Tannin-Resorcinol-Formaldehyde Resin and Flax Fiber Biocomposites

A. Sauget*[,1], X. Zhou[1] and A. Pizzi[1,2]

[1]LERMAB-ENSTIB, University of Lorraine, 27 rue Philippe Seguin, BP 1041, 88051 Epinal, France
[2]King Abdulaziz University, Jeddah, Saudi Arabia

Received October 01, 2013; Accepted December 16, 2013

ABSTRACT: Tannin-resorcinol-formaldehyde (TRF) resin shows a good compatibility with natural flax fibers and yields composite materials of good mechanical properties when using paraformaldehyde as a hardener. Different formulations, curing parameters and processes such as high-temperature curing in press or spray-drying have been explored in order to adapt this resin to composite manufacturing and to improve the properties of this new material. Additional testing has been performed on the TRF resin by thermomechanical analysis to observe its reactivity at different pH and with the use of different hardeners.

KEYWORDS: Biocomposites, tannin resin, natural matrix, natural fibers

1 INTRODUCTION

In recent years, bio-based materials have seen a renewal of interest due to the increasing scarcity of fossil resources and the growing demand of consumers for green products. The research on the subject of tannins is an example of this recent trend: tannin-based adhesives for wood [1–3], tannin-based matrix for composites [4–6], tannin-based foams [7–12], and so on. Vegetable tannins are a wide family of natural phenolic molecules produced by the majority of plants, divided in two major classes: hydrolyzable tannins and condensed tannins. Among them, condensed mimosa tannin is obtained from the bark of the mimosa tree and is composed of polymerized flavone units, mostly prorobinetinidins [1–4] and profisetinidins. The reactivity of the aromatic rings of these flavonoids is close to phenol and they can be hardened by auto-condensation or by reaction with common hardeners such as aldehydes. In this way tannins have been widely used for decades as industrial thermosetting adhesive for wood products.

The TRF resin initial formulation is a coldset exterior grade adhesive for wood, usually using paraformaldehyde as hardener. The TRF adhesive has existed and been produced on an industrial scale for a long time [13]. This resin is bonded by hydrogen bonds and van der Waals forces to hydroxyl groups of the wood components (cellulose, hemicellulose, etc.). However, since the formulations were developed empirically during the 1970s, not much was known and reported about its chemical constitution and reactions. Recently, work has been performed to study the composition and reactivity of this adhesive by MALDI-ToF and ^{13}C NMR analysis in order to create lightweight sandwich panels of tannin foam/tannin composites [14]. Despite a good reactivity of this adhesive with ligno-cellulosic materials [13], no attempts have yet been made to create composites by reaction of TRF resin with natural fibers.

Hence, this paper deals with the preparation of fiberboard composites using the TRF resin as a matrix and nonwoven fiber mats of flax fibers as reinforcement, in an attempt to create a new bio-based composite material. Since TRF is a very strong wood adhesive used in humid conditions, these composites should present good mechanical properties with a better water resistance than composites using the tannin/hexamine matrix described in previous studies. Flax fibers were chosen as they are the most widely produced natural fibers in Europe (100000 ha/year) and, more specifically, in France, where 75% of the European flax is produced [15].

---

*Corresponding author: alix.sauget@univ-lorraine.fr

DOI: 10.7569/JRM.2013.634128

2 EXPERIMENTAL

2.1 Materials

The fiber mats used for the experiments were purchased from EcoTechnilin (Yvetot, France). These mats were 100% flax fiber mats mechanically carded, cross-lapped and bonded by needle punching. They had a surface mass of 600g/m² for a thickness of 3mm. The fibers were kept at moisture content between 5% and 8% (on dry mass) during storage. Chemical analysis of the flax fiber (Table 1) was done by Cetelor (Epinal, France). The flax fibers have a Young's modulus between 50 and 70 GPa with a tensile strength from 500 to 900 MPa. Their elongation at break is lower than glass, between 1.3 and 3.3%, where glass is 5.1±0.3%.

- The tannin extract used for the preparation of the resin was commercial mimosa tannin extract (non-sulfited, hot water extracted) from Silvateam (San Michele Mondovi, Italy).
- Resorcinol, furfuryl alcohol, *p*-toluenesulfonic acid and hexamethylenetetramine were purchased from Acros Organics (Geel, Belgium).
- Formaldehyde 37% in solution was purchased from Roth (Karlsruhe, Germany).
- Sodium hydroxide 33% in solution was purchased from Carlo Erba Reagents (Val de Reuil, France).
- Paraformaldehyde was purchased from Merck (Darmstadt, Germany).
- Methanol was purchased from VWR Prolabo (Fontenay-sous-Bois, France).

2.2 Preparation of the TRF Resins

The different formulations are described in Table 2 and Table 3. The resins were prepared as followed, based on the work of Pizzi and Roux [13]. First, water and methanol were mixed together in a balloon with cooling column using a mechanical stirrer and heated to 40°C with a water bath to ease the dissolution of tannins. Mimosa tannin powder was then added and dissolved in the solution. Resorcinol was added and dissolved. Formaldehyde solution and sodium hydroxide were added. The solution was brought to 70°C for 1 h with continuous stirring and then cooled down. For the TMA analysis at different pH, additional sodium hydroxide solution or *p*-toluenesulfonic acid (PTSA) solution was then added to adjust the pH, while still stirring. The solution was stored in hermetic containers. The TRF resins prepared this way were 60% bio-based, the biomaterial part being the polyflavonoids.

Table 1 Flax fibers chemical composition (mass percentages) from Normandy. Other = tannins, minerals salts, starch, galactan.

	Cellulose	Hemicellulose	Lignin	Pectin	Waxes	Other
Flax fiber composition	65,9%	12,7%	14,8%	1,6%	2,7%	2,4%
Standard deviation	1,14	1,40	0,70	0,50	0,07	0,34

Table 2 TRF coldset initial formulation at pH 8 (mass percentages).

Resin	Tannin	Resorcinol	Water	Methanol	Formaldehyde	Sodium hydroxide
TRF	35,10	17,50	33,31	9,86	2,12	2,11

Table 3 Adjusted pH formulations (masses, in grams).

Resin	Initial TRF (pH 8, 55% dry content)	Sodium hydroxide (solution, 40%)	PTSA (solution, 65%)
TRF pH 4	40,00	–	6,42
TRF pH 10	40,00	3,27	–

2.3 Spray-Drying of the TRF Resin and Preparation of Additional Formulations

In order to use solvents other than water, TRF resin was spray dried using a Minispray Dryer B-290 from Büchi (Flawil, Switzerland). The TRF resin was first diluted five times to lower the dry content of the solution from 54.7% to 10.9% and ease the spray-drying process. The dry resin powder was collected and stored in hermetic containers.

Two different solvents other than water were used: furfuryl alcohol and a mixture of 70% ethanol and 30% water (Table 4). Furfuryl alcohol was chosen for its reactivity with flavonoid compounds [8], thus making it an active solvent (contrary to water); it could be linked by direct reaction on active sites of polyflavonoids or by formation of methylene bridges with formaldehyde. For these the solvent was heated to 40°C in a balloon with cooling column using a water bath to ease the dissolution of TRF powder prepared with the spray-dryer. The TRF powder was added while stirring with a mechanical stirrer. The solution was then cooled down to 20°C. These mixtures were not stored as they were prepared right before use.

2.4 Viscosity

A DV-II+ viscometer from Brookfield Engineering Laboratories (Middleboro, Massachusetts, USA) with a n°4 spindle was used to perform viscosity analysis of the resins at a room temperature of 20°C. The rotation speeds were 10, 20, 50 and 100 rpm.

2.5 Gel Time

Gel time was measured using test tubes in a water bath at 100°C and 2 g of resin were stirred with a spring-shaped wire until the gelation occurred, i.e., when it was not possible to move the wire in the tube anymore.

2.6 TMA

For thermomechanical analysis (TMA), an adhesive joint of 300 g/m² was created by spreading 27 mg of the resin to analyze between two 18*5*0.6 mm thick layers of beech plywood. The heating cycle was from 25°C to 250°C at a range of 10°C/min. Storage modulus, loss modulus and tan δ were recorded.

Table 4 Formulations using a mixture of ethanol and water (TRF-Eth) and furfuryl alcohol (TRF-Fur) as solvents (mass percentages).

Resin	TRF powder	Water	Ethanol	Furfuryl alcohol
TRF-Eth	40	18	42	–
TRF-Fur	40	–	–	60

2.7 Preparation of the Composites

Hardener—paraformaldehyde 10, 16, 18 or 29% based on the solid mass of the resin— was added to the resin at ambient temperature (20°C) and mechanically stirred for 5 minutes.

The fiber mats were cut from the initial mat at the size of 170 × 100 mm. The samples were marked for fiber orientation, the strength properties being slightly different between the 0° and 90° orientation, due to the carding and cross-lapping in the manufacturing process.

The mats were impregnated with the TRF resin by hand, using a metallic roller. The resin was spread on the surface of the fiber mat and forced to go in it by using the roller. The impregnation is considered to be correct when the resin reaches the fibers in the core of the mat, which is easily achieved with thin fiber mats like the 3-mm-thick ones used in this experiment. This manual process causes a slight scattering of the fiber content of the final material, which was between 35.6% and 37.8% (dry mass of fibers on the dry mass of the composite).

The pre-pregs (pre-impregnated mats) were then air dried to reach the desired equilibrium moisture content before pressing the composites. A full-drying + rehydration process, that has been proven working with another tannin resin [6], has also been investigated; some pre-pregs were stored for 24 hours and then a calculated amount of water was sprayed over the two sides of the pre-preg to adjust the overall moisture content. Mass uptake of the pre-pregs was measured on a 1/100th gram scale during spraying until the required value was reached.

The pressing was performed on a hydraulic press with heating plates at different temperatures ranging from 150°C to 190°C, using 1.5-mm-thick steel bar gauges. The cycle consisted of an initial stage at high pressure (8 MPa, 30 s) used to crush the pre-preg to the gauge's thickness and a hardening stage at 0.5 MPa of various duration, depending on the pressing temperature (Table 5). The pressing at ambient temperature

Table 5 Press cycles.

Press temperature	8.0 MPa Stage	0.5 MPa stage
150	30 s	14 min 30 s
170	30 s	09 min 30 s
190	30 s	06 min 30 s

(20°C) was performed using wooden plates and hand clamps for 7 days.

The composites prepared this way were 75% biobased on a dry material basis; they contain 37% fibers and 63% resin, which itself is made of 60% of biomaterials (tannins).

2.8 Tensile Testing

All samples were stored in the same conditions (room temperature at 20°C and relative humidity 62%) to ensure that their moisture content was the same before testing. The panels were then cut in 150 × 20 mm samples to perform traction mechanical testing and calculate both modulus of elasticity (MoE) and tensile strength (TS). The tests were performed on an Instron 4467 testing machine with a load cell of 30 kN. Eight samples were tested for each parameter.

2.9 Water Resistance Testing

All samples were stored in the same conditions (room temperature at 20°C and relative humidity 62%) to ensure that their moisture content was the same before testing. The panels were then cut into 50 × 50 mm samples for 24 h cold water resistance testing, which was performed following the French standard NF EN 622-2 [16]. Four samples were tested for each parameter.

3 RESULTS AND DISCUSSION

3.1 Composites preparation with stock TRF and 16% pF

The first composites were made using the cold-setting properties of the TRF resin, mixed with 16% fine powder paraformaldehyde based on solid resin content as an hardener, without any prior drying of the solvent. Despite a relatively high viscosity of 600 cP at 20°C, the resin was easily impregnated thanks to the good compatibility of tannins with ligno-cellulosic fibers. The water content of the pre-pregs was 60% on a dry material mass basis. The composite showed a good resistance, meaning the hardening of the TRF was effective. But with time, the composite slowly warped to finally adopt in less than one day a shape that made the material unusable (Figure 1). The excess of water in the resin is not a problem in the case of thin adhesive joint usually used to bond wood, as it is absorbed by the wood itself. With this composite, the water was trapped in the material under pressure between the two plates. It remained in the composite during the hardening and only started to evaporate when the plates were removed, causing the deformation as the material retracted. Thin tannin-based composites are known to be very sensitive to moisture content changes [5]. Hence, no mechanical testing was performed on this material.


Figure 1 The deformation of a TRF composite.

3.2 Composite Preparation with High-Temperature Curing and Pre-pregs Drying

To avoid the warping caused by the excess of water in the pre-pregs, a high-temperature curing step was added to the process. Right after the impregnation of the mats with the same TRF formulation and 16% paraformaldehyde, meaning at a water content of 60%, the pre-pregs were pressed at 150°C for 15 min then cooled down and aged at room temperature (20°C) for a minimum duration of seven days before any mechanical testing. To study the influence of the water content of the pre-preg at the pressing stage on the properties of the cured composite, other pre-pregs were stored at room temperature after the impregnation to let the water evaporate in order to reach the water contents of 23%, 17% and 11% (on a dry material mass basis). Once those values were reached, the pre-pregs were also hot-pressed and aged in the same conditions. The composites produced with this process were perfectly flat (Figure 2) and usable for testing. Mechanical properties measured in tensile testing are presented in Figure 3. The average density of those composites using water-based TRF was 1.21 g/cm^3 (with a standard deviation of 0.075).

The Young's modulus increases with the decreasing quantity of MC (moisture content), from 4.2 GPa at 60% MC to 5.0 GPa at 17% MC, which is 19% better. Then it starts to decrease when the pre-preg is too dry: 4.6 GPa at 11% MC. Tensile strength seems to decrease with the water content, but the standard

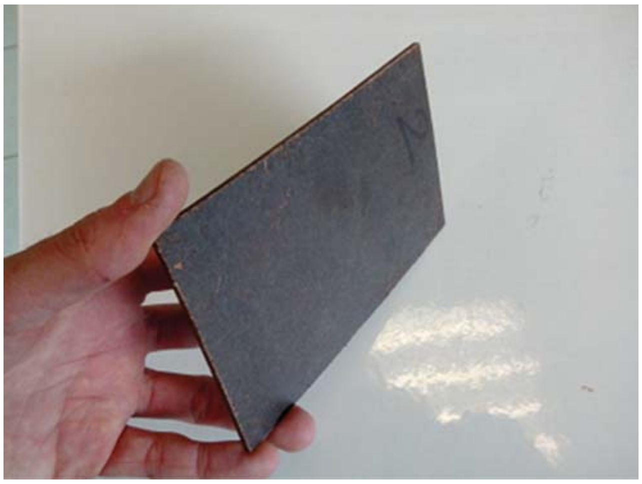

Figure 2 Flat TRF composite.

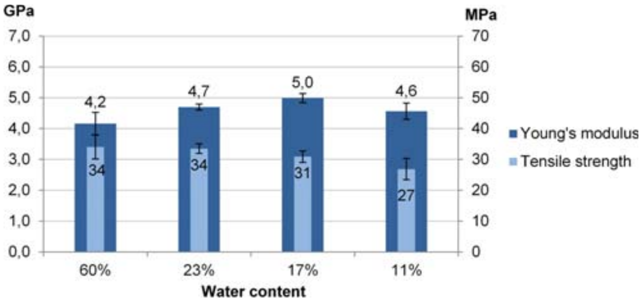

Figure 3 Mechanical properties of different water content TRF composites cured at 150°C (error bars: standard deviation).

deviation is too high to assure this trend with certainty. The water content is known to have a marked effect on the crosslinking abilities of tannin-based resins, enabling the mobility of flavonoid oligomers [5,6], which is essential for their good polymerization. This is why mechanical properties start to decrease if the water content decreases below a certain level; the chemical compounds cannot properly bond together. Conversely, too high of an amount of water in prepregs is also damaging because some water is trapped in the composite as an inert compound that does not play a role in its mechanical resistance in addition to causing some spreading of the pre-preg when pressing it [5]. Thus, the adequate level of water needs to be used to ensure good curing while preventing such problems.

3.3 Composites Preparation with Different Hardener Contents

The hardener proportion of 16% based on solid content used in the initial formulation was optimum in the case of wood bonding with thin adhesive joint.

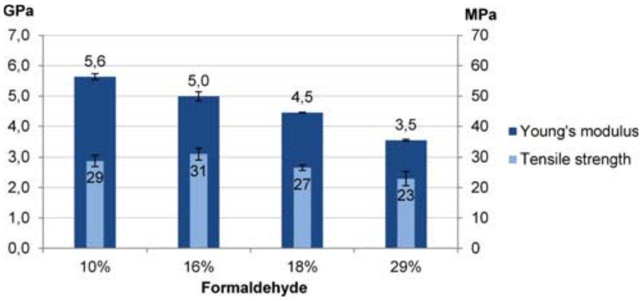

Figure 4 Mechanical properties of different hardener content TRF composites, cured at 150°C (error bars: standard deviation).

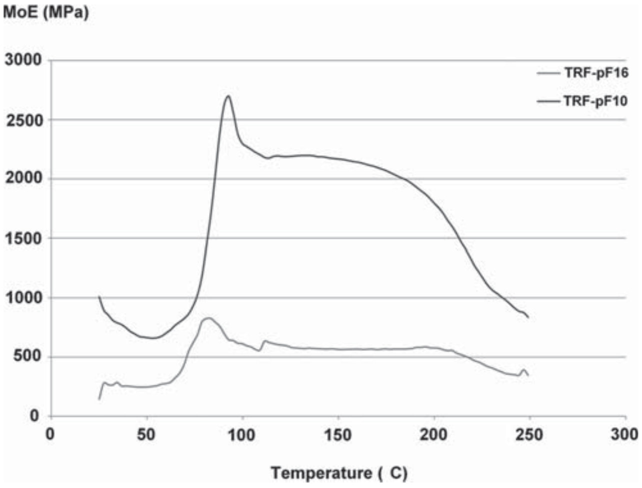

Figure 5 TMA curves of TRF resin with 10% and 16% pF.

Other proportions were tested in order to observe the differences in the case of composites fabrication: 10%, 16%, 18% and 29% paraformaldehyde based on solid content of TRF. Increasing the quantity of pF (paraformaldehyde) causes a decrease of the Young's modulus, the highest being 5.6 GPa for 10% pF and the lowest 3.5 GPa for 29% pF, which is 38% less (Figure 4). The trend is quite the same with the tensile strength, though the scattering of the values does not allow us to see which value gives the best result between 10% pF (29 ± 1.77 MPa) and 16% pF (31 ± 1.84 MPa).

The TMA analysis performed at the middle of their pot life, 100 min after the hardener was mixed into the resin, confirms that a TRF with 10% pF has a theoretically higher MoE than with 16% pF (Figure 5); the plateau (stabilization of the MoE before the thermal degradation of the resin that occurs around 200°C) is at 600 MPa for 16% pF and at 2400 MPa for 10% pF. On the other hand, higher pF quantities lead to composites with higher water resistance (Table 6). This decrease of mechanical properties might be explained by a too fast hardening caused by high quantities of pF; an immobilization of the network occurred early on,

Table 6 Water resistance of TRF composites cured at 150°C.

Water content	pF content	24h cold water swelling (%)	Mass uptake (%)
17%	10%	19 ± 3,0	22 ± 1,5
	16%	09 ± 0,8	19 ± 1,2
	18%	11 ± 0,9	19 ± 1,5
	29%	06 ± 1,4	17 ± 1,2

hence crosslinking (linkage of macromolecular chains by the formation of transversal bounds) stopped when it was at a lower extend. Oppositely, water resistance is improved; this higher crosslinking level due to high pF quantities gives a stronger, more rigid network with better resistance against water. The average density of those composites was still 1.21 g/cm^3 (with a slightly higher standard deviation of 0.076).

3.4 Composite Preparation with Dried and Re-humidified Pre-pregs

A full-drying + rehydration process that has been used with another tannin-based resin [6] was tested by storing the pre-pregs for 24 hours and spraying water over its two sides to adjust the overall moisture content before pressing. This process allows a better control of the overall moisture content across the composite section. Yet the overall properties of those materials were lower than the ones directly dried and pressed—Young's modulus from −9% to −45% and tensile strength from −4% to −55% (Figure 6)—the highest losses being for the composites using the lowest amount of paraformaldehyde hardener.

The main reason for those lower mechanical properties is the cold-setting properties of the TRF resin. As soon as the hardener is added, polymerization starts even at room temperature (TRF could be used to glue wood at 10°C in 24 h [14]). Higher pF causes earlier immobilization of the hardened network, due to faster reaction time, thus lower proportion of crosslinks per unit volume. Another reason might be that after 24 hours of pre-drying storage most of the resin is already hardened on the fibers of the mat and do not react as well as when it is pressed right after impregnation; only some groups of already polymerized chains may react one with each other, leading to a weaker network. This also explains why the loss is less important for the high pF quantities; in those cases the network is already poorly crosslinked with short chains due to the important proportion of hardener.

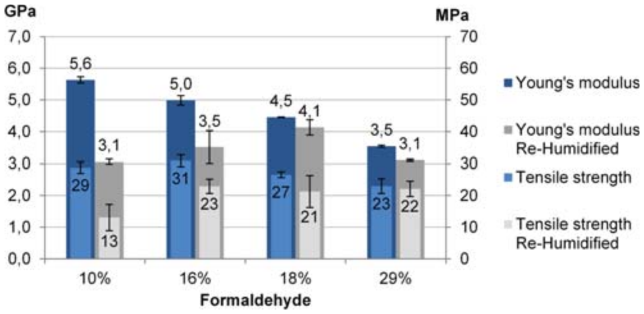

Figure 6 Influence of the re-humidification process on the mechanical properties of different hardener content TRF composites, cured at 150°C (error bars: standard deviation).

3.5 Composite Preparation with TRF Powder in Furfuryl Alcohol or Water/ Ethanol Solvent

The spray drying of the resin carried out with the Minispray Dryer B-290 produces a dry, flour-like powder that could be mixed with various solvents. In furfuryl alcohol, the powder dissolved easily up to 40% solid content. Beyond this point, increasing the solid content increased the viscosity faster than the TRF in water (Figure 7) and the resin became very difficult to incorporate into fibers. Furthermore, TMA analysis indicates better mechanical properties of a resin with 1/3 TRF and 2/3 furfuryl alcohol (Figure 8). In ethanol/water, the TRF followed the same progression and was usable up to 40% solid content.

Thus a TRF to furfuryl alcohol ratio of 2:3 and a TRF to ethanol/water ratio of 2:3 were chosen for the preparation of composites, to keep a high TRF content with a good processability of the resin. The results of mechanical testing are presented in Figure 9, using specific modulus and specific strength because those three composites have very different densities: 1.24 g/cm^3 for the water-based material, 0.99 g/cm^3 for the furfuryl alcohol-based material and 0.84 g/cm^3 for the water/ethanol-based material. Furfuryl-based composites have lower Young's modulus than the water-based ones but better tensile strength (+45%). Composites using ethanol/water do not show better Young's modulus but higher tensile strength (+64%). The material is less rigid (lower Young's modulus) but with better resistance (higher tensile strength) when using furfuryl alcohol: it gives a better distribution of stresses making the network more "elastic" and thus can support higher load. The improvement of resistance caused by ethanol/water solvent might be due to higher volatility of ethanol which is easily evacuated during the curing process,

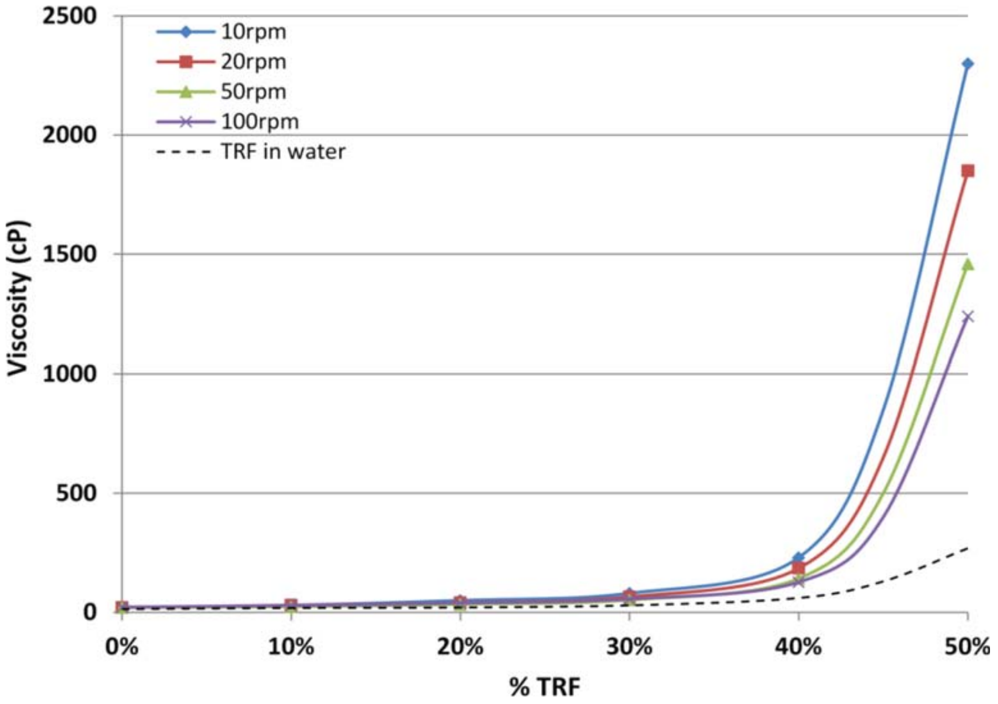

Figure 7 Viscosities of TRF/furfuryl alcohol resin.

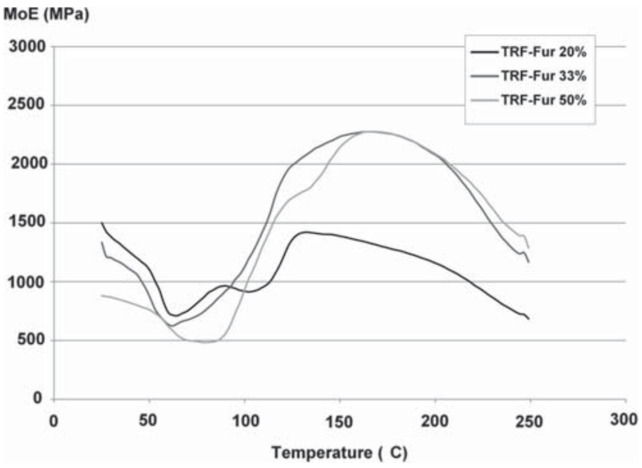

Figure 8 TMA curves of furfuryl alcohol-based TRF resin with 20%, 33% and 50% of TRF content.

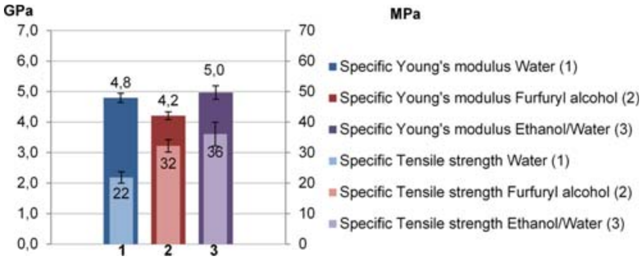

Figure 9 Mechanical properties of water-based, furfuryl alcohol-based and ethanol/water-based TRF composites, cured at 170°C with 10% pF (error bars: standard deviation).

hence in the end there is less inert liquid trapped in the material.

3.6 TMA Analysis to Observe the Behavior of the Resin, and to Determine Possible Ways of Improvement

3.6.1 Different pH (4-8-10)

The testing at 100°C shows that resins of high pH hardened much faster (Table 7). The solidification at pH 10 even starts after only 20 s of heating. At pH 10 the gelation of the resin happened within minutes, making the preparation of the TMA samples difficult; at this pH it takes only 300 s to reach the gel point at room temperature (20°C), compared to at least 3 hours at pH 8. This is due to the combined effect of the activation of the flavonoids B-ring [17] and the increasing reactivity of the A-ring [13] that occurred at pH 10 and higher (see carbon cycles on Figure 10), the reactivity of the A-ring being the main cause. The polymerization reaction occurred much more slowly at pH 4 for the opposite reason but yet leads to relatively high modulus (Figure 11): the slower the polymerization is, the higher the ultimate strength of the network will be. However it should be kept in mind that if a fast pressing time is required, it is likely that a faster setting resin is better than a slow setting one, because after a short curing time a very slow setting resin is even much less crosslinked.

Table 7 Gel times of TRF resins.

	pH4	pH8	pH10
Gel time at 100°C with 16% pF (s)	540	30	27

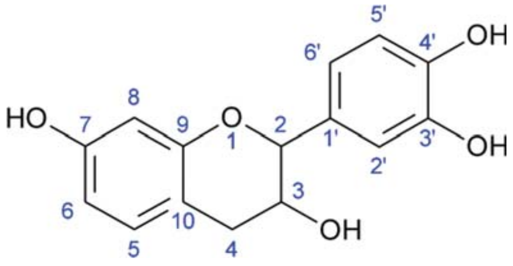

Figure 10 Carbon cycles of a flavonoid unit (fisetinidin).

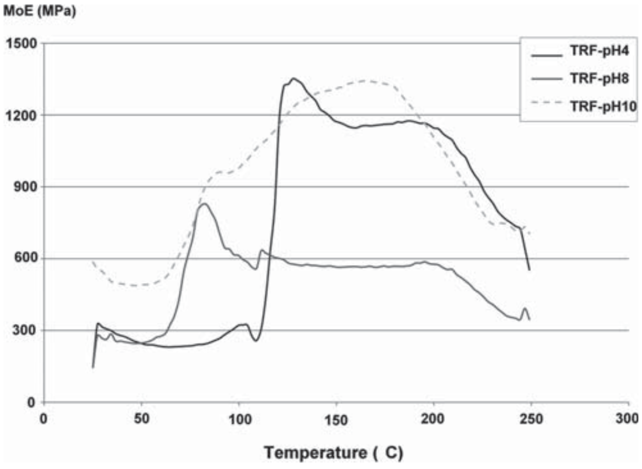

Figure 11 TMA curves of TRF resin at pH 4, pH 8 and pH 10.

3.6.2 *Different Hardeners*

Hexamethylenetetramine (hexamine) was used to replace paraformaldehyde as a hardener. It is a hardener of interest as it is known to lead to composites with very low formaldehyde emissions, as the unstable intermediary molecules that should turn into formaldehyde (Figure 12) immediately react with the negatively charged tannins, resorcinol or other highly reactive phenol [1]. The hexamine (1) hydrolyzes under the action of heat to form a linear component (2) that is then hydrolyzed into smaller imines (3), at a minimum temperature of 65°C (higher temperatures meaning an equilibrium displaced in favor of the decomposition of hexamine). These components will slowly turn back into hexamine at ambient temperature. Two of these imines could form unstable ethers (4). The imine (3) could also turn into imino-aminomethylene bases (5-6-7), the latter (7) possess a strong single negative charge which is the species that will react with tannins to create aminomethylene bridges. Hexamine was added as a saturated solution (850 g/L = 45% solid content) in the TRF resin at pH 8. The TMA analysis performed at t = 5 min, 55 min and 105 min after the addition of hardener all revealed an important increase of the maximum Young's modulus: +92% at t = 5 min (from 2092 MPa to 4025 MPa), +146% at t = 55 min (from 3113 MPa to 7667 Mpa; see Figure 13), which is the most remarkable, and +79% at t = 105 min (from 2699 MPa to 4824 MPa). This makes the hexamine a suitable hardener for TRF resin with the additional benefit of reducing VOCs (volatile organic compounds) emissions. This improvement can be explained by the high reactivity of those unstable hexamine by-products with

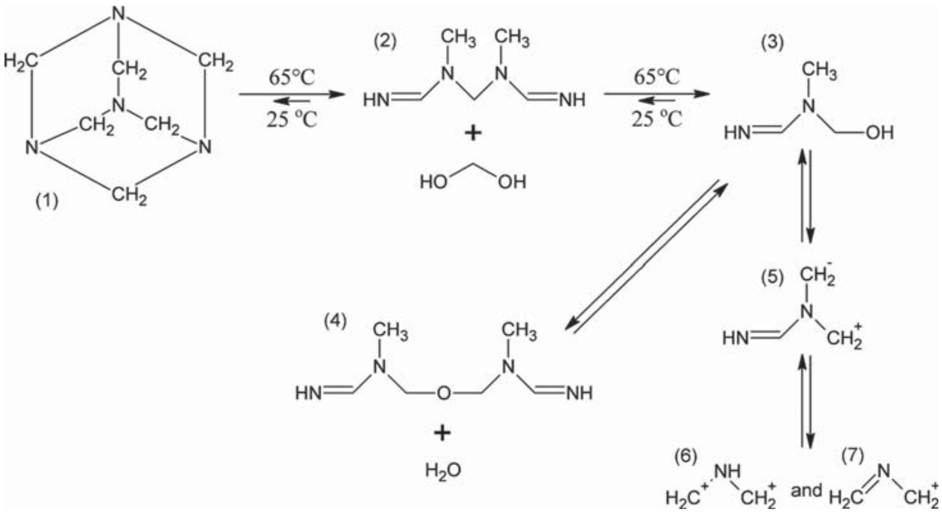

Figure 12 Decomposition of hexamine [1].

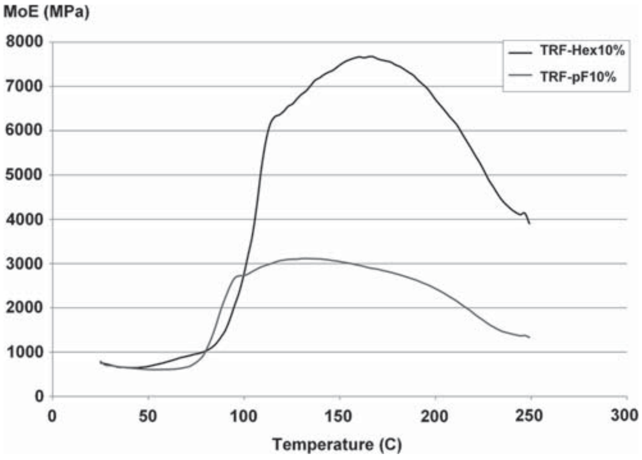

Figure 13 TMA curves of TRF resin with 10% hexamine or paraformaldehyde as a hardener.

tannins, which were recently used for making solid high density bio-based composites [4–6].

4 CONCLUSION

Biocomposites from tannin-resorcinol-formaldehyde coldset adhesive and flax fibers were successfully created using a hot-curing process to get rid of the excess of water, reaching the NF EN 622-2 requirements for fiberboards [16]. The best results that even meet the most restrictive class of this norm, namely the "materials under high strain and wet environment," were obtained using moderate amounts of hardener: 16% paraformaldehyde is the best compromise with a Young's modulus of 5 GPa with a water swelling of 9% and 10% paraformaldehyde give better mechanical properties (5.6 GPa) to the cost of water resistance, which is significantly reduced (19% swelling). This material could thus be used for various applications: exterior grade panels (water-resistant furniture or construction materials), automotive, etc. The possibility of spray drying the TRF resin is of a great interest; the powder could be stored for a virtually unlimited duration and it could be mixed into other solvents. The use of different solvents other than water might be a way to improve the strength of the composite and needs to be further explored. Additional experimentation on pH and hardeners of TRF resin also opens new possibilities; slow setting but high resistance matrix at low pH, or reduction of formaldehyde emissions through the use of hexamine instead of paraformaldehyde, might also increase the composite mechanical properties. Another trail could also be investigated to reduce those emissions even further by replacing the formaldehyde in the first step of the synthesis of the resin with different aldehydes such as glyoxal.

REFERENCES

1. A. Pizzi, Recent developments in eco-efficient bio-based adhesives for wood bonding opportunities and issues. *J. Adhes. Sci. Technol.* **20**, 829–846 (2006).
2. H. Lei, A. Pizzi, and G. Du, Environment-friendly, mixed tannin/lignin wood resins. *J. Appl. Polym. Sci.* **107**, 203–209 (2008).
3. F. Pichelin, M. Nakatani, A. Pizzi, S. Wieland, A. Despres, and S. Rigolet, Structural beams from thick wood panels bonded industrially with formaldehyde-free tannin adhesives. *For. Prod. J.* **56**, 31–36 (2006).
4. A. Pizzi, R. Kueny, F. Lecoanet, B. Massetau, D. Carpentier, A. Krebs, F. Loiseau, S. Molina, and M. Ragoubi, High resin content natural matrix–natural fibre biocomposites. *Ind. Crops Prod.* **30**, 235–240 (2009).
5. A. Nicollin, R. Kueny, L. Toniazzo, and A. Pizzi, High density biocomposite from natural fibers and tannin resin. *J. Adhes. Sci. Technol.* **26**, 1537–1545 (2012).
6. A. Sauget, A. Nicollin, and A. Pizzi, Fabrication and mechanical analysis of mimosa tannin and commercial flax fibers biocomposites. *J. Adhes. Sci. Technol.* **27**, 2204–2218 (2013).
7. N.E. Meikleham, and A. Pizzi, Acid and alkali-setting tannin-based rigid foams. *J.Appl. Polym. Sci.* **53**, 1547–1556 (1994).
8. A. Pizzi, G. Tondi, H. Pasch, and A. Celzard, Matrix-assisted laser desorption/ionization time-of-flight structure determination of complex thermoset networks: Polyflavonoid tannin–furanic rigid foams. *J. Appl. Polym. Sci.* **110**, 1451–1456 (2008).
9. G. Tondi, and A. Pizzi, Tannin based rigid foams: Characterisation and modification. *Ind. Crops Prod.* **29**, 356–363 (2009).
10. G. Tondi, V. Fierro, A. Pizzi, and A. Celzard, Tannin-based carbon foams. *Carbon* **47**, 1480–1492 (2009).
11. G. Tondi, C.W. Oo, A. Pizzi, A. Trosa, and M.F. Thevenon, Metal adsorption of tannin-based rigid foams. *Ind. Crops Prod.* **29**, 336–340 (2009).
12. G. Tondi, W. Zhao, A. Pizzi, V. Fierro, and A. Celzard, Tannin-based rigid foams: A survey of chemical and physical properties. *Bioresour. Technol.* **100**, 5162–5169 (2009).
13. A. Pizzi, and D.G. Roux, The chemistry and development of tannin-based weatherand boil-proof cold-setting and fast-setting adhesives for wood. *J. Appl. Polym. Sci.* **22**, 1945–1954 (1978).
14. X. Zhou, A. Pizzi, A. Sauget, A. Nicollin, X. Li, A. Celzard, K. Rodec, and H. Paschd, Lightweight tannin foam/composites sandwich panels and the coldset tannin adhesive to assemble them. *Ind. Crops Prod.* **43**, 255–260 (2013).
15. C. Meirhaeghe, Evaluation de la disponibilité et de l'accessibilité de fibres végétales à usages matériaux en France. ADEME study (2011).
16. Fibreboards - Specifications - Part 2: Requirements for hardboards, European Norm EN 622–2 (2003).
17. D.G. Roux, D. Ferreira, H.K.L. Hundt, E. Malan, Structure stereochemistry and reactivity of natural condensed tannins as basis for their extended industrial application. *Appl. Polym. Symp.* **28**, 335–353 (1975).