A ^{13}C NMR Study of Polyflavonoid Tannin Adhesive Intermediates. II. Colloidal State Reactions

A. PIZZI* and A. STEPHANOU

Department of Chemistry, University of the Witwatersrand, Johannesburg, South Africa

SYNOPSIS

Water solutions of 40–50% polyflavonoid tannin extracts appear to be in a colloidal state. This is caused by both the presence of noticeable amounts of hydrocolloid gums as well as the presence of higher molecular mass tannins. ^{13}C NMR analysis appears to confirm that during chemical treatment, reactions occur in these colloidal solutions that would not be likely to occur in noncolloidal solutions as used in model compound experiments. These reactions centre on the role of the organic anhydride used during treatment, and lead to intramicellar direct α-set attack or to acetylation of the tannin followed by a rapid rearrangement again to an α-set attack, which is similar to both a Kolbe reaction and a Fries rearrangement. This eventually leads to accelerated cross-linking of the tannin-formaldehyde adhesive prepared from the chemically modified tannin extract. It appears that such reactions and rearrangements are performance determining in the case of the two lower-reactivity tannins examined, mimosa and quebracho; have some noticeably positive effects on the higher reactivity pine tannin, and appear instead to have a deleterious effect on the other higher reactivity tannin, namely pecan nut tannin. The reasons for such behaviour are briefly discussed. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The structural modifications induced by the chemical treatment detailed in the previous paper[1] are not the only performance-determining reactions that occur during the chemical modification of polyflavonoid tannin extracts into tannin adhesives intermediates. Of importance, and not considered up to now, is the presence in the tannin extract of consistent amounts of polymeric carbohydrates (hydrocolloid gums)[2,3] extracted together with the tannin. These polymeric carbohydrates contribute to maintaining the water solutions of tannin extracts in the colloidal state, rendering possible reactions on the tannin that otherwise are not or are less likely to occur in a just-water solution. The reactions that occur appear to rely on the surfactant-like action of the hydrocolloid gums and also of the tannin polymer itself, hence on their capability to form micelles in water. These reactions also appear to contribute to the enhancement of the performance of the modified tannin extracts as thermosetting tannin-formaldehyde wood adhesives. It must be pointed out that both the structural modifications described in the previous paper[1] and the reactions described in the present one are not very extensive, considering the small proportion of chemicals used; but their effect often determines the performance of the adhesive.

EXPERIMENTAL

^{13}C NMR

Solutions of ^{13}C NMR spectra were obtained on a Bruker AC200 FT-NMR spectrometer at a frequency of 50.3 MHz and with the sample spectra at 25 Hz. Chemical shifts were calculated relative to $(CH_3)_3Si(CH_2)_3SO_3Na$ for NMR control. $(CH_3)_3Si(CH_2)_3SO_3Na$ was dissolved in D_2O, run separately, and the shifts for the four signals were set. All the spectra were run overnight. Acquisition time was of 1.08 s and number of transients was approximately 10000. All spectra were run with identical

* To whom correspondence should be addressed. Present address: ENSIB, University of Nancy, B.P. 1041, Epinal, France.

Journal of Applied Polymer Science, Vol. 51, 2125–2130 (1994)
© 1994 John Wiley & Sons, Inc. CCC 0021-8995/94/132125-06

Table I Carbonyl and Methyl Groups ^{13}C NMR Bands of Chemically Treated Tannins and Models

	C=O (181–182 ppm)	$-CH_3$ (25 ppm)	Applied Performance of Tannin as Adhesive
Treated mimosa extract	21	38	Marked performance improvement
Treated quebracho extract	35	55	Marked performance improvement
Treated pine extract	61	147	Partial to marked performance improvement
Treated pecan nut extract	130	210	Little or no performance improvement
Treated catechin monomer	448	1350	—
Treated catechin/gum arabic mix	356	1070	—

relaxation delay of 5 s and were accurate to 1 ppm. The spectra were run with nOe enhancement, spectral width was 15000 Hz, digital resolution 0.925 Hz/point with exponential multiplication. The WALTZ decoupling programme was used. Typical spin-lattice relaxation times were not measured but standard values shown in the literature were used.[1,4] The ^{13}C NMR band intensities reported in the tables are integrated intensities. The samples were prepared by diluting 40% mass/mass aqueous solutions of tannin extracts, before and after treatment, with D_2O in 1 : 4 mass proportion, except for monomeric catechin alone for which deuterated methanol was used as the solvent. Distortionless enhancement by polarization transfer (DEPT) ^{13}C NMR spectra were also obtained to add confirmatory evidence of correct assignment for CH—, $-CH_2-$, $-CH_3$ and quaternary carbon shifts. The ^{13}C NMR band intensities were reported to a 100% band intensity for the C3′, C4′ 145–146 ppm band, for parity of comparison, for the untreated tannin extracts. The chemically treated tannin extracts were reported to the same intensity of the C1′ band at 131 ppm, also for parity of comparison with the untreated samples. Results are shown in Table I for the tannin extracts and on Table II for model compounds. The 60–90 ppm region relating to the signal from the hydrocolloid gums present in the extracts was not reported in the tables because this region has already been examined in depth.[1]

Chemical/Heat Treatment

The chemical/heat treatment was used on the following solutions:

1. 50% mimosa tannin extract in water;
2. 45% natural quebracho tannin extract in water;
3. 45% natural pine tannin extract in water;
4. 45% pecan nut tannin extract in water.

The above were treated on tannin extract solids with 3.5% by mass of acetic anhydride at 80°C, under mechanical stirring for 45 min, followed by 5.5% by mass NaOH solids (as a 30% water solution) at 90°C, under mechanical stirring, for a period of 3 h, then cooled rapidly to ambient temperature and the pH adjusted to 7.0 for all four cases before ^{13}C NMR analysis was carried out. Catechin monomer (A.R. grade) was treated only with acetic anhydride at 80°C for 1 h in the following two cases:

1. 25% catechin monomer alkaline water solution + 3.5% acetic anhydride, by mass, on catechin solids;
2. 25% catechin monomer and 15% gum arabic alkaline water solution + 3.5% by mass acetic anhydride on catechin solids.

Zeta (ζ) Potentials

The zeta potentials were obtained by using a Rank Brothers particle microelectrophoresis apparatus

Table II Comparative ζ Potentials Measurements in mV of Untreated Tannin Extracts, Models, and Synthetic Resins

Mimosa tannin extract 40%	11.3
Quebracho tannin extract 40%	14.5
Pine tannin extract 40%	2.4
Pecan nut tannin extract 40%	4.9
Gum arabic 23%	5.2
Catechin/gum arabic mix 23%	5.2
Synthetic PF resin 40% solids	0.9
Synthetic UF resin 40%	0.3
Treated mimosa extract 40%	4.0

using its standard thin-walled flat cell and 10 mA current.[5] Zeta potential is physically significant in media of high dielectric constant such as water. The tannin extracts zeta potential was measured for all of them at pH 5, 40% solids content, 25°C.

Particle Board Preparation

To the tannin extract solutions unmodified and modified by the chemical heat treatment, at a solid content of 35%, were added 10% mass/mass of 96% fine paraformaldehyde powder as hardener. The pHs of the tannin extract were adjusted to current optimal pHs for application on pine wood substrates for a standard laboratory press time and press cycle under laboratory conditions. These were much slower than industrial pressing conditions; this was done to determine the maximum strength of each tannin-formaldehyde adhesive under ideal conditions. The pHs of operation used, for modified and unmodified tannin extracts were, respectively: mimosa, 7.0; quebracho, 7.2; pine, 4.8; pecan nut, 5.6. One layer duplicate exterior grade particle board from industrial core particles of *Pinus radiata,* each board of dimensions 400 × 350 × 12 mm were prepared. The conditions of preparation used to determinate maximum strength achievable were 7.5 min press time at 200°C press temperature, 24 kg/cm^2 pressure, and 22% moisture content with a press cycle of 2 min from contact to maximum pressure and holding maximum pressure, followed by 2.5 min at a pressure of 10 kg/cm^2 and ending with 3 min of pressure at 2 kg/cm^2. The boards were tested for internal bond strength normal to the board plane when dry and after 2 h boiling followed by 16 h drying at 105°C, according to established standard specifications.[6-9]

DISCUSSION

All the reactions influenced by the colloidal state of the tannin extract solution have the organic anhydride used for modification as a source, be it acetic or maleic anhydride. In this regard the ^{13}C NMR bands of interest are those characteristic of the C6′, and C5′/C2′ carbons belonging to the flavonoid units B-rings, respectively at 120–121 ppm, and at 115–117 ppm. The NMR bands in the carbonyl region also appear to be of importance, mainly the 181–184 ppm band belonging to the acid residue of the anhydride and the ester band at 159–160 ppm. In the previous article[1] the free C6 and C8 bands and C4–C8 link band as well as the C3 band in the model compounds studies were shown to sometimes undergo unforeseen behaviour.

The chemical heat treatment of the tannin extracts appears to affect the relative intensity of the C6′ band to a small extent, but the intensity of the C5′/C2′ band is markedly affected (Table I in part I).[1] The C6′ band is superimposed to the small band of C4–C6 interflavonoid link of units with resorcinol A-rings; its increase or decrease in intensity might well mean that some autocondensation or cleavage, respectively, of such a link might occur. In the case of mimosa tannin the relative intensity of this band only increases slightly or not at all. It decreases slightly (5%) for quebracho, and it hardly decreases at all for pine tannin, which is expected due to the low level or absence of resorcinol-type units in this tannin. Pecan nut tannin instead shows a clear increase in relative band intensity, although this is small (7%). The C4–C8 link band involving resorcinol-type units is superimposed equally to the C5′/C2′ band. In the case of the C5′/C2′ band, marked variations in relative intensity occur as a consequence of the chemical/heat treatment. As the interflavonoid link involving a resorcinol-type unit is not easily cleaved,[10] such marked variations in this band intensity could be ascribed to some C4–C8 interflavonoid autocondensation in the case of mimosa and pecan nut tannins in which this band relative intensity increases by +8 and +12%, respectively (Table I in part I).[1] However, in the case of quebracho and pine tannin a decrease in relative intensity of −21 and −18%, respectively (Table I in part I) appears to infer the attack of a chemical species at C5′ or C2′ or both. Such a deduction appears also to be confirmed by the behaviour of these ^{13}C NMR bands in the case of model compounds being used (Table II in part I).[1] Thus, catechin monomer, and particularly catechin monomer/gum arabic mixtures, when treated with acetic anhydride, show a marked decrease of all the C6′, C5′, and C2′ bands relative intensities (C6′, −32%; C5′, −19%; C2′, −28% in catechin; = −46, −26, −48% in catechin/gum arabic). No cleavage of the interflavonoid link between resorcinol-type units can occur in the model compounds case: this is because first catechin is a monomer, and second because catechin does not have a resorcinol A-ring. No condensation by C2 or C4[2,10,11] open heterocycle is likely to occur on the B-ring sites because this has very low reactivity being exclusively catecholic. No phlobatannin[12] or catechinic acid[10] rearrangements can be involved as such rearrangements do not involve the C6′, C5′, and C2′ sites on the B-ring, hence, the deduction

that what occurs is an attack at these sites by a chemical species derived from the anhydride.

Such an occurrence appears to be inferred by the variation in relative bands' intensity of the free C6 and C8 sites on the A-rings for both tannins and models. Although in the latter such variations possibly also indicate autocondensation, the extent and irregularity of their decrease possibly indicates that the same attack described for the B-ring also occurs on the reactive sites of the A-ring. Confirmatory indications that the attacking chemical species is anhydride derived can be obtained by the variation in relative intensities, to the rest of the spectrum and in relation to each other, of the $-CH_3$ (25 ppm) and C=O (181–184 ppm) bands derived from the anhydride residues in both the treated tannins and model compounds (Table I in part I).[1] In Table I the reported applied effectiveness of the anhydride treatment for the four tannin extracts and model compounds are compared to the relative intensities of the $-CH_3$ and C=O bands, as well as with the $\zeta+$ potential for each system as a measure of colloidal behaviour. Passing from the noncolloidal to the colloidal state, the model compounds' relative band intensities appear to indicate that 20% or more of the anhydride does not convert to acid (applied results previously reported[13,14] showed that this varied between 25 and 40% according to treatment conditions). Table I also shows that this effect of the anhydride treatment is most marked for mimosa and quebracho tannin extracts; it is noticeable but somewhat lower for pine tannin, but it is least marked for pecan nut tannin, in good agreement with applied results.

All of what has been described appears to indicate that a so-called α-set attack[15–17] of the CH_3CO residue from the anhydride occurs on the phenolic A- and B-nuclei of some of the flavonoid units of the tannins. That this reaction is facile in concentrated water solutions of natural tannin extracts should be expected due to the colloidal micellar state caused by the presence of hydrocolloid gums. For the same reason it is more noticeable in water solutions of catechin monomer in which colloidal behaviour is imparted by the presence of gum arabic. When the solution is not colloidal, the anhydride is hydrolyzed to acid much more extensively. Anhydrides, both acetic and maleic, are not miscible with water and hence the reaction has a considerable time in which to take place. The hypothesis can be advanced that part of the anhydride has time to migrate from its state as a water dispersion to within the hydrophobic micellae. Within the micellae both acetylation of hydroxy groups as well as α-set[18] attack by the CH_3CO fragment on the aromatic A- and B-rings should occur. It is likely that in an acid environment acetylation might occur, followed by the formed ester rearrangement[16–18] to an α-set attack; thus the equivalent of a Fries rearrangement after a Friedl–Krafts acylation,[18] as soon as the 2nd state of the treatment, NaOH addition, is carried out.

The first question to be asked is: does acetylation or α-set attack occur? After chemical treatment an ester band often appears as a clear shoulder at 159–160 ppm in treated tannins, coupled to a noticeable decrease of relative intensity of the band characteristic of C5 and C7; this might indicate some ester formation at the $-OH$ groups of the flavonoid A-rings. Catechin monomer when treated with anhydride does not show any esterification and no ester band appears. The lack of colloidal state thus ensures that most of the anhydride hydrolyses to acid, but some limited α-set attack still occurs. With the catechin/gum arabic mix, esterification appears to occur and the ester band at 159–160 ppm can be noticed. Thus, with tannin extracts both some esterification and α-set attack on the phenolic nuclei appears to occur. The final effect on the adhesive performance of these two reactions is likely to be the same because esters moieties rearrange into α-set attacks, with additional cross-linking through another cross-linking mechanism, leading to curing acceleration, even in synthetic phenol-formaldehyde resins.[16] The direct α-set attack during treatment might contribute to some increase in degree of polymerization of the tannin. Both reactions instead are likely to contribute to faster gel times and greater cross-linking of the tannin-formaldehyde adhesive on curing. The second question of interest is how colloidal are the tannin extracts? The $\zeta+$ potentials, which are correlated to the extent of colloidal state of a solution, are reported for the four natural tannin extracts, the model compounds, and for some comparison materials in Table II. These show that the colloidal state of a water solution of tannin is quite definite, and does not disappear even after the chemical/heat treatment used.

All the above indicate why the extent of anhydride improvement of the different tannin extracts differs, apart from structural modifications already described.[1] In mimosa, quebracho, and pine extracts, where the content of hydrocolloid gums is noticeable, the effect of the anhydride treatment will be more marked. In pine, such a treatment, while still improving the extent of cross-linking (by α-set) and strength of the cured adhesive, does not appreciably accelerate tannin-formaldehyde gel times due to the already fast-reacting phloroglucinol-type units. For

Table III Results of Particle Board Prepared With Untreated and Chemically Treated Tannin Extracts

	IB Dry (MPa)	IB After 2 h Boil + 16 h Drying (MPa)	Board Density (g/cm^3)
Mimosa, natural	0.50	0.20	0.709
Mimosa, treated	0.58	0.51	0.700
Quebracho, natural	0.45	0.16	0.704
Quebracho, treated	0.60	0.54	0.700
Pine, natural	0.72	0.30	0.702
Pine, treated	0.71	0.49	0.700
Pecan nut, natural	1.11	0.69	0.699
Pecan nut, treated	1.08	0.71	0.700
Standard requirements	> 0.55	> 0.45	—

12-mm thick particle board, 200°C press temperature. pHs: mimosa, 7.0; quebracho, 8.0; pine, 4.8; pecan, 5.6. At best pHs of operation for the standard press time used. IB, internal bond strength.

mimosa and quebracho, faster gel times are observed due to the slower-reacting resorcinol-type units predominant in these tannins. In pecan nut tannin extract the low proportion of carbohydrates and near absence of hydrocolloid gum (the colloidal nature of the extract solution being due mostly to the high molecular weight tannins) coupled with the additional cross-linking mechanism already described[1] would lead to very little improvement of the anhydride treatment and to no noticeable difference in gel times, which is indeed what was observed.[1] It is interesting to note that such an accelerating effect of organic anhydrides on synthetic phenol-formaldehyde resins has also been reported,[17] the effect being even more pronounced than in tannins due to the much slower-reacting nature of phenol-formaldehyde resins.

Variations of ^{13}C NMR band intensities related to the carbohydrate region of the spectra can also be noticed. Their variation and their significance on the performance of tannin-formaldehyde adhesives has already been reported extensively elsewhere.[2,14,18]

In conclusion both structural modifications of tannins that occur independently of the colloidal state of the solution,[1] as well as reactions that are dependent on the colloidal state, can greatly contribute to the improvement in performance of tannin extracts as tannin-formaldehyde adhesives. ^{13}C NMR has proven to be an excellent technique in following the complex modifications induced in the tannin extracts by the simple chemical/heat treatments used to improve the performance of tannin-formaldehyde wood adhesives.

It is of interest to report results of properties of tannin-formaldehyde adhesives using the four modified and four natural tannin extracts, as well as results of particle board produced with them. These are shown in Table III. It is easy to see the major improvement in wet strength and swelling achieved by the chemical treatment of the tannin extract, particularly for the two slow reacting tannins, mimosa and quebracho. The improvement is definite in the case of pine tannin but of lower importance to the final results. The treatment is completely inconsequential to pecan nut tannin. These applied results are typical and confirm what can be deduced by ^{13}C NMR analysis.

REFERENCES

1. A. Pizzi and A. Stephanou, *J. Appl. Polym. Sci.*, to appear.
2. A. Pizzi, in *Wood Adhesives Chemistry and Technology*, Vol. 1, Chap. 4, A. Pizzi, Ed., Dekker, New York, 1983.
3. Leather Industries Research Institute, 1965, *Modern Applications of Mimosa Extract*, Grahamstown, South Africa, pp. 34–35.
4. E. Breitmaier and W. Voelter, *Carbon-13 NMR Spectroscopy*, 3rd ed., VCH, Weinheim, 1987.
5. Rank Brothers, *Operating Instructions and Manual for the Particle Microelectrophoresis Apparatus Mark II*, Cambridge, England.
6. British Standard BS 1204–1965, 1965, *Specification for Synthetic Resin Adhesives, Parts 1 and 2.*
7. Deutschen Normenansschuss, 1967, *Specification for Particle Board*, DIN 68761 (3)-1967.
8. South African Bureau of Standards, 1980, SABS 1300–1980, *Specification for Particle Board, Exterior and Flooring Type.*

9. British Standard BS 2604, part 2, 1970, *Specification for Resin Bonded Wood Chipboard; BS 1811, part 2, 1969, Methods of Test for Wood Chipboard and Other Particle Board.*
10. R. W. Hemingway, P. E. Laks, G. W. McGraw, and R. E. Kreibich, in *Wood Adhesives in 1985: Status and Needs,* Forest Products Research Society, Madison, WI, 1986, pp. 159–169.
11. G. W. McGraw, T. G. Rials, J. P. Steynberg, and R. W. Hemingway, in *Plant Polyphenols,* R. W. Hemingway and P. Laks, Eds., Plenum Press, New York, 1992.
12. D. G. Roux, in *Adhesives From Renewable Resources,* R. W. Hemingway and A. H. Conner, Eds., Plenum, New York, 1989.
13. A. Pizzi, Ph.D. Thesis, University of the Orange Free State, Bloemfontein, South Africa, 1977.
14. A. Pizzi, *Forest Prod. J.,* **28,** 12, 42 (1978).
15. P. H. R. B. Lemon, *Int. J. Mater. Prod. Technol.,* **5,** 1, 25 (1990).
16. A. Pizzi and A. Stephanou, *J. Appl. Polym. Sci.,* **49,** 2157 (1993).
17. A. Pizzi and A. Stephanou, *J. Appl. Polym. Sci.,* to appear.
18. A. Pizzi and A. Stephanou, *Holzforschung und Holzverwertung,* **45,** 30 (1993).
19. R. T. Morrison and R. N. Boyd, *Chimica Organica,* Ambrosiona, Milano, 1965.

Received April 28, 1993
Accepted July 29, 1993