Rheology of Polyflavonoid Tannin–Formaldehyde Reactions Before and After Gelling. II. Hardener Influence and Comparison of Different Tannins

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ABSTRACT: Good correspondence of the gel-time values obtained by two different methods, $G' = G''$ and $1/\eta_0 \rightarrow 0$, was observed for different types of natural and modified tannin extracts. The pH presents the predominant effect on both the activation energies and the gel times observed, while the proportion of a paraformaldehyde hardener has a much lesser effect on these parameters. The rate constants of the different phases of the reaction of polycondensation with formaldehyde, both before and after the gel point, were obtained for the six commercial tannin extracts tested. The viscoelastic properties of the different tannins/formaldehyde gels were measured. The gel stiffness S, relaxation coefficient n, and relaxation time λ were determined and their dependence on the proportion of the formaldehyde hardener, on the temperature, and on the type of tannin was determined. The gel stiffness S appears to be influenced considerably by the proportion of the formaldehyde hardener. Its value decreased as the percentage of the hardener increased: This was due to early network immobilization and the resulting lower level of crosslinking resulting from it. The influence on S of the temperature is not very pronounced. The relaxation coefficient n appears to depend mainly on the reactivity of the tannin used: The faster reactivity, the higher was the value of n. This appears to be valid exclusively in tannin extracts where the colloidal state is still present, while it is not valid in extracts where the colloidal state was eliminated by, for example, solvent extraction. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 864–871, 2002

Key words: rheology; polyflavonoids; adhesives; resins; polycondensation; gelation; networks

INTRODUCTION

After having defined, sorted out, and sometimes even modified the relevant calculation and measurement methods for the polycondensation reaction of mimosa tannin extract with 5% paraformaldehyde before, at, and after the gel point, the predefined methods[1] were used to compare different natural and modified commercial polyflavonoid tannins. Thus, the methods were used to test the rheological characteristics of the reaction with formaldehyde of (i) a pure procyanidin tannin, natural pine bark tannin extract[2,3]; (ii) a predominantly prodelphinidin tannin (8:1 prodelphinidin:procyanidin mass ratio[3,4]), natural pecan nut membrane tannin extract; (iii) two prorobinetinidin/profisetinidin mixed tannins, namely, natural mimosa and quebracho tannin extracts, although of somewhat different prorobinetinidin/profisetinidin ratios and secondary structure[5–8]; (iv) a pure quebracho tannin obtained by carbohydrate elimination by solvent extraction of the correspondent natural extract[9–13]; and (v) a modified commercial quebracho tannin adhesive intermediate obtained by a series of acid/base hydrolysis and other treatments.[14,15]

EXPERIMENTAL

The polycondensation reactions with formaldehyde of water solutions of commercial polyflavonoid tannin extracts of mimosa (*Acacia mearnsii*) bark tannin extract, natural quebracho (*Schinopsis balansae*) wood tannin extract, pine (*Pinus radiata*) bark tannin extract, pecan (*Carya illinoensis*) nut membranes tannin extract, and, furthermore, of two modified quebracho tannin extracrs, exactly as reported in the Experimental section of the preceding article,[1] were carried out.

The solutions were tested with a Rheometrics controlled stress rheometer RS-500 with parallel-plate geometry for all the measurements; the plate diameter used was 40 mm and the gap in between the parallel plates was 0.3 mm. A humidity cover plus a solvent trap based on a film of silicone oil applied to the perimeter of the plates were used to prevent solvent evaporation.

In reference to the preceding article,[1] during oscillatory rheological measurements, the shear was applied sinusoidally at a deformation amplitude (γ_{max}) of 5%—hence, sufficiently weak not to destroy the

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TABLE I
Effect of Percentage Paraformaldehyde Hardener on the Gel Time and Energy of Activation of Mimosa Tannin Extract–Formaldehyde System

Percentage	Gel times (s)					Activation energy (kJ/mol)
	Temperature (°C)					
	65	70	75	80	85	
5% HCHO	6657	3680	2250	1275	760	108.6
8% HCHO	5071	2852	1869	947	522	113.5
12% HCHO	4573	2400	1533	738	410	120.6

structure of the gel or of the network which forms as the tannin–formaldehyde reactions proceed. For each tannin, the measurements were repeated at four to five different temperatures and at five different frequencies. From these measurements, the in-phase elastic modulus G', the out-of-phase viscous modulus G'', the complex modulus G^*, and the complex viscosity η^* were obtained. Their values extrapolated to zero frequency were used. The measurements at five different angular frequencies correspond to five values of viscosity, which, reported as a function of the frequency, allow the calculation by linear regression of the viscosity at zero frequency η_0^*, obtained from the value of the intersection on the y axis. The moduli at zero frequency, G_0', G_0'', and G_0^*, are also obtained in the same manner during the whole polycondensation reaction, before and after the gel point. The coefficient of correlation of these linear regressions was never lower than 0.94.

RESULTS AND DISCUSSION

An increase in the proportion of the paraformaldehyde hardener on the mimosa tannin–formaldehyde reaction results in shorter gel times. This effect is clearly shown in Table I, where the gel point was calculated by the $1/\eta_0 \to \infty$ method. In the same table, one can note the influence of the formaldehyde proportion on the energy of activation of the reaction, with the energy of activation increasing slowly from 5 to 12% paraformaldehyde. The higher the proportion of formaldehyde, the faster is the reaction, leading to earlier immobilization of the network and to diffusional problems.

As in the case of the mimosa tannin extract, it is interesting to compare the gel points of the other tannins obtained by the same rheometry method. One point that must be made clear first is that, as for all phenol–formaldehyde reactions, the gel time of a tannin–formaldehyde system depends markedly on the pH. The choice was then either to keep all the gel times of the tannins at the same pH, results which are already available by other techniques,[15] or to keep the gel times at the operational pH's at which the tannins are used industrially for this application. The second approach was chosen (see the Experimental section for the pH of the different tannins used) as the difference in reactivity between different tannins is well known to be quite considerable[16–18]; corrections of the pH are given in the Experimental part. This notwithstanding, a definite range of temperatures, different for each tannin, had to be chosen to take into account the still very marked differences in their reactivity. In Table II are reported the comparative values of the gel time for the different tannins calculated by the method $G'_0 = G''_0$, and in Table III are reported the same obtained by the $1/\eta_0 \to \infty$ method. Not only is there good correspondence of the results obtained by using the two methods, but the trends outlined are, further-

TABLE II
Gel Times and Energy of Activation of Different Tannin–Formaldehyde Systems Obtained by Rheology Method 1 ($G' = G''$)

Temperature (°C)	Gel times (s) $G' = G''$ method					
	Pecan	Pine	Mimosa	Natural quebracho	Quebracho QS	Quebracho adhesive intermediate
40	5765					
45	3325	7695				
50		4105				
55	865	2105				7045
60	410	1050				4205
65			6625			2535
70			3730	11,575		1570
75			2275	7105	15,230	965
80			1285	4805	9280	
85			745	3135	5415	
90					2045	
Activation energy (kJ/mol)	109.3	116.9	114.8	96.4*	137.5	94.1

*Activation energy calculated without anomalous result at 65°C (not presented).[18]

TABLE III
Gel Times and Energy of Activation of Different Tannin–Formaldehyde Systems
Obtained by Rheology Method 2 ($1/\eta_0 \to 0$)

Temperature (°C)	Gel times (s) $1/\eta \to 0$ mMethod					
	Pecan	Pine	Mimosa	Natural Quebracho	Quebracho QS	Quebracho Adhesive Intermediate
40	5767					
45	3380	7770				
50		4046				
55	889	2087				7020
60	402	1070				4173
65			6657			2572
70			3680	11,335		1553
75			2250	7016	15,321	948
80			1275	4939	9335	
85			760	2246	5601	
90					2159	
Activation energy (kJ/mol)	108.6	116.3	115.2	107.4*	133.9	94.7

*Activation energy calculated without anomalous result at 65°C (not presented here).[18]

more, supported by the applied FESYP standard test which compares the times needed to reach gelling at 100°C,[15,19] which gives the following results:

pecan < pine < quebracho adhesive intermediate
  58s   74s   207s

< mimosa < natural quebracho < quebracho QS
   368s   1444s   2314s

As regards the activation energies of the reactions, considering the reactivity of the different tannin systems, one needs to strictly use the same interval of temperature. But due to the considerable difference in reactivity, this has not been always possible. Thus, the activation energies for pine and pecan tannin are comparable but they are not comparable with the activation energy of the less reactive mimosa tannin which was determined at a higher temperature range. The activation energies of natural mimosa and quebracho tannin extract can be compared, but the result obtained is the inverse of what would be expected from the results obtained by other techniques for these two tannins.[15,20] There are two possible reasons for this anomalous result: (i) The DPn of quebracho is 6.5, while that of mimosa is 4.9.[9,21] Thus, the quebracho tannin molecule will become immobile earlier and the reaction will present a lower energy of activation. This explanation is very doubtful as quebracho polyflavonoids are known to undergo depolymerization reactions by cleavage of the interflavonoid bonds simultaneously to the polycondensation with formaldehyde.[8,22–24] (ii) The polymeric carbohydrates are in greater proportion and of much higher molecular mass in quebracho tannin extract, conferring to it a much more marked colloidal behavior than that of the mimosa tannin extract.[9,11–13,24–29]

It has also been shown that the addition of polymeric carbohydrates to synthetic phenolic resin confer to these a colloidal behavior and that this shortens the gel time considerably: It almost halves the gel time of a phenolic resin[30] due to the high concentration of reagents within the micelles and lowers considerably the reaction's energy of activation. There might be a contribution due to this characteristic to the lower energy of activation of the more colloidal quebracho extract. This effect has an evident counterpart in the markedly higher activation energy and slow gelling rate of the quebracho QS tannin, which had no colloidal character whatsoever due to the removal of all carbohydrates by organic solvent extraction. The contribution of the colloidal state is not the predominant effect in the adhesive intermediate, where chemical treatment has considerably decreased by hydrolysis of the polymeric carbohydrates, but has not completely eliminated, the colloidal characteristics of the tannnin extract. The adhesive intermediate is used at a pH of 7.4—hence, at a pH at which the rate of reaction of any tannin with formaldehyde is considerably higher. It is the predominance of the higher pH effect that causes the much lower activation energy and gel times observed in Tables II and III.[15]

In Figure 1(a,b) is shown the variation of the rate constants k_1 and k_4, respectively, before and after the gel point, as a function of the temperature and of the % paraformaldehyde hardener used. The trends outlined by these two rate constants as a function of the percentage hardener are the same as what was obtained for the rate constants k_2, k_3, k_5, and k_6 and the values of these are stored elsewhere.[18] Figure 1(a)
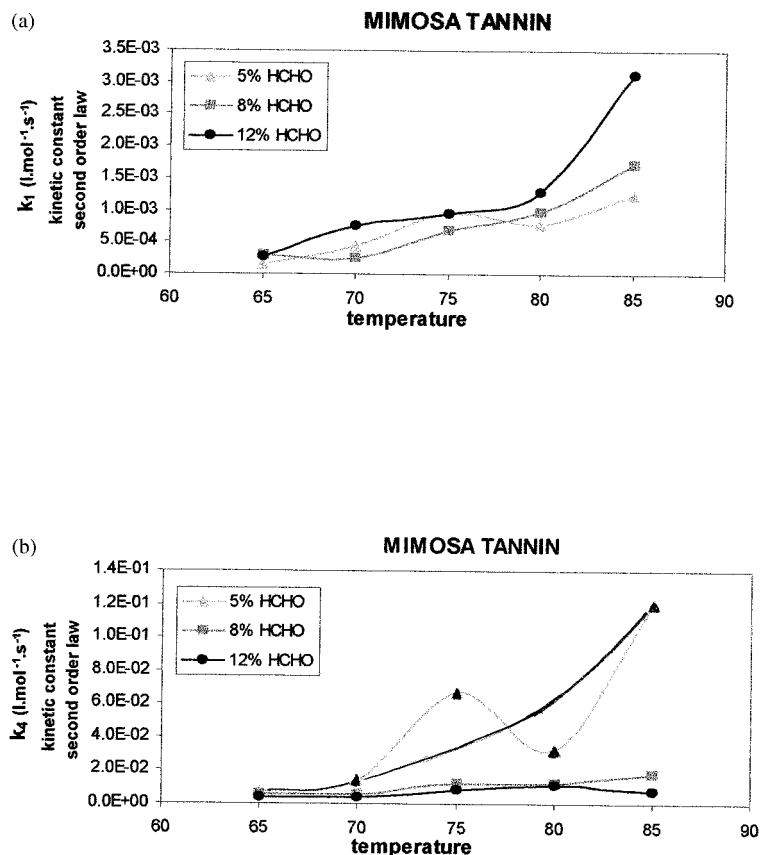
Figure 1 Influence of the proportion of paraformaldehyde hardener [(▲) 5%, (■) 8%, and (●) 12% on mimosa tannin extract solids] on the value of the second-order rate constant: (a) variation of rate constant k_1 of the first reaction phase well before the gel point; (b) variation of rate constant k_4 of the first reaction phase immediately after the gel point.

indicates that, before the gel point, the reaction becomes faster the higher the proportion is of the formaldehyde hardener used, as would be expected. Figure 1(b), instead, indicates that, after the gel point, the reverse trend applies: The reaction is faster at a lower proportion of the hardener. This is again an effect of the early immobilization of the network at a higher hardener proportion and of the consequent diffusion problems.

As regards the rate constants for the different tannins, it is interesting to remark that the characteristic $k_1 > k_3 > k_2$ second step slowdown of the reaction before the gel point noticed for the mimosa tannin extract occurs only for quebracho, the only other profisetinidin/prorobinetinidin tannin, and its derivatives quebracho QS and quebracho adhesive intermediate.[18] For the faster-reacting procyanidin- and prodelphinidin-type pine and pecan tannin extracts, only two phases exist: the phase corresponding to the k_2 failing to occur and the reaction accelerating before the gel point; hence, $k_3 > k_1$. After the gel point, the rate constants were calculated both on the basis of a second-order law as well as on the basis of a diffusion-controlled model, with similar trends being noted.[18] While a few interesting observations could be made,

such as that pecan tannin, being faster before the gel point than is pine tannin, becomes slower after the gel point, the trends of the different rate constants (reported elsewhere[18]) after the gel point are rather confused. The only remark that can be made is that diffusion, oligomer size, and possibly other not easily identifiable factors are at play, rendering impossible, with the data available, any generalization of conclusions as regards the rate constant trends after the gel point.[18]

Viscoelastic properties of gel

As the tannin–formaldehyde reaction proceeds, the reaction mix passes from a viscous liquid state to a gelled rubber and, eventually, to a gelled glass state. Already at the gel point, the reaction mix neither behaves any more as a viscous liquid nor yet as a gelled glass, but is in a viscoelastic state called a critical gel.[31] Critical gels exhibit an unusually simple and regular relaxation behavior, which can be described by a simple power law[32–37]:

$$G(t) = St^{-n} \tag{1}$$

where S is commonly called the gel stiffness and n is the critical relaxation exponent. It has been shown[38,39]
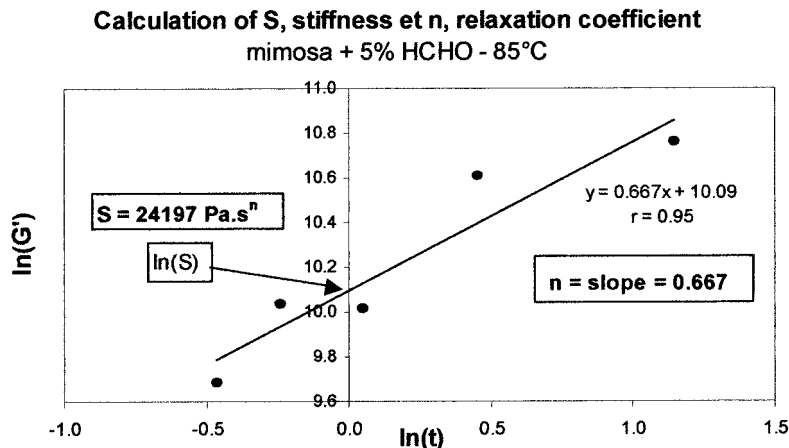
Figure 2 Example of graphical determination of the critical gel stiffness S and of the relaxation coefficient n for the mimosa tannin extract + 5% paraformaldehyde system reacted at 85°C.

that the critical gel state is fragile when the gel stiffness S is low and the relaxation coefficient n is high (i.e., $n \rightarrow 1$). Vice versa, the critical gel is rather stiff when S is high and n is low (i.e., $n \rightarrow 0$). The mathematical expression correlating S and n derived from these experimental observations is

$$S = G_0 \lambda_0^n \quad (2)$$

where G_0 is the modulus of the polymer plateau—hence, the modulus of the final crosslinked network, and λ_0 is the time of the highest relaxation of the molecular precursor, equally defined as the relaxation time at the gel point ($G' = G''$).[40,41] Lower values of λ_0 indicate the presence of a high proportion of short linear oligomers, while higher values of λ_0 indicate a higher proportion of longer oligomers. At the gel point, λ_0 is obtained experimentally from the viscosity at zero frequency η_0 equal to the product $G_0 \lambda_0$. The problem with this approach is that the rheometer is limited by its maximum torsion couple. Thus, the highest value which can be measured for the elastic modulus G'_∞ is imposed by the equipment used and

corresponds to the highest value of the torsion couple of the rheometer. The elastic modulus of the final polymer network is then quite likely higher than G'_∞, but the technical limit characteristics of the rheometer do not allow measurement of the real value of the elastic modulus of the totally networked polymer. It is for this reason that, in this study, λ_0 is calculated from the zero-frequency viscosity η_0 experimental data.

The gel stiffness S and the relaxation coefficient n were determined as shown in Figure 2, by reporting the value of the elastic modulus G'_0 at the five frequencies used as a function of these frequencies. It is possible and easier (Fig. 2) to model, with good correlation, the increase of ln G'_0 as a function of ln(t). The linear equations for the influence of the amount of the hardener in the case of mimosa tannin and for the influence of the different tannins were calculated, and from these, the values of S, n, and λ_0 were obtained. These are shown in Tables IV and V. The influence of the temperature in the range studied is not very pronounced as the variations observed do not show a definite trend for S, n, or λ_0 (Table IV). The influence of the percentage paraformaldehyde added appears to

TABLE IV
Dependence of the Values of Gel Stiffness S, Relaxation Coefficient n, and Relaxation Time λ_0
from the Percentage Paraformaldehyde (Mimosa Tannin Extract)

Measurement		Temperature (°C)					Average value
		65	70	75	80	85	
S gel rigidity (Pa.s)	5% HCHO	26,397	25,235	26,239	21,616	24,197	24737
	8% HCHO	20,952	12,679	18,431	10,324	17,384	15964
	12% HCHO	(26,957)	12,621	17,567	15,988	11,929	14527
n relaxation coefficient	5% HCHO	0.565	0.364	0.724	0.402	0.667	0.544
	8% HCHO	0.418	0.787	(1.142)	(1.532)	0.250	0.485
	12% HCHO	(0.258)	0.562	0.594	0.420	0.649	0.556
λ_0 relaxation time (s)	5% HCHO	0.624	0.656	0.677	0.662	0.633	0.650
	8% HCHO	0.737	0.648	(0.385)	(0.318)	0.665	0.683
	12% HCHO	0.774	0.756	0.660	0.624	0.642	0.691

TABLE V
Viscoelastic Properties of Different Tannin–Formaldehyde Systems as Represented from the
Average Values of Gel Stiffness S, Relaxation Coefficient n, and Relaxation Time λ_0

Measurement	Pecan	Pine	Mimosa	Natural Quebracho	Quebracho QS	Quebracho adhesive intermediate
S gel rigidity (Pa.s)	199	2185	24,737	24,289	25,094	16,662
n	1.294	1.246	0.544	0.445	0.720	0.872
λ_0	0.715	0.566	0.650	0.678	0.658	0.610

have more influence and shows a definite trend (Table IV). The value of S, the gel stiffness, decreases as the percentage of the hardener increases. This is due to the faster reaction due to the higher concentration of one of the reagents and the consequent earlier immobilization of the network due to the faster rate of reaction. The value of λ_0, characteristic of the length of the segment between two crosslinking nodes, also depends on the concentration of the paraformaldehyde hardener, although it is much less sensitive to it than is S. The slowly increasing values of λ_0 indicate a higher proportion of longer oligomers being due to a faster linear growth of the polymer and to the same early immobilization of the network at higher hardener concentrations, yielding less densely crosslinked networks (Table IV). The trend in gel stiffness and relaxation time is maintained when comparing the behavior of different tannins in Table V, namely, the faster the reaction (the more reactive the tannin is), the lower is the gel stiffness S and slightly higher is the value of λ_0. The same trend was observed in thermomechanical analysis tests of the same tannins + paraformaldehyde systems,[42] but with considerably smaller differences between the same tannins as shown in Table V. It is then evident, from the results in Table V, that the rheology is more sensitive than is the thermomechanical analysis, as well as markedly exaggerating the differences in the gel and network rigidity due to the type of tannins or to other factors. Applied results of these systems on wood particleboard have shown also that other factors other than gel stiffness have a dominant influence on the performance of the system, such as the viscoelastic dissipation of the energy of a hardened network.[43]

The relaxation coefficient n appears also to depend on the relative reactivity of the tannin used. In Table V, the more reactive is the tannin, and the faster is this reaction with formaldehyde, the higher is the value of n. This is valid for all the tannins, the colloidal state of which has not been altered (the first four in Table V) or, although altered, still conserves evident colloidal behavior (the last one in Table V).[24–29] As the colloidal state is eliminated, such as by complete elimination of the colloidal carbohydrates, such as for quebracho QS, this does not appear to be valid any more. The variation of λ_0 with the type of tannin is rather small, with

the relaxation time decreasing as the reactivity of the tannin and its rate of reaction with formaldehyde increase, with pecan tannin giving the only anomalous result (Table V). This again confirms that the slower the reaction the higher is the value of λ_0 and the lower is the proportion of longer oligomers.

In Figure 3(a,b) are shown curves of the variation of the energy of activation of the reactions as a function of viscosity η_0. There are three main types of curves which occur. The curve in ref. 1 (Fig. 2), characteristic of the reaction of mimosa with 5% paraformaldehyde, has already been ascribed[1] to the sequence of three distinct phases of the reaction: a first phase of linear growth of the polymer, showing increasing energy of activation; a second phase in which branching starts to occur, showing a plateau of the value of the energy of activation; and the third phase of gel formation in which the observed apparent decrease of the energy of activation, which is measured on the liquid fraction, is only due to the decrease in sol proportion of the system. For the same reaction (with 5% paraformaldehyde) with the more reactive pine and pecan tannins, only two phases appear, namely, the first phase and the plateau phase [Fig. 3(a)]. It must be noted that, while for mimosa the zero-frequency viscosity is reached at the end of the reaction, a value of almost 40,000 Pa s, for the same reaction with pecan and pine tannins, the maximum values reached are, respectively, only 3500 and 8000 Pa s. Equally, the plateau is reached at viscosities of 7000, 400, and 80 Pa s for mimosa, pine, and pecan tannin extracts, respectively. This is again a clear indication of the very early immobilization of the network in formation for pine and pecan tannins and the reason why only two phases are observed in Figure 3(a). The same type of two-phase curve shown in Figure 3(a) also occurs for mimosa tannin when higher amounts of the paraformaldehyde hardener are used. This is also due to an increase in the reaction rate, but, in this case, as a consequence of the higher concentration of the hardener used.

The third type of curve is shown in Figure 3(b) and is characteristic of all the different types of quebracho tannins tested. In Figure 3(b), the first phase, again the increase in the instantaneous activation energy due to the diffusion problems caused by the linear growth of the polymer is followed by a rather brutal decrease of
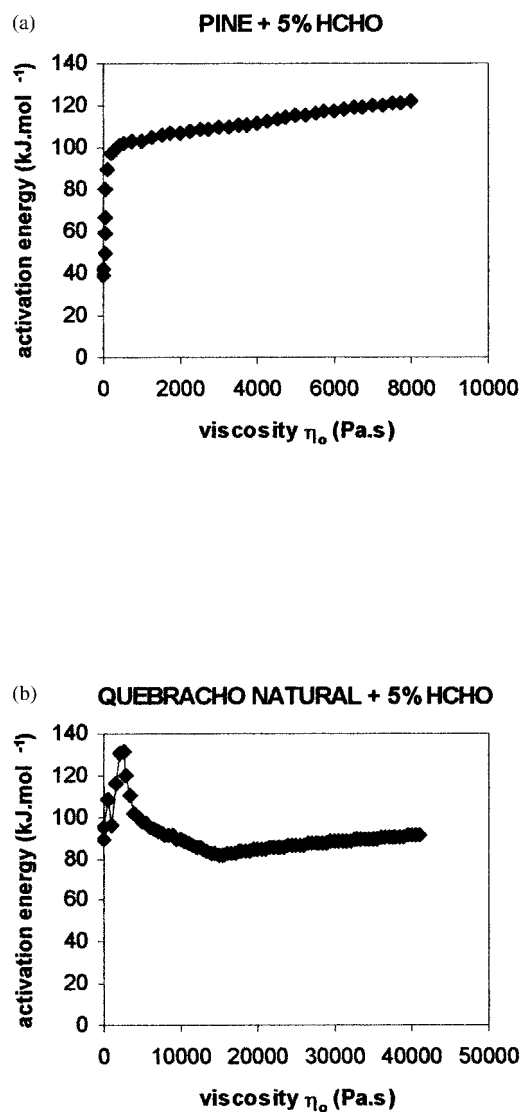
(a)

(b)

Figure 3 Variation of the instantaneous energy of activation as a function of the viscosity η_0 of (a) the reaction of pine bark tannin extract + 5% paraformaldehyde and of (b) the reaction of quebracho wood tannin extract + 5% paraformaldehyde.

the instantaneous energy of activation. This is due to the already-remarked[8,22–24] behavior of quebracho tannin to depolymerize by cleavage at the interflavonoid bond. This initially lessens drastically and rapidly diffusion hindrance and, hence, the energy of activation of the forward polycondensation. The forward polycondensation reaction starts again to predominate as the reaction approaches the gel point and a third phase becomes then noticeable in which the decrease of the instantaneous activation energy becomes progressively less important. Once reached and after the gel point, in Figure 3(b) (this is the inflexion point at about 15,000 Pa s), the energy of activation starts to increase again, but much slower due to the immobilization of the network. The same trend is

observed for the graphs of quebracho QS and quebracho adhesive intermediate (not shown here),[18] but with very different intensities. In the case of the adhesive intermediate, the trends and the slope of the curves in the different phases are considerably more marked than in Figure 3(b). For the desugared quebracho QS, the starting point of the instantaneous energy of activation is much lower (30 kJ/mol) due to the purity of the tannin extract, and the max value of the energy of activation is the same as for natural quebracho but occurs at 4000 Pa s rather than at 2000 Pa s as in Figure 3(b). Furthermore, the extent of the decrease of the instantaneous energy of activation due to depolymerization is very much smaller than in Figure 3(b); before that, the energy of activation settles down to a constant value plateau (an energy of activation of approximately 125 kJ/mol as related to natural quebracho's value of 90 kJ/mol).

CONCLUSIONS

Good correspondence of the gel-time values obtained by the two different methods $G' = G''$ and $1/\eta_0 \to 0$ was found for all the different types of natural and modified tannin extracts. The pH presents the predominant effect on both the activation energies and the gel times observed while the percentage of the paraformaldehyde hardener has a much lesser effect on these parameters. The rate constants of the different phases of the reaction of polycondensation with formaldehyde, both before and after the gel point, were obtained for the six commercial tannin extracts tested and the viscoelastic properties of the different tannins/formaldehyde gels were measured and the inffluence of different parameters on the gel stiffness S, relaxation coefficient n, and relaxation time λ were determined.

References

1. Garnier, S.; Pizzi, A.; Vorster, O. C.; Halasz, L. J Appl Polym Sci, in press.
2. Sealy-Fisher, V. J.; Pizzi, A. Holz Roh Werkstoff 1992, 50, 217.
3. Pizzi, A.; Stephanou, A. J Appl Polym Sci 1993, 50, 2105.
4. McGraw, G. W.; Rials, T. G.; Steynberg, J. P.; Hemingway, R. W. In Plant Polyphenols; Hemingway, R. W.; Laks, P. E., Eds.; Plenum: New York, 1992; pp 979–990.
5. Pizzi, A. In Wood Adhesives, Chemistry and Technology; Pizzi, A., Ed.; Marcel Dekker: New York, 1983; Vol. 1.
6. Roux, D. G. In Mimosa Extract; LIRI Leather Industries Research Institute: Grahamstown, South Africa, 1965; pp 33–51.
7. Abe, I.; Funaoka, M.; Kodama, M. Mokuzai Gakkaishi 1987, 33, 582.
8. Pasch, H.; Pizzi, A.; Rode, K. Polymer 2001, 42, 7531.
9. Thompson, D.; Pizzi, A. J Appl Polym Sci 1995, 55, 107.
10. Trosa, A. Doctoral Thesis, University Henri Poincaré–Nancy 1, Nancy, France, 1999.
11. Pizzi, A; Trosa, A.; Stracke, P. Final report, European Commission Research Contract FAIR-TC 95-0137, 1996–1998.
12. Masson, E.; Merlin, A.; Pizzi, A. J Appl Polym Sci 1996, 59, 1181.

13. Masson, E.; Pizzi, A.; Merlin, A. J Appl Polym Sci 1996, 60, 1655.
14. Pizzi, A.; Stephanou, A. Holz Holzver 1993, 45(2), 30.
15. Pizzi, A. Advanced Wood Adhesives Technology; Marcel Dekker: New York, 1994.
16. Stephen, J. J Chem Soc 1951, 646.
17. Roux, D. G. J Soc Leath Trades Chem 1952, 36, 274.
18. Garnier, S. Doctoral Thesis, University Henri Poincaré–Nancy 1, Nancy, France, 2002 (all additional data not shown in this article are stored and easily accessible in this document).
19. FESYP, European Federation of Panel Manufacturers: Standard Methods.
20. Rossouw, D. duT.; Pizzi, A.; McGillivray, G. J Polym Sci Chem Ed 1980, 18, 3323.
21. Fechtal, M.; Riedl, B. Holzforschung 1993, 47, 349.
22. Pizzi, A.; Stephanou, A. J Appl Polym Sci 1993, 50, 2105.
23. Pizzi, A.; Stephanou, A. J Appl Polym Sci 1994, 51, 2109.
24. Pizzi, A.; Stephanou, A. J Appl Polym Sci 1994, 51, 2125.
25. Pizzi, A.; Meikleham, N.; Stephanou, A. J Appl Polym Sci 1994, 54, 1827.
26. Garnier, S.; Pizzi, A.; Vorster, O. C.; Halasz, L. J Appl Polym Sci 2001, 81, 1634.
27. Merlin, A.; Pizzi, A. J Appl Polym Sci 1996, 59, 945.
28. Masson, E.; Pizzi, A.; Merlin, A. J Appl Polym Sci 1997, 64, 243.
29. Garcia, R.; Pizzi, A.; Merlin, A. J Appl Polym Sci 1997, 65, 2623.
30. Gay, K.; Pizzi, A. Holz Roh Werkstoff 1996, 54, 278.
31. Vilgis, T. A.; Winter H. H. Coll Polym Sci 1988, 266, 494
32. Chambon, F.; Winter, H. H.: Polym Bull 1985, 13, 499.
33. Winter, H. H., Chambon, F. J Rheol 1986, 30, 367.
34. Chambon, F.; Winter, H. H. J Rheol 1987, 31, 683.
35. De Rosa, M. E.; Winter, H. H. Rheol Acta 1994, 33, 220.
36. De Rosa, M. E., Mours, M.; Winter, H. H. Polym Gels Networks 1997, 5, 69.
37. Winter, H. H.; Mours, M. Adv Polym Sci 1997, 134, 165.
38. Winter, H. H.; Izuka, A.; De Rosa, M. E. Polym Gels Networks 1997, 5, 69.
39. De Rosa, M. E.; Mours, M.; Winter, H. H. Polym Gels Networks 1997, 5, 69.
40. Halasz, L.; Vorster, O. C.; Pizzi, A.; van Alphen, J. J Appl Polym Sci 2000, 75, 1296.
41. Halasz, L.; Vorster, O. C.; Pizzi, A.; Guasi, K. J Appl Polym Sci 2001, 80, 898.
42. Garnier, S.; Pizzi, A. J Appl Polym Sci 2001, 81, 3220.
43. Mittal, K.; Pizzi, A. Adhesion Promotion Techniques; Marcel Dekker: New York, 1999.