J. Mater. Environ. Sci. 4 (4) (2013) 496-501
ISSN : 2028-2508
CODEN: JMESCN

Polenta cornstarch-mimosa tannin-based urea formaldehyde adhesives for interior grade particleboard

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Received 16 Dec 2012, Revised 3 Jan 2013, Accepted 3 Jan 2013

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Abstract

This study investigated the physical properties (rheological and thermogravimetric) of adhesive mixtures of (i) polenta cornstarch, (ii) -mimosa tannin, and (iii) -urea formaldehyde (UF) and various mechanical properties (internal bond, modulus of rupture and modulus of elasticity, surface soundness and withdrawal of screws) of laboratory particleboard made with such adhesive mixtures. It was found that the best results were given with the mass ratio of 10:4:86 for polenta cornstarch, mimosa tannin and UF resin. Both, the polenta cornstarch and the mimosa tannin were introduced into the UF resin in order to replace a certain proportion of the UF resin.

The laboratory results showed that particleboards bonded with the optimal mixture of polenta cornstarch, mimosa tannin and UF resin exhibited better mechanical properties than boards made from commercial UF resins. Rheological results show excellent structural stability of the mixture. The formaldehyde emission levels from the boards were lower by 18% to those obtained from boards bonded with the control UF. UF resins, hence, could be partially substituted by addition of polenta cornstarch and mimosa tannin barks extracts.

Keywords: Mimosa tannin; Particleboard; Polenta cornstarch; Urea formaldehyde.

Introduction

Urea-formaldehyde adhesives are used in the production of interior-grade particleboards, plywood, and oriented strandboard (OSB). These resins are the most important type of the so-called aminoplastic resins [1]. Currently, approximately 6 billion tons of UF resins are produced per year worldwide, based on a usual solids content of 66% by mass [1]. Formaldehyde can be emitted in the production and the use of wood products bonded with UF resins. These problems push the wood industry to investigate using natural and economical products as substitutes for UF resins [2-7].

Starch is the major carbohydrate reserve in higher plants. It is a biodegradable polysaccharide, produced in abundance at low cost, and exhibits thermoplastic behaviour. Therefore, it has become one of the most promising candidates as substitutes for UF resins. Numerous studies have been conducted to optimize the performance of starch-based resins [8-12]. Starch yields adhesives with excellent affinity for polar materials such as cellulose. In this regard, starch based adhesives wet the polar surface of cellulose, penetrate into crevices and pores and, thus, form strong adhesive bonds. The bonding is the result of both mechanical interlocking and Van der Waals forces [8]. In order to improve the reactivity of active sites the cornstarch was heat treated at 80°C [13].

Mimosa bark tannin is another renewable resource which can be used for replacing petroleum-derived phenolic compounds. Mimosa bark tannins (*Acacia mearnsii*) have been used as fortification to UF resins in order to produce particleboard and plywood. Mimosa bark tannins have higher reactivity with formaldehyde [14, 15]. In addition, tannin-UF adhesives can reduce the tendency of the resin to migrate into the interior of high-moisture veneers due to the broader molar mass distribution of tannin-based adhesives [16].

In this work the rheological behaviour of a polenta cornstarch-mimosa tannin-UF mixture (10 : 4 : 86 mass ratio) [17] as well as the mechanical properties (internal bond, surface soundness, thickness swelling, porosity, modules of rupture MOR and modulus of elasticity MOE, withdrawal of screws) and the formaldehyde emission of laboratory particleboard using this mixture as adhesive were investigated.

2. Materials and methods

Unmodified commercial grade cornstarch (extra pure) was supplied by ACROS ORGANICS (New Jersey, US); the moisture content was in the range of 10 to 12%. Commercial flavonoid mimosa barks tannin (Acacia mearnsii, Mimosa OP) was provided from SILVATEAM (Cuneo, Italy). Commercial liquid UF resin for particleboard production and Maritime pine (*Pinus pinaster*) particles were supplied by EGGER-ROL (Rion des Landes, France). The UF resin had a density of 1280–1290 kg/m3, a pH of about 8.5–9, a U/F molar ration of 1/1.05 and a viscosity of 350–600 mPa.s, all measured at 20 ± 2°C; the gel time was 40-50 seconds at 100°C. The content of free formaldehyde is maximum 0.15 % based on the liquid resin.

2.1 Preparation of the UF resin mix and the adhesive mix

The UF resin mix used for the various tests consisted of 90 g of the liquid resin, 6 g of aqueous ammonium nitrate hardener (SOLAN 50), and 4 g of the aqueous paraffin emulsion (REDEMUL 456). In order to prepare the optimal mix of polenta cornstarch, mimosa tannin, and UF resin (10 : 4 : 86 mass ratio), a quantity of water (33 g) was heated to 80 ° C before adding the 10 g cornstarch [17]. Then 4 g mimosa tannin was added. The mixture was mechanically stirred until the swelling of the cornstarch happened. Finally, the resin was cooled to room temperature before mixing with 86 g UF resin mix as described above. The adhesive mix had a viscosity of 400 mPa.s measured at 20 ± 2°C. The adhesive mixture optimization was performed on the basis of mechanical and physical tests. This heat treatment (at 80°C) is designed to activate the active sites of the natural starch polymers [13].

2.2 Particleboard preparation and testing

Laboratory particleboards of dimension 350 mm x 350 mm x 14 mm were prepared. The total addition of (i) the commercial UF resin as control and (ii) the adhesive mix of polenta cornstarch, mimosa tannin, and UF resin (with mass proportions of 10 : 4 : 86) was 9 %; the press time was 7.5 min at 195°C press temperature and a maximum pressure of 2.5 MPa. Particles were dried to approximately 3 % moisture content prior to application of the resin mix or the adhesive mix. The target board density was 657 kg/m3. The 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) [18], static bending as modulus of rupture (MOR) and modulus of elasticity (MOE) [19], thickness swelling (after 24 hours) [20], withdrawal of screws [21] and surface soundness [22].

2.3 Rheological characterization

The adhesives were tested with a rotary rheometer ARES (New Castle, US) with parallel plates geometry; the plate diameter used was 25mm and the gap between the plates was 1.5mm. The experiments were carried out in an environment with constant temperature (25°C). Silicone oil was used to prevent water evaporation. Three replicates were used for optimal adhesive mix.

2.4 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was used to determine the thermal stability and degradation of the adhesive mix using a TGA Q50 thermogravimetric apparatus. Investigation was done for the optimal adhesive mix as mentioned above. Ten milligrams of each cured sample were placed on a balance located in the furnace and heat was applied over the temperature range from room temperature to 600 °C at a heating rate of 5 °C/min in air. Mass losses vs. temperature thermograms were obtained showing the different decomposition processes. Three replicates were used for optimal adhesive mix.

2.5 Density and porosity

The apparent density of the particleboard was determined by measuring the mass and volume, while material density of the board was measured with a Helium pycnometer Accupyc 1330 (Micromeritics, Norcross, USA). Porosity (voids between the particles) was calculated by the equation according to Rahman equation [23, 24]:

$$e = 1 - \frac{\rho_{ap}}{\rho_m}$$

where e, ρ_{ap} and ρ_m are porosity, apparent density (kg/m3) and material density (kg/m3) respectively.

2.6 Formaldehyde emission by desiccator method

The formaldehyde emissions from the particleboard were determined according to the standard [25]; the 24-h desiccator method uses a common glass desiccator with a volume of 10 L. Eight test pieces, with dimensions of 150 x 50 x 10 mm3, which were cut from the particleboard, are positioned in the desiccator. The formaldehyde released from the test pieces at 23 ± 2 °C and 50 ± 10% relative humidity during 24 h is absorbed in a Petri dish filled with 30 ml of distilled water and determined photometrically. Ten replicates were used for UF control and optimal adhesive mix.

2.7. Statistical analysis

The tests experiments concerning the Particleboard characterisation were repeated ten times. Means and standard deviations of data were calculated. The analysis of variance (ANOVA) was applied for the analysis of the results of table 1. For each analysis, significance level of 5% was assumed. All statistical analyses were carried out using the software Statgraphics Plus 5.1 (Stat-point Technologies, Inc.).

3. Results and discussion

Dynamic oscillatory measurements were carried out in order to examine the structural stability of the optimal adhesive mix of polenta cornstarch, mimosa tannin, and UF resin mix (mass proportions 10 : 4 : 86. In the complex modulus, the elasticity or the energy stored in the material during deformation is shown by the storage shear modulus G’, whereas the viscous property or the energy dissipated as heat can be described by the loss shear modulus G’’. These parameters were monitored as function of time and temperature pointing out the physical properties of adhesive. In Figure 1 the rheological curves of the adhesive mix described above measured at 25 °C, 1 % strain and 1 rad/s are shown. Here, it can be observed that the dynamic modules (G' and G") remain constant and parallel with increasing time. That shows excellent structural stability of the resin. On the other hand, this Figure 1 shows a predominant elastic character of the adhesive (G’>G’’).
TGA can check the thermal decomposition and thermal stability of the resins.

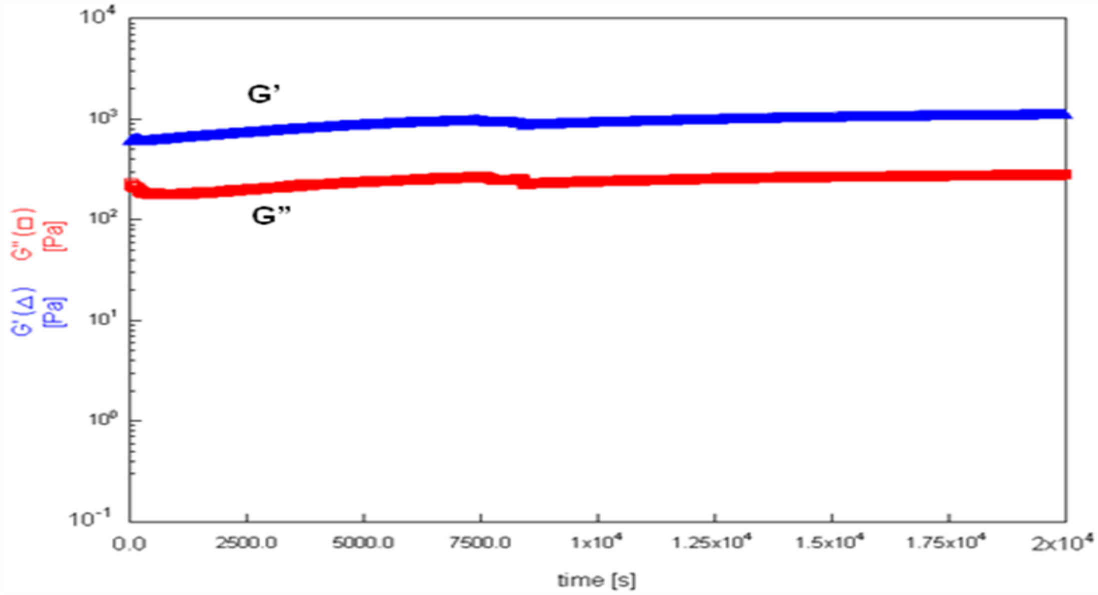

Figure 1: Time sweep of storage modulus (G’) and loss modulus (G’’) of the adhesive mix of polenta cornstarch, mimosa tannin, and UF resin mix (composition 10:4:86 mass proportions) resins at 25°C; 1rad/s and 1% strain.

Figure 2 shows the thermogravimetric (TGA) curve and the mass loss per time (DTG) of the optimal adhesive mix as described above when heating in air atmosphere at a rate of 5 °C/min. TGA curves reveal the remaining mass of the samples in relation to time (the temperature of thermal degradation). The DTG curve shows that there are four steps of mass losses at around 110 °C, 245 °C 270 °C and 300 °C, corresponding respectively (i) to moisture release, (ii) decomposition of the polenta cornstarch, (iii) of the mimosa tannin, and finally (iv) of the UF resin. The most probable phases formed during the decomposition of the polenta cornstarch-mimosa tannin-UF-adhesive mix resins were levoglucosan, besides complex gases, catechol and water liberated [13, 26, 27]. It should be mentioned that such high temperatures do not occur during the board production and during any use of the boards.

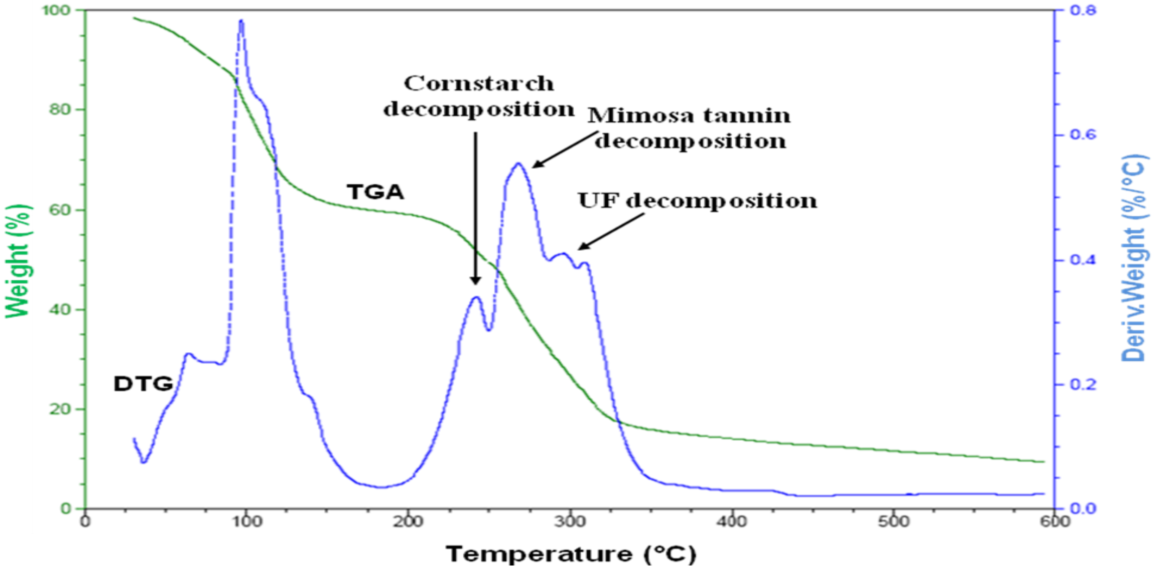

Figure 2: TGA and DTG curves of the adhesive mix of polenta cornstarch, mimosa tannin, and UF resin (10 : 4 : 86 mass proportions); temperature increase = 5°C/min.

After hardening, we tested kinetic cooling effect on the mechanical performance of our resins. Figure 3 shows the temperature dependence of storage (G') and loss (G'') modules of the polenta cornstarch-mimosa tannin-UF resin mix (10:4:86 mass proportions) when cooling from 125 to 25°C at 1 rad/s, 0.05% and 2°C/min.

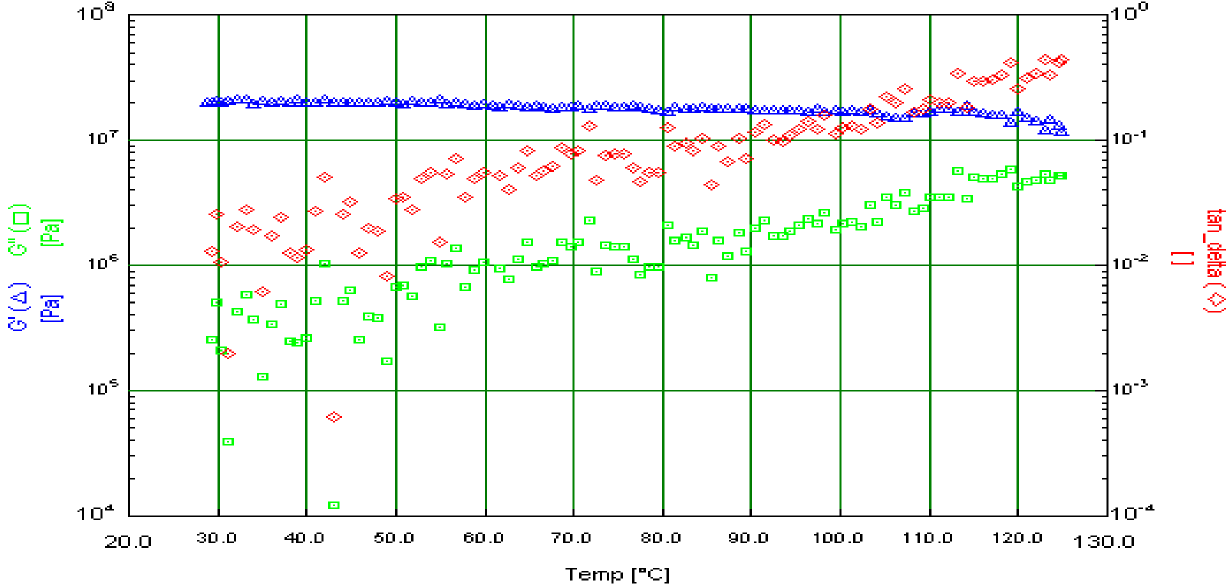

Figure 3: Temperature dependence of storage (G') and loss (G'') modules of the adhesive mix of polenta cornstarch, mimosa tannin, and UF resin mix (10:4:86 mass proportion) when cooling from 125 to 25°C; test conditions in the rheometer: 1 rad/s, 0.05 %; cooling speed 2°C/min.

The elastic modulus (G') values remain almost constant as a function of temperature. This result indicates that cooling has absolutely no effect on the elastic properties of the adhesive. However, the viscous modulus (G'') values decrease linearly with temperature. This is normal, since cooling the resin becomes more solid.

The mechanical properties (internal bond, surface soundness, modules of rupture MOR, modulus of elasticity MOE and withdrawal of screws), thickness swelling, porosity and formaldehyde emission of the particleboards made using (i) the described adhesive mix of polenta cornstarch, mimosa tannin, and UF resin mix (10 : 4 : 86) and (ii) a commercial UF resin as control are illustrated in Table 1.

Table 1: Summary of the test results of the particleboards (pressed at 195 °C and 7.5 min). Ten replicates of each adhesive. S.D.: standard deviation.

Resins	Average panel density (Kg/m^3)	Dry IB, (MPa) Mean ±S.D	MOE (MPa) Mean ±S.D	MOR (MPa) Mean ±S.D	TS, (%) Mean ±S.D	SS, (N/mm^2) Mean ±S.D	WS, (daN)	Porosity (%)	Formaldehyde emission (mg/100g) Mean ±S.D
Control UF	656	0.48 ± 0.03^{a}	2481 ± 92^{a}	15 ± 0.6^{a}	14 ± 1.6^{a}	1.63 ± 0.13^{a}	70^{a}	50^{a}	3.7 ± 0.12^{a}
Polenta cornstarch:mimosa tannin:UF (10:4:86)	657	0.69 ± 0.05^{b}	3175 ± 227^{b}	19 ± 1.5	14 ± 1.6^{a}	1.65 ± 0.14^{b}	50^{b}	53^{b}	3.0 ± 0.09^{b}
Requirements EN 312 (P4 boards)	*	> 0.35	> 2300	> 15	< 15	> 1	*	*	*
Requirements EN 312 (P2 boards)	*	> 0.35	> 1600	> 13	< 15	> 1	*	*	*

IB: internal bond
TS: Thickness swelling
SS: Surface soundness
S.D: standard deviation
WS: Withdrawal of screws
MOR: modulus of rupture
MOE: modulus of elasticity
NF EN: European standard
a,b values with the same superscript letters were not significantly different

Conclusion

A polenta cornstarch-mimosa tannin-UF (10 : 4 : 86; mass proportions) adhesive mixture is easy to prepare. A simple mixing of a mimosa tannin, Polenta cornstarch solution and UF resin provides a high mechanical performance. Results of the laboratory studies indicate that the optimal polenta cornstarch-mimosa tannin-UF (10 : 4 : 86; mass proportions) mixture can be used successfully as a wood adhesive for interior grade particleboard. Moreover, the formaldehyde emission levels obtained from boards bonded with polenta cornstarch-mimosa tannin-UF (10 : 4 : 86) adhesive mixture were lower to those obtained from boards made with control UF. Extension of these results to the industrial particleboards production is in progress.

Acknowledgements

We gratefully acknowledge the financial support from the "Conseil Général des Landes" (Aquitaine, France).

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(2013) ; http://www.jmaterenvironsci.com