

Article

Effect of Surface Modification on the Properties of Buckwheat Husk—High-Density Polyethylene Biocomposites

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Abstract: This study focuses on the production and characterization of biocomposites based on a thermoplastic polymer (high-density polyethylene, HDPE) and a biosourced filler (buckwheat husk, BHS) to develop more sustainable composites. Compounding was performed via twin-screw extrusion with three different types of BHS. In the first series, untreated BHS was directly mixed with the polymer matrix, while the second series used mercerized BHS and the third series used pretreated BHS with a coupling agent (polyethylene grafted with maleic anhydride, MAPE) in solution. The samples were prepared at different concentrations (10, 20, 30, 40 and 50 wt.% of BHS) to compare with the neat matrix (0%). All the samples were finally produced by compression molding and then cut to get the specimens for characterization. The latter included morphological (scanning electron microscopy), physical (density and hardness) and mechanical (tension, flexural and impact strength) properties. Based on the results obtained, it was observed that most of the mechanical and physical properties were improved, especially when the BHS was pretreated in solution before its introduction into the polymer matrix. The results showed that 30 wt.% of BHS in HDPE was the optimum for most of the properties investigated.

Keywords: polyethylene; buckwheat husk; interfacial treatment; maleated polyethylene; mechanical properties



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1. Introduction

Over the past 20 years, biosourced particles have been used as fillers and reinforcements in low melting points thermoplastic resins and thermosets [1,2]. In particular, thermoplastic composites have attracted interest due to their easy production and good properties (wide range), but most importantly (as of today) because of their recyclability. These materials also have other advantages including low cost, availability, renewability and the possibility to increase the specific properties (per unit weight) of composites such as rigidity, stiffness and strength, while reducing carbon emissions [3–5]. Although a great deal of research has been conducted on the subject of biocomposites and various products that are now available on the market, there is still interest to pursue these investigations on different residues (agricultural, forest, etc.) and to better understand how the processing methods and conditions/parameters, as well as the composition/formulation, affect the final properties of these materials to develop new biocomposites with improved performances for novel applications [6]. Buckwheat husk (BHS) is a good example of agricultural by-product that can be applied as a biofiller for the production of polymer composites [7,8]. Buckwheat is currently consumed in the form of flour, groat, etc., which includes noodles accounting for more than 96% of the total processed form. The worldwide average annual production of buckwheat over the last decade was 1.9 million tons [7], leading to a high amount of residues. These residues are generated during the processing of buckwheat grain

into groats, which is 25–30% of the weight of the whole buckwheat grain [8]. Therefore, applications must be developed for these residues.

Buckwheat husk has been reported to be an effective sorption material for the removal of heavy metals ions and oils from aqueous solutions [9]. Another application is in the preparation of activated carbon to produce supercapacitor electrodes for lithium-ion (Li-ion) batteries [10,11]. For polymer composites production, buckwheat husks have been introduced into different matrices including polypropylene (PP) [12–14], polyethylene (PE) [15,16], polylactic acid (PLA) [16–18], polyurethane (PUR) [2,19] and epoxy (EP) [20–22]. Most of these composites were prepared via twin-screw extrusion followed with compression or injection molding [12], as well as rotational molding [16]. In most cases, a morphological characterization was performed to explain the thermal and mechanical properties of these potentially biodegradable biocomposites.

As for any particle, biosourced fillers in thermoplastic resins require good adhesion/compatibility with the matrix to improve the dispersion and homogeneity, leading to optimized properties. However, the cellulose inside BHS has a highly hydrophilic character due to its three hydroxyl groups in its monomer unit, while the majority of polymers are hydrophobic [23]. This difference is the main origin of poor intrinsic compatibility between both materials. Interfacial adhesion/compatibility must be improved; however, this comes with a cost [12].

The objective of this work is to determine the possibility of using BHS as a biofiller in thermoplastic resins and to determine the effect of its concentration on the physical and mechanical properties of the resulting biocomposites. As a first step, high-density polyethylene (HDPE) was selected as the matrix due to its availability, commodity and easy processing/recyclability. To improve the final properties, the neat BHS particles were compared with different modifications including mercerization and coupling agent.

2. Experimental

2.1. Materials

In this work, high-density polyethylene (HDPE) HD 6719 with a density of 950 kg/m³ and a melt flow index of 19 g/10 min (2.16 kg/190 °C) was used as the matrix. Buckwheat husk was purchased from Moulins de l'Isle-aux-Coudres (Quebec, QC, Canada) and used as a biofiller. The materials were sieved to keep only particles between 250 and 500 microns. For surface treatment, different chemicals were used, as follows: sodium hydroxide (NaOH), hydrochloric acid (HCl) and xylene (laboratory purity grade) from Fisher Chemicals (Waltham, MA, USA), as well as maleic anhydride grafted polyethylene (MAPE) supplied by Westlake Chemical Corporation (Houston, TX USA) under the trade name of Epolene C-26. Its melting temperature and density are 121 °C and 919 kg/m³, respectively.

2.2. BHS Surface Treatment

Surface treatment of the buckwheat husk was performed in two steps. The first step was a standard mercerization in an alkaline treatment (MEC). The main reason is to wash the surface (remove impurities) and make the -OH groups more available. The particles were first dried overnight in an oven at 80 °C. Then, a 5 wt.% alkaline (NaOH) solution was prepared by dissolving 50 g of NaOH in 1000 mL of distilled water. The BHS particles were soaked in the solution with a 1:10 ratio (100 g particle in 1000 mL of solution). The suspension was mixed with a mechanical stirrer for 10 min at room temperature. Then, the BHS particles were filtrated and washed with distilled water to remove the remaining NaOH solution. Finally, the particles were neutralized with dilute acetic acid, rinsed with water and dried overnight in an oven at 80 °C. In the second step, 1 wt.% of MAPE was dissolved in xylene at 90 °C under mechanical stirring. Subsequently, a suspension of 10 wt.% of BHS was prepared and the treatment was conducted for 30 min at 90 °C with high intensity mixing. Finally, the buckwheat husks were recovered via filtration and then dried at 80 °C in an oven to eliminate the remaining solvent. Overall, three series

of samples were prepared using different BHS: untreated (UC), mercerized (MEC) and grafted with MAPE (MAC).

2.3. Composites Preparation

Different BHS (untreated and treated) concentrations (between 0 and 50 wt.% in steps of 10 wt.%) were used to study the effect of this parameter on the properties of the biocomposites. The materials were melt-blended in a Leistritz (Nurnberg, Germany) ZSE-27 co-rotating twin-screw extruder to produce the pellets. The twin-screw extruder had a L/D ratio of 40 (D = 27 mm) and the screw speed was set at 95 rpm. The following temperature profile was applied: 160, 160, 160, 160, 165, 165, 165 and 170 °C with a circular die (2.7 mm in diameter) at 170 °C to obtain a total flow rate of 4 kg/h. The HDPE was fed in zone 1 (main feeder), while the BHS was introduced via a side-stuffer in zone 4 (total of 10 zones). The extrudates were cooled down in a water bath (room temperature) and pelletized with a model 304 (Conair, Stamford, CT, USA). Finally, the pellets were dried overnight in an oven at 80 °C to eliminate any residual humidity. After drying, each formulation was placed in a metal (stainless steel) mold with dimensions of 21 cm × 21 cm × 2.5 mm. Compression molding was performed on a laboratory scale press (Carver Inc., Wabash, IN, USA) using the following sequence: preheating for 3 min at 175 °C, pressing for 5 min under a load of 3 tons and finally cooling (circulating water) until 35 °C before removing the pressure to open the mold. The resulting biocomposites were later cut into the different geometries to perform all the characterizations as described next.

2.3.1. Characterization

Morphology

The biocomposites were cryogenically fractured with liquid nitrogen and their surfaces (exposed cross-sections) were coated with gold/palladium under vacuum. Then, micrographs were taken on a scanning electron microscope (SEM) FEI Inspect (Hillsboro, OR, USA) model F50 at 15 kV. Different magnifications were used to observe and characterize the microstructure in terms of fiber state (adhesion and dispersion) in the matrix.

Density/Hardness

Density was measured using a gas pycnometer model ULTRA-PYC 1200e (Quantachrome Instrument, Boyton Beach, FL, USA). Nitrogen (N₂) was used as the gas phase and the results reported are the average of three measurements for each sample. Hardness (Shore D) was measured using a hardness tester (PT Instruments, Williamsburg, VA, USA) model 307L following ASTM D2240. The reported values are the average and standard deviation of at least 10 measurements.

2.3.2. Thermal Properties

Thermogravimetric Analysis (TGA)

The thermal stability of the matrix (HDPE), filler (BHS) and the composite treated with 30% wt. (30% of BHS + C26) was evaluated with thermogravimetric analysis (TGA) for the weight curves and their derivatives (DTG). The tests were performed on a Q5000 IR (TA Instruments, New Castle, DE, USA) on samples around 5–15 mg with a heating rate of 10 °C/min between 30 and 850 °C under a nitrogen atmosphere.

Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) studies were conducted on a Perkin-Elmer model DSC-2. Each sample was weighed and placed in a sealed aluminum pan and heated at 10 °C/min from 20 to 200 °C under a flow of dry nitrogen (20 mL/min). The crystallinity level (X_c) was calculated according to:

$$X_c (\%) = (100) \Delta H_m / (x \Delta H_{ref}) \quad (1)$$

where ΔH_m is the experimental heat of fusion, ΔH_{ref} is the theoretical heat of fusion of fully crystalline polyethylene (293 J/g) and x is the weight fraction of HDPE in the composite.

2.4. Mechanical Properties

Tensile and flexural properties were measured on a universal testing machine Instron model 5565 (Norwood, MA, USA) with a 500 N load cell. For tension, type V dog bone specimens were used according to ASTM D638. The tests were performed at room temperature and a crosshead speed of 5 mm/min. The tensile properties (modulus, strength and elongation at break) are reported based on the average of five samples. For flexion, three-point bending tests were performed according to ASTM D790 at room temperature using a crosshead speed of 2 mm/min and a span length of 60 mm. Five specimens were cut with dimensions of 80 mm \times 12.7 mm \times 2.5 mm (rectangular bars) to report the average and standard deviation for modulus and strength. Notched Charpy impact tests were performed on an impact tester Tinius Olsen model 104 (Horsham, PA, USA) with a 1.22 J (242 g) pendulum according to ASTM D256. For each composition, ten rectangular samples (80 mm \times 12.7 mm \times 2.5 mm) were cut and notched at least 24 h before the test with a model ASN (Dynisco, Franklin, MA, USA). The values represent the average and standard deviation of ten repetitions.

3. Results and Discussion

3.1. Morphological Characterization

To produce good mechanical properties for thermoplastic composites, not only a large contact surface area is required, but also good compatibility (adhesion) between all the phases is necessary. Figure 1 presents typical SEM micrographs of the biocomposites. The first column reports the structure of samples based on untreated (UC) BHS. It can be seen that poor adhesion occurred between both phases; i.e., interfacial voids and defects will highly reduce the stress transfer between the phases due to intrinsic incompatibility between BHS (hydrophilic) and HDPE (hydrophobic). Particle pull-out is also clearly seen, especially as BHS concentration increases (30–40%). In the second column, the particles were mercerized (NaOH treatment), which produced a better wettability by the matrix, leading to better contact between both phases. This reduces some interfacial defects; however, incompatibility still exists and limits the adhesion of particles to the matrix, as observed from the different surface textures: tearing and microcracks. Once again, this phenomenon is more important at higher concentrations. In the third column, a more homogeneous distribution of particles is observed with very few defects in the morphology. The presence of a coupling agent (MAPE) on the particles' surface definitely improved the adhesion/compatibility with the polymer. This improved particle–matrix interface allows for better mechanical stresses transfer as discussed later. In general, it has been observed that the adhesion between the particles and the matrix is strong when using a treated particle and a coupling agent. Some microcracks can be seen, which might be related to samples preparation (cryogenic fracture) and/or differential shrinkage (different coefficient of thermal expansion) between both phases leading to particle detachment. However, the presence of MAPE is bridging the gap due to covalent bonds being produced between the hydroxyl (OH) groups of BHS and the maleic anhydride groups of MAPE, as well as physical entanglement occurring between the PE chains in MAPE and HDPE [24]. Similar results have been reported for other systems including composites based on PE with agave [25] and coir fibers [26], where the use of a coupling agent (MAPE) had a positive effect on the mechanical properties.

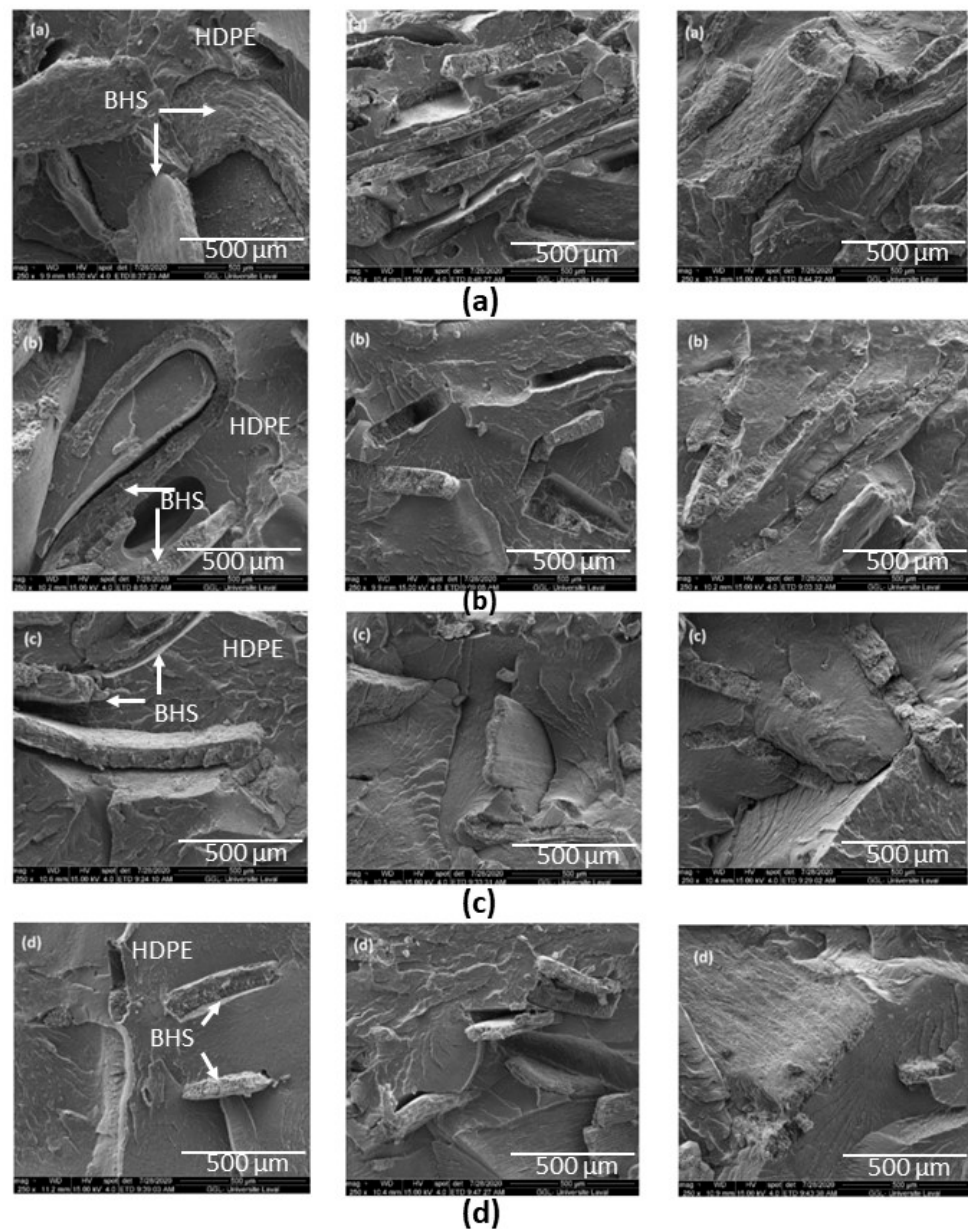


Figure 1. SEM micrographs ($250\times$ magnification) of the HDPE biocomposites with different concentrations of buckwheat husk: (a) 40%, (b) 30%, (c) 20% and (d) 10%. The first column is based on untreated particles (UC), while the second column refers to mercerized BHS (MEC) and the third column is for BHS with MAPE (coupling agent).

3.1.1. Density

One important property of polymer composites is their density, especially for automotive, construction and packaging applications. It also gives information on possible voids (porosity generated during molding) and interfacial defects (particle–matrix adhesion). These defects were partially observed in Figure 1 and the results are presented in Table 1. It can be seen that the biocomposites densities are all above the neat HDPE value (952 kg/m^3) but to a different extent, however, as they represent a balance between the components density (BHS = 1422 kg/m^3 [12] and MAPE = 919 kg/m^3) and the amount of voids/defects in the structure. As expected, the highest density (1188 kg/m^3) was obtained with the 50% MAPE-treated biocomposites which had the highest concentration of particles and limited porosity/defects.

Table 1. Density ($\pm 1 \text{ kg/m}^3$) of the biocomposites.

BHS Content (wt.)	Untreated BHS (UC)	Mercerized BHS (MEC)	MAPE-Treated BHS (MAC)
10	997	955	979
20	998	970	1013
30	1019	1052	1018
40	1082	1070	1103
50	1145	1090	1188

3.1.2. Thermal Properties

Thermogravimetric Analysis (TGA)

Figure 2 presents the thermal decomposition of the raw materials. The degradation of HDPE started around $430 \text{ }^\circ\text{C}$ and finished around $500 \text{ }^\circ\text{C}$ (Figure 2a) with a maximum rate of degradation at $480 \text{ }^\circ\text{C}$ (Figure 2b), indicating good thermal stability for the range of processing conditions used in this study ($170\text{--}175 \text{ }^\circ\text{C}$). The thermal decomposition of BHS is composed of several steps with an initial loss of 6% between 80 and $180 \text{ }^\circ\text{C}$ due to dehydration, followed by the degradation of all constituents: lignin (30 wt.%), cellulose (30 wt.%) and hemicellulose (10 wt.%). As expected, the main stages are related to the carbohydrate components [2]. The thermal decomposition of pure hemicellulose occurs from 250 to $300 \text{ }^\circ\text{C}$, while cellulose decomposes around $350\text{--}390 \text{ }^\circ\text{C}$. Lignin thermal decomposition is usually observed from 250 to $500 \text{ }^\circ\text{C}$ and the maximum rate of degradation is observed at $357 \text{ }^\circ\text{C}$ [27]. Thus, the third and final stage, starting around $350 \text{ }^\circ\text{C}$, is associated with the decomposition of lignin and carbonaceous components [28]. In the case of 30 wt.% of BHS composite, the thermal decomposition is a combination of HDPE and BHS, with a maximum rate of degradation at $350 \text{ }^\circ\text{C}$ corresponding to BHS and the other maximum at $483 \text{ }^\circ\text{C}$ corresponding to HDPE.

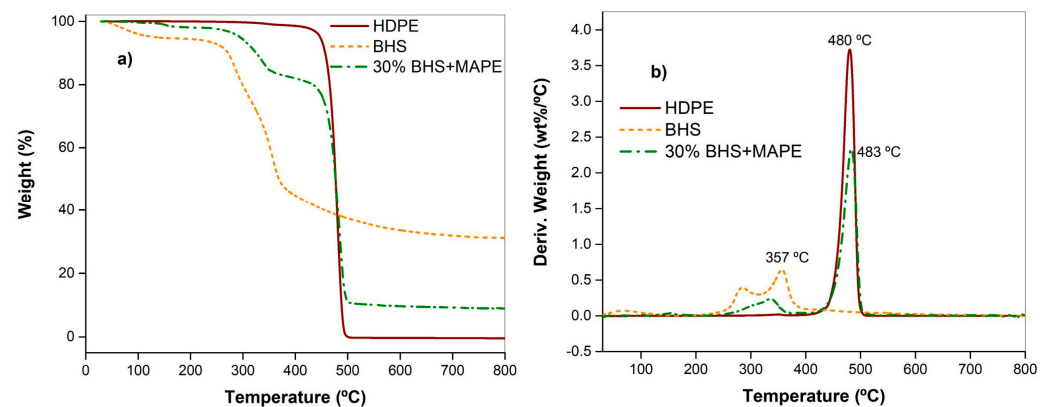


Figure 2. Thermogravimetric analysis (a) and the derivative (b) curves of the neat materials under a nitrogen atmosphere.

The DSC curves for HDPE and 30 wt.% of BHS composite are shown in Figure 3. It can be seen that the presence of BHS does not significantly modify the matrix properties because similar melting temperatures ($130 \text{ }^\circ\text{C}$) and crystallinities (65%) are observed.

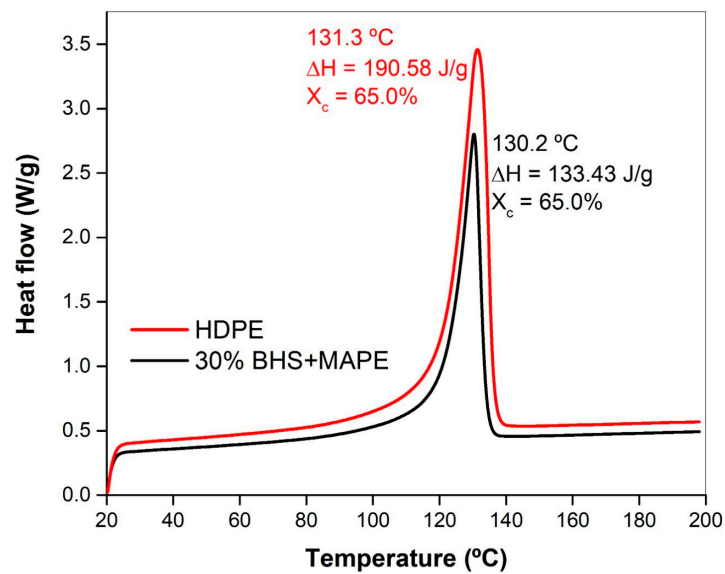


Figure 3. Differential scanning calorimetry thermograms of the matrix (HDPE) and the 30% of BHS + MAPE composite.

3.2. Mechanical Properties

3.2.1. Hardness

Hardness data are presented in Figure 4. The value for neat HPDE is 67 Shore D, which slightly increases with increasing BHS content. There is also a slight increase depending on the particle treatment used. In general, the untreated particles (UC) led to about 5% hardness increase, while the mercerized particles (MEC) generated 8% higher values and the coupling agent addition (MAC) produced a 11% increase compared to the neat polymer (HDPE). The variation in hardness represents a balance between the presence of BHS particles that are harder than the matrix (increased hardness) and the presence of (surface) defects making the material softer (lower hardness). This is the reason why hardness increases with BHS concentration and why the addition of a coupling agent gives the highest values (less defects/voids).

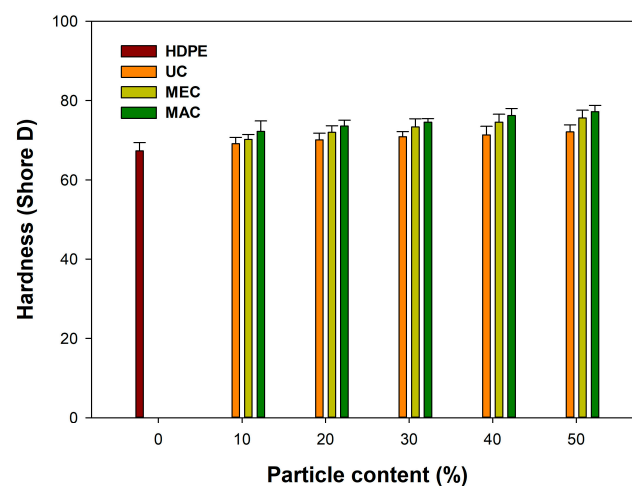


Figure 4. Hardness as a function of BHS content for different treatments.

3.2.2. Tensile Properties

Figure 5 shows the effect of BHS concentration on the tensile properties of the bio-composites. In Figure 5a, the tensile modulus for the neat polymer is 400 MPa and slightly increases (424, 437 and 440 MPa) for untreated particles (UC) at a low content (10, 20 and

30 wt.%), while higher compositions (40 and 50 wt.%) show a decreasing trend down to 390 and 368 MPa, respectively. This modulus loss is associated with poor interfacial interaction between the particles and the matrix (Figure 1), as reported in several studies for untreated particles [15,29]. For the mercerized particles (MEC), a similar trend is observed; however, higher moduli are obtained for all the concentrations studied. This is associated with better dispersion and wettability of the particle after mercerization. On the other hand, the presence of a coupling agent produced a continuous increase for the range investigated (10 to 50 wt.%) up to 460 MPa (15% improvement) at 30 wt.% particle content. Additionally, MAC treatment shows an additional increase in TM of only 2% compared to MEC treatment.

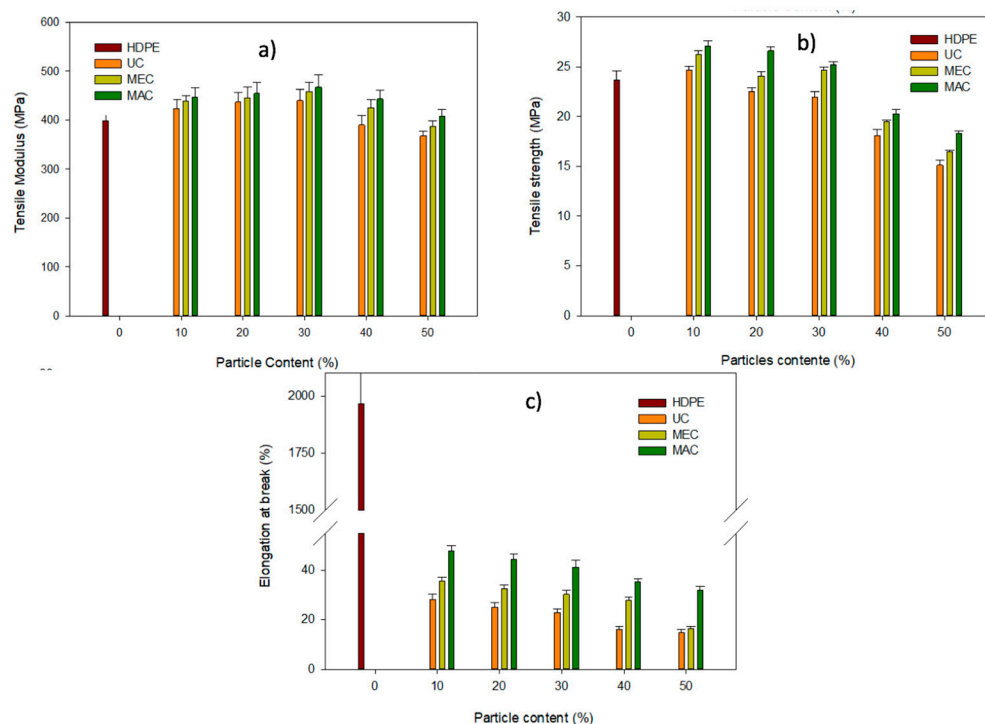


Figure 5. Tensile properties of HDPE and the biocomposites with different BHS contents and treatments: (a) modulus, (b) strength and (c) elongation at break.

Figure 5b reports on the tensile strength results. The value for the neat HDPE is 24.0 MPa and serves as a basis of comparison. In general, the tensile strength decreases with increasing BHS content due to poor adhesion between the particles and the matrix (Figure 1). MEC treatment followed by MAC treatment results in an improvement for compositions up to 30% (27.1, 26.6 and 25.2 MPa for 10, 20 and 30 wt.%, respectively). Formulations with 40 and 50 wt.% show a TS decrease mainly due to particle–particle contact, which creates some defects. Similar results were reported by Abele et al. [30]; however, they used PP as a matrix and injection molding to prepare their samples. In their case, the optimum result was obtained around 40% of BHS.

Figure 5c compares the elongation at break for the three types of biocomposites. The general trend is a substantial decrease in the elongation at break for all the BHS formulations. As expected, adding rigid particles limits possible deformation in the polymer structure (macromolecule mobility) and creates some defects in the chain entanglements, destroying the structural integrity of HDPE. The trend is different, however, as performing a treatment improves adhesion/compatibility and thus makes the structure more rigid and less deformable before complete rupture [16,29]. Nevertheless, less defects are generated, leading to slightly higher deformability of the biocomposites. On average, the values are 33% higher for MAC compared to MEC, which are 30% higher than UC.

Figure 6 presents the flexural results for HDPE and the biocomposites. The flexural modulus of the neat matrix is 813 MPa and the biocomposites have a maximum value around 30–40 wt.% for both UC and MEC. On the other hand, the presence of a coupling agent (MAC) produces a linear increase with a slope of 14 MPa/%BHS, leading to a maximum flexural modulus of 1614 MPa at 50 wt.%. For the flexural strength, a similar trend to the tensile strength (Figure 5b) is observed. In this case, all the values for MAC samples are higher than for the neat HDPE (18.4 MPa), leading to a maximum of 22.0 MPa between 20 and 30 wt.% of BHS with a flexural modulus of 20.4 MPa at 50 wt.%.

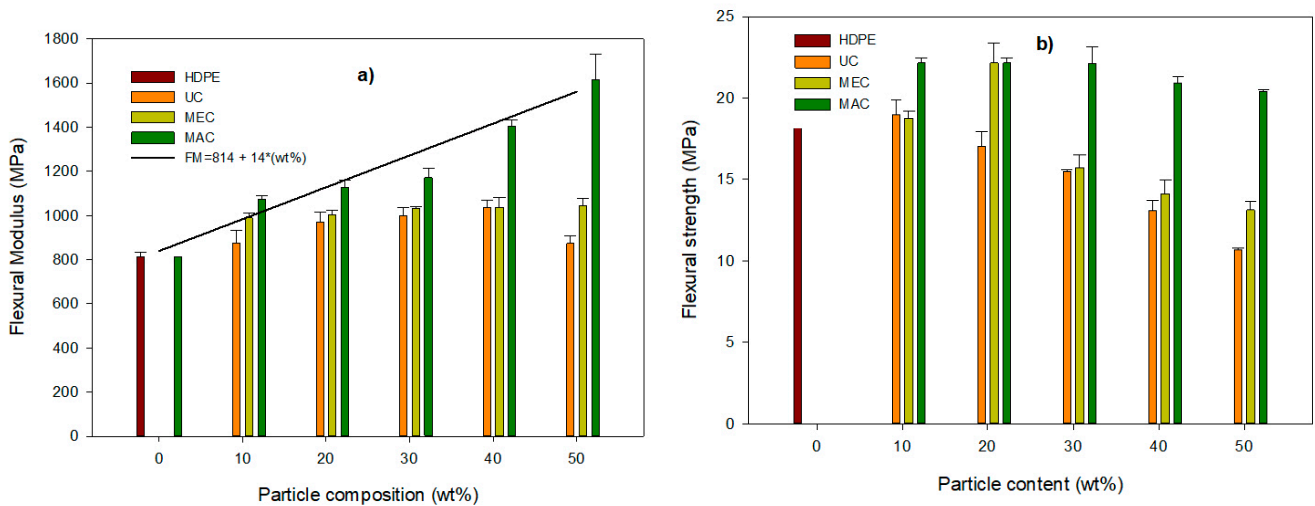


Figure 6. Flexural properties of HDPE and the biocomposites with different BHS contents and treatments: (a) modulus and (b) strength.

Another important mechanical characterization for polymer composites, especially for outdoor and material handling applications, is impact strength, which represents the capacity of a materials to absorb mechanical energy at high strain rate. Here, notched Charpy impact resistance was carried out and the results are presented in Figure 7. Similar to most of the results in the literature [12,16,24,25], the impact strength decreases with increasing particle content similar to tensile elongation at break (Figure 5c), and the same reasons can be used to explain the trend: more defects with less mobility of the polymer chain to deform and absorb the mechanical energy applied. Even if the particle treatments were applied (MEC and MAC), negligible difference was observed for this property. Based on the results of Figure 7, a general linear decrease is observed with increasing BHS content leading to a slope of $-1.3 \text{ J/m}/\% \text{BHS}$ from the neat HDPE value (115 J/m).

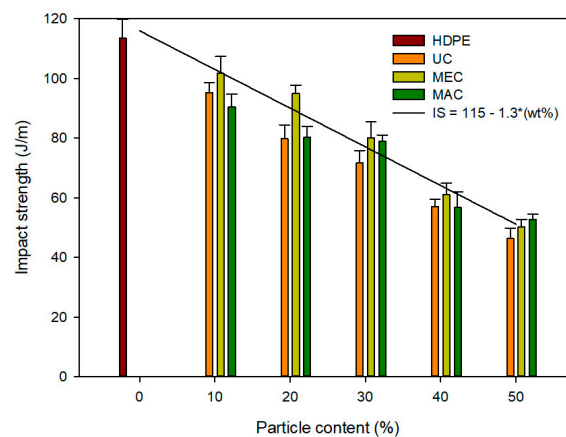


Figure 7. Charpy impact strength of HDPE and the biocomposites with different BHS contents and treatments.

Based on all the characterization performed, the best sample seems to be the 30 wt.% of BHS composite with a coupling agent (MAPE) as it is the one having the highest tensile strength (25.2 MPa) and flexural strength (22.0 MPa), while having good flexural modulus (1171 MPa) and tensile modulus (346 MPa), without losing too much elongation at break (28.5%) and impact strength (57 J/m) compared to the neat matrix (HDPE). This biocomposite is only 7% higher in density, but has 14% higher hardness, while having a high biosourced content (30 wt.%).

To complete the analysis, Figure 8 presents a comparative analysis between the mechanical properties of 30 wt.% of BHS with the matrix. For an easy comparison, the properties of the biocomposites were normalized using the neat HDPE. It can be seen that all the values are above unity, which indicates improvement, with the exception of impact strength. The hardness and elongation at break were not included in Figure 8. Hardness increased by 5–11% depending on the treatment type, while the elongation at break decreased by 98% compared to neat HDPE. The mechanical properties for this composite are similar to other green composites, where the changes are in agreement with the review paper of Kuram (2021) [29]: the elastic modulus, tensile strength, flexural modulus and hardness are generally improved by 1–115%, 12–212%, 10–46% and 5–8%, respectively, depending on the matrix and natural fiber used. However, a drop in elongation at break, flexural strength and impact strength is expected by 10–98%, 0–85% and 68–92%, respectively, depending on the type of natural fiber and matrix used.

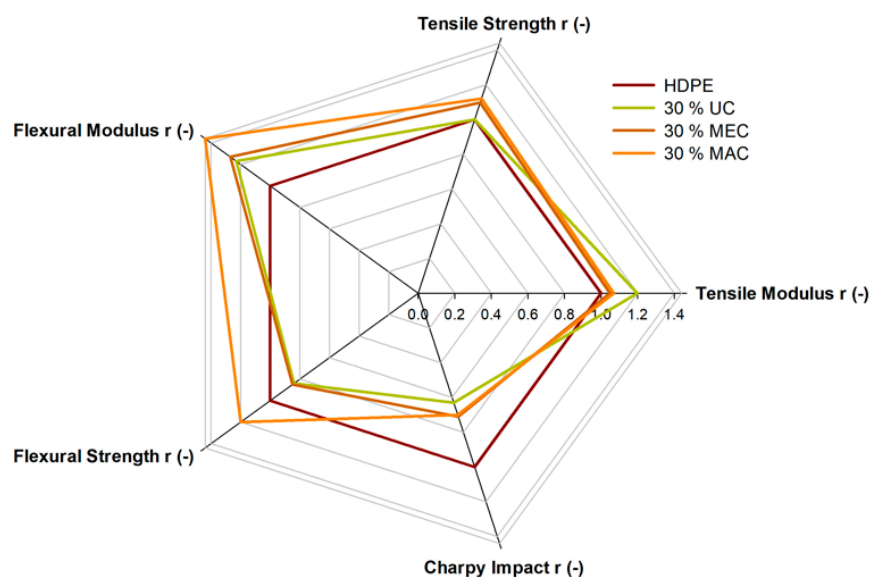


Figure 8. Normalized mechanical properties (with respect to the neat HDPE) for the untreated (UC) and treated (MEC, MAC) biocomposites with 30 wt.% of BHS.

4. Conclusions

In this work, buckwheat husks (BHS) as agricultural residues were used as biofillers inside high-density polyethylene (HDPE) to determine the effect of its addition on the physical (density and hardness), thermal (DSC and TGA) and mechanical (tension, flexion and impact) properties. In particular, the following three series of biocomposites were produced to investigate the effect of particle–matrix interfacial adhesion: untreated particles, mercerized particles and particles grafted with a coupling agent (maleated polyethylene, MAPE). The samples were compounded via twin-screw extrusion and compression molded.

From the results obtained, it can be concluded that different treatment led to different mechanical behavior of the biocomposites. In most cases, the addition of a coupling agent (MAPE) performed best as it improved the flexural modulus and strength, as well as the tensile modulus and strength compared to untreated and mercerized particles. However, the best overall performance was obtained at 30 wt.% of BHS with MAPE, as

this biocomposite had the higher tensile strength (12%), flexural strength (20%), tensile modulus (7%) and flexural modulus (44%) compared to the neat matrix (HDPE).

These preliminary results open the door for more development on buckwheat husks in biocomposites. Possible development can be performed using a biosourced or a recycled matrix to improve the sustainability of the final materials, as well as to optimize the processing and formulation for a better mechanical response. Finally, more characterization can be performed to determine their processability (rheology), long term properties (fatigue, creep, relaxation, etc.), component interaction (FTIR, NMR, Raman, etc.) and other characteristics (degradation, fire resistance, etc.). All these aspects will be studied in a future investigation.

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