Phenol Model Compound Controls, and for Control Noncrosslinkable Linear Polymer Entanglement Networks

Tannin alone, pH 4.5	54(7)	63(9)	[77(17)]	—	92(21) <sup>a</sup>	103(23)	[110(19)]	124(7)	142(5)
Tannin alone, pH 9.5	51(12)	63(13)	[75(7)]	—	93(4)	104(9)	115(12) <sup>a</sup>	125(12) <sup>a</sup>	138(5)
+Paraformaldehyde, pH 4.5	54(9)	63(15)	78(22) <sup>a</sup>	—	92(23)	100(31) <sup>a</sup>	110(14)	129(4)	141(—)
+Paraformaldehyde, pH 7.2	[59(27)]	[65(41)]	76(32) <sup>a</sup>	86(21)	—	107(7) <sup>a</sup>	115(10)	130(11)	142(6)
+Hexamine, pH 4.5	53(2)	69(5)	78(10)	[88(21)]	93(17)	106(27) <sup>a</sup>	117(17)	—	139(6)
+Hexamine, pH 9.5	52(16)	65(16) <sup>a</sup>	—	86(8)	99(11)	—	113(10)	125(10)	140(4)
+Furfuryl alcohol, pH 4.5	—	—	71(15)	88(17) <sup>a</sup>	—	101(19)	112(28) <sup>a</sup>	129(12)	143(7)
+Furfuryl alcohol, pH 9.5	50(18)	58(19) <sup>a</sup>	—	86(8) <sup>a</sup>	—	105(12) <sup>a</sup>	115(11)	131(7)	146(3)
+Paraform.-urea, pH 4.5	49(5)	67(12)	79(17) <sup>a</sup>	87(15)	—	103(22) <sup>a</sup>	110(22)	126(13)	138(10)
+Paraform.-urea, pH 7.2	54(7)	69(29)	80(25) <sup>a</sup>	90(24) <sup>a</sup>	—	107(5)	—	126(4)	138(6)
+MDI, pH 4.5	51(8)	61(15) <sup>a</sup>	73(16)	—	91(19)	102(27)	120(11)	134(9)	148(2)
+MDI, pH 9.5	51(6)	66(15)	75(18) <sup>a</sup>	88(18) <sup>a</sup>	—	106(10)	—	128(8)	145(4)
+MDI-paraform., pH 4.5	56(19)	62(15)	75(18)	—	96(12)	108(23) <sup>a</sup>	118(10)	131(9)	151(2)
+MDI-paraform., pH 7.2	54(12)	62(22)	78(28) <sup>a</sup>	—	[↓ 92]	104(20) <sup>a</sup>	[↓ 109]	122(6)	136(6)
Phloroglucinol-form.	—	—	76(8)	—	93(34) <sup>b</sup>	104(32) <sup>a</sup>	121(4)	—	144(13)
Resorcinol-form.	—	—	—	—	96(18) <sup>a</sup>	109(40) <sup>b</sup>	122(9)	—	139(—)
Pyrogallol-form.	—	—	—	—	—	102(18) <sup>a</sup>	116(38) <sup>b</sup>	—	141(14)
Catechol-form.	—	—	—	—	—	—	115(5)	—	141(50) <sup>b</sup>
Linear vnylic	—	—	—	—	—	105(11) <sup>a</sup>	116(8) <sup>a</sup>	—	—
Linear CMC	50(1)	63(2)	—	89(10) <sup>a</sup>	—	—	112(35)122(33)	130(28) <sup>a</sup>	—
Starch	57(1)	—	—	82(6)	92(7)	—	—	129(1)	165/179
				87(1)	—	109(31) <sup>a</sup>	—	—	141(3)

The relative intensities of each first-derivate peak for each system are reported in parenthesis and are normalized to render possible comparison between different systems.

() Indicates relative peak intensity.

[] Indicates important first-derivate peaks or shoulders, which do not appear in each of the 3 replicates of each experiment.

↓ Indicates an important, sudden descending (negative) peak.

<sup>a</sup> Major first-derivate peaks corresponding to major variations of modulus.

<sup>b</sup> Only for the simple phenols controls: the most intense first-derivate peak.

tannin only, only patterns noticeable in the higher temperature region (beyond its first peak at 129°C, then 145, 160, and 176°C), a strong pattern of peaks at 68 and 94°C and a negative peak at  $\pm 95$ –107°C is noticeable, this being valid at both pH 4.5 and pH 7.2 and also in the presence of silica.

A few general considerations on the results shown in Tables I and IV can also be made. In Table I, the first-derivate peak at 80–88°C is predominant in intensity only when nitrogen is present in the crosslinking bridges. The case of pine tannin + SiO<sub>2</sub> at pH = 9.5 in which autocondensation is very evident is the only one in which high-intensity, 51 and 63°C, first-derivate peaks are present. For pine tannin + paraformaldehyde at pH = 7.2, the 4 peaks characteristic of the reaction of phloroglucinol with formaldehyde are all present and are all major peaks. The negative (descending slope) peaks for pine tannin + hexamine and pine tannin + paraformaldehyde are important internal rearrangement peaks of the benzylamine bridges formed, namely,  $-\text{CH}_2\text{NHCH}_2- \rightarrow -\text{CH}_2- + \text{HCHO} + \text{NH}_3$ . As a consequence, the novel systems tannin + furfuryl alcohol + SiO<sub>2</sub> are formulations also worth pursuing. Pine tannin alone also presents some intense first-derivate peaks, which are a consequence of the autocondensation because they correspond to the reaction of the phloroglucinol group, confirming that in this tannin at the pHs used, the ionic autocondensation route is the most important one.<sup>3,4</sup> As regards Table V, silica appears definitely to be of some importance in the case hardened by addition of furfuryl alcohol at pH 9.5, a pH at which furfuryl alcohol does not self-condense. The furfuryl alcohol first-derivate peak patterns are mostly different from the other hardeners patterns; however, in their case, it is clearly the phloroglucinol anion that drives the reaction, even in alkaline pH by reacting with the  $-\text{CH}_2\text{OH}$  group of the furfuryl alcohol.

It is also interesting to observe the results in Table II for the slower quebracho tannin. For quebracho, the autocondensation plateaus start at much higher temperatures (118–128°C and 148–149°C) than pine tannin, and, hence, quebracho should give by autocondensation weaker networks and a worse performance, which indeed the applied results confirm it does.<sup>13</sup> This leaves the polycondensation plateaus much clearer and well distinct from the autocondensation ones than in the case of pine. The first fast phenol gelation peak occurs at a temperature higher than in pine tannin, namely, 109–114°C (against pine's, 101–

106°C), indicating that the main phenol involved in the polycondensation reactions is resorcinol rather than phloroglucinol, in line with the known structure of this tannin<sup>14</sup> and its applied gel time values.<sup>15</sup> The presence of pyrogallol in the B-ring of this tannin is noticeable only in 2 cases, namely hexamine at pH 7.3, and paraformaldehyde/MDI, also at pH 7.3. The less-intense catechol plateau is also noticeable at approximately the same temperature, but phloroglucinol participation is noticeable in several cases by the existence of the plateau starting at 145–149°C, although its contribution to the modulus is small (as would be expected from the small amount of phloroglucinol type A-rings present in this tannin<sup>14</sup>), indicating that, contrary to the thought that in slower reacting tannins, the phloroglucinol is present exclusively as its unreactive "angular tannin" form (thus, with all reactive sites blocked),<sup>16</sup> this is not the case, and that some proportion still capable to react with hardeners is present. In certain cases, such as hexamine at pH 7.2, this is supported by the existence of some other plateaus clearly belonging to phloroglucinol A-rings, such as at 101°C. As regards paraformaldehyde, the main networking reaction is clearly and almost exclusively its reaction with resorcinol-like A-rings. This is also the case for hexamine at pH 10.3, while for hexamine at pH of 7.3, a definite contribution from the reaction of tannin autocondensation is definitely noticeable (120°C). In this latter case, only early reorganization of possibly benzylamine bridges is already observable from the lower modulus values after the 120°C plateau, indicating that better strength performance should be obtained at higher pH with hexamine (as observed with applied results<sup>17–20</sup>). In the case of furfuryl alcohol, in line with the neutral and alkaline pHs used for the reactions, but contrary to the case of the more reactive pine tannin, there is no trace of furfuryl alcohol self-condensation having any influence on the modulus of the total system, with furfuryl alcohol reacting and behaving a bit as paraformaldehyde. At least with quebracho, this hardener should constitute a feasible alternative to paraformaldehyde. Paraformaldehyde/MDI behaves exactly as paraformaldehyde with none of the advantages noticeable by the use of this hardener with pine tannin. In all quebracho tannin cases, in which MDI is present, as well as in all the cases in which hexamine is present, one can notice, or at least they are better distinguishable, the plateaus characteristic of the reaction with the catechol B-rings, but why this should be so is not clear.

In Table VI, the results of quebracho tannin with all the different hardeners in presence of  $\text{SiO}_2$  are shown. The main point that emerges is that the formation of networks occurs, mostly earlier, when  $\text{SiO}_2$  is present. The main conclusion that can be drawn from this is that whatever the type of polycondensation hardener used, the quebracho tannin (and other profisetinidin–prorobinetinidin tannins) rate of hardening and the tightness of the final network formed will always be improved when  $\text{SiO}_2$  is present, a result that confirms what was found previously (in the preceding article).<sup>8,13</sup>

As then polycondensation and autocondensation always coexist during hardening of the tannin by whatever means, it is interesting to compare the apparent, approximate contribution of the 2 types of condensation for the different cases examined. This is shown in Table VII. For quebracho tannin alone, it is clear that polycondensation is by far the predominant reaction (the same being true for other profisetinidin–prorobinetinidin tannins). From applied results previously reported,<sup>13</sup> it is also clear that the higher the value of the modulus (in parentheses in Table VII), due to polycondensation, the greater the water resistance of the finished network. The higher the value of the total modulus (thus, of polycondensation + autocondensation), the greater the dry strength of the joint. Thus for quebracho tannin, in the absence of silica, for autocondensation + polycondensation-dependent total strength of the joint, MDI/paraf.  $\approx$  paraf./urea  $>$  paraf.  $>$  furfuryl alc.  $>$  tannin alone  $>$  hexamine; and for polycondensation-dependant water resistance of the joint, MDI/paraf.  $\approx$  paraf./urea  $>$  paraf.  $>$  hexamine  $\approx$  furfuryl alc.  $\approx$  tannin alone.

It is also clear that addition of  $\text{SiO}_2$  increases autocondensation to an extreme value and that its effect is particularly beneficial to the performance of the weaker formulations. Thus, the approximate proportions of polycondensation to autocondensation in presence of  $\text{SiO}_2$  become 47 : 53%, 69 : 31%, 88 : 12%, and of 36 : 64%, respectively, for the hexamine, paraf.–urea, MDI–paraf., and furfuryl alcohol, all at pH 7.3 (compare with results in the absence of  $\text{SiO}_2$  in Table VII). This also shows why hexamine addition never yields with quebracho tannin (or its equivalents, such as mimosa tannin) an exterior-grade, water-resistant joint.<sup>21</sup> Addition of silica then should be beneficial for the furfuryl alcohol system dry strength, with wet strength remaining unaltered. In pine tannin

**Table VI** Temperatures (in °C) of Start of Plateaus for Quebracho Tannin +  $\text{SiO}_2$  Modulus Increase Curves

	Modulus	
	Relative	(GPa)
Tannin alone, pH 7.3	1.16	1.86
Tannin alone, pH 10.3	1.30	2.08
+ Paraformaldehyde, pH 7.3	1.16	1.86
+ Hexamine, pH 7.3	1.11	1.78
+ Hexamine, pH 10.3	1.35	2.16
+ Furfuryl alcohol, pH 7.3	1.11	1.78
+ Furfuryl alcohol, pH 10.3	1.21	1.94
+ Paraform.–urea, pH 7.3	1.42	2.28
+ MDI, pH 7.3	1.37	2.19
+ MDI, pH 10.3	1.57	2.51
+ MDI–paraform., pH 7.3	1.07	1.71

	123(84)	109(73)	—	84(73)	103(84)	123(89)	123(91) <sup>a</sup>	—	—	148(100) <sup>a</sup>	—	—	1.16
	123(89)	103(84)	—	84(73)	103(84)	123(89)	123(91) <sup>a</sup>	—	—	141(91) <sup>a</sup>	—	—	1.30
	—	—	—	—	—	—	—	134(94)	—	—	151(100) <sup>a</sup>	—	1.16
	116(88)	108(46)	—	—	130(93)	—	—	143(99)	—	143(99)	151(100)	—	1.11
	—	102(83)	—	80(73)	—	—	—	143(93)	—	143(93)	150(95) <sup>a</sup>	160(100) <sup>a</sup>	1.35
	—	—	—	—	—	—	—	—	—	142(98)	150(99) <sup>a</sup>	—	1.11
	—	96(77)	—	—	—	—	—	—	—	145(94)	—	—	1.21
	[120(57)]	[105(26)]	—	80(79)	—	—	—	—	[137(94)]	—	151(99)	159(100) <sup>a</sup>	1.42
	114(74)	[97(44)]	—	[85(10)]	—	—	—	—	—	145(93)	152(98)	162(100) <sup>a</sup>	1.37
	113(81)	—	—	—	129(89)	—	—	—	—	146(97)	151(100) <sup>a</sup>	161(99)	1.57
	—	101(57)	—	81(61)	135(94)	—	—	—	—	139(98)	150(100) <sup>a</sup>	—	1.07

The percentages of the final value of the relative modulus for each system reached at each plateau are reported in parenthesis.

<sup>a</sup> Highest modulus plateau. When two occur there is a decrease of modulus between the two plateaus.

**Table VII** Relative Percentages of the Contribution to the Total Modulus of Polycondensation and Autocondensation for Pine and Quebracho Tannins

	Polycondensation (%)	Autocondensation (%)	Total Modulus(GPa)
<i>Pine tannin</i>			
Tannin alone, pH 4.5	—	100	1.50
Tannin alone, pH 9.5	—	100	1.74
+Paraformaldehyde, pH 4.5	63	37	1.56
+Paraformaldehyde, pH 7.3	89	11	2.28
+Hexamine, pH 4.5	71	29	1.55
+Hexamine, pH 9.5	91	9	1.88
+Paraform-urea, pH 4.5	47	53	1.70
+Paraform-urea, pH 7.3	80	20	2.45
+MDI-paraform., pH 7.3	80	20	2.46
+SiO <sub>2</sub> , pH 4.5	—	100	1.60
+SiO <sub>2</sub> , pH 9.5	—	100	1.23
<i>Quebracho tannin</i>			
Tannin alone, pH 7.3	—	100	1.37
Tannin alone, pH 10.3	—	100	1.58
+Paraformaldehyde, pH 7.3	84	16	1.94
+Hexamine, pH 7.3	55	45	0.81
+Hexamine, pH 10.3	92	8	1.37
+Furfuryl alcohol, pH 7.3	43	57	1.56
+Furfuryl alcohol, pH 10.3	—	—	—
+Paraform-urea, pH 7.3	75	25	2.13
+MDI, pH 7.3	84	16	1.94
+MDI, pH 10.3	88	12	1.88
+MDI-paraform., pH 7.3	91	9	2.22
+SiO <sub>2</sub> , pH 7.3	—	100	1.86
+SiO <sub>2</sub> , pH 10.3	—	100	2.08

instead, it is quite evident that addition of silica is very little, or not beneficial at all<sup>13</sup>:

A general conclusion that can be made is that the more important the polycondensation, the more the entanglement peaks and plateaus move to lower temperature and the more they are less intense. Also, in most cases, the proportion contribution to final joint strength by the autocondensation tends to decrease with a pH increase (Table VII), at least for the more used hardeners, such as hexamine and paraformaldehyde and paraform. mixed with other reactives, this improving the contribution of the polycondensation more than that of the autocondensation.

## CONCLUSION

The curves of increase of modulus as a function of temperature obtained by TMA of joints bonded with different polyflavonoid tannins-hardener systems

show a succession of different plateaus. Equally, the increase of modulus first-derivate curves show a succession of several peaks. Both show considerable apparent variability in relative intensity and sometimes in the relative position on the thermogram due to the superimposition of the series of polycondensation reactions of the different phenolic nuclei with each different hardener on the pattern induced by the noncrosslinked entanglement networks formed by the linear increase of the polymer in the early stages of the polycondensation. The more marked the polycondensation, the earlier entanglement networks appear, and the lower the temperature at which they appear. Autocondensation is always shown to participate to the formation of the final, hardened tannin network, more or much less markedly according to the hardener used. Addition of SiO<sub>2</sub> increases autocondensation, and its addition is particularly beneficial to the performance of the slower reacting profisetinidin and/or prorobinetinidin tannins, such as quebracho tannin, and of the weaker formulations thereof.



It is also clear that in complex systems in which reactive sites of very different reactivity coexist on the same molecule, such as phloroglucinol and catechol on a flavonoid tannin unit, the traditional identification of gel point and start of vitrification from features of the TMA modulus curve loses its accepted significance. In the context, for example, of a four-step modulus increase curve, the effective gel point temperature cannot be the temperature of the first start of the uprise because this is most likely the pseudo gel point yielded by the start of the entanglement network formation. Equally, the first-derivate first peak for the first modulus curve step, hence, the first flex point of the modulus curve, cannot be the start of vitrification but only the start of immobilization of a purely entanglement network. The successive flex points and plateaus on the modulus curve clearly indicate that the "comfortable" concept of the correspondence of gel point and start of vitrification developed for single-step modulus increase curves is grossly inadequate for multistep modulus increase curves. It also infers that the concepts of gel point and, particularly of vitrification in relation to modulus curves of complex systems, must be reevaluated and redefined. A complex system, as those presented, cannot present 4 gel points and 4 start of vitrification points. It is clear that the modulus curve flex points, hence, the first-derivate peaks, represent (1) first (when it can be observed), the rigidification of an entanglement network of linear polymers, hence, a pseudovitrification; (2) second (or the first if the previous one is absent or not noticeable), the real start of vitrification due to the start of covalent tridimensional crosslinking induced by the more reactive sites of the molecule (phloroglucinol and resorcinol A-rings in the case of the tannins); and (3) the further tightening of the network induced by the reaction and further crosslinking of the less reactive sites present on the same molecule.

Thus, in complex systems, gel and vitrification appear to be rather senseless concepts, while one should rather talk of progressive formation and further tightening of a network by a series of the following successive mechanisms: entanglement

followed by first crosslinking, followed by further crosslinking through less-reactive sites.

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## REFERENCES

1. S. Yin, X. Deglise, and D. Masson, *Holzforschung*, **49**, 575 (1995).
2. R. Riesen and H. Sommerauer, *Anal. Lab.*, **15**, 30 (1983).
3. K. Hofmann and W. G. Glasser, *Thermochim. Acta*, **166**, 169 (1990).
4. A. Pizzi and A. Stephanou, *J. Appl. Polym. Sci.*, **51**, 2109 (1994).
5. F. Probst, M.-P. Laborie, A. Pizzi, A. Merlin, and X. Deglise, *Holzforschung*, **51**, 459 (1997).
6. A. Pizzi, *J. Appl. Polym. Sci.*, **63**, 603 (1997).
7. A. Pizzi, F. Probst, and X. Deglise, *J. Adhes. Sci. Technol.*, **11**, 573 (1997).
8. R. Garcia, A. Pizzi, and A. Merlin, *J. Appl. Polym. Sci.*, **65**, 2623 (1997).
9. N. Meikleham, A. Pizzi, and A. Stephanou, *J. Appl. Polym. Sci.*, **54**, 1827 (1994).
10. J. F. Walker, *Formaldehyde*, Reinhold, London, 1964.
11. R. Garcia and A. Pizzi, *J. Appl. Polym. Sci.*, to appear.
12. N. Meikleham and A. Pizzi, *J. Appl. Polym. Sci.*, **53**, 1547 (1994).
13. A. Pizzi, N. Meikleham, B. Dombo, and W. Roll, *Holz Roh Werkstoff*, **53**, 201 (1995).
14. I. Abe, M. Funaoka, and M. Kodama, *Mokuzai Gakkaishi*, **33**, 582 (1987).
15. A. Pizzi, *Advanced Wood Adhesives Technology*, Marcel Dekker, New York, 1994.
16. A. Pizzi, *Wood Adhesives, Chemistry and Technology*, Marcel Dekker, New York, 1983.
17. A. Pizzi and P. Tekely, *Holzforschung*, **50**, 277 (1996).
18. H. Heinrich, F. Pichelin, and A. Pizzi, *Holz Roh Werkstoff*, **54**, 262 (1996).
19. A. Pizzi, P. Stracke, and A. Trosa, *Holz Roh Werkstoff*, **55**, 168 (1997).
20. S. Wang and A. Pizzi, *Holz Roh Werkstoff*, **55**(3), 174 (1997).
21. A. Pizzi, J. Valenzuela, C. Westermeyer, *Holz Roh Werkstoff*, **52**, 311 (1994).