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Effect of plasma treatment on the properties of Arundo Donax L. leaf fibres and its bio-based epoxy composites: A preliminary study

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ABSTRACT

A preliminary investigation about the effect of plasma treatment on the properties of natural fibres extracted from the leaf of the giant reed Arundo Donax L. and their compatibility with a bio-based epoxy resin is performed. To this aim, the influence of plasma treatment on the functional groups and on the thermal behaviour of fibre were investigated using Fourier transform infrared spectroscopy and thermogravimetric analysis. Moreover, the mechanical characterization of fibres was performed through fibre tensile tests. Short randomly oriented fibres/bio-based epoxy composites were manufactured by hand lay-up method followed by compression moulding, varying both fibres weight content and length. The influence of plasma treatment was evaluated by performing quasi-static and dynamic mechanical tests on the composites. Changes in the surface functional groups are obtained whereas neither the thermal stability nor the tensile properties of fibres are influenced by plasma treatment. Characterizations of the composites showed remarkable enhancements of mechanical properties, indicating that plasma treatment improves fibre/matrix adhesion. SEM micrographs showed that the resin better adheres around treated fibres compared to untreated ones.

1. Introduction

Natural fibre-reinforced composites have been deeply studied in the last decade due to their specific properties and their clearly positive environmental impact. The use of vegetable fibres instead synthetic ones (i.e. glass, carbon or kevlar fibres) presents many advantages such us low-cost production and processing, safe handling, reduced energy consumption and large availability. For these reasons, lignocellulosic fibres constitute an interesting alternative to traditional synthetic fibres in composite materials [1–6].

During last years, some authors proposed to use less common natural fibres (if compared to flax, hemp, jute, kenaf and sisal, for instance) such as okra [7], isora [8], ferula [9], althaea [10], piassava [11], sansevieria [12], buriti [13], artichoke [14] and culms of giant reed [15] as reinforcement for composite materials.

In this work, a new kind of fibres, extracted from the leaf of the giant reed Arundo Donax L., is investigated as a potential reinforcement in polymer composites.

The giant reed Arundo Donax L. is a perennial rhizomatous grass, widely diffused all around the world, from the temperate areas of the Europe (mainly in the countries of the Mediterranean area as Sicily) to the eastern countries as China and Japan, since it can be easily adapted to different climatic conditions (Fig. 1).

Moreover, it is a potentially high-yielding non-food crop, which is actually used for the production of energy and paper pulp [16]. In addition, the giant reed Arundo Donax L. grows plenty and naturally and, thanks to its high growth rate, represents an invasive species which disposal could result to be difficult. It was recently considered for the manufacturing of chipboard panels alternative to the wood-based ones [17] and to be applied as reinforcement of thermoset [18] and thermoplastic [19] matrix polymer composites as well as to partially replace sand in concrete mixes [20].

As well known, the use of natural fibres, as an alternative to the synthetic ones, as reinforcement of composite materials, has received growing attention, owing to their specific properties, price, advantages for health, and recyclability. Due to the above reasons, natural fibres begin to be used as reinforcement of composite materials for engineering applications. In particular, Alomayri et al. [21] produced via layup technique geopolymer composites reinforced with different layers of woven cotton fabric, showing that the mechanical properties (i.e. flexural strength,

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Fig. 1. Arundo Donax plant.

flexural modulus, impact strength and fracture toughness) of cotton fabric reinforced geopolymer are superior to the neat geopolymer matrix. Moreover, they showed that all the mechanical properties are improved by increasing the cotton fibre contents, due to the unique properties of cotton fibres in withstanding greater bending and fracture forces than the more brittle geopolymer. Yan et al. [22] analysed the flexural behaviour (i.e. three and four point bending) of plain concrete and coir fibre reinforced concrete beams externally strengthened by flax fabric reinforced polymers. The experimental results showed that the peak load, flexural strength, deflection and fracture energy of both plain concrete and coir reinforced concrete enhance with increasing of confinement flax layers. Yan and Chouw [23] compared the compression behaviour of coir fibre reinforced concretes confined with glass/carbon and flax fibre reinforced polymers. They showed that the confinement effectiveness of flax FRP confined normal strength concrete is comparable to those of glass/carbon confined normal strength concrete, although the tensile strength of flax FRP samples is significantly lower than that of glass/carbon ones. The same authors studied the lateral crushing behaviour of empty and polyurethane-foam filled flax fabric reinforced epoxy composite tubes as function of tube thickness, tube inner diameter and foam filler [24]. The comparison with existing tubes shows that natural flax/epoxy tube can be considered as good alternative to aluminium tube and to glass/carbon composite tube as energy absorbers. Hakamy et al. [25] studied the influence of calcined nanoclay and chemical treatment on the microstructure and mechanical properties of treated hemp fabric-reinforced cement nanocomposites. The experimental results showed that alkali-treated hemp fabric reinforced cement composites exhibit higher flexural strength when compared to their non-treated counterparts and the mechanical properties are improved due to calcined nanoclay addition. Moreover, it was found that calcined nanoclay behaves not only as a filler to improve the microstructure, but also as the activator to facilitate the pozzolanic reaction and thus improved the adhesion between the treated hemp fabric and the matrix.

In addition to their encouraging features, natural fibres present also some drawbacks like low mechanical properties, poor compatibility with polymeric matrix and high moisture absorption of fibres. These features result in a low ability to transfer stress from matrix to fibre in addition to dimensional changes of fibres that may lead to microcracking of composites, thus reducing their mechanical properties.

In order to improve the performances of natural fibre reinforced composites by improving fibre-matrix compatibility, the surface properties of natural fibres can be modified by means of adequate treatments (i.e. chemical or physical ones). In particular, physical modifications induced by plasma treatment of the reinforcement surface can improve the compatibility with the polymer matrices. Atmospheric plasma is interesting due to it is cost effective, continuous in operation and provides a relatively uniform and stable treatment throughout the surface [26]. Depending on the material to be treated, plasma flow can cause ablation, cross-linking or surface activation. Ablation consists of the removal of organic residues as well as surface layers at a molecular level. Cross-linking occurs as a result of the interaction between two or more radicals leading to the formation of covalent links whilst surface activation increases the surface energy as a result of generation of polar groups on the reinforcement surface [27]. This kind of treatment is widely used for common natural fibres [28–30] because, differently from chemical treatments, it is a simple process without any pollution which can be considered as dry and clean. Moreover, plasma treatment is also used to improve the surface characteristics of synthetic fibres like carbon [31,32] glass [33] and Kevlar [34,35] or inorganic fillers as marble powder [36].

The goal of the present paper is the evaluation of the feasibility of bio-based, low environmental impact composites reinforced with fibres extracted from the leaf of the giant reed Arundo Donax L.

The surface functional groups and the thermal stability of untreated and plasma treated arundo fibres were determined by Fourier transform infrared spectroscopy (ATR-FTIR) and thermogravimetric (TGA) analyses, respectively. Moreover, the effect of plasma treatment on fibre tensile properties was determined by through single fibre tensile tests.

As a preliminary study, short randomly oriented fibres/bio-based epoxy composites were manufactured by hand lay-up method followed by compression moulding, varying fibre weight fraction (i.e. 2.5% and 5%) and length (i.e. 1 cm and 3 cm). The influence of plasma treatment was evaluated by performing quasi-static and dynamic mechanical tests. Furthermore, scanning electron microscopy (SEM) was used to investigate the fracture surface morphologies of the plasma treated and untreated composites.

2. Experimental details

2.1. Materials

The giant reed Arundo Donax L. consists of culms, which grow up to 6 m. Since the leaves are placed in correspondence of each internode, spaced 10–30 cm [37], each culm carries up to 30 leaves. Furthermore, each leaf can reach a length up to 80 cm and a width up to 7.0 cm [38].

In this work, leaves ranging from 20 cm to 25 cm were separated from the culms immediately after collecting the fresh plant from a plantation in the area of Palermo (Sicily). Then, fibres with a length between 15 cm and 20 cm were extracted from the leaf by mechanical separation by traditional combing process with a metal teeth brush. The obtained fibres were then dried at 103 °C for 24 h in an oven to remove the moisture content (Fig. 2).

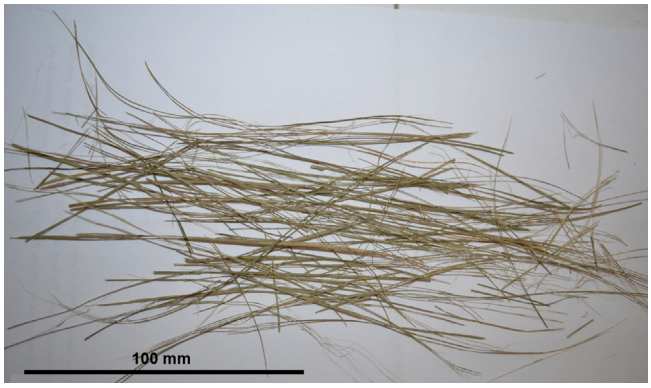

Fig. 2. Arundo leaf fibres after drying.

It is well known that lignocellulosic fibres show a non-uniform cross section and irregular shape. For this reason, the diameter of fibres extracted from the leaf of Arundo Donax L. was measured through optical observations by using an optical microscope model MS5 by Leica (Wetzlar, Germany) at three different locations along the single fibre: bottom, middle and top. The apparent cross-sectional area of each fibre was then calculated assuming a circular cross-section and, as suggested by the literature [7,39] by averaging fibre diameter.

A bio-based epoxy Super Sap™ 100 resin by Entropy Bio-Resins Co (San Francisco, CA, USA) mixed with its Super Sap™ 1000 Hardener (2:1 mix ratio by volume) was used as matrix of the bio-epoxy composites. Table 1 shows the main properties of the bio-based epoxy matrix, as reported in the supplier datasheet. The bio-based epoxy is a resin made from up of 37% bio-content obtained as co-products of other green industries including wood pulp and bio-fuels production. It is classified as a USDA (United States Department of Agriculture) BioPreferred^{SM} Product using ASTM D 6866 standard [40] and has a total calculated biomass of 50% [41]. Four bio-epoxy composites were manufactured by varying both the fibre weight fraction (i.e. 2.5% and 5%) and the length of randomly oriented fibres (i.e. 1 cm and 3 cm). For each condition, bio-epoxy resin was reinforced with untreated and plasma treated fibres in order to evaluate the effect of plasma treatment on the mechanical performances of composites.

Composite panels were manufactured by hand lay-up method followed by compression moulding: i.e., chopped fibres were prepared and were impregnated with the bio-based epoxy matrix in a mould having dimension 200 mm × 100 mm × 3 mm. Curing was done at 25 °C for 7 days as suggested in the supplier's datasheet, under a constant pressure of 1 kPa. Afterwards, specimens for quasi-static and dynamic characterizations were cut by using a diamond saw.

2.2. Plasma treatment

Plasma treatment was performed using a plasma reactor model Tucano by Gambetti (Binasco, Italy), with a chamber with volume of about 5.5 L. The process was carried out in four steps: i) reaction chamber from ambient pressure to 0.2 mbar; ii) stabilization of the inner pressure (5 s); iii) air inlet and plasma reaction (during plasma treatment the total pressure was 0.5 mbar); iv) venting to ambient pressure (about 150 s). In particular, arundo fibres were exposed to a plasma power of 150 W for 120 s.

Table 1
Main properties of the bio-based epoxy resin Super Sap™ 100/1000.

Performance data		Processing data	
Tensile modulus [GPa]	2.62	Mix ratio by volume	2:1
Tensile strength [MPa]	56.5	Mix ratio by weight	100:48
Elongation at break [%]	7.0	Density at 25 °C [g/cm^3]	1.09
Flexural modulus [GPa]	2.28	Viscosity at 25 °C [cPs]	600
Flexural strength [MPa]	77.0	Pot life at 25 °C [min]	25
Compression strength [MPa]	72.1	Tack free time at 25 °C [h]	4
Hardness (Shore D)	70–80	Full Cure time at 25 °C [days]	7

2.3. Characterization methods

2.3.1. Thermal analysis

Thermogravimetric analysis (TGA) was carried out to define the thermal stability of untreated and plasma treated arundo fibres by using a thermobalance TG/DTA NETZSCH (Selb, Germany), model TG 449 F1 Jupiter. Particularly, powdered samples were placed in a alumina pan and heated from 30 to 1000 °C at a heating rate of 10 °C/min in nitrogen atmosphere.

2.3.2. Fourier transform infrared spectroscopy

The effect of plasma treatment on functional groups of arundo fibres was investigated by attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) analysis. IR spectra were recorded with a resolution of 2 cm^{-1} in the range of 4000–500 cm^{-1}, by using a spectrometer model spectrum Two by Perkin Elmer (Waltham, MA, USA), operating in attenuated total reflectance (ATR) mode.

2.3.3. Single fibre tensile tests

A population of 50 fibres for each condition (i.e. untreated and plasma treated fibres) were mechanically tested in tension, according to ASTM standard method D 3379 standard [42], using an U.T.M. model Z005 by Zwick-Roell (Ulm, Germany) equipped with a load cell of 200 N. The displacement rate was set equal to 1 mm/min and gauge length to 30 mm.

Since the mechanical properties of natural fibres present high scatter due to their intrinsic characteristic (e.g. irregular shape, age of the plant, fibre extraction processes and natural defect), the results were statistically analysed using an ad-hoc code developed in Matlab® environment [43]. In particular, a statistical approach is required to evaluate the mechanical properties: i.e. the experimental data were statistically analysed using a two-parameter Weibull distribution [44,45].

2.3.4. Quasi-static flexural tests on composites

Quasi-static flexural tests were performed on composites according to ASTM D 790 standard [46]. To this aim, an U.T.M. model Z005 by Zwick-Roell (Ulm, Germany), equipped with a 5 kN load cell, was used. Five prismatic samples (3 mm × 10 mm × 96 mm) for each condition were tested in three point bending configuration. The span and the crosshead speed were set equal to 80 mm and 1.5 mm/min, respectively.

2.3.5. Dynamic mechanical tests on composites

Dynamic mechanical analysis was carried out on composites using a dynamic mechanical analysers model DMA + 150 by Metravib (Acoem Group, Limonest, France), equipped with a load cell of 150 N.

The experiments were performed under tensile mode at a frequency of 1 Hz. Prismatic samples of size 3 mm × 3 mm × 45 mm were used. The tests were conducted at temperatures from room to 160 °C with heating rate of 2 °C/min, under nitrogen atmosphere.

2.3.6. Morphological analysis

Scanning electron microscopy (S.E.M.) analysis was performed on the flexural fractured surfaces of composites by using a Phenom World (Eindhoven, Netherlands) scanning electron microscopy,

model Phenom Pro X. Before analysis, each sample was sputter-coated with a thin layer of gold to avoid electrostatic charging under the electron beam.

3. Results and discussion

3.1. Fibres

3.1.1. Thermal analysis

The thermal stability of natural fibres is known to be one of the limiting factors in their use as reinforcement in composite structures [7–14,47]. The results of the thermal analysis of untreated Arundo leaf fibre are shown in Fig. 3.

The DTG curve of the arundo fibre shows an initial peak between 30 °C and 130 °C (loss in weight about 6%), which corresponds to the vaporization of absorbed water. After this peak, the curve exhibits two degradation steps. In particular, thermal degradation of the fibre starts at 210 °C (i.e. onset degradation temperature) and the first degradation shoulder peak occurs at about 285 °C [7,14,15]. This is attributed to the thermal depolymerisation of hemicelluloses and pectin and the glycosidic linkages of cellulose (19% weight loss). The major second peak, at about 340 °C, is due the degradation of α-cellulose (30% weight loss) [48]. Similar peaks were observed at 321 °C, 308.2 °C, 298.2 °C, 309.2 °C, 352 °C and 320 °C for bamboo, hemp, jute, kenaf fibres [49], artichoke [14] and arundo fibres extracted from the culm [15], respectively. The degradation of lignin, whose structure is a complex composition of aromatic rings with various branches, happens at a very low weight loss rate within the whole temperature range from ambient to temperatures higher than 700 °C [7,14,50].

Furthermore, thermal analysis shows that the arundo leaf fibre is stable until around 210 °C, value similar to those of other natural fibres like okra (220 °C), hemp (250 °C), curaua (230 °C), kenaf (219 °C), Jute (205 °C) [7], sisal (230 °C) [48], bagasse (222 °C) and bamboo (214 °C) [49], artichoke (230 °C) [14] and arundo fibres extracted from the culm (275 °C) [15], respectively. This temperature is higher than the polymerization process temperature so that the arundo leaf fibre is not subjected to thermal degradation during the curing process.

By observing Fig. 4, it is possible to notice that plasma treated fibre show similar behaviour to untreated one, thus indicating that plasma treatment does not influence its thermal stability.

3.1.2. Fourier transforms infrared spectroscopy

ATR-FTIR assignment of functional groups of untreated and plasma treated arundo leaf fibres can be seen in Fig. 5. The peak at

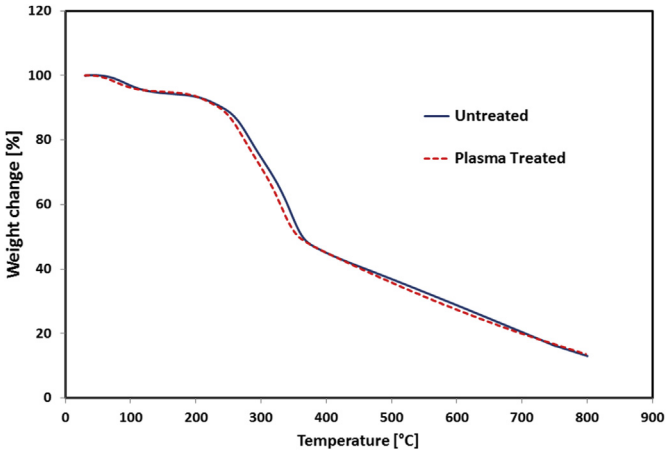

Fig. 4. TG curves of untreated and plasma treated fibres.

3340 cm^{-1} can be caused by the O–H stretching vibration and hydrogen bond of the hydroxyl groups ([9,50]). The peaks at 2929 cm^{-1} and 2859 cm^{-1} are the characteristic band for the C–H stretching vibration from CH and CH_2 in cellulose and hemicellulose components [51] while the absorption band centred at 1737 cm^{-1} can be attributed to the C=O stretching vibration of the acetyl groups in hemicellulose [52].

The peak centred at 1652 cm^{-1} may be explained by the presence of water in the fibres [52] while the little peak at 1521 cm^{-1} is attributed to C=C stretching of benzene ring of the lignin [7]. The absorbance at 1430 cm^{-1} is associated to the CH_2 symmetric bending [53]. The peaks observed at 1379 cm^{-1} and 1344 cm^{-1} are attributed to the bending vibration of C–H and C–O groups of the aromatic ring in polysaccharides [54] while the absorbance peak centred at 1251 cm^{-1} is due to the C–O stretching vibration of the acetyl group in lignin [55]. The peak at 1165 cm^{-1} is associated to C–O–C stretching vibration of the pyranose ring in polysaccharides [50].

The changes due to the plasma treatment is notable just in the range of 800–1100 cm^{-1}, where new small peaks are evident. In particular, a change from shoulder to peak is observed at 1106 cm^{-1} and a new peak at 1060 cm^{-1} appears after plasma treatment. This means that plasma treatment modifies the structure of the fibre surface: the C–O–C symmetric glycosidic stretching or ring stretching mode at ~1100 cm^{-1} and the C–OH stretching vibration of the cellulose backbone at 1060–1050 cm^{-1} (C–O secondary

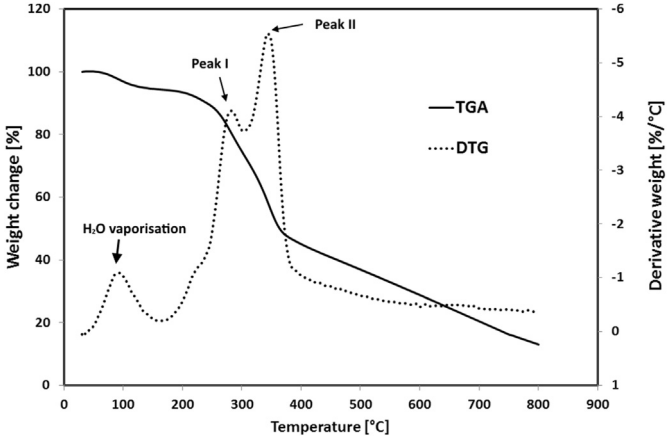

Fig. 3. TG and DTG curves of untreated arundo leaf fibres.

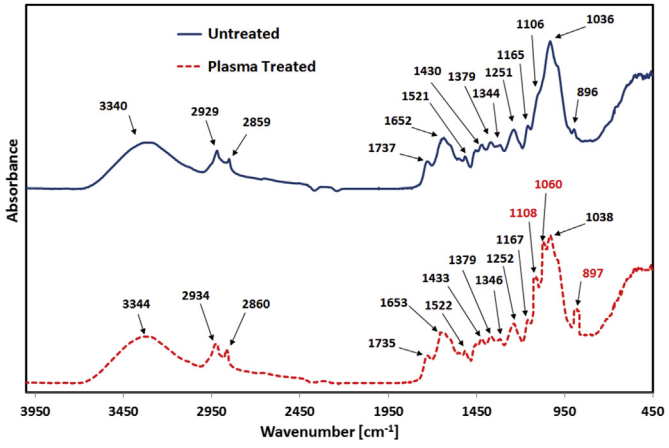

Fig. 5. FTIR spectra of untreated and plasma treated arundo leaf fibres.

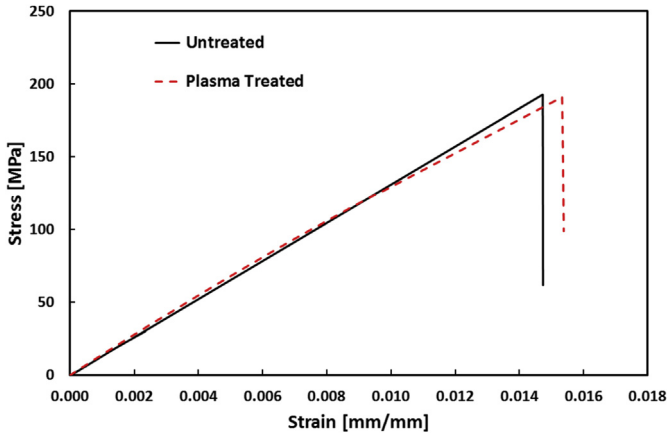

Fig. 6. Typical stress-strain curves of untreated and plasma treated fibres.

alcohol) arise from the polysaccharide components (mainly cellulose) [28,56].

The intense band, centred at 1036 cm^{-1}, can be associated to the C–O stretching modes of hydroxyl and ether groups in cellulose [51] whereas the little peak at 896 cm^{-1} can be attributed to the presence of b-glycosidic linkages between the monosaccharides [7]. By observing the spectrum of plasma treated fibre, an appreciable change in the intensity of this peak is evident, as already found by other authors [28,57]: this may be due to cleaning effect of plasma treatment on the fibre surface.

3.1.3. Single fibre tensile tests

Similarly to other lignocellulosic fibres [7,14,15,58], arundo leaf fibres show a brittle behaviour under tensile conditions with a drop of load corresponding to the fibre failure. No noticeable change in the stress-strain tensile curve of the plasma treated fibres was found: this means that plasma treatment does not influence the tensile behaviour of arundo leaf fibres (Fig. 6).

As well known, results of tensile tests on natural fibres are difficult to analyse because of the observed high scatter. This is related to three main factors, mainly consisting in parameters and conditions of the test, area measurements and natural plant characteristics. In particular, this latter factor is influenced by source and age of the plant, the presence of defects and the fibre extraction procedure [43].

For all of these reasons, a statistical approach is required in order to evaluate the tensile properties of natural fibres. The experimental data were statistically analysed using a two-parameter Weibull distribution [7,14,43,44].

Fig. 7 shows the Weibull distributions for (a) tensile strength, (b) Young's modulus and (c) strain at failure of untreated arundo leaf fibres. It can be seen that this model provides a good fitting of the data for both mechanical properties. Similarly, Weibull's statistical analysis was applied on the experimental tensile results of plasma treated fibres. For sake of conciseness, the Weibull distributions are not shown while the statistical parameters of both fibres (i.e. untreated and plasma treated) are reported in Table 2. The Weibull fitting parameter allows to statistically describe and evaluate the mechanical properties of natural fibres. In particular, a shape factor is related to the reliability of the experimental data. As higher is the shape factor as more reliable is the result of the analysis. Moreover, higher shape parameter is equivalent to lower coefficient of variation in a normal distribution. The scale parameter defines the position of the Weibull curve. As shown in Table 2, the tensile properties are just slightly influenced by plasma treatment [28].

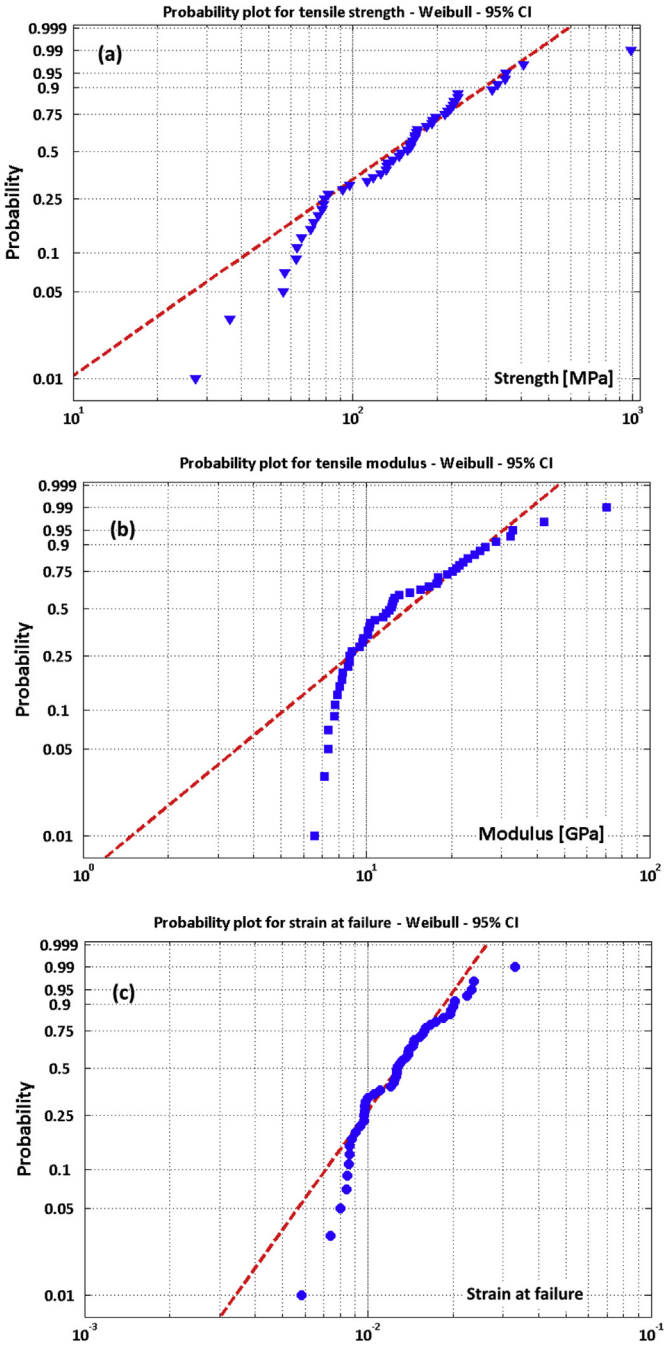

Fig. 7. Weibull distribution for (a) tensile stress, (b) deformation and (c) Young's modulus of arundo leaf fibres.

Table 3 shows that mechanical properties of untreated arundo leaf fibre are comparable to those of other less common natural fibres investigated as potential reinforcement in polymer matrix composites.

3.2. Composites

3.2.1. Quasi-static flexural tests

Fig. 8 shows the results of quasi-static flexural tests for untreated and plasma treated bio-epoxy composites, at varying both fibre weight content and length. In particular, both composites show increments in modulus if compared to the neat resin (i.e.

Table 2
Characteristic statistical parameters for tensile properties of arundo leaf fibres.

		Scale	Shape[a]	Mean value	Stand dev.	Median	Correlation[a]
Untreated	Strength[MPa]	193.47	1.42	173.90	146.09	152.81	0.98
	Modulus [GPa]	18.04	1.64	15.96	11.17	12.17	0.97
	Strain at failure [mm/mm]	0.0153	2.74	0.0136	0.00515	0.0127	0.98
Plasma Treated	Strength [MPa]	192.32	1.67	170.45	97.25	132.60	0.99
	Modulus [GPa]	17.98	1.75	14.90	3.28	11.35	0.99
	Strain at failure [mm/mm]	0.0155	2.86	0.0138	0.00213	0.0128	0.99

[a] Dimensionless.

Table 3
Mechanical properties of untreated arundo leaf fibres and some less common natural fibres from literature.

Fibre	Tensile strength [MPa]	Young's modulus [GPa]	Strain at failure [%]	References
artichoke	201	11.6	–	[10]
okra	281	16.5	–	[3]
ferula	475	52.7	4.2	[5]
althaea	415	65.4	3.9	[6]
piassava	77	2.93	10.45	[7]
alfa	250	20	–	[36]
sansevieria	50–585	2.5–7.8	2.8–21.7	[8]
arundo culm	248	9.4	3.24	[11]
arundo leaf	**193.5**	**18**	**1.53**	//

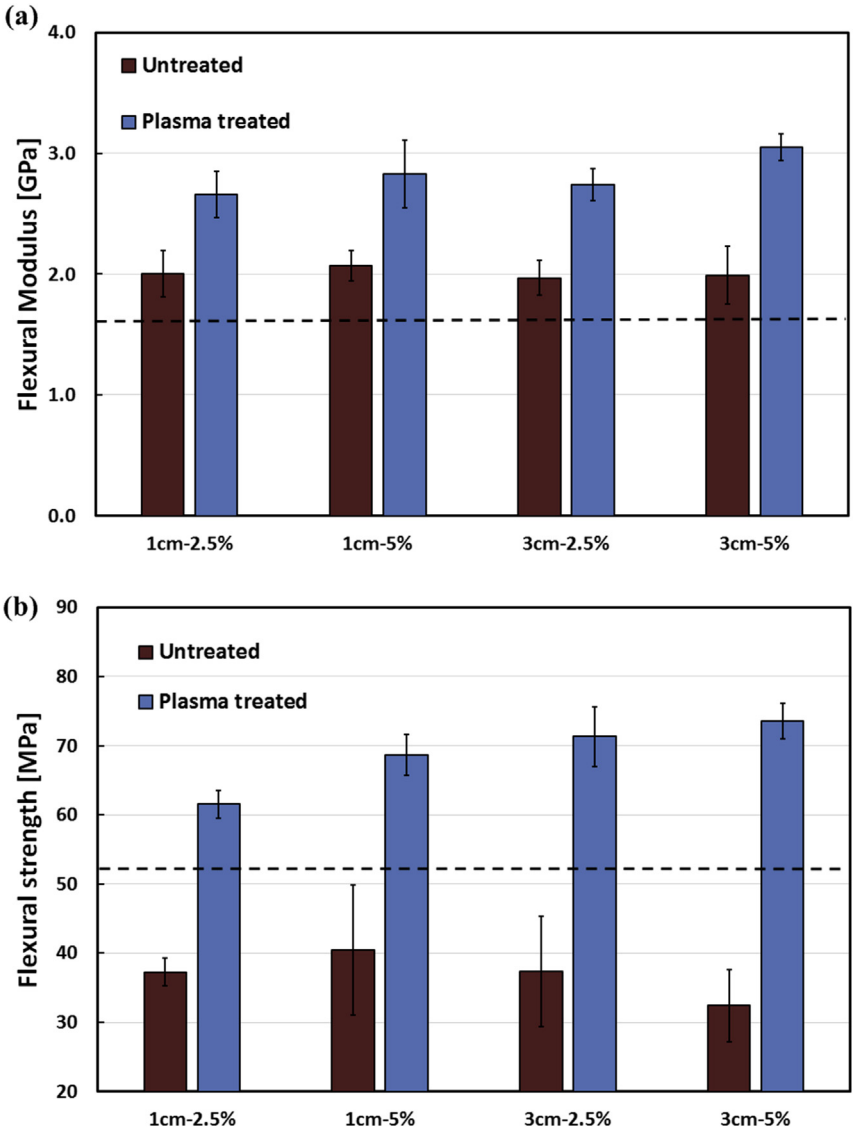

Fig. 8. Quasi-static flexural properties of bio-epoxy composites.

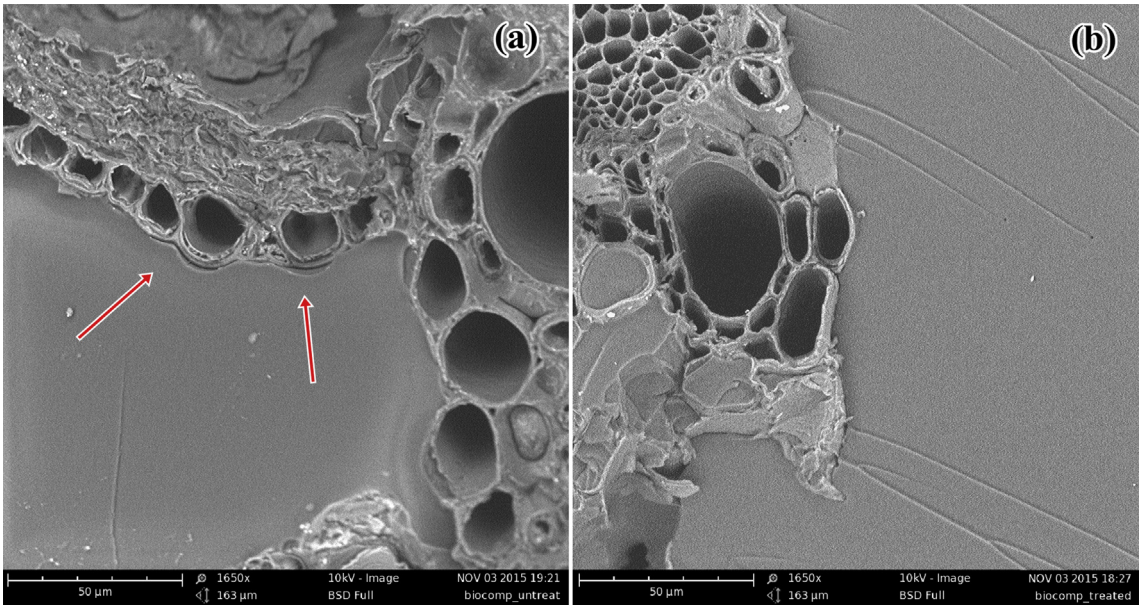

Fig. 9. SEM micrographs of the fractured surfaces of (a) untreated and (b) plasma treated arundo fibre/bio-epoxy composites.

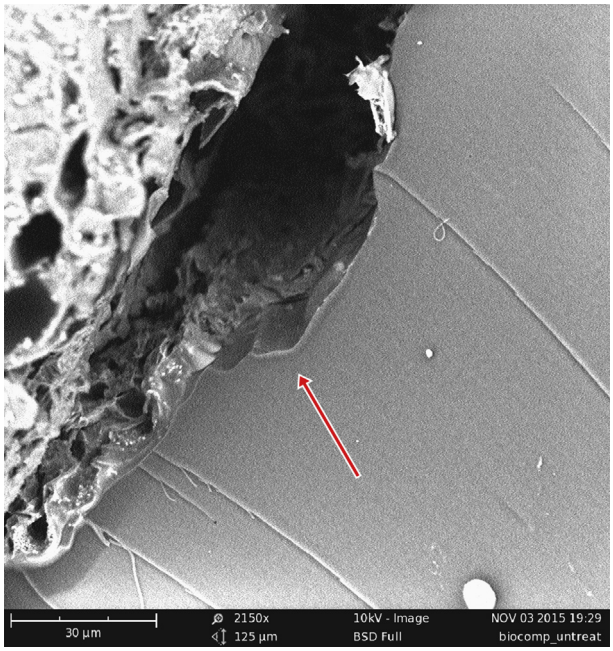

Fig. 10. Evidence of fibres pull-out mechanism on the fractured surfaces of untreated arundo fibre/bio-epoxy composites.

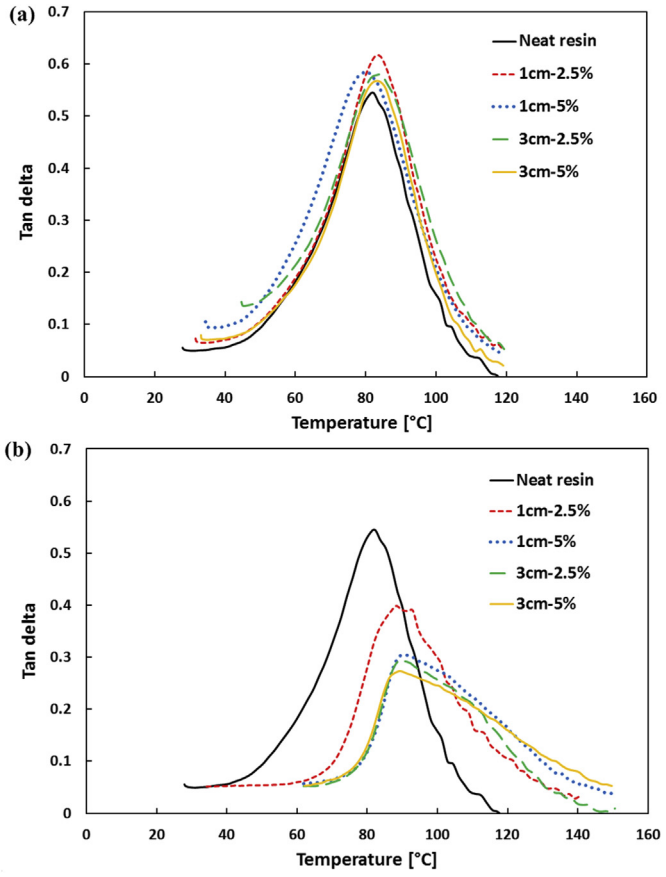

Fig. 11. Variation of Tanδ with temperature for (a) untreated and (b) plasma treated arundo fibre/bio-epoxy composites.

1.66 GPa, indicated by the black dashed in Fig. 8a), regardless of fibre weight content and length. As concerns untreated composites, flexural modulus does not depend from the fibre weight content and length. This can be explained taking into account two competitive contributions to the material stiffness: (i) greater amount of reinforcement increases the composite stiffness and longer fibres guarantee larger interface area, leading to better matrix-fibre shear stresses transmission; (ii) the number of interfaces increases by increasing both fibre weight content and length leading thus, in turn, to a worsening of the composites properties, due to the weak fibre-matrix adhesion. For plasma treated composites, the beneficial effect of the treatment on the fibre-matrix compatibility leads to the above increment of the flexural modulus.

Fig. 8b shows the results concerning the flexural strength. As highlighted above, an increment in interface area between low

Table 4
Dynamic mechanical analysis results.

		Tg [°C]	Tanδ max	E_{room} [GPa]
	Neat Resin	82.2 ± 0.85	0.53 ± 0.02	1.63 ± 0.01
Untreated	1cm-2.5%	82.7 ± 0.10	0.60 ± 0.02	2.13 ± 0.03
	1cm-5%	80.3 ± 0.43	0.58 ± 0.02	2.01 ± 0.18
	3cm-2.5%	81.8 ± 1.16	0.56 ± 0.02	1.88 ± 0.07
	3cm-5%	82.7 ± 0.87	0.57 ± 0.02	2.02 ± 0.02
Plasma Treated	1cm-2.5%	89.1 ± 0.7	0.40 ± 0.07	2.53 ± 0.02
	1cm-5%	90.4 ± 1.35	0.30 ± 0.03	2.84 ± 0.05
	3cm-2.5%	90.5 ± 1.21	0.30 ± 0.03	2.54 ± 0.01
	3cm-5%	89.8 ± 0.53	0.27 ± 0.03	3.03 ± 0.01

compatible materials (i.e. untreated arundo fibre and bio-epoxy matrix) leads to the statistical increment of voids and defects, which promote premature failures of the composites. In particular, the flexural strength of untreated composites is lower than that of neat resin (i.e. 53.4 MPa) and an high scatter was registered, regardless of fibre weight content and length. Improving the interface quality by plasma treating the fibres, an increase in flexural strength is observed up to reach 73.5 MPa for the 3cm-5% composites.

By observing the SEM micrographs on the fractured surfaces shown in Fig. 9, it is possible to confirm that the bio-epoxy resin better adheres around plasma treated fibres, in comparison to untreated fibres. In particular, Fig. 9a shows the presence of large debonded area in correspondence of the untreated fibre-matrix interface (indicated by the arrows) that acts as crack nucleation zones, thus decreasing both tensile modulus and strength of the composites. This is mainly due to the low compatibility between the hydrophilic natural fibre and the hydrophobic polymer used as matrix. On the other hand, Fig. 9b highlights the beneficial effect of plasma treatment on the fibre-matrix compatibility: i.e. the composites are characterized by continuous and regular interfaces. Moreover, there is no evidence of fibre pull-out mechanisms. This means that, if arundo leaf fibres are plasma treated, a very high degree of matrix adhesion is achieved, thus confirming the validity of this dry and clean method in the enhancement of the mechanical properties of polymer based composites reinforced with natural fibres.

Furthermore, by observing in Fig. 10 the SEM micrograph at high magnification of the fractured surface of an untreated arundo fibre/bio-epoxy specimen, it is possible to note an area affected by fibre pull-out phenomena, confirming the need to improve the fibre-matrix interaction.

3.2.2. Dynamic mechanical tests

Fig. 11 shows tan delta (also named damping factor) variation with the temperature for neat resin (continuous black line), untreated and plasma treated composites. Incorporation of fibres in a polymeric matrix affects the damping behaviour of the composites, which is due both to shear stress concentrations at the fibre-matrix interfaces and to the viscoelastic energy dissipation in the matrix [59,60]. Hence, it depends on the fibre-matrix adhesion: i.e. a weak fibre-matrix adhesion leads to higher values of tan delta [59,61] while a good fibre-matrix adhesion limits the mobility of the polymer chains, thus reducing the damping and shifting the glass transition (T_g) to higher temperatures [18].

In particular, from Fig. 11a and Table 4, it is possible to observe slight increases in the tan delta peak values of untreated composites in comparison to that of the neat resin. This is due to the weak fibre-matrix compatibility, thus resulting in a bad interface quality. Consequently, there is no noticeable change in the glass transition temperature between composites and neat resin, thus indicating no restriction to the macromolecules chain motion due to presence of the untreated fibres within the bio-epoxy matrix. Vice versa, plasma treated composites experience different behaviour, as shown in Fig. 11b and Table 4. In particular, regardless fibre weight content and length, the tan delta peak values of the composites are lower than that of the neat resin, confirming the enhancement of the fibre-matrix interface properties due to the plasma treatment. Due to this beneficial effect, the treated fibres hinder the polymeric chain mobility, thus resulting in an increase of the glass transition temperature (i.e. up to 89.8 °C for 3cm-5% composites) in comparison to the neat resin (i.e. 82.2 °C).

Table 4 also reports the Young moduli measured at room temperature for all the investigated composites. These last results confirm the trends of the quasi-static moduli, discussed in the Section 3.2.1.

4. Conclusions

The goal of the present paper is to evaluate the feasibility of bio-based, low environmental impact epoxy composites reinforced with fibres extracted from the leaf of the giant reed Arundo Donax L. As a preliminary study, bio-based epoxy composites reinforced with low content of short randomly oriented fibres were manufactured and tested in order to evaluate the effect of plasma treatment on the fibre-matrix compatibility.

The surface functional groups and the thermal stability of Arundo leaf fibres were determined by Fourier transform infrared spectroscopy (ATR-FTIR) and thermogravimetric (TGA) analyses, respectively. The effect of plasma treatment on fibre tensile properties were determined by through single fibre tensile tests.

Short randomly oriented fibres/bio-based epoxy composites were manufactured by hand lay-up method followed by compression moulding, varying fibre weight fraction (i.e. 2.5% and 5%) and length (i.e. 1 cm and 3 cm). The influence of plasma treatment was evaluated by performing quasi-static and dynamic mechanical tests. Furthermore, scanning electron microscopy (SEM) was used to investigate the fracture surface morphologies of the plasma treated and untreated composites.

From the experimental results, it was possible to state that:

- Plasma treated fibres show similar thermal behaviour to untreated ones, thus indicating that plasma treatment does not influence their thermal stability;
- The tensile properties (i.e. Young modulus, tensile strength and strain at failure) of arundo leaf fibres are just slightly influenced by plasma treatment;
- FTIR analysis shows that plasma treatment modifies some functional groups of arundo leaf fibre evidencing the cleaning effect of plasma treatment on the fibre surface;
- The morphological analysis evidences the beneficial effect of plasma treatment on fibre-matrix adhesion;
- Plasma treatment leads to significant improvements of quasi-static flexural properties (i.e. both modulus and strength) of the bio-epoxy composites, regardless of fibre content and length;
- DMA results confirm the weak compatibility between untreated fibres and bio-epoxy matrix and the enhancement of the fibre-matrix interface properties due to the plasma treatment.

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References

[1] Gurunathan T, Mohanty S, Nayak SK. A review of the recent developments in biocomposites based on natural fibres and their application perspectives. Compos Part A;77:1–25.
[2] Yan L, Chouw N, Jayaraman K. Flax fibre and its composites - a review. Compos Part B 2014;56:296–317.
[3] Akil HM, Omar MF, Mazuki AAM, Safiee S, Ishak ZAM. Abu Bakar A. Kenaf fiber reinforced composites: a review. Mater Des 2011;32:4107–21.
[4] Ku H, Wang H, Pattarachaiyakoop N, Trada M. A review on the tensile properties of natural fiber reinforced polymer composites. Compos Part B 2011;42:856–73.
[5] Koronis G, Silva A, Fontul M. Green composites: a review of adequate materials for automotive applications. Compos Part B 2013;44:120–7.
[6] La Mantia FP, Morreale M. Green composites: a brief review. Compos Part A 2011;42:579–88.
[7] De Rosa IM, Kenny JM, Puglia D, Santulli C, Sarasini F. Morphological, thermal and mechanical characterization of okra (Abelmoschus esculentus) fibres as potential reinforcement in polymer composites. Compos Sci Technol 2010;70:116–22.
[8] Mathew L, Joseph KU, Joseph R. Isora fibre: morphology, chemical composition, surface modification, physical, mechanical and thermal properties - a potential natural reinforcement. J Nat Fibres 2006;3:13–27.
[9] Seki Y, Sarikanat M, Sever K, Durmuşkahya C. Extraction and properties of Ferula communis (chakshir) fibers as novel reinforcement for composites materials. Compos Part B 2013;44:517–23.
[10] Sarikanat M, Seki Y, Sever K, Durmuşkahya C. Determination of properties of Althaea officinalis L. (Marshmallow) fibres as a potential plant fibre in polymeric composite materials. Compos Part B 2014;57:180–6.
[11] d'Almeida JRM, Aquino RCMP, Monteiro SN. Tensile mechanical properties, morphological aspects and chemical characterization of piassava (Attalea funifera) fibers. Compos Part A 2006;37:1473–9.
[12] Sathishkumar TP, Navaneethakrishnan P, Shankar S, Rajasekar R. Characterization of new cellulose sansevieria ehrenbergii fibers for polymer composites. Compos Interfaces 2013;20:575–93.
[13] da Silva Santos R, de Souza AA, De Paoli MA, de Souza CML. Cardanol formaldehyde thermoset composites reinforced with buriti fibers: preparation and characterization. Compos Part A 2010;41:1123–9.
[14] Fiore V, Valenza A, Di Bella G. Artichoke (Cynara cardunculus L.) fibres as potential reinforcement of composite structures. Compos Sci Technol 2011;71:1138–44.
[15] Fiore V, Scalici T, Valenza A. Characterization of a new natural fiber from Arundo donax L. as potential reinforcement of polymer composites. Carbohydr Polym 2014;106:77–83.
[16] Papazoglou EG, Karantounias GA, Vemmos SN, Bouranis DL. Photosynthesis and growth responses of giant reed (Arundo donax L.) to the heavy metals Cd and Ni. Environ Int 2005;31:243–9.
[17] Flores JA, Pastor JJ, Martinez-Gabaroon A, Gimeno-Blanes FJ, Rodriguez-Guisado I. Arundo donax chipboard based on urea-formaldehyde resin using under 4 mm particles size meets the standard criteria for indoor use. Ind Crops Prod 2011;34:1538–42.
[18] Fiore V, Scalici T, Vitale G, Valenza A. Static and dynamic mechanical properties of Arundo Donax fillers-epoxy. Mater Des 2014;57:456–64.
[19] Fiore V, Botta L, Scaffaro R, Valenza A, Pirrotta A. PLA based biocomposites reinforced with Arundo donax fillers. Compos Sci Technol 2014;105:110–7.
[20] Ismail ZZ, Jaeel AJ. A novel use of undesirable wild giant reed biomass to replace aggregate in concrete. Constr Build Mater 2014;67:68–73.
[21] Alomayri T, Shaikh FUA, Low IM. Synthesis and mechanical properties of cotton fabric-reinforced geopolymer composites. Compos Part B 2014;60:36–42.
[22] Yan L, Su S, Chouw N. Microstructure, flexural properties and durability of coir fibre reinforced concrete beams externally strengthened with flax FRP composites. Compos Part B 2015;80:343–54.
[23] Yan L, Chouw N. Natural FRP tube confined fibre reinforced concrete under pure axial compression: a comparison with glass/carbon FRP. Thin-Walled Struct 2014;82:159–69.
[24] Yan L, Chouw N, Jayaraman K. Lateral crushing of empty and polyurethane-foam filled natural flax fabric reinforced epoxy composite tubes. Compos Part B 2014;63:15–26.
[25] Hakamy A, Shaikh FUA, Low IM. Effect of calcined nanoclay on microstructural and mechanical properties of chemically treated hemp fabric-reinforced cement nanocomposites. Constr Build Mater 2015;95:882–91.
[26] Baltazar-y-Jimenez A, Bistritz M, Schulz E, Bismarck A. Atmospheric air pressure plasma treatment of lignocellulosic fibres: impact on mechanical properties and adhesion to cellulose acetate butyrate. Compos Sci Technol 2008;68:215–27.
[27] Kafi AA, Magniez K, Fox BL. A surface property relationship of atmospheric plasma treated jute composites. Compos Sci Technol 2011;71:1692–8.
[28] Bozaci E, Sever K, Sarikanat M, Seki Y, Demir A, Ozdogan E, et al. Effects of the atmospheric plasma treatments on surface and mechanical properties of flax fiber and adhesion between fiber–matrix for composite materials. Compos Part B 2013;45:565–72.
[29] Sun D, Stylios GK. Investigating the plasma modification of natural fiber fabrics-The effect on fabric surface and mechanical properties. Text Res J 2005;75:639–44.
[30] Yuan X, Jayaraman K, Bhattacharyya D. Plasma treatment of sisal fibres and its effects on tensile strength and interfacial bonding. J Adhes Sci Technol 2002;16:703–27.
[31] Lee H, Ohsawa I, Takahashi J. Effect of plasma surface treatment of recycled carbon fiber on carbon fiber-reinforced plastics (CFRP) interfacial properties. Appl Surf Sci 2015;328:241–6.
[32] Xie J, Xin D, Cao H, Wang C, Zhao Y, Yao L, et al. Improving carbon fiber adhesion to polyimide with atmospheric pressure plasma treatment. Surf Coat Technol 2011;206:191–201.
[33] Encinas N, Lavat-Gil M, Dillingham RG, Abenojar J, Martínez MA. Cold plasma effect on short glass fibre reinforced composites adhesion properties. Int J Adhes Adhes 2004;48:85–91.
[34] Guo F, Zhang ZZ, Liu WM, Su FH, Zhang HJ. Effect of plasma treatment of Kevlar fabric on the tribological behavior of Kevlar fabric/phenolic composites. Tribol Int 2009;42:243–9.
[35] Sun Y, Liang Q, Chi H, Zhang Y, Shi Y, Fang D, et al. The application of gas plasma technologies in surface modification of aramid fiber. Fibers Polym 2014;15:1–7.
[36] Fiore V, Di Bella G, Scalici T, Valenza A. Effect of plasma treatment on mechanical and thermal properties of marble powder/epoxy composites. Polym Compos 2016. http://dx.doi.org/10.1002/pc.23937. in press.
[37] Shatalov AA, Pereira H. Influence of stem morphology on pulp and paper properties of Arundo donax L. reed. Ind Crops Prod 2002;15:77–83.
[38] Everett TH. The New York botanical garden illustrated encyclopedia of horticulture. 1980. ed. Routledge, New York.
[39] Silva FA, Chawla N, Toledo Filho RD. Tensile behavior of high performance natural (sisal) fibers. Compos Sci Technol 2008;68:3438–43.
[40] ASTM D 6866–11. Standard test methods for determining the biobased content of solid, liquid, and gaseous samples using radiocarbon analysis. 2011.
[41] Masoodi R, El-Hajjar RF, Pillai KM, Sabo R. Mechanical characterization of cellulose nanofiber and bio-based epoxy composite. Mater Des 2012;36:570–6.
[42] ASTM D 3379–75. Standard test method for tensile strength and young's modulus for high-modulus single-filament materials (Withdrawn 1998). 1989.
[43] Liu D, Han G, Huang JH, Zhang Y. Composition and structure study of natural *Nelumbo nucifera* fiber. Carbohydr Polym 2009;75:39–43.
[44] Weibull W. A statistical theory of the strength of materials. Ing Vetenskaps Akad Handl, 151; 1939. Stockholm.
[45] Andersons J, Sparniņš E, Joffe R, Wallström L. Strength distribution of elementary flax fibres. Compos Sci Technol 2005;65:693–702.
[46] ASTM D 790–10. Standard test methods for flexural properties of unreinforced and reinforced plastics and electrical insulating materials. 2010.
[47] Monteiro SN, Calado V, Margem FM, Rodriguez RJS. Thermogravimetric stability behavior of less common lignocellulosic fibers - a review. J Mater Res Technol 2012;1:189–99.
[48] Albano C, Gonzalez J, Ichazo M, Kaiser D. Thermal stability of blends of polyolefins and sisal fiber. Polym Degrad Stab 1999;66:179–90.
[49] Yao F, Wu Q, Lei Y, Guo W, Xu Y. Thermal decomposition kinetics of natural fibers: activation energy with dynamic thermogravimetric analysis. Polym Degrad Stab 2008;93:90–8.
[50] Yang H, Yan R, Chen H, Lee DH, Zheng C. Characteristics of hemicellulose, cellulose and lignin pyrolysis. Fuel 2007;86:1781–8.
[51] Paiva MC, Ammar I, Campos AR, Cheikh RB, Cunha AM. Alfa fibres: mechanical, morphological and interfacial characterization. Compos Sci Technol 2007;67:1132–8.
[52] Biagiotti J, Puglia D, Kenny JM. A review on natural fibre-based composites-Part I. J Nat Fibers 2004;1:37–68.
[53] Sgriccia N, Hawley MC, Misra M. Characterization of natural fiber surfaces and natural fiber composites. Compos Part A 2008;39:1632–7.
[54] Le Troedec M, Sedan D, Peyratout C, Bonnet J, Smith A, Guinebretiere R, et al. Influence of various chemical treatments on the composition and structure of hemp fibres. Compos Part A 2008;39:514–22.
[55] Liu W, Mohanty K, Drzal LT, Askel P, Misra M. Effects of alkali treatment on the structure, morphology of native grass fibers as reinforcements for polymer matrix composites. J Mater Sci 2004;39:1051–4.
[56] Spinace MAS, Lambert CS, Fermoselli KKG, De Paoli MA. Characterization of lignocellulosic curaua fibres. Carbohydr Polym 2009;77:47–53.
[57] Sinha E. Effect of cold plasma treatment on macromolecular structure, thermal and mechanical behavior of jute fiber. J Ind Text 2009;38:317–39.
[58] Fiore V, Scalici T, Nicoletti F, Vitale G, Prestipino M, Valenza A. A new eco-friendly chemical treatment of natural fibres: effect of sodium bicarbonate on properties of sisal fibre and its epoxy composites. Comp Part B 2016;85:150–60.
[59] Shanmugam D, Thiruchitrambalam M. Static and dynamic mechanical properties of alkali treated unidirectional continuous palmyra palm leaf stalk fiber/jute fiber reinforced hybrid polyester composites. Mater Des 2013;50:533–42.
[60] Fiore V, Di Bella G, Valenza A. The effect of alkaline treatment on mechanical properties of kenaf fibers and their epoxy composites. Compos Part B 2015;68:14–21.
[61] Martinez-Hernandez AL, Velasco-Santos C, De Icaza M, Victor MC. Dynamic mechanical and thermal analysis of polymeric composites reinforced with keratin biofibers from chicken feathers. Compos Part B 2007;38:405–10.