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Multilayer cotton fabric bio-composites based on PLA and PHB copolymer for industrial load carrying applications

Daniele Battegazzore[a]*, Tobias Abt[b], Maria Lluisa Maspoch[b], Alberto Frache[a]

[a]Dipartimento di Scienza Applicata e Tecnologia, Politecnico di Torino, sede di Alessandria, Viale Teresa Michel 5, 15121 Alessandria, Italy

[b]Centre Català del Plàstic (CCP)-Unversitat Politècnica de Catalunya BarcelonaTech (EEBE-UPC). C/Colom, 114, Terrassa 08222, Spain

*Corresponding author: Tel/Fax: +390131229343/+390131229399; e-mail address: daniele.battegazzore@polito.it

ABSTRACT

The thermo-mechanical and impact behavior of bio-based polymers reinforced with a multilayer cotton fabric were determined and assessed for the potential use in building, furniture or automotive applications. The measured properties were compared to other composites with similar natural fabric content or to international standard requirements. Flexural properties of PLA composites fully satisfied the requirements for heavy duty load-bearing boards in humid condition (EN 312 standard), while the PHB copolymer composites still satisfied the conditions for load-bearing boards. The HDT evaluation through the dynamic mechanical thermal analysis revealed the great increase (+53°C) in the temperature for PHB composites that reached 123°C, potentially extending their application fields to automotive applications. For this focus, the Charpy impact strengths were also investigated. One of the highest values reported in the literature (54.5 kJ/m^2) was reached with PHB, superior to what is commercially used for the interior part of the cars. Furthermore, an epoxy functional additive was employed and was found to reduce the void content and increase the flexural properties and the impact strength.

Keywords

A. Fabrics/textiles; A. Polymer-matrix composites (PMCs); B. Thermomechanical; B. Impact behavior; Film stacking.

1. INTRODUCTION

The development of continuous fiber reinforced composites is essential for manufacturing materials for load-bearing/structural applications. Carbon, glass, aramid and boron fibers are very common for high-performance composite reinforcements in aerospace, automotive, construction and sporting applications. However, these fibers/fabrics have some drawbacks such as the high cost, the non-recyclability, the high health risk and the high energy consumption [1]. The search for new high-performance materials at affordable costs has recently been jointed to the environmental and sustainable awareness.

In several works high-performance natural fiber composite systems for structural applications were developed using continuous textile reinforcements. Nevertheless, the developed materials cannot directly compete in terms of strength with carbon or glass fiber composites [2] or are vulnerable to environmental attacks [3]. For this reason, it has been proposed that natural fiber reinforced composites are limited to use in low to medium load-bearing applications in indoor components. However, limited research work has been performed to fill the gap between high-performance fabrics and natural fabrics [1].

Actually, the majority (85%) of the global fiber reinforced plastics market is based on E-glass composites [4]. The remaining part of the market is divided between 7% of wood-plastic composites, 4% of cotton fiber composites and less than 2% of plant fiber composites, but all have a great opportunity for market capture in the next future [4].

By commercial application, the majority of natural fiber reinforced plastics produced in the EU are used for non-structural automotive components, which are manufactured primarily via compression molding [4]. Up to 30 % of these are based on thermoset matrices, while the rest is based on thermoplastics and is used for side and door panel, seat back, boot lining, spare tire lining, hat rack, business table, pillar cover panel, dashboard, instrumental panel and headliner panel, underbody protection trim [5]. Among the used thermoplastics, the majority are polyolefins; completely renewable bio-based materials (matrix and filler) are rarely investigated or adopted [6-9].

The automotive industry requires composite materials that meet specific performance criteria [5]. Typical requirements include the flexural properties, impact strength and maximum operating temperature which are investigated in this article and compared to other results.

The design of the optimal material for a specific application is the key point of the engineering work and, generally, there is no single material that simultaneously meets all the requirements.

Indeed, Pickering et al. [10] reported in a recent review that fiber reinforced epoxy composites typically demonstrated the highest strength among all the composites. On the other hand, they also noted that cotton fibers lead to high impact strength but lower tensile strength and stiffness with respect to other natural fibers, nevertheless they may be applied for impact stressed components like interior parts of cars. In contrast to conventional materials, bio-based polymers and natural fiber composites save non-renewable energy and reduce other environmental impacts, therefore, they should be incentivized for a sustainable future [11, 12]. In this innovative scenario, a literature review made by Pandey et al. [13] reported the production and the mechanical characteristics of composites with different types of natural fibers (cotton, hemp, kenaf and man-made cellulose fibers) with PLA at a fiber weight fraction from 30 to 50%, obtained by compression molding. Tensile and impact characteristics were investigated, reaching the best properties with man-made Lyocell fibers (82 MPa and 39.2 kJ/m^2, respectively). There are very few available studies about the flexural properties and impact behavior of natural fiber reinforced bio-polymers, as opposed to the great amount of research and applied solutions in petroleum-derived non-biodegradable polymers [7, 14-16].

Other than automotive applications, natural fiber reinforced composites are being considered to complement or to replace wood, for the manufacture of fiberboard, decking and furniture padding, for applications in building products such as door shutters, panels, door frames and roofing sheets [17-20]. Dittenber et al. [12] reviewed the possibility to use natural fiber reinforced polymer composites for applications in infrastructure. They reported that the use of primary structural applications would be of particular interest in countries such as India, where wood is often scarce.

In order to develop and optimize a bio-material for the reported application fields, a system that has proved promising with only one layer of fabric [21], was studied in a multilayer layout. This scale-up was necessary to compare the composite properties with commercial standards in order to compete with consolidated materials in generic load carrying applications.

The composites reinforced with cotton fabric were prepared using a film stacking procedure with two bio-polymers: poly(lactic acid) and poly(3-hydroxybutyrate-co-3-hydroxyhexanoate). The fabric used was a commercially available fabric but wastes as second-hand clothes, linen or production cuttings could be potentially used for the same purpose [22]. By this way, a reduction in the transfer to the landfill and thus a further enhancement of the sustainability could be achieved. The contribution of a chain

extender/coupling agent on the thermo-mechanical and impact behavior of such multilayer composites was also investigated and discussed in order to optimize the properties.

In a previous work [21] the validity of the process on one-layer composite was studied, as well as the chemical/physical investigation of the additive function and the potential recyclability. In the present article, the focus is instead on applications linked to industrial exploitation.

2. MATERIALS AND METHODS

2.1 Materials

2.1.1. Matrices

Poly(lactic acid) (in the text coded as PLA), INGEO 3051D grade, purchased from NatureWorks LLC and Poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (coded as PHB), AONILEX X131A grade, purchased from Kaneka Corporation were used. PLA and PHB were dried at 80°C for 5 h in a convection oven before the foil preparation. Following the ASTM D792 method, the density was determined (1.25±0.01 for PLA and 1.21±0.01 g/cm³ for PHB copolymer).

2.1.2. Cotton fabric

Cotton twill fabric with a mass per unit area of 165 g/m^2 and a density of 1.53±0.03 g/cm³ was cut in 15×15 cm^2 square samples and dried for 5 h in a ventilated oven at 100°C. The fabric was used without any chemical pre-treatment. The used cotton fabric was characterized from a morphological and mechanical point of view in a previous article [21].

2.1.3. Coupling agent/Chain extender

A commercial epoxy functional oligomeric acrylic polymer (Joncryl ADR-4368 from BASF Corporation, coded as “J” in the text) was used as coupling agent/chain extender as already demonstrated in a previous article [21].

2.2. Coupling agent application on fabric

The coupling additive was deposited on the surface of the fabric with a method already used and proved to be effective [21]. Tetrahydrofuran (purity: 99%) from Sigma-Aldrich was used to dissolve the Joncryl ADR-4368 additive. A percentage ranging from 7.5 to 9.2% with respect to the original fabric weight was added on the cotton fabric.

2.3. Composite preparation

The multilayer composite panels were produced using a film-stacking procedure where dry fabric layers and matrix foils (thickness 0.2 mm) were piled up alternately with a method already used [21]. An IQAP LAP PL-15 hot plate press (IQAP Masterbatch group SL, Barcelona, Spain) equipped with temperature and pressure-controlled plates was used.

The stacked plies were placed in a mold of 150×150×4 mm^3 size. Ten matrix sheets and nine fabric layers were pressed to make a nine-layer reinforced composite (9L). Layers of fabrics were oriented alternatively at 0° (warp) and 90° to the roll direction of the fabric (weft), starting and ending with the warp direction (namely, symmetric cross-ply laminate). After a pre-heating time of 3 min, a 5 MPa pressure was applied and removed several times (8-10) for 1 min to degas the composite minimizing the void generation. Subsequently, a compressive force of 10 MPa was applied for 3 min and the plates were cooled at -50°C/min to room temperature. The measured final thickness of the nine cotton layer composite was 3.8-4.0 mm and the cotton weight fraction in the 34-37% range, as reported in Table 1. From the weight of fibers used to make the laminate and the final laminate weight, the mass fraction was calculated. The reference samples of neat PLA and PHB were produced with a single compression molding procedure in the mold of 150×150×4 mm^3 size.

All the composite plates were cut with a band saw into specific sizes for various analyses and the edges finished with sandpaper to have straight and smooth surfaces. The specimen dimensions were 60×15×4 mm^3 for three-point bending, DMTA and impact tests.

Table 1. Codes, composition, thickness, density and porosity percentage of cotton fabric composites.

Sample code	Fabric mass fraction [%]	Additive J mass fraction [a] [%]	Fabric volume fraction [%]	Thickness [mm]	Density measured [g/cm^3]	Porosity [b] [%]
PLA	-	-	-	3.90±0.05	1.25±0.01	-
PHB	-	-	-	3.85±0.05	1.21±0.01	-
PLA9L	34.5±1.0	-	30.0±1.0	3.80±0.05	1.24±0.01	8.4±0.5

PLA9LJ	37.1±1.0	3.2	32.5±1.0	3.85±0.15	1.28±0.01	4.6±0.5
PHB9L	33.5±1.0	-	28.4±1.0	4.00±0.05	1.24±0.01	6.0±0.5
PHB9LJ	35.2±1.0	2.8	30.0±1.0	3.95±0.05	1.27±0.01	3.2±0.5

a) mass fraction of J additive was calculated from fabric weight increase after treatment

b) Porosity = (measured density - density calculated from mass fraction / calculated density)*100

2.4. Characterization techniques

The composite cross sections obtained from a brittle fracture in liquid nitrogen or after Charpy tests were pinned up on stabs with conductive adhesive tapes, sputtered with gold and studied using a LEO-1450VP Scanning Electron Microscope (working distance 15mm, accelerating voltage 20kV).

The densities of the matrices, fabric and composites were determined following ASTM D792 method. The differences between the measured densities and the calculated ones are reported in Table 1 as porosity. The procedure details used are reported in a previous work [21].

Flexural tests (three-point bending) were performed at room temperature (23±1°C) using a Zwick Roell Z10 machine equipped with a load cell of 1 kN. The tests followed the ISO 14125 standard, using a crosshead speed of 1 mm/min and a span length of 50 mm. Five specimens were used for each formulation and the average values and corresponding standard deviations were calculated. These tests provided the flexural modulus (E_f) and the flexural strength (σ_f) of the composites.

Dynamic mechanical thermal analysis (DMTA) in dual cantilever configuration was performed on a DMA Q800 (TA Instruments). A temperature range from 30 to 120ºC, heating rate of 3ºC/min, 1 Hz frequency and 0.05% of oscillation amplitude in the strain-controlled mode were adopted. The storage modulus (E') was registered.

The Heat Deflection Temperature (HDT) was extrapolated from the storage modulus plot. The HDT at 1.82 MPa was determined as the temperature at which the storage modulus achieves 800 MPa in the DMTA tests, following a method proposed in the literature [23, 24].

Charpy unnotched impact strength according to ISO 179-1 was obtained with a Zwick HIT 5.5P testing machine operated with a pendulum size of 5 J. Rectangular 60×15×4 mm^3 and unnotched specimens were used. To determine the impact strength, 5 specimens were tested edge-wise.

The specimens for all the mechanical tests were conditioned for minimum 48 h at 23±1°C and 30% relative humidity in a desiccator chamber with a water-saturated $MgCl_2$ solution.

3. RESULTS AND DISCUSSION

Nine multilayer fabric composites (9L) with 4 mm thickness and around 35 wt.-% of fabric content were prepared with the film stacking procedure. This step was necessary to test and compare the properties with standards in order to compete with consolidated commercial materials in load carrying applications.

3.1. Composites density and porosity

Common manufacturing-induced defects, especially in multilayer composites, are voids between the fabric and the matrix [25, 26]. Generally, they have dramatic effects on the mechanical strength [27] and moisture penetration [28] in the composites. For these reasons, the composite density was evaluated and the void content (reported as porosity) was calculated and reported in Table 1.

The fabric content in one layer (1L) composites was around 25 wt.-% [21]. Once the layers were increased to nine layers and the ratio fabric/foil was 9:10, the fiber content increased to around 34 wt.-%. As far as porosity was concerned, 2 % was found for 1L composites [21] and it was in the range of 6–8 % for 9L. Similar results have been obtained by other researchers [29-31]. Generally, the higher the fiber volume fraction, the higher is the amount of porosity. This is probably due to air being trapped between the layers which is not released during compression molding procedure. Nevertheless, it can be seen that the J additive in the amount of around 3 wt.-% in the 9L composites slightly increased the densities of the composites and also significantly decreased the void contents, as already seen in the one layer composites [21]. This fact is fundamental since Madsen et al. [30] have shown that the effect of porosity on material stiffness is approximated by an exponential factor of the porosity volume fraction. Conversely, it was also reported that void content up to 4% has minimal effect on fiber composite properties [32]. The 9L samples are over this threshold and the 9LJ around this value. This fact will be taken into consideration during the mechanical discussion.

3.2. Composite morphology

From SEM cross sections in Figure 1, a constant spacing of around 100 μm between the fabric layers in both matrices is maintained. This analysis is essential to verify the integrity and alignment of the fabric

within the composite. The used production technique allowed to obtain a composite with clear and regular spacing between the fabric layers.

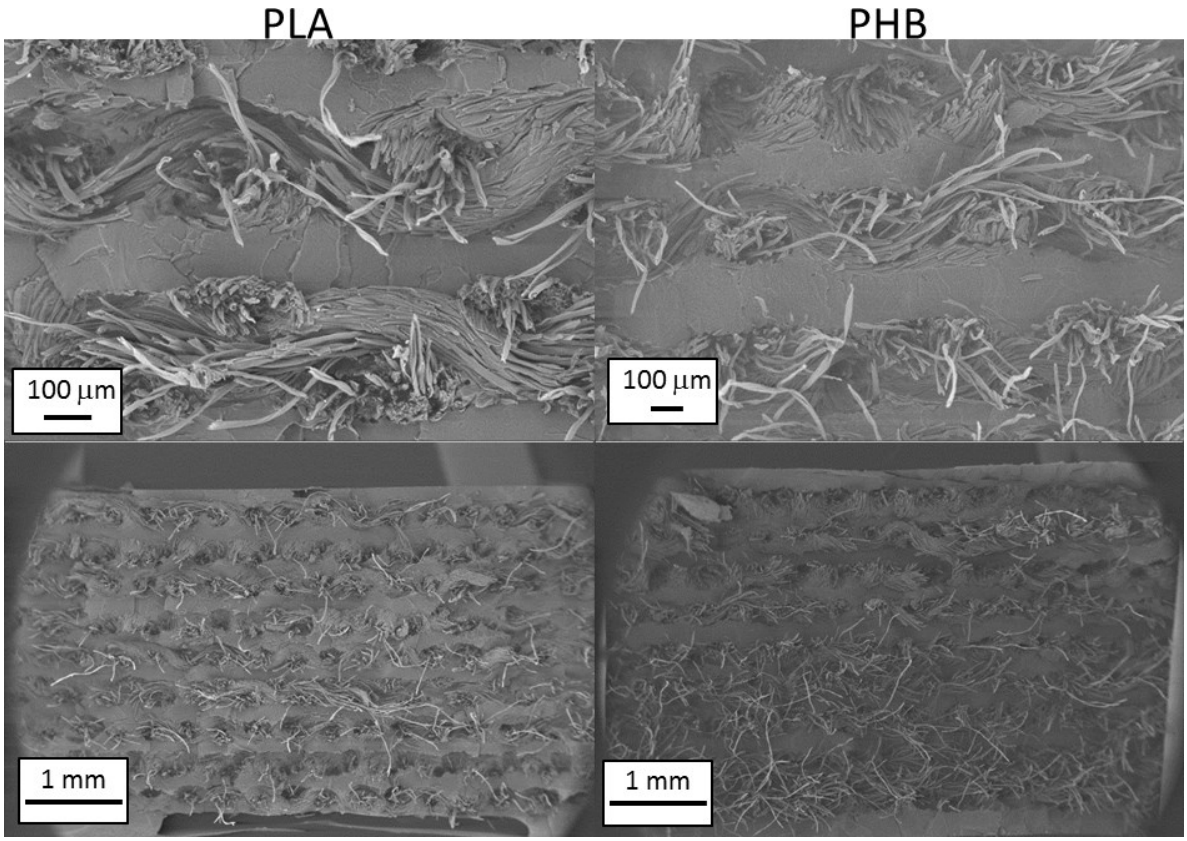

Figure 1 SEM images of PLA9L and PHB9L samples.

3.3. Composite mechanical characterization

The multilayer composites were mechanically analyzed in bending and impact configurations. Furthermore, the storage modulus versus temperature was monitored with a DMTA equipment and the HDT was evaluated.

Data for PLA in Table 2 and PHB in Table 3 show the flexural modulus, flexural strength, storage modulus at 30°C, HDT and impact strength values of matrices and their composites. To have a visual comparison between the matrices (grey area) and the composites, these data are also graphically reproduced in Figure 2. By this way, it is easy to simultaneously compare all the properties of the composites and to evaluate the effect of the J additive (dotted lines) with respect to the not treated fabric composites (continuous lines).

Table 2 Flexural properties, modulus from DMTA, HDT and impact results of PLA and 9 layer composites.

		PLA	PLA9L	PLA9LJ
3 point bending	E_f [MPa]	3092 ± 123	4642± 165	4559 ± 52
	ΔE_f [%]	-	+50	+47
	σ_f [MPa]	101.5 ± 3.0	105.5 ± 2.9	107.8 ± 2.5
	$\Delta\sigma_f$ [%]	-	+4	+6
DMTA	E' at 30°C [MPa]	3262	4104	5547
	ΔE' [%]	-	+26	+70
HDT from DMTA	HDT 1.81 MPa* [°C]	61	63	66
Impact	[kJ/m^2]	15.7 ± 3.0	28.6 ± 3.0	37.7 ± 14.2
	Δ [%]	-	+82	+140

* Calculated with E' data = 800MPa

Δ = (value composite – value matrix) / value matrix * 100

Table 3 Flexural properties, DMTA, HDT and impact results of PHB and 9 layer composites.

		PHB	PHB9L	PHB9LJ
3 point bending	E_f [MPa]	1486 ± 25	2552 ± 217	2927 ± 327
	ΔE_f [%]	-	+72	+97
	σ_f [MPa]	38.5 ± 1.0	42.6 ± 2.5	54.2 ± 2.8
	$\Delta\sigma_f$ [%]	-	+11	+41
DMTA	E' at 30°C [MPa]	1735	2769	3645
	ΔE' [%]	-	+60	+110
HDT from DMTA	HDT 1.81 MPa* [°C]	70	119	123
Impact	[kJ/m^2]	8.3 ± 1.0	54.5 ± 5.9	40.7 ± 4.5
	Δ [%]	-	+557	+390

* Calculated with E' data = 800MPa

Δ = (value composite – value matrix) / value matrix * 100

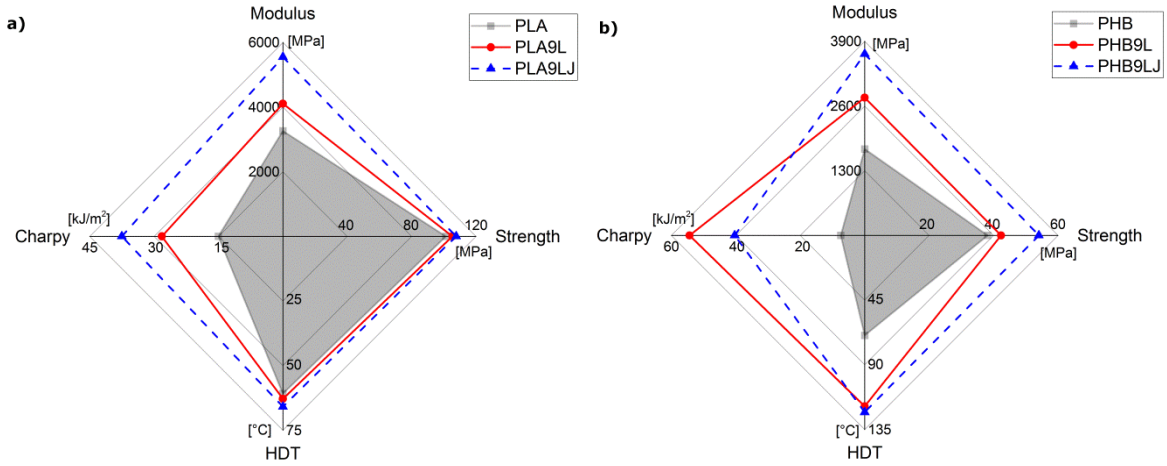

Figure 2. Flexural modulus, strength, HDT and impact results (Charpy) of PLA (a) and PHB (b) matrices and 9 layer composites

The fabric-based composites exhibited 1.5 times the flexural modulus of neat PLA and more than 1.7 times in the case of PHB. Measurements obtained by DMTA showed similar results, although if smaller increases of 26% and 60% were found.

These enhancements should be roughly between what was reported in warp (MD) and weft (TD) directions of the one layer composites in tensile mode [21]. Indeed, the cotton fabrics in the 9 layer composites were stacked with alternative orientations of 0º–90º (MD-TD-MD-…), thus a behavior in between the two orientations was expected. From this simple calculation a tensile modulus increase of 55% for PLA and of 101% for PHB were expected. Conversely, the modulus increase registered in the 9L composites was significantly lower than foreseeable by the average value between MD and TD. Only the action of the J additive in the systems was able to bring back the increase to supposed values.

These results confirm that the reduction in porosity generated an improvement in the properties and at the same time it was verified [21] that the additive acted as an effective chain extender and adhesion promoter which had a positive effect on the rigidity of the materials.

As far as flexural strength is concerned, only a small increase was registered in the PLA composites (4-6%). This result is justified by the fact that PLA has a high flexural strength (101 MPa), close to the tensile strength of cotton in MD (165 MPa) and even significantly higher than in TD (78 MPa) [21]. For this reason, a greater enhancement in the PHB matrix was expected, which had a flexural strength (38 MPa) lower than the one of PLA. However, a considerable increase (+41%) was found only for the PHB9LJ composite, significantly higher than the counterpart without the use of J additive (+11%). Again,

this result could be ascribed to the higher porosity found in 9L with respect to 9LJ and to the adhesion promoter effect.

According to the EN 312 standard for particleboards in furniture application, seven classes are defined for different environment application from P1 to P7. The minimum requirements for P4 (non load-bearing boards for use in humid conditions), P5 (load-bearing boards for use in humid conditions) and P7 (heavy duty load-bearing boards for use in humid conditions) are shown with dashed lines in Figure 3, the areas above and to the right of this boundary lines are suitable for these purposes. All our PLA/cotton fabric composites satisfied the highest requirements of 22 MPa for what concerns the strength and 3.35 GPa for the modulus (green dotted line in Figure 3) [33]. Also the PHB fabric composites satisfy the strength, but not the modulus for the highest class. Indeed, in Figure 3 the property indicator of PHB9L sample falls exactly on the limits for P5 (violet line σ= 20 MPa and E= 2.55 GPa) while the PHB9LJ sample is within the area between P5 and P7. The J additive action in the PHB system is therefore essential to broaden the field of use of the multilayer composite.

Also several types of wood (Douglas-Fir, Western Hemlock, Ponderosa Pine, Plywood) are taken in consideration and discussed [34]. The flexural strength of the PLA-based composites are better than the properties measured for the reported engineered wood products (85-27 MPa) but the modulus is less than half. The PHB composites have a flexural strength comparable to the one of Ponderosa pine (35-65 MPa) but also a lower flexural modulus (6.9-8.9 GPa) (see the orange area in Figure 3).

This brief comparison suggests that the same loading as wood could be carried by the bio-based composites, but bigger deformations due to the lower stiffness will be found. However, the fabric composites' evident drawback is the density, significantly higher than those of engineered wood products (320–810 kg/m^3) [34]. On the other hand, an advantage over wood is the easy ability to be shaped including hollow sections to achieve lightweight structures.

At the end, other studies on thermoplastic polymers with natural fabrics, adopting compression molding procedure and similar weight fraction were considered and flexural characteristics are shown in Figure 3. The results obtained with PHB (34-35 wt.%; 28-30 vol.%) are comparable with reported data obtained with PP (PP-jute 37 wt.% [35], PP-kapok/cotton 28 vol.% [36]) but using a completely bio-based and biodegradable system. On the other hand, the use of a conventional and not bio-based system with glass fibers (PP-GF 28 vol.% [36]) gave the best results in PP. Nevertheless, higher flexural performances than

PP-GF are obtained with PLA composites. Indeed, they are in the upper right part of the graph, where the characteristics are maximized for both modulus and strength. In this context, PLA9L and PLA9LJ (34-37 wt.%; 30-32 vol.%) resulted better than PLA-bamboo (51 vol.%) [31] reported in the literature and comparable to PHB-lyocell (30 wt.%) with the fibers mainly oriented in the testing direction [37]. Better results are obtained with PLA-lyocell (30 wt.%), PLA-kenaf (40 wt.%) and PHB-kenaf (40 wt.%) by the same authors but always parallel to the main fiber direction [37]. These last best results are probably due to the fiber orientation and also to the better mechanical characteristics of the fiber used. Indeed, the same system of PLA-kenaf with the same fabric content (37 vol.%) was investigated by Huda et al. [15] and gave extremely different and low results. It is certainly that cotton fabric is not the best solution to maximize the composite flexural properties, but it accounted for 79 % of the total amount of natural fibers produced in the world in 2013 [38]. Thus, it has been also investigated for the possibility to recycle such high amounts of fabric in the composite field, as recently proposed by Temmink et al. [22].

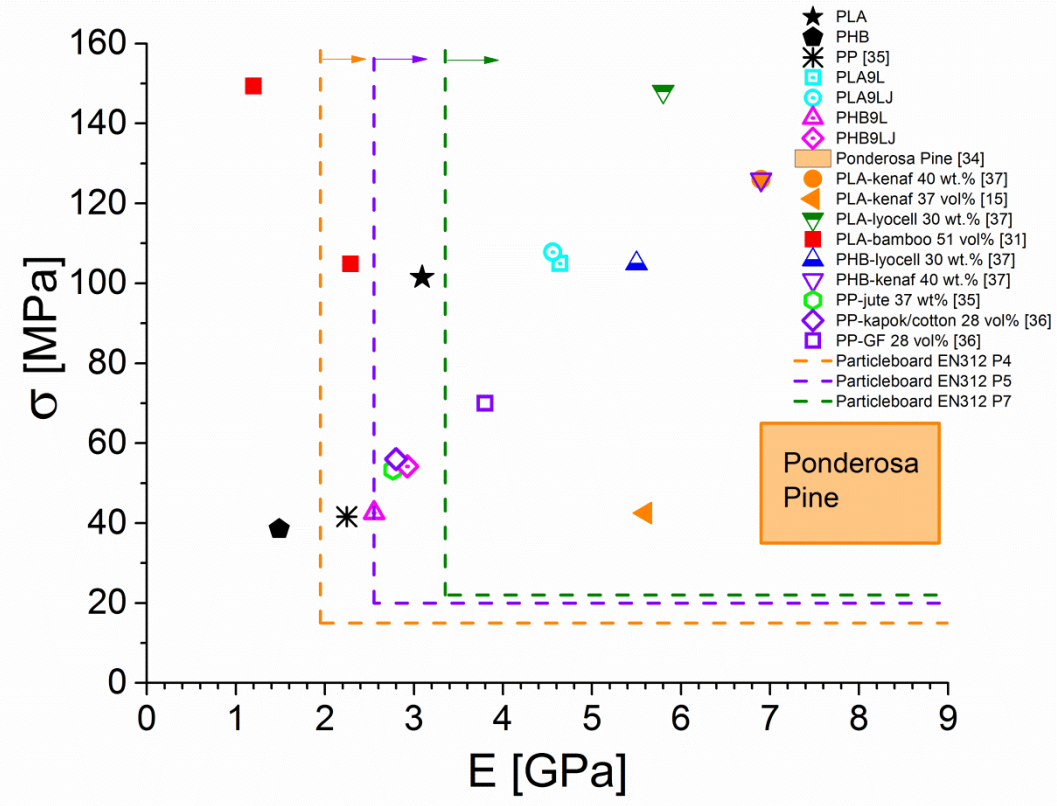

Figure 3. Flexural strength (σ) versus flexural modulus (E) of multilayer composites and various natural fabric thermoplastic composites (data from [15, 31, 34-37]).

3.4. HDT from DMTA analyses

The dynamic thermo-mechanical analysis in the dual cantilever mode was used in order to establish the effect of the temperature on the storage modulus of 9L bio-composites. Figure 4 reports the trend of the storage modulus (E') *vs*. temperature for the PLA- (a) and PHB-based (b) 9L composites. In the same graphs, a dotted horizontal line at 800 MPa is reported to visualize the HDT value. Indeed, the intersection between this line and the modulus curves correspond to the HDT temperatures at 1.82 MPa reported in Table 2.

The thermo-mechanical aspects are fundamental for renewable polymers that generally show poor mechanical properties with increasing temperature. Indeed, the neat PLA showed a deep drop of E' at around 60°C that also corresponds to the HDT value (61°C). The PHB modulus variation is more gradual than PLA, but, anyway, presents a mitigate fall down from 50 to 90°C that reflects an HDT value at 70°C. From an overall consideration, once the composites with cotton were tested, a general increase in E' was observed.

For all the formulations based on PLA, the thermo-mechanical property collapse occurs around 60-65°C. DMTA data and the calculated HDT confirm that PLA-based bio-composites may be used only below such temperature. Unfortunately, also the J additive is able to increase the HDT value of only 5°C, namely from 61 to 66°C.

In the case of amorphous or predominantly amorphous polymers, like PLA, the increase in HDT is mainly linked to the increase in the crystallinity. The PLA cotton fabric system has a crystallinity of 8.2 % [21] too low to allow a substantial increase in the HDT. An increase in the crystallinity could be achieved by annealing the material which, added to the fiber reinforcement, may drastically increase its thermo-mechanical properties, as already verified in the PLA-talc system [39]. Unfortunately, this solution is difficultly adopted in the industrial field for the treatment costs, but it remains an opportunity.

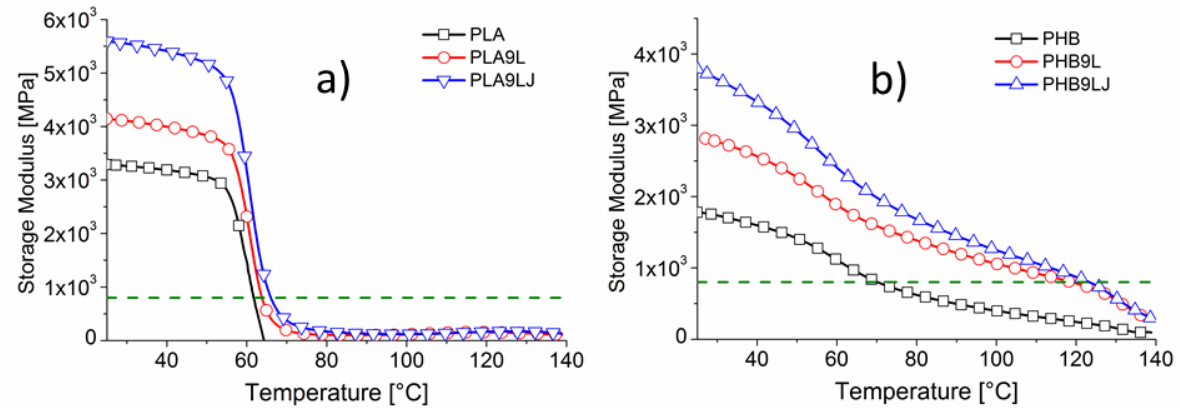

Figure 4 Storage modulus E' of a) PLA-, b) PHB-based composites with HDT dotted lines.

As far as PHB was concerned, the bio-composites exhibited higher storage modulus than the neat matrix even at high temperatures (>80°C) (Figure 4). The PHB is a semi-crystalline polymer with crystallinity around 26% [21]. Consequently, its loss of mechanical property in temperature is more gradual. The addition of fabric is able to increase the HDT (+49°C) because the material is now rigid enough to remain above the 800 MPa threshold. Only a slight increase is recorded with the addition of J (+4°C) revealing that the better stress transfer obtained at room temperature are not reflected in a great HDT enhancement. As far as HDT absolute value is concerned and considering PHB-based composites, Singh et al. [40] have reported an HDT of 134°C (+24°C as compared to neat PHBV) for composite with 40 wt.-% of wood fiber.

Summing up, the high thermo-mechanical performances (HDT=123°C) obtained in the PHB multilayer composites widely increase the opportunities for their employment in applications at high temperature.

3.5. Impact tests

Table 2 reports the impact strengths of PLA and PHB reinforced composites for different laminates. The impact properties of the composites followed the trend obtained in the flexural tests. The impact strength was around 28.6 and 37.7 kJ/m^2 for PLA9L and PLA9LJ, respectively. The variation in impact strength of the composites was significantly influenced by the J additive (see Table 2, Figure 2 and Figure 5). Graupner et al. [41] have found a value of 28.7 kJ/m^2 in the Charpy impact test for cotton-PLA (40wt.%) in MD, the same value as in this study (Figure 5). Comparable results were also obtained with PLA-bamboo at 51 vol.% [31], PLA-lyocell with 6 layers [42] and PP-jute at 37 wt.% [35] (Figure 5). On the other hand, better results are reported with PLA-lyocell with 8 multilayers and 50 wt.% [42] or

preferentially oriented in MD at 30 wt.% [37] while worse ones with PLA-kenaf 40 wt.% [41], PLA-hemp 40 wt.% [41], PLA-flax 40 wt.% [43] and PHB-kenaf 40 wt.% [37] were reported (Figure 5).

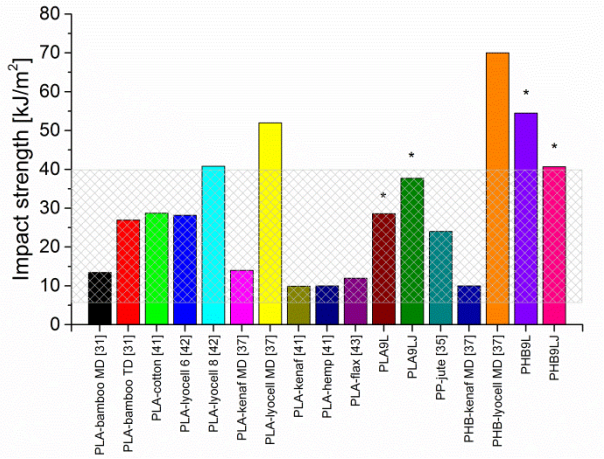

Figure 5 Unnotched Charpy impact strength of natural fiber composites. Data from [31, 35, 37, 41-43]) and from present work (marked with *).

Remarkable high impact strengths were registered for PHB laminates that reach mean values of 54.5 and 40.7 kJ/m^2 for PHB9L and PHB9LJ, respectively (see Table 2, Figure 2 and Figure 5).

Only a few investigations are reported in the literature for this matrix and comparisons are difficult for the different analysis methods and setups. However, the best results reported by Graupner et al. [37, 41] with PHB-lyocell at 30 wt.% tested in the MD gave 70 kJ/m^2, not so higher than the 54 kJ/m^2 obtained with the not oriented PHB9L composite. Graupner et al. [37, 41] have also reported that the impact strength of commercially used natural fiber reinforced composites for interior parts of cars ranges from 6 to 40 kJ/m^2. This data range is highlighted in Figure 5 with a grid. Following this rough subdivision, it is possible to define the composites with PLA suitable and comparable with currently adopted solutions in terms of impact property and the PHB even over such requirements.

The results obtained with PHB matrix are much higher than those obtained with the PLA, despite the PHB has a lower impact strength value than the PLA. The first experimental evidence is the visual appearance of the samples after the impact test. The PLA-based samples are all fractured into two parts, while the PHB-based composites do not have a two-part fracture, but only bending and folding of the sample (Figure 6). Consequently, the energy used to fracture the PHB samples does not generate two new

complete surfaces, but it is not easy to evaluate if this area of separation is different when the J additive is used. Surely a variation in the fracture area influences the impact strengths obtained.

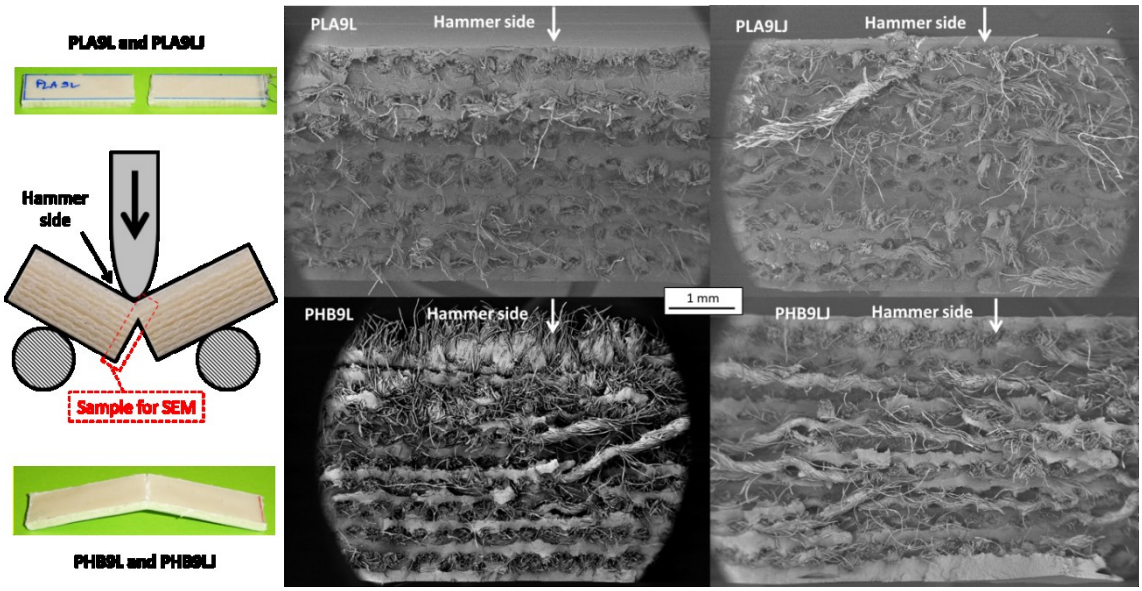

Figure 6 SEM magnifications after Charpy impact tests of natural fiber composites.

It is well known that the fiber pull-out from the matrix is a process that dissipates large amounts of energy, a fundamental aspect for the impact tests. Fiber pull-out during the tensile tests was evidenced by morphological studies in the previous work [21]. This behavior could be partly responsible for the high impact strength of the composites prepared. To verify this aspect, the fracture surfaces of the samples after the impact tests were analyzed with SEM (Figure 6).

PLA-based composites present the fiber break without a large pull-out from the matrix surface. Conversely, the PLA9LJ sample has a more extensive pull-out (compare the pictures in Figure 6). Such feature is expected and here verified from the hypotheses made that the J additive works as a chain extender of the PLA without substantially modify the adhesion. The registered increase in the impact strength is therefore explained with two concurrent effects: firstly, the pull-out of the fibers, secondly the increase in the length of the polymer chains. Indeed, the high molecular weight chains are more difficultly ordered decreasing the crystallinity, as previously reported [21]. It is also well known that the same polymer, if is less crystalline, is able to absorb more energy to the impact [44].

Nevertheless, relatively better results were achieved with the PHB matrix than with PLA. In this case, the samples did not separate during the Charpy test (Figure 6) and were manually separated to observe the cross-section by SEM. A large fiber pull-out is visible in the untreated material (PHB9L) which increases going towards the surface hit by the hammer (Figure 6).

The remarkable 6.5-fold increase of impact strength with respect to the PHB neat value was reduced by the J additive to around 4.9-fold increase. Thus, the J additive had a negative effect on the impact behavior of the PHB composites. This may be ascribed to the better adhesion properties between the matrix and the fibers which limit the pull-out visible from the Figure 6 and hence the energy dissipation during the impact. Other times in the literature have been found similar behaviors: untreated sisal fiber has been shown to give a ten-fold increase in Charpy impact strength compared to polyester alone, but acetylation, alkali and silane treatments have a drastic negative influence on the composite behavior [45].

4. CONCLUSIONS

Multi-layer bio-composites consisting of poly(lactic acid) or poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) matrices film stacked with cotton twill fabric were produced. The layers of the fabric resulted to be regularly spaced with around 100 μm of gap. The composites porosity was assessed to be 6-8%, but the epoxy functional oligomeric acrylic additive (Joncryl ADR-4368) was able to reduce porosity to 3-4% and to improve the stress transfer, which resulted in better flexural properties. A possible application as load-bearing boards according to the EN 312 standard or substitution of engineering woods in mean load-bearing applications were verified. Furthermore, DMTA analyses also shown that the cotton fabric composites caused a consistent increase in the HDT temperature in the PHB matrix from 70 to 123°C, increasing the service temperature. Finally, the impact test of composites reached values comparable to composites used in automotive applications. The remarkable impact resistance of 54 kJ/m^2 was reached in the case of PHB9L. The Joncryl additive acted mainly as a chain extender in the PLA and gave a substantial increase in the impact strength of PLA. In contrast, J acted as an adhesion promoter and made the PHB composites more susceptible to impact. From these results, it is possible to choose the right composite for a characteristic application, i.e. the formulations with PLA are preferable for the load-bearing boards in the furniture application while PHB for the automotive field where screening is made on HDT and impact strength. The J additive can play a key role in some cases as flexural properties of

PHB or impact test in PLA. The studied multilayer bio-composites are verified suitable for the use in applications such as furniture or automotive, bringing additional sustainability properties not owned by the conventional fossil-based composites. Further investigations have to be carried out to determine the biodegradability/compostability of these laminated composites.

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Figure Captions

Table Captions