**Utilization of Spent Sulfite Liquor in Combination with Wheat Flour for particleboards manufacture**

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**Abstract**

Nowadays, the majority of adhesives used in particleboards manufacture are formaldehyde-based, a compound classified as human carcinogen. Due to health concerns, there is an increasing demand for safer and eco-friendly adhesives.

In this work a low-cost formulation based on thick spent sulfite liquor (TSSL), a byproduct from the acidic sulfite wood pulping process, and wheat flour (WF), was developed.

This combination was tested for the production of three-layer particleboards, 15 mm thick and density of (650 ± 20) kg m−3, at different manufacturing conditions. The produced particleboards presented better performance than those manufactured solely with TSSL, with internal bond strength (0.46 N∙mm-2) above the requirements of the standard EN 312 for standard particleboards type P2 (0.35 N∙mm-2).

1. Introduction

Europe produces about 29 million m3 of particleboards per year, and this value is expected to continue growing [1]. Nowadays, the majority of adhesives used in particleboards manufacture are synthetic, mainly formaldehyde-based, due to their high reactivity, good binding strength and low prices [2]. Nevertheless, they release formaldehyde, a toxic chemical compound obtained from non-renewable resources and classified as human carcinogen. Due to health concerns, there is an increasing demand for safer and eco-friendly adhesives.

Spent sulfite liquor is a byproduct from the acidic sulfite wood pulping process and is majorly burnt for energy production and regeneration of the pulping chemicals, being only 2 % used in industrial processes [3]. These liquors are usually concentrated using multiple evaporators resulting in thick spent sulfite liquor (TSSL) [4]. The major components of TSSL obtained from the acidic magnesium-based sulfite pulping of *Eucalyptus globulus* are lignosulfonate lignin (58 % of dry solids), ashes (24 % of dry solids) and sugars (16 % of dry solids) [4].

There is a high amount of works reporting the application of spent sulfite liquor (SSL) as adhesive, but its industrial application is reduced, mainly due to the longer pressing times and lower performance when compared to synthetic resins. To improve the properties of SSL as adhesive, various studies reported combination with synthetic resins, such as phenol-formaldehyde and urea-formaldehyde. However, information on its association with other natural products is scarce.

Wheat flour (WF) is a low-cost natural product, obtained from wheat grains that consists mainly of starch (72.8 %) and proteins (7.8 %) [5]. It is widely used as an extender for synthetic resins in wood products [6].

In an attempt to developed a low-cost bioadhesive, with good binding properties, a formulation comprising SSL (84 %) and wheat flour (16 %) was developed. This combination was tested for the production of three-layer particleboards, 15 mm thick and density of (650 ± 20) kg m−3, at different manufacturing conditions.

**2. Materials and Methods**

**2.1. Materials**

Thick spent sulfite liquor (53-59 wt. % solids content) from acidic magnesium–based sulfite pulping of *Eucalyptus globulus*, was kindly supplied by Caima – Indústria de Celulose SA (Constância, Portugal). Wheat flour was a 55 type commercial product obtained from Pingo Doce (Lisboa, Portugal) with the following composition: 76.2 % of carbohydrates; 12.5 % of water, 10.0 % of proteins and 1.3 % of lipids. Wood particles were supplied by Sonae Arauco Portugal, SA. (Oliveira do Hospital, Portugal). Unless stated otherwise, all other chemicals were provided by Euroresinas – Indústrias Químicas, S.A. (Sines, Portugal).

**2.2. Methods**

**2.2.1. Thick spent sulfite liquor and wheat flour blend**

In a jacketed glass reactor vessel equipped with a condenser, a heating thermostatic bath circulator and an overhead stirrer, 84 parts of TSSL were blended with 16 parts of WF (solids/solids). Then the mixture was stirred at 97 ºC, or room temperature, for 70 minutes. The final solids content was adjusted to about 57 % with deionized water.

**2.2.2. Resin physicochemical characterization**

**Viscosity:** viscosity (expressed in mPa.s) was measured with a Brookfield DV-II+ programmable viscometer at 25 °C.

**pH:** pH values were measured with a InLab Routine Pro combined pH glass electrode with integrated temperature probe.

**2.2.3. Particleboards production**

Particleboards were produced by spraying the resin formulation onto the wood chips (2-3.5 % moisture content), in a laboratory glue blender. The resin solids, on dry wood chips, were 13.2 % or 20.0 %. After blending, a three-layer particle mat was hand formed into a flexible aluminum container (220×220×80 mm). The percentage of wood particles per layer was: 20 % in the upper surface layer, 62 % in the core layer and 18% in the bottom surface layer. The final particleboard density was (650 ± 20) kg·m−3. The hand formed aluminum containers were pressed in a parallel plate hot-press, set in order to simulate a typical particleboard continuous pressing operation. The pressing times were 300, 420 and 600 seconds and the pressing temperature 190 °C. The final thickness of the panels was 15 mm. Three panels were produced for each pressing time.

**2.2.4. Particleboards characterization**

After pressing, panels were stored in a conditioned room (20 °C, 65 % RH) and the density (EN 323), moisture content (EN 322), internal bond strength (IB) (EN 319) and thickness swelling (EN 317) were tested accordingly to the European standards.

**3. Results and discussion**

**3.1. Binder basic properties**

The characteristics of TSSL and TSSL mixed with WF at room temperature and 97 ºC (TSSL+WF-RT or TSSL+WF-97, respectively) are presented in Table 1. All the resins, present a low pH, ranging from 2.79 to 2.88, resulting from the characteristic low pH of TSSL. Regarding the viscosity, TSSL+WF-97 has the highest viscosity (505 mPa s), but a substantially higher value was expected, since the mixture was prepared at a temperature higher than the gelatinization temperature of wheat flour starch granules, which ranges from 61 to 75 ºC [6]. This indicates that the gelatinization of the starch granules, at 97 ºC was inhibited. This effect is in agreement with the work of Richardson *et al.* [7] who demonstrated that lignosulfonates delay swelling of the starch granules. The mechanism suggested for this effect is the molecular adsorption of lignosulfonates onto the granules surface, hindering transport to and from the granules.

**Table 1.** Final properties of TSSL, TSSL mixed with wheat flour (84:16) at room temperature (TSSL+WF-RT) and at 97 ºC (TSSL+WF-97).

|  |  |  |
| --- | --- | --- |
| **Resin/ Properties** | **pH** | **Viscosity (mPa.s)** |
| **TSSL** | 2.79 | 115 |
| **TSSL+WF-RT** | 2.83 | 230 |
| **TSSL+WF-97** | 2.88 | 505 |

This effect allowed the mixture prepared at 97 ºC maintain an acceptable viscosity for being applied on wood particles by spraying and tumble mixing.

**3.2. Binding performance in particleboards**

To assess the binding performance of the developed mixtures, particleboards (PB) were produced with the TSSL and TSSL+WT mixtures. The content of binder solids on dry wood chips (20 or 13.2 %), and particleboards pressing time, were also studied.

**Figure 1.** Internal bond strength of particleboards produced with TSSL and TSSL+WF mixture mixed at room temperature and 97 ºC (TSSL+WF-RT and TSSL+WF-97, respectively) as a function of different pressing times. Particleboards were manufactured with 20 % or 13.2 % of binder solids relative to dry wood particles, and pressed at 190 ºC (IB values shown in legend).

Figure 1 presents the internal bond strength (IB) values obtained for different pressing times and binder/wood ratios. All the particleboards produced with the TSSL+WT formulations presented higher IBs than the PBs produced solely with TSSL. Even when the PBs were produced with lower contents of TSSL+WF mixture, the IBs were higher.

For all the binders, the best pressing time was 600 seconds. The PBs produced with TSSL presented an IB (0.30 N·mm-2) above the requirements of the standard EN 312 for particleboards type P1 (0.24 N·mm-2), and the TSSL+WF PBs complied the requirements of the standard EN 312 for particleboards type P2 (0.35 N·mm-2).

Regarding the binder content, the PB produced with the highest TSSL+WF-RT binder content (20 %) presented better performance than the PB produced with a 13.2 % of resin solids on dry wood chips. Despite that, the TSSL+WF-97 binder, yielded slightly better IB values at 13.2 % resin content than TSSL+WT-RT at 20 %. This demonstrates the positive effect of preparing the binder at 97 ºC, as the heating treatment increased the binder viscosity, controlling its wood penetration and avoiding starved bond-lines. Additionally, it may have caused the leakage of some amylose from the starch granules, increasing the number of hydroxyl groups available for interaction with wood surface.

Despite of the good internal bond strengths, none of the particleboards produced presented resistance to water, having disintegrated after 24 hours immersed in water at 20 ºC. Nonetheless, they can be used for interior applications, since water resistance is not a requirement for dry conditions applications. Finally, chemical cross-linkers like diisocyanates or dialdehydes can be added to the TSSL+WF binder in order to increase water resistance.

**4. Conclusion**

A bio-based and low-cost adhesive was developed and tested in the present workby combining TSSL with WF. The results showed that when TSSL is combined with WF, particularly when mixed at 97 °C, the final binder performance is improved. Particleboards with internal bond strength of 0.46 N∙mm‑2 were obtained, which is above the requirements of standard EN 312 for particleboards type P2 (0.35 N∙mm-2).

In the present work, it was also observed that the starch granules present in the wheat flour don´t open during the binder preparation at 97 ºC, due to inhibition of gelatinization caused by TSSL. This allowed the final binder mixture to have sufficiently low viscosity for particleboards production.

The only limitation of the particleboards in terms of performance had to do with lack of water resistance. Nonetheless, they are suitable for dry conditions application. Use of chemical cross-linkers would allow surpassing this problem.

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References

[1] European Panel Federation. Market information. http://europanels.org/facts--figures/market-information. Published 2015. Accessed November 22, 2017.

[2] M. Dunky. Urea — formaldehyde (UF) adhesive resins for wood. *International Journal of Adhesion and Adhesives*, 18:95-107, 1998.

[3] M. Euring, A. Kirsch, P. Schneider, A. Kharazipour. Lignin-Laccase-Mediator-Systems (LLMS) for the Production of Binderless Medium Density Fiberboards (MDF). *Journal of Materials Science Research*, 5(2):7, 2016.

[4] A. Marques, D. Evtuguin, F. Magina, A. Prates. Chemical Composition of Spent Liquors from Acidic Magnesium–Based Sulphite Pulping of *Eucalyptus globulus*. *Journal of Wood Chemistry and Technology*, 29(4):322-336, 2009.

[5] Instituto Nacional de Saúde Doutor Ricardo Jorge. Detalhe alimento Farinha de Trigo Tipo 55. http://www2.insa.pt/sites/INSA/Portugues/AreasCientificas/AlimentNutricao/AplicacoesOnline/TabelaAlimentos/PesquisaOnline/Paginas/DetalheAlimento.aspx?ID=IS415. Published 2010. Accessed November 29, 2017.

[6] S. D’Amico, M. Hrabalova, U. Müller, E. Berghofer. Bonding of spruce wood with wheat flour glue-Effect of press temperature on the adhesive bond strength. *Industrial Crops and Products*, 31(2):255-260, 2010.

[7] G. Richardson, Y. Sun, M. Langton, A. Hermansson. Effects of Ca- and Na-lignosulfonate on starch gelatinization and network formation. Carbohydrate Polymers. 57(4):369-377, 2004.