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Original Research Paper

Effect of filler load and high-energy ball milling process on properties of plasticized wheat gluten/olive pomace biocomposite

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ABSTRACT

The increase of particles surface area can optimize the dispersion state of biocomposite components and enhance their properties. First in this paper, we aimed to elaborate a novel biocomposite without any treatments. Plasticized wheat gluten (WG), was filled with 0–20% of olive pomace (OP) powder. The second objective was the improvement of biocomposite properties using physical treatment. High-energy ball milling process was applied on the blend of wheat gluten and olive pomace powders (MPs). The grinding effect of particle shape, size and distribution in biocomposite was characterised by particle size distribution using a laser-light diffraction and by SEM analysis. The cryo-fractured surface of selected films, mechanical properties, moisture absorption and thermal properties of both biocomposites were described in details. It was found that the sensitivity of biocomposites to moisture absorption was reduced with the increase of filler content after the applying of high-energy ball milling process. The thermal stability of OP biocomposite decreased with the increase of loading, while that of MPs was unaffected by high-energy ball milling process. This process affects the physical and morphological characteristics of the powders. The mechanical properties were improved by grinding process at filler content lower than15%.

1. Introduction

Given growing environmental concerns, biodegradable polymers have received much attention in academia and industry in the past two decades [1]. Moreover, governments in many countries are supporting usage of green products [2] and renewable resources such as agricultural byproducts. Wheat gluten is an interesting candidate because it is a low-cost raw material, renewable and available [3]. It has remarkable viscoelastic properties, ability to cross-link upon heating and low water solubility. From the chemical standpoint, gluten is composed of two storage proteins, gliadin and glutenin. Wheat gluten-based materials can be obtained by thermoplastic processing, which consists in mixing proteins and plasticizer by a combination of heat and shear [4]; followed by a thermo-mechanical treatments (e.g. compression moulding) [5]. Protein-based materials have been explored as potential materials because of their good barrier properties against oxygen and aroma compounds [4]. However, wheat gluten-based materials have drawbacks that can limit their applications, such as their brittleness and their high moisture sensitivity [6]. This requires an improvement of theirs properties by reinforcement of plasticized wheat gluten to produce a novel biocomposite with characteristics that hold great promise [7].

Raw fibres/particles have been largely exploited as reinforcements into polymer matrices as a substitute to the used synthetic fillers. The natural fillers can be obtained from both forestry and agricultural resources [8], among them, olive pomace which is a by-product of olive oil production industry. Considerable amounts of these wastes are produced and present an environmental hazard in olive oil producing countries. Therefore, there is an urgent need to treat these materials safely [9]. In Algeria, huge amounts of olive pomace are generated; it represents 10^5 t per year, this amount of agrowastes is usually burned [10], however, they can be an important source of renewable fillers since they give bio-based composites unique properties by improving their mechanical properties and water resistance [11]. It contains a great amount of cellulose, hemicelluloses, and lignin. To produce biocomposites with good mechanical properties, a strong adhesion has to be obtained by interfacial interactions, including mechanical interlocking,

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chemical bonding and physical adhesion [12]. There has been a lot of research on various methods to improve adhesion between biocomposite components [13]. High-energy ball milling process is a cost-effective and eco-friendly physical technique [14]. Materials with novel microstructures and properties have been synthesised via this process, using planetary ball mill [15]. High-energy ball milling process combined friction, collision and shear resulting from the grinding balls and the container wall [16]. This particle-size reduction technique can increase the surface area and improves interface adhesion in the materials by particle distribution enhancement in the biocomposite [17]. However, the particle size can be expected to influence a range of mechanical properties [18]. The present work aims to elaborate a biocomposite based on plasticized wheat gluten with glycerol containing 0–20% of OP. To improve OP biocomposite properties, high-energy ball milling process was applied to produce MPs biocomposite. The properties of boths biocomposites, in function of filler contents, were studied. Grinding effect on shape, size and distribution of particles in the biocomposite were characterised by particle size distribution (PSD) using a laser-light diffraction and SEM analysis. The cryo-fractured surface of selected biocomposites was observed using SEM analysis. The particle-size reduction effect on mechanical properties, moisture absorption, mass loss, micropores ratio and thermal properties of biocomposites were also investigated.

2. Experimental work

2.1. Chemical

Analytical grade glycerol (≥99%) was purchased from Sigma Aldrich (Saint-Louis, United States).

2.2. Raw materials

Wheat gluten was obtained from Tereos Syral (Marckolsheim, France). Chemlal olive pomace (OP) was obtained from a local olive refinery in the area of Fenaia-Ilmaten (Bejaia, North-east of Algeria), and washed with hot tap water to remove all water-soluble impurities, followed by drying at room temperature. The product was ground using an electrical grinder (IKA model-A11, Staufen, Germany) and was sieved using standard 125 μm sieve.

2.3. Particle size distribution (PSD)

The particle size distribution of wheat gluten, OP and MPs powders were determined using a laser-light diffraction unit (Mastersizer S, Malvern Instruments Ltd., Worcestershire, UK) equipped with 300 RF lens. The diameters D (v, 0.10), D (v, 0.50) and D (v, 0.9) at 10% (small particles), 50% (medium size particle), 90% (large coarse particle), respectively and volume mean diameter (D [4.3]) were computed.

2.4. High-energy ball milling process

A planetary ball mill (model PM400, Fritsch, Haan, Germany) was used to grind the dry blend of this study. Using 250 mL capacity stainless steel milling jars and lids, charged with spherical zirconia (ZrO) balls (10 mm diameter) as grinding media. The powder (g) to media (g) ratio was maintained at 1:10 for all milling experiments. The speed of ball milling was set at 150 rpm. The duration of milling was 10 h. Grinding was performed as follows: 35 g of the blend of powders (wheat gluten and olive pomace) labelled MP_s, and 47 spherical zirconia balls were placed in the jars, which was filled with 80 vol% of ZrO balls and powders. The rate of each blend compounds was shown in Table 1. After treatment, the milled blend of olive pomace and wheat gluten powders, named Milled powders (MPs) was collected after removing the balls, then mixed with a plasticizer in order to manufacture the biocomposites.

Table 1
Composition of plasticized Wheat Gluten (WG) and biocomposites, all percentages were calculated on a dry weight basis.

Biocomposite names[a]		Sample compositions (%, w/w)	
		Wheat gluten	Powder (filler)
WG		65	0
OP_5	**MPs_5**	60	5
OP_10	**MPs_10**	55	10
OP_15	**MPs_15**	50	15
OP_20	**MPs_20**	45	20

[a] **WG:** plasticized Wheat Gluten. All materials were plasticized with 35 (%, w/w) of glycerol, and the composition of WG and biocomposites were calculated on a dry weight. The indexes 5, 10, 15, 20 represent the percentage of powder. **OP:** Olive Pomace powder, **MPs:** Milled Powders.

2.5. Preparation of biocomposites

Processing of [19,20] was adopted to elaborate biocomposites, wheat gluten and dried OP powder were firstly hand mixed to the desired proportions (Table 1). Then, the resulting powder was mixed with glycerol (35%, based on total dry weight) in a two-blade counter-rotating batch mixer, turning at 3:2 differential speed (Brabender, Duisburg, Germany). For the milled powders, glycerol (35%, based on total dry weight) was directly mixed with MPs powder to the desired proportions (Table 1). The mixtures were performed by mixing at a speed of 100 rpm during 15 min at 70 °C. The blends were then thermo-moulded in a heated press (Carver hot press model-2629, Wabash, United States) at 120 °C. Approximately, 4 g of the blends were placed between two aluminium sheets in a rectangular mould (80 × 40 mm) for 10 min without pressure, followed by 3 min under a pressure of 15 MPa. Then they were removed from the mould and cooled at room temperature. The thickness of the resulting films was approximatively 0.5 mm. Prior to the tensile test, the films were conditioned into a desiccator producing 43% relative humidity at 24 °C for one week.

2.6. Scanning electron microscopy (SEM)

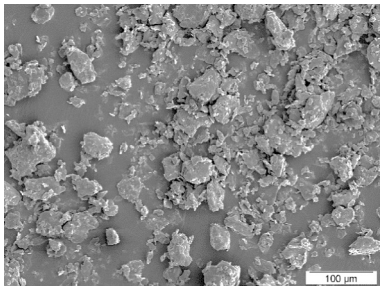
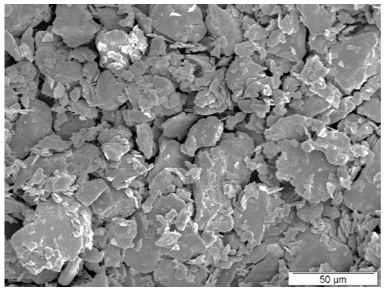
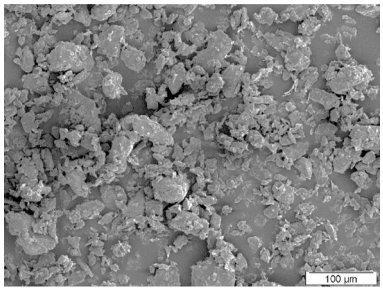
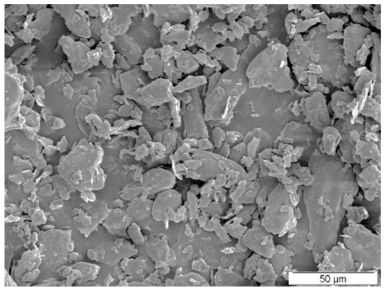
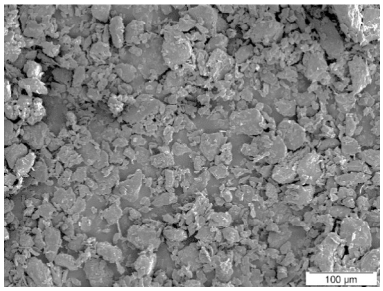
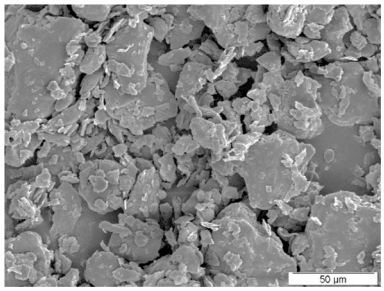
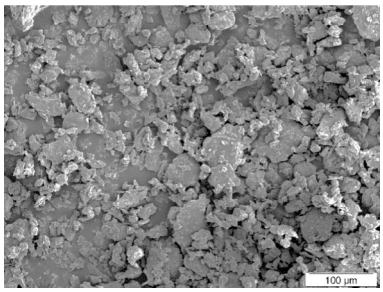
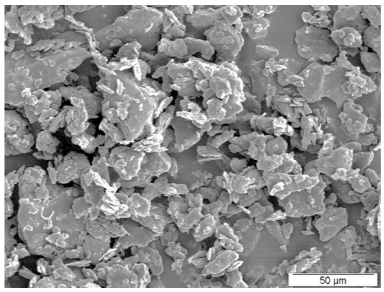
The micrographs of morphology observation of MPs powder contains 5, 10, 15 and 20 (%, w/w) of OP powder (Table 2), WG films, selected biocomposites (OP_10 and MPs_10) (Table 3), were obtained using 8 kV secondary electrons microscopy (JEOL JSM-6100, Tokyo, Japan). Each material sample was frozen in liquid nitrogen and fractured. All samples (MP_s powders and cryo-fractured biocomposites) were coated with gold/palladium on a JEOL JFC-1100E ion sputter coater (Tokyo, Japan) before observation.

2.7. Micropore ratio estimation

The micropore ratio (%) of biocomposites (Table 3) were derived from SEM images. To investigate the repeatability of the results, a minimum set of five similar images in term of magnifications (×300), and contrast for each films were processed by ImageJ software (ver. 1.49, NIH, Maryland, USA), using manual threshold-based segmentation algorithm. The results were reported as mean ± standard deviations (S.D).

Before ImageJ analysis steps [21,22], which are detailed below, the SEM images needs to be calibrated to their scales:

Table 2
Micrographs at two magnifications (×250 and ×300) of MPs powder, contains 5, 10, 15 and 20 (%, w/w) of OP powder.

	SEM observation of MP_S powders Magnification (×250)	Magnification (×300)
MPs_5		
MPs_10		
MPs_15		
MPs_20		

i. The images (8-bit) level brightness and contrast were processed to achieve a reasonable resolution in order to heighten the pores.
ii. Then, SEM images were processed using a low/high defaults threshold filter, with a lower limit which varies with the image and higher limit which have maximum of 255. This filtering is needed for the automatic edge detection and insures accurate morphology measurements.
iii. Thresholding operation is critical; identified micropores, properly, by manual thresholding displays a "halo effect" showing pixels of red color filling the micropores. This step should b performed with care in order to distinguish between the micropores, statches granules, inclusions and other possible defects.
iv. The binary images were then analyzed using the "analyse particles" tool built in ImageJ, the results produced contain the total number of identified pores, total pores area, the arithmetic average pore area and the percentage of area covered by pores, which is defined as micropores ratio.

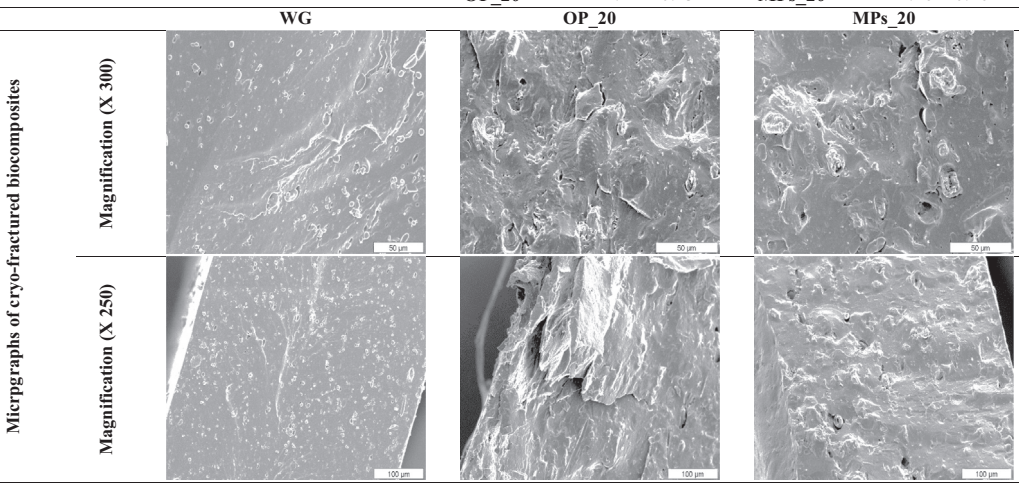
The statistical analysis with one–way analysis of variance (ANOVA) followed by Tukey's test using JMP software (Ver. 7, SAS, North Carolina, USA), were used to show if there are significant differences between OP and MPs biocomposites in term of their micropore ratio ($p < 0.05$).

2.8. Tensile test

The tensile test was performed using a universal testing machine (AGS-X, Kyoto, Japan) equipped with trapezium x software (Kyoto, Japan), with a 500 N load cell at room temperature and with a crosshead speed of 10 mm min^{-1}. Before testing, biocomposites containing 0 to 20% of OP or MPs powder were cut into dumbbell-shaped (10 × 5 mm), the thickness was measured in three different places with a calliper. Young's modulus, tensile strength and elongation at break were tested from eight replicates for each sample, the mean value and standard deviation were determined for each of these parameters. A one–way analysis of variance (ANOVA) followed by a Tukey's test using JMP software

Table 3
Micropores ratio (%) of biocomposites contain 0 to 20 (%, w/w) of OP or MPs powder and micrographs of WG, OP_20 and MPs_20 biocomposites.

Parameters			Biocomposites			
Micropore ratio (%)	WG	1.06 ± 0.45^{abc}	OP_5	1.10 ± 0.32^{ab}	MPs_5	1.16 ± 0.41^{ac}
			OP_10	1.13 ± 0.46^{ab}	MPs_10	1.20 ± 0.45^{ac}
			OP_15	1.18 ± 0.41^{ab}	MPs_15	1.22 ± 0.30^{ac}
			OP_20	1.22 ± 0.43^{ab}	MPs_20	1.26 ± 0.46^{ac}



The results of the micropore ratio (%).are reported as means ± S.D. Same letters (a–c) in the same column refer to the means that are not statistically different according to ANOVA and Tukey's test ($p < 0.05$); the results are ranked in decreasing order: a > b > c.

(Ver 7, SAS, North Carolina, USA), were used to show if there are significant differences between OP and MPs biocomposites in term of Young's modulus, tensile strength and elongation at break. Evaluations were based on the $p < 0.05$ significance level.

2.9. Moisture absorption

Square samples of approximately (1 × 1 cm) were cut from the biocomposites containing 0–20% of OP or MPs powder, firstly these samples were conditioned into a desiccator containing silica gel at room temperature until constant weight was reached. After the measurement of the initial dry weight (W_i) three replicates per sample were stored at 24 °C into desiccators containing saturated salt solutions of $CaCl_2$, K_2CO_3, NaBr and K_2SO_4 producing relative humidity respectively of 35, 43, 58 and 98%. When equilibrium was reached, the equilibrium weight (W_{eq}) was measured. At high relative humidity levels (98% RH), water droplets condensed on the samples surfaces. Before measuring their mass, the surfaces were carefully wiped with absorbing paper. After equilibrium, the samples were dried again over silica gel and the final weight after mass loss (W_f) was measured.

The moisture absorption (Eq. (1)) and mass loss (Eq. (2)) were then calculated as:

$$\textit{Moisture Absorption}\ (\%) = \frac{W_{eq} - W_i}{W_i} \times 100 \quad (1)$$

$$\textit{Mass Loss}\ (\%) = \frac{W_i - W_f}{W_i} \times 100 \quad (2)$$

2.10. Thermogravimetric analysis (TGA)

The thermograms of weight loss and derivative weight loss of powders, WG films and selected biocomposites (OP_10, OP_20, MPs_20 and MPs_20) were carried out with a thermogravimetric analyzer (SETARAM 92-12, Frankfurt, Germany) equipped with software Setsoft 2000 (Frankfurt, Germany). Thermogravimetric analysis (TGA) was done under nitrogen flux at 1.8 L h^{-1}. Approximately, 20 mg of each sample were placed in crucibles and analysed over a temperature range of 20–500 °C with a heating rate of 5 °C min^{-1}. All samples were dried about one week in desiccator containing silica gel before testing.

3. Results and discussion

3.1. Particles size distribution (PSD) of powders

Fig. 1 shows the particle volume distributions of OP and wheat gluten in function of the mean diameter of the particles in the powders. The OP powder and wheat gluten had, respectively, 54 μm and 45 μm, mean diameters. The distribution of OP powder presents two peaks, the first one is higher and larger, between 10 and 100 μm, is attributed to agglomerates of finer particles. The second peak is weaker with a size between 100 and 1000 μm, disappeared after mixing and milling with wheat gluten powder. A Gaussian distribution between 10 and 100 μm is obtained for wheat gluten powder. The means diameters of milled powders contain 5, 10, 15 and 20% of OP powder were close to those of wheat gluten and OP powders; which were 48 μm for MPs_5, 50 μm for MPs_10, 47 μm for MPs_15 and 53 μm for MPs_20.

Incorporating OP powder from 5 to 20% in wheat gluten powder didn't produce any change in their particle size distribution. The milled powders exhibited a broader distribution with an irregular shape and distorted close larger particle sizes, showing a higher agglomeration degree, as observed in the SEM micrograph (Table 2). OP powder is a hard material and is probably more resistant than wheat gluten. Some small particles were formed on the surface of others larger particles during the milling process and the particles agglomeration occurred. This might be due to the fact that the fresh surface formed, due to high-energy ball milling process, then the produced particles with high surface energy prefers to agglomerate [23]. These agglomerates can influence the biocomposites properties.

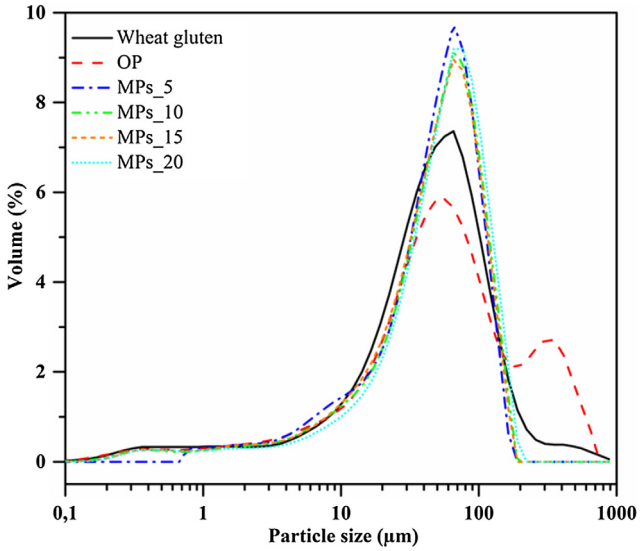


Fig. 1. Size distribution of wheat gluten, OP and MPs powders.

3.2. SEM observation of MPs powders

SEM micrographs of MPs contain 5 to 20% of OP powder grounded under the dry milling condition is shown in Table 2 at two magnifications (×250 and ×300). The high-energy ball milling process plays a major role affecting the dimensional and topological characteristics of powders. It is also known that the milling methods affect the shape of the granules [24]. Particles in the initial mixture were affected by the cold working conditions. The impact and shear forces were generated by the milling media. Therefore, an amount of the particles increased in size and they agglomerated to form larger particles. The fine particles sized in the sub-micrometre range.

For all MPs, the fine particles adhere to the surface of the other larger particles with a rougher surface. During the progressive modifications induced by high-energy ball milling process, it seemed that particles were grounded from external portions. This observation was approved by the fact that coarsest particles did not disappear, but were surrounded by small particles deriving from them [25]. As the fragments decreased in size, fracture resistance and the tendency to agglomerate, are increasing and particle fineness approached a limit [26]. These agglomerates were more observed in MPs that contained more than 10% of OP powder.

3.3. SEM of cryofractured biocomposites and micropores ratio

SEM micrographs taken at the break surface of WG films, OP_20 and MPs_20 biocomposites fractured under liquid nitrogen at room temperature, were presented in Table 3 at two magnifications (×250 and ×300), for each material the goal is to display the filler dispersion within the plasticized wheat gluten and the interfacial adhesion between the biocomposite components [27].

The surfaces of the materials showed a visible difference. WG films presented a homogeneous surface, this may be due to a complete blend of wheat gluten powder in glycerol during the manufacturing process. However, granular particles were observed outside the fractured WG surface, that could be the residual starch existing in industrial wheat gluten powder used to produce these materials. Small holes which are labelled as micropores, were observed on the WG films surface, these micropores have an effect on material properties.

The micrographs of OP_20 and MPs_20 biocomposites at two magnifications (×250 and ×300) show heterogeneous and rough surfaces and a dense bulk phase, which is typical in brittle fracture. Small agglomerates and several holes (micropores) can be observed on the fractured surface of the biocomposite as a consequence of poor interfacial adhesion in the biocomposite. Spherulite-like domains were also observed. The agglomerates that took part in the micropores formation were more important for MPs_20 compared to those of OP_20 biocomposite. This occurred after applying a high-energy ball milling process.

The micropores ratio estimation (%) of all OP and MPs biocomposites were derived from images processing of three similar images in term of magnification (×300), and they were presented in Table 3. The micropores ratio of OP and MPs biocomposites increased without significant differences compared to that of WG films ($p > 0.05$). It has been described that the micropores ratio in the produced biocomposites influences their mechanical strength and water absorption [19]. In this work, the micropores ratio effect on biocomposites properties will be discussed.

3.4. Mechanical properties

The effect of the OP powder incorporation in plasticized wheat gluten and the effect of high-energy ball milling process of the MPs powder on the mechanical properties were detailed in Fig. 2.

Fig. 2a shows a stress-elongation relationship of biocomposites containing 0–20% of OP powder. A typical curve similar to those of thermoplastic materials was obtained for WG films. With increasing the OP powder content, the elongation at break decreased. These curves are typical of brittle materials. Fig. 2b shows a stress-elongation relationship of biocomposites that contains 0 to 20% of MPs powder, and demonstrates curves similar to those of thermoplastic materials for filler content ≤10%. The elongations of MPs biocomposite are close to that of WG films, these biocomposites became more rigid and brittle for reinforcement ≥15%. Mechanical properties of these biocomposites were detailed through the study of more specific parameters (Young's modulus, tensile strength and elongation at break), were summarised in Fig. 3.

It can be observed on plots shown in Fig. 3a that Young's modulus for OP biocomposites increased and was higher than that was observed in the case of WG films ($p < 0.05$). The Young's modulus of MPs biocomposites increased with the increase of powder content ($p < 0.05$).

The Young's modulus values of MPs biocomposite were close to those of OP biocomposite except for MPs_10 biocomposite, which was 42.13% higher than that of OP_10 biocomposite ($p < 0.05$). Tensile strength (Fig. 3b) of WG films was unaffected by incorporation of 5% of OP powder. It decreased for OP_10 biocomposite and was 15.32% inferior to that of WG films ($p < 0.05$). Then they increased. The tensile strength of MPs_5 biocomposite was close to that of WG films ($p > 0.05$); it increased with loading ≥ 10% of MPs. For MPs_20 biocomposite, tensile strength decreased and it value was close to that of OP_20 biocomposite.

With increasing of OP powder content (Fig. 3c), elongation at break decreased while incorporating OP powder. The OP_20 biocomposite was brittle and it elongation at break was 45.46% less than that of WG films ($p < 0.05$). For MPs_5 biocomposite, the elongation at break was close to that of WG films and was improved by 27.50% compared to OP_5 biocomposite ($p < 0.05$). After that, it decreased and the obtained values were close to those of OP biocomposite for loading ≥10% ($p > 0.05$).

The Young's modulus improvement of biocomposites is due to a higher stiffness resulting from an increase of OP or MPs filler content compared to that of the WG; as a consequence of incorporating the rigid filler. The efficiency of reinforcements against rupture

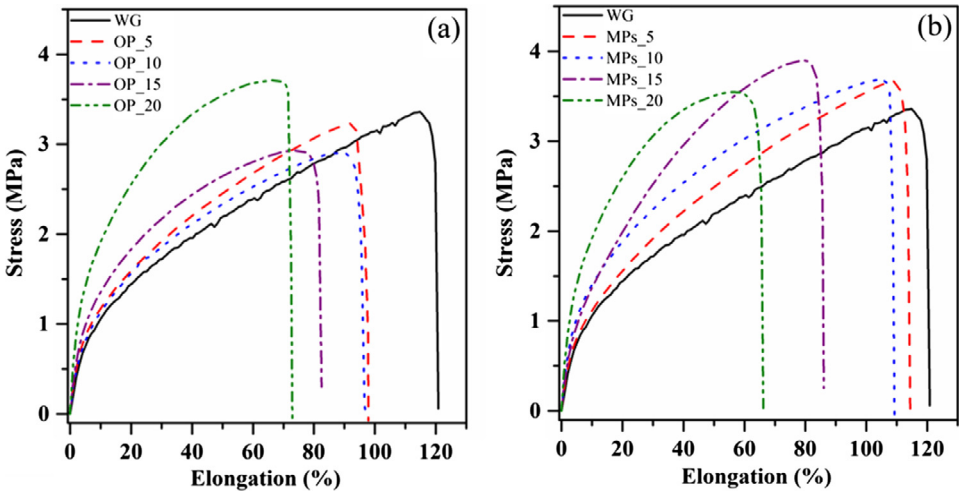


Fig. 2. Stress–Elongation relationship of OP (a) and MPs (b) biocomposites containing 0–20 (%, w/w) of powder content.

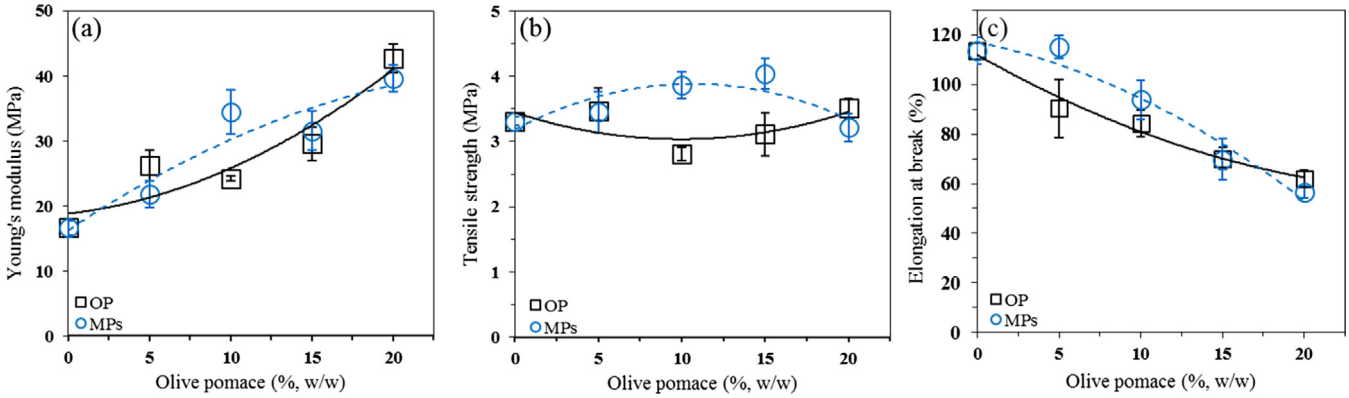


Fig. 3. Young's modulus (a), tensile strength (b) and elongation at break (c) of OP and MPs biocomposites containing 0–20 (%, w/w) of powder content.

depends on filler distribution in the matrix, volume fraction, interfacial wettability and their orientations [28].

Compared with the strength values of OP biocomposite, the tensile strength of MPs biocomposite was enhanced. This is due to the high-energy ball milling process applied on the dry blend of powders before biocomposites manufacturing, which improves the strength of the interfacial bonding [29]. When the MPs powder content exceeded a certain value (>15%), the interface bonding in biocomposite was influenced by the produced agglomerates, which became weaker.

The high-energy ball milling process improves the elasticity of MPs biocomposites at lower reinforcement. After that, the hardness of the filler is more pronounced. The presence of micropores (Table 3), considered as defects and imperfections resulting from the biocomposites processing, create stresses concentration zones favorable to the initiation and propagation of fatigue microcracks, that decrease decrease mechanical properties [21]. However, these biocomposites were more brittle at high filler content ($\geq$15%). This was also due to a poor interfacial adhesion.

The high-energy ball milling process improved the mechanical properties of MPs biocomposites at lower filler content. The increase of loading induces an increase of the stiffness.

3.5. Moisture absorption and mass loss

Water sensitivity is an important criterion for many materials applications. Results obtained following the moisture absorption test at 35%, 43%, 58% and 98% relative humidity (RH) of OP and MPs biocomposites are shown in Table 4. The moisture absorption is dependent on the atmosphere relative humidity and less on the biocomposite [27].

At 35% RH, the moisture absorption of OP biocomposite remains stable with the increase of OP powder content, without significant difference. However, the moisture absorption of MPs biocomposite decreased with incorporating 5% of filler. After that, they remain stable up to 15% of MPs powder content ($p > 0.05$).

At 43% and 58% RH, the moisture absorption decreased with increasing of OP or MPs powder content ($p > 0.05$). In 98% RH, the moisture absorption decreased significantly for both biocomposites. Moisture absorption of MPs_20 biocomposite decreased by 15.70% compared to that of OP_20 biocomposite and by 29.19% compared to that of WG films ($p < 0.05$). The moisture absorption was reduced by incorporating both powders, but an important reduction of absorption was obtained for MPs biocomposites. This is due to the high-energy ball milling process, which improves the filler particles distribution in the plasticized wheat gluten.

With increasing OP or MPs powder content, the lignin (a hydrophobic component) content in these fillers increased and reduces the hydrophilicity of the blend [20]. The micropores ratio (Table 3) present in the biocomposites, can promote the moisture absorption of biocomposites. However, a reduction in moisture absorption caused by the wax present in the powder particles was more pronounced [30].

Table 4
Moisture absorption at 35%, 43%, 58% and 98% RH; and Mass loss of biocomposites containing 0 to 20 (%, w/w) of OP or MPs powder during moisture absorption experiments at 98% RH.

Biocomposite name	Moisture absorption (%)				Mass loss (%)
	35% RH	43% RH	58% RH	98% RH	98% RH
WG	2.83 ± 0.16^{ab}	5.24 ± 0.24^{a}	10.68 ± 0.25^{a}	59.14 ± 0.20^{ab}	16.17 ± 0.24^{ab}
OP_5	2.65 ± 0.34^{ab}	4.83 ± 0.33^{ab}	10.28 ± 0.05^{a}	61.65 ± 0.37^{a}	18.16 ± 0.47^{a}
OP_10	3.73 ± 1.50^{a}	4.57 ± 0.26^{abc}	10.07 ± 0.18^{ab}	57.06 ± 0.26^{b}	14.90 ± 0.47^{ab}
OP_15	2.42 ± 0.31^{ab}	3.82 ± 0.13^{c}	9.12 ± 0.24^{bc}	52.66 ± 0.85^{c}	15.16 ± 0.38^{abcd}
OP_20	2.14 ± 0.36^{ab}	4.07 ± 0.27bc	8.85 ± 0.51^{c}	49.17 ± 0.20^{c}	12.27 ± 0.78^{abcd}
MPs_5	0.89 ± 0.28^{bc}	2.18 ± 0.44^{d}	8.95 ± 0.40^{c}	52.32 ± 0.23^{d}	15.68 ± 0.99^{abc}
MPs_10	1.23 ± 0.12^{bc}	2.45 ± 0.08^{d}	8.74 ± 0.13^{c}	49.51 ± 0.87^{d}	12.58 ± 0.87^{cd}
MPs_15	1.31 ± 0.15^{bc}	0.49 ± 0.76^{e}	5.83 ± 0.33^{d}	47.87 ± 0.37^{e}	16.28 ± 0.31^{ab}
MPs_20	0.14 ± 0.44^{c}	1.59 ± 0.09^{de}	6.90 ± 0.41^{d}	41.45 ± 1.52^{e}	13.86 ± 2.51^{bcd}

Results are reported as means ± S.D. Same letters (a–e) in the same column refer to means that are not statistically different according to ANOVA and Tukey's test ($p < 0.05$); the results are ranked in decreasing order: a > b > c > d > e.

During the moisture absorption experiments, water droplets condensed on the sample surfaces when the relative humidity is high (98% RH), leading to extraction of soluble compounds from the blends. This mass loss can be attributed to the glycerol migration from the material [20]. Table 4 shows the mass loss of OP and MPs biocomposites after moisture absorption at 98% RH level.

3.6. Thermogravimetric analysis

The thermal stability of natural fillers incorporated into a natural polymer is of great importance for biocomposites manufacturing since it affects their processability, physical and mechanical behaviours [24].

Fig. 4 shows the weight loss and derivative weight loss of wheat gluten and olive pomace powders, which were due to the formation of volatile products after thermal degradation. This was displayed as a function of temperature between 20 and 500 °C under atmospheric nitrogen.

The wheat gluten powder was characterized by two peaks of decomposition. The first peak located from 20 to 150 °C was due to the free and bonded water loss; whereas the second peak (close 278 °C) was related to the proteins volatilization. The thermal degradation of OP powder exhibited three steps of decomposition. An initial peak between 20 and 150 °C represents the mass loss of absorbed moisture; the second peak of decomposition at about 150–314 °C was attributed to thermal depolymerization of hemicelluloses. The major third decomposition peak at from 314 to 380 °C was attributed to cellulose decomposition [31]. Lignin presents a broad peak, degrading between 220 and 500 °C, and it was found that the decomposition occurs in three stages. Below 220–250 °C, condensation and splitting of the side chains take place between 300 °C and 400 °C, active pyrolysis leads to the formation of free radicals. Above 400 °C, decomposition was associated with a series of degradation and condensation reactions with an accumulation of aromatic products [32].

The Fig. 5a and a′ shows the thermograms of weight loss and derivative weight loss of WG films, OP_10 and OP_20 biocomposites. Thermograms of MPs_10 and MPs_20 biocomposites were shown in Fig. 5b and b′. The thermal degradation of WG under nitrogen showed a four-stages decomposition. The first stage corresponds to the water loss was between 25 and 150 °C. The second stage is related to the volatilization of glycerol was between 150 and 270 °C. The third stage consists in the breakage of the covalent peptide bonds between the amino acid residues, that varied from 270 to 360 °C. The last stage is associated with the cleavage of S—S, O—N, and O—O bonds from protein molecules, it was between 360 and 384 °C [33].

With incorporating of 10 or 20% of OP or MPs powder; it was observed that after the weight loss due to water and glycerol loss, wheat gluten was degraded between 270 and 300 °C. This phenomenon was followed by the degradation of powder compounds from 300 to 360 °C. The degradation of cellulosic materials happens at a temperature higher than 300 °C. The thermal stability of OP biocomposite decreased with incorporating filler although

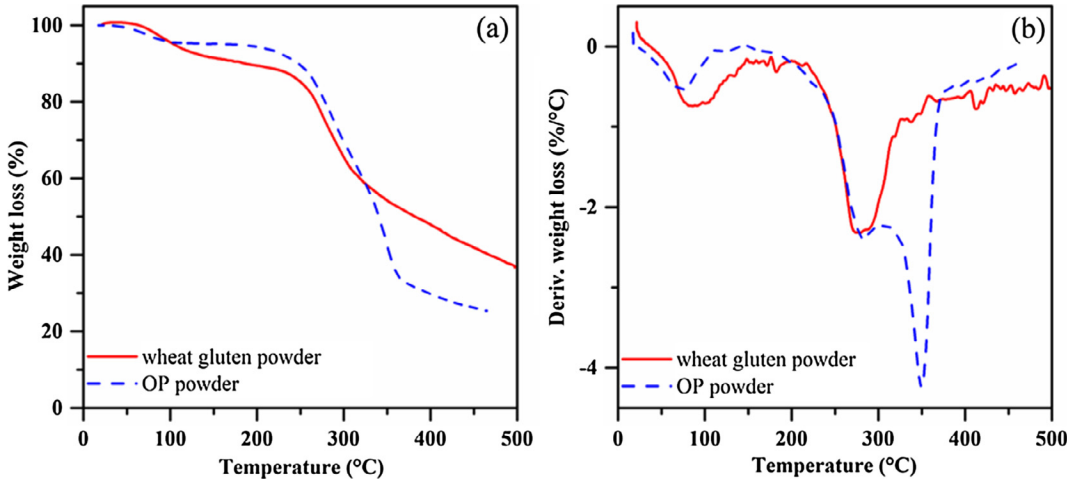


Fig. 4. Thermograms of weight loss (a) and derivative weight loss (b) of wheat gluten and Olive Pomace (OP) powders.

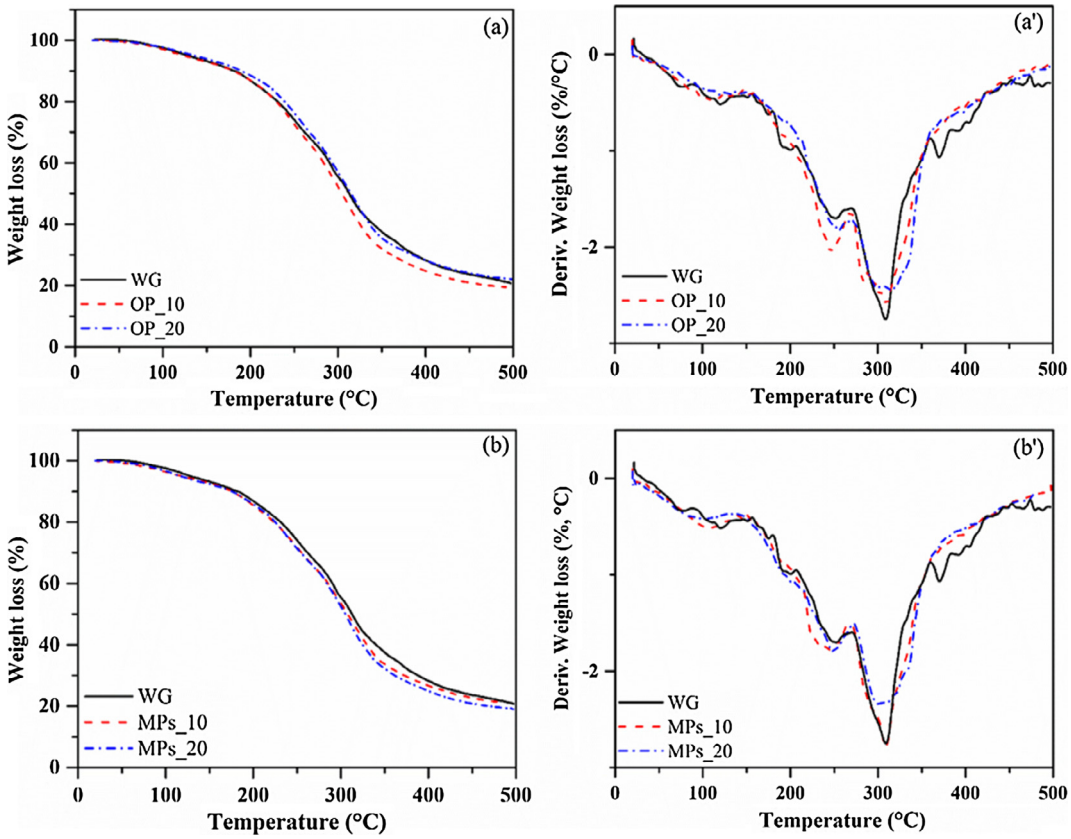


Fig. 5. Thermograms of weight loss and derivative weight loss of WG, OP_10, OP_20 (a and a′); WG, MPs_10 and MPs_20 (b and b′) biocomposites.

that of MPs biocomposite was unaffected. However, the high-energy ball milling process did not seem to affect their thermal properties [24].

4. Conclusion

Biocomposite properties do not only depend on the particle size, it appears that quality of filler dispersion, interface adhesion and particle loading, are also very important parameters. The optimum performance of a biocomposite requires a homogenouse dispersion of the filler particles within plasticized wheat gluten. Reinforcement of WG with OP powder to produce a biocomposite has opened a new bio-resource of lignocellulosic filler. OP and MPs biocomposites were produced using the conventional blending and high-energy ball milling process. High reinforcement increases the stiffness of biocomposite. The sensitivity of MPs biocomposites to moisture absorption was reduced with the increase of filler content incorporated. The thermal stability of OP biocomposite decreased with the increase of loading, while that of MPs biocomposite was unaffected by physical treatment. The high-energy ball milling process applied, affects physical and morphological characteristics of the olive pomace particles. The mechanical properties were improved at lower filler content (<15%). The particle size was not affected by high-energy ball milling process.

In summary, these results showed that the reinforcement of plasticized wheat gluten with OP powder was a promising biocomposite materials in form of biodegradable films that could be used in several fields, such as for food packaging. The high-energy ball milling process was an interesting way to produce the biocomposites and to improve their properties, but with increasing the ratio of hard particles until a critical ratio was reached at 15% of loading, where non-uniform dispersion of filler appeared and increased the tendency of particles to agglomerate. This agglomerations limited the stress transfer between the filler particles and WG, caused cracks to initiate and propagate more easily. Thus, the resulting biocomposite was brittle and presented a lower mechanical properties.

Even if this results seem very promising, further biomposites properties improvements are needed to enlarge their application potential and for an industrial production.

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