Binderless Composites from Pretreated Residual Softwood

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Received 10 August 1998; accepted 3 February 1999

ABSTRACT: Residual softwood was thermomechanically pretreated and used to produce composites with no synthetic binders. The lignocellulosic material was steam exploded with a thermomechanical aqueous vapor process in a continuous tubular reactor. The study attempts to use the intrinsic bonding capacity of the steamed fiber, which is due to the plastification of the lignin. Chemical and structural changes in the pretreated substrate were evaluated by analytical characterization and scanning electron micrographs (SEM). The effect of the pressing conditions was evaluated in accordance with the physicomechanical responses of the composites. The physical and mechanical properties of the panels obtained were tested using UNE EN Spanish standard-European standards. In order to get more information about the degree of adhesion between the lignin and the fibers, SEM micrographs were taken of the broken surfaces of the material tested by the internal bond method. The results show that the thermomechanical pretreatment, pressing temperature, and time have a great effect on the mechanical and physical properties of binderless composites. The steam explosion aqueous vapor pretreatment is a good way for conditioning softwood sawdust for production of composites. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2485–2491, 1999

Key words: binderless panels/composites; physicomechanical properties; thermomechanical aqueous vapor steam process; lignin

INTRODUCTION

From an environmental and economic point of view, the production of binderless boards is beneficial: first, because waste lignocellulosic materials are recyclable and renewable[1–4]; second, because there are no synthetic resin binders in the panel production process. Generally, these resins come from fossil resources, which are not renewable and make the product expensive. No curing period is needed because there are no synthetic adhesives,[5] which is an economic saving. Neither do these panels have any formaldehyde emissions, which are subject to very severe legislation. Therefore, although the pretreatment process has an energy cost, the resulting composite material is environment friendly.[6]

Since thermomechanical fibers were seen as good fillers in composites based on plastic polymers and pretreated wood fibers, it has been both interesting and useful to evaluate the pretreated residual softwood as a raw material.[1,2,7–10]

The aim of this study is to evaluate the suitability of thermomechanical aqueous vapor pre-

Correspondence to: J. Salvadó.

Contract grant sponsor: Spanish Government; contract grant number: QFN95-4720.

Contract grant sponsor: Generalitat de Catalunya; contract grant number: GSR96.

Contract grant sponsor: Universitat Rovira I Virgili.

Journal of Applied Polymer Science, Vol. 73, 2485–2491 (1999)

 CCC 0021-8995/99/122485-07

Table I Average Composition and 95% Confidence Interval for the Softwood Mixture (Original and Pretreated)[a]

Fraction	Original Material	Pretreated Material
Solubilization	—	31.4
Ash	0.4 ± 0.1	0.2 ± 0
Hot water extractives	7.4 ± 1.4	6.5 ± 1.6
Ethanol/toluene extractives	3.3 ± 1.4	5.0 ± 1.5
Klason lignin	25.1 ± 0.8	21.1 ± 2.3
Glucose	38.2 ± 0.7	37.7 ± 2.6
Other sugars	28.5 ± 1.6	9.0

[a] Results based on 100 g of Dry Solid Basis (% DSB).

treated fiber as a raw material in the production of composites. There are several papers that deal with binderless panels made with steamed fiber by different processes,[5,10–15] but their results are difficult to correlate with our study because they used different raw materials, different pretreatment conditions, a different press process, and even different conditioning.

The main reaction produced during the steam explosion process is the autohydrolysis of the constituent polymers. The hemicelluloses are hydrolyzed, the cellulose is slightly depolymerized, and the lignin is melted and progressively depolymerized into low molecular weight macromolecules.[16] This process increases the accessibility, separates the main components of lignocellulosic materials, and enables the fiber to be conditioned so that it can be used in chemical fractionation, biotechnological conversion, and panel production.

EXPERIMENTAL

Lignocellulosic Substrate

The experiments were carried out using a mixture of softwood residues, particularly spruce (*Abies alba*) and pine (*Pinus insignis*) harvested in Lleida, Catalonia, in the northeast of Spain. The ground material was sieved at 100 mesh (0.150 mm). The substrate average composition is shown in Table I. The moisture content of the fiber was 7%.

Steam Explosion Pretreatment

The hydrolytic pretreatment was carried out in a continuous tubular reactor capable of processing up to 100 kg h^{-1} of aqueous suspension with a solid consistency of 7% (w/w), which has been described elsewhere.[17] Pretreatment was conducted at a temperature of 217°C, 22 bar vapor pressure, and a residence time of 2.8 min. The R_o severity factor was used,[18] which groups the treatment temperature and time into a single variable, and in this case the log R_o = 3.9 (pretreatment severity factor). This severity factor was used because previous scanning electron microscopy (SEM) studies demonstrated that this severity was sufficient to ensure that the lignin polymer melted. The average composition of the pretreated fiber is shown in Table I.

Analytical Methods

The original and pretreated substrates were chemically analyzed using the following standard methods: American Society for Testing and Materials (ASTM) E-871-82 for moisture content; ASTM D-3516-76 for ash content; ASTM D-1111-84 for hot-water extractives, and ASTM D-1107-84 for ethanol/toluene extractives. Klason lignin was measured using the ASTM D-1106-84 method. Carbohydrates were analyzed by high performance liquid chromatography.[19]

Pressing Conditions

The pretreated material was air dried to a moisture content of 7 %, which is near to equilibrium in atmospheric conditions. The panels were 31 × 31 × 0.35 cm^3 in volume. The press cycle consisted of three stages[15]: The first one had a maximum pressure of 4.2 MPa for 5 min at the desired temperature; the second, called the breathing stage, was needed to release the steam produced during the first step and to prevent blowouts (1 min); the third step was a pressing stage with a pressure of 4.2 MPa for the desired time (5, 10, 15 min) at target temperatures of 175, 200, 215, 225, and 230°C. Temperatures above 230°C ignited the pretreated material. These values are between the target pressing temperatures and pressing times found in the literature.[5,10–15]

Previous studies have shown that panels with high densities have the best mechanical properties.[20] The target density of the panels in this work was set at 1000 kg/m^3.

Control Panel

Pressing conditions of 200°C and 10 min (midrange for both temperature and time) were

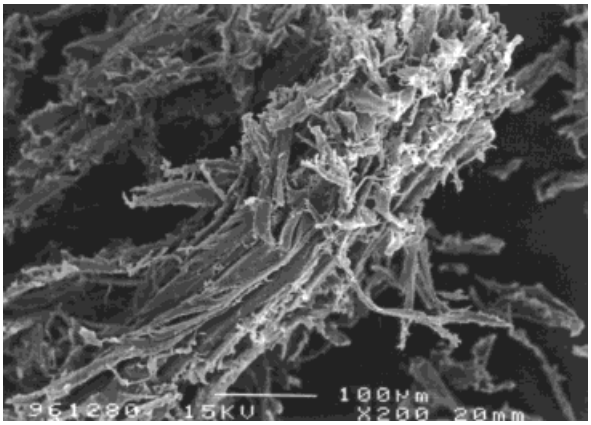

Figure 1 SEM micrograph of aqueous vapor exploded fibers.

used with unpretreated material to provide a control for the physical and mechanical changes.

Physical and Mechanical Tests

The panels were characterized using the following physical and mechanical UNE EN Spanish standard-European standards: 32294 for the humidity; 32594 for preparing the panels in the same environmental conditions, 65% relative humidity and 20°C; 32394 for density; 31794 for thickness swelling (TS) and water absorption (WA); 31094 for modulus of elasticity (MOE) and strength (in a bending test); 31994 for internal bond (IB). An accelerated aging test, called the T-313 method, was also carried out using the 32194 method, and the TS and the IB were then performed again.

Scanning Electron Micrographs

The SEM technique was used to find out information about the structural changes caused by the pretreatment and about the broken surfaces after the mechanical tests.[21] Samples (pretreated fibers and broken surface panels) were dried using the critical-point technique[22] and prepared on a stub and sputter coated with gold. They were metalled at 0.05 mbar and 30 mA, and observed at acceleration voltages of 15 kV and a distance of 20 mm. For magnification, a JEOL JSM6400 scanning electron microscope was used.

RESULTS AND DISCUSSION

Structural Changes

Structural changes in the pretreated fiber were qualitatively evaluated with SEM micrographs. A selected micrograph of pretreated fibers at 217°C with a residence time of 2.8 min ($\log R_o = 3.9$) is shown in Figure 1. At this severity, some shrinkage folds can be seen on the fiber surfaces and there was some defibration. The same behavior has been seen elsewhere else.[22] Because of these changes, the contact surface increased, which facilitated the adhesion of the panels.[23] In some magnifications of these micrographs (Fig. 2) some lignin droplets can be observed. These spherical particles of lignin, formed due to the phenomenon of coalescence, ranged from 100 to 400 nm in size.

Chemical Changes

Variations in the chemical composition of the pretreated fiber were studied in order to evaluate the effect on the physical and mechanical properties of the panels. The results of the characterization were found as an average value of triplicates with a 95% confidence interval and are shown in Table I. When the severity increased, the solubility also increased. Simultaneously, both kinds of polymers in the pulp, hemicelluloses and cellulose, decreased. Klason lignin decreased slightly from 25.1% DSB (dry solid basis) to 21.1% DSB. Organic extractives (organic-soluble lignin) increased from 3.3 to 5.0% DSB. It should be pointed out that although the lignin content seemed to decrease, it became more superficial and accessible for bonding, as seen in the micrographs. The ash content of the fiber also diminished and this is a desired aspect in bonding quality.[24,25] A more detailed study of the effect of the pretreatment on the chemical composition of the lignocellulosic material can be found in the literature.[26,27]

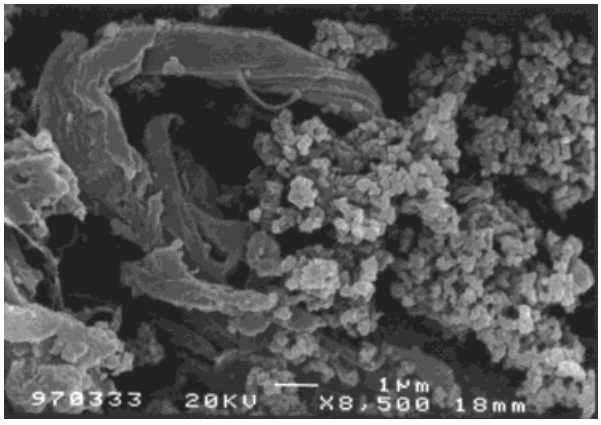

Figure 2 SEM micrograph of a pretreated fiber with droplets of lignin.

Table II Average % of Humidity and 95% Confidence Interval for the Panels[a]

Pressing T (°C)	Pressing Time (min)		
	5	10	15
175	3.7 ± 0.2	3.2 ± 0.9	3.3 ± 0.2
200	3.7 ± 0.3	3.2 ± 1.1	3.3 ± 0.3
215	3.4 ± 0.1	3.6 ± 0.2	3.4 ± 0.2
225	3.8 ± 0.1	2.9 ± 0.9	3.0 ± 0.6
230	3.4 ± 0.2	3.4 ± 0.0	3.4 ± 0.2

[a] Control panel (200°C, 10 min): 3.9 ± 0.4. Results based on 100 g of Dry Solid Basis (% DSB).

Physical Properties

Moisture

All panels had a moisture content between 3 and 4%. Table II lists the moisture values for the panels. There are no significative differences between the moisture of the different panels with a probability of 95%.

Density

The panel densities for the different pressing conditions are listed in Table III. The average values of 9 repetitions are presented with a confidence interval of 95%. The density of the control panel was 956 ± 49 kg/m^3.

Water Absorption and Thickness Swelling

The WA and TS after 24 h in water are shown in Figure 3 and 4, respectively.

Water absorption values are between 36 and 72% (% weight gained). Thickness swelling varies between 12 and 37%. The general trend is to get better results (less TS and WA) at high temperatures and pressing times. The higher the temperature is the lower the influence of the pressing time. At 225°C, WA and TS seem to stabilize. For the control panels, WA was 204% and TS 80%. Even the worst results for panels made with pretreated material had much better physical characteristics than the control panels. Analysis of variance tests and the least significant difference test, $\alpha = 0.05$ (α is the significance level), show that for pressing temperatures higher than 215°C the TS and WA tend to be constant.

Table III Density (kg/m^3) Values of the Panels[a] at Different Pressing Conditions[b]

Pressing T (°C)	Pressing Time (min)		
	5	10	15
175	971 ± 32	1063 ± 54	1060 ± 72
200	952 ± 25	936 ± 20	1036 ± 43
215	1000 ± 8	965 ± 56	990 ± 24
225	996 ± 35	963 ± 18	1016 ± 51
230	992 ± 38	979 ± 9	995 ± 27

[a] Control panel (200°C, 10 min): 956 ± 49.
[b] Results are the average value with the confidence interval at a level of significance of 95%.

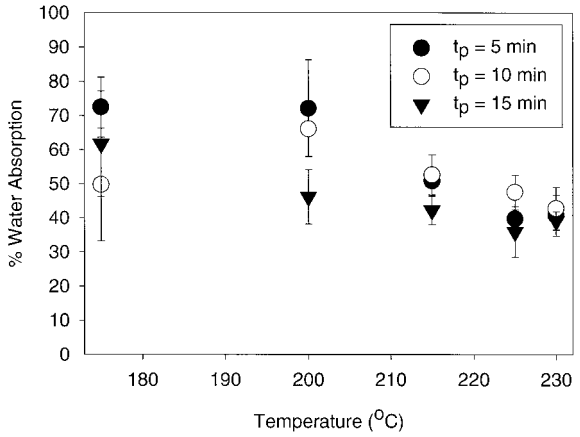

Figure 3 Water absorption after 24 h immersion of the binderless panels at different pressing times (min) and temperatures (°C). WA for Control panel: 204%. Results are the average value with the confidence interval at a level of significance of 95%.

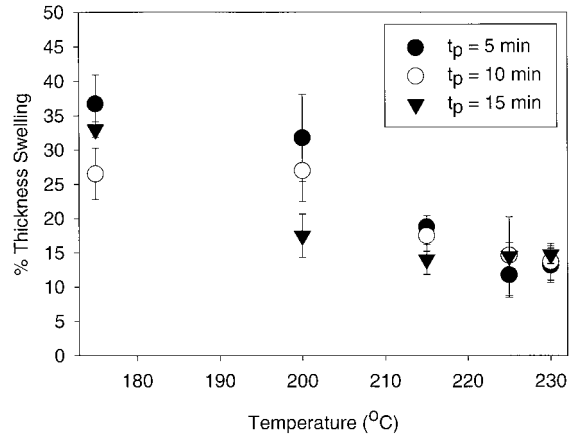

Figure 4 Thickness swelling after 24 h immersion of the binderless panels at different pressing times (min) and temperatures (°C). TS for Control panel: 80%. Results are the average value with the confidence interval at a level of significance of 95%.

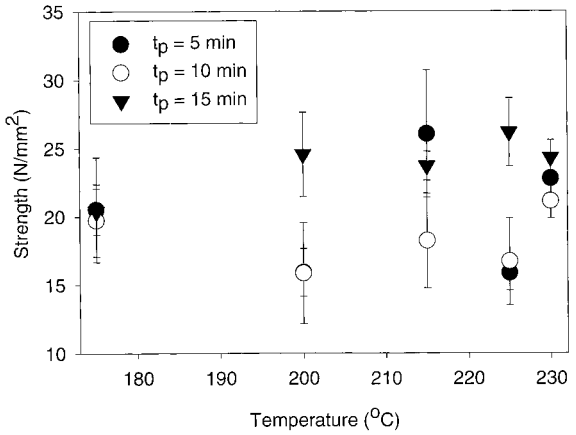

Figure 5 Strength of the binderless panels at the different pressing times (min) and temperatures (°C). Strength of control panel: unable to perform the test due to poor binding. Results are the average value with the confidence interval at a level of significance of 95%.

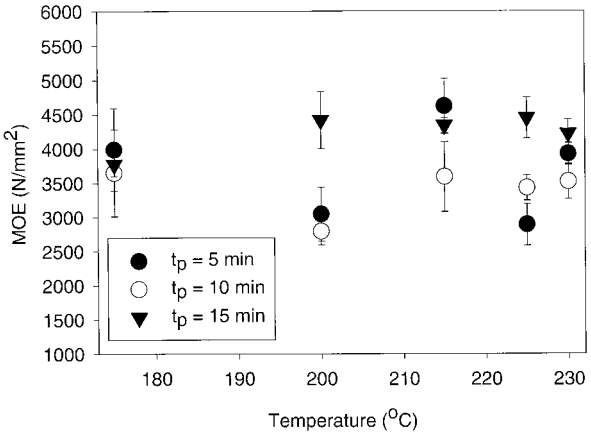

Figure 6 MOE of the binderless panels at the different pressing conditions varying time (min) and temperature (°C). MOE of control panel: unable to perform the test due to poor binding. Results are the average value with the confidence interval at a level of significance of 95%.

All these physical values are similar to others found in literature.[1,13,15,28,29] This behavior is in accordance with the chemical and structural changes observed in the thermomechanically treated softwood fiber, which gave it a better water resistance.[30,31]

Mechanical Properties

Strength properties are shown in Figure 5 as a function of pressing conditions. The values (9 repetitions) range from 15.9 to 26.2 N/mm^2. There seems to be a slight increase in strength if the extreme temperatures studied are compared. In general, a pressing time of 15 min gives better results than 5 and 10 min, which are very similar except for 215°C, 5 min. There is a wide dispersion of results at this last point. It was observed in most cases that strength was high when density was also high. More data are needed to establish a more consistent conclusion.

MOE values are presented in Figure 6. Since these results came from the same test as the strength property, the tendency is the same. Values were between 2800 and 4600 N/mm^2.

The strength and MOE results showed that panels pressed at the highest temperatures and longest times were not the strongest. This is probably because the strength of the bonds between polymers decreases at longer times and higher temperatures.[23]

Control panel had so poor mechanical properties that neither the strength nor the modulus of elasticity could be tested.

Internal bond is the cohesion between the fibers determined by applying a perpendicular force to the panel faces so as to separate them. The results are plotted in Figure 7 and show that in most cases, except for $T = 175$°C, the IB values for $t_p = 10$ min (t_p is the pressing time) are lower than for $t_p = 5$ min. It can also be observed that the lowest panel densities are for $t_p = 10$ min, except for $T = 175$°C. For IB values at other pressing times and temperatures, there seems to be the same dependence between this mechanical

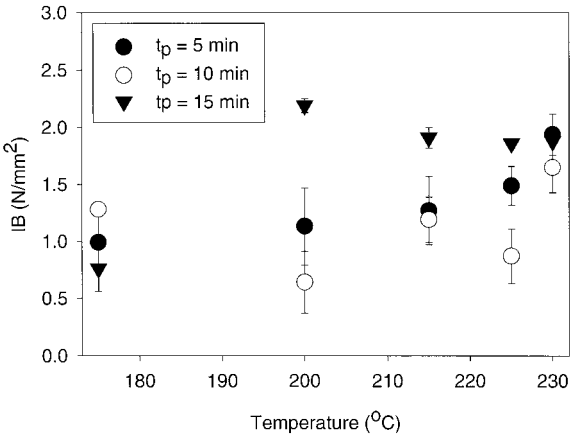

Figure 7 IB of the binderless panels at the different pressing times (min) and temperatures (°C). IB of control panel: unable to perform the test due to poor binding. Results are the average value with the confidence interval at a level of significance of 95%.

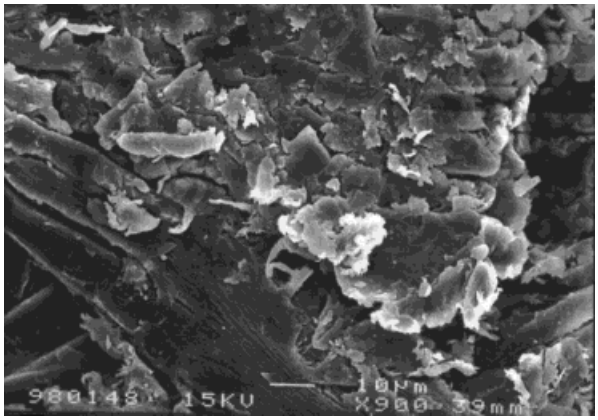

Figure 8 SEM micrograph of a broken surface after the IB test for a panel made at 200°C for 15 min.

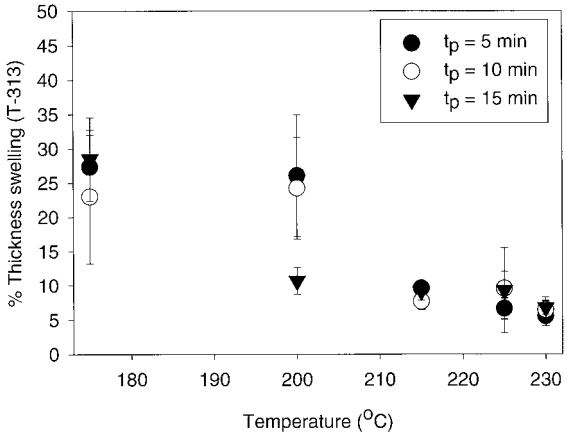

Figure 9 Thickness swelling after the accelerated aging test T-313. Results are the average value with the confidence interval at a level of significance of 95%.

property and density. Besides, a temperature of 175°C is shown to be insufficient to produce a panel with good mechanical properties.

It should also be pointed out that, at high temperatures, pressing time has less influence on IB and that even for short pressing times the polymers that make up the fibers can adhere.

This behavior agrees with the glass transition values, in the dry state, found in the literature: cellulose (≈ 220°C), hemicelluloses (≈ 170°C) and native lignin (≈ 200°C).[32]

Control panel had so poor mechanical properties that the IB could not be tested.

SEM micrographs were taken in order to get more information about the interface between the fibers and the lignin polymer. Figure 8 shows the broken surface after the IB test for a panel made at 200°C 15 min (the best results for IB). It can be seen that at 200°C for 15 min the lignin can flow and cover the lignocellulosic fibers, and that interfiber cohesion is greater than in other panels. A temperature of 200°C with a fiber humidity of 7% is enough to make the lignin soften, flow, and surround the fibers. Some authors have pointed out that the lignin also recovers the hemicelluloses and cellulose and prevents the hydrophilic groups of these two sugar polymers from taking up water.

Accelerated Aging Test

The thickness swelling test was carried out after the accelerated aging procedure, T-313, and the results are shown in Figure 9. The values range between 5 and 28%, which are lower than the values before the aging test and the same tendency is observed. It can be seen that panels pressed at low temperatures and short pressing times did not behave well, but above 215°C the thickness swelling seemed to be constant for all the pressing times.

The internal bond property was also evaluated in the panels subject to the accelerated aging test. The values are shown in Figure10. The effect of the aging test on this kind of panel seemed to decrease the IB property by 45–50%. After the aging test, the relationship between IB and the pressing temperature is clearer.

CONCLUSIONS

The results demonstrate that binderless panels made with this pretreated material have better

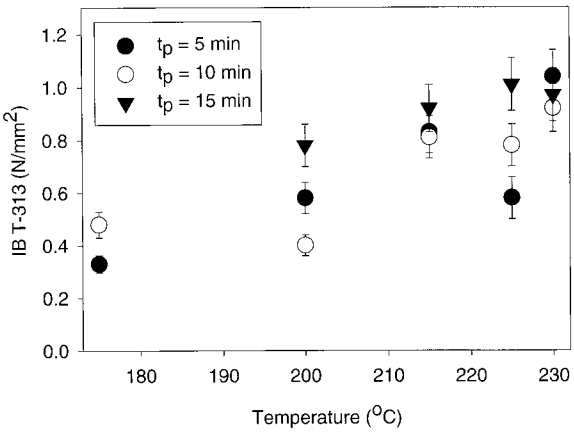

Figure 10 IB after the aging test T-313 of the binderless panels at the different pressing times (min) and temperatures (°C). Results are the average value with the confidence interval at a level of significance of 95%.

mechanical properties than the panels made from unpretreated material (the mechanical properties of control panels could not be tested due to their poor qualities). There are several reasons for this: the structural changes in the pretreated fiber, the fact that lignin has better access to the fiber surface, and the decrease in the hemicellulose content in the fiber, which affects the water resistance of the panel.

The pressing temperature should be at least 200°C to ensure that the lignin can melt and flow in situ between the fibers. The general trend is that the best physical and mechanical properties are best at the highest temperatures tested; in these conditions, 230°C, the panel properties are the same for the different pressing times studied. This means that the processing time can be shorter in an eventual commercial production. This is desirable from an environmental and economical point of view.

Some authors[28,30,31] have related the water resistance of the panels to the partial hydrolysis of hemicelluloses due to the thermomechanical pretreatment. This is also the case in this study.

Depending on the size of the particle used, the surface of the panels has a smooth appearance and does not need a sanding stage, which is an energy saving. The panels also seemed to have good machineability when the panels were cut.

The pretreatment increases the intrinsic bonding properties of wood, and also its resistance to water.

In the future, research could be done on the effect of the severity of the thermomechanical aqueous vapor continuous pretreatment on the panels made with such residual raw material, in an attempt to evaluate how the different constituent polymers affect the characteristics of the panels.

The authors are indebted to the Spanish Government and the Generalitat de Catalunya (Catalan Local Government) for financial support, project number GSR96 for quality groups and project number QFN95-4720, and a grant from the Universitat Rovira i Virgili (Catalunya).

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