

A preliminary assessment on the preparation of Spirulina/PE blends by compression molding

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Abstract

Substituting petrochemical plastics with biobased plastics from natural feedstock offers an environmentally friendly alternative to reduce the carbon footprint. Proteins are promising biopolymers that can be transformed into plastics and sourced from various types of biomass, such as microalgae. Microalgae, particularly spirulina, is considered an excellent renewable resource for bioplastic production due to its high protein content. This study focuses on the characterization of spirulina-polyethylene (PE) composites molded by compression molding technology. Both washed (for salt removal), and unwashed biomass were used in order to explore a potentially more sustainable and cost-effective option. Various loadings of both biomass types (5-30% by weight) were investigated, and the mechanical (tensile, flexural, and impact resistance) as well as thermal properties (thermogravimetric analysis and differential scanning calorimetry) of the resulting composites were determined. The mechanical properties remained nearly unchanged compared to neat PE when the biomass content was kept under 10 wt% for both the washed and unwashed biomass. At higher biomass loadings, a reduction in mechanical performance was observed; however, the molded parts maintained good aesthetics and acceptable properties. Despite the predictable adverse changes in thermal behavior, the processability of the materials was not affected. Differential scanning calorimetry indicated that total plasticization of the biomass protein was not achieved during the molding process. Additionally, no significant differences were found between the washed and unwashed biomass, suggesting that using unwashed biomass could be more economically and environmentally beneficial.

Keywords: compression molding; microalgae; plasticization; spirulina; mechanical properties; biocomposite

1. Introduction

It is well known that the extensive use of petroleum-derived materials poses significant environmental challenges. These materials contribute to greenhouse gas emissions during their production and result in the accumulation of non-biodegradable waste in the environment [1]. Bio-based plastics derived from natural feedstock offer a biodegradable alternative to conventional plastics, degrading more quickly and thus reducing

waste [2, 3]. Biobased plastics can be produced from starch and cellulose, such as polylactic acid, cellulose acetate, and thermoplastic starch; in the recent years, more attention has been paid to biopolymers derived from natural protein that can be processed thermomechanically [2].

Most research on protein-based plastics has focused on terrestrial crops. Soybean and casein have been widely studied and used to produce bioplastic items, including films [2]. Despite the long history of using proteins for plastic materials, their adoption has not been as common as for other naturally derived polymers, such as starch or cellulose due to their physical stability over time, and concerns about using potential food resources for the chemical sector [4]. Microalgae have a high protein content and are considered a promising alternative biomass for bioplastic production. The advantages of using microalgae include a higher yield, faster growth, cultivation in different types of water media (seawater, freshwater, and wastewater), without competing with food applications [5]. Furthermore, microalgae consume small amounts of water, have low production costs and do not require prior treatment to isolate proteins for plastic fabrication, thus enhancing their cost-effectiveness and scalability [6].

The transformation of microalgae protein into bioplastics has been extensively studied in the literature [2, 5, 7–11], with *Chlorella* and spirulina (a cyanobacteria, not a microalgae itself) being the most studied ones owing to their ease of processing and large-scale production for nutraceutical purposes [5, 12, 13].

In the present study, spirulina biomass was used after being washed and directly used without previous washing for salt removal. The influence of the presence of salts was studied for the first time in a previous work of the authors of this study [14], in which a beneficial effect of using non-washed biomass on the properties of compression molded items was obtained, due to the potential environmental and economic benefits of not having to use potable water to wash the biomass.

To convert proteins into useful materials, they must be modified. Solvent casting is a common laboratory-scale method for converting protein solutions into films, but molding and extrusion are more scalable and industrially relevant [15, 16]. In such processes, proteins are plasticized and heated above their softening or glass transition temperatures to become malleable and form cohesive materials, resulting from chain interdiffusion [15]. Various systems have been employed to promote the plasticization of microalgae protein, including internal mixers [17], roller mixers [18], and micro twin-screw extruders [10]. Plasticizers such as glycerol play a crucial role in enhancing the flexibility and elongation of bioplastics from microalgae [13, 16]. Although replacing conventional plastics entirely with microalgal bioplastics would be ideal, 100% bioplastics generally have inferior physical and mechanical properties [13]. To address this, conventional polymers such as PE, PP, PU, or PVA have been blended with microalgae [2, 5, 7–9, 18–21]. On the other hand, the hydrophilic nature of biomass and the hydrophobic nature of the polymer matrix often require compatibilizers like maleic anhydride to improve the mechanical properties of the resulting biocomposites [7, 10].

The plasticization of algae protein can occur separately or simultaneously with polymer processing. Compression molding is a commonly explored process for producing microalgae-polymer composites [7, 16];

to obtain molded parts, the biomass and the polymer (and additives if needed) are placed inside a mold, where elevated pressure and temperature are applied. Different processing parameters have been found in the literature, with a molding time from 3 to 20 min, pressure from 20 kPa to 10 MPa and temperatures from 130-160°C [16]. Some studies have adapted variations of the process without compression to obtain parts of different sizes and shapes. Some authors have also processed the microalgae/polymer blend in molds without any pressure [7], obtaining prototypes of different shapes and sizes. Further exploration is needed to establish the optimal conditions for plasticizing microalgae without thermal degradation and achieving suitable mechanical properties.

This study explored a simple method where PE and spirulina were manually mixed and processed by compression molding. The process aimed to promote biomass denaturation and thermomechanical plasticization while mixing with the polymer and molding the mixture. Both washed spirulina biomass and non-washed – as a more environmentally friendly and cost-effective alternative – were used. Unlike other studies, this research avoided plasticizers and compatibilizers, considering a maximum biomass load of 30 wt% and spirulina's higher compatibility with PE compared to other microalgae [2]. The study examined the influence of the biomass weight percentage and the salt content on the mechanical and thermal properties of the composites.

2. Materials

Polyethylene (Revolve N-461 from Matrix Polymers), in powder form, was used as the polymer matrix in all the experiments. Polyethylene (PE) has a low melting point, which allows the use of low temperatures to mix with the microalgae, reducing the risk of biomass thermal degradation.

A. platensis (spirulina) biomass was kindly supplied by Instituto Tecnológico de Canarias (ITC). The harvesting of the biomass was performed as described in [22]. Two different biomasses were provided: dried washed spirulina (Sp) and dried unwashed material (Sp.N.W), both as a powder obtained after spray drying.

3. Methods

3.1. Composite preparation

Before mixing, the materials were dried at 60°C for 24 h for PE and for 6 h for biomass to avoid their thermal degradation. The samples were designated with the letter C (compression molding), followed by the matrix (PE), the percentage of biomass (5-30% by weight) and the biomass (Sp: spirulina, Sp.N.W: non-washed spirulina).

Samples were produced in an aluminum mold of 190 × 190 mm in a Collin P200 PM hot press. 100 g of the manually mixed materials was introduced into the mold allowing 3-mm thick plates to be obtained. Previous tests conducted with the microalgae and PE allowed the processing cycle to be defined: heating to 160°C at 5

bar for 6 min, followed by a stage of higher pressure (50 bar) for 4 min, and with a last cooling stage, performed under the same pressure. The plates were then die-cut to obtain standardized test bars.

3.2. Composite characterization

The tensile, flexural and impact properties were determined according to UNE 527-2:2012, UNE 178:2019, and ISO 180:2001/A2:2013, respectively. A universal testing machine from Dongguan Liyi Test Equipment (model LY-1065) was employed for the tensile and flexural tests (test rates of 2 mm/min, for the tensile elastic modulus, and 10 mm/min for ultimate strength); for the impact tests, a 5.5 J pendulum and an impact rate of 3.5 m/s were used (Dongguan Liyi Test Equipment, LY-XJJD 50). Six specimens were tested for each property. Differential scanning calorimetry (DSC) was conducted in a PerkinElmer DSC 4000 apparatus. Specimens of 9-12 mg were put in closed aluminum pans in an N₂ atmosphere. The specimens were heated from 30°C to 200°C at the heating rate of 10°C/min, cooled down to 30°C and heated again to 200°C at the same rate. The melting temperature for the first heating (T_{m1}) and the second one (T_{m2}) as well as the crystallization temperature (T_c) were determined. Cold crystallization was not observed in any of the tests. The melting (ΔH_{m1} , ΔH_{m2}) and crystallization (ΔH_c) enthalpies were also determined and used to determine the degree of crystallization.

A thermogravimetric analyzer, TGA 4000 by Perkin Elmer, was utilized to determine the thermal stability. The specimens (2-5 mg) were heated from 30 to 600°C at the heating rate of 10°C/min, with nitrogen as the purge gas. The TG and DTG curves were used to determine the weight loss, DTG peak values, residual char and to identify the temperatures at which 5% ($T_{5\%}$), 10% ($T_{10\%}$), and 50% ($T_{50\%}$) weight loss occur.

FTIR spectra were obtained in a Spectrum Two spectrophotometer from Perkin Elmer, in the attenuated total reflectance (ATR) mode, in the range from 4000 to 500 cm⁻¹ (resolution of 4 cm⁻¹ and 12 scans/specimen).

SEM analysis was conducted in a Hitachi TM3030 tabletop microscope, at the acceleration of 15 kV. The specimens were sputtered with a thin layer of Pd/Pt in a SC 760 apparatus from Quorum Technologies. The biomass, the surface of the molded plates and the breakage section of the samples after the tensile test were observed.

4. Results and discussion

4.1. Biomass processability

Both biomasses were characterized in a previous work of the authors [14]. Thermal characterization was useful to choose the conditions for compression molding. The TG curves of Sp and Sp.N.W are presented in Figure 5, together with those for the composites. The thermal decomposition of both biomasses was divided into three stages. First, the evaporation of water and also, in a minor amount, volatile components took place between 30 and around 140°C, respectively, for both biomasses. The weight loss obtained in this temperature range was 9.26±1.12% for Sp and 7.90±2.46% for Sp.N.W. After that, protein, lipid and carbohydrate thermal degradation occur. For Sp, this degradation occurred in two steps: the first one between 140 and 240°C with a weight loss

of $5.73 \pm 0.12\%$ and after that, a weight loss of $56.87 \pm 1.37\%$, with a final residual char of $27.95 \pm 2.27\%$ at the end of the test (600°C). For Sp.N.W, there was also two-step degradation but at different temperatures, indicating that the presence of salt in the biomass alters its thermal behavior. In this case, there was a first weight loss of 29.40 ± 1.19 , between 140 and 320°C , followed by a second one of $22.25 \pm 1.13\%$. As expected, due to the presence of salts in Sp.N.W, its residual char level was considerably higher ($40.45 \pm 0.51\%$).

The DSC curves corresponding to the first heating are also included together with the composite curves in Figure 6. As can be seen, both biomasses showed a high peak (only observable during the first heating carried out in DSC) between 110 and 190°C that could be attributed to protein denaturation [2]. The area of the peak was higher for Sp (as it possesses more protein in proportion) and it was centered at $158.6 \pm 4.7^\circ\text{C}$. For the non-washed spirulina, the temperature of the highest peak was a little lower ($146.4 \pm 1.9^\circ\text{C}$).

Taking into consideration the different behavior observed between the biomasses during the thermal characterization, better processability could be expected for the non-washed biomass as protein denaturalization takes place earlier and degradation starts slightly later; it is essential to achieve high denaturation of the protein but without degradation. The maximum temperature of 160°C was chosen for the compression molding cycle. For this temperature, less than a 10% weight loss was obtained for both the biomasses, corresponding mostly to moisture evaporation; hence, both biomasses are suitable to be processed with PE. With respect to protein denaturation, in order to use protein to obtain plastic materials, their structure must be significantly denatured to linearize the molecules and transform them into ones similar to conventional plastic molecules [23]. In this case, the processing temperature is slightly higher than the one for the protein denaturation of both biomasses, although the desirable complete denaturation of the protein was not achieved, as seen later; from the area under the curve at DSC, denaturation of 58% and 88% was achieved for Sp and Sp.N.W, respectively.

4.2. Visual evaluation

A good distribution of the biomass in the matrix was obtained for all the molded parts since they displayed a uniform color. In the case of the spirulina composites, the pieces had a very dark green color (almost black) quite similar for all the percentages of biomass tested. For the non-washed spirulina, as the original biomass exhibited a different color, the composites also had a different one. In this case, they were characterized by a greenish brown color and there were more differences between the formulations, as can be seen in Figure 1. Also in Figure 1, it can be observed that in the case of the upper surface of the pieces, there were some light spots (more substantial for the higher loads) as a consequence of the presence of internal bubbles. In relation to the surface touch, both sides of the plate had a smooth surface without the presence of substantial porosity.

In Figure 2, SEM micrographs of the surface of a composite containing 15 wt% Sp.N.W are presented; a smooth surface with a limited presence of pinholes or biomass particles can be observed.

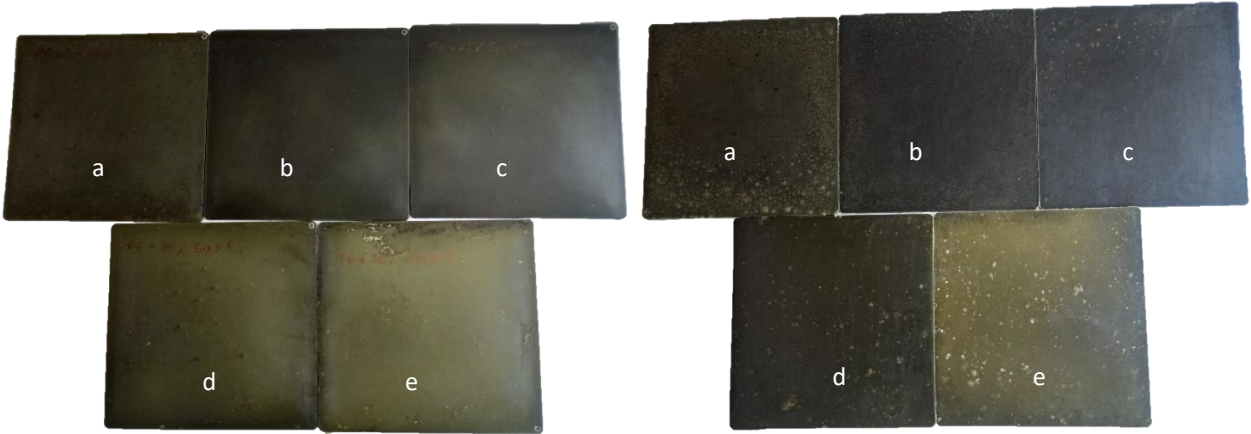


Figure 1. Pictures of composites obtained by compression molding with non-washed spirulina: a) 5 wt%, b) 10 wt%, c) 15 wt%, d) 20 wt% and e) 30 wt%. Left are undersides of pieces, right, upper surface

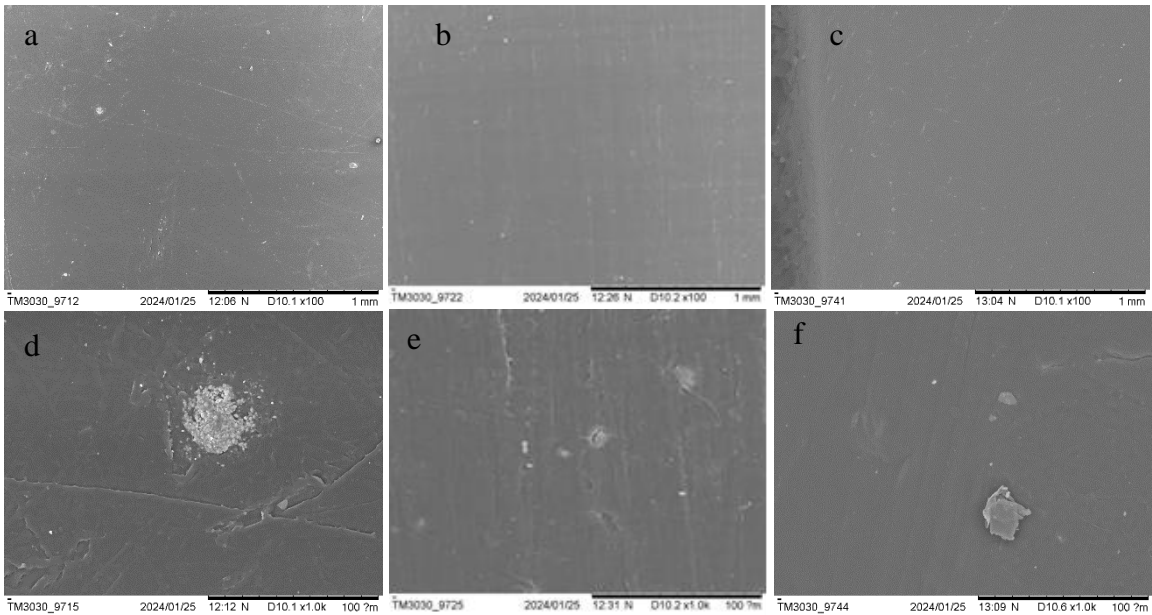


Figure 2. SEM micrographs of SP.N.W. composite surfaces a) 10 wt%, b) 15 wt%, c) 30 wt% (magnification x100), and d), e) and f) for same composites at x1000 magnification

With respect to the density of the composites, determined by measuring the dimensions and the weight, a reduction in this value could be expected as a consequence of the filler [24]. However, in this case, as partial plasticization of the biomass can take place during the molding process, it is more difficult to draw conclusions.

The density tends to slightly grow with the biomass content until 20 wt%; for 30 wt% it again decreased, being more for evident for the Sp biomass, possibly owing to porosity and the presence of voids.

4.3. Mechanical characterization

The mechanical properties determined for the composite materials obtained with both biomasses (Sp and Sp.N.W) are shown in Figure 3. Regarding the tensile properties, a gradual reduction in the maximum strength was observed with the increased biomass, for both of them. For the maximum content of biomass tested (30 wt%) a reduction of 62% and 58% in the property was observed for Sp and Sp.N.W, respectively. In the case of the tensile elastic modulus, no significant differences were observed for any of the biomass loadings. On the other hand, the flexural behavior was less sensitive to the introduction of the biomass into the matrix. Although a slight reduction of the flexural strength was observed when the percentage of biomass was increased, only a maximum 20% reduction was observed for the 30 wt% load for both biomasses. The flexural elastic modulus remained unaltered or slightly raised. Finally, there were no significant differences in the impact strength until a 15 wt% load (for both biomasses), after which the property was reduced, particularly for the 30 wt% ratio (a 70% reduction for both biomasses).

On the other hand, if the mechanical properties of the composites with the same biomass proportion are compared, no differences can be found between using spirulina or non-washed spirulina. For some formulations, statistically significant differences were observed in some properties, but these differences were small, being in some cases favorable for Sp, while in others for Sp.N.W. Therefore, there is no clear trend regarding which biomass exhibited better behavior than the other one; in contrast with the behavior previously observed by authors for rotomolded composites [14], the Sp.N.W composites exhibited better performance.

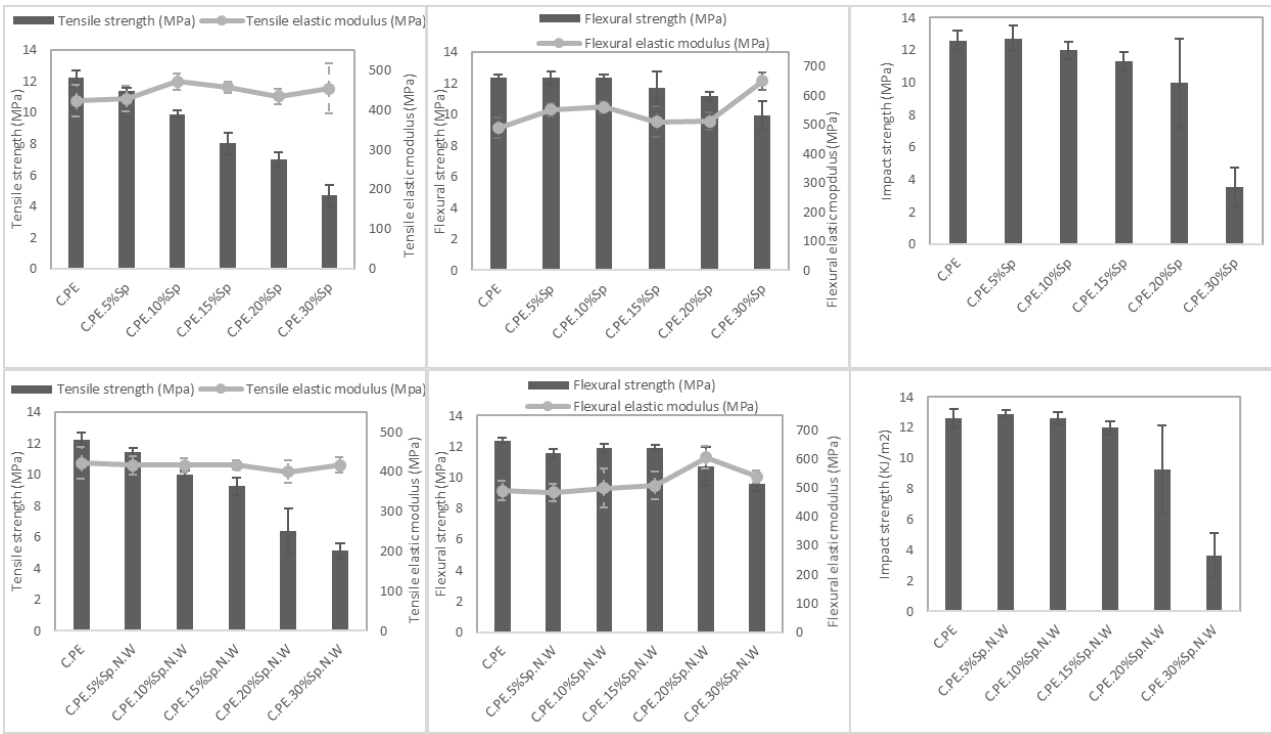


Figure 3. Mechanical properties of washed spirulina (above) and non-washed spirulina (below) composites (tensile, flexural and impact strengths, from left to right)

Therefore, in general terms, the composites obtained with both biomasses by means of compression molding exhibited acceptable mechanical properties. Spirulina (washed and unwashed) can be introduced into the PE matrix up to 10 wt% without significant reductions in any of the properties, compared to neat PE. The values of the obtained mechanical properties are comparable with previously published works. For example, Zeller et al. [2] obtained values of tensile strength of around 8 MPa and 3.5 MPa for the PE-spirulina composites obtained by compression with 24 wt% and 35 wt% spirulina, respectively, and utilizing glycerol as the plasticizer. In the present work, values close to 7 and 5 MPa were obtained for loads of 20 wt% and 30 wt%, with the advantage that neither glycerol nor any other additive was used during the process. The values of the tensile elastic modulus are not comparable since glycerol increases plastic flexibility, and thus the values are quite lower. Otsuki et al. [18], for their part, produced *Chlorella*-PE composites by the heat-pressurizing method and they received higher mechanical properties (for example for a 30 wt% load, around 12 MPa tensile strength), but they needed to use chemically modified PE with maleic anhydride, which allowed them to obtain a composite with a tensile strength more than two-fold greater than that of a composite derived from unmodified PE.

4.4. Scanning electron microscopy (SEM)

Figure 4 shows the appearance of the biomasses obtained by SEM. Both biomasses present particle sizes of less than 50 μm, but a different shape and surface appearance can be observed. The spirulina biomass has an

irregular shape, while the non-washed biomass possesses a more spherical shape resulting from the presence of salts incrustated in its surface, which could have affected the filler-matrix interaction. The breaking section of the tensile bars was also observed utilizing SEM. The images revealed good distribution of the filler particles along the matrix, although slight agglomeration can be observed in some areas owing to the higher affinity of the biomass particles for themselves than for the matrix. It seems that the Sp particles are more integrated in the matrix than the Sp.N.W ones, which can be explained by their different particle shape, and also because the presence of salts on the surface could have hindered the attachment to the polymer. Nonetheless, this aspect did not have an effect on the mechanical properties, as seen before.

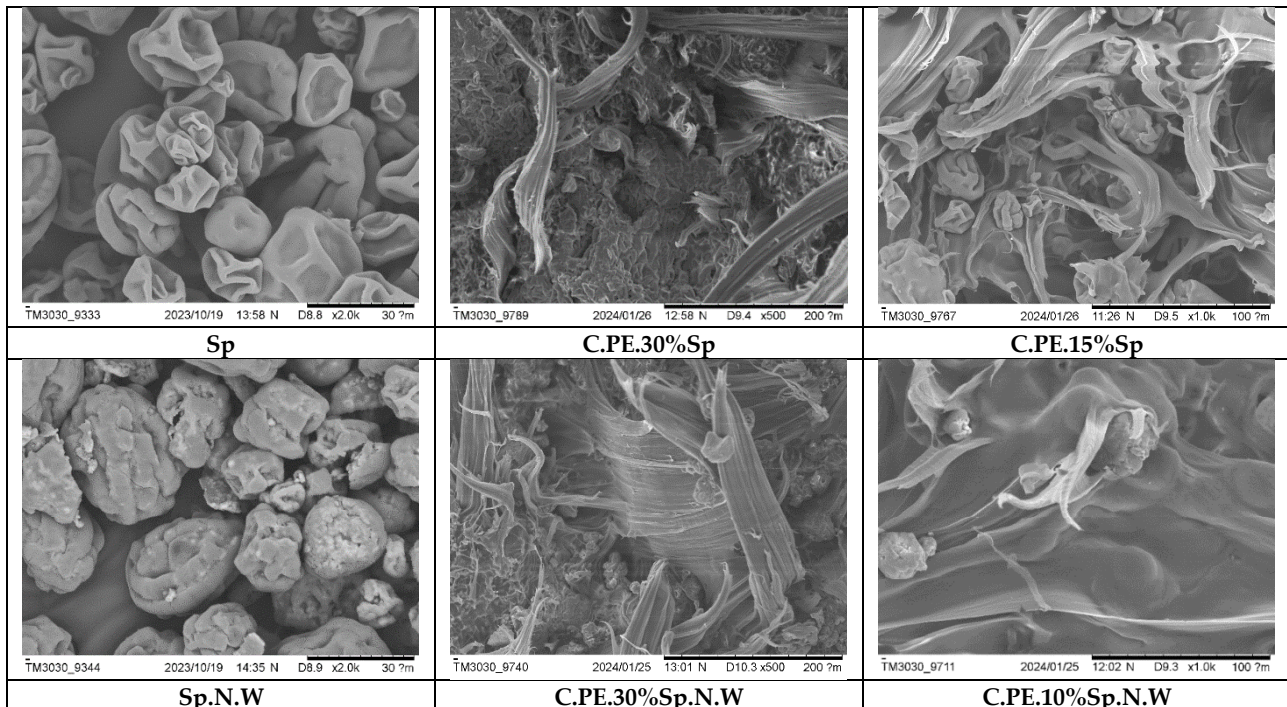


Figure 4. SEM micrographs of Sp and Sp.N.W biomasses and fracture surface of tensile specimens

On the other hand, in the case of the Sp composites, it can be seen that the particles tend to agglomerate in some areas (C.PE.30%Sp micrograph in Figure 4), which could indicate that plasticization of the biomass happened in these areas. The fracture surfaces show that the plastic matrix underwent deformation, but the mentioned presumable plasticized zones did not exhibit this capacity for deformation. In other areas, the microalgal fraction acted more like a filler as the particles were not plasticized, and in some cases air gaps between the biomass particles and the PE matrix can be observed, although compared with other published works using natural fillers, their presence was smaller in the present study. This could be explained by the high protein content present in the biomass, which could improve the interactions of the filler with the matrix [24]. It should also be noted that, as indicative of good interaction, the particles were not pulled out of the polymeric matrix subjected to plastic deformation, as can be seen in Figure 4 (C.PE.10%Sp.N.W).

Nevertheless, the interaction between the biomass (hydrophilic) and the matrix (hydrophobic) could be improved by using a compatibilizer, like in the study of Otsuki et al., who obtained a composite of *Chlorella* with PE chemically modified with maleic anhydride (MPE), the compatibilizer most commonly used in microalgae composites. It can be observed in the SEM micrographs of the fractures that the *Chlorella* grains were firmly embedded in the modified PE matrix, without the presence of air gaps, and that when the samples were strained to failure, the *Chlorella* grains on the fracture were broken, suggesting that the interactions between *Chlorella* and PE were stronger than those between the *Chlorella* particles. In other studies, the addition of maleic anhydride as compatibilizer also increased the homogeneity and flexibility of the products [7, 19].

4.5. FTIR

The FTIR spectrum of the composite samples did not reveal any remarkable aspects. All the composites showed strong bands corresponding to PE, and other less intense bands corresponding to the biomasses that become more intense with the filler loading. Particular bands associated with the creation of bonds between the matrix and the biomass were not observed, unlike other studies, for example, the work of Otsuki et al., which confirmed the successful formation of a *Chlorella*-MPE composite, obtained by means of solid-phase reactions, observed in IR spectroscopy [18].

4.6. Thermal characterization

From the TG curves (Figure 5), it can be observed that while the degradation of pure PE is a one-step process, the composite curves show two degradation steps, corresponding to the two materials in the composite.

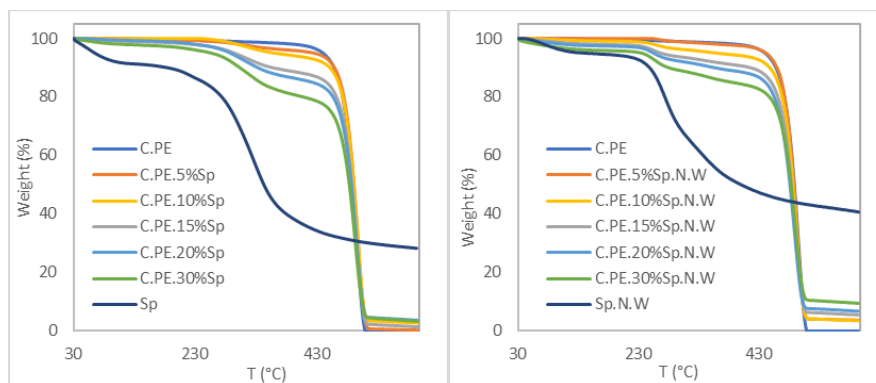


Figure 5. Thermogravimetric (TG) curves for washed spirulina (left) and non-washed spirulina (right) composite materials

The addition of the biomass resulted in a reduction in the thermal stability of the materials (Table 1), as expected. If the values of T5% are compared, it can be seen that its value was considerably reduced. For the maximum amount of load, reductions of 42% and 47% in the T5% values were obtained for C.PE.30%Sp and C.PE.30%Sp.N.W, respectively, compared with neat PE. Even though the T5% values significantly exceed the molding temperature used for composite preparation (160°C), the observed adverse changes will not affect the

processability of the material. On the other hand, the values of residual mass grew with incorporation of the biomass, this increase being higher for the Sp.N.W composites.

Table 1. Temperatures at which 5% (T5%), 10% (T10%), and 50% (T50%) weight loss occur, residual mass obtained in thermogravimetric analysis, and density values of Sp and Sp.N.W composites

Specimen	% biomass	Density (g/cm ³)	T _{5%} (°C)	T _{10%} (°C)	T _{50%} (°C)	Residual mass (%)
C.PE	0	0.91	440	459	490	0
C.PE.5%Sp	5	0.92	426	460	492	0.3
C.PE.10%Sp	10	0.92	361	452	491	2.7
C.PE.15%Sp	15	0.93	294	358	488	1.4
C.PE.20%Sp	20	0.95	288	334	488	3.7
C.PE.30%Sp	30	0.87	257	304	484	3.3
C.PE.5%Sp.N.W	5	0.92	443	461	489	3.7
C.PE.10%Sp.N.W	10	0.92	361	449	487	3.5
C.PE.15%Sp.N.W	15	0.94	268	417	485	5.5
C.PE.20%Sp.N.W	20	0.93	255	358	482	6.8
C.PE.30%Sp.N.W	30	0.90	235	281	484	9.4

On the other hand, no significant changes in the thermal properties (including characteristic temperatures of melting and crystallization) were observed during differential scanning calorimetry analysis. The DSC curves obtained for the first heating of the cycle are displayed in Figure 6. The composites presented a melting peak at around 130°C, whose area increased with the polyethylene content. In some cases, a second endothermic peak, corresponding to protein denaturation, appears. The arbitrariness in the observation of the protein denaturation event can be due to the fact that total plasticization of the biomass was not achieved during compression molding, along with the certain inhomogeneity of the material.

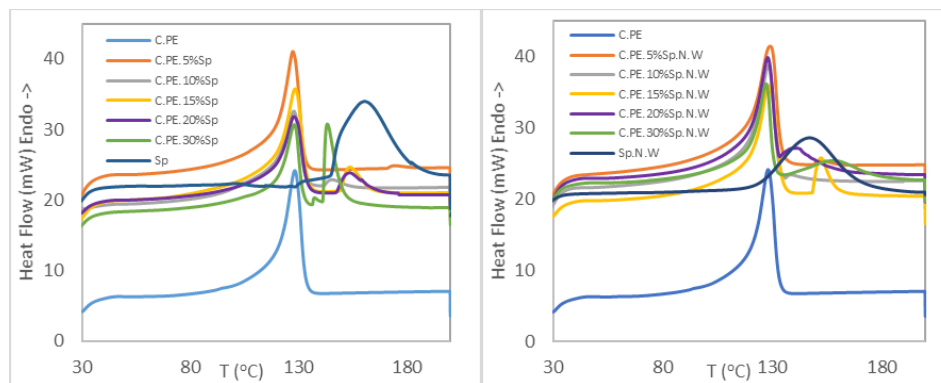


Figure 6. DSC curves for washed spirulina (left) and non-washed spirulina (right) composite materials

As mentioned earlier, in order to use soy proteins to produce plastics, their structure must be significantly denatured, although total denaturation is difficult since the temperatures at which proteins soften are high and often close to their degradation temperatures [15]. To promote linearization, the protein can be dissolved in a solvent and chemically altered to break the disulfide bonds. Further denaturation can be achieved using an extrusion process that heats the protein structure. The combination of heat and shearing transforms the protein

into a material that behaves similarly to traditional petrochemical-based thermoplastics. This route could be a good option to explore in the future to increase the percentage of incorporated biomass as it has been satisfactory used by other researchers. For instance, by using glycerol – the most used plasticizer in bioplastic production using microalgae [13] – improvements in flexibility and elongation were achieved even with high weight percentages of microalgae [16].

5. Conclusions

Spirulina-PE composites with up to a 30 wt% loading were successfully compression molded without using any previous melt compounding operation or any additives like compatibilizers or plasticizers. Composites with up to 10 wt% biomass can be produced without affecting the mechanical properties of the material, comparing with neat PE. Moreover, previous washing of the biomass is not necessary as the presence of salts did not affect the materials properties.

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