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Composites with hemp reinforcement and bio-based epoxy matrix

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ABSTRACT

The use of natural fiber reinforcements for the production of ecofriendly composites has arisen considerable interest both in thermoplastic and thermoset based materials. In the latter case, the matrix is often an epoxy based polymer, which allows remarkable performance, but that cannot be considered eco-friendly since it is non-biodegradable and is produced from non-renewable sources. This strongly impairs the environmental friendly character of the resulting composite material. The aim of this work was to study the characteristics and performance of a thermoset bioepoxy resin, which is partly based on natural components, to be used in hemp reinforced laminates. The permeability of the hemp fabric as well as the rheological and thermal behavior of the resin were studied in view of their fabrication by resin infusion techniques. The results showed that laminated composites could be easily obtained with a vacuum assisted resin transfer molding process. Static, dynamic and vibration-damping tests were performed to evaluate limits and potentials of such biocomposites.

1. Introduction

The applicative interest for natural fibers as reinforcement in composites as alternative to more conventional glass and carbon fibers is continuously growing for a large number of products. In addition to being biodegradable and from renewable sources, they are economical and have remarkable mechanical performance in relation to specific weight. In particular, their use in composites leads to benefits in terms of impact resistance, vibration and noise damping, thermal insulation, which are expected to be comparable or even superior to glass fiber reinforced plastics [1–3]. Critical aspects for the use of vegetal fibers in a number of applications remain their mechanical performance in absolute terms, their processing temperature limits, their sensitivity to humid conditions and environmental degradation. In consideration of prospected application areas, extensive research activity has been dedicated to the development of natural fibers reinforced thermoplastics, either biodegradable or non-biodegradable. At present, thermoplastic matrices reinforced with natural fibers are increasingly used for the production of panels or frames employed in the automotive field and in the building constructions [1–4].

While a wide range of biodegradable thermoplastic polymers is today commercially available and extensively developed (for instance PLA, MaterBi and other starch based polymers), eco-friendly thermoset matrices can still be considered in an initial study phase [2,5,6]. Although not biodegradable, thermoset resins with a significant content of renewable vegetable component can be considered a significant improvement toward fully eco-compatible composites. Bio-thermosets, particularly epoxy based resins, are finding increasing success and are marketed by different manufacturers.

The problems connected with the use of oil resources for the production of conventional polymeric materials and polymer composites employed in packaging, toys, house appliances, PC, audio/video sets, as well as in vehicles components (e.g., interiors, dampers, accessories) or construction items (e.g., pipes, gutters, frames, panels) are well known; the difficulties of reuse and disposal of such objects represent further serious drawbacks to their employment. The extension of applications of vegetable fibers as reinforcing materials is contributing to the growth of a new class of materials with better environmental compatibility not only in terms of easier reuse, recycle or disposal [1–4]. These materials are in fact based on renewable sources and require lower energy consumption for their manufacture, compared to conventional composites. Interest in these materials, since a few years ago quite marginal, has partially extended to primary industrial sectors like the automotive one. Moreover, glass fibers, the traditional reinforcement for polymer composites, and carbon fibers, pose serious doubts over the safety for the health of workers operating with them. Natural fibers are presently considered a potential valid

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alternative to glass and inorganic fibers in a number of applications, where global optimized performance, including a life cycle assessment, is needed [7]. A present limit to their extensive use in different fields is certainly the limited knowledge of their actual properties and potentials, and the lower performance when compared with the traditional materials they are intended to substitute. Interest in vegetable fibers is not only based on ecological aspects; in fact, they possess good mechanical performance, particularly in relation to their low specific weight and low price. As a matter of fact, their cost is generally lower than that of the polymers they can be added to: the expected improvement in terms of strength and stiffness with an overall reduction of the polymer consumption (it should be considered that in present applications, fibers are added up to more than 50% of the total material), suggests their use even when the application does not strictly require reinforced materials. Moreover, composites containing vegetable fibers present good vibration and acoustic damping capacity which could be well exploited in a number of automotive and house appliances [1,2]. However the optimization of their performance in this field is still far from being reached and requires further research efforts.

In many applications, which necessitate of high performance like those in the automotive, nautical and aeronautical constructions, in addition to those required in the civil and industrial sectors, the need to satisfy resistance, stiffness, lifetime and reliability requirements, involves the use of thermoset polymeric matrices. In comparison with the thermoplastic matrices, thermosets have advantages related also with the processing techniques; they are good either for small and large scale productions and imply a lower working temperature with consequent minor degradation of the natural reinforcing fibers. The possibility to use lamination techniques with lower temperatures and with low pressure technologies can significantly broaden their exploitation.

At present, available thermoset biodegradable matrices for demanding structural applications are not known; however, not biodegradable resins but with a significant content of components coming from renewable vegetable materials, having good performance are already marketed (e.g., by Entropy Resins Inc., Eco Green Resins, LLC, DSM); still, there is a poor knowledge of their properties and their potential use for the manufacturing of composites reinforced with natural fibers.

It is important to emphasize that a number of vegetable fibers such as hemp, flax or kenaf, which are common reinforcements in natural composites for civil and industrial applications, find adequate growth conditions in many different world areas and can significantly improve non-food agriculture development in these regions.

In previous research activities, biocomposites based on thermoplastic matrices reinforced with natural fibers were investigated as a resource for new materials. Different composites, based on traditional polymers (polypropylene, polyethylene) or biodegradable polymers (polylactic acid – PLA, blends of PLA with polyethylene glycol-PEG) reinforced with a number of fibers (kenaf, jute, flax, cellulose microfibrils) have been produced and characterized. Such materials demonstrated good potentials in a number of applications, particularly those requiring vibration absorption capacity; different processing technologies where also investigated [8–15]. In general, however, due to limited matrix properties and processing difficulties, applications requiring relatively high mechanical performance are prevented. Thermoset matrices, such as epoxies, present better mechanical performance and superior adhesion with reinforcing fibers, including natural fibers, and are therefore better suited for structural applications. Thermoset resins, also allow the use of advanced close-mold processing methods, such as RTM, which involve lower impact in working environment, and yet, high reinforcement contents and performance.

In this work, a preliminary evaluation of an epoxy resin partly made of renewable bio-sources with two long gel time hardeners, suitable as matrix for natural fiber composites, was carried out. The first phase consisted in a general characterization of materials, studying fabric permeability and rheological behavior of the thermoset matrix, as well as curing rates at different processing temperatures.

In a second phase hemp/bioepoxy composite laminates were produced by RTM technique; they were then characterized in terms of some mechanical properties; vibration damping capacity, moisture absorption and fire response.

2. Experimental

Two Bio Epoxy systems (01 S and 01 F – provided by ALPAS srl, Italy) were selected for the production of laminates. System Bio Epoxy 01 S was then chosen for further composite testing due to its longer gel time, which suits best for the RTM technology. In Table 1, the main characteristics of the resin systems are reported as specified by the manufacturer.

The resin viscosity variation during curing was measured at different temperatures to get information about the proper processing conditions; tests between 20 °C and 50 °C, by means of a rotational rheometer (TA Instruments AR 2000) were carried out.

Hemp fabric (from Assocanapa), 240 g/m^2, plain weave, was employed as reinforcement of composite panels produced by RTM. Fabric permeability was evaluated, on the basis of Darcy's law, by measuring the flowing rate of silicon oil (viscosity 350 mPa s at 25 °C) along fabric layers with an applied known pressure gradient [16]. Fig. 1 shows the mold, with a glass window, used for the permeability measurements.

DSC (differential scanning calorimetry) tests were employed to evaluate the curing characteristics and to determine curing cycles suitable for RTM production. A TA Instruments DSC 2920 was used. In a first set, repeated runs were carried out for each test. The first run was conducted from 20 to 180 °C with a variable heating rate (Table 2), and then back at a constant rate of 20 °C/min; the reaction peak data were recorded. The second run was conducted from −20 °C to 100 °C with a rate of 30 °C/min to measure T_g after curing.

In a second set of tests, two different cure/post-cure cycles applied to composite panels were compared (Table 2). In the first case, the resin was cured at room temperature for 24 h and post cured at 120° for 2 h. In the second case, the resin was cured at 120 °C for 2 h and post cured at 180 °C for 2 h. DSC tests after cure/post-cure show that in the second case the glass transition temperature is consistently higher and resin crosslinking is practically complete. This second cycle was then selected for composite laminates production.

Composite plates were manufactured with a resin transfer molding process (RTM), using a MVP Hypaject MK III resin injection system and a heated aluminum mold (Figs. 2–4). Resin was previously degassed in a vacuum and injected at room temperature while the mold was preheated at 30 °C. Inlet injection pressure was set at 0.5 bar, while partial vacuum (−0.5 bar) was applied at the mold vent. After completion of the injection, the mold was heated for the cure process at 120 °C for 2 h. A post cure at 180 °C for 2 h followed the opening of the mold and extraction of the laminate. Lamination sequence was [0°/0°/45°/45°/0°/45°/45°/0°/0°]; laminates with about 40% vol. fiber content were produced.

Water absorption tests of hemp/bioepoxy specimens cut from the laminates were carried out by water immersion according to the ASTM D570 standard. Laminates mechanical properties were

Table 1
Thermoset resin characteristics.

Characteristics	Resin + Hardener	
	Bio Epoxy 01 F	Bio Epoxy 01 S
Viscosity (mPa s @23 °C)	2000–4000	200–500
Bio content per mass	21–30%	21–30%
Gel time (min @23 °C)	25	40
Thin film set (h @23 °C)	6	8
Hardening cycle	7–10 days @25 °C Post cure recommended	7–10 days @25 °C Post cure recommended
Young modulus (MPa)	3450	3310
Tension stress (MPa)	65	64
Flexural modulus (MPa)	3030	3170
Flexural stress (MPa)	93	94
Max deformation (%)	5	6
T_g (°C)	65	62

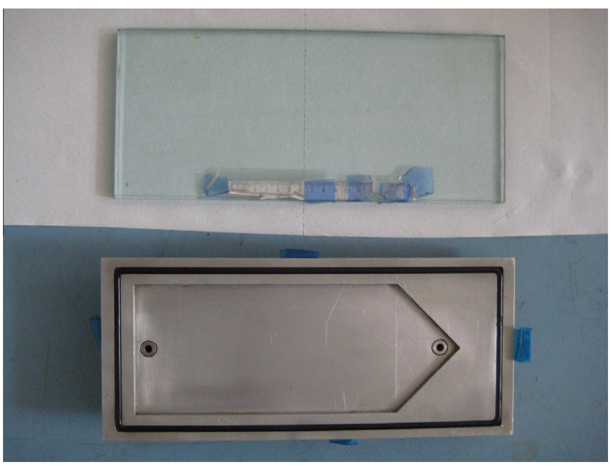

Fig. 1. RTM mold used for permeability tests. Resin inlet/outlet holes are visible.

Fig. 2. Resin injection system – temperature and pressure control.

Table 2
DSC test results. Glass transition after different curing cycles.

Curing cycle	T_g (°C)
20 °C to 180 °C, 1 °C/min	62
20 °C to 180 °C, 5 °C/min	55
20 °C to 180 °C, 10 °C/min	55
20 °C to 180 °C, 20 °C/min	57
24 h @ 25 °C + 2 h @ 120 °C (cycle 1)	55
2 h @ 120 °C + 2 h @ 180 °C (cycle 2)	65

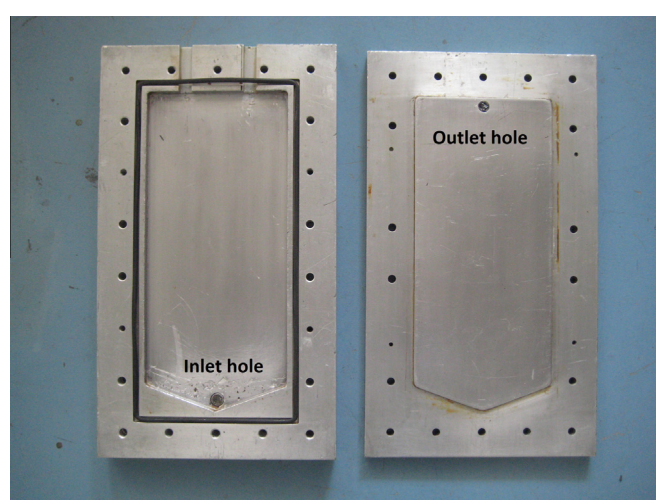

Fig. 3. Composite laminates production mold.

evaluated with static tensile and flexural tests, according to ASTM D 3039 and D 7264. Strain gages were employed for strain measurements during tensile tests. Measurements of the damping ratios at low frequencies were obtained with forced vibration torsional dynamic tests (TA Instruments AR2000). Tests at higher frequencies were conducted in accordance with the ASTM E 756 standard, consisting in a modal free–free analysis (Fig. 5 shows the test layout). Specimens dimensions were 300 × 50 mm with a thickness of 3.5 mm. Three different free inflexion lengths were chosen.

Fracture surface of hemp laminates were observed by a SEM Hitachi TM3000 at different magnifications to examine laminates and fiber failure features.

Flammability tests of laminates were conducted according to standards ASTM D 635 and D 3801. The main differences between the two is in the position of the specimen, horizontal and vertical respectively. Fig. 6 shows the test layout in accordance with the ASTM D 635 standard. Specimens dimensions were 125 × 13 mm with a thickness of 3.5 mm.

Fig. 4. Temperature control of the mold electric heater.

Fig. 5. Test layout for free–free vibration tests.

Fig. 6. Flammability test: horizontal set up.

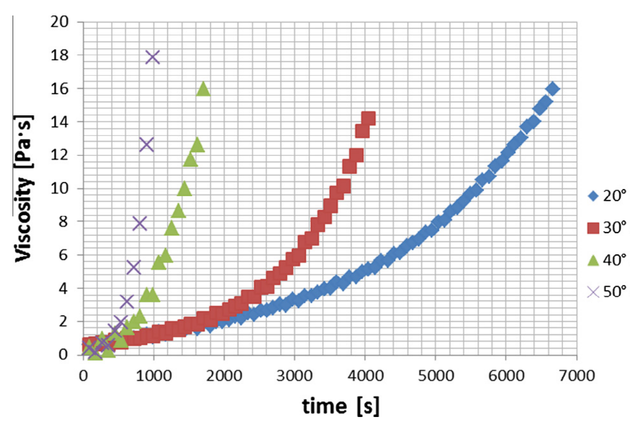

Fig. 7. Curing curves at different temperatures.

3. Results and discussion

In resin infusion based processes, such as RTM or VaRTM, rapid and full resin infusion can be obtained provided processing conditions are consistent with material characteristics. Low resin viscosity, adequate gelation time, high fabric permeability usually allow to get easy and rapid mold filling. Fig. 7 reports the measured viscosity evolution with time at different curing temperatures for the selected bioepoxy system (Bio Epoxy 01 S). The reported curves give useful information about resin flow capability during infusion, particularly in large and complex molds. On the other hand, the ability for the resin to fully impregnate the reinforcement and to fill all the parts of the mold cavity is related also to fabric reinforcement permeability. Hemp permeability measurements (Fig. 8) were carried out at fiber volume contents in the range of actual composite laminates. Porosity Φ indicates the ratio between the air volume and the total volume; fiber volume fraction is therefore equal to $(1 - \Phi)$. In Table 3, the measured permeability values of hemp and other types of fabric are calculated according to Darcy's law. Comparing these with the more classic glass and carbon fabrics, at the same porosity, the permeability of hemp results consistently higher [16]. This is possibly related to the markedly higher diameter of hemp fibers (at least 20–40 μm) compared to glass and carbon fibers (7–12 μm). It is interesting to note also that the measured permeability are even higher than those estimated in natural fiber mats, notwithstanding in the latter case considered fiber volume contents were consistently lower [5]. This is possibly related to the presence of preferential resin paths within the fabric lay-up.

Composite laminates with hemp reinforcement were produced by RTM. With the process parameters selected (mold temperature 30 °C, $\Delta P = 1$ bar), injection was completed within few minutes, i.e. well before an appreciable resin viscosity increase. Homogeneous filling and no visible defects or voids were detected in the produced laminates.

Most natural fibers suffer of high moisture absorption, which may affect dimensional stability and durability. As a matter of fact, plain hemp fibers can absorb as much as 33% [17]. In Fig. 9, the measured water absorption of laminates as a function of time shows a maximum increase of 11%. It can be observed, however, that the absorption rate is quite slow and equilibrium is reached after about 10 days; this suggests that short term contact with humid conditions may be acceptable for the material.

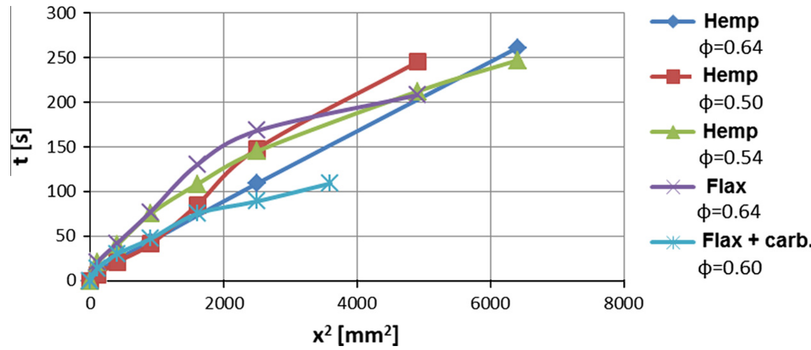

Fig. 8. Comparison of the permeability of the different materials tested.

Table 3
Permeability test results. Data obtained with different fabrics (flax, flax/carbon, glass, carbon) are reported as comparison.

	Φ Porosity	n Layers	s (mm) Thickness	ΔP (bar)	K_x (m^2) Equivalent permeability
Hemp	0.64	6	2.5	0.14	1.70E−9
Hemp	0.5	5	1.5	0.16	0.91E−9
Hemp	0.55	6	2	0.22	1.01E−9
Hemp (45°)	0.64	6	2.5	0.14	1.49E−9
Flax	0.58	5	2.5	0.25	0.82E−9
Flax + Carbon	0.60	6	2	0.22	1.41E−9
Glass [16]	0.51–0.59	–	–	–	6E−11–20E−11
Carbon [16]	0.44–0.56	–	–	–	2E−11–7E−11

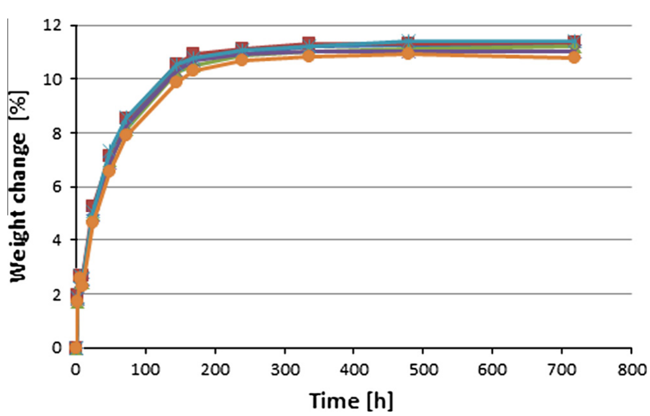

Fig. 9. Water absorption tests.

Table 4
Static tensile test results.

Ultimate tensile stress (MPa)	Max strain (tens) (%)	Young modulus (tens) (MPa)
63	1.8	5870

Prospected applications for composites are often related to their efficiency in sound insulation and mechanical vibration damping. Static and dynamic mechanical tests show that, a significant increase of stiffness is obtained by the addition of natural fibers (Table 4). In Fig. 10 it can be shown how the bio epoxy resin reduces the ultimate stress of the material compared to a reference traditional HexFlow® RTM6 epoxy, but significantly increases the plastic field, thus enhancing its toughness. The damping properties of hemp reinforced laminates are quite promising, compared to traditional glass fiber reinforced composites. The damping ratios at low frequencies (up to 100 Hz) obtained with forced vibration torsional dynamic tests and the damping ratios obtained with flexural vibration mode tests at higher frequencies (up to 3800 Hz), conducted in accordance with ASTM E 756, are within a range of 0.015–0.025.

The results of both torsional and flexural damping tests are compared in Fig. 11. It can be observed that, notwithstanding the different testing modes and techniques, a fair agreement is found. The measured damping values are significantly higher than those measured in glass/epoxy composites, which fall in the 0.005–0.015 range [18,19].

This behavior is usually attributed also to the fibrillar nature of vegetable fibers; fibril to fibril slippage is considered one of the main vibration energy absorption mechanism. Observations of rupture surfaces (Fig. 12) evidencing a quite irregular fracture surface of hemp fibers, and their fibrillated nature further support such considerations.

Natural based composites are considered for non load-bearing, critical applications such as secondary structures or internal insulating panels of civil buildings, automobiles or aircrafts. This leads to the necessity to evaluate their flammability; in fact, it is expected that the presence of natural fibers may bring to poor fire resistance. In Table 5 the linear burning rate defined is reported.

As a matter of fact, the burning tests have confirmed a quite poor fire resistance, with a burning rate of about 14.6 mm/min, which is comparable with that of a polyethylene (approximately 15 mm/min). No data could be gained from the vertical test due to the instantaneous firing up of the specimen. It is apparent that, for their employment, such composites need the addition of fire retardant additives.

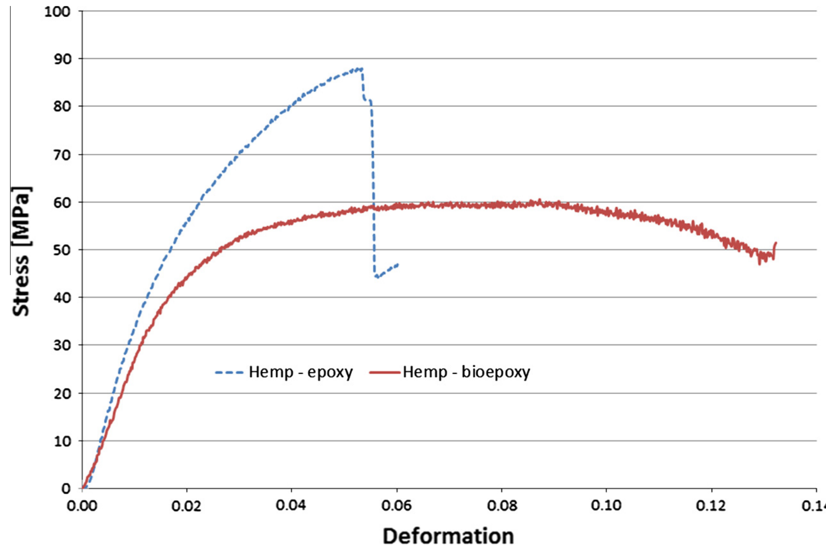

Fig. 10. Resin influence on the toughness of the composite in the bending test.

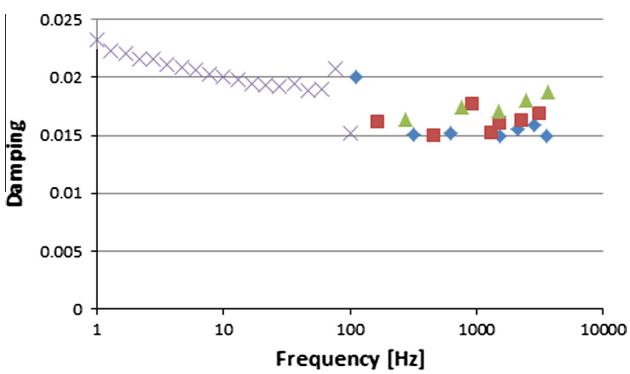

Fig. 11. Damping ratios at all the frequencies tested.

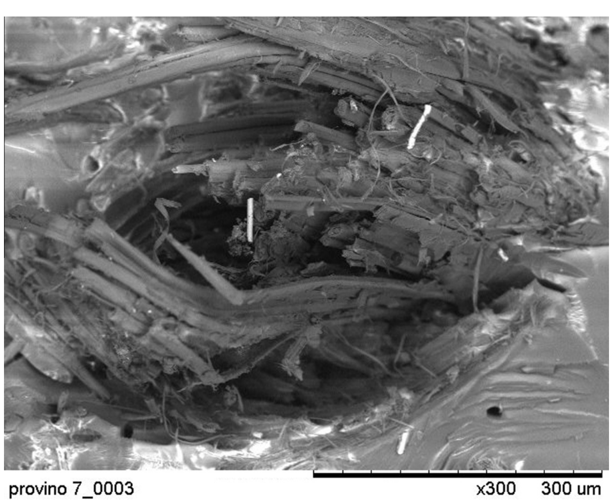

Fig. 12. Fracture surface of a tensile tested laminate.

4. Conclusions

In this work the rheological and mechanical characteristics of a bio-based thermoset resin and composites has been investigated.

Table 5
Flammability test results.

	Time (s)	*V* (mm/min)
Specimen 1	320	14.6
Specimen 2	303	14.85
Specimen 3	315	14.28

Laminated composites reinforced with hemp fibers have been easily manufactured using a very promising vacuum assisted resin transfer molding process. The composites mechanical properties in relation to their low density, and the damping characteristics highlighted from the vibrational tests, show an interesting possible application in secondary structures and insulating panels.

The high water absorption and burning rate, mainly due to the characteristics of the natural reinforcement, are substantial drawbacks. The results suggest that still much work must be done mainly to improve resin glass transition and biobased components content on one side and to improve composite fire and water absorption response on the other.

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