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To cite this version:
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Journal: Holz als Roh- und Werkstoff
Manuscript ID: HRW-08-0144.R1
Manuscript Type: ORIGINALARBEITEN / ORIGINALS
Date Submitted by the Author: 09-Apr-2009
Complete List of Authors: MOUBARIK, Amine; Université de Pau et des Pays de l'Adour, SYLVADOUR CHARRIER, Bertrand; Université de Pau et des Pays de l'Adour, SYLVADOUR CHARRIER, Fatima; Université de Pau et des Pays de l'Adour, SYLVADOUR Allal, Ahmed; Université de Pau et des Pays de l'Adour, Equipe de physique et Chimie des Polymères Pizzi, Antonio; Université de Nancy 1, ENSTIB
Keywords: Cornstarch, Formaldehyde, Hexamine, Mimosa tannin, Quebracho tannin, Wood adhesives, Wood composites
Development and optimization of a new formaldehyde-free cornstarch and tannin wood adhesive

A. Moubarik, B. Charrier, A. Allal, F. Charrier, A. Pizzi

Abstract

The development and optimization of a new, environment-friendly adhesive made from abundant and renewable cornstarch and tannin is described in this study. At present, the production of wood composites mainly relies on petrochemical- and formaldehyde-based adhesives such as phenol-formaldehyde (PF) resins and urea-formaldehyde (UF) resins. Formaldehyde-free cornstarch plus tannin adhesives were evaluated for mechanical and physical properties (shear strength, rheological characterisation and thermogravimetric analysis).

First, optimized conditions for the preparation of cornstarch-sodium hydroxide wood adhesives were determined. The parameters studied were the following: total solids content of the adhesives, sodium hydroxide concentration and sodium hydroxide/cornstarch volume ratio. The highest shear strength results appeared to be 0.5 sodium hydroxide / cornstarch volume ratio when using concentrations of cornstarch (65 % p/v H₂O) and sodium hydroxide (33 % p/v H₂O).

The optimum cure temperature was 170°C and the cure time 4min. The addition of two types of tannin-based adhesives, Mimosa and Quebracho, with hexamethylenetramine (hexamine) hardener to the cornstarch-sodium hydroxide formulation improved the shear strength and decreased the viscosity of adhesives.

Entwicklung und Optimierung eines neuen, formaldehydfreien Holzklebstoffes auf Maisstärke- und Tanninbasis

Zusammenfassung


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1 Introduction

One of the main concerns of the 21st century is the environment. The environment has become a subject of constant attention and has become a focal point of our life and welfare (Meyer et al. 1986 a, b, c).

Formaldehyde-based wood adhesives such as phenol-formaldehyde, urea-formaldehyde and melamin-urea-formaldehyde are derived from petrochemicals, which are non-renewable and therefore ultimately limited in supply (Li et al. 2004). Moreover, formaldehyde is considered a priority pollutant by the United States Environmental Protection Agency. Its emission into the environment and exposure of workers at manufacturing facilities continues to be a major safety concern (Keith and Telliard 1979, Myers 1986).

Efforts are made to develop durable adhesives using phenolic substitutes (Thompson 1991). Other investigators have utilized renewable natural polymers to replace phenol in phenol-formaldehyde adhesives (Conner et al. 1989, Conner 1989). Lignin, a highly branched natural phenolic polymer and a by-product of the pulping industry, is an abundant renewable resource at
low cost (Pizzi 2006). Tannin is another example of such a renewable material and has been used
to substitute tannin for the synthetic phenolics in wood adhesives (Pizzi 2006).
Starch is one of the most abundant natural polymers (Imam et al. 1999). Starch has been used as
an adhesive in a wide range of products, including binders, sizing material, glues and pastes
(Imam et al. 1999, Yazaki and Collins 1997). More recently, the development of a starch-based
wood adhesive for interior applications has been described (Imam et al. 1999). Starch yields
adhesives with excellent affinity for polar materials such as cellulose. Ideally, the contact angle
between the adhesive and the substrate should be small. This allows the adhesive to wet the
surface and spread uniformly in a thin film with a minimum of voids. In this regard, starch based
adhesives wet the polar surface of cellulose, penetrate crevices and pores and, thus, form strong
adhesive bonds (Imam et al. 1999).
Among the possible alternatives, tannin is an excellent renewable resource which can be used for
replacing petroleum-derived phenolic compounds. The major species from which it can be
obtained are Mimosa, Quebracho and Radiata pine. The use of hexamine as a hardener for a
tannin, hence, a tannin-hexamine adhesive, is a very environment-friendly proposition. $^{13}$C-NMR
has confirmed (Pichelin et al. 1999, Kamoun et al. 2003) that the main decomposition of
hexamine under such conditions is not directly due to formaldehyde. It rather proceeds through
reactive intermediates, hence, mainly through the formation of reactive imines and
iminoaminomethylene bases. $^{13}$C-NMR has also confirmed (Pichelin et al. 1999, Kamoun et al.
2003) that in the presence of chemical species with very reactive nucleophilic sites, such as
condensed flavonoid tannins, hexamine is not 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 imines and iminoaminomethylene intermediates initially
formed in its decomposition do react with the phenolic species present without ever passing
through the formation of formaldehyde (Pizzi and Tekely 1995, 1996; Pizzi et al. 1996; Kamoun
et al. 2003).
Initial investigations on the use of wattle tannin in starch corrugating adhesives were carried out
at the Division of Forest Products, CSIRO, in 1968. As an alternative material to resorcinol was
urgently needed in 1969, the project was extended to include some studies designed to establish
reasons for the poor performance of water-resistant starch adhesives (McKenzie and Yuritta
1972). Further research and developments in the field of fortified starch adhesives with wattle
tannin were carried out in South Africa (Saayman and Brown 1977). Industrial production with
one such system started, however, in South Africa in the late 1970’s (Custers et al. 1979).
In this study, the mechanical properties (shear strength) and physical properties (rheological and thermogravimetric analysis) of cornstarch-tannin adhesives with hexamine as hardener was investigated.

2 Experimental methods

2.1 Preparation of cornstarch-tannin adhesives and preparation of two-ply wood composites bonded with the cornstarch-tannin adhesives.

Cornstarch water solutions were prepared at six different concentrations namely 12, 25, 50, 65, 75 and 90%, by dissolving cornstarch in deionised water, stirring at room temperature, and adding sodium hydroxide (Mw = 40.00) at different concentrations (5, 15, 33, 50 and 75%) as hardeners. The resulting adhesives were mixed for 45 min at room temperature and then used for bonding wood veneer.

In order to improve the shear strength of cornstarch-sodium hydroxide adhesives, the two types of tannin, Mimosa and Quebracho, were added in proportions of 5%, 10%, 20%, 30%, 40% and 50% by weight on cornstarch solids content; hardener content used was 5 percent hexamine by weight on tannin extract solids content. The hexamine was dissolved in water to yield a 30 percent concentration solution in water prior to adding to the tannin solution to form the glue-mix.

Maritime pine veneer with a thickness of 3 mm was cut to rectangular specimens $2.5 \times 11.5 \text{ cm}^2$ (according to British Standard 1204, 1965, part 2, for synthetic resins adhesives). The adhesive was applied to one side of each piece of veneer. The application area was $2.5 \times 2.5 \text{ cm}^2$ for each veneer. The spread rate of the adhesive was 120-150 g/m$^2$ on a dry weight basis (Nihat and Nilgül 2002, Pizzi 1977). Two adhesive-coated veneer boards were lapped together with the grain parallel to each other and then pressed at 0.45 MPa (Fig. 1). The press temperature and press time were varied for the determination of their effects on the strength of wood composites. After bonding, the assemblies were conditioned in a Vötsch climate room (25°C and 65% humidity) for 24 hrs. Five hundred samples were prepared for mechanical tests.

2.2 Mechanical properties
The shear strength of the wood composite was determined on an Instron testometric M500-50 AT testing machine. The crosshead speed was 1 mm/min. The load at fracture was measured, and reported as shear strength. Every experiment was repeated; at least, ten replicates and their standard deviations were calculated.

2.3 Rheological characterization

The adhesives were tested with an advanced rheometric expansion system (ARES) with parallel plate’s geometry, which was used for all the measurements; the plate diameter used was 25mm and the gap between the parallel plates was 1.5mm. Silicone oil was used to prevent water evaporation.

2.4 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was carried out with a TGA Q50 thermogravimetric apparatus. Ten milligrams of each cured sample was placed on a balance located in the furnace and heat was applied over a temperature range from room temperature to 600 °C at a heating rate of 5 °C/min in air.

2.5 Solid phase $^{13}$C NMR analysis

The solid state $^{13}$C NMR spectra of the cornstarch, cornstarch-NaOH, mimosa tannin-hexamine and cornstarch-NaOH-MT-H resin systems used, were acquired at ambient temperature by using a Bruker 400 MHz spectrometer. Powdered samples were packed in 4-mm zirconia rotors, sealed with Kel-F™ caps and spun at 6 KHz and at a contact time of 3.5 ms. Chemical shifts were determined relative to tetramethyl silane (TMS) used as control.

3 Results and discussion

First, the conditions for the preparation of cornstarch-sodium hydroxide wood adhesives were optimized. Parameters like total solids content of adhesives, sodium hydroxide concentration,
sodium hydroxide/cornstarch volume ratio, reaction time and reaction temperature were studied. These parameters were varied and their effect on shear strength was studied.

3.1 Effects of the total solids content of adhesives on shear strength

The results presented in Table 1 show the effect of cornstarch concentration on shear strength. Table 1 shows that there is an optimum level of cornstarch to be added during formulation to obtain optimal shear strength. As the cornstarch concentration increases, the shear strength and percentage of wood failure increase too. The shear strength increases up to approximately 65\% and remains unchanged with a further increase in cornstarch concentration. A total solid content of 65\% appears to be optimal. Furthermore, the test revealed that in most cases, joint failure was cohesive in the wood (wood failure) and not due to failure either at the interface or of the adhesive itself. It is interesting to note that, when the total solids content was higher than 65\%, the cornstarch-sodium hydroxide adhesive became so viscous that it was difficult to apply.

3.2 Effects of sodium hydroxide concentration on shear strength

The results of the effect of sodium hydroxide concentration on the shear strength are shown in Table 2. It can be seen from Table 2 that shear strength values and percentage wood failure increase up to a sodium hydroxide concentration of 33\%. Beyond this a decrease in shear strength and percentage of veneer failure is observed. It has been shown that the presence of sodium hydroxide accelerates the reaction between the two polymers amylose and amylopectin due to an increase in pH of the basic medium (Yazaki and Collins 1997; Kennedy 1989; Leach et al. 1961; Champagne et al. 1985). It is concluded that 33\% sodium hydroxide concentration is optimal for the preparation of cornstarch-sodium hydroxide adhesives.

3.3 Effects of sodium hydroxide/cornstarch volume ratio on shear strength

Table 3 reports the results of the effect of sodium hydroxide/cornstarch volume ratio on shear strengths of wood composites. It is observed that shear strength and percentage of veneer failure increase up to sodium hydroxide/cornstarch volume ratio of 0.5. Beyond this a decrease in shear
strength is observed. At higher sodium hydroxide/cornstarch volume ratios, it appears that
crosslink formation is hindered, which reduces the rate of crosslink formation and decreases
shear strength (Saayman and Brown 1977, Custers et al. 1979).

Comparative solid state CP-MAS $^{13}$C NMR spectra of cornstarch and NaOH/cornstarch were also
done. The comparative $^{13}$C NMR spectra in Figure 2 show that some low molecular weight
compounds were produced. This is evident from the appearance of new peaks in the 18-40 ppm
and 127-135 ppm region. The production of these low molecular weight compounds is due to the
dissociation of intermolecular hydrogen bonding in the amylopectin (Tako and Hizukuri 2002;
Yamamoto et al. 2006).

The alkaline solution reduces the rigidity as well as the stability of the molecular organization of
starch. Therefore, the mobility of the amylose chains is increased, which contributes to the loss of
granule architecture (Cardoso 2007).

3.4 Effects of hot-press temperature on shear strength

In Table 4, the results of the effect of reaction temperature on the preparation of adhesives are
shown. The adhesives were prepared at 60°C, 80°C, 120°C, 140°C, 160°C, 170°C, 180°C and
200°C. Shear strength and percentage of veneer failure increase with increasing temperature from
80°C to 170°C, and then decrease (Table 4). It appears that crosslink formation starts at 80°C.
However, at this temperature, the rate and the extent of crosslink formation are low. With the
increase in temperature, rate and extent of network formation increase (Mozaffar et al. 2004).
This causes the increase in shear strength. With increasing the reaction temperature to 200°C, a
decrease in shear strength and percentage of veneer failure is observed. This appears to infer that
170°C is the optimal polymerization temperature.

Using TGA, the thermal decomposition and thermal stability of the adhesive are assessed. Figure
3 shows the TGA curve and its derivative (DTG) of the adhesive at different temperatures. The
TGA curve shows that there is an evident mass loss at 175 °C. From this temperature onward the
curve decreases initially, indicating cornstarch decomposition. This means that the optimum cure
temperature was 170 °C. The results obtained by thermogravimetric analysis confirm the results obtained by the shear strength tests.

### 3.5 Effects of hot-press time on shear strength

The shear strength significantly increased when the hot-press time was increased from 2 to 4 min (Table.5). A longer hot-press time means more energy is needed for cross-linking. This is the reason for the improvement of the mechanical properties with increasing press time. Further increase in hot-press time from 4 to 25 min had little effect on the shear strength. With increasing the reaction time to 25 min, a decrease in shear strength was observed. The resin still set but the prolonged reaction time appeared to cause the breakdown of some fraction of the hardened network resulting in a decrease in the shear strength observed (Mozaffar et al. 2004). From the above, it appears that, a reaction time of 4 min is optimal for the preparation of cornstarch-NaOH resin.

The results in Figure 4 appear to confirm this. Figure 4 shows the variation of the viscoelastic parameters (G’ and G’’) with time at 170 °C, 1 % strain and 1 rad/s. Here, it can be observed that the elastic modulus (G’) and viscous modulus (G’’) increase progressively with increasing the time up to 4 min. Beyond this a sharp decrease in G’ and G’’ is observed. This indicates that the optimum cure time is 4 min. Thus, this rheological characterization confirms the results obtained by the shear strength tests.

### 3.6 Improvement of the shear strength with two types of tannin, hardened with hexamine.

The shear strength of the cornstarch-NaOH wood adhesives was then improved by addition of two types of tannin-based adhesives, mimosa and quebracho, using hexamine as hardener.

The results of the effect of addition of tannin (Mimosa or Quebracho) and hexamine on shear strength are shown in Table 6. This clearly illustrates that, in both cases, shear strength increases with an increase of the tannin percentage up to 10%. Beyond this level a decrease in shear strength is observed. A decrease in shear strength is attributed to the high amount of hardener (hexamine); which makes the adhesive very viscous. The addition of mimosa tannin and hexamine (Cornstarch-NaOH-MT-H) improves the mechanical properties of 16% compared to the cornstarch-NaOH adhesives alone.
Pizzi (2006) reported that in the case of Mimosa tannin hardened with hexamine, di- and tri-
benzylamine bridges were formed, this being stable bridges. Figure 5 shows this mechanism.

In Figure 6, the comparative solid state CP-MAS $^{13}$C NMR spectra of cornstarch, NaOH/cornstarch, mimosa tannin/hexamine and cornstarch-NaOH-MT-H adhesive are shown. The spectra in Figure 6 show that no differences were noticeable between the three solid states CP-MAS $^{13}$C NMR spectra of the NaOH/cornstarch, mimosa tannin/hexamine and cornstarch-NaOH-MT-H adhesive. This indicates that the two materials function as a polymer blend rather than co-reacting. One definite interaction is that the use of NaOH necessary for cornstarch also favours the condensation reaction of mimosa tannin with hexamine (Pizzi 1994).

### 3.7 Viscosity of the natural wood adhesives

The results in Table 7 compare the viscosity of the three natural wood adhesives prepared under their optimal conditions (Cornstarch-NaOH, Cornstarch-NaOH-MT-H and Cornstarch-NaOH-QT-H). Viscosity is measured by the advanced rheometric expansion system (ARES) at 25°C. Table 7 indicates that the addition of tannin (Mimosa or Quebracho) and hexamine to the first formulation (cornstarch-NaOH) decreases the viscosity of the natural adhesives. The addition of tannin mimosa and hexamine (Cornstarch-NaOH-MT-H) decrease the viscosity of 25% compared to the cornstarch-NaOH adhesives (Pizzi 1994; Li and Maplesden 1998). It is clear that cornstarch-NaOH-MT-H wood adhesive, is the best formulation because it improves the shear strength of 16% and decreases the viscosity of 25% compared to the cornstarch-NaOH adhesives.

### 3.8 Comparison of the mechanical properties of cornstarch-tannin adhesives with commercial adhesives

The cornstarch-NaOH-MT-H adhesive prepared at optimized conditions was compared with three different types of industrial wood adhesives (urea-formaldehyde, polyvynylacetate adhesive and a polyurethane adhesive) for their mechanical properties (Table 8). The results show that the cornstarch-NaOH-MT-H natural adhesive has comparable mechanical properties to the ones of commercial adhesives under the testing conditions used.

### 3.9 Effects of moisture and liquid water on shear strength
Table 9 shows the effects of moisture (65, 80 and 90% relative humidity) on the mechanical properties of cornstarch-NaOH-TM-H, urea formaldehyde, vinyl and polyurethane adhesive. After bonding, the assemblies were conditioned in a Vötsch climate room (25°C; 65, 80 and 90% relative humidity) for 7 days. Ten samples were prepared for each resin. It can be seen from Table 9 that Cornstarch-NaOH-TM-H, urea formaldehyde vinyl adhesive and polyurethane adhesive had similar shear strength values at 25°C and 65% relative humidity. Furthermore, the experimental results showed that there was no shear strength deterioration observed between 65% and 90% relative humidity. The results indicate that under moisture conditions, formaldehyde-free cornstarch-NaOH-TM-H adhesive is capable of giving shear strength results which are comparable to those obtained with synthetic resins.

Data for shear strength after 2 hours immersion in liquid water (pH= 7 and 25°C) are summarised in Table 10. After immersion, two-ply wood bonded with cornstarch-NaOH-TM-H resin exhibited poorer values of shear strength compared to samples bonded with the commercial resins (urea formaldehyde, Vinyl and Polyurethane adhesive). These natural adhesives are developed exclusively for interior grade panels, hence for an application different from the traditional tannin adhesives. For this reason their resistance to liquid water has no particular importance.

3.10 Effects of storage time of cornstarch-NaOH-MT-H adhesives on shear strength

The cornstarch-NaOH-MT-H adhesive was prepared, and then stored at room temperature for various times before being applied to the wood veneers to determine the effect of storage time on the shear strength of the joint. With increasing storage time, the shear strength decreased (Figure 7). When the cornstarch-NaOH-MT-H adhesives were stored at room temperature for one day, the shear strength was significantly lower than at a storage time of 45 min. The data fitted well the following equation, using the software: ‘Table Curve’ (2D Windows V2.03).

\[
\sigma = 1.56 + 3.67 \exp\left(-\frac{t}{9.39}\right)
\]  

(1)
where \( \sigma \) is the shear strength (MPa) and \( t \) the time (days). The adjusted \( R^2 \) value was 0.99, indicating a good fit. The decline of shear strength with storage time is still not fully understood.

4 Conclusion

Cornstarch was used with tannin to form a natural wood adhesive. The cornstarch-tannin adhesive is easy to prepare. The adhesive was developed and optimized for wood bonding. In some countries, cornstarch and tannin are inexpensive renewable polymers. The cost of this adhesive appears to be lower than that of the synthetic phenolic resins traditionally used for wood adhesives. Its main advantage is that it contains no formaldehyde or phenol, both of which are considered as environmental pollutants.

Research is in progress to further improve cornstarch-tannin adhesive formulations by employing other nonvolatile, non-toxic aldehyde hardeners (glyoxal or dioxal).

Acknowledgements

The authors would like to thank the "Conseil Général des Landes" (Aquitaine, France) for providing financial support.

References


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Cardoso MB (2007) from rice starch to amylose crystals: alkaline extraction of rice starch, solution properties of amylose and crystal structure of \( \nu \)-amylose inclusion complexes. Université Joseph Fourier, Grenoble I, France.


Table 1

<table>
<thead>
<tr>
<th>Number of prepared adhesives</th>
<th>Total solids content (%)</th>
<th>Sodium hydroxide concentration (%)</th>
<th>Sodium hydroxide/corn starch volume ratio</th>
<th>Reaction temperature (°C)</th>
<th>Reaction time (min)</th>
<th>Shear strength, (SD), MPa</th>
<th>Veneer Failure (%)</th>
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**Table 2**

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Table 5

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<th>Sodium hydroxide concentration (%)</th>
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<th>Reaction temperature (°C)</th>
<th>Reaction time (min)</th>
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<th>Veneer Failure (%)</th>
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### Table 6

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<th>Hardener</th>
<th>Tannin</th>
<th>Percentage of tannin (%)</th>
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Table 7

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<th>Wood adhesives</th>
<th>Viscosity, Pa s</th>
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<td>Cornstarch-NaOH</td>
<td>61239 ± 5045</td>
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<tr>
<td>Cornstarch-NaOH-MT-H</td>
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<tr>
<td>Cornstarch-NaOH-QT-H</td>
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<tr>
<td>Wood adhesives</td>
<td>Shear strength, MPa</td>
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<tr>
<td>--------------------------------</td>
<td>---------------------</td>
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<tr>
<td>Cornstarch-NaOH-MT-H</td>
<td>5.21 ± 0.05</td>
</tr>
<tr>
<td>Urea-formaldehyde</td>
<td>5.87 ± 0.15</td>
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<tr>
<td>Vinyl adhesive</td>
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<td>Polyurethane adhesive</td>
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### Table 9

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<th>Vötsch climate room conditions</th>
<th>Shear strength, MPa; Mean ± SD</th>
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<tr>
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<td>Cornstarch-NaOH-MT-H</td>
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<tr>
<td>25°C and 65% R.H</td>
<td>5.21 ± 0.05</td>
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<td>25°C and 80% R.H</td>
<td>5.35 ± 0.11</td>
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<td>25°C and 90% R.H</td>
<td>5.17 ± 0.04</td>
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Table 10

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<tr>
<th></th>
<th>Shear strength, MPa; Mean ± SD</th>
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<tr>
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<td>Cornstarch-NaOH-MT-H</td>
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<td>Before immersion</td>
<td>5.21 ± 0.05</td>
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<td>After immersion</td>
<td>1.07 ± 0.24</td>
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<td>Retention (%)</td>
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Fig. 1

Maritime Pine

0.45 MPa

3 mm

2.5 cm

Adhesive (120-150 g/m²)

Shear strength test

11.5 cm

2.5 cm
Fig. 2

Glucose

NaOH/cornstarch

Cornstarch

180 160 140 120 100 80 60 40 20 ppm

1 2 3 5 6 1 2 3 5 6
Fig. 3

175°C

Cornstarch decomposition
Fig. 4
Fig. 6

Mimosa tannin

NaOH/cornstarch

Mimosa tannin/hexamine

Cornstarch/NaOH/MT/H

![Graph showing chemical structures and spectra](image-url)
Fig. 7
Table 1. Effects of total solids content of cornstarch-sodium hydroxide adhesives on shear strength (sodium hydroxide (33%)/cornstarch volume ratio was fixed at the level 0.5; 0.45 MPa; 180°C and 5 min). Ten replicates for each total solid content. SD: Standard deviation.

Table 2. Effect of sodium hydroxide concentration on shear strength (sodium hydroxide/cornstarch (65%) volume ratio was fixed at the level 0.5; 0.45 MPa; 180°C and 5 min). Ten replicates for each NaOH concentration. SD: Standard deviation.

Table 3. Effects of sodium hydroxide/cornstarch volume ratio on shear strength (cornstarch (65%), sodium hydroxide (33%), 0.45 MPa; 180°C and 5 min). Ten replicates for each sodium hydroxide/cornstarch volume ratio. SD: Standard deviation.

Table 4. Effects of hot-press temperature on shear strength (sodium hydroxide (33%)/cornstarch (65%) = 0.5; 0.45 MPa and 5 min). Ten replicates for each hot-press temperature. SD: Standard deviation.

Table 5. Effects of hot-press time on shear strength (sodium hydroxide (33%)/cornstarch (65%) = 0.5; 0.45 MPa and 170°C). Ten replicates for each hot-press time. SD: Standard deviation.

Table 6. Effects of tannin (Mimosa and Quebracho) and hexamine on shear strength at 170°C and 4 min. SD: Standard deviation.

Table 7. Results of viscosity of the three natural wood adhesives prepared under their optimal conditions at 25°C.

Table 8. Mechanical properties of cornstarch-NaOH-MT-H adhesive and commercial adhesives.

Table 9. Shear strength values after 7 days in a Vötsch climate room (25°C; 65%, 80% and 90% relative humidity). Ten replicates for each resin. SD: Standard deviation.

Table 10. Shear strength values before and after 2 h of immersion in water. Ten replicates for each resin. SD: Standard deviation.
**Figure 1.** Schematic representation of wood sample preparation using cornstarch-tannin crosslinked adhesives. Step A: pressure at 180°C and 0.45 MPa, step B: shear strength test after 24 hrs in a Vötsch climate room (25°C and 65% humidity).

**Figure 2.** Comparative solid state CP-MAS $^{13}$C NMR spectra of cornstarch and NaOH/cornstarch.

**Figure 3.** TGA and DTG curves of cornstarch-NaOH adhesives, $\beta = 5^\circ$C/min.

**Figure 4.** Time evolution of storage modulus ($G'$) and loss modulus ($G''$) of cornstarch-NaOH adhesive at 25°C; 1rad/s and 1%.

**Figure 5.** Schematic diagram of the reaction between tannin and hexamine.

**Figure 6.** Comparative solid state CP-MAS $^{13}$C NMR spectra of cornstarch, NaOH/cornstarch, mimosa tannin/hexamine and cornstarch/NaOH/MT/H.

**Figure 7.** Effects of storage time of the cornstarch-NaOH-MT-H adhesive on shear strength.

---

Tabelle 1
Einfluss des Gesamt-Feststoffgehalts des Maisstärke-Natriumhydroxid-Klebstoffs auf die Scherfestigkeit (Natriumhydroxid (33%)/ Maisstärke Volumenverhältnis 0,5; 0,45 MPa; 180°C und 5 Minuten). Zehn Proben je Gesamtfeststoffgehalt. SD: Standardabweichung

Tabelle 2
Einfluss der Natriumhydroxidkonzentration auf die Scherfestigkeit (Verhältnis von Natriumhydroxid/Maisstärke (65%) = 0,5; 0,45 MPa; 180°C und 5 Minuten). Zehn Proben je Natriumhydroxidkonzentration. SD Standardabweichung

Tabelle 3
Einfluss des Volumenverhältnisses von Natriumhydroxid und Maisstärke auf die Scherfestigkeit (Maisstärke 65%, Natriumhydroxid 33%; 0,45 MPa; 180°C und 5 Minuten). Zehn Proben je Natriumhydroxid/Maisstärke Volumenverhältnis. SD Standardabweichung

Tabelle 4
Einfluss der Temperatur beim Heißpressen auf die Scherfestigkeit (Natriumhydroxid 33%/Maisstärke 65% Volumenverhältnis 0,5; 0,45 MPa und 5 Minuten. Zehn Proben je Pressstemperatur, SD Standardabweichung

Tabelle 5
Einfluss der Pressdauer auf die Scherfestigkeit (Natriumhydroxid 33%/ Maisstärke 65% Volumenverhältnis 0,5; 0,45 MPa und 5 Minuten. Zehn Proben je Pressdauer, SD Standardabweichung

Tabelle 6
Einfluss von Tannin (Mimosa und Quebracho) und Hexamin auf die Scherfestigkeit bei 170°C und 4 Minuten. SD: Standardabweichung

Tabelle 7
Viskosität der drei unter optimalen Bedingungen hergestellten natürlichen Holzklebstoffe bei 25 °C

Tabelle 8
Mechanische Eigenschaften von Maisstärke-NaOH-MT-H Klebstoff und handelsüblichen Klebstoffen

Tabelle 9
Scherfestigkeit nach siebentägiger Lagerung in einem Vötsch Klimaraum (25°C, 65%, 80% und 90% rel. Luftfeuchte). Zehn Proben je Harz. SD Standardabweichung

Tabelle 10
Scherfestigkeit vor und nach 2-stündiger Wasserlagerung. Zehn Proben je Harz. SD Standardabweichung

Abb. 1
Schematische Darstellung der Herstellung der Prüfkörper mit quervernetzten Maisstärke-Tannin-Klebstoffen. Schritt A: Pressdruck 0,45 MPa bei 180°C, Schritt B: Scherfestigkeitsversuch nach 24-stündiger Lagerung im Vötsch Klimaraum (25°C und 65 % Luftfeuchte)

Abb. 2
Festkörper-CP-MAS ^13 CNMR Referenzspektrum von Maisstärke und NaOH/Maisstärke

Abb. 3
TGA und DTG Kurven der Maisstärke-NaOH-Klebstoffe, β=5°C/min

Abb. 4
Zeitlicher Verlauf des Speichermoduls (G') und Verlustmoduls (G'') des Maisstärke-NaOH-Klebstoffs bei 25°C; 1rad/s und 1%.

Abb. 5
Schematische Darstellung der Reaktion zwischen Tannin und Hexamin.

Abb. 6
Festkörper-CP-MAS ^13 CNMR Referenzspektrum von Maisstärke und NaOH/Maisstärke, Mimosatannin/Hexamin und Maisstärke/NaOH/MT/H

Abb. 7
Einfluss der Lagerungsdauer von Maisstärke-NaOH-MT-H Klebstoffen auf die Scherfestigkeit