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A no-aldehyde emission hardener for tannin-based wood adhesives for exterior panels

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Methylolated nitroparaffins, and in particular the simpler and least expensive exponent of their class, namely tris(hydroxymethyl)nitromethane (TN), function well as hardeners of a variety of tannin-based adhesives while affording considerable side advantages to the adhesive and to the bonded wood joint. In panel products, such as particleboard, medium density fiberboard and plywood, the joint performance which is obtained is of the exterior/marine grade type, while a very advantageous and very considerable lengthening in glue-mix pot-life is obtained. Furthermore, the use of this hardener is coupled with such a marked reduction in formaldehyde emission from the bonded wood panel to reduce emission exclusively to the formaldehyde emitted by just heating the wood (and slightly less, thus functioning as a mild depressant of emission from the wood itself). Furthermore, TN can be mixed in any proportion with traditional formaldehyde-based hardeners for tannin adhesives, its proportional substitution of such hardeners inducing a proportionally marked decrease in the formaldehyde emission of the wood panel without affecting the exterior/marine grade performance of the panel. Medium density fibreboard (MDF) industrial plant trials confirmed all the properties reported above, and the trial conditions and results are reported. In the case of cold-setting adhesives for finger-jointing and glulam, tris(hydroxymethyl)nitromethane (TN) can be used to good effect only in radiofrequency curing of such joints, hence also by heat activation, its performance instead not coming up to the requirements of relevant standards in the case of ambient temperature curing due to higher temperature activation characteristics of this hardener.

Ein Härter ohne Formaldehydemission für Holzkleber auf Tanninbasis zum Herstellen von Platten für Außenverwendung

Hydroxymethylierte Paraffine, insbesondere das einfachste und billigste, Tris(hydroxymethyl)nitromethane (TN), eignen sich gut als Härter für eine Reihe von Tanninklebern und bieten zusätzlich zu den Klebeeigenschaften noch beträchtliche Vorteile. Bei der Plattenproduktion, wie Spanplatten, MDF oder Sperrholz, erreicht die Bindung die Qualität für Außenverwendung. Eine günstige Begleiterscheinung ist die beträchtliche Verlängerung der Gelzeit, die dabei erreicht wird. Außerdem gelingt es damit, die Emission von Formaldehyd so stark zu reduzieren, daß nur noch das aus dem Holz bei Erwärmen freigesetzte Formaldehyd entweicht (sogar noch geringfügig weniger; das TN wirkt als Aldehydfänger für die Emission aus dem Holz). Darüberhinaus kann TN für Tanninkleber in allen Verhältnissen mit konventionellen Härtern auf Formaldehyd-Basis gemischt werden. Proportional zur Substitution solcher Härter veringert sich die Formaldehydemission der Platten, ohne deren Qualität oder Festigkeit zu beeinträchtigen. Versuche mit MDF im Industriemaßstab bestätigen diese Laborfunde. Die Ergebnisse und Versuchsbedingungen werden hier vorgestellt. Im Fall von kalthärtenden Klebern für Keilzinken und Brettschichtholz können gute Ergebnisse mit TN nur durch Mikrowellenhärtung erreicht werden. Allerdings werden bei Umgebungstemperatur auch durch Wärmeaktivierung, wegen der höheren Aktivierungscharakteristik dieses Härters, nicht die erforderlichen Standardwerte erreicht.

1 Introduction

Tannin-based wood adhesives have now been used industrially for a long time in several countries for the manufacture of exterior wood panels (Pizzi 1983, 1994). In the last decade several approaches to the preparation of low formaldehyde emission wood panels using these wood adhesives have been developed. This research has centered particularly on the type of hardeners used, among which are the technology for the use as hardeners of hexamine (Garcia and Pizzi 1998a, b; Pichelin et al. 1999; Pizzi 1998; Pizzi et al. 1995a, b), of imino-methylene bases (Pichelin et al. 1999; Pizzi 1998), and the use of the combination of paraformaldehyde with urea (Pizzi et al. 1995). For these panels, emissions well within the emission class 1 have been recorded, both at laboratory and at plant level, with typical emissions being in the order of 0.7–1 mg formaldehyde/100 g panel for the first two systems mentioned, and in the order 2–3 mg formaldehyde/100 g panel for the last of the systems mentioned above.

In the search for hardeners for these adhesives capable of yielding even lower formaldehyde emission, a series of products have shown to yield wood particleboard and plywood of even lower formaldehyde emission while still conserving the characteristic exterior panel performance

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characteristic of tannin adhesives. These products are based on methylolated nitroparaffins of which the more easily obtainable is tris(hydroxymethyl)nitromethane (TN), and which are produced by ambient temperature alkaline reaction of formaldehyde with a nitroparaffin. Combination of these hardeners with other hardeners is also possible.

This paper deals with the performance and emission results obtained with methylolated nitroparaffins as hardeners for thermosetting tannin-based adhesives for plywood and particleboard, as well as for radiofrequency cured, cold-setting tannin-based adhesives for glulam.

2
Experimental

Commercial tannin adhesive resins based on quebracho (*Schinopsis balansae*) and mimosa (*Acacia mearnsii*) tannin extracts were used for all the tests. A commercial PRF resin coupled with a high pH solution quebracho tannin extract according to formulations already reported (Pizzi 1994) was used for the honeymoon separate application cold set adhesive for glulam cured at ambient temperature. A traditional, commercial PRF adhesive using tris(hydroxymethyl)nitromethane (TN) as hardener was also used to prepare test joints according to relevant standards and cured by radiofrequency.

2.1
Thermomechanical analysis (TMA)

A commercial tannin adhesive resins based on quebracho (*Schinopsis balansae*) tannin extract was used for this test using 10% tris(hydroxymethyl)nitromethane (TN) on resins solids as hardener. Triplicate samples of beech wood alone, and of two beech wood plys each 0.6 mm thick bonded with each system, for a total samples dimensions of $21 \times 6 \times 1.2$ mm, were tested in non-isothermal mode between 40 °C and 240 °C at a heating rate of 10 °C/min with a Mettler 40 TMA apparatus in three points bending on a span of 18 mm exercising a force cycle of 0.1/0.5 N on the specimens, with each force cycle of 12 seconds (6 s/6 s). The classical mechanics relation between force and deflection $E = [L^3/(4bh^3)][F/(f)]$ allows the calculation of the Young's modulus E for each case tested. As the deflections f obtained were proven to be constant and reproducible (Pizzi 1997; Pizzi et al. 1997), and as they are inversely related to the values of the modulus, it is often the values of the deflection (in μm) which have been reported in the tables.

2.2
Plywood preparation

5 ply laboratory plywood panels of dimension $400 \times 400 \times 10$ mm were prepared from 2 mm thick okoumé veneers of moisture content of 4% at a glue mix spread of 250 g/m^2 single glueline. The modified quebracho tannin adhesive glue mix at a pH of 9.5 contained up to 12% tris(hydroxymethyl)nitromethane (TN) hardener (see tables) and 10% coconut shell flour 200 mesh. Hot pressing was carried out at 8 kg/cm^2 pressure and 120 °C, for 6 minutes press time. The MUF resin control was a commercial resin of M:U weight ratio of 50:50 and of molar ratio HCHO/-NH_2 = 1.2:1. The panels were cut and tested according to European Norm EN 314-method 5.1.3. for exterior plywood panels and the results obtained are shown in the tables.

2.3
Wood particleboard preparation

Duplicate one layer laboratory particleboard of $350 \times 350 \times 12$ mm dimensions were prepared by adding 9% tannin adhesive resin solids content on dry wood particles, for a percentage moisture content of the resinated particles of 20% and pressed at a maximum pressure of 28 kg/cm^2 followed by a descending pressing cycle, at 190°–195 °C and for pressing times as indicated in the results tables. All the panels had densities comprised between 0.695 and 0.704 g/cm^3. The panels, after light surface sanding, were tested for dry internal bond (I.B.) strength, and for I.B. strength after 2 hours boiling and 16 hours drying at 105 °C tested dried. The results obtained are shown in the Tables.

2.4
Medium density fiberboard (MDF) industrial plant trial

MDF of dimensions $5700 \times 1400 \times 3$ mm were produced from pine wood fibres at a temperature of 180 °C at a maximum pressure of 170 Bar in a 30 daylight press at a pressing time of 22 s/mm, and with application of 14% total solids modified quebracho tannin adhesive using as hardener 16% tris(hydroxymethyl)nitromethane (TN) based on dry tannin extract solids and addition of 2% wax emulsion addition on dry fibre.

2.5
Cold setting resins wood joints

A PRF resin containing 17% resorcinol on total liquid resin prepared in the laboratory according to procedures and formulation already reported (Pizzi 1994), which is based on a formulation in current commercial use, was used for these experiments. Two glue mixes were prepared: (i) PRF resin + 16% TN + 5% coconut shell flour filler and (ii) a separate application system in which one profile was spread with a mix composed of PRF resin + 16% TN (on resin solids, while the other profile was spread with a pH 12 quebracho tannin extract 42% water solution). These were used to bond specimens of $150 \times 20 \times 5$ mm with a bonded overlap of 10 mm according to European Norms EN 301 and 302/1 for phenolic adhesives for structural timber. The resins were cured by radiofrequency curing. The specimens were tested according to European Norm 302/1 treatments A1 and A5. Treatment A1 entails the permanence for 7 days of the bonded specimens in a 65% relative humidity chamber at 20 °C. Treatment A5 entails for the specimens a cycle of 7 days at 65% relative humidity at 20 °C, followed by 6 hours in boiling water, then 2 hours in 15 °C cold water, again followed by conditioning for 7 days at 65% relative humidity and 20 °C before testing. The results obtained are shown in the tables. Samples were also tested for delamination after 72 hours in boiling water according to European Norm EN 310, and showed no delamination.

3 Discussion

The typical ambient temperature (25 °C) pot-life results of mimosa and quebracho tannin-based adhesives with some of the different types of hardeners generally used for them are reported in Table 1. Given the already-known slight difference in reactivity (Pizzi 1994) of the adhesives based on these two different tannins, it is evident that tris(hydroxymethyl)nitromethane (TN) used as a hardener affords a tannin adhesives ambient temperature pot-life considerably longer than all the other most commonly used hardeners. This is a first improvement which can be introduced by using TN as a hardener.

In Table 2 are reported the results of laboratory particleboard prepared when using TN as a hardener alone or in combination with methylolureas hardener (Trosa 1997, 1999) and with silica accelerator of tannin autocondensation (Meikleham et al. 1994; Pizzi et al. 1995). The result indicates that at least for the more reactive mimosa tannin the use of TN alone is capable of giving dry and after boiling internal bond (I.B.) strength results which are comparable with those obtained with both synthetic resins controls as well as with paraformaldehyde hardened tannin adhesives controls (and with other traditional hardeners too). Furthermore, for the TN-hardened tannin adhesives formulations (or co-hardened by TN together with other hardeners) in Table 2, to comparable I.B. levels correspond levels of formaldehyde emission which are considerably lower than what is generally obtainable when using more traditional formaldehyde-based hardeners, and this even for the less reactive quebracho tannin adhesive. The levels of formaldehyde emission from TN hardened tannin adhesives are of the order of just the formaldehyde emitted from the heated wood only and nothing more. This shows that such adhesives can really be classed as zero emission type, and confirms that TN is a completely heat-stable type of hardener, although a lower reactivity one (hence slower-reacting), than most traditional formaldehyde hardeners under their different forms.

Table 1. Comparative effect of tris(hydroxymethyl)nitromethane (TN) hardener and classical hardeners on the pot-life at ambient temperature of modified quebracho and modified mimosa tannin adhesives

Tabelle 1. Vergleich der Wirksamkeit von Tris(hydroxymethyl)-nitromethan (TN) mit klassischen Härtern auf die Topfzeit von modifizierten Quebracho- und Akazien-Tanninklebern bei Raumtemperatur

Hardener	Percentage (%) dry hardener on dry tannin	pH	Quebracho tannin pot-life	Mimosa tannin pot-life
TN	12	4	60 days	40 days
TN	12	6	40 days	30 days
TN	12	10	6 hours	5 hours
methylolureas[(1)]	25	4	22 hours	22 hours
methylolureas[(1)]	25	6	48 hours	40 hours
methylolureas[(1)]	25	10	16 hours	12 hours
paraformaldehyde	8	4	8 hours	6 hours
paraformaldehyde	8	6	6 hours	4 hours
paraformaldehyde	8	10	40 min.	32 min.
formalin[(2)]	8	4	6 hours	5 hours
formalin[(2)]	8	6	3 hours	2.5 hours
formalin[(2)]	8	10	25 min.	20 min.

[(1)]stabilised with ethanolamine
[(2)]active formaldehyde in 37% formalin solution

Table 2. Results of laboratory particleboards bonded with tannin adhesives hardened with tris(hydroxymethyl)nitromethane (TN) and classical hardeners for different glue-mix formulations

Tabelle 2. Ergebnisse an Laborspanplatten, gebunden mit Tanninklebern. Als Härter dienten Tris(hydroxymethyl)-nitromethan (TN) und klassische Härter mit verschiedenen Leimzusammensetzungen

Adhesive system	pH	Press time (s/mm)	I.B. dry (MPa)	I.B. (V100) 2 h boil (MPa)	24 h cold water swelling (%)	Formaldehyde emission (mg/100 g panel)
quebracho + 12%TN	9.5	15	0.7	0	15	0.3
quebracho + 12%TN + 3%silica	9.5	15	0.8	0.23	8	0.3
quebracho + 10%TN + 3%silica	9.5	15	0.7	0.14	10	0.3
quebracho + 8% TN + 15%methylolureas	10	15	0.8	0.19	8	0.5
mimosa + 12% TN	9.5	14	0.8	0.20	7	0.3
mimosa + 12%TN + 3%silica	9.5	14	0.8	0.21	7	0.3
quebracho + 30%methyloureas	9.5	15	0.6	0	16	0.4
quebracho + 30%methylolureas + 3% silica	9.5	15	0.8	0.12	10	0.4
quebracho + 30% trimethylol melamine + 3%silica	9.5	15	0.8	0.15	7	0.5
quebracho + 25%methylolureas + 20%PF resin + 3%silica	9.5	15	0.9	0.32	6	0.6
Controls						
PF commercial	13	18	0.9	0.30	7	3.5
UF commercial	–	12	0.8	0	16	6.0
MUF commercial	–	12	0.8	0.22	9	4.5
Mimosa + 7% paraformaldehyde	8	10	0.8	0.19	8	3.5
quebracho + 7%paraform. + 5%urea	8	12	0.8	0.20	8	3.0
quebracho + 3%silica	10	15	0.5	0	28	0.3
quebracho + 7%paraform. + 5%urea + 3%silica	10	15	0.8	0.20	8	3.0
European Norm requirements			≥0.35	≥0.15		≤6.5

The results in Table 2 also confirm that TN can be used to good effect as a hardener not only alone but even in combination with formaldehyde-based hardeners, even the less performaing ones among them (such as methylolureas). In this regard, it can function as a convenient means to markedly reduce formaldehyde emission from particleboard and similar panels (such as MDF and OSB) when used in combination with traditional, but also less costly hardeners, such as paraformaldehyde and methylol ureas.

In Table 3 are reported the results of plywood panels prepared using quebracho tannin adhesives hardened with different amounts of TN and tested according to European Norm EN 314, class 3, for marine plywood. The results obtained indicate that marine grade plywood can be prepared using TN alone as the sole hardener of quebracho tannin adhesives, and by inference of adhesives from other tannins, quebracho having been chosen here in order to prove the capability of the hardener with the least reactive tannin. Also in plywood the TN hardener can be used in combination with other more traditional formaldehyde based hardeners, showing that synergy between TN and other hardeners exists (Table 3). The higher the proportion of TN used, the better the results obtained, as it could be expected, but the TN being rather more expensive than traditional hardeners, the limit at which the plywood prepared presents performance comparable to a MUF resin of M/U weight proportion of 40/60 is in the order of 8% TN on dry tannin adhesive solids. The same performance can be obtained by decreasing the proportion of TN and progressively substituting it with a traditional hardener, while maintaining performance but gaining considerably on ambient temperature pot-life and on still much lower than usual formaldehyde emission.

In Fig. 1 are shown, respectively, the gel times at 100 °C as a function of solution pH of three different types of tannin, namely modified quebracho, modified mimosa and pine tannin extracts, to which 12% tris(hydroxymethyl)nitromethane (TN) was added as hardener. These are considerably slower at comparable pH than what is reported for the same tannins hardened with paraformaldehyde (Pizzi 1994) but at very high pHs, namely higher than pH 9, they tend to become much closer to the gel times of the same tannins hardened with paraformaldehyde. The characteristic behaviour of tris(hydroxymethyl)nitromethane (TN) of imparting to the tannin adhesive a long pot-life at ambient temperature while maintaining

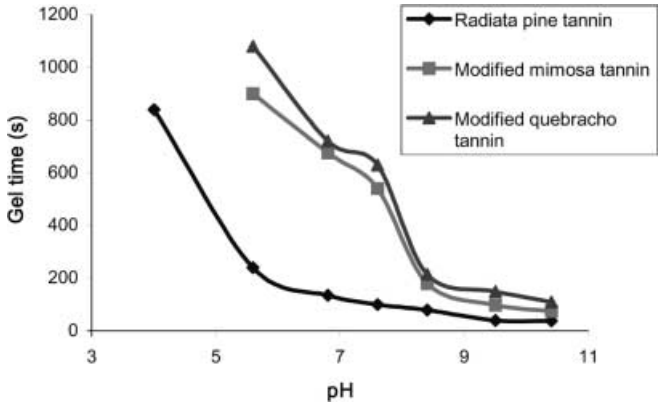

Fig. 1. Gel time curves as a function of pH of radiata pine bark tannin extract, modified wattle (mimosa) tannin adhesive and modified quebracho tannin adhesive with 12% tris(hydroxymethyl)nitromethane (TN) on dry resin solids
Bild 1. Gelzeit in Abhängigkeit vom pH für Tannin aus Kiefernrindenektrakt, für modifizierte Tanninkleber aus Akazien- und Quebrachoextrakten mit 12% Tris(hydroxymethyl)-nitromethan (TN) als Härter (bezogen auf Trockenharz)

an acceptable gel time and rate of hardening at 100 °C and higher temperatures is explained on the base of the results shown in Fig. 2, where the percentage decomposition of

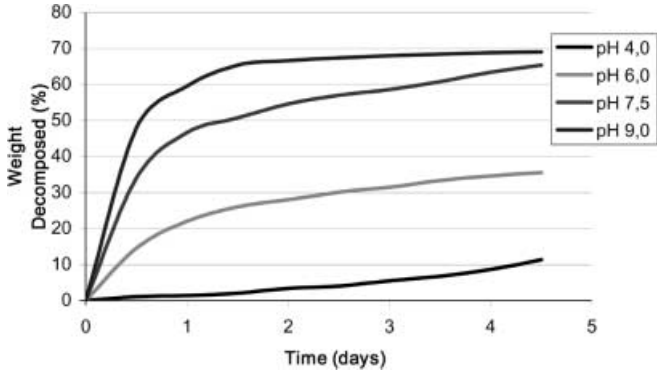

Fig. 2. Curves at different pHs of weight percentage of tris(hydroxymethyl)nitromethane (TN) decomposed to formaldehyde as a function of time at 60 °C
Bild 2. Zersetzung von Tris(hydroxymethyl)-nitromethane (TN) zu Formaldehyd bei verschiedenen pH-Werten als Funktion der Zeit bei 60 °C

Table 3. Results of laboratory plywood bonded with tannin adhesives hardened with tris(hydroxymethyl) nitromethane (TN) and classical hardeners
Tabelle 3. Ergebnisse an Laborspanplatten, gebunden mit Tanninklebern. Als Härter dienten Tris(hydroxymethyl)-nitromethan (TN) und klassische Härter mit verschiedenen Leimzusammensetzungen

Adhesive system	Breaking load (EN 314, class 3, marine ply) (MPa)	Wood failure (%)	Formal. emission (mg/100 g panel)
quebracho + 10%TN	2.1	>80	0.5
quebracho + 8%TN	1.7		
quebracho + 6%TN	0.9		
quebracho + 6%TN + 15% methylolureas	1.9		
quebracho + paraformaldehyde	1.73	>80	7
quebracho + 15% methylolureas control	0.8		
MUF (M/U 50/50) control	2.7	>80	6
MUF (M/U 30/70) control	1.4		
European Norm EN 314 requirement	≥1.0		≤6.5

TN to formaldehyde as a function of the time of its decomposition is shown. The higher the pH, the more stable the TN, and especially at the higher pHs, after an initial surge of decomposition to formaldehyde, a steady state equilibrium between the proportion of TN and formaldehyde is reached, the shift to the right becoming more evident the higher the temperature. Even at higher temperature however, a very considerable proportion of the material has not decomposed to formaldehyde. This means that after adhesive curing, curing due to both the small amount of free formaldehyde present as well as to the undissociated TN itself, as the wood panel cools down the TN↔formaldehyde equilibrium shifts again to the left re-establishing the TN and any small amounts of formaldehyde still free are again trapped in the TN any longer and cannot contribute to emission any longer.

In Table 4 are reported the results of a 4 hours industrial scale plant trial of interior grade medium density fibreboard (MDF) manufactured by the addition of 9% quebracho tannin adhesive catalysed with TN. The results at industrial level for this panel confirm the trends shown in Tables 2 and 3 for particleboard and plywood, indicating a good performance of the panels as regards dry IB strength and bending results (better than the UF control) and very low levels of formaldehyde emission (much lower than the UF control), indeed low enough to really be able to classify them as E0.

To check the performance of TN as a hardener for applications other than for panel products, honeymoon separate application cold-setting adhesives were also used with TN as a hardener for the laboratory preparation of glulam. Two types of tests were carried out: the first by hardening the joints at ambient temperature using a separate application honeymoon system based on a synthetic PRF/tannin 50/50 adhesive (Pizzi et al. 1980; Pizzi and Cameron 1984), and the second using a traditional phenol-resorcinol-formaldehyde (PRF) adhesive hardened by radiofrequency curing. In all the cases the TN was the only hardener used. The results in Table 5 indicate that in the case of ambient temperature curing of even a chemically-accelerated, fast-setting honeymoon adhesive, the performance of the joint falls somewhat short of what is required by the relevant standards, although one imagines that the system could be refined and improved. TN is then a hardener which prefers higher temperature activation to allow the adhesive and the joint to reach the wanted performance. This is in line with the very long pot-life observed in Table 1, this being a

Table 4. Industrial plant trial results for medium density fiberboard (MDF) bonded with modified quebracho tannin adhesive hardened with tris(hydroxymethyl)nitromethane (TN); sanded panels
Tabelle 4. Ergebnisse eines Industrieversuchs mit MDF, gebunden mit einem modifizierten Quebrachotannin. Als Härter wurde Tris (hydroxymethyl)-nitromethan (TN) verwendet. (Geschliffene Platten)

	Quebracho + TN	UF control
Thickness (mm)	3.0	3.0
Density (kg/m^3)	870	870
Cold water swell (20 °C, 24 h)	14%	14%
Bending strength (MPa)	38	30
Internal Bond (IB) strength (MPa)	1.8	1.8
Formaldehyde emission (mg/100 g panel)	0.0	0.9

Table 5. Phenol-resorcinol-formaldehyde (PRF) cold set adhesives hardened with tris(hydroxymethyl)nitromethane (TN), tested according to European Norms EN 301 and EN 302/1 for structural glulam adhesives (N/mm^2)
Tabelle 5. Ein PRF (kalthärtendes Harz), gehärtet mit Tris(hydroxymethyl)-nitromethan (TN). Prüfung der Konstruktionskleber nach EN 301 und EN 302/1 für Brettschichtholz

Treatment type	PRF + TN	PRF + TN + Quebracho	Requirements EN 302/1
A1	1520	1480	≥2000
A5	1240	1260	≥1600

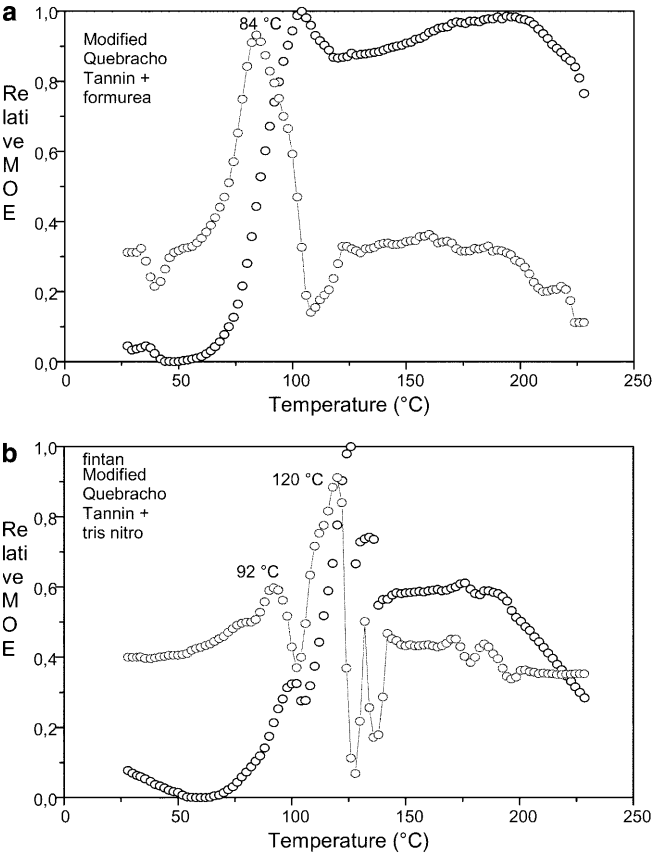

Fig. 3a, b. Thermomechanical analysis (TMA) determined curves of the variation of the relative modulus and of its first derivative as a function of temperature for a beech wood joint bonded with modified quebracho tannin adhesive: **a**) using 14% formurea as hardener; **b**) using tris(hydroxymethyl)nitromethane (TN) (solids on resin solids)
Bild 3a, b. TMA-Kurven der Änderung des relativen E-Moduls und der ersten Ableitung als Funktion der Temperatur, gemessen an einer Buchenholzverbindung. Als Kleber diente ein modifiziertes Quebrachotannin: **a**) mit 14% Harnstoff-Formaldehyd als Härter; **b**) mit Tris(hydroxymethyl)-nitromethane (TN) als Härter (jeweils bezogen auf Trockenmasse)

Table 6. Thermomechanical analysis (TMA) for controls and for joints bonded with modified quebracho tannin adhesive hardened with tris(hydroxymethyl)nitromethane (TN)
Tabelle 6. TMA and Kontrollproben und Verbindungen, die mit einem modifizierten Quebrachotannin-Kleber verleimt waren. Als Härter wurde Tris(hydroxymethyl)-nitromethan (TN) verwendet

Adhesive type	Young's module (MPa)	Minimal bending deflection (μm)	Max. dE/dt first derivative peaks (°C)	
			T_1	T_2
Quebracho + 14%formurea	1107	32	84	–
Quebracho + 16%formurea	1540	23	87	–
Quebracho + 12%TN	1476	24	92	120

considerable advantage in thermosetting adhesives but being a considerable disadvantage for cold setting adhesives, where too long a pot-life infers too low a reactivity of the system at ambient temperature. Radiofrequency curing is necessary as it is a different form of heat activation, and the TN reverts to being an excellent and sufficiently fast hardener while maintaining the advantage of a very long pot-life of the glue-mix.

The performance of beech joints bonded with tannin adhesives when using TN as a hardener was also checked by thermomechanical analysis. The comparative results obtained are shown in Fig. 3a and b, and in Table 6. In Table 6 two points are noticeable, showing that the minimum deflection and maximum modulus obtained with 12% TN are comparable to what is obtained by using 16% formurea as alternative hardener, but better (deflection smaller and modulus greater) than what is obtained with 14% formurea hardener. In Table 6 and in Fig. 3a and b, it is noticeable that two reaction zones occur in the case of tannin hardened with TN while only one occurs when using formurea hardener. The first derivate peak noticeable between 84 °C and 92 °C is the reaction due to the faster formaldehyde with the tannin, while the second, higher temperature first derivate peak at 120 °C is the one due to the reaction with the adhesive of the undissociated TN, and is absent in the formurea or formaldehyde hardened cases. This confirms again both the stability of the TN as its capability to function as an effective hardener for tannin adhesives.

To conclude, methylolated nitroparaffins and in particular the simpler (and least expensive) exponent of their class, namely tris(hydroxymethyl)nitromethane (TN), function well as hardeners of a variety of tannin-based adhesives while affording considerable side advantages to the adhesive and to the bonded wood joint. Thus, in panel products, such as particleboard, medium density fiberboard and plywood, the joint performance obtained is of the exterior/marine grade type, while a very advantageous and considerable increase in glue-mix pot-life is obtained coupled with such a marked reduction in formaldehyde emission from the bonded wood panel to reduce this exclusively to the formaldehyde emitted by heating just the wood (and slightly less). Furthermore, TN can be mixed in any proportion with traditional formaldehyde-based hardeners for tannin adhesives, its proportional substitution of such hardeners, inducing a proportionally marked decrease in the formaldehyde emission of the wood panel. In the case of cold-setting adhesives for fingerjointing and glulam, tris(hydroxymethyl) nitromethane (TN) can be used to good effect only in radiofrequency curing of such joints, hence also by heat activation. Its performance, however, does not come up to the requirements of relevant standards in the case of ambient temperature curing, due to the higher temperature activation characteristics of this hardener.

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