

CONDENSED TANNIN REACTIVITY INHIBITION BY INTERNAL REARRANGEMENTS: DETECTION BY CP-MAS ¹³C NMR

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ABSTRACT

Tannin extracts were prepared from barks of maritime pine (*Pinus maritimus*), aleppo pine (*Pinus halepensis*), Norway spruce (*Picea abies*) and from a mixture of barks of different pine species (*Pinus spp.*, namely 20% black pine (*Pinus thunbergii*) + 30% Scots pine (*Pinus sylvestris*) + 20% maritime pine (*Pinus maritimus*) + 10% Aleppo Pine (*Pinus halepensis*) + 5% Douglas fir (*Pseudotsuga menziesii*) + 15% Norway spruce (*Picea abies*)) at a paper mill. The ¹³C-NMR spectra were carried out from these tannins. Blending systems adhesives were prepared with 5% paraformaldehyde to measure the reactivity by gel time, and to determinate the mechanical resistance by thermomechanical analysis (TMA) and the internal bond strength (IB) according to the European Norm EN-312. The CP MAS ¹³C NMR bands at 163 ppm and the increase number of smaller bands between 20 and 65 ppm clearly indicate that the extraction of procyanidin-type tannins has been incorrect yielded high relative proportions of catechinic acid structures and diarylpropanol-catechinic acid dimer caused by internal flavonoid rearrangement, and causing the blockage of the C6 and C8 reactive sites, rendering unusable the tannin for wood adhesive applications. Thus, the gel times are very long except for the maritime pine tannin with a value of 51 (s). The TMA analysis gave very low MOE values for almost all the tannin extract samples, except for maritime pine. This situation was confirmed by the IB test. Only maritime pine tannin presented a good mechanical resistance with a value of 0.6 (MPa). Only this sample fulfils the standard requested.

Keywords: Catechinic acid, tannins, rearrangements, reactivity inhibition, NMR, wood adhesives.

INTRODUCTION

Natural adhesives were used a lot before the 1930's, and then, they have been almost entirely replaced by synthetic adhesives (Wang *et al.* 2008). However, wood adhesives from renewable raw materials have been a topic with considerable interest for many years. This interest, already present in the 1940's, became bigger with the first world oil crisis in the early 1970's but subsided as the cost of oil decreased. Since the beginning of the 21st century this interest intensified again for a lot of reasons. The main stimulus for today's renewed interest in bio-based adhesives is the acute sensitivity from the general public toward anything concerning the environment and its protection (Pizzi 2006). Health problems that can present symptoms such as the most common of which are eyes irritation and the upper respiratory tract are attributed to the emission of formaldehyde gases (Kim 2009). Also, formaldehyde has been found to produce nasal carcinomas in mice and rats after a prolonged exposure at 14.1 and 5.6 mg/L level, respectively. These findings have led to an intensified interest in the indoor environment (Kim 2009, Kim and Kim 2004, Brown 1999). Consumer products, especially construction materials, are the main source of formaldehyde emissions in the indoor environment. On the other hand, the limited fossil fuels pool and the broad availability of renewable resources are especially appealing as a source

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Received : 06.05.2010 Accepted : 13.12.2010.

of materials and energy (Vazquez *et al.* 2010). For all these reasons, it is necessary to find new natural alternatives to produce wood adhesives.

While the majority the literature on this subject focuses on already commercially available tannins such as mimosa and quebracho, work on pine tannins has yielded perfectly workable formulations some of which have already been used industrially for almost ten years at Masisa Chiguayante plant facility in Chile (Pizzi *et al.* 1993, Pizzi *et al.* 1996) as adhesives for particleboards. The scarcity of commercially available mimosa and quebracho tannins in a period where the interest in adhesives from renewable materials, and the very positive Chilean experience with *Pinus radiata* bark tannins, has prompted a number of investigations in the suitability for wood adhesives application of tannins obtained from the bark of other pine species (Pizzi 1998). Thus also, hybrids adhesives such as tannin/PVAc have been studied as environment-friendly adhesives (Kim 2009) to decrease the formaldehyde emissions.

The purity of vegetable tannin extracts is very different from one to another. The non-tannin fraction, mainly sugars and hydrocolloid gums, generally does not participate in resin formation with formaldehyde (Pizzi 1982), and there are some differences between different polyflavonoid tannins that can be used for thermosetting wood adhesives. Flavonoid units in such tannin present phloroglucinol or resorcinol A-rings and catechol or pyrogallol B-rings is presented in the figure N°1.

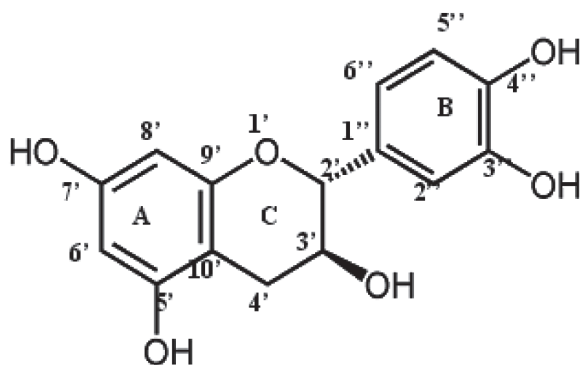


Figure 1. Flavonoid structure.

Since tannin molecules are generally large, the rate of molecular growth in relation to the rate of linkage is high; thus tannin adhesives can tend to have short pot-lives (Pizzi 1982). From the point of view of both molecular size and reactivity, phloroglucinolic tannins are worse than mainly resorcinolic tannins as shown by their relative gel times at their pH's of lower reactivity: 950 (s) for wattle tannin extract (resorcinolic) against 65 (s) for pine tannin extract (phloroglucinolic). Molecular size reduction is difficult and therefore it does not offer a practical solution (Pizzi 1982).

Different works have been developed about the tannin extraction with the aim of improving their quality and yield. Thus, different additives have been added to improve some properties, such as sulphites, allow limiter the tannin auto-condensation and the phlobaphenes formation (Sealy-Fischer and Pizzi 1992), as well as to break the interflavonoides link, or to do the tannin polymers more soluble because they are smaller (Pizzi 1983). The urea allows coverall to increase the yield extraction (Sealy-Fischer and Pizzi 1992), and the amoniac allow the tannin use with a better adhesive aptitude (Panamgama 2006). However, some manipulation errors in extraction, drying conditions generally could cause this unusual behaviour, and this paper sets out to explain what rearrangement occurs in the tannin to inhibit its reactivity to the point of even inhibiting gelling altogether.

EXPERIMENTAL

Extractives preparation

Tannin extracts were prepared from the barks of maritime pine (*Pinus maritimus*), aleppo pine (*Pinus halepensis*), Norway spruce (*Picea abies*) and from a mixture of barks of different pine species (*Pinus spp.*, 20% namely black pine (*Pinus thunbergii*) + 30% Scots pine (*Pinus sylvestris*) + 20% maritime pine (*Pinus maritimus*) + 10% Aleppo Pine (*Pinus halepensis*) + 5% Douglas fir (*Pseudotsuga menziesii*) + 15% Norway spruce (*Picea abies*)) at a paper mill. All these are composed of procyanidin-type tannins. The tannin samples were extracted in the standard manner (Sealy-Fischer and Pizzi 1992) by extracting 100 grams bark with 500 ml water solution of 2% Na₂SO₃ + 0.5% NaHCO₃ at 75°C for 1 hour, with the exception of the maritime pine for which an industrially water extracted material was used produced by DRT (Dérivés Résiniques et Térpeniques, France). The samples for which a catechinic acid rearrangement was required to study the appearance of the ¹³C NMR spectra were dried in an oven for 20 days at 45-50°C and pH 8-9 after extraction prompting the catechinic acid rearrangement described for pure catechin model compounds under these conditions by Sears *et. al.* (1974) and Kiatragrajai *et. al.* (1982), according to figure N°2. The industrial sample was obtained after spray-drying to ensure minimization or absence of the same rearrangement.

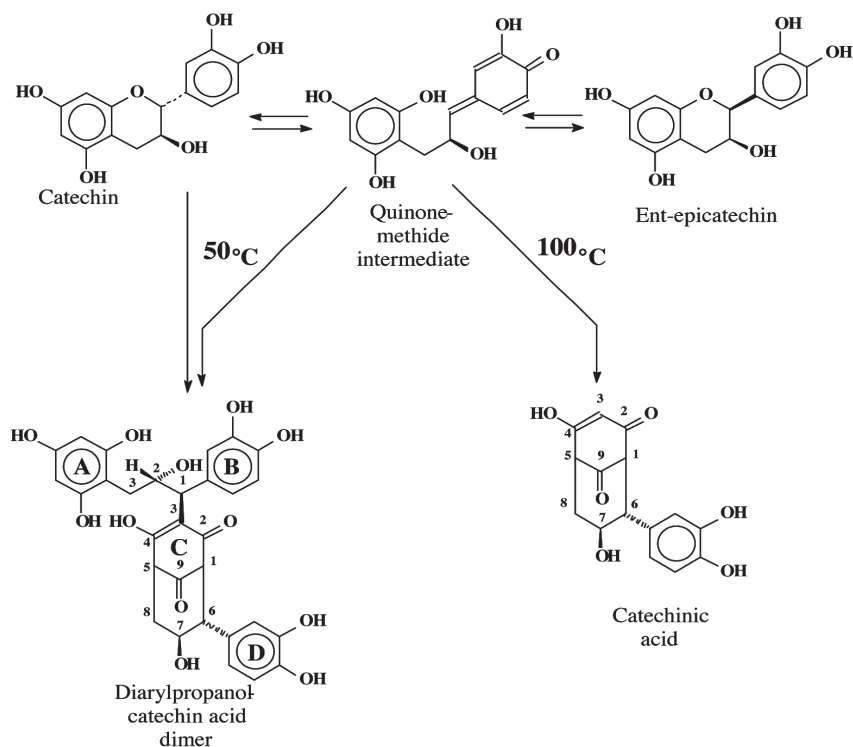


Figure 2. Base catalyzed reactions of (+) catechin at pH12 (Kiatragrajai *et al.* 1982).

¹³C NMR analysis

The dried powder sample were analysed by solid state CP MAS (cross-polarisation/magic angle spinning) ¹³C NMR spectroscopy. Spectra were obtained on a Bruker AVANCE II 400 MHz spectrometer operating at a frequency of 100.6 MHz and a sample spin of 12 kHz, using a recycling delay of 1s and a contact time of 1 ms. Number of transients was about 15000, and a 53 kHz decoupling field. Chemical shifts were determined relative to tetramethyl silane (TMS) used as control. Spectra, accurate to 1 ppm, were recorded with suppression of spinning side bands.

Gel time

The gelation is defined as the point at which the resin ceases to be a viscous liquid and become a soft, elastic, rubbery solid (Pizzi and Stephanou 1993). Triplicate samples at 45% tannin solution in water to which 5% paraformaldehyde on tannin extract solids content had been added were prepared. The samples initial pH is indicated in the table N° 1. In the Norway spruce, Aleppo pine and the mixed pine species had high initial pH compared with Maritime pine, for this reason the initial pH was diminished to pH 5. Gel time tests were conducted at 100 °C, Five (g) of liquid was weighed in a glass test tube, and then placed in a boiling water bath. The wire spring was manually moved rapidly upward and downward, and the time for gelation was measured using a stopwatch.

Table 1. Gel times for different procyanidin type tannins extracted under different conditions.

Specie	Hardener	pH	Get time (s)
Control: Commercial <i>Pinus maritimus</i>	Paraformaldehyde	5.2	51
Control: Commercial <i>Pinus radiata</i>	Paraformaldehyde	5	80
Norway Spruce (<i>Picea abies</i>)	Paraformaldehyde	10	3060
		8,2	2160
	Hexamethylenetetramine	10	6000
		8,2	4200
Aleppo pine (<i>Pinus halepensis</i>)	Paraformaldehyde	4,95	3360
		9	1740
		10,2	2490
	Hexamethylenetetramine	10,2	2754
Mixed pine species (<i>Pinus spp</i>)	Paraformaldehyde	5	3300
		9	2280
		10	2352
	Hexamethylenetetramine	9,7	2610

Thermomechanical analysis TMA

The hardening reaction of one resin system or glue mixes can be evaluated by TMA, by the study of the rigidity of the wood-resin joint as a function of temperature. Thus, the different system adhesives tannins were thermomechanically analyzed under the same conditions. The formulations were identical to gel time formulations. Triplicate samples of beech wood alone, and of two beech wood ply each 0.6 mm thick, bonded with each system, for a total samples dimension of 20×5×1.1mm were tested in non-isothermal mode between 25 °C and 250 °C at a heating rate of 10 °C/min, 30 mg of resin, with a Mettler 40TMA 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 $E = [L^3/(4bh^3)] [\Delta F/(\Delta f)]$ allowed the calculation of the Young's modulus E for each case tested. Deflection curves that allow MOE determination are obtained by the three-points bending TMA mode. The MOE of the wood joints bonded with different resin systems give a good indication of the final strength of the adhesive system tested and the possible end performance of the adhesive system tested.

Internal bond strength IB

Duplicate one-layer laboratory particleboards of dimensions 350 mm×310 mm×14 mm were prepared, using only enter particles of beech (*Fagus sylvatica*) and Norway spruce (*Picea abies*) wood mixture. The resin solid load was maintained at 10% of the tannin resin on dry wood particles. All particleboards were tested for dry internal bond (IB) strength according to the European Standard EN-312.

RESULTS AND DISCUSSION

The gel time results in table N° 1 indicates that for industrially extracted samples the gel times with paraformaldehyde hardener at pHs of around 5 were fast as expected of procyanidin-type tannin extracts (Pizzi 1994). However, procyanidin-type tannins that were laboratory extracted and dried in an oven first for a number of days at a temperature of 50°C, followed by further days of drying at 45°C, even if the pH was low at around 4-5, as their natural pH (8-9) thus in non ideal conditions for maximum to catechinic acid rearrangement and diarylpropanol-catechinic acid dimer, showed gel times which were far too long. Moreover they did not gel well but remained exceedingly soft. The difference was major, between the 50-90 seconds recorded for the normally extracted and spray-dried commercial tannin extracts (Pizzi 1994), and the rest at 50-80 minutes gel time (Table 1). In addition, at very high pHs the reactivity of normally extracted procyanidin-type tannins is of around 20-30 seconds. This result indicated that a great proportion of the available C6 and C8 reactive sites of the flavonoid structure were blocked, and thus unavailable for reaction with paraformaldehyde. The catechinic acid rearrangement shown in figure N° 2 shows that blocking a great proportion of C6 and C8 sites available for reaction, thus slowing down considerably and sometime even stopping altogether gelation of the tannins with hardeners. It was then of interest to examine these tannins by ¹³C NMR spectroscopy to observe whether catechinic acid and apparently diarylpropanol-catechinic acid dimer had been formed (Hashida and Ohara 2002).

About the base-catalyzed reactions of (+)-catechin, (Figure N° 2), several investigations have been reported (Hashida and Ohara 2002, Sears *et al.* 1974). At 25 °C, ent-epicatechin is formed by epimerization at C-2 position of pyran-ring, whereas catechin acid is obtained in high yield in the reactions at 100 °C (Hashida and Ohara 2002; Kiatgrajai *et al.* 1982, and Sears *et al.* 1974). These reactions are supposed to proceed through opening of the pyran-ring to give the quinone-methide intermediate, followed by reclosure of pyran-ring or by nucleophilic attack of carbanion at C-8 position on the C-2 position of quinone-methide intermediate. A radical reaction mechanism is also proposed because these reactions are inhibited by the exclusion of oxygen (Kennedy *et al.* 1984, Hashida and Ohara 2002). Previously (Ohara and Hemingway 1991) showed that at intermediate temperature (40 °C), diarylpropanol-catechin acid dimer is produced together with catechin acid. There are other compounds are produced in low yield on that condition but they are not been identified (Hashida and Ohara 2002).

The ¹³C NMR spectra in figure N°3 show a maritime pine tannin extract (Fig. N° 3a), and the rearranged of Norway spruce extract (Fig. 3b), Aleppo pine extract (Fig. N° 3c), and mixed pine species extract (Fig. N° 3d) samples. The ¹³C NMR chemical shift assignments for the tannins are indicated on the spectra themselves corresponding to the relevant notations on the catechin and catechinic acid formulas. The rearranged tannin samples show signals for the catechinic acid C2 (176-180 ppm), C4 (163 ppm), C6, C3 (around 110 ppm), C7, C1, C5 and C8 (37-40 ppm). Only the spectra in Figures 3c, 3d, show presence of the C9 position (190-200 ppm). The majority of these peaks are relatively small although clearly indicating the presence of noticeable proportions of catechinic acid (Pretsch *et al.* 1998, Werhli and Wirthlin 1978). This is explained by the fact that only some of the flavonoid structures have converted to catechinic acid and diarylpropanol-catechinic acid dimer rearranged due to the lower temperature of drying and high pH of the samples (Figure N° 2). However, one peak is very sensitive to the presence of catechinic acid and is always present, very sharp and evident, where no other equivalent peaks are present for non-rearranged flavonoid structures. In normal flavonoid tannins the two peaks at 155 and 144 ppm are characteristic and clearly visible. But only where a consistently

high proportion of catechinic acid is high peak at 163 ppm does appear transforming the peak couple in a three peaks set (Figs. 3b, c and d). The second best indication of the presence of catechinic acid is the series of peaks between 20 and 65 ppm. In this range are generally found the C3, C6' and the unreacted C4 of normal flavonoids. However, in the case of the catechinic acid rearrangement, some sharp peaks appear corresponding to the C1, C7, C6, C5, C8 (Fig. 3b and 3d) and 1', 2' and 3' (Figure N° 2 and N° 3c) where these ones are clearly present (Figure N° 3b and 3d). The third indication of the presence high proportions of catechinic acid structures is its C2 peak presenting a sharp peak at around 176-177 ppm (clearly visible in Figures N° 3b and 3d) (Pretsch *et al.* 1998, Werhli and Wirthlin 1978). This is not always clearly obvious and thus cannot be totally relied on. As for the causes of the rearrangement, they appear to be the very long time exposure during the drier (20 days), at low temperature (50-45°C) and high pH samples that caused the rearrangement to occur under these relatively mild conditions. Differently from Hashida and Ohara (2002), while the shifts around 65 ppm as they find indicate the presence of catechinic acid-like molecules, the more obvious band at 163 ppm is an even clearer and more noticeable indication of such flavonoid rearrangements (table N°2).

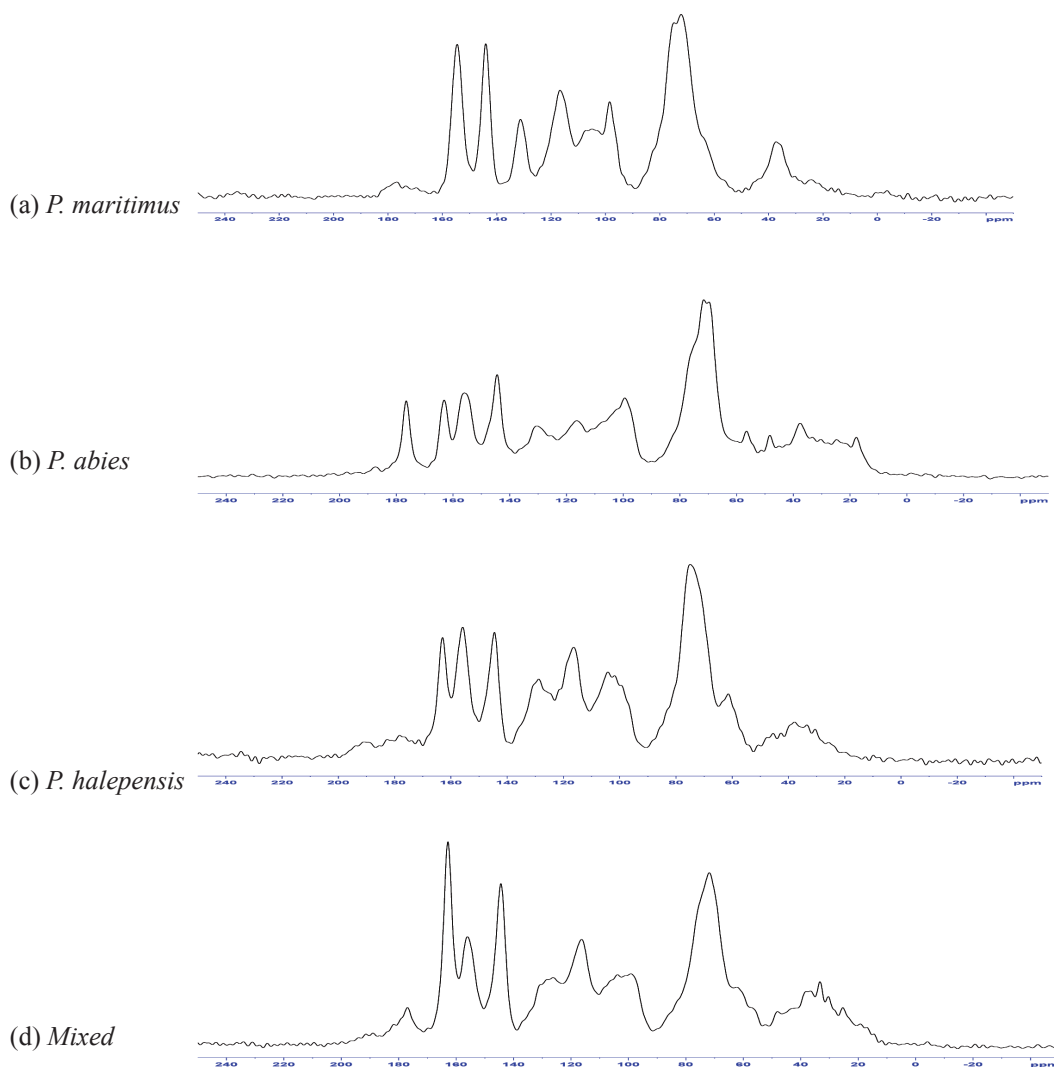
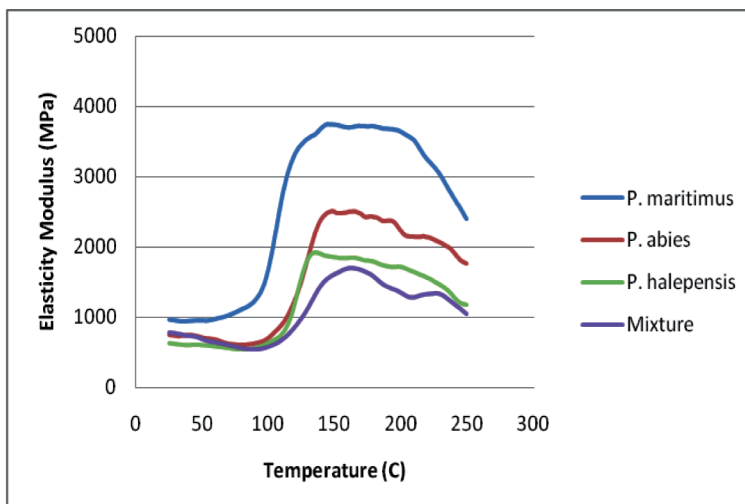


Figure 3. CP MAS ^{13}C NMR solid state spectra of (a) *P. maritimus*, (b) *P. abies*, (c) *P. halepensis*, and (d) mixture tannin extract species showing catechin acid rearrangement.

Table 2. ^{13}C NMR Chemical shifts to the rearranged samples results.

Chemical shifts		<i>P. maritimus</i>	<i>P. abies</i>	<i>P. halepensis</i>	Mixture
C9	190-120	Absent			
C2	176-180				
C4	163	Absent			
C6, C3	110				
C8, C7, C5, C1	37-40	Absent			
C5', C7'	156-157				
C9'	155				
C3'', C4''	145-146				
C1'	131				
C6''	120-121				
C5'', C2''	115-117				
Phloroglucinol interflavonoid	110		Absent	Absent	Absent
C10'	101				
C6'	96-98				
C8'	95-96				
C2'	91-82				
C3'	67-68				
Catechic acid	31-32				
C4'	27-28				

The TMA analysis showed low Elasticity Modulus (MOE) for *P. halepensis*, *P. abies* and the bark mixture tannin adhesives (Figure N° 4). The maximal value registered with these tannins was hardly 2.500 (MPa). Nevertheless, the maritime pine situation was different. The elasticity modulus for this specie presented a maximal value of 3.744 (MPa). The MOE of the wood joints bonded with different resin systems gives a good indication of the final strength of the adhesive system tested and the possible final performance of the adhesive system tested.

**Figure 4.** Thermomechanical test comparison by elasticity's modulus (MOE).

The results of the TMA tests were confirmed by preparing and testing laboratory particleboard panels. Thus, in table N° 3 the IB results from particleboard prepared using the different extracts are shown. The IB results from particleboards tannins are in direct relation with the TMA analysis. The registered value didn't reach the minimal requirements demanded by the European Norm, except for the particleboard prepared with maritime pine tannin. This result was able to satisfy the dry IB strength requirement of >0.35 (MPa) of the relevant European Norm EN 312 for interior grade panels, to press time of 7.5 (min), and at 195 (°C). There are not available reactive sites in *P. abies*, *P. halepensis* and the bark mixed tannin studied. Then, there was not to cross linking between the adhesive and the wood, even using paraformaldehyde as a hardener.

Table 3. Internal bond results.

Formulation	Density (kg/m ³)	IB (MPa)
<i>P. maritimus</i>	700	0,6±0,09
<i>P. abies</i>	700	0,08±0,01
<i>P. halepensis</i>	692	0,03±0,02
Mixed	690	0,01±0,00

CONCLUSIONS

The CP MAS ¹³C NMR bands at 163 ppm, and the increase number of smaller but clearly defined bands between 20 and 65 ppm can be taken as a clear indication that the extraction of procyanidin-type tannins has been incorrect yielding high relative proportions of catechinic acid structures, caused by internal flavonoid rearrangement, and causing the blockage of the C6 and C8 reactive sites, rendering unusable the tannin for wood adhesive applications. This was confirmed by the gel time and the mechanical tests (TMA and IB). Only maritime pine with a strength of 0.6 (MPa) satisfy the European Norm EN-312 request.

It is important to note that alkaline pHs of the tannins extracted (8-9) noticeable proportions of flavonoid units to catechinic acid rearranged and other compounds have been formed if the temperature is sufficiently low (around 45-50 °C), and the time at which the tannin extract is maintained at such a temperature is sufficiently long, such as for days.

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