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PREPARATION AND MECHANICAL CHARACTERIZATION OF PARTICLEBOARD MADE FROM MARITIME PINE AND GLUED WITH BIO-ADHESIVES BASED ON CORNSTARCH AND TANNINS*

Amine Moubarik¹⁻³, Ahmed Allal³, Antonio Pizzi², Fatima Charrier¹ and Bertrand Charrier¹

ABSTRACT

In this presented work, we describe the development and characterization of a new, environmentally friendly adhesive derived from cornstarch and tannins. The production of wood composites mainly relies on the petrochemical-based and formaldehyde-based adhesives such as urea formaldehyde (UF), phenol formaldehyde (PF) and melamine urea formaldehyde (MUF), which can generate under certain conditions, problems for health and environment. The aim of our work is to replace totally these synthetic resins. In order to evaluate the quality of cornstarch-tannin adhesives, particleboards were produced and physical and mechanical properties were investigated. These physical properties included rheological, thermogravimetric analysis and solid phase ¹³C NMR analysis of resins. Internal bond, surface soundness, modules of rupture and modulus of elasticity mechanical properties of particleboards bonded with cornstarch-tannin adhesives were also determined.

Particleboards bonded with formaldehyde-free cornstarch-tannin adhesive showed comparable mechanical properties to the panels made with the commercial UF resins and satisfied the exigencies of panels for interior fittings used in dry medium (P2) according to European norms EN 312 (2004). Beyond 4 hours, rheological characterization show excellent structural stability of cornstarch-tannin adhesive.

Keywords: Bio-adhesives; Cornstarch; Tannin; Particleboard; Wood adhesive.

INTRODUCTION

Formaldehyde based resins including UF, PF and MUF are the three most commonly used binders in wood composite industry. Moreover, formaldehyde is considered a priority pollutant by the United States Environmental Protection Agency. Its emission in the environment and workers exposure to it at manufacturing facilities continues to be a major safety concern (Keith and Telliard 1979, Myers 1986). Several efforts have been made to reduce or replace formaldehyde contents in adhesive formulations (Mozaffar *et al.* 2004, Nihat and Nilü 2002, Pizzi 1977, Yoosup *et al.* 2008) or to develop adhesives from natural materials (Pizzi 2006, Pizzi and Tekely 1995, Pichelin *et al.* 2006, Yuan and Kaichang 2007).

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 in 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).

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Recently, there have been growing interests on tannin based resins. Tannins are naturally occurring phenolic compounds, which have been a subject of extensive research leading to development of a wide range of industrial applications (Pizzi 1993). Tannin is the renewable resource which is most widely used in adhesive production. Wattle bark tannins (*Acacia mearnsii*) adhesives have been used without fortification to bond hardwood species in Brazil (Coppens *et al.* 1980; Santana and Sobral, 1983) and China (Zhao *et al.* 1994).

Further research and developments in the field of fortified starch adhesives with wattle bark 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 physical properties (rheological, thermogravimetric and solid phase ^{13}C NMR analysis) of adhesives and mechanical properties (modulus of rupture "MOR", modulus of elasticity "MOE", internal bond strength and surface soundness) of particleboards manufactured using formaldehyde-free cornstarch-tannin adhesives were investigated.

EXPERIMENTAL METHODS

Unmodified commercial grade cornstarch (extra pure) was obtained from ACROS ORGANICS; the moisture content was in the range of 10 to 12%. A sodium hydroxide ($M_w = 40.00 \text{ g/mol}$) was purchased from VWR prolabo. Commercial flavonoid mimosa barks tannin (*Acacia mearnsii*, Mimosa OP) was provided from SILVATEAM (Italy). The hardener, hexamethylenetetramine 99% (hexamine), was supplied by Aldrich. Commercial resol-type liquid UF resin (which is a particleboard binder resin), was supplied by EGGER (Rion des Landes).

Maritime pine (*Pinus pinaster*) veneer was provided by sawmill Ets Labadie (Roquefort - France) Sd (moisture content around 8-10%).

Preparation of cornstarch-tannin adhesives

To prepare 500 g of adhesive, cornstarch water solution was prepared at 65% (p/v) concentration, by dissolving 130 g of cornstarch in 200 ml of deionised water and stirred at room temperature, to which 13 g of wattle tannin are added. Hardener content used was 5 percent hexamine by weight on tannin extract solids content. The hexamine was dissolved in water to yield a 30% concentration solution in water before being added to the cornstarch-tannin solution. The solution was mixed and 100 ml of sodium hydroxide (33%) was added. The resulting adhesives were mixed for 45 min at room temperature then used to bond particleboard.

Particleboard preparation and testing

Laboratory particleboards of dimension 350 mm x 350 mm x 14 mm were prepared. The total resin solid by weight was 10 % for the commercial UF and cornstarch-tannin adhesives. In the case of the cornstarch-tannin adhesives, hot pressing was carried out at 25 kg/cm² pressure and 170 °C, for 7.5 minutes press time (optimal conditions) (Moubarik *et al.* 2010a). While particleboard bonded with commercial UF resin has assembled and hot pressed under 25 kg/cm² pressure at 195°C, for 7.5 minutes press time. Particles were dried to approximately 3 % moisture content prior to application of resin. Aimed board density was 657 kg/m³. The fabricated particleboards were pre-conditioned at 25°C and 65 % relative humidity in a Vötsch climate room for a week before testing. All tests were carried out to the appropriate European Standards. The tests performed on the specimens were internal bond strength perpendicular to the plane of the board (IB) (EN 319, 1993), static bending [modulus of rupture (MOR) and modulus of elasticity (MOE)] (EN 310, 1993) and surface soundness (EN 311, 1993).

Rheological characterization

The adhesives were characterized with an rotary rheometer (ARES) in the parallel plates geometry, which was used for all the measurements; plates of diameter 25 mm and a gap of 1.5 mm. Silicone oil was used to prevent water evaporation. To be in the linear regime the strain value was set as 1%.

Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was used to determine the thermal stability and degradation of cornstarch-tannin adhesives. TGA was done using 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 the temperature range of room temperature to 600 °C at a heating rate of 5 °C/min in air. The derivatives of the weight loss vs. temperature thermograms were obtained to better show the different decomposition processes.

Formaldehyde emission by desiccator method

The formaldehyde emissions from the particleboard were determined according to the European Norm (ISO/CD 12460-4) using a glass desiccator. The 24-h desiccator method uses a common glass desiccator with a volume of 10 L. Eight test pieces, with dimensions of 150 mm x 50 mm x 14 mm, which were cut from particleboard, are positioned in the desiccator. The formaldehyde released from the test pieces at 23 ± 2 °C and $50 \pm 10\%$ relative humidity, during 24 h is absorbed in a Petri dish filled with a 30 ml of distilled water and determined photometrically. Three replicates were used for each adhesive.

Solid phase ^{13}C NMR analysis

The solid state ^{13}C NMR spectra of the cornstarch, NaOH/ cornstarch, mimosa tannin/hexamine and cornstarch/NaOH/ mimosa tannin/hexamine adhesive systems used, were acquired at ambient temperature by using a Bruker 400 MHz spectrometer. Powdered samples were packed in a 4-mm zirconia rotors, sealed with Kel-FTM caps and spun at 7 kHz and at a contact time of 3.5 ms. Chemical shifts were determined relative to tetramethyl silane (TMS) used as control.

RESULTS AND DISCUSSION

Physical properties of cornstarch-tannin adhesives

Dynamic oscillatory measurements (time sweep) were carried out in order to examine the stability of cornstarch-tannin adhesives. In the complex modulus, the elasticity can be described by the storage shear modulus G' , and the viscous property can be described by the loss shear modulus G'' . Figure 1 show the variation of the elastic modulus G' and viscous modulus G'' with time at 25 °C, 1 % strain and 1 rad/s of formaldehyde-free cornstarch-tannin adhesives. It can be seen that dynamic modulus (G' and G'') increase progressively with time up to 4 hours. Beyond this they remain constant. That shows excellent structural stability of the adhesive. On the other hand, this figure shows a predominant elastic character of the adhesive ($G' > G''$).

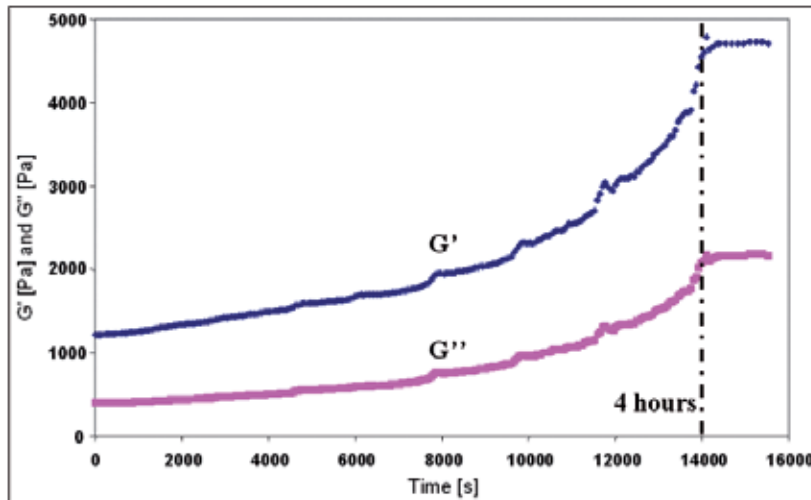


Figure 1. Time evolution of storage modulus (G') and loss modulus (G'') of cornstarch-tannin adhesive at 25°C, 1rad/s and 1%.

TGA can check the thermal decomposition and thermal stability of adhesives. Figure 2 shows the thermogravimetric TGA curve and its derivative (DTG) of the cornstarch-tannin adhesive in air atmosphere at a heating rate of 5 °C/min. The DTG curve shows that there are two obvious mass losses at 175 °C and 225 °C. The decomposition of the cornstarch is produced at about 175 °C, whereas the decomposition of the wattle tannin starts at 225 °C. The results obtained with thermogravimetric analysis confirm that 170 °C is the optimal polymerization temperature. Pyrolysis of starches at 175 °C in a stream of air has been described to give CO_2 , CO, water, acetaldehyde, furan and 2-methyl furan (Bryce and Greenwood, 1963). For cornstarch, levoglucosan is usually the main constituent of the decomposed products, besides complex gases and water liberated (Greenwood 1967). The curve also shows that thermal degradation began to occur only after the materials have absorbed certain amounts of heat energy. The heat initiated the degradation processes and the breaking down of the structure by causing molecular chain ruptures.

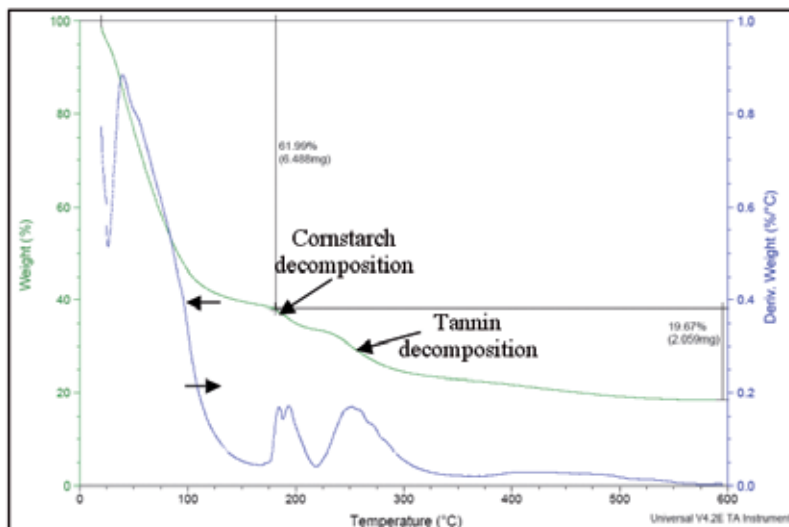


Figure 2. TGA thermograms of cornstarch-tannin adhesives under air atmosphere at 5 °C/min.

Figure 3 shows the time dependence of G' and G'' for cornstarch-tannin adhesive, at 85 °C, 1 % strain and 1 rad/s. The results obtained by this technique show two stages. In the course of the first stage (between 0 and 1500s), both dynamic modulus (G' and G'') increase progressively with

increasing time which may be due to the removal of water. This stage corresponded to the water evaporation. In the second stage (between 1500 and 3000s), G' and G'' increases shortly with time. It corresponded to the activation of polymerization. The foam formation induces the decrease of the complex modulus at the end of experiment. Results show the double effects of the temperature, (water evaporation and activation of polymerization). Moubarik *et al.* (2010b) have demonstrated that the cornstarch-tannin adhesives have a rheological behaviour of a gel.

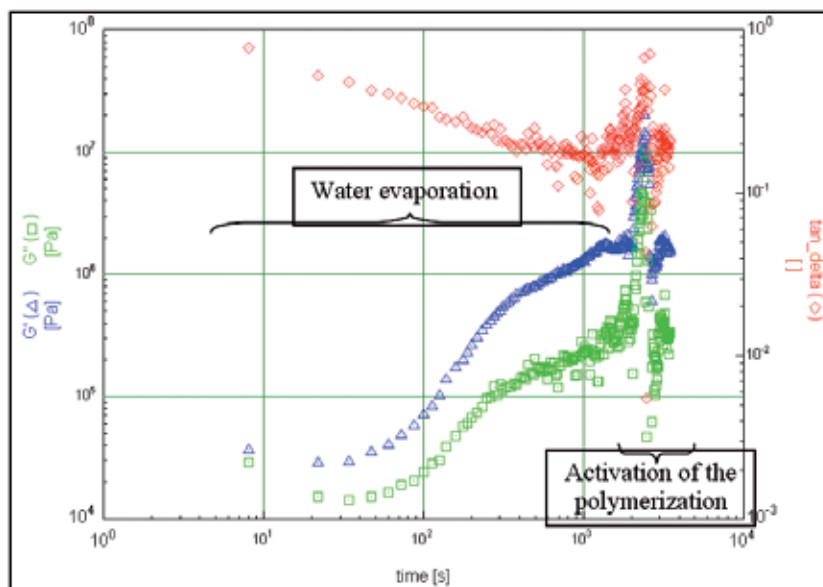


Figure 3. Time evolution of storage modulus (G') and loss modulus (G'') of cornstarch-tannin adhesive at 85°C, 1rad/s and 1%.

In Figure 4 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 comparative ^{13}C NMR spectra of cornstarch and NaOH/cornstarch 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).

The spectra in Figure 4 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 sure interaction is that the use of NaOH necessary for cornstarch favours also the condensation reaction of mimosa tannin with hexamine (Pizzi 1994).

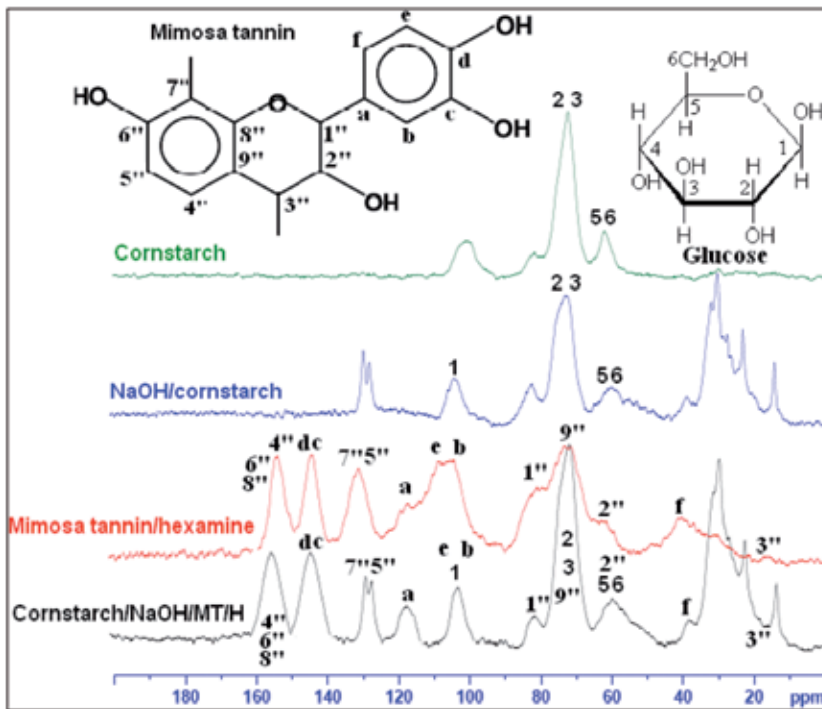


Figure 4. Comparative solid state CP-MAS ¹³C NMR spectra of cornstarch, NaOH/ cornstarch, mimosa tannin/hexamine and cornstarch/NaOH/mimosa tannin/hexamine.

The mechanical properties (internal bond, surface soundness, modulus of rupture and modulus of elasticity) and formaldehyde emission data of the particleboards made using cornstarch-tannin are illustrated in Table 1. Panels bonded with cornstarch-tannin adhesive showed comparable mechanical properties to the panels made with the commercial UF resins and satisfied the exigencies of panels for interior fittings used in dry medium (P2) according to European norms EN 312 (2004). Of particular note in Table 1 is the formaldehyde emission tests performed on the particleboards according to the European Norm (ISO/CD 12460-4). The formaldehyde emission results are, however, considerably lower than those observed for the commercial UF resin. Emission values of 0.2 mg formaldehyde/100g of particleboards in Table 1 are only due to the formaldehyde generated just by the heating of wood, and are not due to the adhesive.

Table 1. Summary of the test results of the particleboards made using cornstarch-tannin and commercial UF resins. Ten replicates of each adhesive. S.D: standard deviation

Wood adhesives	IB (N/mm ²) Mean ± S.D	MOR (N/mm ²) Mean ± S.D	MOE (N/mm ²) Mean ± S.D	Surface soundness (N/ mm ²) Mean ± S.D	Formaldehyde emission (mg/100g) Mean ± S.D
Control UF	0.48 ± 0.03	15 ± 0.60	2481 ± 92	1.63 ± 0.13	3.62 ± 0.19
Cornstarch-tannin	0.45 ± 0.04	17 ± 0.60	2307 ± 74	1.57 ± 0.11	0.20 ± 0.08
P2 (EN 312, 2004)	> 0.35	> 13	> 1600	> 0.8	-

P2: Panels for interior fittings used in dry medium

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. Biodegradation studies show that the environment-friendly cornstarch-tannin adhesive improves the total resistance of the two-ply wood composites (Moubarik *et al.* 2009).

CONCLUSIONS

The present investigation on the use of cornstarch and tannin to prepare a natural wood adhesive shows that particleboard panels bonded with cornstarch-tannin adhesive showed comparable mechanical properties to the panes made with the commercial UF resins and satisfied the exigencies of panels for interior fittings used in dry medium (P2) according to European norms EN 312 (2004). Moreover, the formaldehyde emission levels obtained from boards bonded with cornstarch-tannin adhesive were considerably lower to these obtained from boards made with control UF. Rheological studies have shown that beyond 4 hours, cornstarch-tannin adhesives exhibit an excellent structural stability.

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

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