Revalorisation of *Posidonia Oceanica* as Reinforcement in Polyethylene/Maleic Anhydride Grafted Polyethylene Composites

D. Puglia*, R. Petrucci, E. Fortunati, F. Luzi, J.M. Kenny and L. Torre

Materials Engineering Center, UdR INSTM, University of Perugia, Strada Pentima Bassa, 4, Italy

Received December 12, 2013; Accepted February 17, 2014

ABSTRACT: *Posidonia Oceanica* waste was used as reinforcement in a polyethylene matrix and the obtained composites were characterised by a tensile test and morphological analysis. The fibrous material derived from *P. Oceanica* wastes was characterised by morphological, thermal and chemical analysis, and a subsequent treatment with sodium hydroxide (NaOH) at different weight content (2, 5 and 10 wt%) was considered as an optimised method for surface modification of pristine fibres (PO). The TGA analysis and morphological investigation of the treated fibres selected the 5 wt% of NaOH as the best treatment. Matrix compatibilisation with maleic anhydride grafted polyethylene was also considered and the effect on both grafting procedure and alkali treatment was studied for composites containing 20 wt% of fibres. The results confirmed that it is possible to aim for a revalorisation of coastal algae and seaweed wastes as raw material for polyolefin matrix composites, even without applying a strong chemical treatment to the waste.

KEYWORDS: Natural sources, polyolefin matrix, algae, waste revalorisation, polyethylene

1 INTRODUCTION

Recently, there has been considerable expansion in the research and development of natural fibres as a reinforcement phase in thermoplastic resin matrix. These reinforced plastics serve as an inexpensive, biodegradable, renewable, and nontoxic alternative to glass or carbon fibres [1, 2]. The various advantages of natural fibres over man-made glass and carbon fibres are their low cost, low density and competitive specific mechanical properties and reduced energy consumption, as well as their biodegradability. Natural fibres coming from industrial crops such as flax, kenaf, jute, etc., have been extensively reported in some cases as having comparable properties to traditional fibres such as glass fibre. The use of these fibres is attractive from both a technical and environmental point of view, but it is also important to consider fibrous wastes as potential candidates for green composites [3, 4]. It is possible to find fibrous materials as wastes derived from different industrial processes, i.e., husk rice, almond husk, olive pits, sawdust, sugar cane bagasse, etc. [5–9]; while great amounts of biomass (pine needles, algae wastes, leaves from deciduous forests, corn stalks, wood wastes, etc.) are continuously generated, and some of their final uses include composting, fuel manufacturing, conversion to thermal energy, etc. [10–12]. In some cases it is possible to find new attractive uses for these biomass wastes, as for fibrous wastes derived from algae such as Zostera seagrass [13] or *Posidonia Oceanica* [14, 15]. The *Posidonia Oceanica* is a Mediterranean endemic alga which appears in large amounts in the form of balls (aegagropili) along many coastal beaches as a consequence of storms that tear off leaves, stems and, in some cases, the whole plant. These wastes reach the seacoast and the continuous movement over the sand causes the formation of round balls. These balls are removed from tourist beaches in order to obtain quality awards. Some studies have focused on the potential use of this fibrous waste as filler in potato starch-based films with varying amounts of *P. Oceanica* in the 10–30 wt% range

---

Corresponding author: debora.puglia@unipg.it

DOI: 10.7569/JRM.2013.634134

with interesting results [15]; the fibre from *Posidonia* was hot-pressed with wheat gluten protein as binder-matrix material to obtain a new set of polymer composites fully based on renewable resources [14].

Thermoplastic materials that are currently dominant as matrices for natural fibres are polypropylene (PP), polyethylene, and poly(vinyl chloride), while thermosets such as phenolics and polyesters are common matrices. For this purpose, organic matrix resin reinforced with natural fibres such as jute, kenaf, sisal, coir, straw, hemp, banana, pineapple, rice husk, bamboo, etc., have been explored over the past two decades [16]. Considering the practical use of natural fibre-reinforced polymeric composite, there is an increasing demand (e.g., from automotive companies) for formulations with sound abatement capability as well as reduced weight for fuel efficiency. Natural fibres possess excellent sound absorbing efficiency and are more shatter resistant and have better energy management characteristics than glass-fibre-reinforced composites [17]. However, the main disadvantage of natural fibre/plastic composites is the poor compatibility between the mainly hydrophobic polymer matrix and the hydrophilic fibres. This leads to the formation of a weak interface, which results in poor mechanical properties, where the stress transfer at the interface between two different phases is determined by the degree of adhesion. A strong adhesion at the interfaces is needed for an effective transfer of stress and load distribution throughout the interface [18, 19]. Thus, in order to improve the mechanical properties of composites, an improvement in the compatibility between the fibres and the matrix has to be made, i.e., a third component, the so-called compatibiliser, has to be used or the fibres have to be surface modified prior to the preparation of the composites [20, 21]. Formation of an interphase between the lignocellulosic phase and the polymer matrix phase, with polymer chains bonded onto the fibres particles, is probably the best solution to the problem. Complete matrix fusion to facilitate thorough fibre impregnation, formation of strong fibre/matrix interfacial bonding, and matrix-to-fibre stress transfer efficiency are vital requirements for the manufacture of reliable, eco-friendly natural composites that possess better mechanical properties and withstand environmental attacks. For this purpose, Bledzki and Gassan [22] have stated that the quality of the fibre/matrix interface is significant for the application of natural fibres as reinforcement fibres for plastics. Physical and chemical methods can be used to optimise this interface. These modification methods have a different efficiency for the adhesion between matrix and fibre. However, the main problem of natural fibre/polymer composites is the incompatibility between the hydrophilic natural fibres and the hydrophobic thermoplastic matrices. It necessitates the use of compatibilisers or coupling agents in order to improve the adhesion between fibre and matrix [23, 24]. Matrix or fibre modification is therefore necessary to improve the compatibility between fibre and matrix. Maleated polyolefins are often used to modify the matrix in order to guarantee the interaction between the anhydride groups of maleated coupling agents and the hydroxyl groups of natural fibres [25, 26].

Examples of how the grafted matrices can modify the behaviour of composites based on agro residual wastes are reported in literature [27–29], while few investigations can be found on how residual renewable resources, such as algae, can be successfully incorporated in modified polyolefins [30, 31].

As an example, in Luan *et al.* [32, 33] the effects of two additives (carbon nanotubes and MAPP (maleic anhydride grafted polypropylene) modifier) on polypropylene/seaweed (PP/SW) biocomposites were investigated by dynamic rheological characterisation and a synergistic effect was observed. Moreover, surface modification of natural fibres with sodium hydroxide can be considered as one alternative method aimed at improving the adhesion between the fibre surface and the polymer matrix, not only modifying the fibre surface but also increasing fibre strength [23]. Specifically, the alkali treatment of natural fibres was extensively considered in the literature as a possible functionalisation method for polyolefin-based composites [34, 35], while few reported attempts are available for direct or mediated alkali treatment of seaweed [36, 37]. *Posidonia Oceanica* is a Mediterranean endemic alga characterised by relatively high amounts of extractives, especially for ethanol/toluene extractives (10.7%) and ash content (12%), with a relatively high cellulose content (40%). The lignin content is close to that of softwood, while the amounts of holocellulose and cellulose were similar to those found in wood and non-wood plants. These important fractions allow envisaging the valorisation of such crops as cellulose derivatives and/or as lignocellulosic fibres for fibre-reinforced composite materials or papermaking applications [38].

In the present work, pristine and alkali treated short fibres extracted from *Posidonia Oceanica* aegagropili were used as reinforcement phase both in neat polyethylene matrix (HDPE) and maleic anhydride grafted polyethylene/HDPE blend. Preliminary analysis of the fibres was performed in order to verify the morphology and thermal stability of the fibre before and after the treatment with sodium hydroxide, with the aim of selecting the best treatment to be applied on the pristine fibres; after that, different composite systems containing untreated and treated fibres, such as neat or grafted polyethylene matrix, were produced and characterised. The mechanical characterisation and the morphological analysis of the polyolefin after the introduction of the *Posidonia* sea waste were performed, and the results were revised by trying to identify the role of the *Posidonia* in polyolefin-based matrices in order to understand how compatibilisation of the two combined systems (matrix and fibre) could modify the mechanical performance of the produced materials.

2 EXPERIMENTAL

2.1 Materials

Posidonia Oceanica waste balls (PO) were collected from the Campello Beach in Alicante (Spain) by Aitex (Alcoy, Alicante, Spain) without any cleaning process; they were washed and rinsed several times with distilled water in order to eliminate the sand and other soil contaminants after a milling stage aimed at converting them into a short fibre form to use in the composite approach. The final length of the fibres was in the 2–10 mm range. Alkaline treatment of the fibres was performed by boiling the fibres for 1.5 h at 98°C in a deionised water solution of sodium hydroxide at different weight percent (2, 5 and 10 wt%, namely PO2A, PO5A and PO10A, respectively); after the treatment, the fibres were washed with distilled water several times and dried in a oven at 60°C for 24 h. High density polyethylene supplied by Polimeri Europa (designed as Eraclene® BC 82, HDPE) was used as thermoplastic matrix. A high density polyethylene grafted with maleic anhydride (designed as Fusabond® MB265 D, PE-g-MA) obtained from DuPont, was employed as a compatibiliser between the above-mentioned matrix and the *P. Oceanica* fibres extracted from the waste balls. Different composites were realized and the codes used for the identification of the materials are reported in Table 1.

2.2 *Posidonia Oceanica* Waste Ball Treatment and Characterisation

The morphology of the extracted fibres from *P. Oceanica* balls was investigated by a field emission scanning electron microscope (FESEM, Supra 25-Zeiss). The *P. Oceanica* fibres were swollen in distilled water before FESEM observation. A 1 wt% aqueous solution of fibres was stirred for 4 h at room temperature. The solution was then subjected to 1 h sonication over 12 h in 10 min intervals in order to loosen up the particles. A few drops of the suspension were cast onto silicon substrate, vacuum dried for 2 h and gold sputtered before the analysis. The same procedure was applied for the preparation of alkali treated fibres. Fourier infrared (FTIR) spectrum of *Posidonia Oceanica* extracted fibres embebbed in KBr discs was recorded using a Jasco FT-IR 615 spectrometer in the 400–4000 cm^{-1} range, in transmission mode. Thermogravimetric measurements (TGA) of pristine *Posidonia Oceanica* extracted fibres were performed by using a Seiko Exstar 6300 analyser, in order to evaluate the thermal stability of the natural fibre and to select the temperature process in the following composite production. Heating scans from 30 to 900°C at 10°C min^{-1} in nitrogen atmosphere were performed.

The fibres treated with the different amounts on sodium hydroxide were also characterised in order to establish the best conditions of treatment.

2.3 Composite Processing

Neat PE, PE/PE-g-MA blend and composite formulations reinforced with untreated and alkali treated *Posidonia Oceanica* extracted short fibres were manufactured using a twin-screw microextruder (Dsm Explore 5&15 CC Micro Compounder) and the mixing process parameters (60 rpm screw speed, 3 min mixing time and temperature profile: 170 – 185 – 200°C) were modulated in order to optimise the material final properties. In order to obtain the desired specimens for the following characterisation, a DSM Xplore 10-mL injection

Table 1 Material formulations.

Materials	Matrix (%)	Compatibilizer (%) (PE-g-MA)	Fiber content (%) (untreated)	Fiber content (%) (alkali treated)
PE	100	–	–	–
PE/PE-g-MA	90	10	–	–
PE/20PO	80	–	20	–
PE/20PO5A	80	–	–	20
PE/PE-g-MA/20PO	90	10	20	–
PE/PE-g-MA/20PO5A	80	10	–	20

moulding machine (T_{mould} = 30°C, $P_{injection}$ = 9 bar, $T_{injection}$ = 190°C) was used and ISO 527–2/1BA tensile dog-bone bars were produced.

Composite formulations based on PE/PE-g-MA were produced considering a 90/10 (wt%) ratio of neat polymer and compatibiliser, while the composites were realized considering a fixed amount of 20 wt% of *P. Oceanica* fibres in respect to neat matrix (or blend). These specific amounts were selected for comparison, taking into consideration that this content of natural fibre typically acts as a real reinforcement in the polymeric composites

2.4 Composite Characterisation

Mechanical behaviour of neat and grafted polyethylene systems and *P. Oceanica* fibre-based composite was evaluated by failure tensile test of dog-bone-shaped specimens using a digital Lloyd instrument LR 30K on the basis of UNI EN ISO 527:2012 with a crosshead speed of 5 mm/min and a load cell of 30 kN. The data are expressed as mean value and standard deviation of at least five measurements.

Fractured samples from tensile tests were observed by field emission scanning electron microscope (FESEM, Supra 25-Zeiss) in order to evaluate the fibre/matrix interactions. Prior to the sample observation, the fractured surfaces were covered with a gold layer (sputtering conditions: A for 40 s at 0.08 bar, by using an AGAR, Auto Sputter Coater).

3 RESULTS AND DISCUSSION

3.1 Characterisation of *Posidonia Oceanica* Pristine Fibres

The algae cleaning from the sea sand has been developed and short fibres were extracted from *Posidonia Oceanica* balls (Figure 1a). The cleaning and extraction processes are based on a whirlpool technique and, after drying, the material obtained has considerably clean short fibres. Basically, the main observation is that the raw biomass has a typical compact lignocellulosic fibrous structure. Indeed, like all lignocellulosic-based fibres, the *Posidonia Oceanica* ones are formed by several microfibres (Figure 1b), which are linked together by lignin [39]. As it is possible to observe, a large diameter distribution characterised the extracted fibres and the dimensions vary from about 150 μm to about 40 μm with

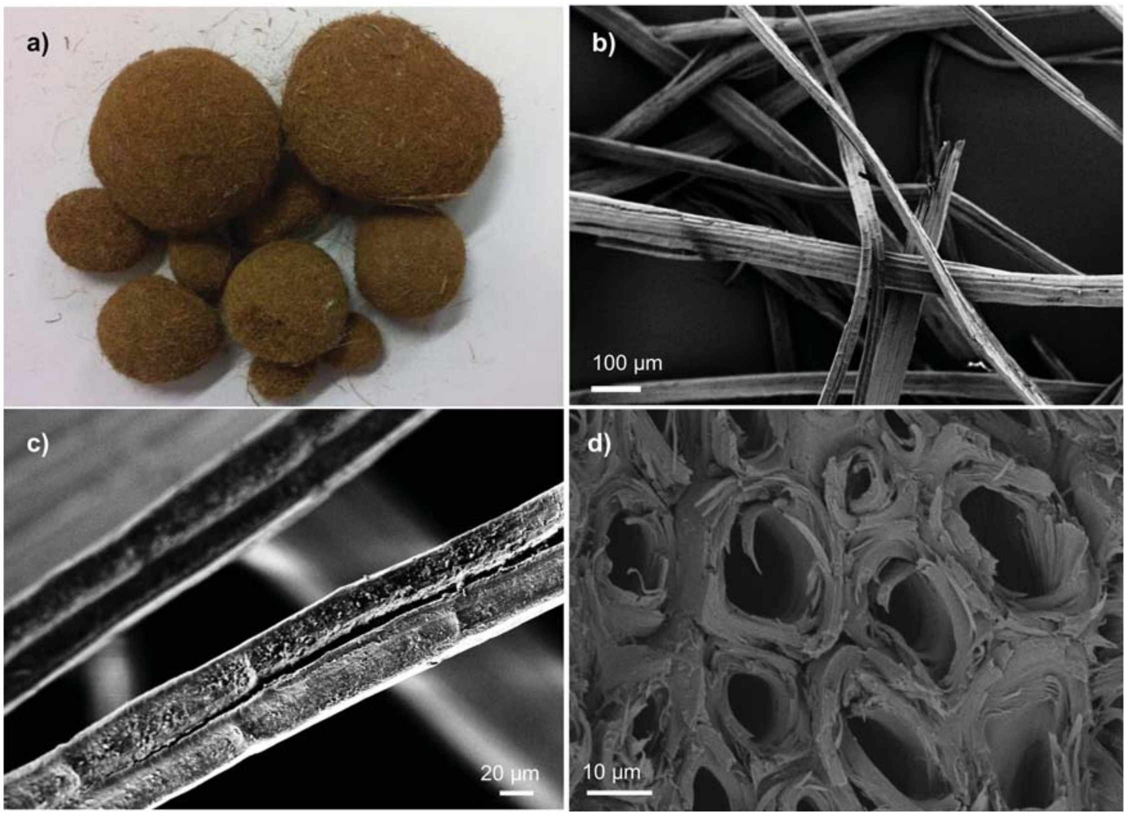

Figure 1 (**a**) *P. Oceanica* balls collected from the sea and FESEM images of fibers from *P. Oceanica* aegagropili: (**b,c**) fibres configuration and (**d**) internal structure.

an average diameter of (84 ± 26) μm, calculated on 50 measurements. It is worthwhile to point out, as shown in Figure 1c and d, that the fibres have a hollow structure, with the epidermis normally covered by a cuticle and walls usually thickened and lignified [40, 41]. This fibrous configuration (relatively high aspect ratio) can suggest their application as a reinforcement inside the common thermoplastic (general purpose or biobased) polymer matrices.

A FTIR analysis of the *Posidonia Oceanica* (PO) fibre was also performed, and typical peaks are shown in Figure 2a. The two peaks at 2918 and 2852 cm^{-1} were due to the asymmetric and symmetric C—H stretching vibrations of aliphatic structures such us CH, CH$_2$, and CH$_3$ groups [42]. The peaks at 1605 and 1432 cm^{-1} were attributed to asymmetric and symmetric C—O stretching of carboxylate (COO$^-$), respectively. The peak at 1605 cm^{-1} could also include C=C stretching of aromatic structures, and the peak at 1432 cm^{-1} could include stretching and O-H deformation of carboxylic groups (COOH). Thus, these spectral bands indicative of carboxylates could include contributions from the vibrations of aromatic and aliphatic carboxylates, and/or aromatic C=C structures [43]. The small peaks at 1273 and 1170 cm^{-1}, and the broad one at 1063 cm^{-1} were probably due to C—O stretching vibrations; particularly, the broad peak at 1063 cm^{-1} was attributed to the C—O vibrations associated with polysaccharide structures [44]. The peak at 898 cm^{-1} could be due to out-of-phase asymmetric ring stretching which, along with the peaks at 1170 and 1063 cm^{-1}, corresponds to cellulose [37, 45, 46].

Residual mass (TG) and derivative weight loss (DTG) curves of *Posidonia Oceanica* fibre (PO) are shown in Figure 2b. The thermal degradation of the *P. Oceanica* fibres shows several stages, indicating the presence of different components that decompose at different temperatures. Dehydration, primary devolatilisation, and consequently char formation are the main steps. There are three main zones in the pyrolytic process. Generally, during pyrolysis, the moisture is removed initially at a temperature below 150°C (the amount of mass loss material in this first step is 15%). Above 150°C and up to 450°C, the chemical bonds of macromolecules break to release the volatile compounds and hemicellulose and cellulose start to break and release more volatiles (a mass loss of 52% was registered in this second step of decomposition, with main temperature peaks detected at 294°C and 335°C). The last decomposition peak, observed at about 460°C and visible as a shoulder of the main peak due to the cellulose decomposition, can be attributed to the degradation of lignin component [47].

3.2 Characterisation of *Posidonia Oceanica* Alkali Treated Fibres

Figure 3 shows the morphological, thermal and chemical characterisation of alkali treated *Posidonia Oceanica* fibres with increasing NaOH content. As it is possible to observe, the pristine fibres (Panel A: a and b) appear separated

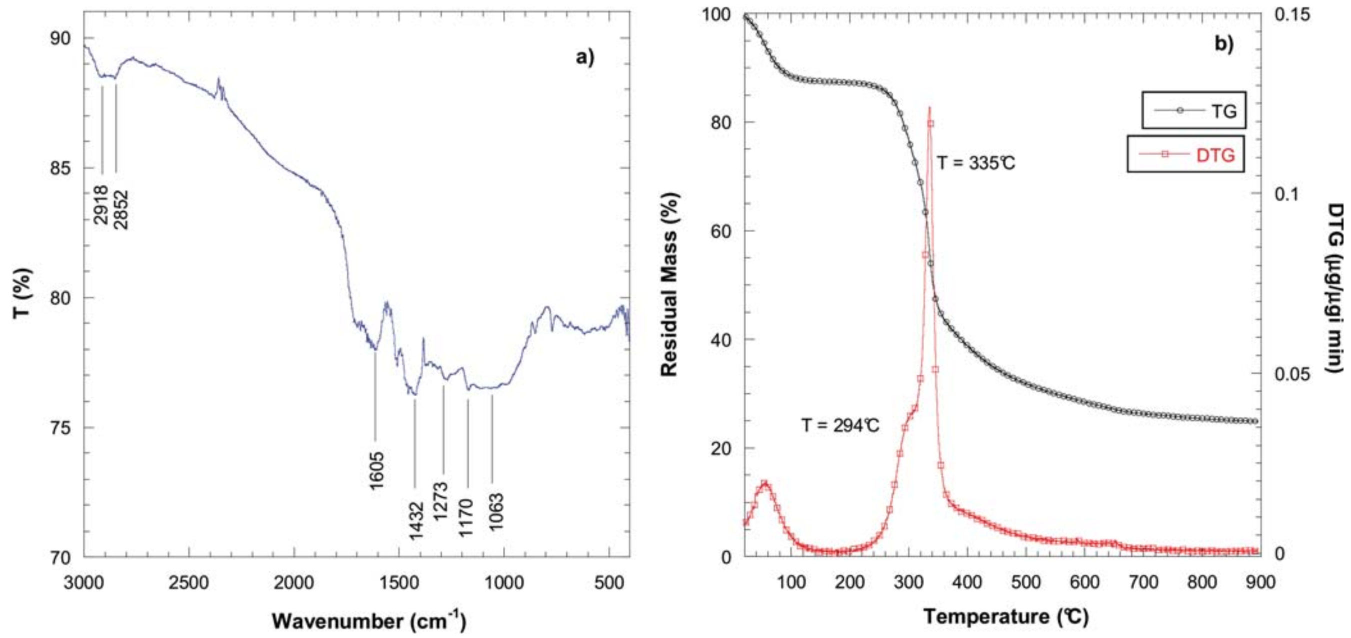

Figure 2 (**a**) FTIR spectrum and (**b**) weight loss and derivative weight loss curves of *P. Oceanica* pristine fibre.

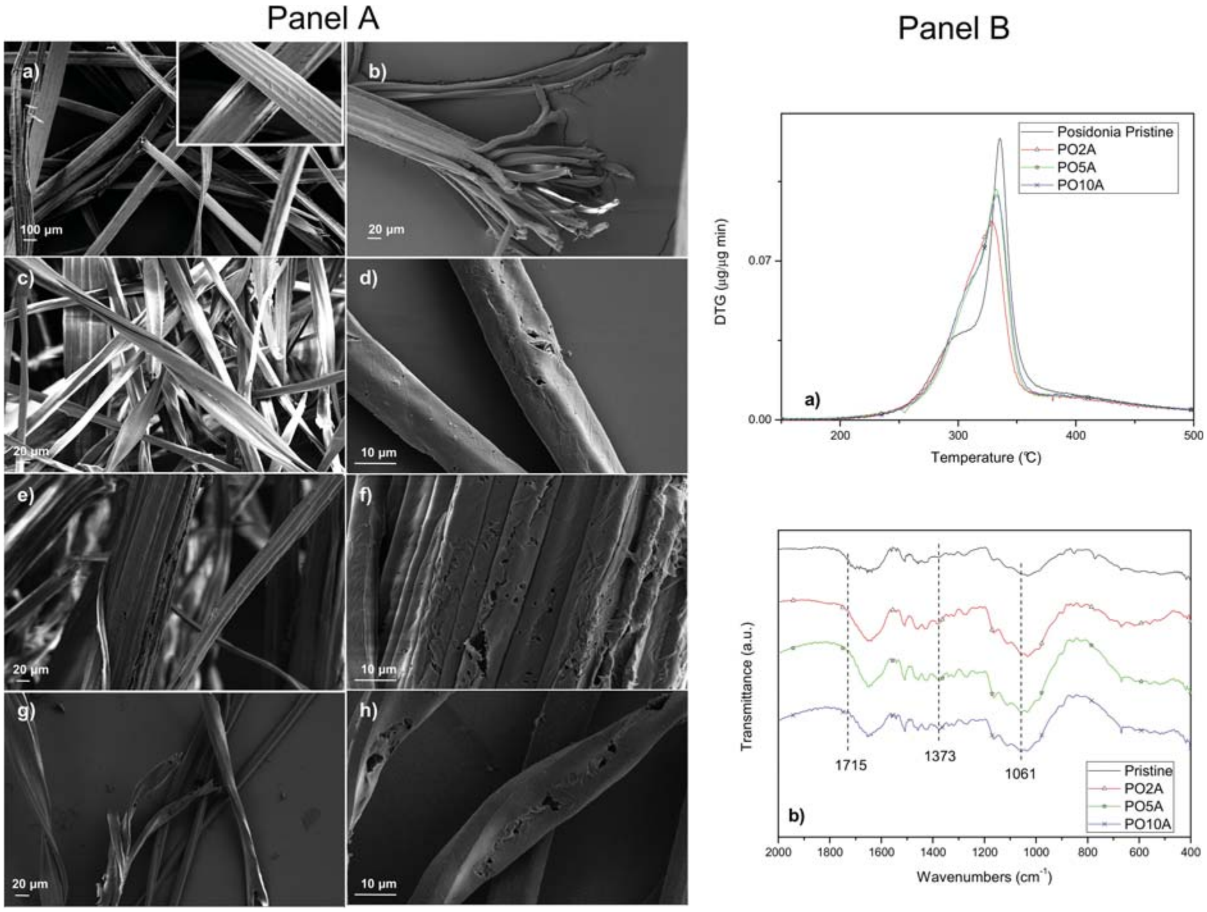

Figure 3 Panel A: FESEM images of (**a**) pristine and (**b**) alkali treated *P. Oceanica* fibres at different NaOH content (2 wt%: **c** and **d**; 5 wt%: **e** and **f**; 10 wt%: **g** and **h**). Panel B: (**a**) DTG curves and (**b**) FTIR spectra of pristine and alkali treated *P. Oceanica* fibres at different NaOH content.

into individual microfibrils, well individualized and with a regular, smooth and clean surface. A soft defibrillation process was induced in the case of treatment with NaOH, and the micrographs obtained in the case of POA2 fibres (2 wt% NaOH, Panel A: c and d), POA5 fibres (5 wt% NaOH, Panel A: e and f) and POA10 fibres (10 wt% NaOH, Panel A: g and h) confirm that the increasing content of sodium hydroxide seems to be detrimental from the point of view of surface regularity of the fibres, since a more porous structure was observed. In detail, it can be observed that different percentages of NaOH caused different levels of treatment on the fibre surface. For 2 wt% NaOH-treated fibre, some impurities can still be observed though, after the chemical treatment, a reduction in fibre dimensions was evident with an average diameter of (12 ± 3) µm. When the fibre was treated with 5 wt% NaOH and 10 wt% NaOH, some holes were observed, indicating that the caustic soda had removed a larger amount of the soluble substances from the respective layers, but the effect seems to be comparable in the case of POA5 fibres and POA10 fibres also in terms of final diameter (11 ± 2) µm in both cases. Alkali treatment is believed to have cleared the micropores in fibres and roughened the fibre surface, as a consequence of the removal of the impurities on the surface of the fibres [48]. Even if a porous surface of the fibres was observed, a compact and non-defibrillated structure of the macrofibril was obtained, indicating that this level of mercerisation treatment could not be efficient for the elimination of whole content of lignin and hemicellulose components from the pristine fibres.

This result was confirmed by thermal analysis reported in Figure 3 (Panel B: a). For all the studied alkali treated *Posidonia Oceanica* fibres, the main degradation peak was shifted to lower temperatures (333°C for POA5 and POA10, 328°C for POA2, with respect to the initial 335°C for pristine fibres) with a slightly reduced thermal stability in comparison with pristine fibres. Moreover, a less intense peak centered at 290°C attributed to the decomposition of hemicellulose fraction was detected for alkali treated *Posidonia Oceanica* fibre with respect to pristine fibre [49]. This might be caused by the alkali treatment, which reduced the hemicelluloses and lignin content of the fibre. As a result, fibres should become more hydrophobic, enhancing the possibility for better adherence to the matrix. Even in the case of thermal analysis, no substantial differences were registered for POA5 fibres and POA10 fibres.

The FTIR analysis reported in Figure 3 (Panel B: b) confirms the results of thermogravimetric analysis. The pristine fibres show a peak due to the residual hemicellulose at 1715 cm^{-1} that was not so evident for the alkali-treated fibres. Moreover, a shift of the peak at 1061 cm^{-1} of the original 1056 cm^{-1} related to the xylane and the glycosidic linkages of hemicellulose was detected for the three treated fibres. This shift proves the partial removal of hemicellulose fraction from the pristine fibres. The peak at 1373 cm^{-1} was due to the C-OH stretching of the hydrogen bond intensity of crystalline cellulose. These peaks remained unchanged for alkalized fibres, suggesting that the treatment did not affect the cellulose structure of the fibre.

On the basis of the previously obtained results, the 5 wt% of NaOH was selected as the less detrimental and useful treatment to be applied on pristine *Posidonia Oceanica* fibres for further evaluation of the treatment effect on the mechanical properties of the produced composites due to fibre surface modification.

3.3 Mechanical and Morphological Properties of *Posidonia Oceanica* Fibre-Based Composites

Figure 4 shows the stress-strain curves for neat PE and PE/PE-g-MA blend (Figure 4a), while in Figure 4b the results of a tensile test for the produced composites are reported.

As commonly observed in grafted systems, grafting of maleated polyolefins leads to a significant increase in the plastic region of the stress-strain curve in comparison to the neat matrix (Figure 4a). Despite a yield stress in the grafted system, a significant hardening of the specimen necked region occurs and the related deformation becomes very relevant, with the elongation at break for the grafted matrix that amounts to 343%, approximately two times higher than the neat polymer (Table 2).

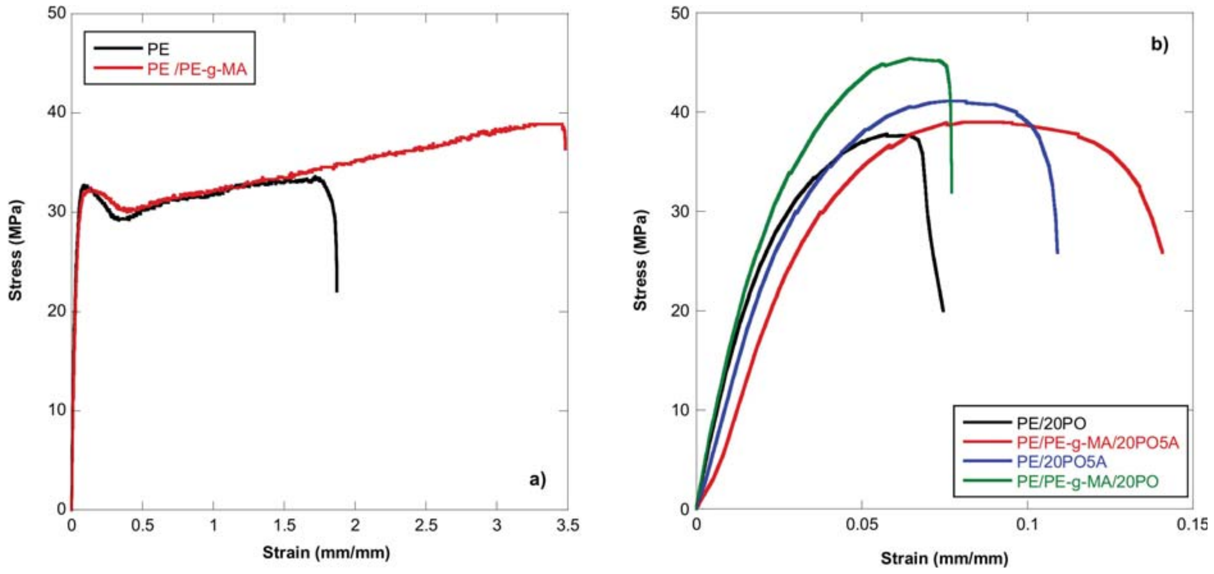

Figure 4 (**a**) Stress-strain curves for neat PE and PE/PE-g-MA blend and (**b**) *P. Oceanica* fibre-based composites.

Table 2 Results of tensile tests for the neat matrix and *Posidonia Oceanica* fibre-based composites.

Materials	Tensile Strength (MPa)	Young's Modulus (GPa)	Elongation at Break (%)
PE	36.64 ± 1.31	1.30 ± 0.12	177.53 ± 9.09
PE/PE-g-MA	38.86 ± 0.79	1.03 ± 0.06	343.15 ± 8.44
PE/20PO	38.71 ± 1.69	1.54 ± 0.04	7.81 ± 0.70
PE/20PO5A	40.55 ± 0.56	1.09 ± 0.04	10.5 ± 0.64
PE/PE-g-MA/20PO	45.58 ± 0.21	1.55 ± 0.08	7.30 ± 0.45
PE/PE-g-MA/20PO5A	39.58 ± 0.71	1.15 ± 0.07	13.65 ± 1.45

The material hardening also leads to an increase of the related strength at break. Finally, the PE/PE-g-MA blend also shows a lower Young's modulus than the neat PE matrix.

The addition of the *P. Oceanica* short fibres to the thermoplastic systems leads to a significant increase of the tensile strength and a considerable decrease of the elongation at break (Figure 4b). In particular, the plastic deformation occurring after the yielding point can be considered nearly negligible for all the composite systems. The inclusion of treated fibres, even in both the case of neat or grafted polymer, shows a decrease in the material tensile modulus. On the other hand, the composites containing untreated fibres have a slightly higher modulus than the matrix.

On the basis of the obtained results, it can be concluded that the best performance in terms of strength and stiffness could be attributed to the system based on the untreated *Posidonia* fibres and the grafted matrix, meaning that the alkaline fibre treatment of *Posidonia Oceanica* negatively affected the mechanical performance of the composites.

The FESEM images obtained from analysis of the specimens surfaces after the tensile test (Figure 5)

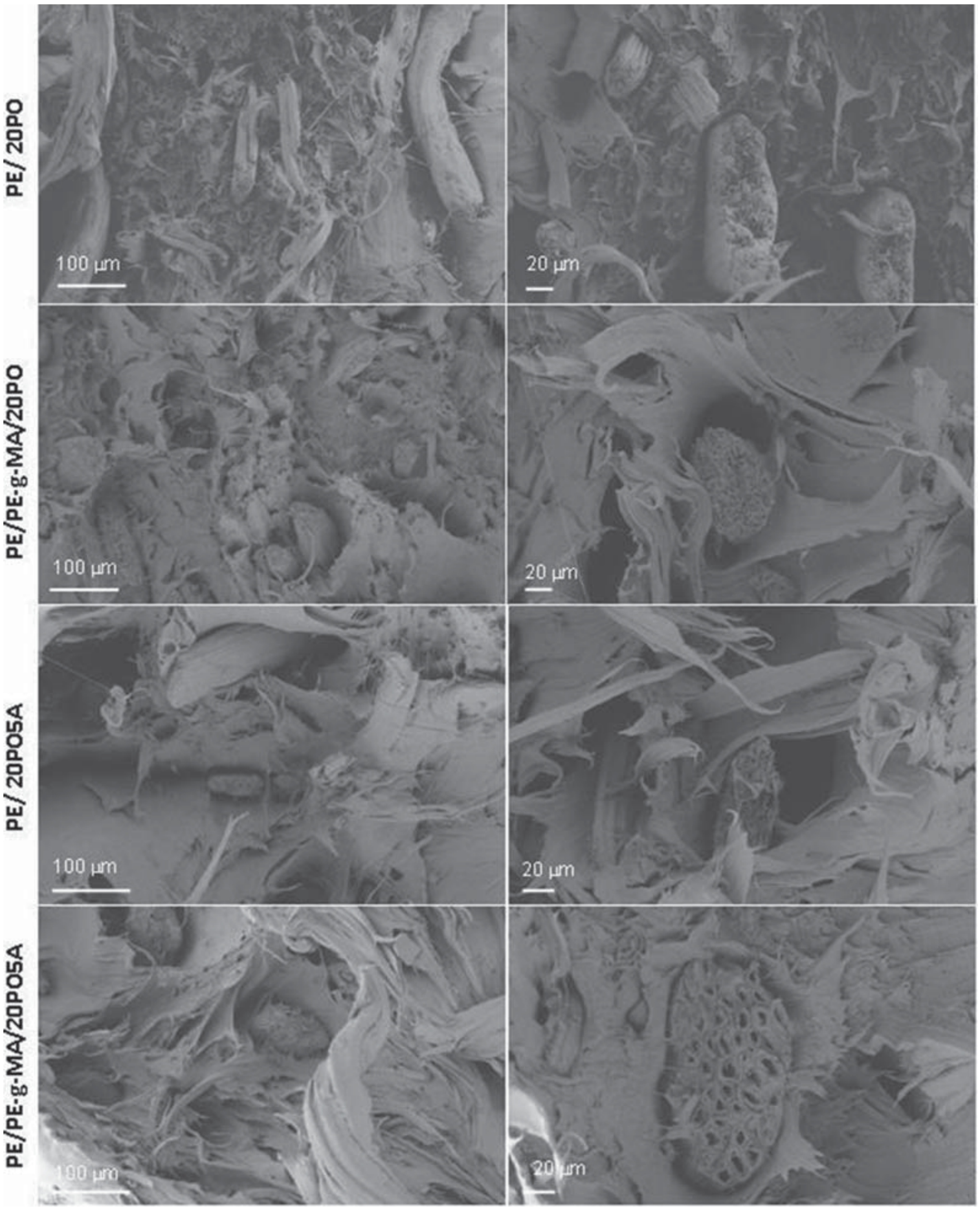

Figure 5 FESEM images of composite fracture surfaces at different magnifications.

confirmed the previous results, evidencing a very good fibre homogeneity inside the matrix, as well as a good interface between the matrix itself and the fibres in the case of composites containing untreated fibres (PE/20PO and PE/PE-g-MA/20PO); while a poor interface was detected in the case of composites containing alkali-treated fibres (PE/20PO5A and PE/PE-g-MA/20PO5A). Moreover, the addition of the compatibiliser determined a change in the matrix morphology with improved interfacial adhesion and reduced pull-out phenomena, which can be ascribed to the occurrence of chemical interactions between maleic anhydride and the hydroxyl groups on the fibre surface [50]. These micrographs also confirm that sodium hydroxide treatment could weaken the degree of adhesion at the interface between the matrix and the fibre, and also suggest that sodium hydroxide treatment alone may not be sufficient to strengthen the degree of adhesion at the interface. Further chemical treatments may be required to improve the strength of the sodium hydroxide treated natural fibre composites. On the basis of the mechanical response of all the tested composites, it can be concluded that, in the case of polyethylene-based composites containing fibres extracted from *P. Oceanica*, the compatibiliser has a significant role in the improvement of such properties, while the alkaline treatment seems to weaken the interface within this specific fibre.

4 CONCLUSIONS

The manufacture of composites based on *Posidonia Oceanica* wastes and thermoplastic matrix is an interesting solution to the management problem associated with algae accumulation. Therefore, this solution is attractive from both a technical and environmental point of view. These composites are reinforced with renewable waste resources and could find interesting applications at an industrial level. A polyethylene/polyethylene grafted with maleic anhydride blend was considered as polymer matrix and a 20 wt% of fibre extracted from *P. Oceanica* waste balls was added to the blend. An optimised alkaline treatment was used in order to investigate the combined effect that a compatibiliser and a chemical surface agent could have on this specific fibre when included in a polyolefin matrix. The effect of an increasing NaOH content (2, 5 and 10 wt%) on thermal, chemical and morphological behaviour of the fibres was investigated and the results confirmed that a 5 wt% NaOH treatment could be considered useful and not detrimental for the fibres. Composites based on *P. Oceanica* were successfully produced by a melt-blend compounding followed by an injection moulding procedure. The FESEM investigation of the composite fracture surfaces evidenced a good fibre homogeneity inside the polymer matrix with a very good interface between the matrix and the reinforcement phase in the case of untreated fibres, while the mechanical performance of the different composites seems to be unaffected or worsened in the case of alkali treated fibres. The results underlined and proved that it is possible to aim for a revalorisation of coastal algae and seaweed wastes as raw material for polyolefin matrix composites, even without applying a strong chemical treatment to the waste.

ACKNOWLEDGEMENT

The Authors acknowledge the financial support of SEAMATTER: Revalorisation of coastal algae wastes in textile nonwoven industry with applications in building noise isolation, LIFE11 ENV/E/000600, Funding Program: LIFE+. Call 2011

REFERENCES

1. J. Biagiotti, D. Puglia, and J.M. Kenny, A review on natural fibre based composites-part I: Structure, processing and properties of vegetable fibres. *J. Nat. Fibres* **1**, 37–68 (2004).
2. D. Puglia, J. Biagiotti, and J.M. Kenny, A review on natural fibre based composites-part II: Application of natural reinforcements in composite materials. *J. Nat. Fibres* **1**, 23–65 (2004).
3. T. Mukherjee and N. Kao, PLA based biopolymer reinforced with natural fibre: A review. *J. Polym. Environ.* **19**, 714–725 (2011).
4. S. Kalia, L. Avérous, J. Njuguna, A. Dufresne, and B.M. Cherian, Natural Fibres, Bio- and Nanocomposites. *Int. J. Polym. Sci.*, **2011**, 2 (2011), Article ID 735932, doi:10.1155/2011/735932.
5. S. Kumagai and Y. Matsuo, Composite produced from rice husk and chopped carbon fiber without using any binders. *Ind. Crop. Prod.* **43**, 640–647 (2013).
6. R.L. Quirino and R.C. Larock, Sugarcane bagasse composites from vegetable oils. *J. Appl. Polym. Sci.* **126**, 860–869 (2012).
7. J.E. Crespo, L. Sanchez, F. Parres, and J. Lopez, Mechanical and morphological characterization of PVC plastisol composites with almond husk fillers. *Polym. Compos*. 28, 71–77 (2007).
8. E. Garcia-Hernandez, A. Licea-Claverie, A. Zizumbo, A. Alvarez-Castillo, and P.J. Herrera-Franco, Improvement of the interfacial compatibility between sugar cane bagasse fibers and polystyrene for composites. *Polym. Compos*. **25**, 134–145 (2004).
9. W. Yamsaengsung and N. Sombatsompop, Interfacial adhesion and molecular diffusion in melt lamination of wood sawdust/ebonite NR and EPDM. *Polym. Compos.* **30**, 248–256 (2009).
10. V.J.P. Vilar, C.M.S. Botelho, and R.A.R. Boaventura, Copper removal by algae *Gelidium*, agar extraction algal

waste and granulated algal waste: Kinetics and equilibrium. *Bioresour. Technol.* **99**, 750–762 (2008).

11. J.G. Wu, X. Zhang, J.L. Wan, F.Y. Ma, Y. Tang, and X.Y. Zhang, Production of fiberboard using corn stalk pretreated with white-rot fungus *Trametes hirsute* by hot pressing without adhesive. *Bioresour. Technol.* **102**, 11258–11261 (2011).
12. M. Chauhan, M. Gupta, B. Singh, A.K. Singh, and V.K. Gupta, Pine needle/isocyanate composites: Dimensional stability, biological resistance, flammability, and thermoacoustic characteristics. *Polym. Compos.* **33**, 324–335 (2012).
13. P. Davies, C. Morvan, O. Sire, and C. Bale, Structure and properties of fibres from sea-grass (*Zostera marina*). *J. Mater. Sci.* **42**, 4850–4857 (2007).
14. B. Ferrero, T. Boronat, R. Moriana, O. Fenollar, and R. Balart, Green composites based on wheat gluten matrix and *Posidonia oceanica* waste fibres as reinforcements. *Polym. Compos.* **34**, 1663–1669 (2013).
15. R. Khiari, Z. Marrakchi, M.N. Belgacem, E. Mauret, and F. Mhenni, New lignocellulosic fibres-reinforced composite materials: A stepforward in the valorisation of the *Posidonia oceanica* balls. *Compos. Sci. Technol.* **71**, 1867–1872 (2011).
16. O. Faruk, A.K. Bledzki, H.P. Fink, and M. Sain, Progress report on natural fibre reinforced composites. *Macromol. Mater. Eng.* **299**, 9–26 (2013), doi:10.1002/mame.201300008.
17. R. Malkapuram, V. Kumar, and Y.S. Negi, Recent development in natural fibre reinforced polypropylene composites. *J. Reinf. Plast. Comp.* **28**, 1169–1189 (2009).
18. K.L. Fung, R.K. Y. Li, and S.C. Tjong, Interface modification on the properties of sisal fibre-reinforced polypropylene composites. *J. Appl. Polym. Sci.* **85**, 169–176 (2002).
19. A.K. Mohanty, L.T. Drzal, and M. Misra, Novel hybrid coupling agent as an adhesion promoter in natural fiber reinforced powder polypropylene composites. *J. Mater. Sci. Lett.* **21**, 1885–1888 (2003).
20. D.F. Caulfield, D. Feng, S. Prabawa, R.A. Young, and A.R. Sanadi, Interphase effects on the mechanical and physical aspects of natural fibre composites. *Angew. Makromol. Chem.* **272**, 57 (1999).
21. A. Beshay and S.V. Hoa, Improved interface bonding between cellulosic fibres and thermoplastics. *Sci. Eng. Compos. Mater.* **2**, 85–98 (1992).
22. K. Bledzki and J. Gassan, Composites reinforced with cellulose based fibres. *Prog. Polym. Sci.* **24**, 221–274 (1999).
23. X. Li, L.G. Tabil, and S. Panigrahi, Chemical treatments of natural fibre for use in natural fibre-reinforced composites: A review. *J. Polym. Environ.* **15**, 25–33 (2007).
24. Y. Xie, C.A.S. Hill, Z. Xiao, H. Militz, and C. Mai, Silane coupling agents used for natural fibre/polymer composites: A review. *Compos. A Appl. Sci. Manuf.* **41**, 806–819 (2010).
25. T.J. Keener, R.K. Stuart, and T.K. Brown, Maleated coupling agents for natural fibre composites. *Compos. A Appl. Sci. Manuf.* **35**, 357–362 (2004).
26. L. Sobczak, O. Brüggemann, and R.F. Putz, Polyolefin composites with natural fibres and wood-modification of the fibre/filler–matrix interaction. *J. Appl. Polym. Sci.* **127**, 1–17 (2013).
27. Y. Habibi, W.K. El-Zawawy, M. M. Ibrahim, and A. Dufresne, Processing and characterization of reinforced polyethylene composites made with lignocellulosic fibres from Egyptian agro-industrial residues. *Compos. Sci. Technol.* **68**, 1877–1885 (2008).
28. A. Bilal, R.J.T. Lin, and K. Jayaraman, Analysis of the mechanical properties of rice husk reinforced polyethylene composites using experiments with mixtures. *Adv. Mater. Res.* **747**, 395–398 (2013).
29. Tisserat, L. Reifschneider, N. Joshee, and V.L. Finkenstadt, Properties of high density polyethylene–Paulownia wood flour composites via injection moulding. *BioResources* **8**, 4440–4458 (2013).
30. K.J. Sim, S.O. Han, and Y.B. Seo, Dynamic mechanical and thermal properties of red algae fibre reinforced poly(lactic acid) biocomposites. *Macromol. Res.* **18**, 489–495 (2010).
31. I.N. Sim and S.O. Han, Effect on modified nanoclay on dynamic mechanical and thermomechanical properties of natural fibre/polypropylene biocomposites. *J. Adhes. Sci. Technol.* **27**, 1313–1323 (2013).
32. L. Luan, W. Wu, M.H. Wagner, and M. Mueller. Seaweed as novel biofiller in polypropylene composites. *J. Appl. Polym. Sci.* **118**, 997–1005 (2010).
33. L. Luan, W. Wu, and M.H. Wagner, Rheological behaviour of lubricating systems in polypropylene/seaweed composites. *J. Appl. Polym. Sci.* **121**, 2143–2148 (2011).
34. J.A. Khan, M.A. Khan, and R. Islam, Effect of mercerization on mechanical, thermal and degradation characteristics of jute fabric-reinforced polypropylene composites. *Fibres Polym.* **13**, 1300–1309 (2012).
35. C. Qin, N. Soykeabkaew, N. Xiuyuan, and T. Peijs The effect of fibre volume fraction and mercerization on the properties of all-cellulose composites. *Carbohydr. Polym.* **71**, 458–467 (2008).
36. D.L. Arvizu-Higuera, Y. Elizabeth Rodríguez-Montesinos, J. Iván Murillo-Álvarez, M. Muñoz-Ochoa, and G. Hernández-Carmona, Effect of alkali treatment time and extraction time on agar from *Gracilaria vermiculophylla*. Dev. Appl. Phycol. **2**, 65–69 (2009).
37. A. Coletti, A. Valerio, and E. Vismara. *Posidonia oceanica* as a renewable lignocellulosic biomass for the synthesis of cellulose acetate and glycidyl methacrylate grafted cellulose. *Materials* **6**, 2043–2058 (2013).
38. R. Khiari, M.F. Mhenni, M.N. Belgacem, and E. Mauret, Chemical composition and pulping of date palm rachis and *Posidonia oceanica*—A comparison with other wood and non-wood fibre sources. *Bioresour. Technol.* **101**, 775–780 (2010).
39. M.C. Ncibi, V. Jeanne-Rose, B. Mahjoub, C. Jean-Marius, J. Lambert, J.J. Ehrhardt, Y. Bercion, M. Seffen, and S. Gaspar, Preparation and characterisation of raw chars and physically activated carbons derived from marine *Posidonia oceanica* (L.) fibres. *J. Hazard. Mater.* **165**, 240–249 (2009).
40. M. Belzunce, R.M. Navarro, and H.F. Rapoport, *Posidonia oceanica* seedling root structure and development. *Aquat. Bot.* **88**, 203–210 (2008).

41. W.D. Larkum, R.J. Orth, and C.M. Duarte, *Seagrasses: Biology, Ecology and Conservation*, Springer, Dordrecht, the Netherlands, 51-87 (2006–2007).
42. P. Francesca, M. Sara, and T. Luigi, New biosorbent materials for heavy metal removal: Product development guided by active site characterization. *Water Res.* **42**, 2953–2962 (2008).
43. R.R.E. Artz, S.J. Chapman, A.H.J. Robertson, J.M. Potts, F. Laggoun-Defarge, S. Gogo, L. Comont, J.R. Disnar, and A.J. Francez, FTIR spectroscopy can be used as a screening tool for organic matter quality in regenerating cutover peatlands. *Soil Biol. Biochem.* **40**, 515–527 (2008).
44. M. Grube, J.G. Lin, P.H. Lee, S. Kokorevicha, Evaluation of sewage sludge-based compost by FT-IR spectroscopy, *Geoderma* **130**, 324–333 (2006).
45. M. Izquierdo, P. Marzal, C. Gabaldon, M. Silvetti, and P. Castaldi, Study of the interaction mechanism in the biosorption of Copper(II) ions onto *Posidonia oceanica* and peat. *CLEAN Soil Air Water* **40**, 428–437 (2012).
46. A. Cocozza, A. Parente, C. Zaccone, C. Mininni, P. Santamaria, and T. Miano. Chemical, physical and spectroscopic characterization of *Posidonia oceanica* (L.) Del. residues and their possible recycle. *Biomass Bioenergy* **35**, 799–807 (2011).
47. A. Chadlia and M.M.Farouk. Chemical modification of Posidonia with cyclic anhydrides: Effect on thermal stability. *Carbohydr. Res.* **345**, 264–269 (2010).
48. M.M. Kabir, H. Wang, K.T. Lau, and F. Cardona, Effects of chemical treatments on hemp fibre structure. *Appl. Surf. Sci.* **276**, 13–23 (2013).
49. T. Fisher, M. Hajaligol, B. Waymack, and D. Kellogg, Pyrolysis behaviour and kinetics of biomass derived materials. *J. Anal. Appl. Pyrolysis* **62**, 331–349 (2002).
50. M. Pracella, Md. M. Ul Haque, and V. Alvarez, Functionalization, compatibilization and properties of polyolefin composites with natural fibers. *Polymers* **2**, 554–574 (2010).