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**Development and optimization of a new formaldehyde-free  
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# 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 H<sub>2</sub>O) and sodium hydroxide (33 % p/v H<sub>2</sub>O). 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 hexamethylenetetramine (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

In dieser Studie wird die Entwicklung und Optimierung eines neuen, umweltfreundlichen Klebstoffes auf Basis der nachwachsenden und reichlich vorhandenen Rohstoffe Maisstärke und Tannin beschrieben. Gegenwärtig werden zur Herstellung von Holzwerkstoffen Klebstoffe auf Öl- und Formaldehydbasis, wie zum Beispiel Phenolformaldehyd-Harz (PF) und Harnstoffformaldehyd-Harz (UF), verwendet. Die mechanischen und physikalischen Eigenschaften (Scherfestigkeit, rheologische Eigenschaften und thermogravimetrische Analyse) von Klebstoffen auf Maisstärke und Tanninbasis wurden untersucht.

Zunächst wurden die optimalen Bedingungen zur Herstellung von Maisstärke-Natriumhydroxid-Holzklebstoffen bestimmt. Dabei wurden die Parameter Gesamt-Feststoffgehalt der Klebstoffe, Natriumhydroxidkonzentration und das Volumenverhältnis von Hydroxid und Maisstärke untersucht. Die höchste Scherfestigkeit ergab sich bei einem Volumenverhältnis von 0,5 bei einer Maisstärkekonzentration von 65% p/v H<sub>2</sub>O und einer Natriumhydroxidkonzentration von 33% p/v H<sub>2</sub>O. Die optimale Aushärtungstemperatur lag bei 170°C und die Aushärtungszeit bei 4 Minuten. Durch Zugabe zweier verschiedener Tannin basierter Klebstoffe, Mimosa und Quebracho, mit Hexamin als Härter, zur Maisstärke-Natriumhydroxid-Rezeptur wurde die Scherfestigkeit verbessert und die Viskosität der Klebstoffe verringert.

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## 1 Introduction

One of the main concerns of the 21<sup>st</sup> 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

1 low cost (Pizzi 2006). Tannin is another example of such a renewable material and has been used  
2 to substitute tannin for the synthetic phenolics in wood adhesives (Pizzi 2006).

3 Starch is one of the most abundant natural polymers (Imam et al. 1999). Starch has been used as  
4 an adhesive in a wide range of products, including binders, sizing material, glues and pastes  
5 (Imam *et al.* 1999, Yazaki and Collins 1997). More recently, the development of a starch-based  
6 wood adhesive for interior applications has been described (Imam *et al.* 1999). Starch yields  
7 adhesives with excellent affinity for polar materials such as cellulose. Ideally, the contact angle  
8 between the adhesive and the substrate should be small. This allows the adhesive to wet the  
9 surface and spread uniformly in a thin film with a minimum of voids. In this regard, starch based  
10 adhesives wet the polar surface of cellulose, penetrate crevices and pores and, thus, form strong  
11 adhesive bonds (Imam *et al.* 1999).

12 Among the possible alternatives, tannin is an excellent renewable resource which can be used for  
13 replacing petroleum-derived phenolic compounds. The major species from which it can be  
14 obtained are Mimosa, Quebracho and Radiata pine. The use of hexamine as a hardener for a  
15 tannin, hence, a tannin-hexamine adhesive, is a very environment-friendly proposition. <sup>13</sup>C-NMR  
16 has confirmed (Pichelin *et al.* 1999, Kamoun *et al.* 2003) that the main decomposition of  
17 hexamine under such conditions is not directly due to formaldehyde. It rather proceeds through  
18 reactive intermediates, hence, mainly through the formation of reactive imines and  
19 iminoaminomethylene bases. <sup>13</sup>C-NMR has also confirmed (Pichelin *et al.* 1999, Kamoun *et al.*  
20 2003) that in the presence of chemical species with very reactive nucleophilic sites, such as  
21 condensed flavonoid tannins, hexamine is not a formaldehyde-yielding compound. It neither  
22 decomposes to formaldehyde and ammonia in an acid environment nor to formaldehyde and  
23 trimethylamine in an alkaline environment (Pizzi and Tekely 1995, 1996; Pizzi *et al.* 1996,  
24 Kamoun *et al.* 2003). The very reactive imines and iminoaminomethylene intermediates initially  
25 formed in its decomposition do react with the phenolic species present without ever passing  
26 through the formation of formaldehyde (Pizzi and Tekely 1995, 1996; Pizzi *et al.* 1996; Kamoun  
27 *et al.* 2003).

28 Initial investigations on the use of wattle tannin in starch corrugating adhesives were carried out  
29 at the Division of Forest Products, CSIRO, in 1968. As an alternative material to resorcinol was  
30 urgently needed in 1969, the project was extended to include some studies designed to establish  
31 reasons for the poor performance of water-resistant starch adhesives (McKenzie and Yuritta  
32 1972). Further research and developments in the field of fortified starch adhesives with wattle  
33 tannin were carried out in South Africa (Saayman and Brown 1977). Industrial production with  
34 one such system started, however, in South Africa in the late 1970's (Custers *et al.* 1979).

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3 In this study, the mechanical properties (shear strength) and physical properties (rheological and  
4 thermogravimetric analysis) of cornstarch-tannin adhesives with hexamine as hardener was  
5 investigated.  
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## 8 9 10 **2 Experimental methods**

### 11 12 13 **2.1 Preparation of cornstarch-tannin adhesives and preparation of two-ply wood** 14 **composites bonded with the cornstarch-tannin adhesives.** 15 16

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19 Cornstarch water solutions were prepared at six different concentrations namely 12, 25, 50, 65,  
20 75 and 90%, by dissolving cornstarch in deionised water, stirring at room temperature, and  
21 adding sodium hydroxide ( $M_w = 40.00$ ) at different concentrations (5, 15, 33, 50 and 75%) as  
22 hardeners. The resulting adhesives were mixed for 45 min at room temperature and then used for  
23 bonding wood veneer.  
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28 In order to improve the shear strength of cornstarch-sodium hydroxide adhesives, the two types  
29 of tannin, Mimosa and Quebracho, were added in proportions of 5%, 10%, 20%, 30%, 40% and  
30 50% by weight on cornstarch solids content; hardener content used was 5 percent hexamine by  
31 weight on tannin extract solids content. The hexamine was dissolved in water to yield a 30  
32 percent concentration solution in water prior to adding to the tannin solution to form the glue-  
33 mix.  
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38 Maritime pine veneer with a thickness of 3 mm was cut to rectangular specimens  $2.5 \times 11.5 \text{ cm}^2$   
39 (according to British Standard 1204, 1965, part 2, for synthetic resins adhesives). The adhesive  
40 was applied to one side of each piece of veneer. The application area was  $2.5 \times 2.5 \text{ cm}^2$  for each  
41 veneer. The spread rate of the adhesive was 120-150  $\text{g/m}^2$  on a dry weight basis (Nihat and  
42 Nilgöl 2002, Pizzi 1977). Two adhesive-coated veneer boards were lapped together with the grain  
43 parallel to each other and then pressed at 0.45 MPa (Fig. 1). The press temperature and press time  
44 were varied for the determination of their effects on the strength of wood composites. After  
45 bonding, the assemblies were conditioned in a Vötsch climate room (25°C and 65% humidity) for  
46 24 hrs. Five hundred samples were prepared for mechanical tests.  
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### 55 56 **2.2 Mechanical properties** 57 58 59 60

1 The shear strength of the wood composite was determined on an Instron testometric M500-50 AT  
2 testing machine. The crosshead speed was 1 mm/min. The load at fraction was measured, and  
3 reported as shear strength.  
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5 Every experiment was repeated; at least, ten replicates and their standard deviations were  
6 calculated.  
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## 9 10 11 **2.3 Rheological characterization**

12 The adhesives were tested with an advanced rheometric expansion system (ARES) with parallel  
13 plate's geometry, which was used for all the measurements; the plate diameter used was 25mm  
14 and the gap between the parallel plates was 1.5mm. Silicone oil was used to prevent water  
15 evaporation.  
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## 23 24 **2.4 Thermogravimetric analysis (TGA)**

25 Thermogravimetric analysis (TGA) was carried out with a TGA Q50 thermogravimetric  
26 apparatus. Ten milligrams of each cured sample was placed on a balance located in the furnace  
27 and heat was applied over a temperature range from room temperature to 600 °C at a heating rate  
28 of 5 °C/min in air.  
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## 36 37 **2.5 Solid phase <sup>13</sup>C NMR analysis**

38 The solid state <sup>13</sup>C NMR spectra of the cornstarch, cornstarch-NaOH, mimosa tannin-hexamine  
39 and cornstarch-NaOH-MT-H resin systems used, were acquired at ambient temperature by using  
40 a Bruker 400 MHz spectrometer. Powdered samples were packed in 4-mm zirconia rotors, sealed  
41 with Kel-F™ caps and spun at 6 KHz and at a contact time of 3.5 ms. Chemical shifts were  
42 determined relative to tetramethyl silane (TMS) used as control.  
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## 50 51 **3 Results and discussion**

52 First, the conditions for the preparation of cornstarch-sodium hydroxide wood adhesives were  
53 optimized. Parameters like total solids content of adhesives, sodium hydroxide concentration,  
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1 sodium hydroxide/cornstarch volume ratio, reaction time and reaction temperature were studied.  
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3 These parameters were varied and their effect on shear strength was studied.  
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### 6 **3.1 Effects of the total solids content of adhesives on shear strength**

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10 The results presented in Table 1 show the effect of cornstarch concentration on shear strength.  
11 Table 1 shows that there is an optimum level of cornstarch to be added during formulation to  
12 obtain optimal shear strength. As the cornstarch concentration increases, the shear strength and  
13 percentage of wood failure increase too. The shear strength increases up to approximately 65%  
14 and remains unchanged with a further increase in cornstarch concentration. A total solid content  
15 of 65% appears to be optimal. Furthermore, the test revealed that in most cases, joint failure was  
16 cohesive in the wood (wood failure) and not due to failure either at the interface or of the  
17 adhesive itself. It is interesting to note that, when the total solids content was higher than 65%,  
18 the cornstarch-sodium hydroxide adhesive became so viscous that it was difficult to apply.  
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### 33 **3.2 Effects of sodium hydroxide concentration on shear strength**

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36 The results of the effect of sodium hydroxide concentration on the shear strength are shown in  
37 Table 2. It can be seen from Table 2 that shear strength values and percentage wood failure  
38 increase up to a sodium hydroxide concentration of 33%. Beyond this a decrease in shear strength  
39 and percentage of veneer failure is observed. It has been shown that the presence of sodium  
40 hydroxide accelerates the reaction between the two polymers amylose and amylopectin due to an  
41 increase in pH of the basic medium (Yazaki and Collins 1997; Kennedy 1989; Leach *et al.* 1961;  
42 Champagne *et al.* 1985). It is concluded that 33% sodium hydroxide concentration is optimal for  
43 the preparation of cornstarch-sodium hydroxide adhesives.  
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### 52 **3.3 Effects of sodium hydroxide/cornstarch volume ratio on shear strength**

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56 Table 3 reports the results of the effect of sodium hydroxide/cornstarch volume ratio on shear  
57 strengths of wood composites. It is observed that shear strength and percentage of veneer failure  
58 increase up to sodium hydroxide/cornstarch volume ratio of 0.5. Beyond this a decrease in shear  
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1 strength is observed. At higher sodium hydroxide/cornstarch volume ratios, it appears that  
2 crosslink formation is hindered, which reduces the rate of crosslink formation and decreases  
3 shear strength (Saayman and Brown 1977, Custers *et al.* 1979).  
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8 Comparative solid state CP-MAS  $^{13}\text{C}$  NMR spectra of cornstarch and NaOH/cornstarch were also  
9 done. The comparative  $^{13}\text{C}$  NMR spectra in Figure 2 show that some low molecular weight  
10 compounds were produced. This is evident from the appearance of new peaks in the 18-40 ppm  
11 and 127-135 ppm region. The production of these low molecular weight compounds is due to the  
12 dissociation of intermolecular hydrogen bonding in the amylopectin (Tako and Hizukuri 2002;  
13 Yamamoto *et al.* 2006).  
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20 The alkaline solution reduces the rigidity as well as the stability of the molecular organization of  
21 starch. Therefore, the mobility of the amylose chains is increased, which contributes to the loss of  
22 granule architecture (Cardoso 2007).  
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### 33 **3.4 Effects of hot-press temperature on shear strength**

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36 In Table 4, the results of the effect of reaction temperature on the preparation of adhesives are  
37 shown. The adhesives were prepared at 60°C, 80°C, 120°C, 140°C, 160°C, 170°C, 180°C and  
38 200°C. Shear strength and percentage of veneer failure increase with increasing temperature from  
39 80°C to 170°C, and then decrease (Table 4). It appears that crosslink formation starts at 80°C.  
40 However, at this temperature, the rate and the extent of crosslink formation are low. With the  
41 increase in temperature, rate and extent of network formation increase (Mozaffar et al. 2004).  
42 This causes the increase in shear strength. With increasing the reaction temperature to 200°C, a  
43 decrease in shear strength and percentage of veneer failure is observed. This appears to infer that  
44 170°C is the optimal polymerization temperature.  
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52 Using TGA, the thermal decomposition and thermal stability of the adhesive are assessed. Figure  
53 3 shows the TGA curve and its derivative (DTG) of the adhesive at different temperatures. The  
54 TGA curve shows that there is an evident mass loss at 175 °C. From this temperature onward the  
55 curve decreases initially, indicating cornstarch decomposition. This means that the optimum cure  
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1 temperature was 170 °C. The results obtained by thermogravimetric analysis confirm the results  
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3 obtained by the shear strength tests.  
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### 6 **3.5 Effects of hot-press time on shear strength**

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10 The shear strength significantly increased when the hot-press time was increased from 2 to 4 min  
11 (Table.5). A longer hot-press time means more energy is needed for cross-linking. This is the  
12 reason for the improvement of the mechanical properties with increasing press time. Further  
13 increase in hot-press time from 4 to 25 min had little effect on the shear strength. With increasing  
14 the reaction time to 25 min, a decrease in shear strength was observed. The resin still set but the  
15 prolonged reaction time appeared to cause the breakdown of some fraction of the hardened  
16 network resulting in a decrease in the shear strength observed (Mozaffar *et al.* 2004). From the  
17 above, it appears that, a reaction time of 4 min is optimal for the preparation of cornstarch-NaOH  
18 resin.  
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27 The results in Figure 4 appear to confirm this. Figure 4 shows the variation of the viscoelastic  
28 parameters ( $G'$  and  $G''$ ) with time at 170 °C, 1 % strain and 1 rad/s. Here, it can be observed that  
29 the elastic modulus ( $G'$ ) and viscous modulus ( $G''$ ) increase progressively with increasing the  
30 time up to 4 min. Beyond this a sharp decrease in  $G'$  and  $G''$  is observed. This indicates that the  
31 optimum cure time is 4 min. Thus, this rheological characterization confirms the results obtained  
32 by the shear strength tests.  
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### 40 **3.6 Improvement of the shear strength with two types of tannin, hardened with hexamine.**

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43 The shear strength of the cornstarch-NaOH wood adhesives was then improved by addition of  
44 two types of tannin-based adhesives, mimosa and quebracho, using hexamine as hardener.  
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49 The results of the effect of addition of tannin (Mimosa or Quebracho) and hexamine on shear  
50 strength are shown in Table 6. This clearly illustrates that, in both cases, shear strength increases  
51 with an increase of the tannin percentage up to 10%. Beyond this level a decrease in shear  
52 strength is observed. A decrease in shear strength is attributed to the high amount of hardener  
53 (hexamine); which makes the adhesive very viscous. The addition of mimosa tannin and  
54 hexamine (Cornstarch-NaOH-MT-H) improves the mechanical properties of 16% compared to  
55 the cornstarch-NaOH adhesives alone.  
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1 Pizzi (2006) reported that in the case of Mimosa tannin hardened with hexamine, di- and tri-  
2 benzylamine bridges were formed, this being stable bridges. Figure 5 shows this mechanism.  
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6 In Figure 6, the comparative solid state CP-MAS  $^{13}\text{C}$  NMR spectra of cornstarch,  
7 NaOH/cornstarch, mimosa tannin/hexamine and cornstarch-NaOH-MT-H adhesive are shown.  
8 The spectra in Figure 6 show that no differences were noticeable between the three solid states  
9 CP-MAS  $^{13}\text{C}$  NMR spectra of the NaOH/cornstarch, mimosa tannin/hexamine and cornstarch-  
10 NaOH-MT-H adhesive. This indicates that the two materials function as a polymer blend rather  
11 than co-reacting. One definite interaction is that the use of NaOH necessary for cornstarch also  
12 favours the condensation reaction of mimosa tannin with hexamine (Pizzi 1994).  
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### 19 20 21 **3.7 Viscosity of the natural wood adhesives**

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24 The results in Table 7 compare the viscosity of the three natural wood adhesives prepared under  
25 their optimal conditions (Cornstarch-NaOH, Cornstarch-NaOH-MT-H and Cornstarch-NaOH-  
26 QT-H). Viscosity is measured by the advanced rheometric expansion system (ARES) at 25°C.  
27 Table 7 indicates that the addition of tannin (Mimosa or Quebracho) and hexamine to the first  
28 formulation (cornstarch-NaOH) decreases the viscosity of the natural adhesives. The addition of  
29 tannin mimosa and hexamine (Cornstarch-NaOH-MT-H) decrease the viscosity of 25%  
30 compared to the cornstarch-NaOH adhesives (Pizzi 1994; Li and Maplesden 1998).  
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33 It is clear that cornstarch-NaOH-MT-H wood adhesive, is the best formulation because it  
34 improves the shear strength of 16% and decreases the viscosity of 25% compared to the  
35 cornstarch-NaOH adhesives.  
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### 43 44 **3.8 Comparison of the mechanical properties of cornstarch-tannin adhesives with** 45 **commercial adhesives**

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48 The cornstarch-NaOH-MT-H adhesive prepared at optimized conditions was compared with  
49 three different types of industrial wood adhesives (urea-formaldehyde, polyvinylacetate adhesive  
50 and a polyurethane adhesive) for their mechanical properties (Table 8). The results show that the  
51 cornstarch-NaOH-MT-H natural adhesive has comparable mechanical properties to the ones of  
52 commercial adhesives under the testing conditions used.  
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### 59 60 **3.9 Effects of moisture and liquid water on shear strength**

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3 Table 9 shows the effects of moisture (65, 80 and 90% relative humidity) on the mechanical  
4 properties of cornstarch-NaOH-TM-H, urea formaldehyde, vinyl and polyurethane adhesive.  
5 After bonding, the assemblies were conditioned in a Vötsch climate room (25°C; 65, 80 and 90%  
6 relative humidity) for 7 days. Ten samples were prepared for each resin. It can be seen from  
7 Table 9 that Cornstarch-NaOH-TM-H, urea formaldehyde vinyl adhesive and polyurethane  
8 adhesive had similar shear strength values at 25°C and 65% relative humidity. Furthermore, the  
9 experimental results showed that there was no shear strength deterioration observed between 65%  
10 and 90% relative humidity. The results indicate that under moisture conditions, formaldehyde-  
11 free cornstarch-NaOH-TM-H adhesive is capable of giving shear strength results which are  
12 comparable to those obtained with synthetic resins.  
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22 Data for shear strength after 2 hours immersion in liquid water (pH= 7 and 25°C) are summarised  
23 in Table 10. After immersion, two-ply wood bonded with cornstarch-NaOH-TM-H resin  
24 exhibited poorer values of shear strength compared to samples bonded with the commercial  
25 resins (urea formaldehyde, Vinyl and Polyurethane adhesive). These natural adhesives are  
26 developed exclusively for interior grade panels, hence for an application different from the  
27 traditional tannin adhesives. For this reason their resistance to liquid water has no particular  
28 importance.  
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### 37 3.10 Effects of storage time of cornstarch-NaOH-MT-H adhesives on shear strength

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39 The cornstarch-NaOH-MT-H adhesive was prepared, and then stored at room temperature for  
40 various times before being applied to the wood veneers to determine the effect of storage time on  
41 the shear strength of the joint. With increasing storage time, the shear strength decreased (Figure  
42 7). When the cornstarch-NaOH-MT-H adhesives were stored at room temperature for one day,  
43 the shear strength was significantly lower than at a storage time of 45 min. The data fitted well  
44 the following equation, using the software: 'Table Curve' (2D Windows V2.03).  
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$$\sigma = 1.56 + 3.67 \exp\left(-\frac{t}{9.39}\right) \quad (1)$$

1 where  $\sigma$  is the shear strength (MPa) and  $t$  the time (days). The adjusted  $R^2$  value was 0.99,  
2 indicating a good fit. The decline of shear strength with storage time is still not fully understood.  
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## 6 **4 Conclusion**

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10 Cornstarch was used with tannin to form a natural wood adhesive. The cornstarch-tannin  
11 adhesive is easy to prepare. The adhesive was developed and optimized for wood bonding. In  
12 some countries, cornstarch and tannin are inexpensive renewable polymers. The cost of this  
13 adhesive appears to be lower than that of the synthetic phenolic resins traditionally used for wood  
14 adhesives. Its main advantage is that it contains no formaldehyde or phenol, both of which are  
15 considered as environmental pollutants.  
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23 Research is in progress to further improve cornstarch-tannin adhesive formulations by employing  
24 other nonvolatile, non-toxic aldehyde hardeners (glyoxal or dioxal).  
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Table 1

Number of prepared adhesives	Total solids content (%)	Sodium hydroxide concentration (%)	Sodium hydroxide/corn starch volume ratio	Reaction temperature (°C)	Reaction time (min)	Shear strength, (SD), MPa	Veneer Failure (%)
1	12	33	0.5	180	5	1.96 (0.62)	0
2	25	33	0.5	180	5	2.32 (0.11)	0
3	50	33	0.5	180	5	3.28 (0.22)	33
4	65	33	0.5	180	5	3.76 (0.11)	66
5	75	33	0.5	180	5	3.84 (0.22)	66
6	90	33	0.5	180	5	3.88 (0.39)	66

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Table 2

Number of prepared adhesives	Total solids content (%)	Sodium hydroxide concentration (%)	Sodium hydroxide/corn starch volume ratio	Reaction temperature (°C)	Reaction time (min)	Shear strength, (SD), MPa	Veneer Failure (%)
1	65	5	0.5	180	5	3.07 (0.35)	33
2	65	15	0.5	180	5	3.32 (0.16)	33
3	65	33	0.5	180	5	3.76 (0.11)	66
4	65	50	0.5	180	5	3.42 (0.07)	33
5	65	75	0.5	180	5	3.37 (0.35)	33

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Table 3

Number of prepared adhesives	Total solids content (%)	Sodium hydroxide concentration (%)	Sodium hydroxide/corn starch volume ratio	Reaction temperature (°C)	Reaction time (min)	Shear strength, (SD), MPa	Veneer Failure (%)
1	65	33	0.2	180	5	3.25 (0.30)	33
2	65	33	0.5	180	5	3.76 (0.11)	66
3	65	33	0.8	180	5	2.93 (0.16)	33
4	65	33	1.2	180	5	3.56 (0.05)	33
5	65	33	1.5	180	5	3.44 (0.11)	0
6	65	33	2	180	5	2.88 (0.18)	0

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Table 4

Number of prepared adhesives	Total solids content (%)	Sodium hydroxide concentration (%)	Sodium hydroxide/corn starch volume ratio	Reaction temperature (°C)	Reaction time (min)	Shear strength, (SD), MPa	Veneer Failure (%)
1	65	33	0.5	60	5	2.78 (0.08)	0
2	65	33	0.5	80	5	2.84 (0.16)	0
3	65	33	0.5	120	5	3.73 (0.01)	33
4	65	33	0.5	140	5	4.20 (0.16)	33
5	65	33	0.5	160	5	4.39 (0.05)	50
6	65	33	0.5	170	5	4.54 (0.02)	66
7	65	33	0.5	180	5	3.76 (0.11)	66
8	65	33	0.5	200	5	3.5 (0.54)	50

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Table 5

Number of prepared adhesives	Total solids content (%)	Sodium hydroxide concentration (%)	Sodium hydroxide/corn starch volume ratio	Reaction temperature (°C)	Reaction time (min)	Shear strength, (SD), MPa	Veneer Failure (%)
1	65	33	0.5	170	1	3.03 (0.12)	25
2	65	33	0.5	170	2	3.22 (0.11)	33
3	65	33	0.5	170	4	4.49 (0.30)	66
4	65	33	0.5	170	5	4.54 (0.02)	66
5	65	33	0.5	170	7	3.81 (0.21)	66
6	65	33	0.5	170	10	4.21 (0.15)	66
7	65	33	0.5	170	15	3.94 (0.28)	66
8	65	33	0.5	170	17	4.31 (0.12)	50
9	65	33	0.5	170	20	4.19 (0.13)	33
10	65	33	0.5	170	25	4.12 (0.10)	33

Table 6

Hardener	Tannin	Percentage of tannin (%)	Shear strength, (SD), MPa	Veneer failure (%)
5 percent hexamine by weight on tannin extract solids content	Mimosa	0	4.49 (0.30)	66
		5	4.65 (0.11)	70
		10	5.21 (0.05)	85
		20	4.62 (0.04)	85
		30	4.19 (0.26)	70
		40	3.99 (0.09)	50
		50	3.53 (0.20)	35
	Quebracho	0	4.49 (0.30)	66
		5	4.65 (0.18)	66
		10	5.00 (0.12)	75
		20	4.62 (0.17)	75
		30	4.14 (0.19)	50
		40	3.92 (0.13)	50
		50	3.50 (0.16)	35

Table 7

Wood adhesives	Viscosity, Pa s
	Mean $\pm$ SD
Cornstarch-NaOH	61239 $\pm$ 5045
Cornstarch-NaOH-MT-H	45900 $\pm$ 5840
Cornstarch-NaOH-QT-H	47100 $\pm$ 3010

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Table 8

Wood adhesives	Shear strength, MPa
	Mean $\pm$ SD
Cornstarch-NaOH-MT-H	5.21 $\pm$ 0.05
Urea-formaldehyde	5.87 $\pm$ 0.15
Vinyl adhesive	5.96 $\pm$ 0.47
Polyurethane adhesive	6.03 $\pm$ 0.18

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Table 9

Vötsch climate room conditions	Shear strength, MPa; Mean $\pm$ SD			
	Cornstarch-NaOH- MT-H	Urea formaldehyde	Vinyl adhesive	Polyurethane adhesive
25°C and 65% R.H	5.21 $\pm$ 0.05	5.87 $\pm$ 0.15	5.96 $\pm$ 0.47	6.03 $\pm$ 0.18
25°C and 80% R.H	5.35 $\pm$ 0.11	5.52 $\pm$ 0.12	5.91 $\pm$ 0.19	6.11 $\pm$ 0.21
25°C and 90% R.H	5.17 $\pm$ 0.04	5.51 $\pm$ 0.09	5.71 $\pm$ 0.08	5.87 $\pm$ 0.06

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Table 10

	Shear strength, MPa; Mean $\pm$ SD			
	Cornstarch-NaOH- MT-H	Urea formaldehyde	Vinyl adhesive	Polyurethane adhesive
Before immersion	5.21 $\pm$ 0.05	5.87 $\pm$ 0.15	5.96 $\pm$ 0.47	6.03 $\pm$ 0.18
After immersion	1.07 $\pm$ 0.24	4.21 $\pm$ 0.21	4.93 $\pm$ 0.33	5.39 $\pm$ 0.05
Retention (%)	21	71	83	89

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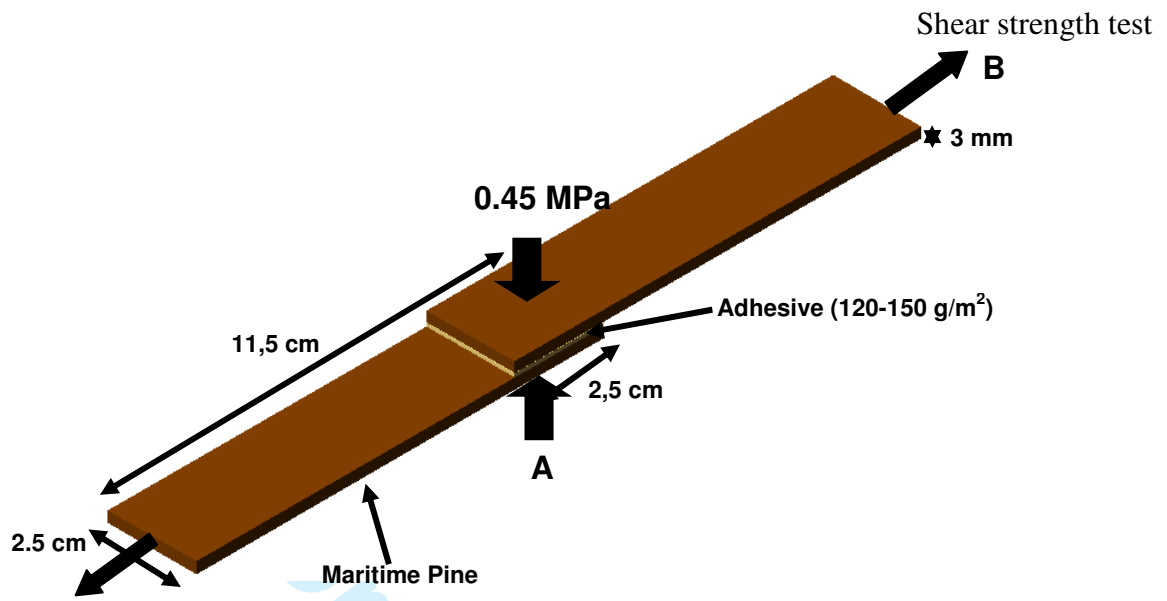


Fig. 1

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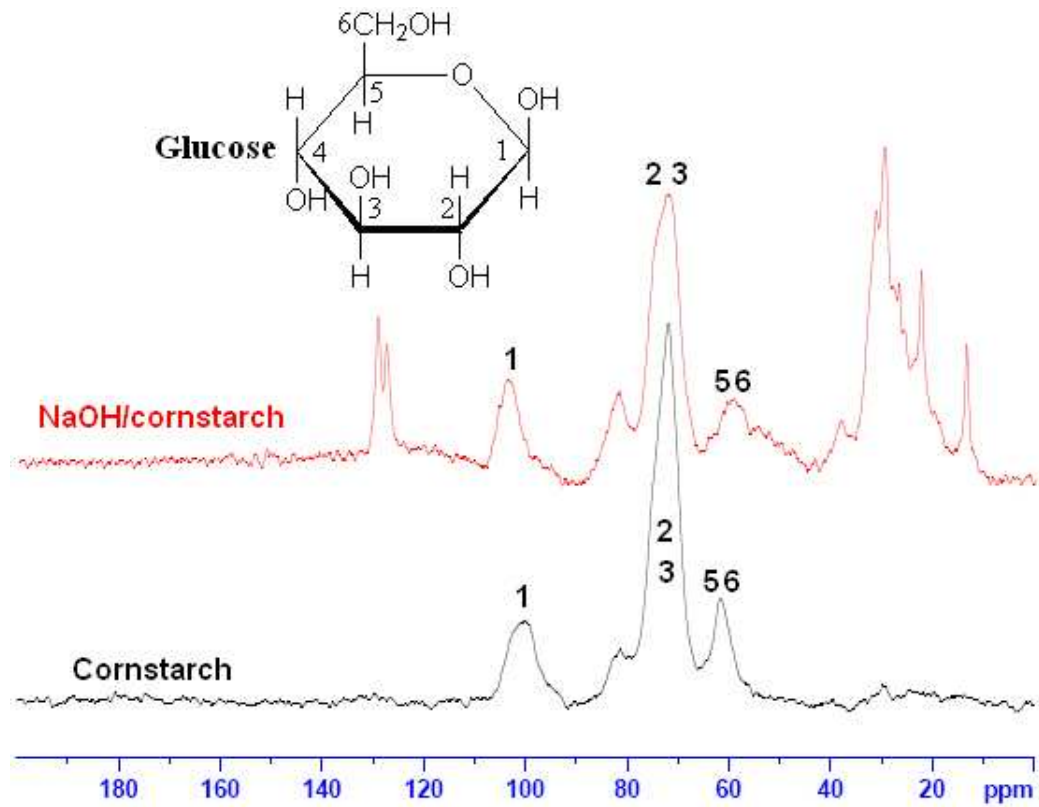


Fig. 2

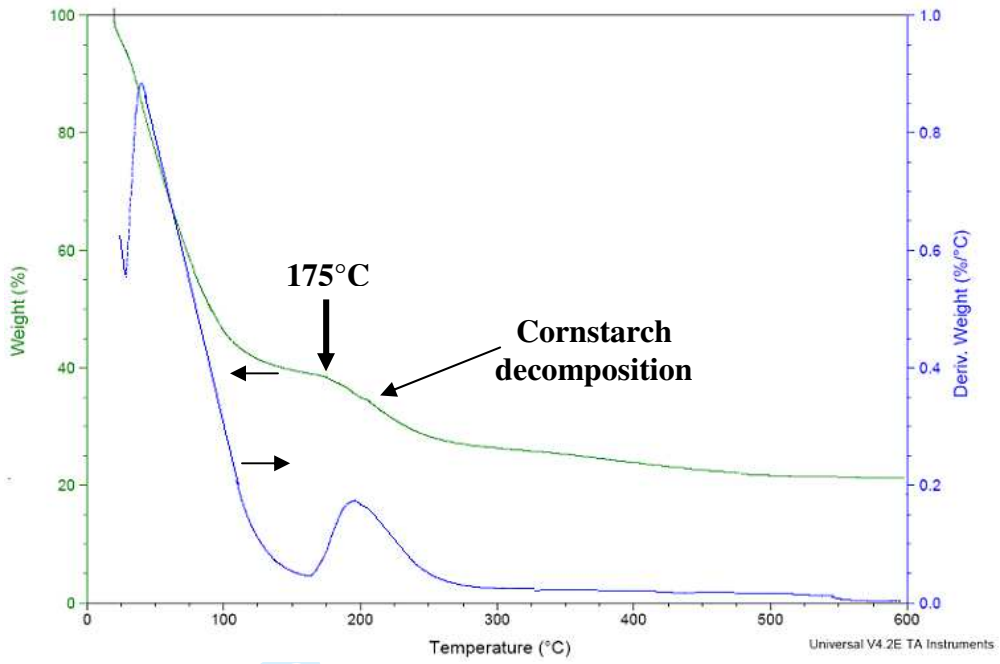


Fig. 3

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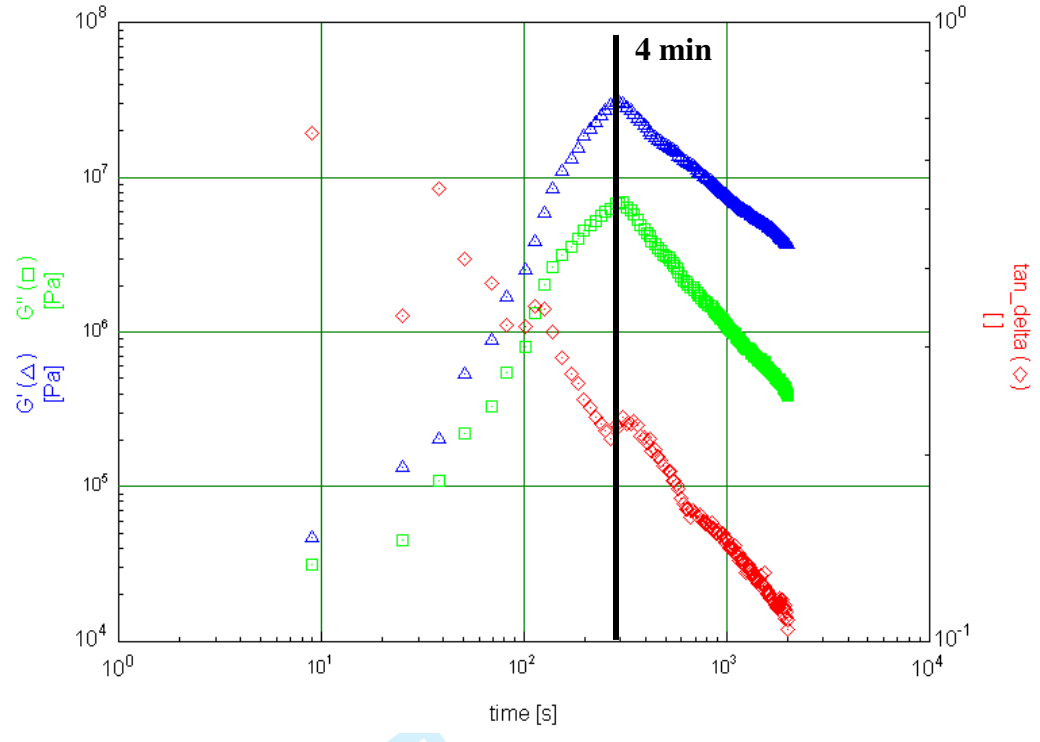


Fig. 4

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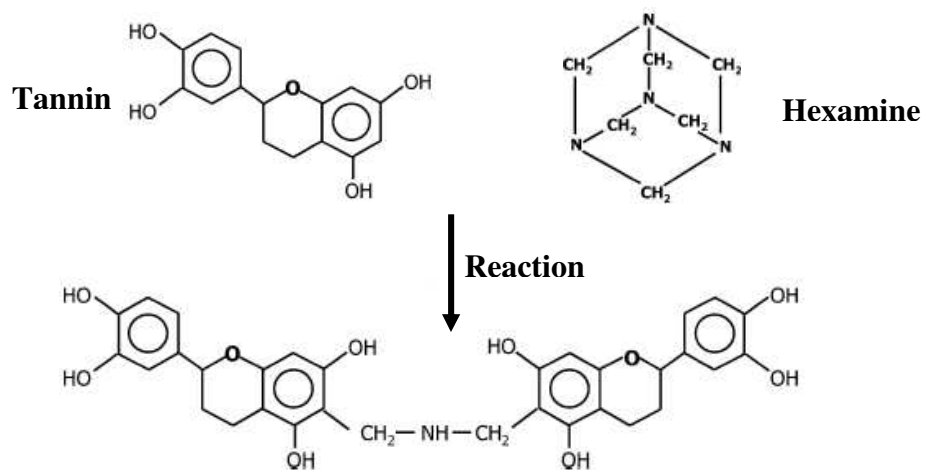


Fig. 5

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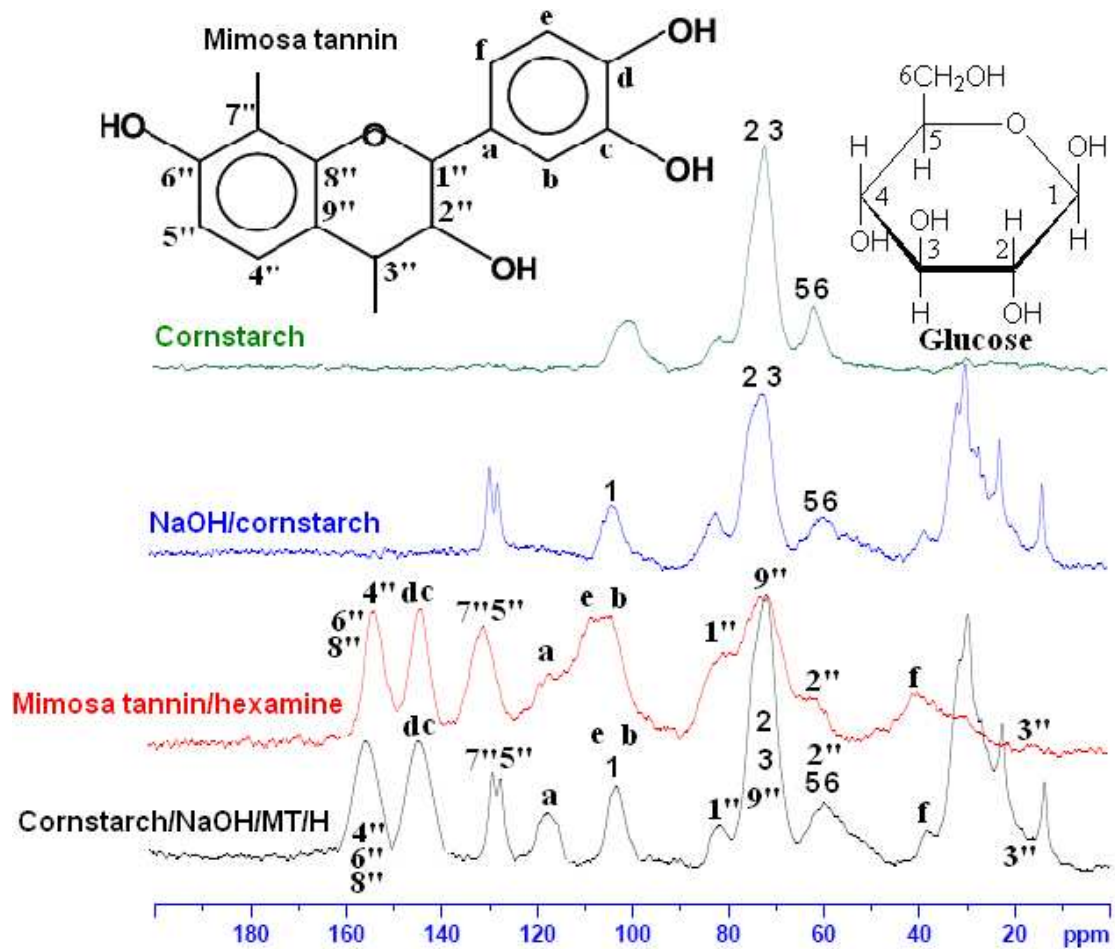


Fig. 6

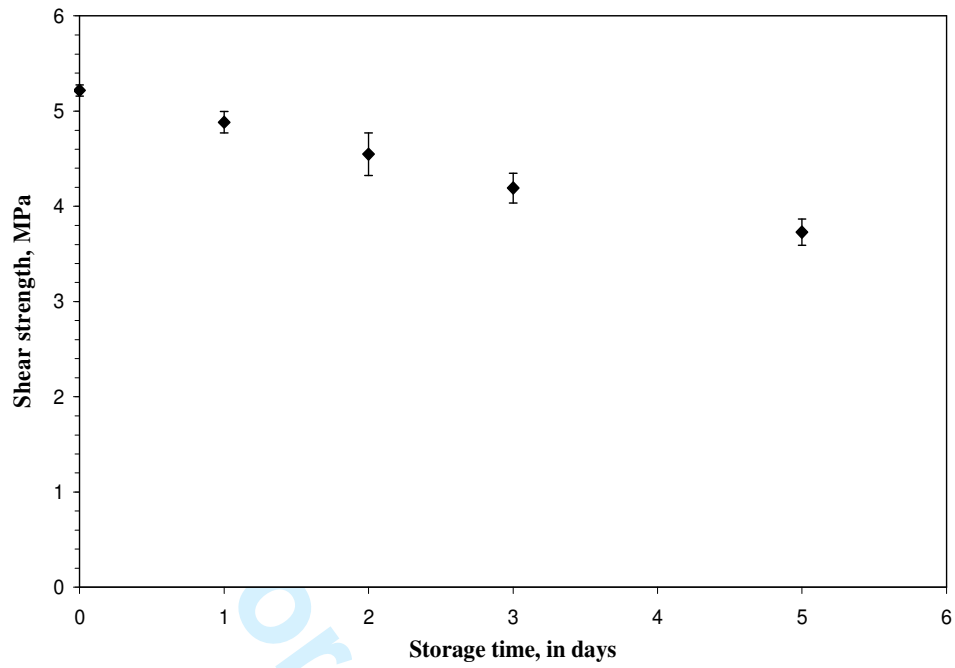


Fig. 7

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3 **Table 1.** Effects of total solids content of cornstarch-sodium hydroxide adhesives on shear  
4 strength (sodium hydroxide (33%)/cornstarch volume ratio was fixed at the level 0.5; 0.45  
5 MPa; 180°C and 5 min). Ten replicates for each total solid content. SD: Standard deviation.  
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10 **Table 2.** Effect of sodium hydroxide concentration on shear strength (sodium  
11 hydroxide/cornstarch (65%) volume ratio was fixed at the level 0.5; 0.45 MPa; 180°C and 5  
12 min). Ten replicates for each NaOH concentration. SD: Standard deviation.  
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17 **Table 3.** Effects of sodium hydroxide/cornstarch volume ratio on shear strength (cornstarch  
18 (65%), sodium hydroxide (33%), 0.45 MPa; 180°C and 5 min). Ten replicates for each  
19 sodium hydroxide/cornstarch volume ratio. SD: Standard deviation.  
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24 **Table 4.** Effects of hot-press temperature on shear strength (sodium hydroxide  
25 (33%)/cornstarch (65%) = 0.5; 0.45 MPa and 5 min). Ten replicates for each hot-press  
26 temperature. SD: Standard deviation.  
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31 **Table 5.** Effects of hot-press time on shear strength (sodium hydroxide (33%)/cornstarch  
32 (65%) = 0.5; 0.45 MPa and 170°C). Ten replicates for each hot-press time. SD: Standard  
33 deviation.  
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37 **Table 6.** Effects of tannin (Mimosa and Quebracho) and hexamine on shear strength at 170°C  
38 and 4 min. SD: Standard deviation.  
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42 **Table 7.** Results of viscosity of the three natural wood adhesives prepared under their optimal  
43 conditions at 25°C.  
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47 **Table 8.** Mechanical properties of cornstarch-NaOH-MT-H adhesive and commercial  
48 adhesives.  
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52 **Table 9.** Shear strength values after 7 days in a Vötsch climate room (25°C; 65%, 80% and  
53 90% relative humidity). Ten replicates for each resin. SD: Standard deviation.  
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57 **Table 10.** Shear strength values before and after 2 h of immersion in water. Ten replicates for  
58 each resin. SD: Standard deviation.  
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3 **Figure 1.** Schematic representation of wood sample preparation using cornstarch-tannin  
4 crosslinked adhesives. Step A: pressure at 180°C and 0.45 MPa, step B: shear strength test  
5 after 24 hrs in a Vötsch climate room (25°C and 65% humidity).  
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10 **Figure 2.** Comparative solid state CP-MAS <sup>13</sup>C NMR spectra of cornstarch and NaOH/  
11 cornstarch.  
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15 **Figure 3.** TGA and DTG curves of cornstarch-NaOH adhesives,  $\beta = 5^\circ\text{C}/\text{min}$ .  
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19 **Figure 4.** Time evolution of storage modulus ( $G'$ ) and loss modulus ( $G''$ ) of cornstarch-  
20 NaOH adhesive at 25°C; 1rad/s and 1%.  
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24 **Figure 5.** Schematic diagram of the reaction between tannin and hexamine.  
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27  
28 **Figure 6.** Comparative solid state CP-MAS <sup>13</sup>C NMR spectra of cornstarch, NaOH/  
29 cornstarch, mimosa tannin/hexamine and cornstarch/NaOH/MT/H.  
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32  
33 **Figure 7.** Effects of storage time of the cornstarch-NaOH-MT-H adhesive on shear strength.  
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36  
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38 Tabelle 1

39 Einfluss des Gesamt-Feststoffgehalts des Maisstärke-Natriumhydroxid-Klebstoffs auf die  
40 Scherfestigkeit (Natriumhydroxid (33%)/ Maisstärke Volumenverhältnis 0,5; 0,45 MPa;  
41 180°C und 5 Minuten). Zehn Proben je Gesamtfeststoffgehalt. SD: Standardabweichung  
42

43  
44 Tabelle 2

45 Einfluss der Natriumhydroxidkonzentration auf die Scherfestigkeit (Verhältnis von  
46 Natriumhydroxid/Maisstärke (65%) = 0,5; 0,45 MPa; 180°C und 5 Minuten). Zehn Proben je  
47 Natriumhydroxidkonzentration. SD Standardabweichung  
48

49  
50 Tabelle 3

51 Einfluss des Volumenverhältnisses von Natriumhydroxid und Maisstärke auf die  
52 Scherfestigkeit (Maisstärke 65%, Natriumhydroxid 33%; 0,45 MPa; 180°C und 5 Minuten).  
53 Zehn Proben je Natriumhydroxid/Maisstärke Volumenverhältnis. SD Standardabweichung.  
54

55  
56 Tabelle 4

57 Einfluss der Temperatur beim Heißpressen auf die Scherfestigkeit (Natriumhydroxid  
58 33%/Maisstärke 65%Volumenverhältnis 0,5; 0,45 MPa und 5 Minuten. Zehn Proben je  
59 Presstemperatur, SD Standardabweichung  
60

Tabelle 5

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3 Einfluss der Pressdauer auf die Scherfestigkeit (Natriumhydroxid 33%/ Maisstärke 65%  
4 Volumenverhältnis 0,5; 0,45 MPa und 5 Minuten. Zehn Proben je Pressdauer, SD  
5 Standardabweichung  
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10 Tabelle 6  
11 Einfluss von Tannin (Mimosa und Quebracho) und Hexamin auf die Scherfestigkeit bei  
12 170°C und 4 Minuten. SD: Standardabweichung  
13  
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15 Tabelle 7  
16 Viskosität der drei unter optimalen Bedingungen hergestellten natürlichen Holzklebstoffe bei  
17 25 °C  
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20 Tabelle 8  
21 Mechanische Eigenschaften von Maisstärke-NaOH-MT-H Klebstoff und handelsüblichen  
22 Klebstoffen  
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25 Tabelle 9  
26 Scherfestigkeit nach siebentägiger Lagerung in einem Vötsch Klimaraum (25°C, 65%, 80%  
27 und 90% rel. Luftfeuchte). Zehn Proben je Harz. SD Standardabweichung  
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30 Tabelle 10  
31 Scherfestigkeit vor und nach 2-stündiger Wasserlagerung. Zehn Proben je Harz. SD  
32 Standardabweichung  
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34

35 Abb. 1  
36 Schematische Darstellung der Herstellung der Prüfkörper mit quervernetzten Maisstärke-  
37 Tannin-Klebstoffen. Schritt A: Pressdruck 0,45 MPa bei 180°C, Schritt B:  
38 Scherfestigkeitsversuch nach 24-stündiger Lagerung im Vötsch Klimaraum (25°C und 65 %  
39 Luftfeuchte)  
40

41 Abb. 2  
42 Festkörper-CP-MAS <sup>13</sup> CNMR Referenzspektrum von Maisstärke und NaOH/Maisstärke  
43  
44

45 Abb. 3  
46 TGA und DTG Kurven der Maisstärke-NaOH-Klebstoffe,  $\beta=5^\circ\text{C}/\text{min}$   
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49 Abb. 4  
50 Zeitlicher Verlauf des Speichermoduls ( $G'$ ) und Verlustmoduls ( $G''$ ) des Maisstärke-NaOH-  
51 Klebstoffs bei 25°C; 1rad/s und 1%.  
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54 Abb. 5  
55 Schematische Darstellung der Reaktion zwischen Tannin und Hexamin.  
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58 Abb. 6  
59 Festkörper-CP-MAS <sup>13</sup> CNMR Referenzspektrum von Maisstärke und NaOH/Maisstärke,  
60 Mimosatannin/Hexamin und Maisstärke/NaOH/MT/H

Abb. 7

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3 Einfluss der Lagerungsdauer von Maisstärke-NaOH-MT-H Klebstoffen auf die  
4 Scherfestigkeit  
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For Peer Review