Contents lists available at ScienceDirect

Composites Part B

journal homepage: www.elsevier.com

# Toward high performance renewable agave reinforced biocomposites: Optimization of fiber performance and fiber-matrix adhesion analysis

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ARTICLE INFO

*Article history:*
Received 6 December 2016
Accepted 11 April 2017
Available online xxx

*Keywords:*
Biocomposites
Agave fibers
Green epoxy
PLA
Micromechanics

ABSTRACT

The increasing sensitivity toward the environmental pollution and the recent laws on the environmental protection, have led to an increasing attention to the so called biocomposites, i.e. to ecofriendly or renewable composite materials, obtained from biopolymers reinforced by natural fibers. Although the contribution of various works reported in literature, focused on biocomposites reinforced by agave fibers, such materials are still exclusively used in the automotive industry for non-structural applications, and the implementation of high performance biocomposites for semi-structural and structural applications, is an expected, but not yet reached objective.

Therefore, the present work aims to give a contribution to reach such an objective, by means of a proper selection of the fiber, in terms of variety, age and position, as well as by the implementation of a new ecofriendly fiber extraction method that allows the user to obtain fibers with improved mechanical performance. In more detail, it is shown that the agave marginata, widespread in the Mediterranean area, provides fiber with performance higher than the agave sisalana commonly considered in literature, and its performance can be furtherly improved by proper optimization of the main influence parameters and the extraction process. On the basis of these optimized fibers, as well as of thermoplastic and thermosetting matrixes, particularly suitable for the manufacturing of high performance ecofriendly biocomposites, an accurate theoretical-experimental analysis on the fiber-matrix adhesion has allowed first to confirm the good adhesion of the agave with epoxy and PLA matrixes, as well as to detect the actual influence of the mercerization treatments and the significant effects of the stiffness of the coupled materials on the potential pull-out and/or debonding damage mechanisms.



## 1. Introduction

The attention to the environmental concerns, has lead in the last years to a recent interest toward ecofriendly and/or renewable materials, among which an important role is played by the so-called biocomposites, i.e. materials generally constituted by an ecofriendly matrix (green polymers or biopolymers) reinforced by natural fibers. Among the various natural fibers, particularly interesting is the agave fiber, characterized by short renewal time, high availability (about 4.5 million tons of agave fibers is produced worldwide every year), possibility of exploiting marginal lands (it is in practice a weed that does not subtract fertile terrains to the agricultural crops), but also good strength and stiffness, along with low cost (about 0.3 €/kg) and good adhesion with many polymer matrixes. Moreover, it has the lowest specific cost in term of stiffness (about 25€/GPa.ton), and a fibrillar structure that make it the natural fiber with the highest thoughness, comparable with that of the glass fibers. For all these reasons, it is a shared opinion that in the current state, the agave fibers are yet underused [1] and the implementation of new biocomposites, especially for semi-structural and structural applications, is an objective strongly expected, but not yet reached.

Several research works reported in literature, deal with the study of the agave fiber for the manufacturing of ecofriendly composite materials; in particular, some works focused on the fiber extraction process [1–4], whereas other works have addressed to the study of the mechanical strength and the relative main influence parameters, focusing on the single fiber [5–10], as well as on the properties of the fiber-matrix interface [11–15] and on the mechanical or chemical treatments aimed to the improvement of the fibers properties and of the adhesion with the polymeric matrixes [16–24]. Few are instead, the works reported in literature that deal with the biocomposites [25–28] and their damage mechanisms, by considering the cases of two-components short [25,26] and long fiber [27,28] biocomposites [25,26], as well as the case of hybrid tri-components [29–33] biocomposites.

The present work is the first one of two research works, carried out under a project partially financed by European funds, with the objective to give a contribution to the development of high performance renewable biocomposites reinforced by agave fibers, that can be used for semi-structural (short fiber) and structural (long fiber) applications. Such an objective is in practice pursued by a proper fiber selection, performed in term of agave variety, age of the leaf, and fiber po-

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http://dx.doi.org/10.1016/j.compositesb.2017.04.011
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sition, but also by the development of an innovative ecofriendly fiber extraction process, that allows to improve significantly the fiber mechanical performance. On the basis of the properties of the so optimized fibers, as well as of the properties of two matrix ("green" epoxy and PLA) potentially suitable to obtain respectively ecofriendly and renewable high performance biocomposites, a systematic theoretical-experimental analysis has allowed an accurate evaluation of the actual fiber-matrix adhesion and of its main influence parameters.

## 2. Fiber optimization

### *2.1. Preliminary fiber analysis*

Most of the works reported in the literature, dealing with agave fibers and relative biocomposites, consider almost exclusively the so called sisal fibers, i.e. the fibers extracted from the agave sisalana, because they are widely and readily available in the market; they are generally long fibers coming from Brazil or other African countries, commonly obtained by decortication from agave leaves of various age, and mainly used for the manufacturing of handicrafts. A simple visual inspection shows that such fibers are in practice constituted by a mixture of fibers having different quality, age, length, cleaning degree, etc. For this reason the experimental tests carried out on such fibers show an high scattering, often higher than 50%, especially in term of strength and stiffness.

In order to obtain agave fibers with high mechanical performance, in the present work the properties of the agave fibers obtained by the "marginata" variety (Fig. 1), widely diffuse in the Mediterranean area, are compared with those obtain form the agave sisalana, considering for both the varieties, plants grown in contiguous experimental fields. In this manner, the possible difference will be due to exclusively to the different variety, being the same the growing conditions (climate, soil, etc.) and the successive fiber extraction process.

The two considered varieties have similar exterior characteristics: long succulent leaves, reinforced by about a thousand of rectilinear longitudinal fibers (Fig. 2); each leaf is in practice a sandwich structure made by drymatter (8%–9%), fibers (3%–4%), cuticle (about 1%) and water (86%–88%). Among the fibers, it is possible to distinguish the so called *mechanical fibers* (structural fibers) concentrated on the leaf perimeter, and the *arch fibers* (non-structural fibers) scattered on the internal vegetal matrix (see Fig. 2a). The fibers exhibit a characteristic yellow color (Fig. 2b), with a typical horseshoe transversal section (see Fig. 2c) with a mean diameter of about 150–200 μm, value that is in practice about 10 times greater than that of the common synthetical fibers used in the Polymer Matrix Composites (PMCs).

As it is seen from the micrograph reported in Fig. 2c, like the sisal fiber, the agave marginata fiber is typically made by many cells or sub-fibers (Fig. 2d), having diameter included between 10 and 30 μm, with walls made by hemicellulose and lignin reinforced by cellulose spirals having winding angle of about 20°; to such a particular fibrillar structure is strictly related the high thoughness of these fibers. The analysis of the mean composition of the examined fibers of agave marginata (69% lignin, 16% hemicellulose, 15% cellulose) and agave sisalana (65% lignin, 13% hemicellulose, 22% cellulose) shows that the agave marginata fiber contain an higher percentage (about +50%) of cellulose. However both the compositions fall in the ranges typically reported in literature for the sisal fibers (40%–88% lignin, 8%–24% cellulose, 2%–28% hemicellulose), which composition can vary significantly with the age of the leaf and the climate of the site where the plant grown [34]. The specific weight of both the fiber types is about 14,4 kN/m$^3$, that is significantly lower than that of the synthetical fibers (from about 17 kN/m$^3$ of the aramid fibers, to about 25 kN/m$^3$ of the glass fibers).

The literature shows that the mechanical properties of the agave fibers can vary into a relatively wide range [34]: the Young modulus is included between 5 and 25 GPa, the tensile strength between 300 and 500 MPa (i.e. about 1/3 of the strength of glass fibers), whereas the failure strain falls in the range 3%–5%. The compatibility with the polymeric matrixes is in general quite good, although often the literature refers to not well documented debonding and/or pull-out phenomena, considered responsible of the premature failure of the corresponding biocomposites.

Moreover, although there are not literature data, it is reasonable to expect that the mechanical properties of the agave fibers can vary besides that with the age of the leaf and the agave variety, also with the particular segment (base, intermediate, apex) of the leaf from which they are extracted, and with the particular extraction method. Therefore, to obtain high quality fibers, suitable to manufacture high performance biocomposites, besides to select properly the agave variety and the mechanical fibers concentrated on the leaf perimeter, it is necessary also to make a proper selection that takes into account the age of the leaves, as well as the segment of the leaf from which they are extracted. Obviously, also the extraction process can have significant effects on the mechanical performance of the fibers, since it can


**Fig. 1.** (a) Exemplary of agave marginata (b) and agave sisalana.

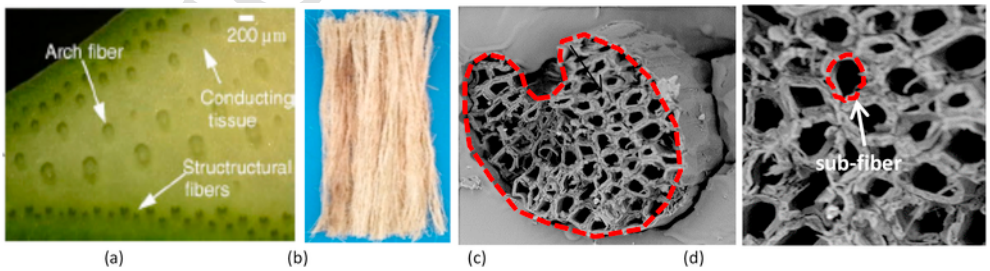


**Fig. 2.** (a) transversal section of the leaf, (b) fibers extracted by decortication, (c) micrograph of the fiber transversal section and (d) sub-fibers.

lead to non-negligible damage of the fibers, or to positive effects (necking, tensile, etc.) that, on the contrary, can also improve significantly their performance.

In the following, therefore, after an accurate study of the influence of the age of the leaf, as well as of the of the segment of the leaf from which the fiber is extracted, an innovative and ecofriendly extraction method that permits to improve both the strength and the stiffness of the fibers, is proposed. Such a method allow to avoid the mercerization treatments that, as it is well known, decreases the eco-compatibility of the fibers and, consequently, of the corresponding biocomposites.

### 2.2. Analysis of the influence of the age and position of the fibers

The effects of both the age and the position, have been preliminarily investigated by considering fibers extracted by decortication from leaves of agave marginata and agave sisalana (Fig. 1), subjected to a successive mercerization treatment under tensile loading [21], that in literature is considered the best treatment to obtain high quality agave fibers. In more detail, the effects of the age, have been analyzed by considering leaves having 1, 2, 3, 4 and 5 year old. A 10 kN BOSE *Biodynamic Electroforce Test Instrument* test machine (see Fig. 3a), equipped with an optical extensometer based on DIC technique (Fig. 3b), have been used to carried out proper tensile tests on 10 specimens for each age considered, and for each agave variety considered.

The following Fig. 4 shows the mean results of the single fiber tensile tests, in terms of Young modulus $E_f$ (Fig. 4a) and tensile strength $\sigma_{f,R}$ (Fig. 4b).

From Fig. 4a it is observed how in practice the stiffness of the fibers increases with the age, with a saturation (maturation) around 4–5 years; moving from 1 to 5 years, it is seen a significant stiffness increment of about +70% (from about 5.5 to about 9.2 GPa for sisalana, from about 8.4 to about 14.5 for marginata). In terms of tensile strength, instead, it is seen relatively lower effects, with a maximum around 4 years: moving from 1 to 4 years it is detected an increment of about +25% (from 253 to 312 MPa for sisalana, from 391 to 492 for marginata). Therefore, without take into account the particular agave variety, it is possible to state that to obtain fibers with high mechanical performance, it is necessary to extract them from agave leaves having 4–5 year old.

In order to investigate the effects due to the position, before the fiber extraction each agave leaf has been divided into three segments having the same length, called A (apex segment), B (intermediate segment) and C (base segment). As an example, the following Fig. 5 shows a specimen of the agave marginata fibers extracted from each segment; similar aspect has been observed for the agave sisalana.

The visual examination of Fig. 5 shows the different quality of the fibers extracted from the three segment of the leaf; in particular, it is seen that the C type fibers (Fig. 5C) are very smeared with vegetal matrix, that is difficult to eliminate, with coarse and irregular bundles, mixed to interrupted and damaged fibers. Significantly superior appear instead the quality of the B type fibers (Fig. 5b), also respect to the A type fibers, that contain also a percentage of interrupted/damaged fibers. The limited quality of the A type fibers appears mainly related to the damage frequently observed in the apex seg-

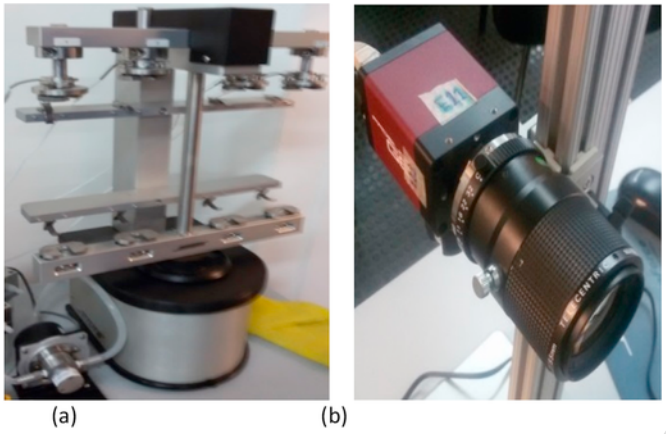


**Fig. 3.** (a) Material test machine type *BOSE Biodynamic Electroforce Test Instrument* and (b) relative optical extensometer, used for the single fiber tensile tests.

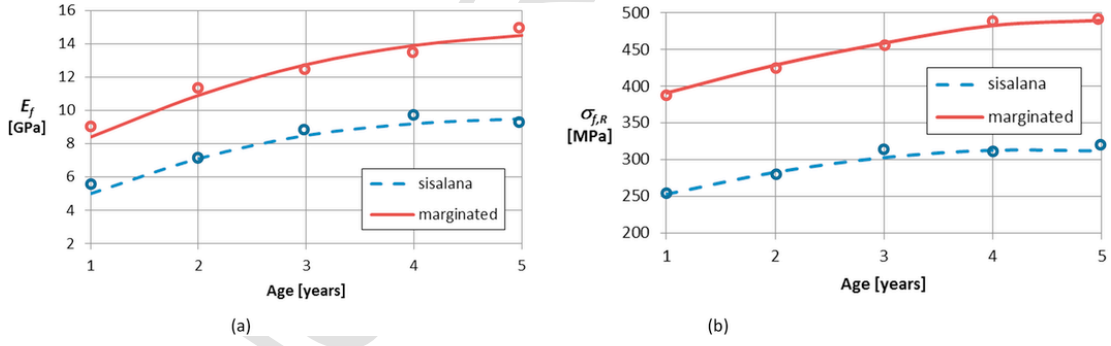


**Fig. 4.** (a) Young modulus and (b) tensile strength of the agave marginata and sisalana fibers (previously subjected to mercerization under tensile loading), vs. the age of the leaf.


**Fig. 5.** Fibers of agave marginata (a) type A, (b) type B and (c) type C.

ment of the leaf, due to the presence of multiple folds and/or longitudinal cracks; the low quality of the C type fibers is instead mainly due the presence in the base segment of a greater percentage of non-structural fibers, that are less robust and difficult to separate from the relative matrix, as well as to the presence of a greater percentage of vegetal matrix, whose elimination leads to a higher damaging of the fiber, that for this reason appears curved and no more rectilinear.

After a proper mercerization treatment, such fibers have been subjected to tensile test by using the same material test machine type BOSE, above mentioned (Fig. 3). The following Fig. 6 shows the mean tensile curves, obtained for the 3 different fiber types, for the agave sisalana (Fig. 6a) and marginata (Fig. 6b).

From Fig. 6 it is observed that the mechanical characteristics of the fibers extracted from the leaf base (C) are significantly lower (−65%) than that of the fiber extracted from the intermediate segment, that are also slightly better (about +15%) than those relative to the fibers extracted from the apex segment (A). Consequently, it is possible to state that, for any variety considered, to obtain high performance agave fibers it is necessary to extract them from the intermediate segment (medium third) of the leaves, discarding properly the fibers of the apex segment and, above all, those of the base segment, that leads to very low quality fibers.

## 3. Optimization of the extraction process

### *3.1. Analysis of the state of the art*

The extraction of the commercially available agave fibers (sisalana), is done through a maceration process and successive scraping of the leaves or, most commonly, by a decortication process followed by a cleaning in abundant water, in order to eliminate completely the non-fibrous material (chlorophyll, juice, cuticle, etc.).

In general, the decortication allows to obtain 2–4% of good quality fibers, whereas the maceration leads to a greater quantity of fibers that appear as an more heterogeneous mixture with a significant percentage of fiber having low quality [34]. However, such processes are usually used for the extraction of fibers addressed to the traditional uses (production of twin, cord, coarse fabrics, carpets and various craft products), for which is not requested an high fiber quality. For this reason, in literature, several fiber treatments aimed to the improvement of the fiber performance and of the fiber-matrix adhesion, have been studied: chemical treatments (with NaOH, $H_2SO_4$, $SiH_4$, $KMnO_4$ etc.), thermal treatments (to increase the fiber crystallinity and then the strength and the stiffness), or treatments with coupling agents (primer, to decrease the fiber hygroscopicity). However, the most used treatment is the mercerization, that consist in placing the fibers into a bath of NaOH solution; it leads in general to a better fiber surface cleaning, as well as to the improvement of the mechanical properties as well as of the fiber-matrix adhesion, due to the increase of the surface roughness and to the partial separation of the sub-fibers with increase of the interface surface (fiber fibrillation) [34]. If the mercerization is performed under tensile loading [22], then it leads to a further improvement of the mechanical performance of the fibers, mainly due to the increase of the winding angle of the hemicellulose spirals, along with a compaction of the materials for the "necking" effects. Usually, it is applied a limited tensile load, generally less than 10% the fiber failure stress, because due the difficulties to obtain a uniform load distribution, the use of greater stresses can lead to easy damaging of the most stressed fibers. Obviously, these treatments should be avoided because the use of NaOH leads to a significant environmental pollution that is not congruent with manufacturing of ecofriendly biocomposites.

### *3.2. New extraction methods proposed*

The manufacturing of high performance renewable biocomposites needs an ecofriendly fiber extraction process, which possibly does not require successive NaOH or similar polluting chemical treatments and, at the same time, it is able to produce fibers with improved mechanical properties. Taking cue from the positive effects of the tensile loading associated with the mercerization, an innovative and ecofriendly fiber extraction process, consisting into the repeated pressing of the leaves by using a common hydraulic press machine (Fig. 7a), alternated to water immersion (to eliminate the residual vegetal matrix), is proposed. In general, three cycles of pressing alternated with three water immersions, are sufficient to obtain good quality fibers. Respect to the decortication, the proposed method leads to a significant improvements of the stiffness and the strength of the fiber. Such a result is essentially related to the benefic longitudinal tensile stresses applied to the fibers, due to the friction forces that occur during the longitudinal matrix shear, caused by the compression (see Fig. 7b).

Obviously, the proposed method is a discontinuous process characterized by relatively low productivity, that needs to be further engineered. In order to increase the productivity, it has been considered also a continuum pressing process, obtained by a rolling mill properly implemented (see Fig. 8a). Obviously, also in this case the matrix shear leads to longitudinal tensile stresses on the fiber (Fig. 8b).

Respect to the simple pressing by hydraulic press, the rolling process is actually characterized by lesser working time, i.e. by greater productivity, but unfortunately the experimental evidence has shown a fiber quality visibly lower, with a non-negligible percentage of damaged/interrupted fibers; the fibers obtained by the hydraulic press appear instead integer, with surfaces more clean and lucid.

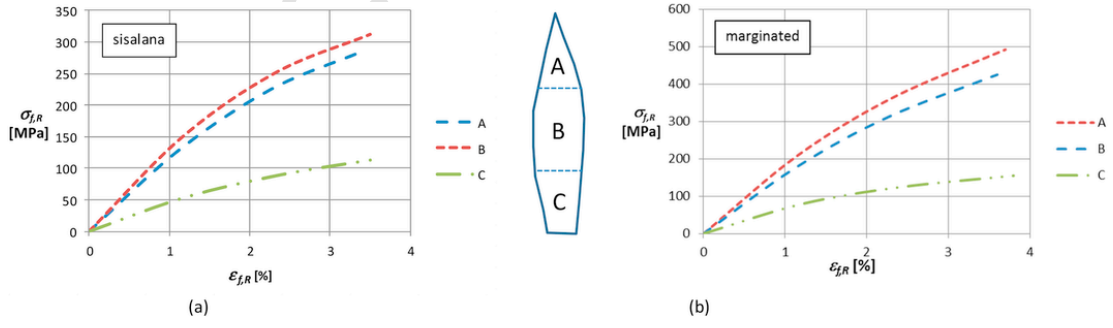


**Fig. 6.** (a) Curve di trazione relative a fibre di agave (a) sisalana e (b) marginata estratte dalle diverse sezioni (A, B e C).

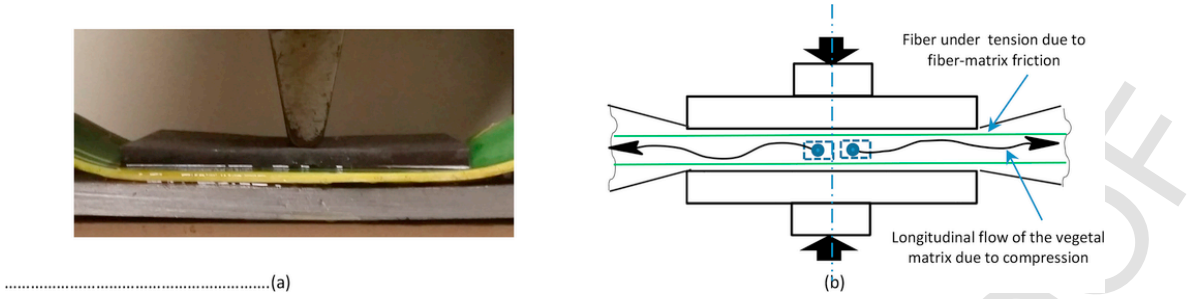


**Fig. 7.** (a) Fiber extraction by pressing process and (b) scheme of the matrix shear due to compression.

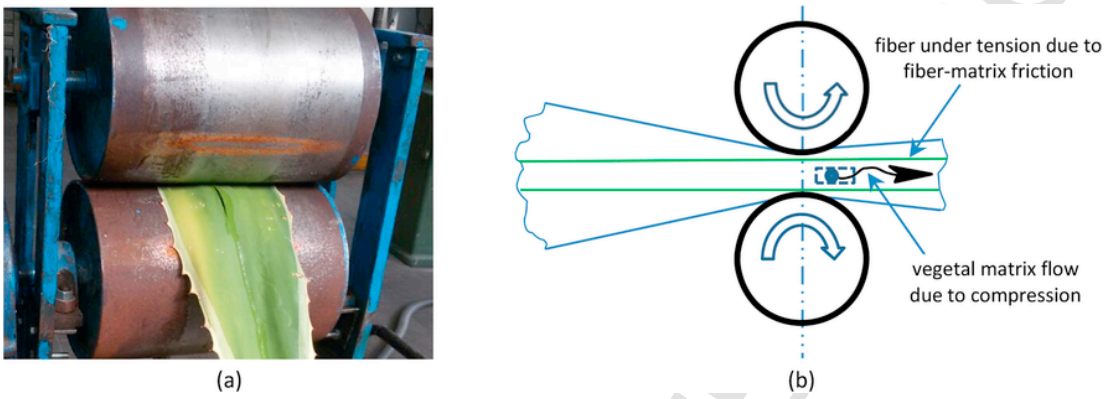


**Fig. 8.** (a) Extraction of the fibers by rolling process and (b) scheme of the vegetal matrix shear and of the relative internal stresses.

### *3.3. Experimental assessment by single fiber tensile tests*

In order to assess the actual improvement of the mechanical characteristics of the fibers extracted by the rolling (R) and the pressing (P) methods proposed, such fibers have been compared with that obtained by decortication (D), also by successive mercerization (M) with and without tensile (T) loading. In detail, in order to compare also the performance of the agave marginata fibers with those of the agave sisalana, proper single fiber tensile tests have been carried out by considering 6 different optimized fiber type (Fig. 9), i.e. extracted from the medium segment of leaves having 4–5 year old. The 6 fiber types are:

- Marginata, extracted by Decortication, Non-treated – called MDN (Fig. 9a);
- Marginata, extracted by Rolling, Non-treated – called MRN (Fig. 9b);
- Marginata, extracted by Pressing, Non-treated – called MPN (Fig. 9c);
- Marginata, extracted by Decortication, Mercerized – called MDM (Fig. 9d);
- Marginata, extracted by Decortication, mercerized un Tensile loading – called MDT (Fig. 9e);

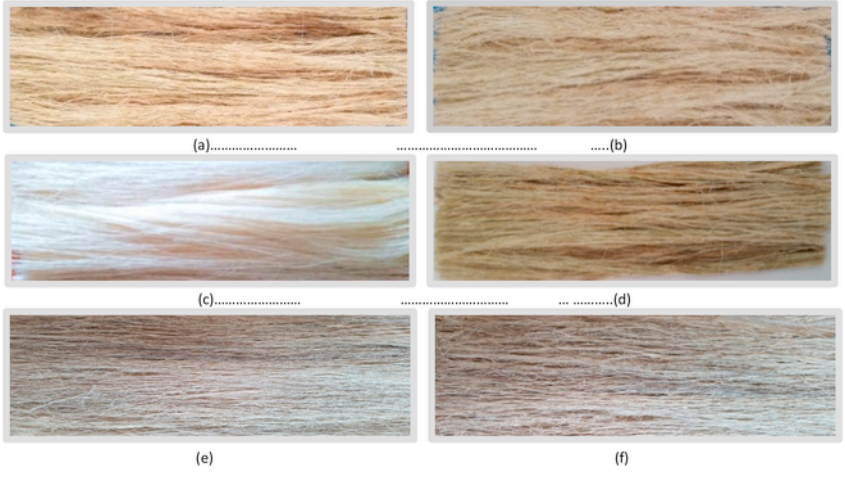


**Fig. 9.** Agave fibers type (a) MDN, (b) MRN, (c) MPN, (d) MDM, (e) MDT and (f) SDT.

- Sisalana, extracted by Decortication, mercerized under Tensile loading – called SDT (Fig. 9f).

The first three fiber types (MDN, MRN and MPN) permit to compare the effects of the two extraction methods proposed, with the traditional decortication, whereas the fourth (MDM) and the fifth (MDT) type allow to compare the effects of the mercerization with and without tensile loading; finally, the fifth and the sixth type allow to compare the effects due the different agave variety.

### *3.4. Experimental characterization by single fiber tensile test*

As above, the characterization of each fiber type, has been performed by mean of fiber lots made with 10 specimens, at the standard environmental condition of 20 °C and 65% of humidity. The mean diameter of each fiber, has been determined by three measures, carried out on three different sections of the gage length, by using a high precision vernier caliper. For each type examined, the corresponding mean tensile curve is reported in the following Fig. 10.

From Fig. 10 it is seen that all the examined fibers, exhibit an elastic behavior that can be approximated by a bilinear diagram with knee corresponding to the strain value of about 1/3 the failure strain. As it has already been observed in literature for similar fibers [7,25], such a progressive stiffness reduction correspond in practice to the partial failure of the weaker sub-fibers. Thanks to the optimization process (all fibers extracted from the intermediate segment of leaves having all the same age), the experimental results are not affected by the typical high scattering of the commercial non-optimized sisal fibers (also more than ±50%), but they exhibit a scattering lower than ±15%, in practice comparable with that of the synthetical fibers. As an example, from Fig. 6a it is possible to observe that the strength of the fibers extracted from leaves having age that falls in the range 1–5 years, is about 200 MPa with a scattering of about ±100 MPa, i. e about ±50%.

The following Table 1 shows the result of the single fiber tensile tests, in terms of tensile strength ($\sigma_{f,R}$), failure strain ($\varepsilon_{f,R}$) and Young modulus ($E_f$).

From the examination of the results reported in Table 1, it is possible to detect that the tensile strength varies significantly with the fiber type, the extraction method and the alkaline treatment, although it remains always relatively high, in the typical range 300–500 MPa, already reported in literature. By excluding the fibers obtained by pressing (MPN), that exhibit a failure strain of about 2%, the failure strain of all the other fibers falls in a quite narrow range, from 3.3% to 3.9%. The Young modulus, instead, varies in a wide range, between 9.3 GPa and 18.7 GPa, and values of about 23.3 MPa, have been also detected.

In detail, concerning the extraction process, the comparative examination of the results relative to the agave marginata extracted by decortication (MDN), rolling (MRN) and pressing (MPN), shows that the rolling leads to fiber properties only slightly better (+10%) than the decortication, whereas the pressing leads to significant improvement of the performance (40% in terms of strength, +100% in terms of stiffness). In other words, the strength improvements obtained by pressing are comparable to that obtained by mercerization (403 MPa versus 399 MPa), whereas in terms of stiffness the pressing leads to higher improvements (18.7 GPa versus 12.7 GPa) that overcome also that obtained by mercerization under tensile loading (MDT, 14.5 GPa). Respect to these latter, the fibers obtained by simple pressing, exhibits a tensile strength slightly lower, of about −18% (403 MPa versus 492 MPa), but they are completely renewable, since they are not subjected to any chemical treatment.

Regarding the comparison between agave marginata and agave sisalana, the experimental results show that the agave marginata mercerized under tensile loading, exhibits mechanical properties significantly higher than those of the agave sisalana (+60% in terms of strength, +50% in terms of stiffness, see Table 1).

Finally, considering the influence of the mercerization, the comparison between mercerized fibers (MDM) and non-treated fibers MDN, evidences how the application of the tensile load (5–10% of the failure stress), allows a further increment of about 25% of the strength and of about 15% of the stiffness.

Respect to the non-treated fiber (MDN), the mercerization under tensile loading, leads to an absolute increment of both strength and

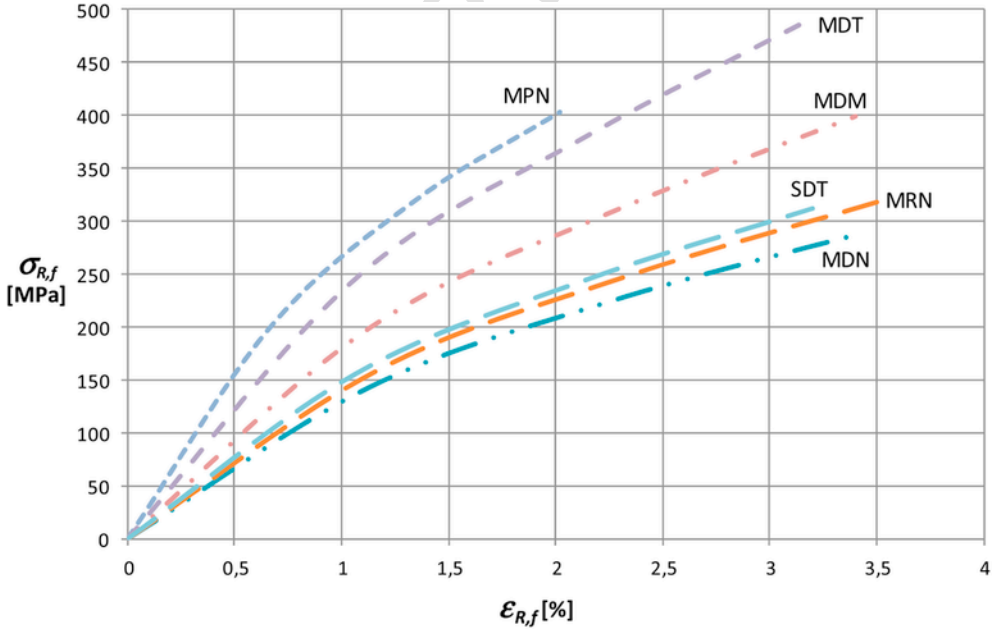


**Fig. 10.** Average curves of single fiber tensile tests, for the various fiber types considered.

**Table 1**
Results of the single fiber tensile tests for the 6 fiber types considered.

| Fibra | $\sigma_{f,R}$ [MPa] | $\varepsilon_{f,R}$ [%] | $E_f$ [GPa] |
|---|---|---|---|
| MDN | 287 | 3,4 | 9,2 |
| MRN | 318 | 3,5 | 9,3 |
| **MPN** | **403** | **2,0** | **18,7** |
| MDM | 399 | 3,3 | 12,7 |
| MDT | 492 | 3,2 | 14,5 |
| SDT | 312 | 3,2 | 9,8 |

stiffness, of about 55%; in detail, the comparison with data reported in literature, shows that the mercerization under tensile loading of the marginata gives higher strength increments with respect to the sisalana (only +30% about). In absolute terms, the marginata extracted by decortication and mercerized under tensile loading, exhibit a stiffness (14.5 GPa) and a strength (492 MPa) greater than about 30% respect to the average values reported in literature for the sisal (11 GPa and 381 MPa).

However, it is important to note that the proposed extraction method based on the simple pressing and water immersion, leads to the maximum absolute stiffness equal to 18.7 GPa, i.e. twice the stiffness of the same fiber extracted by decortication or rolling, and about higher than 30% respect to the fiber mercerized under tensile loading. It is also important to highlight that the fiber stretching due to the pressing, lead to a decreasing of the failure strain inversely proportional to the Young modulus, with value of about 2%. Such a value is ½÷1/3 the typical values (3%–7%) reported in literature for the agave fibers, but it is similar to that detected for other natural fibers as Kenaf, that exhibit better mechanical performance. The low failure strain of the pressed fiber (MPN) is an index of the improved fiber quality since, in accordance with [7], for a natural fiber a low failure strain is always associated to a reduced defects density.

Finally, taking into account the experimental results above exposed in Table 1, it is possible to state that, unlike rolling that damages the fibers due to unavoidable fiber-roll relative motion, the proposed ecofriendly the proposed pressing method leads to significant improvements of the mechanical performance, so that it appear particularly suitable for the development of high performance renewable biocomposites.

## 4. Matrixes selection and characterization

### *4.1. Matrixes selection*

In the field of biocomposites reinforced by natural fibers, the literature [10,34,35] has described the use of thermosetting matrixes for both long and short fibers, showing that the best mechanical performance is obtain in practice by using the epoxy resin, also with proper fiber treatments [10,21,24,34,35] aimed to the improvement of the fiber-matrix adhesion. Unfortunately, as it is well known, the thermosetting matrixes have a low recyclability and therefore its use leads to biocomposites with low environmental compatibility.

In the present work, in order to exploit the good properties of the epoxy resin and limit, at the same time, the environmental impact, a "green" epoxy, obtained partially from biobased glycerol, has been selected; in detail, the green epoxy type *SUPERSAP CNR* with hardener type IHN [36], manufactured by Entropy Resins, Inc. (CA) USA, has been considered.

Among the thermoplastic matrixes, that represent a valid alternative to the thermosetting ones, not only for the greater recyclability, but also for the greater flexibility, lower costs, higher thoughness and easier formability by molding, in the present study the PLA has been selected; in more detail, the PLA type 2002D having melt flow index (210°C/2.16 kg) = 6 g/10 min, melting temperature equal to 151 °C, supplied by Natureworks (Minnetonka, MN, USA), has been used.

In literature, several thermoplastic matrixes have already been considered for the development of biocomposites reinforced with natural fibers, as polyethylene, polypropylene, polystyrene, polyurethane, PVC etc. [10,34], and recently a significant attention is paid to the PLA from same automotive industries [10]; several research works are reported in literature [34,37,38], although they do not deal with the development of structural biocomposites, but rather to other objectives as the use of nanoparticles for an innovative sizing [37], the improvement of ageing effects [38] or the tribological properties [35]. The PLA is one of the most attractive biopolymers to obtain an interesting high performance renewable biocomposite with thermoplastic matrix. It is, in fact, a biocompatible, biodegradable and compostable biopolymer, that can be used for the manufacturing of biocomposites by extrusion and/or injection molding. The PLA is the most used material in modern 3D printers, which technique could be used in the future also for the production of biocomposites. In more detail, the PLA is obtained from dextrose a sugar that can be extracted from the cornstarch by the formation of lactic acid, transformed in lactides (type D, D, and meso) and then polymerized as polylactic acid. Although its characteristics can be varied into a wide range depending to the percentages of the various lactides, it exhibits averagely a Young modulus of about 1.5 GPa, and a good mechanical strength (about 50 MPa). For its high failure strain (in the range 5%–8%), higher than that of most natural fibers, it allows in principle to exploit completely the strength of high performance natural fibers, i.e. to obtain high performance biocomposites.

### *4.2. Matrixes characterization*

In order to have an accurate characterization of the mechanical properties of the two selected matrixes, by using dog-bone and notched rectangular specimens, tensile tests and shear tests (Iosipescu test) have been carried out in accordance with the ASTM standard [39,40]. The following Fig. 11 shows the average curves of the tensile tests (Fig. 11a) and of the shear tests (Fig. 11b), for both the matrixes considered.

From Fig. 11a it is noted that both epoxy and PLA exhibit an almost linear-elastic behavior under tensile loading, with a Young modulus of about 2.8 GPa (epoxy) and 1.25 GPa (PLA), and strength of about 50 MPa (epoxy) and 55 MPa (PLA). Less linear is instead the behavior under shear loading (Fig. 11b), with lower failure shear stress, of about 36 and 38 MPa, respectively for epoxy and PLA. In practice, the two matrixes exhibit very similar strength but different stiffness and, very important, very different failure tensile strain: 2% for epoxy and about 5% for the PLA (value higher than that of the agave fibers).

## 5. Fiber–matrix adhesion and characterization

### *5.1. Fiber-matrix adhesion*

In a high performance biocomposite a good fiber-matrix adhesion is an essential condition to have an efficient load transmission, from matrix to fibers. In the mechanics of composite materials, the fiber-matrix adhesion is considered weak if the composite failure involves the fiber-matrix separation trough debonding and/or pull-out phenomena, with interface failure stresses significantly lower than the matrix ultimate shear stress. As it is well known, for short fiber composites, a low matrix-adhesion can lead to easy debonding of the

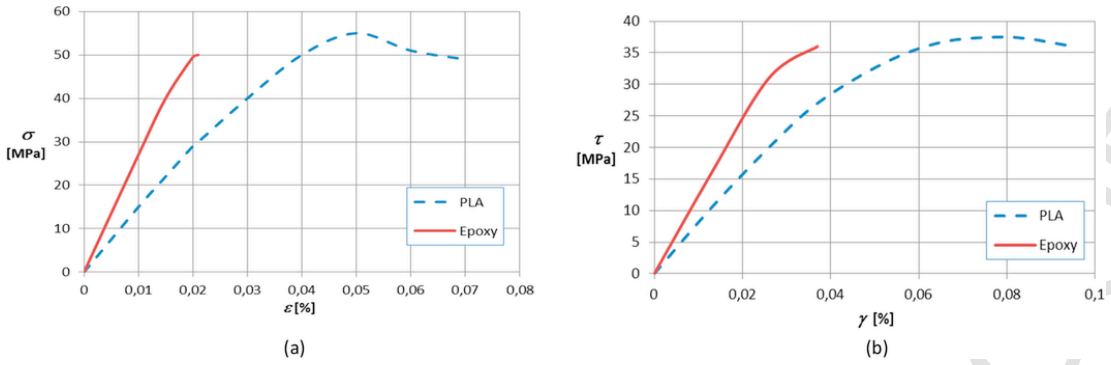


**Fig. 11.** Average tensile test curves (a) and shear curves (b) for the considered green epoxy and PLA.

transversal fibers along with possible pull-out of the longitudinal fibers. In the long fiber composite, instead, a poor fiber-matrix adhesion can lead to debonding phenomena, only in presence of significant and diffuse matrix defects [45]. Within the framework of biocomposites reinforced by natural fibers, the correlation between actual strength and fiber-matrix adhesion is frequently based on an aprioristic and non-rigorous association between low performance and low fiber-matrix adhesion, without to consider other important influence parameters, as the stiffness of the coupled materials and the consequent efficiency of the fiber reinforcing.

In more detail, in the most works reported in literature, the efficiency of the fiber-matrix adhesion is simplistically evaluated by the ratio between the interface mean stress and the matrix failure stress, without taking into account the significant end effects, i.e. the high stress concentrations that are responsible of the possible interface failure. Obviously, this fact lead to an underestimation of the actual fiber-matrix adhesion, which goodness is instead more correctly characterized by ratio $r_a$ between the maximum shear stress $\tau_{max}$ that occurs at the fiber-matrix interface, in the pull-out incipient condition, and the matrix failure shear stress $\tau_{m,R}$, i.e.:

$$r_a = \frac{\tau_{max}}{\tau_{m,R}} \tag{1}$$

It is an index that varies from 0 (null adhesion) to 1 (perfect adhesion); in the common PMCs reinforced by synthetical fibers, such an index takes value that in general are about or higher 0.5. Obviously, pull-out phenomena can occur also in presence of a good fiber-matrix adhesion if the fiber length is lesser than the critical length $l_c$, that is the minimum length that is necessary to obtain the total load transmission from matrix to fiber, that assure the fiber failure for high load applied to the composite. In the framework of Mechanics of Composite Materials, such a critical length is usually computed by assuming for the matrix an elastic-perfectly plastic behavior [42]; for the examined fibers and matrixes, such an approach gives:

$$\begin{aligned} l_c &= d\,\sigma_{f,R}/4\tau_{m,R} \\ &= 0.2\ \text{mm} \\ &* (287 \div 492\ \text{MPa}) / [4\,(36 \div 38)]\ \text{MPa} \\ &= 0.4 \div 0.6\ \text{mm} \end{aligned} \tag{2}$$

In order to contain the end-effects inside to limited fiber segments, in the practice of the composite materials the actual fiber length is fixed in the range 10–100 times the critical length, that for the examined materials gives a minimum length in the range 6÷60 mm.

### *5.2. Theoretical analysis of the stress distribution at the fiber-matrix interface*

The fiber-matrix adhesion can be tested experimentally through single-fiber pull-out test, in accordance with the scheme of Fig. 12:

In a pull-out test, the most efficient approach to correlate the pull-out load and the actual shear stress distribution $\tau(x)$ at the fiber-matrix interface, is the well known bonded joint theory [44], usually presented for plane systems; by adapting such a theory for the axisymmetric system shown in Fig. 12, it follows:

$$\tau(x) = \frac{P\lambda}{2\pi d}\left[\frac{1-S}{1+S}\cdot\frac{Sinh(\lambda x)}{Cosh(\lambda l_e/2)} + \frac{Cosh(\lambda x)}{(D/d)\,Sinh(\lambda l_e/2)}\right] \tag{3}$$

being $\lambda$ the base characteristic of the bimaterial joint and $S$ the so called unbalancing, given respectively by the following relationships:

$$\lambda = \frac{2}{D}\sqrt{\frac{G_m}{E_m}\left[\frac{1+S}{S}\right]} \tag{4}$$

$$S = \frac{E_f d^2}{E_m\left(D^2 - d^2\right)} \tag{5}$$

It is remarkable to observe how Eqs. (3)–(5) indicate that the interface shear stress distribution depends on the stiffness of fiber and matrix, through the unbalancing $S$. In more detail, such a distribution in general is given by an odd function (hyperbolic cosine), which is

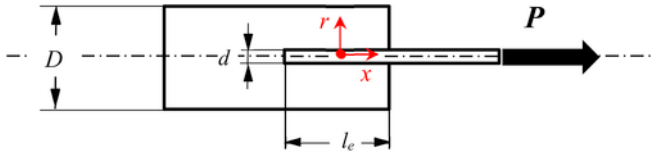


**Fig. 12.** Single-fiber pull-out test.

associated with the load transmission, plus an even function (hyperbolic sine) that is responsible of a non-symmetric distribution with an absolute maximum shear stress peak, that occur always at the attachment edge of the less stiff material [44]. The optimal stress distribution corresponds to the so called balanced joints ($S = 1$) in which the even function is null and equal stress peaks occur at the two attachment edges.

The pull-out tests for both the selected matrixes, epoxy and PLA, and for all the types of fibers considered, have been carried out by fixing $D \approx 10d = 2$ mm. With such values, taking into account of the actual stiffness of the fiber considered, Eq. (5) provides the following values of $S$:

$$S = \frac{E_f d^2}{E_m\left(D^2 - d^2\right)} = \begin{cases} agave - epoxy \rightarrow \left[(9.2 \div 18.7) * 0.2^2\right] \\ agave - PLA \rightarrow \left[(9.2 \div 18.7) * 0.2^2\right] \end{cases}$$

Eq. (6) shows that for any fiber and for both the matrixes considered, $S$ is always less than 1, i.e. the less stiff adherent is always the internal fiber so that the maximum shear stress occur at the attachment edge of the fiber ($x = l_e/2$–see Fig. 12). The following Fig. 13 shows the fiber/matrix interface shear stress distribution evaluate by Eq. (3) for unitary P load, for the various fiber considered and for epoxy (Fig. 13a) and PLA (Fig. 13b).

From Fig. 13 it is seen that, in accordance with the above exposed theory, the maximum shear stresses decrease with the fiber stiffness, and increase with the matrix stiffness. For a given matrix, therefore, the fiber stiffness has a noticeably influence on the pull-out strength of the biocomposite. Unfortunately, such an important correlation has not been evidenced in literature, so that the improvement of the pull-out strength of a biocomposite following a fiber treatment, has often been correlated with the improvement of the fiber-matrix adhesion, when instead the detected effects are due only to the increase of the fiber stiffness, given by the same fiber treatment.

In more detail, Fig. 13a shows that for the green epoxy matrix, the maximum shear stresses, variable from 1.85 to 2.87 MPa, increase of about +55% moving from the most stiff MPN fiber extracted by pressing, to the MDT, to the MDM, to the SDT and then to the MRN which value is near to that of the MDN fiber. For the less stiff PLA matrix, instead, for a given fiber, the maximum stresses are always lower (about −40%), and included between 1.09 and 1.74 MPa. Also for the PLA, such values increase of about +60% when the fiber stiffness decrease, i.e. moving from MPN to MDN, with the same order already observed for the epoxy. The maximum value of the shear stresses, that occurs at the incipient pull-out condition, can be computed by Eq. (3) for $x = l_e/2$ and substituting $P$ with the pull-out load $P_{pull\text{-}out}$ experimentally detected:

$$\tau_{\max} = \frac{P_{pull-out}\lambda}{2\pi d}\left[\frac{1-S}{1+S}\cdot Tanh\left(\lambda\frac{l_e}{2}\right) + \frac{(d/D)}{Tanh\left(\lambda l_e/2\right)}\right] \quad (7)$$

By substituting Eq. (7) into Eq. (1) the expression for the adhesion index is also obtained as:

$$r_a = \frac{\tau_{\max}}{\tau_{m,R}} = \frac{P_{pull-out}\lambda}{2\pi d\tau_{m,R}}\left[\frac{1-S}{1+S}\cdot Tanh\left(\lambda\frac{l}{2}\right) + \frac{(d/D)}{Tanh\left(\lambda l/2\right)}\right] \quad (8)$$

### 5.3. Pull-out test: experimental results

For both the matrixes and for all the fibers considered, the pull-out tests have been carried out by using an overlap length $l_e = 3$ mm (see Fig. 12); the experimental results are synthetically reported in Table 2, along with the maximum stresses evaluated by Eq. (7) and the adhesion index evaluated by Eq. (8). It is also reported the mean shear stress ($\bar{\tau}_m$) at the interface, which is considered often in literature as the reference parameter to evaluate the efficiency of the fiber-matrix adhesion, along with the corresponding adhesion index $r_a^{(*)} = \bar{\tau}_m/\tau_{\max}$. In order to appreciate the effects of the fiber stiffness, in the third column is reported also the Young modulus $E_f$, already reported in Table 1.

From Table 2 it is first observed that the values of the mean shear stress, that vary from 6.44 to 18.47 MPa, are in a good accordance with the values reported in literature for similar biocomposite [37]. In more detail, it is seen how, also without fiber treatments (fiber type MDN, MRN, MPN), the adhesion with epoxy is relatively good with maximum shear stresses always higher than 23 MPa, which correspond $0.64 < r_a < 0.73$. Also, the mercerization improves furtherly the adhesion (see MDM and MDT fibers) with maximum shear stress equal to about 32 MPa, which corresponds an adhesion index of

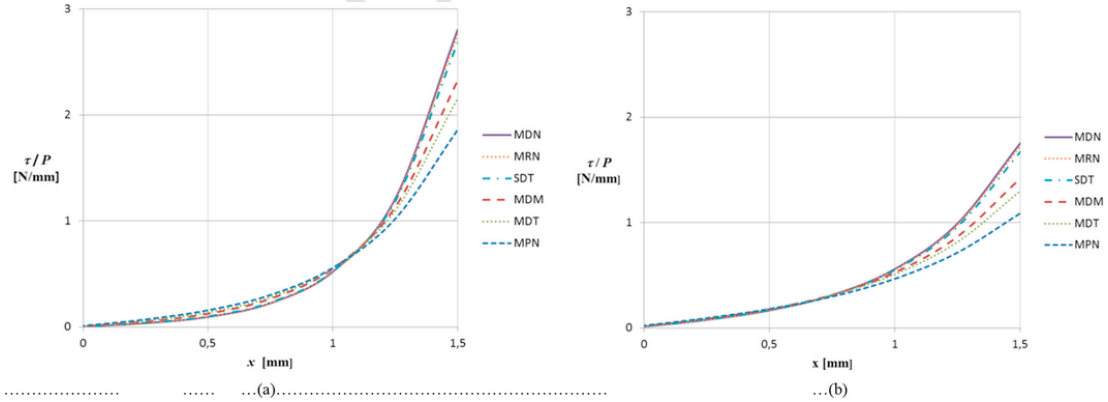


**Fig. 13.** Fiber-matrix Interface shear stress distribution for (a) green epoxy and (b) PLA matrix.

**Table 2**
Results of the pull-out tests for the various fiber types and matrixes considered.

| Fibra | Matrice | $E_f$ [GPa] | $P_{pull\text{-}out}$ [N] | $\tau_{max}$ [MPa] (from Eq. (7)) | $r_a$ (from Eq. (8)) | $\bar{\tau}_m$ [MPa] | $r_a^{(*)}$ |
|---|---|---|---|---|---|---|---|
| MDN | epoxy | 9,2 | 8,1 | 23,12 | 0,64 | 6,44 | 0,17 |
| MRN | epoxy | 9,3 | 9,2 | 28,09 | 0,72 | 7,88 | 0,21 |
| **MPN** | **epoxy** | **18,7** | **13,7** | **26,26** | **0,73** | **10,90** | **0,30** |
| MDM | epoxy | 12,7 | 13,5 | 32,28 | 0,89 | 10,74 | 0,29 |
| MDT | epoxy | 14,5 | 14,2 | 31,52 | 0,87 | 11,30 | 0,31 |
| SDT | epoxy | 9,8 | 10,1 | 27,85 | 0,77 | 8,04 | 0,22 |
| MDN | PLA | 9,2 | 10,3 | 17,61 | 0,46 | 8,20 | 0,21 |
| MRN | PLA | 9,3 | 10,5 | 17,83 | 0,46 | 8,36 | 0,22 |
| **MPN** | **PLA** | **18,7** | **16,1** | **16,75** | **0,44** | **12,81** | **0,33** |
| MDM | PLA | 12,7 | 21,9 | 30,26 | 0,79 | 17,43 | 0,45 |
| MDT | PLA | 14,5 | 23,2 | 29,20 | 0,76 | 18,47 | 0,48 |
| SDT | PLA | 9,8 | 18,3 | 30,06 | 0,79 | 14,57 | 0,38 |

about 0.88 (about +40% respect to the non-treated MDN fiber). However, it is confirmed that, unlike it is stated often in literature, moving from a fiber to an other, an increase (or decrease) of the pull-out load does not correspond necessarily to an increase (or decrease) of the fiber-matrix adhesion, i.e. to a variation of the maximum stress corresponding to the actual pull-out. In accordance with Eqs. (6) and (7), in fact, variations of the pull-out load can be also associated exclusively with variations of the fiber stiffness (and then of the unbalancing *S*), that lead to variations of the shear stress distribution, that is more uniform for stiffer fibers, see Fig. 13. As an example, moving from MRN fiber to the MPN fiber (fibers both without any treatment), that have in practice the same fiber-matrix adhesion (i.e. in practice the same $r_a$ index – see Table 2), it is detected a significant increasing of the pull-out load of about +40% (from 9.2 to 13.7 N), essentially due only to the higher stiffness of the MPN fiber (about double of that of MRN, see third column of Table 2); a qualitatively similar phenomenon occurs moving from the simple mercerization (MDN) to the mercerization under tensile loading (MDT): the adhesion index have a slight decrease (−2% about) whereas, on the contrary, the pull-out load have an appreciable increase (+5%), due to the fiber stiffness increase (about +14%). Finally, the comparison between the mean shear stresses (6.44–11.30 MPa, see the second last column of Table 2) with the matrix failure shear stresses (36–38 MPa), would lead to the erroneous evaluation of the fiber-matrix adhesion, since for all the examined fibers the $r_a^{(*)}$ index is always less than 0.31, whereas the proposed adhesion index $r_a$ takes correctly values always higher 0.64, showing a good fiber-matrix adhesion.

For the PLA, the examination of data reported in Table 2 shows qualitatively similar results; in particular, it is seen that for a given fiber, the pull-out loads are always higher than the epoxy ones. Such a result has led several authors to state that the PLA has an adhesion with the agave fibers, better than that detected with the epoxy resin [37] whereas, instead, such a result is solely due to the lower stiffness of the PLA respect to epoxy. In accordance with Eq. (6), in fact, the lower stiffness of the PLA leads to an higher *S* value (a value closer to the optimal unitary value) with a consequent benefic decreasing of the maximum shear stress (see 4th column of Table 2) provided by Eq. (7). For the PLA, it is detected an adhesion slight lower than the epoxy one, for both non-treated fibers ($r_a$ = 0.45 about, versus about 0.70 of the epoxy resin) and treated fibers ($r_a$ = 0.78 about, versus about 0.88 for the epoxy resin). The improvement of the adhesion given by the mercerization is, however, higher for the PLA (+73% about, versus +40% of the epoxy). Also for the PLA, the comparison between the mean shear stresses, that vary from 8.20 to 18.47 MPa, and the matrix failure stress ($\sigma_{m,R}$ = 38 MPa) would lead erroneously to evaluate as "low" the fiber-matrix adhesion, with values of $r_a^{(*)}$ included in the range 0.22–0.48, whereas the correct $r_a$ index falls in the higher range 0.44–0.79.

Finally, it is possible to state that the agave-epoxy adhesion and the agave-PLA adhesion, is always quite good, also for fibers without none treatment; the adhesion with the epoxy is, however, higher than that with the PLA, although this last exhibits higher pull-out loads, due to its less stiffness that leads to more balanced bi-material systems, i. e characterized by more uniform interface shear stress distribution. The mercerization leads to a further improvement of the fiber-matrix adhesion (increasing higher for the PLA), although significant pull-out strength increments is obtained simply by increasing the fiber stiffness, as it occurs for the more stiff MPN fibers obtained by the extraction method proposed in this work.

## 6. Conclusions

The theoretical-experimental study carried out in the present work, has permitted the optimization of the mechanical characteristics of the agave fibers, as well as the selection of proper matrixes potentially suitable for the manufacturing of ecofriendly high performance biocomposites reinforced by agave fibers. In detail, systematic analyses and experimental single fiber tests, have allowed to evidence that the fiber properties are significantly affected by the age of the leaves: moving from 1 to 4–5 years the strength and the stiffness increase respectively of about +25% and +50%. An even more important role is played by the fiber position: the best mechanical performance correspond to the fibers extracted from the intermediate segment of the leaf, that exhibit strength and stiffness up to about 3 times higher than that of the fiber extracted from the base segment; more limited are, instead, the difference with the fibers extracted from the apex segment (about 15%–20%). To obtain good quality fibers, it is therefore preliminarily necessary to extract these from the intermediate segment of the leaves having age of about 4–5 years. The experimental evidence has shown that such an optimization allows to reduce the typical high scattering of the experimental data, relative the commercial agave fibers (sisal).

Also the agave variety plays an important role on the mechanical performance of the fibers. In detail, the present study has shown that the fiber extracted from the agave marginata, a variety relatively diffuse in the Mediterranean area, exhibits mechanical properties significantly higher than that extracted from the agave sisalana (about +60% in terms of strength and stiffness for fiber mercerized under tensile loading), and therefore the marginata variety should be preferred to the sisalana one, for the manufacturing of high performance biocomposites.

In order to improve furtherly the mechanical properties of the agave fiber, without resorting to chemical treatments, it is proposed an innovative and ecofriendly method for the fiber extraction, based on the simple mechanical pressing of the leaves, alternated to proper water immersions. Such a proposed extraction method, allows to obtain fibers with properties significantly higher than those obtained by the traditional decortication process. The tensile stresses on fibers, due to the friction forces produced by the matrix flow associated with the pressing, leads in fact to benefic effects in terms of fiber compaction, with consequent significant increasing of the strength (about +40%), and especially of the stiffness (about +100%).

However, the development of a high performance biocomposite, goes through not only to an opportune optimization of the mechanical properties of the reinforcing fibers, obtained also through the proposed ecofriendly extraction process, but needs also an appropriate matrix selection and an careful study of the fiber-matrix adhesion. For this reason, an ecofriendly *green* epoxy (thermosetting matrix)

and a PLA (thermoplastic matrix), have been properly selected; they are matrixes potentially very suitable for the above mentioned scope to implement high performance biocomposites. In particular, the green epoxy is suitable for partially recyclable biocomposites, whereas the PLA, thanks to its biodegradability and compostability, allows to obtain completely renewable biocomposites. A systematic study of the fiber-matrix adhesion, carried out by an accurate theoretical analysis and successive single fiber pull-out tests, has shown that both the matrixes lead in general to a good adhesion with the agave fibers (epoxy is better than PLA, with adhesion index always higher than 0.5), also in absence of particular fiber treatments. Moreover, it has been shown that, due to the increase of the unbalancing (toward the optimal unitary values) and the consequent reduction of the interface shear stress peaks, the pull-out strength increases significantly with the fiber stiffness and decreases with the matrix stiffness (PLA is therefore better than epoxy). The best material couple, candidate to obtain a renewable high performance biocomposite, is therefore that constituted by the PLA reinforced by agave marginata fibers extracted by the proposed ecofriendly method, based on the simple pressing. However, in general the mercerization improves furtherly the fiber-matrix adhesion, although the use of NaOH increase the corresponding environmental impact; respect to the non-treated fibers, the effects of mercerization are lower for the epoxy (+40%), higher for the PLA (+73%), that also for this reason remain one of the most interesting matrix for the development of an high performance biocomposite.

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