

Structural beams from thick wood panels bonded industrially with formaldehyde-free tannin adhesives

F. Pichelin
M. Nakatani
A. Pizzi*
S. Wieland
A. Despres
S. Rigolet

Abstract

Mimosa tannin hardened with hexamine at pH 10 has shown both at the laboratory and industrial level to be a formaldehyde-free system, within the limits of sensitivity of the method of Japanese standard JIS A 5908. This useful effect is based on the double mechanism of slow hexamine decomposition to reactive imino-amino methylene bases and their immediately subsequent very rapid reaction with the tannin. Decomposition to formaldehyde can never be reached under the conditions used. This yielded a long ambient temperature pot-life coupled with the fast hardening of the adhesive and fast pressing times of the thick panels by introducing a two-step steam-injection sequence during panel pressing. No formaldehyde emission was found in the panels bonded with such an adhesive system once tested according to the relevant Japanese standard. No free formaldehyde was detected by solid state ^{13}C NMR, nor residual hexamine, in the hardened tannin-hexamine adhesive, although these spectra have to be taken with caution due to the usual peak enlargement and relative lack of sensitivity in solid state NMR spectra. The reactions involved were explained by ^{13}C NMR. The panels obtained satisfied the relevant Japanese standard specification for both internal bond strength and formaldehyde emission.

Japanese standard regulations have become more restrictive (F**** level, JIS A 5908) regarding formaldehyde emissions from wood adhesives, therefore there is increased interest in finding alternative adhesives that will satisfy the stricter requirements. The use of isocyanate adhesives is not a viable solution to the stricter regulations because residual and immobilized isocyanate groups in the hardened adhesive network have still been found, often in considerable proportion, in hardened boards (Wieland et al. 2006, Despres et al. 2006).

Hexamethylenetetramine (hexamine) has already been used industrially for the production of interior-grade tannin-bonded panels of low or no formaldehyde emission (Pizzi 1977, 1999; Pizzi et al. 1994, 1997; Pichelin 1999; Pichelin et al. 1999). In the case of the faster reacting tannins such as pine tannins, exterior-grade panels can also be produced (Pizzi et al. 1994, Pizzi et al. 1997, Pichelin 1999, Pichelin et al. 1999, Pizzi 1999). In this latter application, however, hexamine's

complexation with pine tannin does produce, sometimes too often, aggregates that do not flow as well as one would wish for in adhesive application (Pichelin et al. 1999, Pizzi 1999). This affects the tannin adhesive performance as well as limiting the potential use of hexamine for exterior- and semiex-

The authors are, respectively, Head R&D Panel Products, HSB, Hochschule fur Architektur, Bau und Holz, Univ. of Applied Science, Biel, Switzerland (Frederic.Pichelin@bfh.ch); Project Leader, Wood Project, Urban Infrastructure and Environmental Products Co., Sekisui Chemical Co. Ltd., Kyoto, Japan; Professor (pizzi@enstib.uhp-nancy.fr) and PhD Students, ENSTIB-LERMAB, Univ. of Nancy 1, Epinal, France; and Researcher, LMPC, ENSCMu, Mineral Materials Lab., Mulhouse, France (S.Rigolet@univ-mulhouse.fr). This paper was received for publication in May 2005. Article No. 10057.

*Forest Products Society Member.

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Forest Prod. J. 56(5):31-36.

terior-grade tannin adhesives. In the case of other tannins such as mimosa tannin, this aggregation problem is rather rare, but the panels obtained are of interior grade.

Textbooks report that hexamine decomposes readily to formaldehyde and ammonia in an acid environment and slightly less readily to formaldehyde and to trimethylamine in an alkaline environment (Walker 1964, Meyer 1979). Work on fast-reacting natural and synthetic resins (all deficient in formaldehyde), mainly tannins (Pizzi and Tekely 1995), resorcinol-formaldehyde resins (Pizzi and Tekely 1996), and melamine-formaldehyde resins (Pizzi and Tekely 1996, Pizzi et al. 1996) has shown a different behavior of hexamine. Thus, in the presence of fast-reacting species, hexamine is not at all a formaldehyde-yielding compound. It neither decomposes to formaldehyde and ammonia in an acid environment nor to formaldehyde and trimethylamine in an alkaline environment (Pizzi and Tekely 1995, 1996; Pizzi et al. 1996; Kamoun et al. 2003). The very reactive amino-immine intermediates initially formed in its decomposition do react with the phenolic or aminoplastic species present without ever passing through the formation of formaldehyde (Pizzi and Tekely 1995, 1996; Pizzi et al. 1996; Kamoun et al. 2003). CP-MAS¹³C NMR solid phase spectra of the hardened resins have confirmed this occurrence and shown that the hardened networks present a high proportion of di- and tribenzylamine bridges (-CH₂-NH-CH₂- and -CH₂-N(-CH₂-)-CH₂-), rather than methylene bridges, connecting phenolic or melamine nuclei. These benzylamine bridges (or aminomethylene bridges in the melamine-formaldehyde and melamine-urea-formaldehyde cases) are temperature stable for long periods, even at relatively high temperatures, and dominate resin cross-linking.

This paper deals with the application of a technique called press steam injection, which overcomes the aggregation problems of tannin adhesives mixed with hexamine and greatly upgrades their performance as wood panel adhesives. Techniques and results are reported for very thick panel products, up to 120 mm thickness, and the structural beams cut from the panels. The chemical modifications that led to the performance improvement of panels bonded with tannin-hexamine adhesives were examined by solid phase ¹³C NMR and are explained. The panels obtained and the structural beams obtained from them are for interior use, hence they do not need to withstand a boiling test. Nonetheless, the panels obtained, while not being able to pass the relevant boiling test specification were able to withstand 4 hours in boiling water.

Experimental

Triplicate laboratory panels of dimension 500 by 500 by 25 mm and 500 by 500 by 40 mm were prepared by using very coarse chips (20 to 50 by 3 to 5 by 1 to 5 mm) of a number of different mixed species obtained by recycling structural wood taken out of service, and resinated with a solution of mimosa tannin extract (mimosa-O and mimosa-T ex Tanzania, supplied by Silva, S.Michele Mondovi, Italy) that had a Stiasny value (Stiasny 1905, Hillis and Urbach 1959, Suomi-Lindberg 1985) of 91.2 to 92.2, respectively, to which hexamine hardener was added. The tannin was applied to the wood chips as a 45 percent solution in water. The total resin load used was 7 percent tannin extract by weight on dry wood chips. The tannin extract hardener content used was 5 percent hexamine by weight on tannin extract solids content. The hexamine was predissolved in water to yield a 45 percent concen-

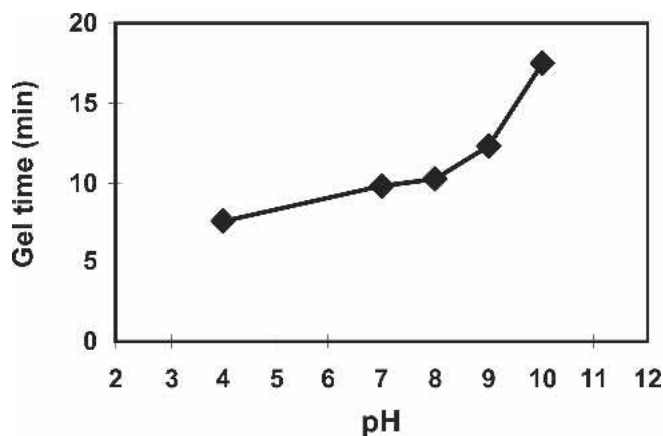


Figure 1. — Hardening time as a function of pH of mimosa tannin solutions hardened with 5 percent hexamethylenetetramine, solids on solids

tration solution in water before being added to the tannin solution to form the glue-mix.

The press times used were 380, 330, and 300 seconds and the target density was 880 kg/m³. The press temperature was 180°C and it involved two steam injections, one brief one at the beginning at a much lower steam pressure and one later at 9 bar steam pressure. The second, main steam injection time was for 60 seconds, with the exception of some of the industrial pilot plant trials where a steam injection time of 120 seconds was used. The results obtained are shown in **Tables 1 and 2**. The gel times at 100°C and viscosity at 25°C of the tannin + hexamine as a function of pH are shown in **Figure 1**. Viscosity of the mimosa tannin/hexamine solutions did not vary much in the pH range 4 to 10: values of 196, 264, and 318 centipoises at pH 4, 7, and 10, respectively. Industrial pilot plant trials were prepared up to a thickness of 120 mm. Formaldehyde emission was measured on the panels according to Japanese Standard JIS A 5908 (JIS 1994), which requires less than 0.3 mg/L formaldehyde emission for F**** class panels.

The solid state ¹³C NMR spectra of the hardened tannin-hexamine resin systems used were obtained on a Bruker MSL 300 FT-NMR spectrometer at a frequency of 75.47 MHz and at a sample spin of 4.0 kHz. The impulse duration at 90 degrees was 4.2 μs, contact time was 1 ms, number of transients was about 1,000, and the decoupling field was 59.5 kHz. Chemical shifts were determined relative to tetramethyl silane (TMS) used as control. The different shifts possible for the different structures were taken from the literature (Pizzi and Tekely 1995, 1996; Pizzi et al. 1996; Pizzi 1999).

Discussion

The results of the hardening time of mimosa tannin extract, with hexamine hardener, as a function of pH are shown in **Figure 1**, which clearly illustrates the well-known fact that the hardening time of tannin adhesives with hexamine hardener lengthens with increasing pH, particularly at alkaline pH (Pizzi 1979, Pichelin 1999, Pichelin et al. 1999). This behavior depends on the rate of decomposition of hexamine, which depends strongly on the pH. The behavior shown in **Figure 1** is expected, as hexamine is a monoprotic base and to react it has to first start decomposing. The more basic the pH, the more difficult it is for the hexamine to start decomposing, thus its decomposition is slower, and as a consequence there is a

Table 1. — Results of thick laboratory panels bonded with tanzanian mimosa tannin + hexamine. Steam injection total duration was 60 seconds.

Tannin type	Hexamine	pH	Resin load	Board thickness	Press time	Board density	Dry IB strength	IB 4 h boil	24 h cold water swelling	Formaldehyde emission ^a
	(%)		(%)	(mm)	(sec)	(kg/m ³)	(MPa)	(MPa)	(%)	(mg/L)
Mimosa-O	5	7.0	7	40	330	0.75	0.37	--	17.1	0.0
	5	8.0	7	40	330	0.75	0.57	--	14.4	0.0
	5	9.0	7	40	330	0.75	0.58	--	14.1	0.0
	5	10.0	7	40	330	0.74	0.73	--	12.8	0.0
Mimosa-T	5	10.0	7	25	380	0.85	0.95	--	12.0	0.0
	10	10.0	7	25	380	0.84	0.71	--	13.8	0.0
	15	10.0	7	25	380	0.81	0.78	--	15.0	0.0
	5	10.0	5	25	380	0.85	0.83	0.06	15.3	0.0
	5	10.0	7	25	380	0.83	0.82	0.07	12.0	0.0
	5	10.0	9	25	380	0.85	0.98	0.09	10.0	0.0
	5	10.0	7	40	330	0.75	0.78	--	12.0	0.0
	Standard requirements (JIS A5908)	--	--	--	--	--	--	≥0.30	--	≤12.0

^aMeasured on panels according to Japanese standard JIS A 5908.

slowing of the availability of the reactive species to cross-link the tannin. The reactivity of the tannin is, however, at its highest at very alkaline pH levels, the same pH levels at which hexamine is slower to decompose down to reactive species. Thus, while the rate-determining step for the hardening time is the slower one of the two, namely hexamine decomposition, once the reactive species start to form, the reaction of the tannin with them is extremely rapid.

It has already been shown that in the presence of fast-reacting species, hexamine neither decomposes to formaldehyde nor yields formaldehyde, but it does yield very reactive amino-imino methylene bases of the type $\text{CH}_2 = \text{N-CH}_2^+$ (Pichelin et al. 1999; Pizzi 1999; Kamoun and Pizzi 2000a, 2000b; Kamoun et al. 2003). This reaction mechanism is based on the capacity of the reactive species present to be able to react with the amino-imino methylene bases $\text{CH}_2 = \text{N-CH}_2^+$ before further decomposition can occur. This is considerably more effective at pH levels where formation of the bases is slower and the reactivity of the capturing species, the tannin, is much higher. It is this slow generation that ensures a too-complete reaction of any intermediate formed with the tannin before any decomposition or evaporation of the intermediate can occur. This is exactly the case for higher alkaline pH levels such as pH 10 or higher. pH 10 is a good compromise, however, because at higher pHs the higher level of alkali content would increase further both water absorption and thickness swelling of the board bonded with such an adhesive system. At much lower pHs, faster decomposition of the hexamine and lower reactivity of the tannin could lead to traces of decomposition to formaldehyde accompanied by its volatilization at higher temperature, in the press, hence leading to loss of cross-linking and lower strength. That this is the case is confirmed by the panel results in **Table 1**.

The results in **Table 1** confirm that the internal bond (IB) strength of the tannin-hexamine adhesives are good and increase with increasing pH. The relevant Japanese standard JIS A 5908 is satisfied at pH 10. But the IB strength becomes progressively lower as the pH decreases, as expected. **Table 1** shows that panel performance worsens, both IB strength and

cold water swelling, when increasing the percentage of hexamine hardener on tannin extract. The main problem appears to be that the increase in the proportion of the relatively sensitive aminic function of the hydroxybenzylamine bridges formed renders the panel more sensitive to water, as can be noted in **Table 1** from the increase in the 24-hour cold water swelling value. Panel performance also appears to improve as resin load increases from 5 to 9 percent, but the IB values are so much higher than what is needed, that it is not really worthwhile to increase the resin load to values as high as 9 percent. **Table 1** confirms that, at the laboratory level, faster press times for a thicker panel are also possible, hence 330 seconds for a 40-mm thickness is equivalent to 8.3 seconds per millimeter of thickness. Of particular note in **Table 1** are the formaldehyde emission tests performed on the panels according to the methods outlined in the Japanese standard JIS A 5908. These results are lower than the level of sensitivity of the method, which is why they are shown as 0.0 in the table. More accurate determination has shown that the emission is much lower even than the formaldehyde generated by the heating of wood. This is quite likely because of ammonia-formaldehyde chemical equilibria due to the presence of hexamine. The industrial pilot plant results in **Table 2** indicate that the IB strength and water swelling results obtained for industrial panels of 40 mm and 120 mm thickness are better than those obtained in the laboratory, and this at rather fast pressing times, namely down to 300 seconds for the 120-mm thickness, equivalent to 2.5 seconds per millimeter of thickness. The formaldehyde emission tests performed on the panels according to the methods outlined in Japanese standard JIS A 5908 again showed zero formaldehyde emission.

The existence of the mechanism outlined above for tannin-hexamine systems has the inherent advantage of a very long pot-life of the glue mix at ambient temperature. It has the disadvantage, however, of being rather slow for normal board pressing conditions where fast pressing rates are essential to panel factory profitability.

It is in this context that steam injection during pressing solves the problem of slow pressing time and slow hardening

Table 2. — Results of thick industrial pilot plant panels bonded with tanzanian mimosa tannin + hexamine.

Tannin type	Hexamine	pH	Resin load	Board thickness	Press time	Board density	Dry IB strength	IB 4 h boil	24 h cold water swelling	Formaldehyde emission ^a
	(%)		(%)	(mm)	(s)	(kg/m ³)	(MPa)	(MPa)	(%)	(mg/L)
Mimosa-T ^b	5	10.0	7	40	300	0.74	0.95	--	9.1	0.0
Mimosa-T ^c	5	10.0	7	120	300	0.75	0.79	--	8.0	0.0
Standard requirements (JIS A5908)	--	--	--	--	--	--	≥0.30	--	≤12.0	≤0.3

^aMeasured on panels according to Japanese standard JIS A 5908.

^bSteam injection total duration = 60 seconds.

^cSteam injection total duration = 90 seconds.

reaction. Steam-injection techniques are used to considerably accelerate the curing of wood panel adhesives, hence shortening markedly panel pressing time. The reaction of decomposition of the hexamine, as well as the reaction of the amino-imino methylene bases intermediates with tannin, are markedly accelerated by the application of steam injection. The resultant tannin-hexamine adhesive has two advantages: 1) long pot-life at ambient temperature; and 2) a fast press time at high temperature when steam injection is applied. It has the added advantage that the intermediate can never reach the formation of formaldehyde during hexamine decomposition. Formaldehyde emission will then be non-existent, within the limits of sensitivity of the method used in Japanese standard JIS A 5908. That this is indeed the case is confirmed by the no formaldehyde emission results of the panels in **Tables 1 and 2**. Furthermore, it has the added advantage that while at pHs much lower than 10, where hexamine decomposition is much faster, small parts of the intermediates can still decompose to formaldehyde, at pH 10 and higher this is not the case. This is confirmed by the evident absence at pH 10 of any tannin-tannin formaldehyde-derived methylene bridges in the ¹³C NMR spectra of hardened tannin-hexamine resins discussed below. The mechanism is shown in **Figure 2**.

Steam injection has also the considerable advantage that if any tannin-hexamine complexes are formed (Pichelin et al. 1999, Pizzi 1999), they have the appearance of non-flowing aggregates, these are dissolved and dissolved well by using steam injection. This is not a problem with the mimosa tannin extract used, where these aggregates form only very rarely, due to its lower number average molecular mass (Fechtal and Riedl 1993, Thompson and Pizzi 1995, Pasch et al. 2001), but it may be a problem with the even better performing pine tannin extract. Steam injection then solves even this problem. The further advantage of tannin resins of this type is that with steam-injection hardening the tannin-hexamine system is not washed out as instead occurs with waterborne phenol-formaldehyde resins. This is a considerable added advantage.

Viscosity of the mimosa tannin/hexamine solutions did not vary much in the pH range 4 to 10, varying between 210 centipoises at pH 4 and 310 centipoises at pH 10. These values made spray application easy in all cases.

Examples of the full-scale structural beams produced are shown in **Figure 3**. These beams are used vertically, as pillars, in the interior of traditional-type Japanese wood houses and have a structural function. The panels are instead used as interior cladding.

Comparative solid state CP-MAS ¹³C NMR spectra of mimosa tannin at pH 4, 7, and 10 hardened with hexamine (pre-

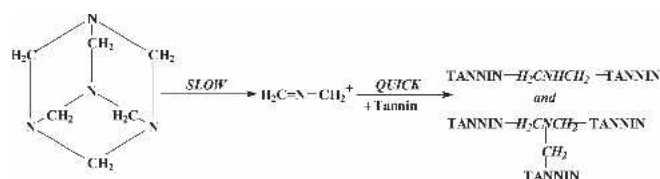


Figure 2. — Mechanism of hexamine decomposition to imino-amino methylene bases in presence of fast-reacting species such as tannins and their fast reaction with tannins to form benzylamine bridges.



Figure 3. — An example of structural pillars prepared by cutting thick panels of coarse chips. These pillars, used vertically, have a structural function in traditional-type Japanese houses now built according to modern principles.

dissolved in solution or added as a solid in one case) were also done. The comparative CP-MAS ¹³C NMR spectra in **Figure 4** are hard to interpret as are all the spectra of hardened tannin adhesives; the widening of solid state spectra peaks makes it more difficult to observe even significant differences. The spectra in **Figure 4** show the hardened flavonoid tannin/hexamine network when the hexamine is added as a water solution to the tannin solution at pH's 4, 7, and 10 or directly as a solid at pH 4. The relation between the various atoms numbers of the flavonoid structure in **Figure 5** and the NMR spectra is discussed below. The spectra show many similarities but nonetheless also show some interesting differences that give an idea why at pH 10 the board results are better than those at pHs 4 and 7 (**Tables 1 and 2**).

The first difference noticeable is that at pH 10 the flavonoids' C3' and C4' peaks at 145 ppm of the flavonoid units is

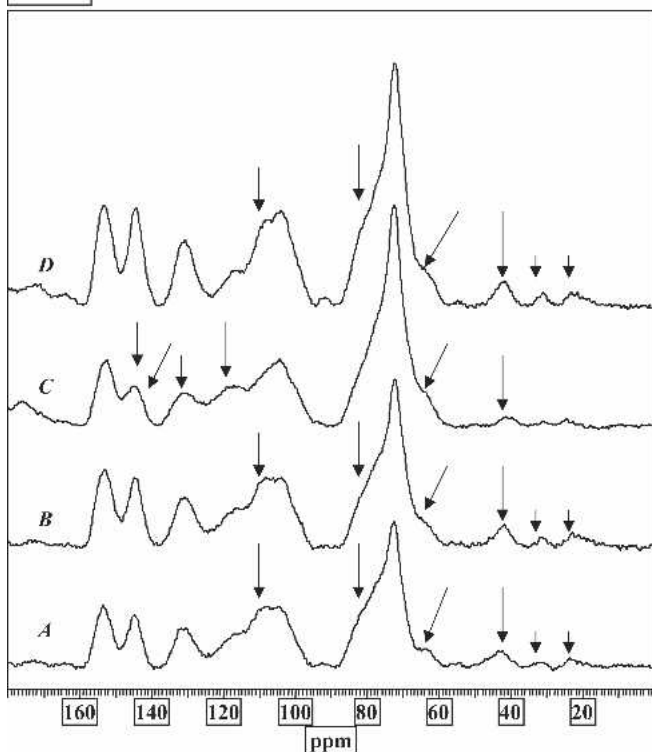


Figure 4. — Comparative solid state CP-MAS ^{13}C NMR spectra of mimosa tannin at pH 4 (A), pH 7 (B), and pH 10 (C) hardened with hexamine predissolved in water, or added as a solid at pH 4 (D).

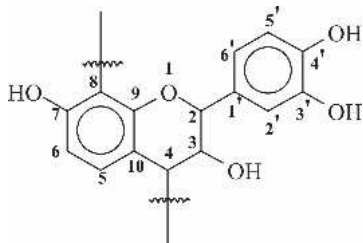


Figure 5. — Schematic structure of the formula of the repeating unit of a flavonoid oligomer with the identifying atom numbers related to the visible NMR bands of Figure 4.

much lower than at pHs 4 and 7 in relation to the control peaks of C5, C7, C9 at 153 to 156 ppm, which remain unaltered. The decrease of the 145 ppm peak indicates the transformation to phenate ions of the phenolic C3' and C4' hydroxygroups on the flavonoid B-ring, implying a considerable increase in its condensation reactivity, but particularly a changed shift due to substitutions on the normally free sites on the B-ring. This is accompanied by the more noticeable appearance of a shoulder at 142 ppm, characteristic of C3', C4' of a B-ring on which multisubstitution has occurred. More direct confirmation appears to be supplied by the noticeable disappearance of the peak at 107 to 112 ppm, indicating a decrease of the open C2' and C5' site on the B-ring simply because these have been substituted. An alternative interpretation of the disappearance of the 107 to 112 ppm peak could be that marked interflavonoid bond cleavage has occurred at pH 10. This is unlikely in the case of mimosa tannin, which is known to never cleave (Pizzi 1983; Pizzi and Stephanou 1993, 1994; Thompson and

Pizzi 1995) at the interflavonoid bond but rather of being prone to preferentially open the C-ring at C2 (Pizzi 1983; Pizzi and Stephanou 1993, 1994; Thompson and Pizzi 1995). The C1' peak at 131 to 132 ppm is also much lower, also confirming that substitution has occurred on the B-ring. A certain extent of the C-ring opening is also noticeable in all the different spectra. This can be deduced by the decrease at pH 10 of the C2 shoulder at 81 to 82 ppm, indicating a decrease of the C2 of the close C-ring form, the slight downfield shift of the C3 shoulder at 67 to 68 ppm, and the presence of the open form of C2 at 31 to 33 ppm.

Also noticeable are three peaks at 23 to 25 ppm, at 31 to 33 ppm, and at 42 to 43 ppm. The peak at 23 to 25 ppm is that of the unreacted C4 of the flavonoids. It is much smaller for the pH 10 case than for the pHs 4 and 7 cases in Figure 4. The 41 to 43 ppm peak is a composition of a peak characteristic of unreacted mimosa tannin but that can also be ascribed to formaldehyde-derived methylene-bridges reacted on the structure of the tannin. These are small but nonetheless noticeable differences at pHs 4 and 7, indicating that some small amounts of formaldehyde might still be produced in the decomposition of hexamine. It is so small to be considered practically absent at pH 10. However, this is clearly not the correct interpretation here. The 41 to 43 ppm peak is the peak of the charged CH_2 carbon of the very reactive amino-imino methylene bases, namely the $\text{CH}_2 = \text{N}-\text{CH}_2^+$ produced on decomposition of hexamine. The former is literally the reactive species that has been proven to derive from hexamine decomposition. Its intensity is particularly low in the pH 10 case, indicating that it has indeed reacted more than in the pH 4 and pH 7 cases. This is confirmed by the peak at 115 to 120 ppm of increased intensity and more clearly discernible for the pH 10 case. This peak is one of the peaks that has been shown to belong to an aromatic carbon to which is attached a benzylamine bridge (Pichelin et al. 1999, Pizzi 1999). In all the spectra, a low intensity broad peak at 53 to 58 ppm is present, this being characteristic of tribenzyl amine nodes in the network (Pizzi and Tekely 1995). It is lower in the pH 10 case, indicating that at pH 10 cross-linking of the network relies less on tribenzylamines than at lower pHs.

An interesting point to note is the absence of unreacted free C6 and C8 sites on the very reactive A-ring, which is a clear indication that these two sites have been totally reacted with benzylamine bridges or they are occupied by the interflavonoid bond. In both cases, they contribute completely to cross-linking. It must be clearly pointed out that this evidence is only circumstantial and that in no way can one assume absence of free formaldehyde at such low levels from broad peaks solid phase NMR spectra. Its absence, or its level too low to be detected, is only based on the test of the panels according to Japanese standard JIS A 5908.

The indication from the CP-MAS ^{13}C NMR spectra is that at pH 10 the B-ring starts to react and to participate in tannin cross-linking, and a more highly cross-linked network will result in higher strength, supporting the results obtained in Tables 1 and 2. Furthermore, the cross-links that exist at pH 10 are due to benzylamine bridges rather than methylene bridges, indicating again that hexamine does not decompose to formaldehyde under the conditions shown, and confirming the zero-emission of formaldehyde from the wood panels produced as presented in Table 1. Thus, the main reactions involved can be summarized as shown in Figure 6.

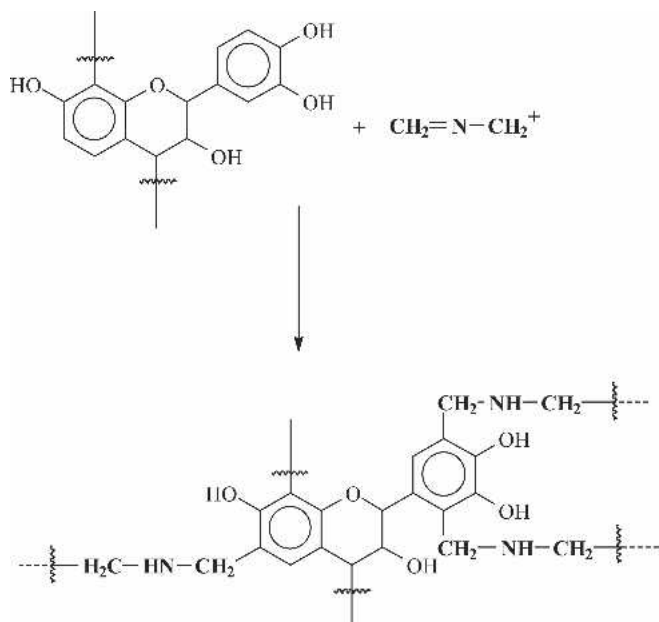


Figure 6. — Schematic example of tannin cross-linking through benzylamine bridges by reaction with imino-amino methylene bases derived by the decomposition of hexamine in presence of tannins.

Conclusions

Mimosa tannin hardened with hexamine at pH 10 has shown both at the laboratory and industrial level to be a formaldehyde-free system, within the limits of sensitivity of the method of Japanese standard JIS A 5908. This useful effect is based on the double mechanism of slow hexamine decomposition to reactive imino-amino methylene bases and their immediately subsequent very rapid reaction with the tannin. Decomposition to formaldehyde can never be reached under the conditions used. This yielded a long ambient temperature pot-life coupled with the fast hardening of the adhesive and fast pressing times for the thick panels by introducing a two-step steam-injection sequence during panel pressing. No formaldehyde emission was found in the panels bonded with such an adhesive system when tested according to the relevant desiccator test (JIS A 5908). This appears to be also supported by the solid state ^{13}C NMR spectra, where free formaldehyde was not detected. These spectra having to be taken with caution, however, due to the usual peak enlargement and relative lack of sensitivity in these types of spectra. In this regard, no residual hexamine was found by solid state ^{13}C NMR for the hardened tannin-hexamine adhesive. The type of reactions involved were explained from the ^{13}C NMR. The panels obtained satisfied the new, relevant Japanese standard specification for both IB strength and formaldehyde emission.

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