Fast Pressing Composite Using Tannin-Furfuryl Alcohol Resin and Vegetal Fibers Reinforcement

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ABSTRACT: Experimental investigations have been carried out on the potential use of tannin-furfuryl alcohol resin for biobased composites using vegetal fiber reinforcement. Results showed that a mixture containing 54% furfuryl alcohol, 45% modified quebracho extract and 0.9% paratoluenesulfonic acid as a catalyst yields a resin that can be used with a nonwoven flax fiber mat to manufacture lightweight composites with good mechanical properties and a very short curing time with a regular hot press. The panels made were tested for tensile and flexural modulus and strength, water resistance and thermo-degradation.

KEYWORDS: Composite, fast curing, furfuryl alcohol, quebracho, tannin

1 INTRODUCTION

In the last decade, considerable progress has been made in the development of plastics and composites from renewable resources, and in particular from agricultural-based materials [1]. The development of “green” composites with both matrix and reinforcement being made from vegetal resources has flourished in the last few years. This has led to a variety of materials giving good results in both performance and economical aspects. While being generally inferior to their synthetic counterparts, they can be favored in a lot of applications that do not require top grade materials. Polylactic acid (PLA) is one of these well-studied materials for its characteristics both as a plastic and a matrix for composites, with works being carried out on structure modifications and filler compatibility [2,3]. Epoxidized vegetal oils can also be used as matrices for biocomposites [4] as well as phenol-furfural resins [5], and there are already on the market composites made out of furanic resins from agricultural byproducts [6]

Vegetal tannins have also been shown suitable for composite making. Their phenolic nature and natural reactivity allows for the development of a variety of adhesives, mainly for wood gluing applications, where they are used either as a substitution for some of the synthetic ingredients [7] or as the main component of the system [8,9]. In recent studies, tannin-based composites have been made using flax fibers and tannin/hexamethylenetetramine (hexamine) as hardener [10] with good results. However the pressing time needed to achieve optimal mechanical properties and stability can be a drawback for some manufacturing processes.

Furfuryl alcohol is known for its strong reactivity under acidic conditions, leading to highly exothermic self-condensation, and has the advantage of being produced by processing agricultural byproducts. Furfuryl alcohol adhesives are already in use, notably for furan no-bake resin, used as binder for sand molds in foundry. Additionally, some work has been achieved on its use as matrix in biobased nanocomposites [11], or as a surface treatment for vegetal fibers in conjunction with chlorine dioxide to increase fiber/matrix bonding [12]

It has been shown that tannin and furfuryl alcohol can react together in acidic conditions [13, 14]. As seen on Figure 1, the furfuryl alcohol reacts with itself leading to chains with three possible results: Structure I is the classical chain condensation, Structure II is the result of the reaction between two hydroxyl groups, and Structure III is due to the rearrangement of the furanic cycle and will

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become the source of crosslinking for furfuryl alcohol (Figure 2A). The tannins tend to form polyflavonoids mainly by C4-C8 linkage (C6-C8 linkage also occurs to a lesser degree), but will also react with the hydroxyl group of a furfuryl alcohol chain in the C6 position, and possibly in the C8 at the end of the flavonoid oligomer (Figure 2B). Chemical modifications of tannin extracts in order to increase their solubility in alcohol and phenol solvents and enhance their reactivity was achieved by Silvachimica and led to the development of tannin-furfuryl alcohol resins for foundry binders that are already available on the market [15]. These adhesives do not have any other industrial application to the author's knowledge. However, tannin-furfuryl alcohol resin alone was shown able to give a thermosetting plastic of interest [14], and therefore, to be a potential candidate for composite materials applications. This paper deals with the development of a fast pressing composite using a tannin-furfuryl alcohol resin catalyzed with paratoluenesulfonic acid and reinforced with a 100% flax fibers nonwoven mat.

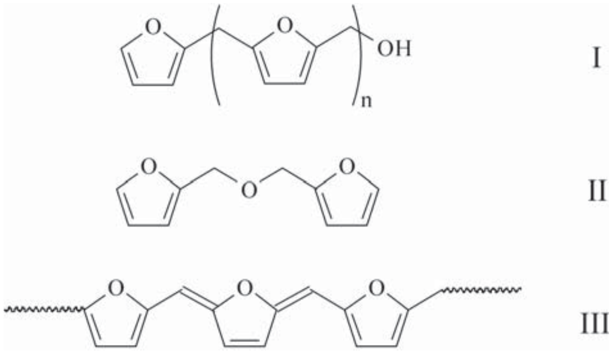

Figure 1 structures resulting from furfuryl alcohol self-condensation. I: classical linear chain, II: reaction between two hydroxyl groups, III: furanic cycle rearrangement.

2 EXPERIMENTALS

2.1 Materials

The fiber mats used were purchased from ECOTECHNILIN (France), and are made of 100% flax fibers mechanically carded, cross-lapped to reach a surface weight of 1200g/m² and bonded by needle punching. The tannins are QSF Quebracho extracts, soluble in furfuryl alcohol, and were obtained from Silvateam (Italy) as a dry powder. Furfuryl alcohol is reagent grade and paratoluenesulfonic acid (pTSA) is used as a 65% solution in distilled water.

2.2 Composite Manufacturing and Sampling

First the resin has to be prepared by dissolving the tannins in furfuryl alcohol. A mass of 96 g of furfuryl alcohol is poured into 80 g of tannin powder (alcohol to tannin ratio 1.2:1). The mixture is then mechanically stirred for 2 h to ensure complete dissolution of the tannins. Then 2.44 g (0.9% weight on dry material basis) of pTSA solution is slowly added to the resin and the mixture stirred for 3 additional minutes.

Fiber mats are cut into 20x25 cm samples and weighted. Then 35 g of resin is spread on each face of the mat and a steel cylinder is used to push the resin in depth. The impregnated mats are then pressed for 100 seconds in a hot press set at 210°C with a pressure of 4MPa using 3 mm gauges between the plates. The panels obtained, despite being hardened, are then put into an oven set at 120°C for 12 h to ensure a full curing of

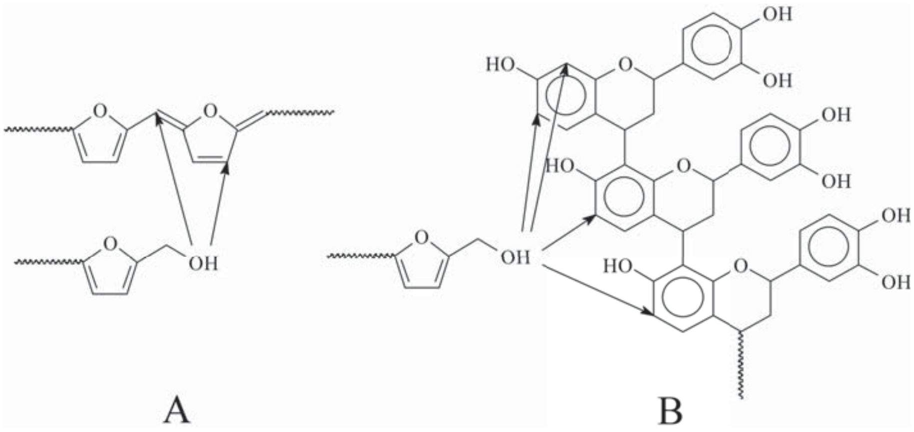

Figure 2 **A**: cross-linking of furfuryl alcohol polymers, **B**: potential reaction sites between polyfurfuryl alcohol's hydroxyl group and flavonoid units.

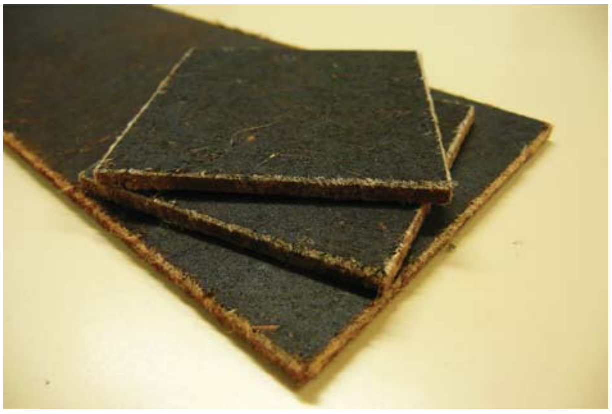

Figure 3 flax fibers reinforced tannin-furfuryl alcohol composites manufactured in this study.

the resin and then conditioned during 48h in controlled atmosphere (20°C, 65%MC). After conditioning, panels are weighted and cut into samples (Figure 3).

For tensile tests, two samples of 170x20 mm were taken out of each panel, two 80x30mm for bending test and three 50x50 mm for water swelling test. The rest is left for hardness measurement. Thermogravimetric analysis (TGA) and Differential thermal analysis (DTA) were made on 100 mg of grinded sample material from the tensile tests.

2.3 Testings

Tensile strength measurements were performed on an INSTRON 4467 Testing machine using a 30kN load cell. Settings were 100 mm between grips and 1 mm/min loading speed. A 3-point bending test was done with an INSTRON 4206 Testing machine and a 1kN load cell. Span was set at 70 mm and load speed at 2 mm/min. Brinell hardness measurement was done using the INSTRON 4467, with a hard steel ball indenter of 10 mm in diameter and a steel strike plate. Speed was set at 0.1 mm/sec and indentation depths at 2.7 mm. Both hardness and elastic recovery were measured. The TGA measurements were made on an ATG Netzsch STA 449 Jupiter machine in inert nitrogen atmosphere. Heating cycle is set for a steep increase to a 103°C plateau, maintained for 30 min to ensure full drying of sample. Then temperature was increased up to 1000°C with a rate of 1°C per minute. Water resistance was tested for 2 h and 24 h in a 20°C water bath, and mass uptake was also recorded.

3 RESULTS AND DISCUSSION

Under the conditions described, the process yielded composites having on average a total mass fiber content of 54.6% and a density of 716kg/m^3, which is under the theoretical maximum density that could be achieved; lignocellulosic material has an estimated density of around 1500kg/m^3 and the measured density of the resin is 1360kg/m^3 [15]. This shows that the material is quite porous. However this porosity is a key feature in the fast pressing process. Under acidic conditions, the furfuryl alcohol reacts with tannins in moderate amounts, and strongly with itself by its characteristic self-condensation mechanism, [13] leading to the formation of a great amount of water [16]. This water needs to be quickly evacuated through the composite during the pressing, as the steam pressure can lead to a spreading of the reinforcement mat as it has been observed in other composites using resins with water as a solvent [17]. Attempts to get a high density composite using a lower curing temperature to reduce steam formation led to considerably longer pressing times and materials that were barely cured after 20 min pressing. Catalyst proportion cannot be increased further as the mixture will reach the threshold of the exothermal self-sustaining condensation at room temperature. As seen on Figure 4, with 1% of pTSA catalyst the pot life does not exceed 8 min.

Despite its lower density compared to classical composite materials, the product showed good mechanical properties and may be suitable for non-structural applications. After pressing, the shape retention is good and no warping has been observed. Mechanical testing showed that the composite Modulus of Elasticity (MOE) in tension is about 2.2 GPa on average, with a tensile strength of 17.4 MPa. The modulus has been measured at 3.1 GPa in bending, with a bending strength of 32 MPa. The Brinell hardness was measured giving 2.55 HBS 10/100, with an elastic recovery of 25%, which is comparable to the properties of untreated beech wood [18]. All properties and their standard deviation are summarized in Table 1.

The TGA analysis of the composite (see Figure 5) reveals that it could withstand temperatures up to 150°C in regular use without damages, the mass variation in the 50 to 100°C being due to sample drying. Here the reinforcement is the first to show the beginning of degradation after 150°C, and the DTA curve follows the same pattern that has been observed for wood pyrolysis [19]. Thus, it presents a shoulder around 250°C that can be mainly attributed to hemicelluloses, and a main peak in the 270 to 330°C range that corresponds to the degradation of cellulose [19]. Cellulose represents a large proportion of the flax fiber weight, usually 70 to 75% [20]. The pyrolysis of the tannin-furanic type matrix occurs in a much broader temperature range, from 200°C to 600°C [15]. The position of the main peak depends on the tannin to furfuryl alcohol ratio. While pure polyfurfuryl

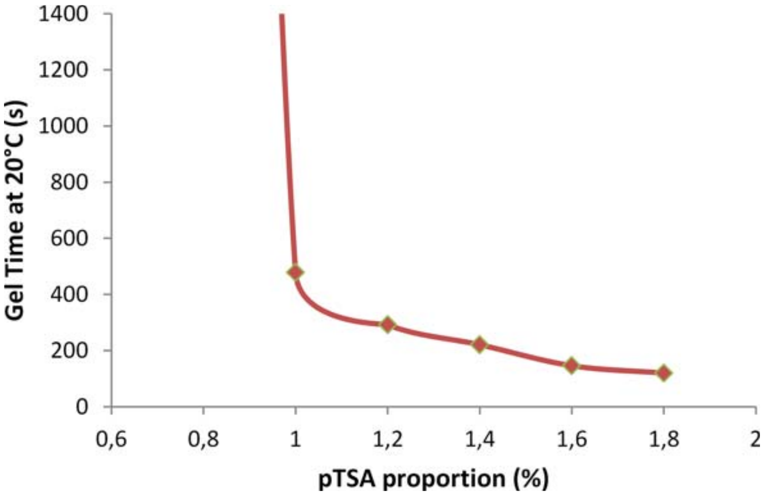

Figure 4 evolution of the gel time at room temperature of the resin with the proportion of catalyst in the mixture.

Table 1 physical and mechanical properties of the composite.

Property		Unit	Average Value	Standard deviation
Tensile	MOE	GPa	2,171	0,145
	Strength	MPa	17,4	2,3
Flexural	MOE	GPa	3,132	0,2
	Strength	MPa	32,2	2,91
Density		kg/m^3	716	25,5
Brinell Hardness		N/mm^2	25,5	0,26
Elastic recovery		%	25,1	1,35

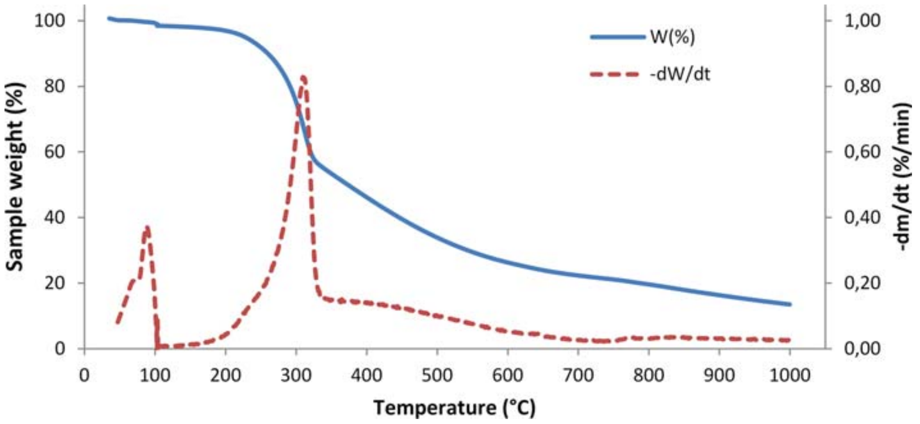

Figure 5 TGA curve of the composite (plain) and differential thermal analysis (dotted).

Table 2 norm EN 622-3 requirements and composite actual performances.

		Non structural		Structural		
		Dry	**wet**	**dry**	**Results**	**Std. deviation**
2h	swelling	–	–	–	4,90%	1,30%
	uptake	–	–	–	11,40%	0,80%
24h	swelling	<15%	<12%	<15%	10,40%	1,60%
	uptake	–	–	–	33%	1,90%
Flexural Strength		> 15MPa	> 18MPa	> 21MPa	32,2MPa	2,91MPa
Flexural MOE		–	–	> 2500MPa	3132MPa	200MPa

alcohol exhibits a main peak around 470°C [21], this moves down to 400°C with a resin containing 25% tannin [15], and in the resins at hand it seems to be more in the 350–370°C range by looking at the shoulder in the DTA curve.

Swelling as well as weight uptake was recorded in cold water for 2 h and 24 h. The composite performed fairly well with an average of only 10.4% after 24 h. Despite not meeting the criteria for exterior grade panels, the material may be suitable for a wide range of uses, including general use in both dry and wet environments, and structural use in dry environment according to the European norm EN 622-3 (shown in Table 2). Additional testing of internal bond would still be needed to ensure that the composite fills all of the norm requirements.

4 CONCLUSIONS

Tannin-furfuryl alcohol resins are potential candidates for biocomposites manufacturing. The combination of acid catalyst and hot pressing of the material allows a fast curing rate, compatible with a lot of applications where high production rates are required, as in the automotive industry. The mechanical properties obtained make it readily usable for some applications, but the possible uses could be further increased by: (i) improving the reinforcement with layered fabrics of unidirectional or 0–90° types, and also (ii) by increasing the overall density to some extent, as long as water evacuation can still take place. Except for the pTSA which represents only 0.5% of the final composite, all the other components are either products of green chemistry or natural resources which make these composites low-ecological-impact materials.

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