

Mechanism of Polyphenolic Tannin Resin Hardening by Hexamethylenetetramine: CP-MAS ^{13}C -NMR

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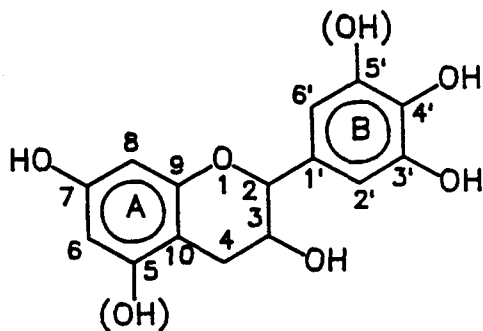
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SYNOPSIS

Polyflavonoid tannins have been shown by ^{13}C -NMR to react with hexamethylenetetramine (hexamine) at considerably higher rates than with phenol with the formation of both benzylamine and methylene crosslinks to form hardened resins. Predominantly prodelphinidin-type tannins appear to present a much higher proportion of benzylamine bridges than of methylene bridges, while in procyanidin-type tannins the proportion of the two types of crosslinks appear to be comparable. The greater the nucleophilicity of the flavonoid tannin A-rings, the greater is the proportion of benzylamine bridges which appear to form. At parity of the type of tannin, the faster the reaction with hexamine, the higher the proportion of benzylamines which appear to form. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Thermosetting polyflavonoid tannin-formaldehyde resins have performed well in industrial applications as phenolic exterior wood adhesives for the last 20 years.¹ Industrial polyflavonoid tannin extracts are polymeric materials composed mostly of flavan-3-ols repeating units and smaller fractions of polysaccharides and simple sugars.¹ Flavonoid units in such tannin extracts present predominantly phloroglucinol or resorcinol A-rings and catechol or pyrogallol B-rings:



The free C6 and/or C8 sites on the A-ring are the ones reactive with formaldehyde due to their strong nucleophilicity to form adhesives.¹ Some tannins present A-rings which are resorcinolic in nature, while others present A-rings which are phloroglucinolic in nature. The resorcinolic A-rings show reactivity toward formaldehyde comparable to resorcinol,¹ while phloroglucinolic A-rings present reactivity comparable to that of phloroglucinol. Assuming the reactivity of phenol toward formaldehyde to be 1 and that of resorcinol and phloroglucinol to be 10 and 100, respectively, the flavonoid resorcinolic A-rings have reactivity of 8–9, while the phloroglucinolic A-rings have reactivity of well over 50. In short, flavonoid tannins are comparable to a high-reactivity phenolic novolak¹ to which a separate hardener must be added for curing.

Hexamethylenetetramine (hexamine) has recently been used instead of formaldehyde to give hardened flavonoid tannin resins.^{2–5} The use of hexamine for exterior tannin adhesives for particleboard has been rendered possible by the use of the faster-reacting, phloroglucinol A-ring flavonoid tannins such as pecan nut tannin (a predominantly prodelphinidin tannin^{6–8}) and pine bark tannin (a procyanidin tannin^{6–8}), but only interior ones with the

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slower-reacting profisetinidin/prorobinetinidin tannins.^{1,2,9}

The formation and hardening of phenolic resins based on phenol and hexamine have been studied at 100°C in some detail.^{10,11} This showed that the resin goes through a stage in which tribenzyl-, dibenzyl-, and monobenzylamines are the crosslinking bridges between the phenolic nuclei. Given times of 1–2 h at 100°C, the benzylamines rearrange to methylene bridges to give dihydroxydiphenylmethanes and higher oligomers with elimination of ammonia. It has also been shown that at 100°C benzylamines constitute the majority of linking bridges up to 15–30 min of reaction and are still present in noticeable proportions (dibenzylamines) even after 1 h of reaction.¹⁰ It has also been shown that the benzylamines form by reaction of phenol with hexamine without previous complete decomposition of the latter to formaldehyde and ammonia. This background raises the question of whether hexamine can be at all considered a formaldehyde-yielding compound when used with fast-reacting tannins considering that at 100°C tannin resins react and harden with it in 40–60 s (the reaction stopping there), this hardening time being much faster than what is obtainable with formaldehyde under identical reaction conditions.^{2–4,12}

This article was aimed at investigating if in the final hexamine-hardened tannin resins the majority of crosslinks is in the form of benzylamines rather than just methylene bridges between the flavonoid nuclei. This investigation was prompted by the almost nonexistence of any formaldehyde emission from tannin resins hardened with hexamine and from the exterior-grade wood particleboard bonded with them.²

EXPERIMENTAL

Spray-dried powders of two commercial polyflavonoid tannin extracts, pecan (*Carya illinoensis*) nut pith tannin extract and pine (*Pinus radiata*) bark tannin extract were used after preparing with them 40% concentration water solutions, adjusting their pH to 4.5 with acetic acid and gelling them at 100°C with 6.5% by weight of hexamine solids on solid tannin extract (the hexamine being added as a 40% solution in water). In the case of pine tannin, a control based on the hardening of the same as above but using 8% paraformaldehyde fine powder by weight on solid tannin extract instead of hexamine was also prepared. The times taken by the two tan-

nins to gel were 45 and 100 s for pecan and pine tannin, respectively. The hardened mass was air-dried at ambient for a few days and then ground to a very fine powder for ¹³C-NMR analysis. Solid-state (CP-MAS) ¹³C-NMR spectra were obtained on a Bruker MSL300 FT-NMR spectrometer, at a frequency of 74.47 MHz. Chemical shifts were calculated relative to TMS for NMR control. All spectra were run overnight. Acquisition time was 0.026 s with the number of transients at about 10,000. All spectra were run with a relaxation delay of 5 s and were accurate to 1 ppm. The spectra were run with the suppression of spinning side bands and a spectral width of 20,000 Hz. Typical spin lattice relaxation times for the types of compounds analyzed were taken from the literature.^{13–15}

DISCUSSION

The CP-MAS ¹³C-NMR spectra of pine tannin alone, pine tannin hardened with formaldehyde, and pine tannin hardened with hexamine are illustrative of what occurs [Fig. 1(a)–(c)]. In the pine tannin hardened with formaldehyde, next to the band at 38 ppm, representative of the unsubstituted C4 site of flavonoid units,⁷ an equally intense band at 36.8–37 ppm appeared, as well as a band at 33 ppm. These bands are known and have been assigned¹⁰ to —CH₂— methylene bridges between phenolic nuclei. Thus, methylene bridges have formed exclusively [Fig. 1(b)], as would be expected in this case. In the spectra [Fig. 1(c)] of pine tannin hardened with hexamine, instead, not only the bands at 37 and 33 ppm appeared, although they are less prominent than in the formaldehyde case, but also clear bands at 57.5, 51, and 45 ppm. These bands have been assigned¹⁰ to tribenzylamines, dibenzylamines, and monobenzylamines, respectively. It is interesting to note that in this case tribenzylamines and monobenzylamines predominate (in phenol itself, dibenzylamines predominate). Thus, in the case of pine tannins, approximately 40–50% of the bridges formed between flavonoid nuclei by reaction with hexamine appear to be methylene bridges while the rest appears to be composed of benzylamine crosslinks. Supporting this view is the variation of the 98 ppm band, representative of free C6/C8 sites [Fig. 1(a) and (b)] and of the 105–110 ppm band, representative of substituted, reacted C6/C8 sites. The 98 ppm band decreases considerably while the 108 ppm band increases markedly after reaction with formaldehyde [Fig. 1(a) and (b)]. This indicates that

the formaldehyde has reacted at the available C6/C8 sites of flavonoid units to form methylene bridges. In pine tannin hardened with hexamine, the same trend is noticeable, with the band at 108 ppm increasing markedly but to a lesser extent than in the pine/formaldehyde case, a new band at 105 ppm appearing, and the band at 98 ppm decreasing sharply, although to a lesser extent than for the pine/formaldehyde case.

Thus, in the case of a fast-reacting phenol such as pine tannin, once the tannin has hardened, a consistently high proportion of crosslinks are in the form of benzylamines; a noticeable proportion of methylene bridges are also present. This is of interest on two counts: First, it means that for high reactivity, fast-hardening polyflavonoid tannins, only partial decomposition to formaldehyde of the hexamine in water solution has occurred; second, such a decreased decomposition has occurred in water solution, at acid pH (pH 4.5). This is a better indication of the relative proportions of methylene and benzylamine bridges than given by previous work on phenol where the reaction was carried out in molten form, in the absence of initial water, rather than in water solution in which hexamine decomposition to formaldehyde is much easier. It also indicates that the only formaldehyde which is likely to have reacted to form methylene bridges is the sum of (i) the small amount of formaldehyde which was originally present in solution due to the equilibrium¹⁶ $\text{hexamine} \rightleftharpoons \text{formaldehyde} + \text{ammonia}$ and (ii) any further formaldehyde derived from this equilibrium before hardening of the tannin occurs. The latter equilibrium must be intended as a dynamic state of the heat-induced decomposition of hexamine to formaldehyde and ammonia. Thus, there are two competitive reactions present initially: (i) the decomposition of the hexamine and (ii) the reaction of amine fragments and of formaldehyde with the phenolic nuclei of the tannin. The higher the reactivity of the tannin, the higher is the proportion of amine fragments which react with it before further decomposition to formaldehyde and the lower is the amount of methylene bridges derived by reaction with formaldehyde. This implies that the nucleophilicity of a procyanidin such as pine tannin is high enough to cause reaction just as rapidly with hexamine and with formaldehyde without any substantial shifts in the hexamine/formaldehyde equilibrium in water. In this respect, the relative proportions of benzyl amine vs. methylene bridges will be clearly dependent on the gel time of the system: The longer the gel time (= the lower the reactivity of the tannin under com-

parable conditions), the greater is the time allowed for hexamine decomposition and, hence, the greater is the proportion of hexamine decomposition to formaldehyde and the greater is the proportion of methylene bridges and, conversely, the lower the proportion of benzylamine bridges.

Pecan nut tannin (predominantly a prodelphinidin⁶⁻⁸) has been shown to be even faster-gelling with hexamine than is pine tannin at parity of reaction conditions [specimens in Figs. 1(c) and 2 gelled at 100°C in 45 s for pecan nut tannin and in 100 s for pine tannin].

In Figure 2, such a difference is also noticeable from the relative proportion of benzylamines and methylene bridges formed. Again, tribenzyl-, dibenzyl-, and monobenzylamine bands at 57.5, 51, and 45 ppm are present, but with dibenzylamines and tribenzylamines being in greater proportion over monobenzylamines than in the case of pine tannin. The proportion of methylene crosslinks is also considerably lower, with the 33 ppm band visible but much smaller and the 37 ppm band being very small. In this tannin, an approximate proportion of 80% or more of the crosslinks present after hardening appears to be in the form of benzylamines. Thus, the rate of hardening of the tannin with hexamine appears to be of some importance, when the reaction is carried out in water (which is the case in the use of these materials for thermosetting wood adhesives¹): The faster hardening the tannin is, the higher the proportion of benzylamine bridges and the lower that of methylene crosslinks. This means that the only formaldehyde capable of reacting as such with the tannin is the one present at the beginning of the reaction due to the $\text{hexamine} \rightleftharpoons \text{formaldehyde} + \text{ammonia}$ equilibrium. To this must be added a further amount of formaldehyde derived from any further decomposition of hexamine at elevated temperature in the short time before the tannin hardens: The faster reacting the tannin, the lower the proportion of this formaldehyde that is available. The temperatures for the use of these materials for wood adhesives never reaches the value of 160°C, at which benzylamines are known to start to rearrange to methylene bridges. The definition obtained in the spectra is less than good, the background noise ratio being more intense than what would be desirable. This is due to the hardened material containing not just 40% hardened resin solids but also 60% water. Further drying of the sample, by application of heat, would further decompose the benzylamine bridges to methylene bridges, changing the results of the analysis and giving a faulty

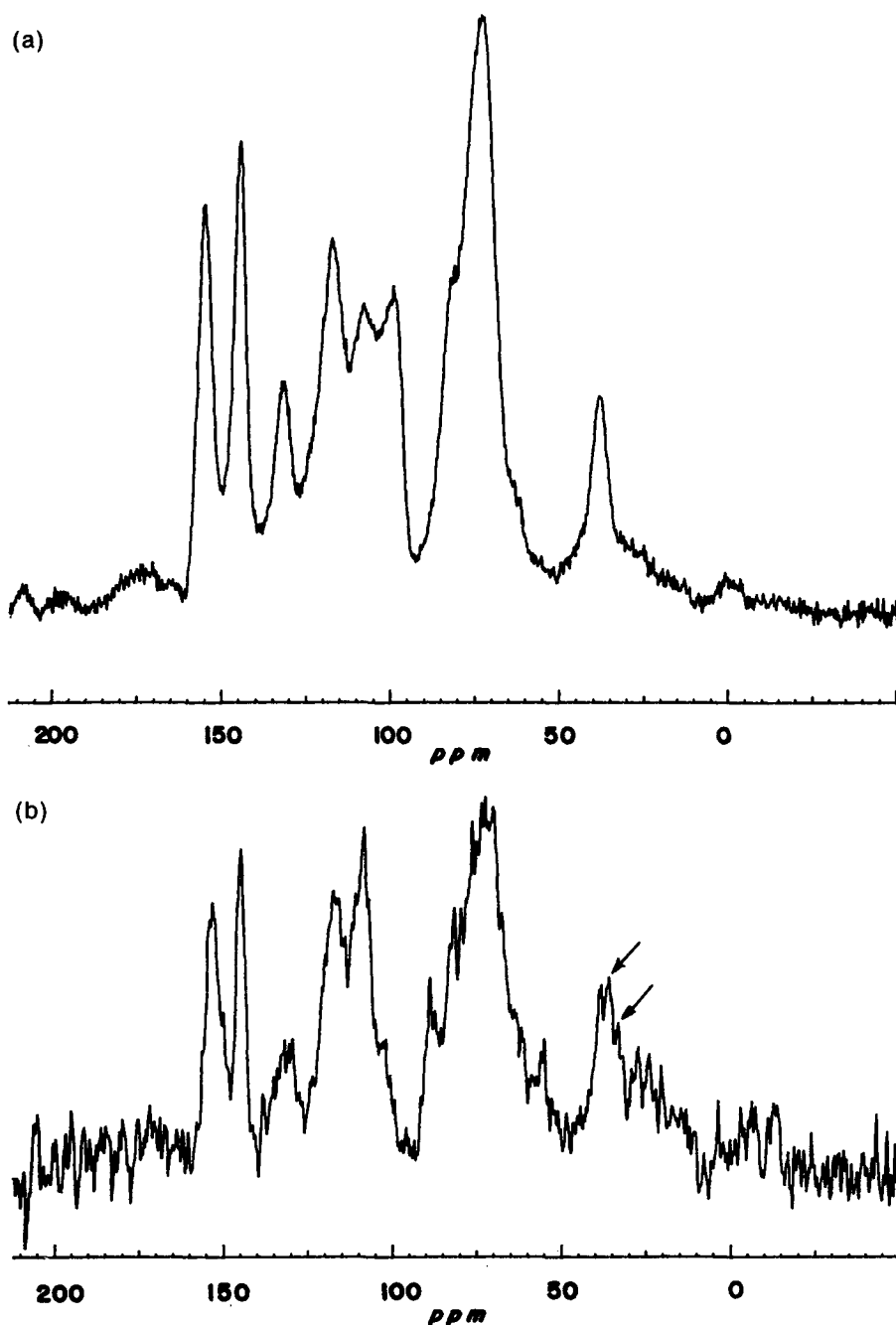


Figure 1 (a) CP-MAS ^{13}C -NMR spectrum of pine tannin extract. (b) CP-MAS ^{13}C -NMR spectrum of pine tannin extract hardened at 100°C with 8% paraformaldehyde. (c) CP-MAS ^{13}C -NMR spectrum of pine tannin extract hardened at 100°C with 6.5% hexamethylenetetramine (hardened in 100 s).

impression of the relative proportions of benzylamine to methylene bridges in the final product.

Application of heat after curing of the resin according to the mechanism presented would also lead to rearrangement of a number of benzylamine bridges

to methylene bridges with liberation of ammonia: In their application as thermosetting wood adhesives, such a rearrangement is likely to occur only to a limited extent, because in industrial practice, the panels are immediately cooled after hot-pressing.¹

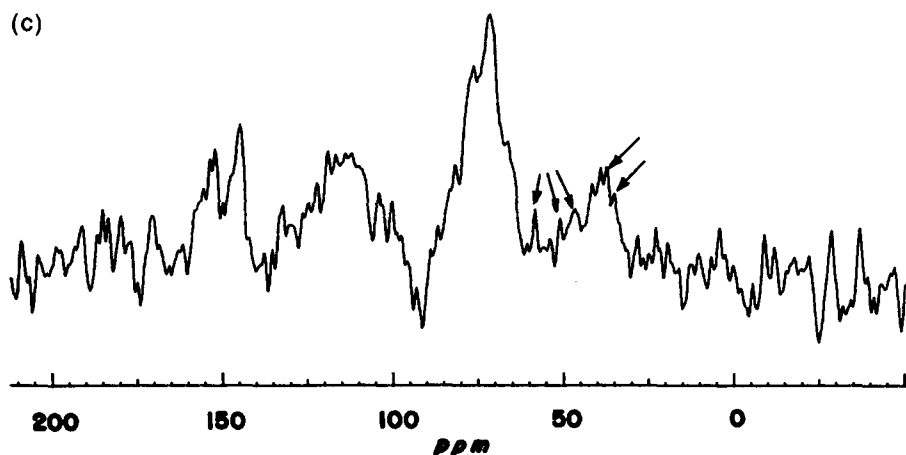


Figure 1 (Continued from the previous page)

In the case of slower-reacting tannins such as profisetinidin/prorobinetinidin^{2,7}-type tannins and mimosa and quebracho tannins,¹⁷ the fastest gel times of these with hexamine are in the order of 120–140 s at 100°C.² This means that for these there will be present in the hardened mass a much higher proportion of methylene bridges and a much lower proportion of benzylamines. Among the latter, monobenzylamines will be predominant, not interflavonoid bridges, and they will render the hardened tannin considerably more susceptible to water attack, as indeed has already been found experi-

mentally^{1,2,5} unless heated for a longer time and at higher temperature after hardening. As the fastest gel times of the different tannins with hexamine have been found to be 37 s for pecan nut tannin,¹⁷ 55–60 s for pine tannin,¹⁷ and 120 and 140 s, respectively, for mimosa and quebracho tannins,^{9,17} this explains the capability of the former two to yield, with hexamine, exterior-grade wood adhesives, while the latter two can only produce interior-grade wood adhesives. Furthermore, the work of Zinke et al.^{18–23} on the reaction of faster-reacting phenols with hexamine also indicates that while dibenzylamine

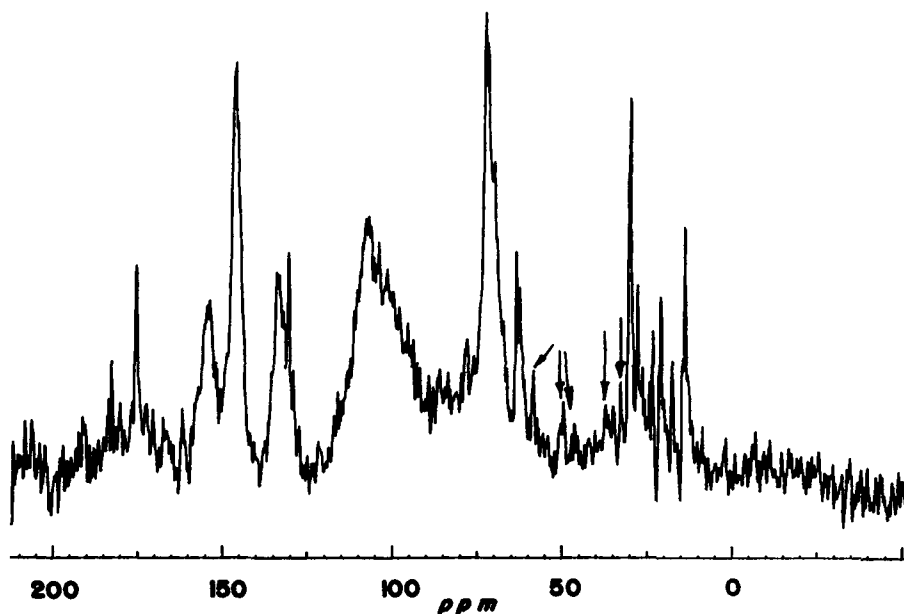


Figure 2 CP-MAS ¹³C-NMR spectrum of pecan nut tannin extract hardened at 100°C with 6.5% hexamethylenetetramine (hardened in 45 s).

would form with both faster- and slower-reacting tannins, tribenzylamines would be much easier to form the faster-reacting the tannin is. It might be that the idea proposed by Hultzs^{23,24} of an initial formation from hexamine of methylene-based reactive fragments such as $^+\text{CH}_2\text{—NH—CH}_2^+$ and $\text{N—(—CH}_2\text{)}_3^+$ is correct, these fragments then attacking the phenolic nuclei. Alternatively, a direct attack, on the phenolic nuclei of the positively charged methylene group vicinal to the only active nitrogen of hexamine (hexamine in solution is monoprotic³), could occur. This, however, it is not possible to deduce, in the case of tannins, with the present limited data.

CONCLUSIONS

In conclusion, polyflavonoid tannins react with hexamine with the formation of both methylene and benzylamine crosslinks. The higher nucleophilicity tannins such as prodelphinidins and procyanidins yield a high proportion of benzylamine bridges, with faster reactions corresponding to increasing proportions of benzylamine bridges. At least for prodelphinidin and procyanidin tannins, hexamine cannot be considered, not in its totality, nor even predominantly, as a formaldehyde-releasing compound, as networking of the resin to hardness does occur mainly by direct reaction of hexamine or hexamine fragments other than formaldehyde on the phenolic nuclei of the polyflavonoid tannins. This appears to confirm the almost nonexistent release of formaldehyde from products bonded with fast-reacting flavonoid tannins hardened with hexamine.^{12,17}

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