Composites & nanocomposites

Chemical modification of hemp fibres by plasma treatment for eco-composites based on biodegradable polyester

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ABSTRACT

In this paper, raw hemp fibres were used to reinforce a commercial biopolyester, namely poly(1,4-butylene adipate-*co*-terephthalate), to achieve eco-composite materials. To promote the adhesion between the polyester matrix and the fibrous reinforcement, chemical modification of fibres surface with coupling agents was accomplished. Usually, the grafting of coupling molecules is carried out involving high amount of solvents. Here, in a general approach of an environmental sustainability, uncut, combed and slightly stretched hemp fibres were treated with a green process based on a novel soft plasma jet device (developed by Nadir Srl). This technique activates the fibres surface and, at the same time, allows the deposition of reactive monomers as coupling agents. Three different monomers were investigated: methyl methacrylate (MMA), (3-aminopropyl)triethoxysilane (APTES) and (3-glycidyloxypropyl)trimethoxysilane. Unmodified and surface-modified fibres were characterized and compared in terms of thermal behaviour and morphological features. Long-fibre eco-composites were then prepared by different compression moulding procedures and characterized by thermal, morphological and dynamic mechanical analysis. Experimental evidences indicated that the cold plasma deposition/grafting treatment was successfully carried out; the composite with the best mechanical performance resulted that obtained by using APTES as coupling agent.

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Introduction

Hemp is generally grown for its bast fibres, used as a raw material for cordage and textile products, and for its pulp used for specialty papers. For many years, hemp has been a traditional crop in Italy; from the late 1990s, hemp cultivation has been reintroduced due to an increasing demand for non-food crops in farming systems and a renewed interest in the use of natural fibres also for non-woven industrial products. The processing of hemp produces significant amounts of secondary products with a low value. Hemp fibres possess some of the best mechanical properties of all natural fibres, and apart textile applications of bast fibres, up to now the short fibres are mainly used for building insulation and fabrication of composite materials [1]. In the latter case, the market of reference is the automotive interior and the composites are based on synthetic plastics. Nevertheless, in the last years, it appears of particular interest the development of fully compostable eco-composite materials based on biodegradable or compostable bioplastics as matrices and low-value hemp fibres and/or shives as reinforcing agents. Yet, the hydrophilic nature of lignocellulosic fibres, due to the presence of hydroxyl groups on their surface, generally results in poor adhesion with polymer matrices, typically hydrophobic, leading to composite materials with low mechanical properties.

Several methods have been investigated to reduce intrinsic hydrophilicity of natural fibres [2–4]. Most of them are based on the chemical modification of fibre surface (acetylation, treatment with organosilanes, isocyanates or specific coupling agents, grafting of polymers), thus involving the use of solvents [5, 6]. More eco-friendly alternatives consist in physical processes, such as corona and plasma treatments and UV irradiation [7, 8]. Among these, plasma technology has been utilized since 1960s to improve the surface properties of fibres in many applications and nowadays is one of the most significant high-tech methods for the modification of wood and other natural fibres.

In particular, surface treatments with plasma sources, working in air at low temperatures and atmospheric pressure, seem to be very promising because they are applicable in large-scale and allow the modification of surfaces that cannot withstand high temperatures. Atmospheric pressure dielectric barrier discharge (DBD) plasma has a great potential for modifying a series of chemical and physical properties of lignocellulosic fibres, from molecular (i.e. generation of hydroxyl, carboxyl, carbonyl, ester or amino groups), to microscopic (i.e. surface smoothing and removal of weak boundary layers), to macroscopic (i.e. modification of surface energy) level [9]. Moreover, depending on the type of the feed gases it is possible to: (1) vary the type of surface modification, with the possibility of introducing different reactive groups; (2) vary the degree of ablation; and (3) reticulate or coat the surface.

It is therefore very interesting to exploit the characteristics of cold atmospheric plasma both to activate the surface of the fibres and to deposit, for example, a reactive monomer. In the literature, few examples of the use of plasma for directly coating the surface of wood and lignocellulosic materials can be found [2, 9]. In the past, DBD technique was used to initiate the grafting of molecules onto lignocellulosics, by employing a two-step procedure [10]: (1) surface activation by plasma and (2) reaction with suitable monomers in solution. More recently, Wielen and Ragauskas [11] used a discharge initiated in situ grafting approach by spraying an acrylamide monomer solution onto the surface of spruce and pine pulps prior to DBD treatment.

Within this frame, the utilization of a cold atmospheric plasma as a green chemical compatibilization technique for the surface modification of natural fibres could be a valid strategy for the preparation of fully sustainable eco-composites endowed with improved mechanical properties.

In the present work, a novel soft plasma DBD jet device (developed by Nadir Srl) was exploited to treat hemp fibres with coupling agents, suitable for enhancing fibres interaction with a polymer matrix. This device allowed both the activation of the fibre surface and the deposition of different reactive monomers, such as methacrylates or organosilanes [12, 13]. The same functionalities are usually grafted on the fibres surface by chemical treatments that involve the use of high amount of solvents.

The so obtained fibres were thermally and morphologically characterized and then incorporated into poly(1,4-butylene adipate-*co*-terephthalate) (PBAT) through a suitable compression moulding procedure. The real composition of the ensuing long fibres eco-composites was estimated by thermogravimetric analysis; their morphology and dynamic mechanical properties were investigated in order to

evaluate the effectiveness of this plasma surface treatment.

Experimental

Materials

A commercial biodegradable, statistical poly(1,4-butylene adipate-*co*-terephthalate) (PBAT) grade (Ecoflex® F Blend A1200), kindly supplied by BASF (Germany), was used as the polyester matrix ($\bar{M}_n = 11.7 \times 10^3$ g mol^{-1}; $\bar{M}_w = 84.4 \times 10^3$ g mol^{-1}; $T_g = -33$ °C; $T_m = 118$ °C, 1:1 adipate/terephthalate units) [14]. Raw hemp fibres of *Carmagnola* variety (HF), from which shives had been previously removed, were kindly supplied by Assocanapa S.r.l. (Italy).

Except where indicated otherwise, chemicals were purchased from Sigma-Aldrich and used as received.

Surface treatment of hemp fibres

Before plasma treatment, HF were mildly treated (HF$_{Na}$) in an aqueous solution of NaOH (0.2 wt%/v) at 20 °C for 48 h, as described in our previous work [14].

The plasma treatment was carried out by using a dielectric barrier discharge (DBD) jet device, patented by Nadir Srl (Fig. 1a) [15]. The plasma jet, deeply described in the paper of Patelli et al. [16], is characterized by two coaxial alumina tubes: the Ar plasma flows in the external tube, while the internal tube is dedicated to carry the precursor vapour from a bubbler. Uncut, combed and slightly stretched HF$_{Na}$ fibres were fixed to a frame and physically and chemically modified by plasma treatment in the presence of suitable reactive monomers, namely methyl methacrylate (MMA), (3-aminopropyl)triethoxysilane (APTES) and (3-glycidyloxypropyl)trimethoxysilane (GLYMO) (Fig. 2). The fixed fibres were treated on both sides in order to allow, as much as possible, a uniform monomer deposition (Fig. 1b). The ensuing fibres were labelled as HF$_{Na}$–MMA, HF$_{Na}$–APTES and HF$_{Na}$–GLYMO, respectively.

In the DBD jet device, Ar or Ar/O$_2$ at 2% of oxygen was employed as carrier gases for the monomers. The fibres were placed at a distance of 2 mm from the plasma nozzle, and the torch was automatically moved thanks to a *x*–*y* plotter (IAI TTA plotter 200 × 200 mm) in order to scan the whole surface.

Treatment parameters were: (1) high voltage power 5 W, radio frequency power 20/30 W; (2) working gas Ar 4.5/5.6 L min^{-1}, carrier gases Ar or Ar/O$_2$ 2.5 or 1 L min^{-1}, respectively; (3) scanning pitch 3 mm, jet advance speed 30 mm s^{-1}; (4) treatment time 15 min on each side of the sample.

Preparation of hemp fibre/PBAT composites

Three different methods for the composites fabrication were investigated (Fig. 3). In Method A, the frame with combed hemp fibres was placed in
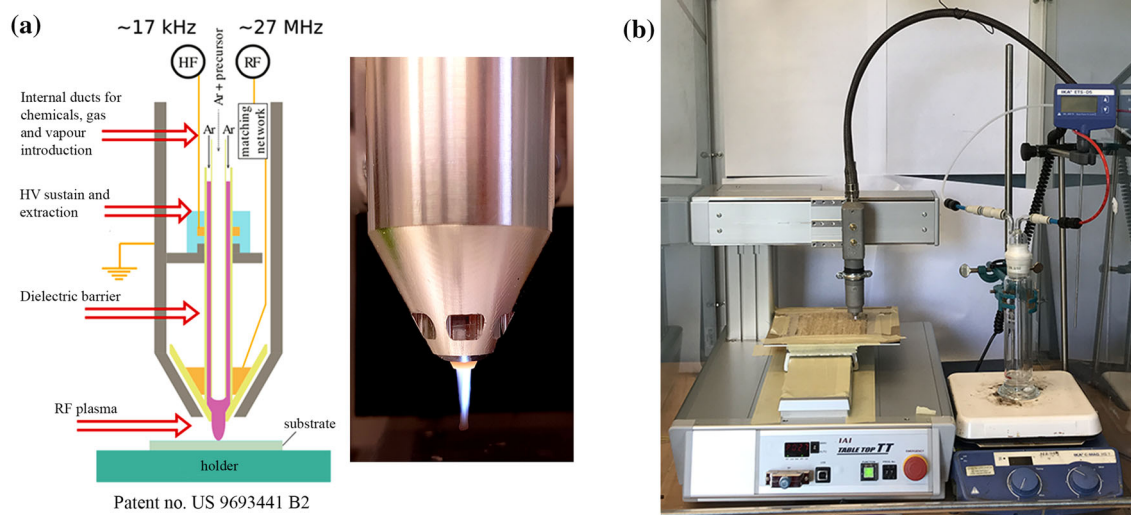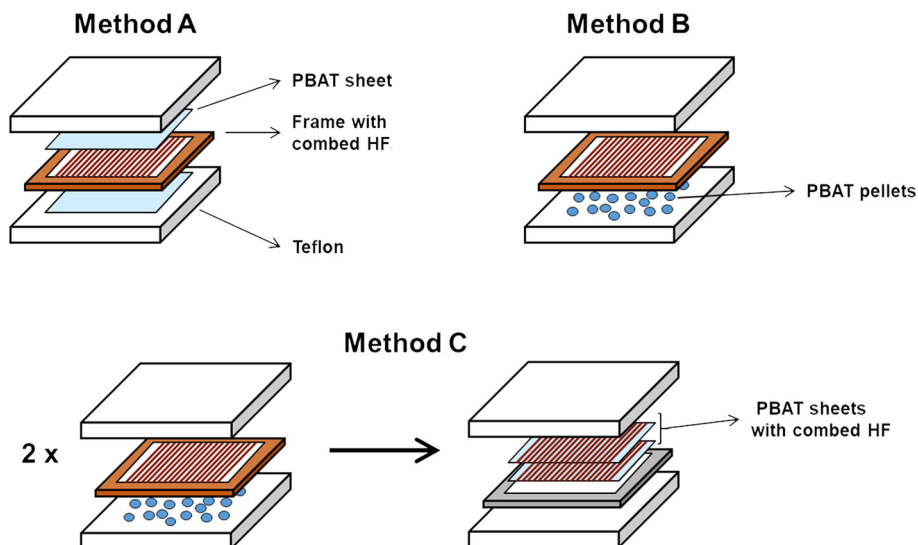

Figure 1 Scheme of the dielectric barrier discharge (DBD) jet device (**a**), fibre treatment (**b**).
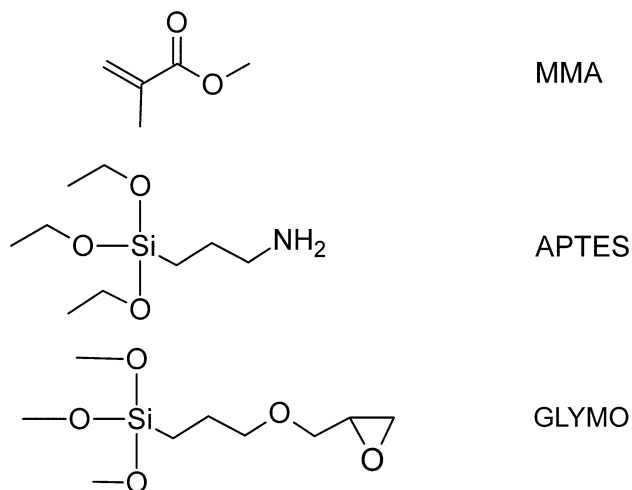
Figure 2 Chemical structure of the molecules used for plasma treatment of hemp fibres.

between two sheets of PBAT (1 mm thick), previously prepared by compression moulding (160 °C, 16 MPa, 4 min); the resulting "sandwich" was then treated at 180 °C, 16 MPa for 4 min. Method B consisted in embedding the fibres directly in the molten polymer (180 °C, 8 min) by moulding at 180 °C, 1 MPa, 7 min. Finally, Method C comprised two steps: (1) preparation of two sheets of PBAT containing pre-impregnated fibres by using Method B and (2) pre-heating and welding of the two pre-impregnated sheets together, with fibres oriented in the same direction, by moulding at 150 °C, 1 MPa, 3 min.

Characterization techniques

Thermogravimetric analysis

Thermogravimetric analysis (TGA) measurements were taken with a PerkinElmer TGA7 analyzer operating in dynamic mode. Samples (about 10 mg) of neat PBAT, fibres and their composites were heated at 10 °C min^{-1} under N$_2$ from 30 to 700 °C (gas flow rate 40 mL min^{-1}).

As concerns the fibres, the temperatures corresponding to the onset of decomposition and the maximum rate of weight loss (T_{onset} and T_{Vmax}, respectively) were determined. The samples of composites were examined for the evaluation of the fibre content.

Scanning electron microscopy

Morphological analysis of fibres was carried out with a Zeiss Supra 40VP FE-SEM instrument operating at 5 kV; whereas the composites were observed with a Hitachi TM3000 benchtop SEM microscope operating at 15 kV. Both fibres and fragile surfaces of composites, fractured in liquid N$_2$, were sputtered with gold using a Quorum Q150R ES sputter coater (2 M Strumenti) at 20 mA for 5 min prior to the observation.

Dynamic mechanical measurements

Dynamic mechanical analysis (DMA) was carried out with a strain-controlled rotational rheometer

Figure 3 Preparation of eco-composites by three different procedures of compression moulding.

MCR301 (Anton Paar) on rectangular (40 × 10 × 1 mm) specimens cut from the composite sheets.

In order to ensure measurements within the linear viscoelastic region, preliminary amplitude sweep tests (AS) were performed at fixed frequency of 1 Hz and 25 °C in the deformation (γ) range from 0.01 up to 100%. Information about the storage (G'), loss (G'') and complex ($G^* = G' + iG''$) moduli was obtained from frequency sweep tests (FS) at 0.1% γ, by varying the frequency from 0.1 to 50 Hz.

Results and discussion

Surface modification of hemp fibres

Raw hemp fibres were surface-modified by plasma treatment using different monomers to make them more compatible with the polyester matrix. The reactions involved in such a process are more complex with respect to the "conventional" reactions: many options are possible as a consequence of the plasma conditions (e.g. type of gas carrier, ratio between gas and precursor, power of the plasma) and mechanisms that in conventional reactions do not occur may take place.

As suggested by Sonnenfeld et al. [17], the deposition process of organosilane precursors is dominated by the polymerization through radicals, constituted by small fragments of the monomers and their subsequent recombination at the treated substrate surface. Similarly, Lecoq et al. [18] assumed that the growth of a plasma polymerized film obtained by APTES monomer occurs through a fragmentation and recombination mechanism which leads to atoms rearrangement to create nitrogen-containing groups like imines, oximes, or amides at the treated surface. Analogous results were obtained by some of the authors in previous works [12, 13] where by plasma polymerization of APTES on titanium-based surface, carried out with the same plasma jet device here used, the formation of the same nitrogen-containing groups was observed. Differently, by using GLYMO as chemical precursor Vangeneugden et al. [19] verified the epoxy ring opening polymerization, with formation of carbonyl groups, and inorganic Si–O–Si cross-linking/condensation. All these research works deal with homogeneous surfaces such as aluminium, silicon

and titanium. Here, the difficulty in determining what happens during the fibres treatments is due to the intrinsic inhomogeneity of the fibres surface. A deep comprehension of the reaction mechanism involved is out of the scope of this work.

However, morphological differences among the fibres differently treated can be assessed by FE-SEM analysis. The as-received hemp fibres (Fig. 4a) are characterized by the presence of hemicellulose, lignin and waxy material that keep bound together the fibres creating a protective layer. As clearly shown in Fig. 4b, after the alkaline treatment the fibres surface appears cleaner and rougher than before this kind of mild mercerization. Analogous results were reported by Mwaiakambo and Ansell [20] for similar concentrations of NaOH. As reported in our previous works [14, 21], FTIR analysis indicated that NaOH treatment leads to the removal of hemicellulose and waxes. After the monomer deposition by plasma treatment, no remarkable changes in surface roughness are appreciable, but a clearly visible, although not entirely homogeneous, polymer-like layer appears on fibres surface (Fig. 4c–f). This is particularly evident on the fibres treated by using APTES as coupling agent (Fig. 4e, f).

TGA results (summarized in Table 1) show that the plasma treatment does not significantly modify the characteristic decomposition temperatures of hemp fibres, thus confirming that cold plasma is a useful soft method to modify the surface of natural fibres without damaging their structure.

PBAT/hemp fibres eco-composites

One of the main aims of this work is the use of an innovative green method to improve the compatibility between non-textile hemp fibres and a biodegradable polyester matrix in order to valorize low-value products and obtain eco-composites with enhanced mechanical properties. In this frame work, a first series of preliminary composites containing as-received HF fibres were fabricated according to the three methods described in "Experimental" section (Fig. 3). The composites preparation was meant to be as easy and smart as possible: the fibres were previously combed and fixed on a frame in order to facilitate the plasma treatment and have the fibrous reinforce already aligned for the subsequent incorporation in the polymer matrix.

Figure 4 FE-SEM micrographs of HF (**a**), HF_{Na} (**b**), HF_{Na}–GLYMO (**c**), HF_{Na}–MMA (**d**), HF_{Na}–APTES (**e**, **f**) fibres.
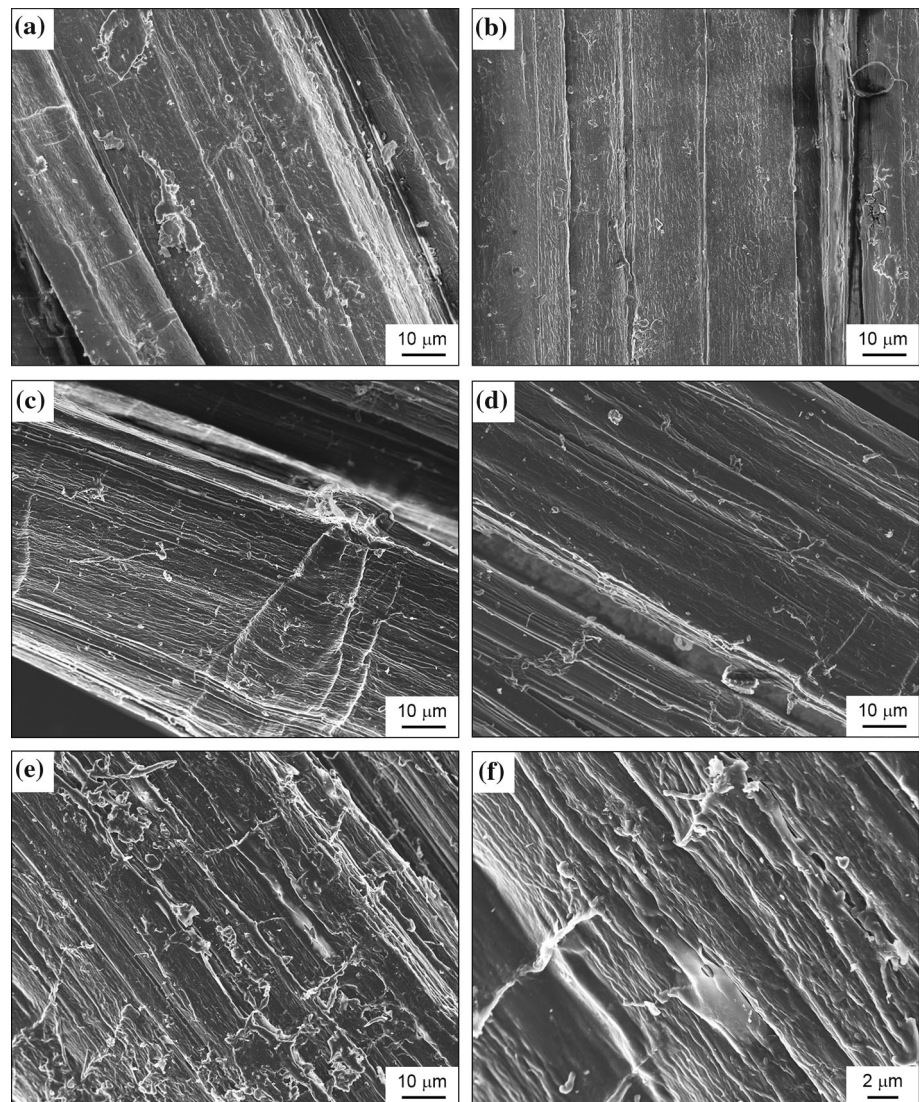
Table 1 Decomposition temperatures of as-received and modified hemp fibres determined by TGA under N_2

| Hemp fibres	T_{onset} (°C)	T_{Vmax} (°C)
HF	349	374
HF_{Na}	344	371
HF_{Na}–GLYMO	344	369
HF_{Na}–MMA	346	371
HF_{Na}–APTES	347	372

The composites cross sections, obtained by fragile fracture in liquid nitrogen, were subjected to morphological analysis to evaluate fibres distribution within the sample.

As visible in Fig. 5a, b, the Method A leads to phase stratification. Despite the high pressure applied during moulding (16 MPa), the polymer does not completely penetrate in between the fibres and tends to symmetrically accumulate in the outer layers of the sheet. As a consequence, the sample under stress is prone to delaminate (Fig. 5a).

A slightly better fibre distribution (Fig. 5c, d) was achieved by embedding the fibres directly into the molten pellets of PBAT (Method B). However, also in this case, the ensuing composite is not homogeneous because the fibres remain predominantly placed on one side of the sheet.

In order to improve the fibre distribution within the sample, a second moulding step was introduced (Method C). In the ensuing composites, hemp fibres

Figure 5 Pictures and corresponding SEM micrographs of samples obtained by Method A (**a**, **b**), B (**c**, **d**), C (**e**, **f**).
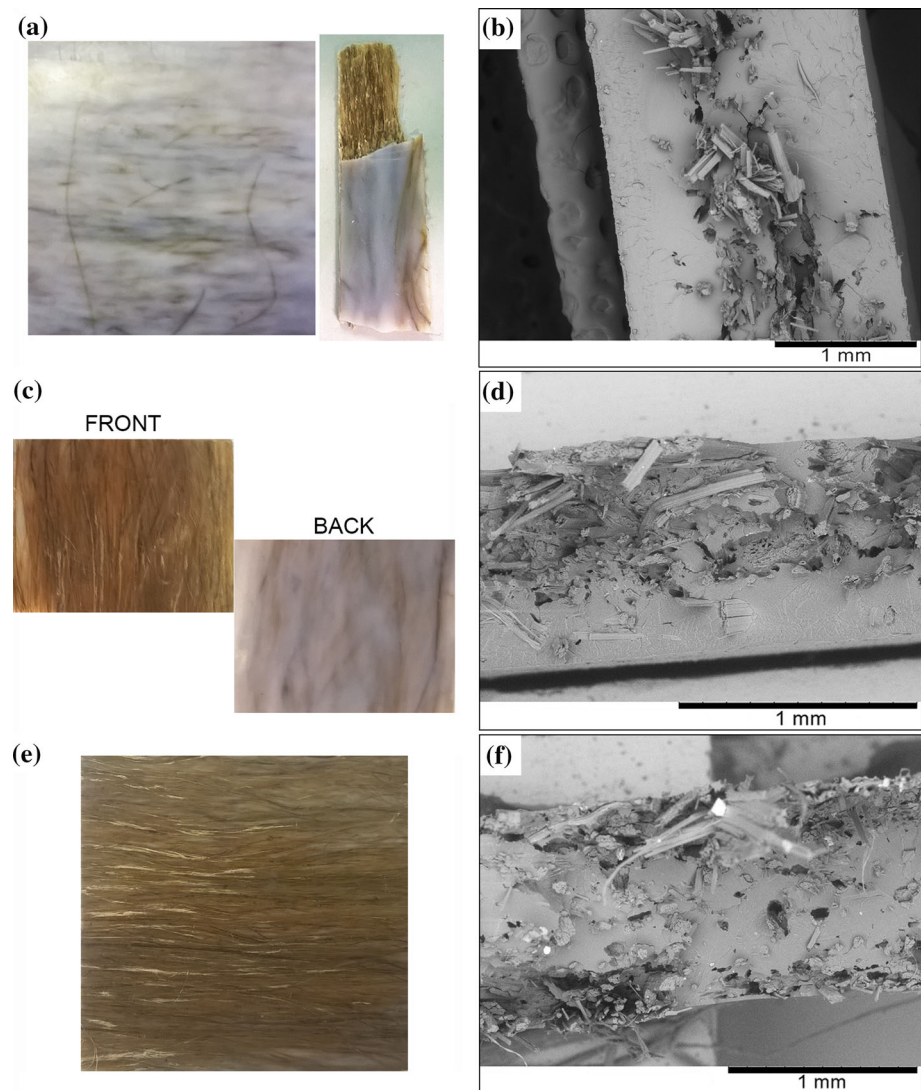

are better distributed across the sample section, as shown in Fig. 5e, f. This last procedure allowed to achieve quite homogeneous composites with a large amount of long fibres bringing about two advantages: (1) samples of different thickness could be prepared by simply layering a variable number of pre-impregnated sheets and (2) these sheets could be stacked with different fibre orientations to obtain cross-ply, angle-ply or quasi-isotropic composites.

Method C was then used to prepare PBAT-based eco-composites (100 × 100 × 1 mm sheets) containing about 40 wt% of long, uni-directionally oriented HF, HF_{Na}, HF_{Na}–MMA, HF_{Na}–GLYMO and HF_{Na}–APTES fibres.

The actual composition of the prepared samples was estimated by TGA. Since the degradation temperatures of the hemp fibres and the polymer matrix are close to each other and the processes partially overlap, the DTG derivative curve was considered. As schematized in Fig. 6, the relative maximum (at about 400 °C) between the two minima of this curve was taken as the temperature to distinguish the two components. Thus, the first weight loss ($\Delta wt_{hemp\ fibres}$) was associated with the hemp fibres degradation, while the second one (Δwt_{PBAT}) with the polyester matrix degradation. The two values, normalized to 100% of weight loss, confirmed the nominal composition of the composite sheets. In order to correctly compare the results of the successive DMA measurements, the weight percentages of each specimen tested were converted into vol%, assuming 1.40 and 1.26 g cm^{-3} the density of fibres and matrix, respectively.
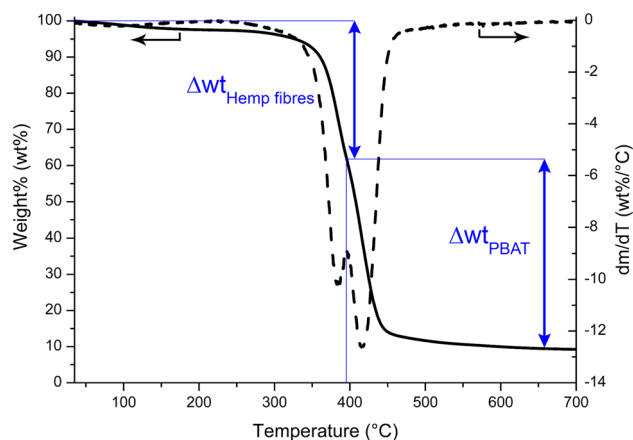
**Figure 6** TGA curve of PBAT + HF and scheme for determination of the fibre amount into the composites.

A careful morphological analysis was carried out by SEM on the surfaces obtained by fragile fracture of the composites in liquid nitrogen. Some representative micrographs are shown in Figs. 7 and 8. The composite containing HF fibres is characterized by many points evidencing fibre pull-out and detachment at the fibre–PBAT interface (Fig. 7a, b). The interaction between phases is only slightly improved after the soda treatment (Fig. 7c, d).

On the whole, the plasma treatment seems to be beneficial for increasing the compatibility between HF fibres and PBAT. However, in the sample containing HF treated with GLYMO (Fig. 8a, b) this effect is poor, while in PBAT + HF_{Na}–MMA (Fig. 8c, d) and especially in PBAT + HF_{Na}–APTES (Fig. 8e, f) composites the fibres appear well attached to the PBAT matrix. Indeed, for these last two samples, one can notice that even where pull-out occurs, the external layer of fibres remains well adhered to the polymer. The different effectiveness of GLYMO and APTES can be explained by taking into account the different partial vapour pressures characterizing the two organosilanes. In fact, although the reactivity of the methoxy groups is higher than that of ethoxy groups [22, 23], the partial vapour pressure of GLYMO is about ten times lower than that of APTES, and this implies that, under the same experimental conditions, the amount of APTES carried by the gas inside the plasma jet device is about ten times higher than that of GLYMO.

These morphological observations are in agreement with DMA measurements, which are a useful and effective tool for determining the viscoelastic properties of polymer and polymer-based composites. As expected, the introduction of long hemp fibres significantly enhances the dynamic mechanical response with respect to that of neat PBAT. More in detail, G' increases, at 0.1 Hz, from 46 to 460 MPa for

**Figure 7** SEM micrographs of PBAT + HF (**a**, **b**), PBAT + HF_{Na} (**c**, **d**) composites.
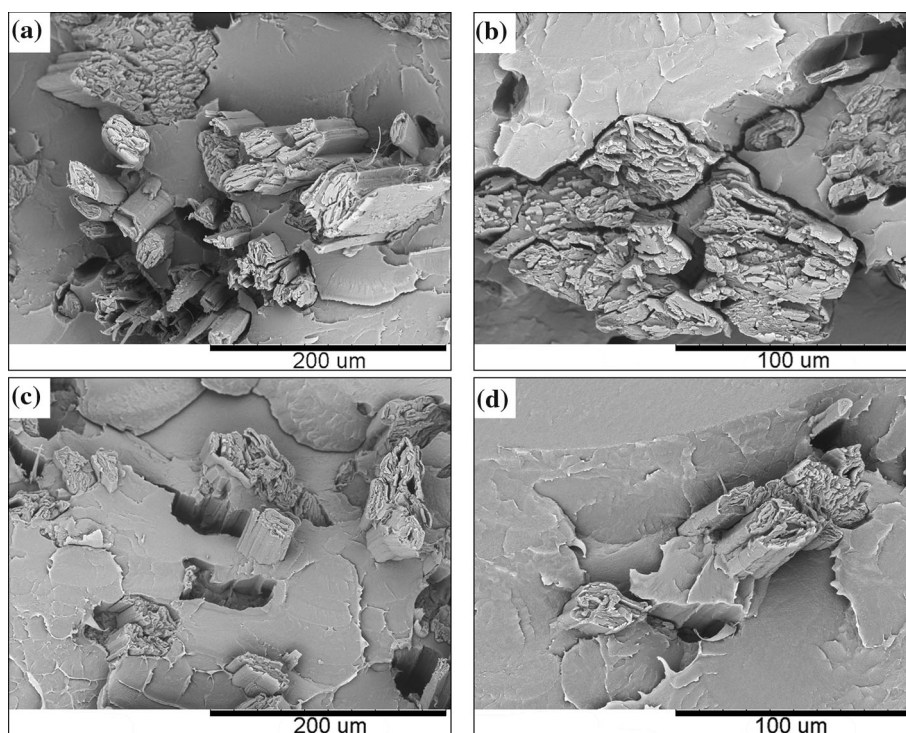
Figure 8 SEM micrographs of PBAT + HF$_{Na}$–GLYMO (**a**, **b**), PBAT + HF$_{Na}$–MMA (**c**, **d**), PBAT + HF$_{Na}$–APTES (**e**, **f**) composites.
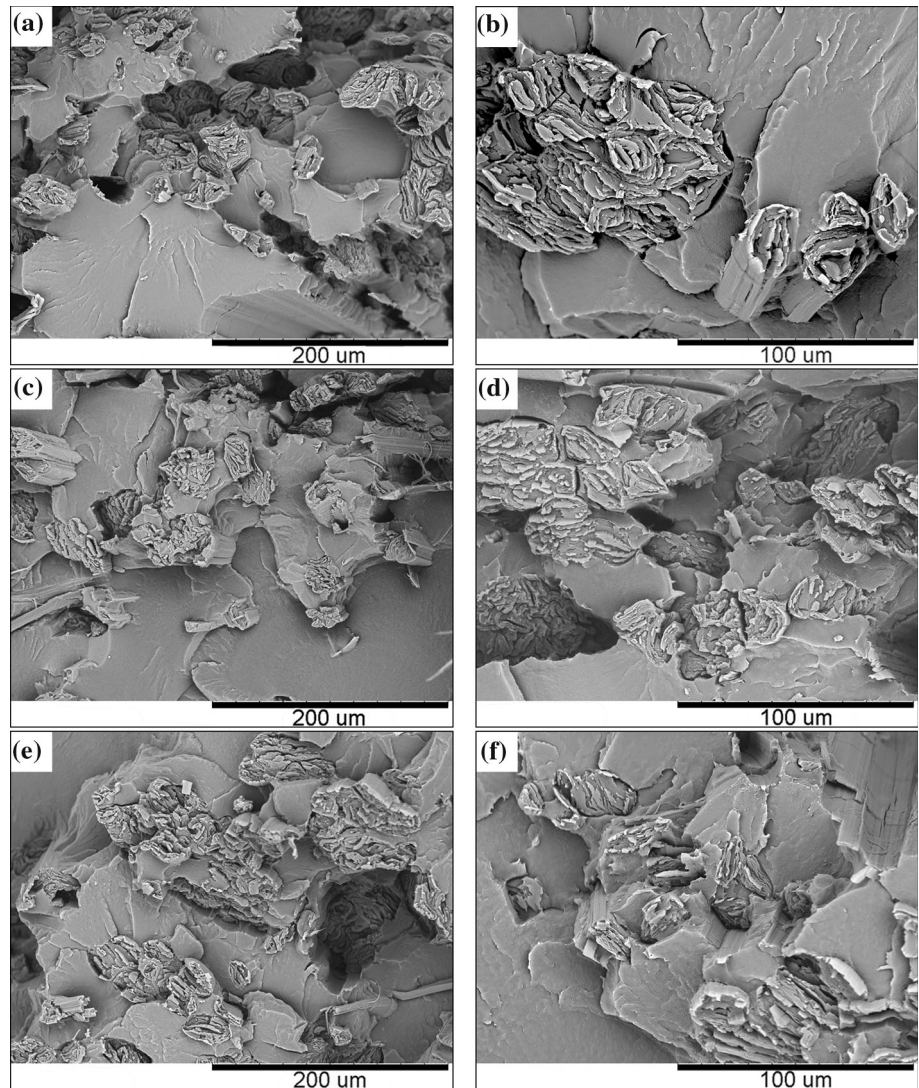
neat polymer and PBAT + HF sample, respectively (inset of Fig. 9).

In order to evaluate the effect of the mere plasma treatment, preliminary mechanical tests were carried out on samples prepared by method A and containing HF fibres, untreated or plasma treated without adding any precursor inside the jet device. No remarkable differences were put in evidence, thus excluding that a gain in mechanical properties originates from an anchoring adhesion mechanism.

In Fig. 9, the comparison of G', normalized with respect to the fibres content, as a function of the frequency for the different composites is reported. A trend is recognizable depending on the fibre treatment: the elastic modulus of the composite containing HF$_{Na}$ is higher than that of the sample containing raw hemp fibres and further improves for the
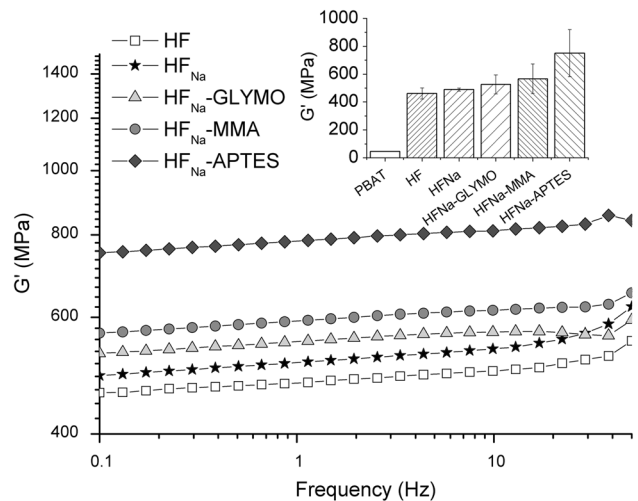
Figure 9 G' versus frequency for the HT-PBAT composites and comparison of the G' values obtained at 0.1 Hz in the inset.

composites containing HF$_{Na}$–GLYMO, HF$_{Na}$–MMA and HF$_{Na}$–APTES. In particular, the plasma treatment carried out using APTES as coupling agent leads to an increment in G' of about 50% with respect to that of PBAT + HF$_{Na}$. The effective reinforcement exerted by the HF$_{Na}$–APTES fibres is highlighted in the bar chart (inset of Fig. 9), where the G' values at 0.1 Hz with the corresponding standard deviation are shown. G' values analogous to those of PBAT + HF$_{Na}$–APTES have been already found in our previous work [14] for a composite prepared in similar conditions and containing HF$_{Na}$ fibres chemically modified by using PBAT macrocyclic oligomers as the coupling agent.

Conclusions

In the present study, eco-composites based on non-textile long hemp fibres and a biodegradable polyester matrix were successfully fabricated. Different procedures were tested to improve the fibres distribution within the polymer matrix. The most promising fabrication method, which could be also potentially effective to obtain composites with different thickness and fibres orientation, was then employed to prepare samples containing about 40 wt% of hemp fibres, unmodified or surface-modified by means of a cold plasma treatment.

After a mild pre-treatment of mercerization, the hemp fibres were chemically compatibilized by using an innovative jet plasma device which allows to directly deposit and grafting the coupling agent onto their surface. Three reactive monomers were used, namely methyl methacrylate (MMA), (3-aminopropyl)triethoxysilane (APTES) and (3-glycidyloxypropyl)trimethoxysilane (GLYMO). The morphological analysis indicates that the fibres were successfully coated by the silane coupling agents, and this results in an improved interaction between the fibrous reinforcement and the polyester matrix. Frequency sweep tests confirmed the positive effect of plasma treatment on the dynamic mechanical behaviour of the composites. By considering PBAT reinforced with as-received or alkaline-treated fibres as references, only a slight increase in the elastic modulus occurs in the samples containing fibres modified with GLYMO and MMA, while a more marked improvement was observed when APTES is used as the coupling agent. The better compatibilization

effect exerted by APTES with respect to GLYMO is ascribable to the higher amount of the former deposited during the plasma treatment because of its higher partial vapour pressure.

The positive influence of silane coupling agents on mechanical properties of natural fibres-reinforced composites has been already observed in the literature; however, the chemical modification is usually carried out by immersing the fibres in a diluted solution of monomer, i.e. non-conveniently in a general perspective of environmental sustainability. On the contrary, our approach allows to obtain composites with enhanced mechanical properties, by using an innovative green process.

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