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Additional Information

**“Development of natural fiber reinforced plastics (NFRP) based on biobased polyethylene
and waste fibers from *Posidonia Oceanica* seaweed”**

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Abstract

In the present study the valorization of wastes from *Posidonia Oceanica* (PO) has been carried out in order to obtain a fully biobased composite material in combination with a biobased polyethylene obtained from sugar cane as matrix. Morphological analysis by scanning electron microscopy (SEM) of the fractured surfaces from impact tests has revealed a homogenous distribution of particles of PO, as a consequence, good balanced properties have been obtained for composites with PO contents in the 5-40 wt. %. Thermal properties of composites have been studied through differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA); the obtained results show an improvement on the thermal degradation. With regard to thermomechanical properties, dynamic mechanical analysis (DMA) results have shown a much enhanced storage modulus (G') as the *Posidonia Oceanica* content increases. Tensile tests have shown a remarkable increase in stiffness with tensile modulus values about 60% higher for composites with 40 wt. % with regard to unfilled material. In a similar way, the flexural modulus is more than twice with regard the unloaded polyethylene. Shore D hardness confirms this improvement on mechanical properties and Charpy Impact Test shows values very similar to sample without PO, so that the intrinsic high impact energy absorption of HDPE is maintained in HDPE-PO composites. The water uptake test determines that the water absorption percent does not exceed 8%, which is relatively low for a high immersion time (5 months), which guarantees a dimensional stability in lifetime for these composites.

1. Introduction

Posidonia Oceanica is a Mediterranean endemic seaweed which covers approximately the 60% of the seabed until 40 m depth [1]. In particular, it represents an extension area of about 2800 km² [2] in the Mediterranean coast of Spain. *Posidonia Oceanica* plays a critical role as it acts as a natural protection of the seabed thus preventing the advance of the erosive process. Moreover is the habitat of more than 400 vegetable and 1000 animal species [3]. Its importance on the overall marine environment, coast and seabed protection and biodiversity are leading factors to advise its legal protection. For example, at European level, it has been included as strictly protected flora specie. (Council Directive 97/62/EC and Regulation (EC) No 1626/94). At state level, countries as France or Spain have protected this flora specie and have declared *Posidonia Oceanica* meadows as zone of conservation [4].

Seasonally *Posidonia Oceanica* detaches rhizomes, calculating a production between 500 and 2000 g dry weight m⁻² per year [5-7], depending on meteorological conditions as winds, storms or marine currents. This accumulation of wastes from *Posidonia Oceanica* on the beach is clearly observable, especially in autumn and winter in the form of leaves, stalks and typical fibrous balls. Thus, each year beaches must be cleaned in order to remove *Posidonia Oceanica* wastes as they cause odors due to its decomposition (and subsequent appearance of insects) and to a negative visual impact, especially for tourism purposes. Mediterranean countries are characterized by a strong beach tourism sector. Presence of big amounts of *Posidonia Oceanica* wastes involves a significant financial cost to the government, which must remove thousand tons of wastes from the beaches in order to obtain quality awards such as the international Blue Flag awarded by the Foundation for Environmental Education (FEE) or the Q for Quality distinction awarded by the Spanish Tourism Quality Institute (ICTE). Traditionally *Posidonia Oceanica* wastes have been collected and used as fodder for livestock, packing glass objects, in traditional medicine due to its anti-inflammatory properties, filtering, etc.; but these activities results in a negligible use of this waste, which can be found in large volumes and carries an economic high cost to be removed from beaches.

In the recent years some authors have studied possible uses of *Posidonia Oceanica* as a renewable adsorbent for dyes or as source of lignocellulosic fibers for the production of pulp and paper [8, 9]. An alternative is to use these wastes as reinforcement fibers in composites with a polymeric matrix thus leading to new natural fiber reinforced plastics (NFRP) which are gaining attractive interest due to recent environmental concerns. The production and use of NFRPs and wood plastic composites (WPCs) have increased considerably during the last decades [10, 11]. WPCs show significant advantages at economical and environmental concerns but also they are attracting from a technical point of view as they can be shaped by conventional manufacturing processes such as hot-press molding, extrusion and injection process [12]. As an alternative to wood, WPCs are characterized by high dimensional stability, lightness, longer lifetime and lower maintenance requirements [13]. WPCs are used in building products that have limited structural requirements. Their utilization in products as industrial flooring, decking, railing, moldings, walls, indoor furniture, automobile interior parts, etc. results in a product market with an annual growth of 18 and 14% in North America and Europe respectively [14]. Moreover, in order to improve the environmentally friendly nature of the WPCs, recycled plastics and biodegradable plastics can be used as matrices which leads to similar mechanical properties to virgin polymers or petro-chemical derived polymers [15, 16]. A step forward in the field of environmentally friendly polymers has been done by Braskem leads industrial production of polyethylene from sugar cane. The different commercial grades of “Green PE” supplied by Braskem offer identical properties as those of the corresponding petroleum-based PE grades but with a remarkable environmental benefit. Production of Green PE does not lead to CO₂ emissions; as it is obtained from sugar cane, it fixes about 2.5 t CO₂/t polymer, while typical CO₂ emissions of a petroleum-based PE are about 2.1 t CO₂/t polymer [17].

In the present work natural fiber reinforced plastics (NFRPs) have been developed by using a biobased HDPE as matrix and waste fibers from *Posidonia Oceanica* as reinforcement in order to give an industrial solution to the problematic associated to seaweed wastes. The influence of the *Posidonia Oceanica* content on the melt viscosity is studied by measuring the Melt Flow Index (MFI) and the dispersion of *Posidonia Oceanica* particles and interaction

fiber/matrix are followed scanning electron microscopy (SEM) analysis. The effect of *Posidonia Oceanica* fibers on thermal behavior of composites is evaluated by differential scanning calorimetry (DSC) and thermogravymetric analysis (TGA) and mechanical properties are obtained by tensile and flexural tests, Charpy's impact test and Shore D hardness. In addition, the effect of temperature on mechanical-dynamical in shear are presented.

2. Experimental

2.1.- Materials

Posidonia Oceanica balls were collected from different beaches located in coast of Valencia (Spain). They were washed with 4% NaOH solution for 24 h to remove impurities such as sand, soil and other contaminants. After this initial process, *Posidonia Oceanica* balls were dried at room temperature and subsequently milled using an ultra-centrifugal mill (Retsch GmbH, Hann, Germany) working at a rotational speed of 6000 rpm to obtain an average particle size of 250 μm .

The selected matrix for composites was a biobased high density polyethylene (HDPE) commercial grade Green HDPE SHA7260 for injection molding supplied by Braskem (Sao Paulo, Brasil). This bio-HDPE is produced from ethanol derived from sugar cane, a fully renewable source. It is characterized by a melt flow index, MFI of 20 g (10 min)⁻¹, a density of 0.956 g·cm³ and a minimum biobased content of 94.5% [17].

2.2.- HDPE-*Posidonia Oceanica* composite preparation

In a first step, the appropriate amounts of bio-HDPE and *Posidonia Oceanica* particles were weighed to obtain different composite formulations (5, 10, 20, 30 and 40 wt. % *Posidonia Oceanica*) and subsequently mechanically mixed in a zip bag. After this, the different formulations were extruded in a twin screw co-rotating extruder at 40 rpm. The temperature profile was 160, 160, 165 and 170 °C. After cooling, the different compounds were pelletized for further processing by injection molding with a Meteor 270/75 (Mateu and Solé, Barcelona,

Spain) using an injection temperature of 190 °C to avoid degradation of the lignocellulosic component. A steel mold with mirror finishing with standardized sample geometries was used.

2.3.- Melt flow index characterization

The melt flow index (MFI) of the pelletized compounds was determined with a plastometer model ATS FAAS by Metrotec (SA Metrotec, San Sebastian, Spain) in accordance with the guidelines of the ISO 1133. The selected temperature and load were 190 °C and 2.16 kg respectively. Every compound formulation was tested at least three times and the average MFI value was calculated.

2.4.- Mechanical characterization

The flexural and tensile properties of the different samples were measured by an electromechanic universal test machine Ibertest Elib 30 (Ibertest S.A.E., Madrid, Spain) following the guidelines of the ISO 178 and ISO 527 respectively. The size of the flexural samples are 80x10x4 ± 2 mm as the normative recommended. The flexural modulus in MPa is determinate according the following expression:

$$E_f = \frac{\sigma_{f2} - \sigma_{f1}}{\varepsilon_{f2} - \varepsilon_{f1}} \quad (1)$$

Where σ_{f1} is the flexural stress measured by the arrow S_1 , and σ_{f2} is the flexural stress measured by the arrow S_2 . The arrow in S_1 and S_2 , correspond to the values of deformation in points $\varepsilon_{f1} = 0.0005$ and $\varepsilon_{f2} = 0.0025$ with the following expression:

$$S_1 = \frac{\varepsilon_{f1} L^2}{6 h} \quad (2)$$

Where S_1 is the arrow in mm, ε_{f1} is the flexural deformation, L is the distance between supports in mm and h is the thickness of the sample.

On the other hand the size of the tensile samples are in weightlifting shape with 150 mm total length and 20 mm broad in the extremes. The narrow part is 60 mm length and 10 mm of broad. The thickness is 4 mm constant in all sample. The tensile modulus is obtained following the next expression:

$$E = \frac{L_0 F}{\Delta l A_0} \quad (3)$$

Where F is the force, L_0 is the original length, Δl is the amount by which the length changes and A_0 is the original cross-sectional area. A load cell of 5 kN was used and the crosshead speed for flexural tests and tensile tests was set to 5 mm·min⁻¹ and 10 mm·min⁻¹ respectively.

The Shored D hardness of HDPE-*Posidonia Oceanica* composites was obtained in a Shore D hardness durometer model 676-D (J. Bot Instruments, Barcelona, Spain) according to ISO 868. On the other hand, the impact energy of notched samples was determined using a 1 J Charpy pendulum following the guidelines of the ISO 179 standard. The size of the samples for Charpy test are 80x10x4 ± 2 mm.

2.5.- Characterization by scanning electron microscopy (SEM)

Fractured surfaces from impact tests of HDPE-*Posidonia Oceanica* composites were observed with a scanning electron microscope (SEM) model Phenom (FEI Company, Eindhoven, The Netherlands). Before observation, samples, mounted on a conductive adhesive tape, were covered with a thin gold-palladium layer. The coating process lasted 120 seconds using the model of sputter-coater Emitech mod. SC 7620 (Quorum Technologies Ltd, East Sussex, UK). Then, samples were observed in the SEM working at an electron acceleration voltage of 5 kV.

2.6.- Thermal analysis of HDPE-Posidonia Oceanica composites

Thermal properties of HDPE-*Posidonia Oceanica* composites were characterized by thermogravimetry (TGA) and differential scanning calorimetry (DSC). Thermogravimetric measurements were carried out in a TGA/SDTA 851 (Mettler-Toledo Inc., Schwerzenbach, Switzerland) and the temperature ranged from 30 °C to 700 °C with a heating rate of 20 °C min⁻¹ under nitrogen atmosphere of 66 mL min⁻¹. Thermal transitions were obtained by differential scanning calorimetry (DSC) using a Mettler-Toledo 821 (Mettler-Toledo Inc., Schwerzenbach, Switzerland) and the temperature program used was from 30 °C to 300 °C at 10 °C min⁻¹ under nitrogen atmosphere of 66 mL min⁻¹. All samples have a weight between 5 and 10 mg.

2.7.- Dynamic mechanical thermal analysis (DMTA) of HDPE-Posidonia Oceanica composites

DMTA was carried out using an AR G2 from TA Instruments (TA Instruments, New Castle, EEUU) in torsion mode. Rectangular samples 40x10x4 mm³ in size were subjected to a temperature ramp from -50 °C up to 100 °C with heating rate of 2 °C min⁻¹ at frequency of 1 Hz and using as a controlled variable the % strain in 0.1. The storage modulus is obtained following the next expression:

$$E' = \frac{\sigma_0}{\varepsilon_0} \cos \delta \quad (4)$$

Where E' is the storage modulus, σ is the stress, ε is the strain and δ is the phase lag between stress and strain.

2.7.- Water uptake of HDPE-Posidonia Oceanica composites

The water uptake test was carried out by immersing samples in distilled water (20 °C) for a 5 months period. Test specimens sized 80x10x4 mm³ and at least five different samples were tested to obtain the average value of each sample. Water absorption percentage was determined by the following expression:

$$WA (\%) = \frac{(M_f - M_o)}{M_o} \times 100 \quad (5)$$

Where WA (%) is the water absorption percentage, M_f is the dry weight of the sample after the corresponding time and M_o is the initial weight of the sample before immersed in water. A measured was taken every week in order to follow the water uptake evolution.

3. Results and discussion

Firstly, the melt flow index (MFI) of HDPE-*Posidonia Oceanica* composites is useful from a manufacturing point of view in order to evaluate the influence of the particle addition on the processability by injection molding of the different composite formulations. Fig. 1 shows the plot evolution of the MFI in terms of the percentage of *Posidonia Oceanica* particle content.

Figure 1

As it can be observed, Fig. 1 shows a clear decreasing tendency in MFI values as the *Posidonia Oceanica* content increases. This reduction of fluidity reached 53% for a sample with 40 wt. % *Posidonia Oceanica*. However, even a MFI of 6.1 g (10 min⁻¹) does not restrict the injection process in an industrial injection molding machine and only some adjustments in pressure in time cycle have to be done. Thus, the incorporation of *Posidonia Oceanica* particles up to 40 wt. % is not a drawback to obtain HDPE-*Posidonia Oceanica* composites in usual manufacturing process used in the plastics industry. This increase in viscosity is typical of polymer-filled systems as the filler increases the shear by restricting polymer chain mobility [11].

To evaluate the particle dispersion and potential interactions among fiber-polymer interface, the morphology of the fractured surfaces from impact tests were observed by scanning electron microscopy (SEM). In Fig. 2a it is possible to observe a moderate surface roughness corresponding to the unfilled HDPE matrix. This morphology is characterized by small crack produced during the advance of the impact test. On the other hand, in the images corresponding to HDPE-*Posidonia Oceanica* composites it is possible to observe an increase in particle presence as *Posidonia Oceanica* content increases. Particles are quite homogeneously distributed

within the thermoplastic matrix, even for the samples with high content of *Posidonia Oceanica* (30 wt. % and 40 wt. % which represents higher volume contents due to the low density of the lignocellulosic waste). Also these images can be useful to determine particle-matrix interactions. As we can see, very small gaps between *Posidonia* particles and the surrounding HDPE matrix can be detected. Even in samples with high *Posidonia* content (Fig. 2e and Fig. 2f) the interaction between the filler and the matrix is acceptable. This suggests that exists an acceptable compatibility between the particle and the polymeric matrix, which is evident from the absence of large gaps between the particles and the polymer matrix. [18]

Figure 2

The thermal properties of the matrix of bio-HDPE and the other materials prepared in this study, has been studied by DSC and TGA. Table 1 summarizes the main parameters obtained with both techniques. Firstly, through DSC, the melting temperature and the degradation temperature of the samples has been studied. The melting temperature of the different composites are slightly above compared with the sample of bio-HDPE without *Posidonia Oceanica*. The difference are less than 3 °C, but could be as a consequence of the presence of phenolic compounds presents in the cells constituting the *Posidonia Oceanica* [19]. The degradation temperature has a similar trend, being slightly higher in composite made with certain *Posidonia Oceanica* content. Some authors has registered similar aspects, with DSC tracings of composites with *Posidonia Oceanica* very similar to the reference sample. Thus, in despite of the introduction of high contents of lignocellulosic fillers, the thermal properties are not affected, in any cases, slightly increased. Some authors justified this behavior as a change of the degradation mechanism. In composites it has been found a complex two-step nucleation-driven reaction, while a polymer without fillers the degradation mechanism is based in a chain scission process [20]. On the other hand, as a consequence, some parameters as the flexibility of the samples or extrusion and injection process are not negatively influenced [21].

On the other hand, thermogravymetric analysis (TGA) shows that *Posidonia oceanica* fibers start to lose weight at about 235 °C with a 50% weight loss close to 550 °C. The degradation of *Posidonia oceanica* corresponds to the first step detected in TGA curves for HDPE-*Posidonia oceanica* composites. However, it should be noted that in all composites, the initial temperature of the first weight loss process is increased up to 15 °C. This suggests that the thermal stability of *Posidonia oceanica* inside the HDPE matrix is slightly increased. Obviously, as the *Posidonia oceanica* content increases in composites the residual mass ratio of this first weight loss process is greater. The second weight loss process corresponds to the degradation of the HDPE polymeric matrix. As it can be seen for the unfilled HDPE, the degradation onset temperature is about 350 °C and almost a 92 wt. % is lost at 520 °C. As observed with weight loss of *Posidonia oceanica* and its degradation process, the degradation onset temperature for the second degradation stage (HDPE degradation) is shifted from 350 °C up to 390.5 °C. Therefore, it seems to be a synergistic effect which delays the onset degradation temperature of both the polymeric matrix as the *Posidonia oceanica* separately which is related with presence of natural phenolic compounds in *Posidonia oceanica* [22]

Table 1

The dynamic mechanical analysis (DMA torsion mode) of composites with different *Posidonia oceanica* contents from -150 °C has shown that the glass transition temperature (T_g) does not change in a remarkable way with a value around -123 °C for both filled and unfilled HDPE which is representative for poor interaction. Thus, the addition of *Posidonia oceanica* does not affect the T_g of the bio-HDPE [21]. Fig. 3 shows the evolution of the storage modulus (G') of the different composites in function of the temperature. The storage modulus is studied to a temperature of -50, since it is not expected that a WPC is subjected in real conditions to temperatures below. At lower temperatures polymers and composites enter in a glassy region characterized by high values of storage modulus but extremely high fragility, which impedes real uses. The storage modulus decreases as the temperature is increased due to softening of

polymer (increase in chain mobility) as we get near the melt temperature. As it can be seen in Fig. 3, the addition of *Posidonia oceanica* waste fibers leads to an increase in storage modulus (G') as observed by a displacement towards higher G' values thus indicating more stiff materials. If we consider a reference temperature of 25 °C, all HDPE-*Posidonia oceanica* composites are characterized by higher storage modulus than the unfilled bio-HDPE: i.e. the addition of a 5 wt. % provides an increment of the storage modulus above 46% and this increase reaches values of almost 118% for composites with 40 wt. % *Posidonia oceanica*. This behavior evidences the reinforcing effect provided by the filler with high cellulose content. Particles immersed in a HDPE polymer matrix act as interlock points which restrict chain mobility and even with a poor polymer-filler interaction, stiffer materials are obtained. [23] It is also important to remark that the increasing tendency for the storage modulus G' is clearly evident for all compositions but very slow differences between 30 wt. % and 40 wt. %. This is important since higher filler addition (over 30 wt.%) does not lead to an increase in storage modulus.

Figure 3

Table 2 shows a summary of the mechanical properties obtained by tensile and flexural tests of HDPE and *Posidoniaeae oceanica* composites. As it can be seen, the tensile modulus of the composites is highly improved as the filler content is increased. The tensile modulus of the unfilled HDPE is close to 373 MPa, and this value is remarkably improved up to values of 521.9 MPa (40% increase) and 600.9 MPa (60% increase) for composites containing 30 wt. % and 40 wt. % *Posidonia oceanica* respectively. These results are in agreement with the previously described DMA results thus indicating a remarkable increase in stiffness. The elongation at break of composites with different *Posidonia oceanica* contents is remarkably reduced from 520% (unfilled HDPE) up to 3.3% for the composite with 40 wt. % *Posidonia oceanica*. This is typical of particle-filled polymer systems with poor or no compatibility between components so that, stress transfer phenomena can't occur and the general behavior of the particle filler is that

of a stress concentrator thus leading to early fracture [24]. With regard to the tensile stress, it remains with interesting values close to 18-19 MPa for all compositions. The effect of the filler is more accurate on flexural properties of HDPE-*Posidonia oceanica* composites. We observe an increasing tendency for flexural strength from 23 MPa (unfilled HDPE) to 30.8 MPa (composite with 40 wt. % *Posidonia oceanica*) and the flexural modulus evolution shows a substantial increase for samples from 723 MPa (unfilled HDPE) up to 1430 MPa and 1762 MPa for composites with 30 wt. % and 40 wt. % *Posidonia oceanica* respectively.

Table 2

The mechanical properties are completed with the study of the Shore D hardness and Charpy's impact test of composites. The results obtained are represented in Fig. 4. Shore D hardness evolution is similar to the previously described mechanical resistance properties such as elastic modulus, flexural modulus and storage modulus. The addition of *Posidonia oceanica* leads to stiffer composites due to the reinforcing effect of the particle-filler which play a key role in restricting polymer chain mobility [25, 26]; i.e. an increase in Shore D hardness of about 11% is achieved with the incorporation of 40 wt. % *Posidonia oceanica*. But usually, one of the main drawbacks of the incorporation particles, fillers and loads to polymeric matrices is the decrease in toughness which represents the ability of the material to absorb energy during the deformation and fracture processes typical of an impact. Toughness is highly dependent on two main factors: supported stress and deformation before fracture. As we have seen previously, the tensile strength remains with almost constant values while the elongation at break suffers a dramatic decrease as the *Posidonia oceanica* content increases. For this reason, the Charpy's impact test was carried out on notched standard samples. The initial impact energy of the unfilled HDPE is around 2.6 KJ m⁻² and as it can be observed, the impact energy for composites with *Posidonia oceanica* is slightly lower than the unfilled material with values of about 2.5 KJ m⁻². This feature is quite interesting and useful in practice because these composites are able to retain similar capacity to absorb impact energy as the unfilled material, but with an advantage of

an overall increase in mechanical resistance properties. It has been reported that the addition of whiskers, particles or loads to polymeric matrices could reduce or even improve the tenacity of polymers depending of the interaction between the matrix and particles [27, 28]. As we have described previously, we have not detected high interaction between the highly hydrophobic HDPE matrix and the highly hydrophilic *Posidonia oceanica* reinforcement but as toughness depends on supported stress and ability to deform, tenacity of HDPE-*Posidonia oceanica* composites remains almost constant as the dramatic decrease in mechanical ductile properties (such as elongation at break) is compensated by an increase in stiffness (moduli) and tensile and flexural strengths. It is possible that the tubular capillary structure of the *Posidonia oceanica* fibers helps to dissipate the energy, thus giving as a consequence a good toughness for composites.

Figure 4

The addition of natural fibers provides multiple advantages from different points of view: economical advantages due to up-grading industrial and/or biobased wastes, environmental advantages due to a reduction in the carbon footprint, biodegradability, etc. and technical aspects as described previously. Nevertheless the addition of natural lignocellulosic particles in products designed to stay in outdoor could have one main drawback: the highly hydrophilicity of the natural fibers. The presence of hydroxyl groups in the structure of cellulose attracts water molecules and moisture, which could modify the dimensional stability of products as decking, walls, flooring, louvers, indoor furniture, etc. [29]. For this reason, it is important to quantify the extent of the water uptake for these composites.

Fig. 5 shows the plot evolution of the water uptake (absorption percentage) of HDPE-*Posidonia oceanica* composites immersed in water for a period of 5 months. Cellulose and hemicellulose presents in *Posidonia oceanica* are characterized by high sensitiveness to water and moisture. As we have described in a previous paper, *Posidonia oceanica* wastes are characterized by a high cellulose and hemicellulose content [18]. For this reason, as the

Posidonia oceanica content in HDPE composites increases, the percentage of absorbed water is greater; i.e., the unfilled HDPE has a weight gain due to water absorption of about 0.32% after an immersion period of 5 months while the composite containing 40 wt. % *Posidonia oceanica* reaches a weight gain of less than 8% after the same period. Compared with other studies, the absorbed water is not high. Klyosov determines typical water absorption for wood plastic composites (WPCs) up to 18% after several months [30]. Other studies carried out with HDPE-based WPCs offer water uptake values of about 15%-16% [31]. On the other hand, it is important to remark that commonly accepted water uptake in wood products is 25% moisture content; this represents the minimum level necessary to start a decrease in mechanical properties and bacterial growth [32]. Thus, the maximum water uptake for HDPE-*Posidonia oceanica* composites with values of 8% for high filler content (40 wt. % *Posidonia oceanica*) guarantees dimensional stability and no growth of bacteria and fungi during the use in outdoor applications.

Figure 5

4. Conclusions

The use of *Posidonia oceanica* as particle filler for NFRP (natural fiber reinforced plastics) is an interesting solution for upgrading this natural waste, that every year is accumulated in beaches and entail an elevated economical cost for local governments. Composites of *Posidonia oceanica* with HDPE derived from sugarcane are fully based on renewable resources and could be used in multiple applications replacing wood and wood like products thus reducing dependency on petrochemical-based materials. Composites with 30-40 wt. % *Posidonia oceanica* are characterized by interesting mechanical performance. The water uptake test guarantees a dimensional stability of these composites for outdoor applications such as decking, flooring, railing, automobile interior parts, indoor furniture, etc. SEM results revealed that *Posidonia oceanica* particles could be dispersed correctly in a green-HDPE matrix and despite poor matrix-filler interaction is obtained, mechanical resistant properties increase and toughness remains almost constant. Addition of *Posidonia oceanica* particles has a

synergistic effect on thermal stability of both waste fibers and HDPE matrix. This work offers new environmentally friendly materials for a wide range of industrial applications as a substitute of wood and wood-like products.

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Figure Caption

Figure 1.- Variation of MFI of the bio-HDPE and WPCs compounds in terms of the wt. % of PO.

Figure 2.- SEM images (500x) of fractured surface from impact test of the composites with (a) 0, (b) 5 wt.%, (c) 10 wt.%, (d) 20 wt.%, (e) 30 wt.%, (f) 40 wt.% of PO loadings.

Figure 3.- Plot evolution of the storage modulus of HDPE composites with different *Posidonia oceanica* contents.

Figure 4.- Plot evolution of the Shore D hardness and Charpy's impact energy of HDPE composites with different *Posidonia oceanica* contents.

Figure 5.- Plot evolution of the water absorption percentage of HDPE composites with different *Posidonia oceanica* contents as a function of immersed time.

Table Captions

Table 1.- Summary of the values obtained by DSC and TGA.

DSC			TGA					
			first weight loss process			second weight loss process		
Sample	Melting Temp, T _m (°C)	Degradation Temperature (°C)	Initial Temp (°C)	End Temp (°C)	Mass Residual Ratio (%)	Initial Temp (°C)	End Temp (°C)	Mass Residual Ratio (%)
P. Oceanica	-	-	235,0	550,0	52,5	-	-	-
HDPE 0 wt, %	137,4	232,5	-	-	-	350,0	520,0	92,8
HDPE 5 wt, %	140,2	233,5	250,0	390,5	4,9	390,5	520,0	86,1
HDPE 10 wt, %	140,5	233,8	250,0	390,5	8,9	390,5	520,0	74,3
HDPE 20 wt, %	138,8	233,8	250,0	390,5	12,1	390,5	520,0	70,4
HDPE 30 wt, %	138,3	233,9	250,0	390,5	13,2	390,5	520,0	68,7
HDPE 40 wt, %	138,4	233,9	250,0	390,5	14,8	390,5	520,0	61,5

Table 2.- Tensile and flexural properties of HDPE composites with different *Posidonia oceanica* contents.

Posidonia oceanica content	Tensile Properties			Flexural Properties	
	Tensile Modulus (MPa)	Tensile Strength (MPa)	Elongation (%)	Flexural Modulus (MPa)	Flexural Strength (MPa)
HDPE 0 wt. %	373 ± 8.6	19.6 ± 0.2	520.1 ± 8.8	723 ± 12.6	23.0 ± 0.4
HDPE 5 wt. %	392 ± 22.1	17.9 ± 1.4	18.9 ± 1.7	888 ± 22.0	25.4 ± 0.5
HDPE 10 wt. %	457 ± 15.6	18.9 ± 0.9	10.5 ± 2.8	1037 ± 25.7	27.0 ± 0.3
HDPE 20 wt. %	474 ± 14.6	19.4 ± 0.5	7.1 ± 0.5	1190 ± 22.9	29.8 ± 0.2
HDPE 30 wt. %	522 ± 10.0	19.5 ± 0.1	5.4 ± 0.3	1430 ± 32.3	30.3 ± 0.2
HDPE 40 wt. %	601 ± 19.8	18.9 ± 0.5	3.3 ± 1.4	1762 ± 22.6	30.8 ± 0.3

Figure 1.- Variation of MFI of the bio-HDPE and WPCs compounds in terms of the wt. % of PO.

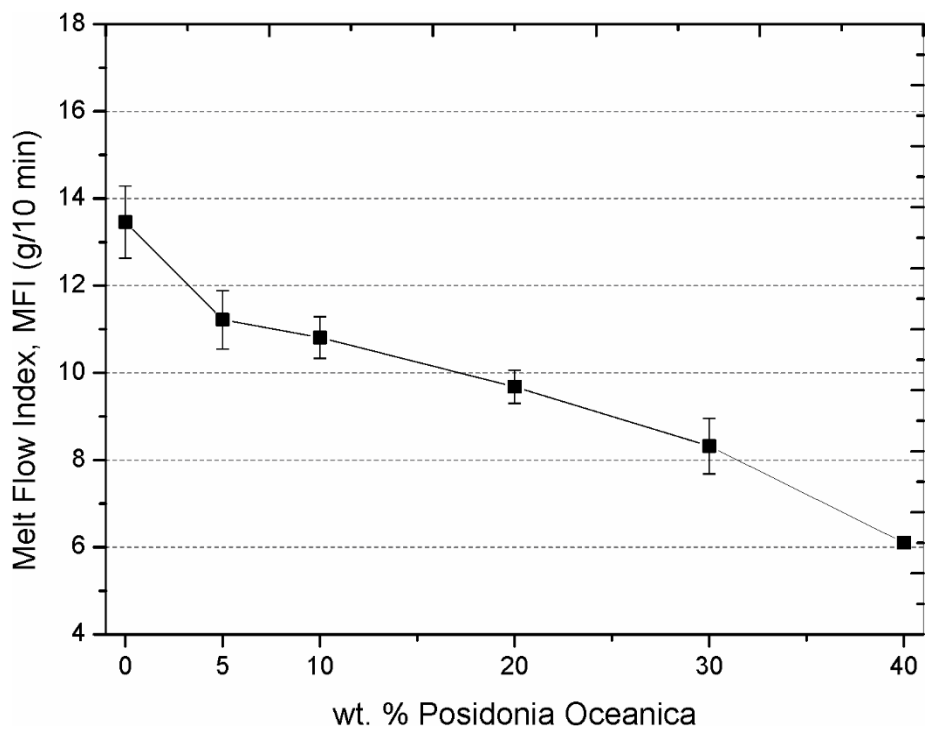


Figure 2.- SEM images (500x) of fractured surface from impact test of the composites with (a) 0, (b) 5 wt.%, (c) 10 wt.%, (d) 20 wt.%, (e) 30 wt.%, (f) 40 wt.% of PO loadings.

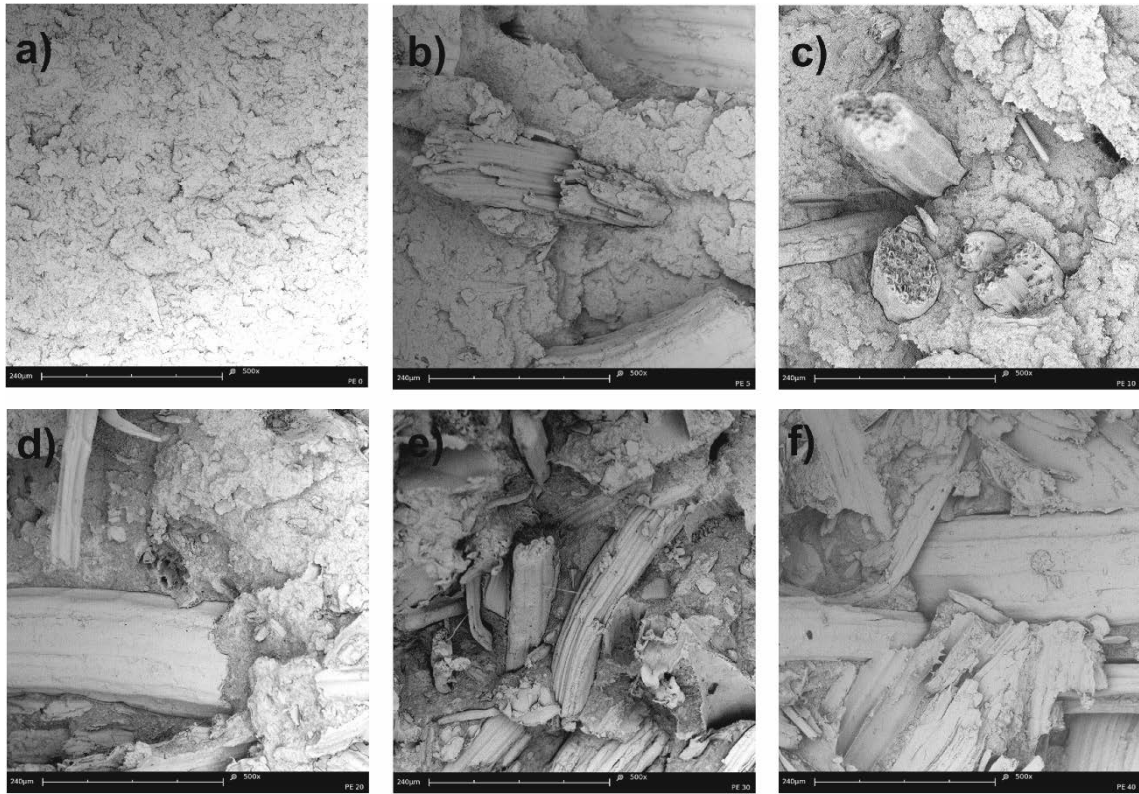


Figure 3.- Plot evolution of the storage modulus of HDPE composites with different *Posidonia oceanica* contents.

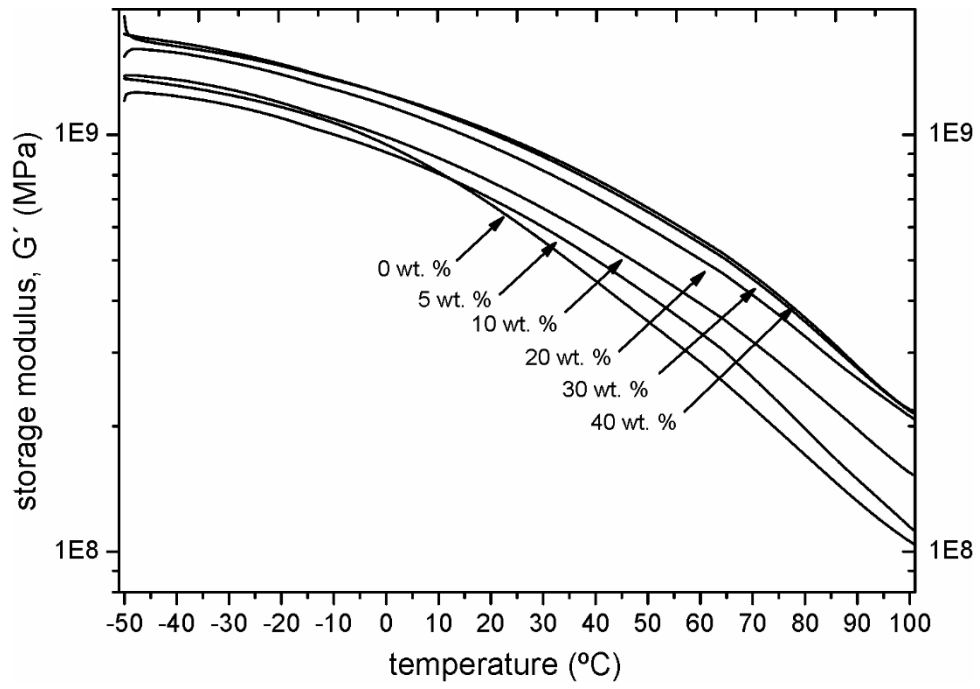


Figure 4.- Plot evolution of the Shore D hardness and Charpy's impact energy of HDPE composites with different *Posidonia oceanica* contents.

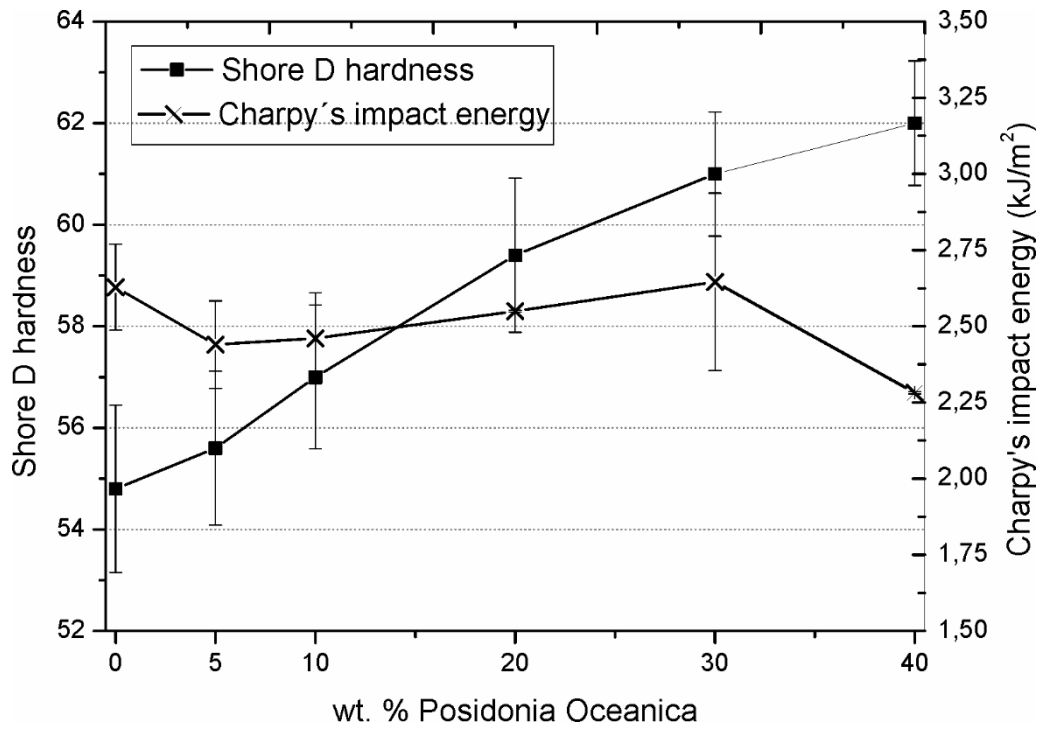


Figure 5.- Plot evolution of the water absorption percentage of HDPE composites with different *Posidonia oceanica* contents as a function of immersed time.

