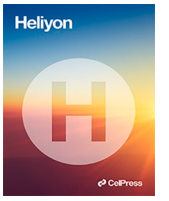
Heliyon 10 (2024) e39713

Contents lists available at ScienceDirect

Heliyon

journal homepage: www.cell.com/heliyon



Research article

Bio-composites from barley, wheat, and cassava flours reinforced with oil palm residues: Characterization and tensile mechanical performance

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ARTICLE INFO

Keywords:
Bio-composites
Oil palm empty fruit bunch
Oil palm kernel shell
Flour
Tensile mechanical properties

ABSTRACT

This study explores the production of bio-composites from barley, wheat, and cassava flours, reinforced with varying ratios of oil palm residues. The research emphasizes principles of circular economy and sustainability. Both flours and reinforcements underwent characterization to elucidate how their physicochemical properties affect the mechanical behavior of the bio-composites. Barley flour exhibited significantly higher levels of protein (11.11 %), crude fiber (5.64 %), and ash (2.80 %) compared to wheat and cassava flours. Conversely, cassava flour stood out for its high carbohydrate concentration (approximately 97.8 % on a dry weight basis). Characterization highlighted enhanced adhesion between reinforcements in bio-composites with cassava flour, alongside morphological distinctions on fractured surfaces. Fourier-transform infrared (FTIR) analysis unveiled several functional groups in the bio-composites, while thermogravimetric analysis delineated five stages of thermal degradation. In terms of mechanical properties, bio-composites with barley flour showed higher elastic modulus values (970.5 MPa), while those with 12 % OPKS exhibited tensile strengths of 1.7–2.1 MPa. The interaction among components emerged as a fundamental factor influencing the mechanical properties of bio-composites, underscoring the necessity of considering reinforcement composition and distribution during fabrication.

1. Introduction

For decades, the overconsumption of non-renewable resources and the disposal of large volumes of plastics have raised concerns about the environmental footprint and sustainability issues [1,2]. Given the impacts on the ecosystem caused by materials derived from petroleum sources, several researchers have focused on developing new green and environmentally friendly materials [1–3]. In this context, PLA (polylactic acid) and PHB (polyhydroxybutyric acid) have emerged as promising alternatives due to their biological

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https://doi.org/10.1016/j.heliyon.2024.e39713
Received 27 May 2024; Received in revised form 21 October 2024; Accepted 22 October 2024
Available online 22 October 2024

base and biodegradability [4]. However, despite their competitive advantages, their high costs limit their applicability. Another sustainable substitute gaining attention is polyvinyl acetate (PVAc), a cost-effective and reasonably biodegradable water-based polymer known for its strong chemical bonding with several substrates, including metallic, plastic, or lignocellulosic materials, owing to its polar nature [5,6]. In the ecological context, initiatives have contributed to producing plastic products made from natural polymeric materials such as lipids, proteins, and polysaccharides [3].

Polysaccharides have recently become central in manufacturing green materials due to their affordability, non-toxicity, availability, and, most importantly, biodegradability [7]. Among them, barley flour stands out for its high content of β-glucan, a crystalline component akin to cellulose that tends to aggregate and exhibit lower solubility, potentially positively influencing mechanical and water vapor barrier performance [8]. Similarly, wheat flour forms a viscoelastic dough when mechanical energy is applied, and water is added, thanks to its structure containing proteins that promote high water retention capacity through intra/intermolecular disulfide bonds [9]. Flours primarily consist of amylose and amylopectin, and their composition from different botanical sources determines their physical and chemical properties [10]. However, the hydrophilic nature of native flour limits its usage, and it offers less mechanical strength than synthetic polymers, with high water permeability. To overcome these shortcomings, thermoplastic flour/-starches have been investigated, which result from blending flour with plasticizers (e.g., sorbitol, glycerol, citric acid, and water) [11].

Thermoplastic flour (TPF) is produced by replacing the hydroxyl groups of flour molecules with hydrogen bonds formed between the plasticizers and the polysaccharide [12]. Under conditions of shear and heat, intermolecular forces are reduced, resulting in higher mobility, making it suitable for processing techniques akin to those of synthetic polymers [13]. However, TPF exhibits similar limitations to flour. To maintain its ecological character, the incorporation of natural fibers as reinforcements is a promising alternative to enhance TPF's mechanical performance [11]. Lignocellulosic fibers, especially those derived from agro-industrial residues, have become focal in the composite materials field due to their affordable cost, low density, high mechanical strength, and sustainability [14,15].

The revaluation of agro-industrial residues emerges as a key opportunity in the bioeconomy. Conventionally, agro-industrial by-products are incinerated or dumped in open landfills, resulting in significant greenhouse gas emissions or decomposition [16]. Among agro-residues sources, those generated by the palm industry are particularly concerning due to their alarming volume. The oil palm crop has been a dynamic industry globally, with numerous applications such as food, biodiesel, cleaning products, cosmetics, plasticizers, and oleochemicals [17]. However, residues produced by these processes, namely oil palm empty fruit bunches (OPEFB) and oil palm kernel shells (OPKS), remain largely untapped. Ongoing research aims to unlock their potential and add value to these byproducts. One potential use of OPEFB fibers and OPKS particles is as reinforcement in polymeric matrices to develop bio-composite materials, enhancing mechanical and thermal properties while reducing processing costs [18]. Nonetheless, like all-natural reinforcement, these fibers/particles have deficiencies associated with their porous structure and high-water absorption capacity, which could be addressed in synergy with different types of matrices [15,19].

Although many studies have explored natural fibers/particles as reinforcements and the development of bio-based matrices, in-depth investigations into specific types of flour/native flour combined with oil palm residues and the impact of proportions of both dispersed and continuous phases have not been thoroughly described. Therefore, this study aimed to develop composite materials using matrices comprising barley flour, wheat flour, cassava flour, and PVAc, along with OPKS and OPEFB. The study assessed the impact of varying proportions of both matrix and reinforcement components on the tensile mechanical, spectrophotometric, and morphological properties of the formulated bio-composites.

2. Methodology

2.1. Materials

Liquid modified commercial polyvinyl acetate resin was utilized, formulated as waterborne with a solid content of 48 ± 3 w/w %. It exhibited Brookfield viscosity (SP1, 12 rpm) ranging between 90 and 110 KU and a density of 1.3 ± 0.05 kg/L at 25 °C. The oil palm residues (OPKS and OPEFB) were provided by Ecuadorian companies located in Quinindé (N 0°20′, W 79°29′) and La Concordia (N 0°00′25″, W 79°23′45″). Cassava flour, wheat flour, and barley flour, all of food-grade quality, were obtained from local suppliers.

2.2. Conditioning of reinforcements

The OPEFB residues were dried at room temperature for 24 h and then ground in a SHINI blade milling machine, model SG-2348E (Ningbo, China). The resulting fibers were sieved through an ASTM mesh No. 50 (length ≈ 297 μm) and dried at 103 °C until a constant weight was achieved. The OPKS residues were processed through a series of grinding steps: two primary grindings in a CONDUX hammer mill (model LHM 20716) followed by two secondary grindings in an ARTHUR THOMAS blade mill (model 3379 - K05) to achieve a fine powder. After grinding, the particles were sifted using an ASTM 100 mesh sieve (particle diameter ≈ 150 μm). Finally, the OPKS powder was dried at 103 °C to attain constant weight [20].

2.3. Preparation of bio-composites

To prepare the matrix, barley flour, wheat flour, and cassava flour were first sifted to avoid clumping. The cold water was added initially, followed by the addition of hot water at 90 °C in a 50:50 ratio. The mixture was stirred until achieving uniform blends, and then it was allowed to cool to room temperature (Ts ≈ 20 °C). PVAc (70 and 80 w/w%) and glycerol as plasticizer (25 w/w%) were

carefully incorporated into the mixture (25 w/w%) until a seamlessly homogeneous texture was achieved for formulation [21]. Subsequently, OPEFB and OPKS were added according to the formulation presented in Table 1.

The samples (matrix + reinforcement) were pelletized. The pellets were processed by compression using a hydraulic press LAB TECH, model LP-S-50 (Mueang Samut Prakan, Thailand). The processing conditions included a temperature of 120 °C, an applied pressure of 150 bar, and a pressing time of 40 min. This temperature was suitable for removing free water from the composite without reaching the decomposition points of the components [21]. When combined with glycerol, it ensured effective wetting, prevented starch retrogradation, and maintained the flexibility of the flours. These conditions are similar to those used in previous research [21, 22].

After processing, the composite was cooled under the same pressure conditions for 15 min before demolding. Plates measuring 150 × 150 mm were produced according to the mold used. The plates were conditioned following ASTM D638-22 standards, at a temperature of 23 ± 2 °C and a relative humidity of 50 ± 10 %, for 48 h. Prior to conducting tensile tests, the thickness of the composite sheets was measured at multiple points, yielding a value of 2.40 ± 0.04 mm.

Fig. 1 depicts a schematic representation of the composite development process.

2.4. Flour and reinforcement characterization

A thorough analysis of the compositions of both flours and reinforcements was carried out according to the standards set by the Association of Analytical Communities (AOAC), the Food and Agriculture Organization of the United Nations (FAO), and the International Code Council (ICC) [23]. This investigation aimed to ascertain the impact of their compositions on the properties of the bio-composites. Various parameters including moisture content (AOAC 925.10), ash (AOAC 923.03), ether extract (AOAC 920.85), protein (AOAC 2001.11), total carbohydrates by difference (FAO), and crude fiber (ICC113) were measured. Furthermore, microscopic analysis of the flours at 400× and 1000× magnifications was conducted to assess the size and shape of their particles and understand how these factors could influence their compatibility with other materials in the bio-composite. The analysis was performed using a Euromex microscope, specifically the Delphi-X Observer model.

For the reinforcements, the content of lignin (ASTM D 1106-21) [24], hemicellulose, and cellulose (ASTM D 1109-21) [25] was determined. Additionally, the specific surface area of the reinforcements was assessed through nitrogen adsorption using a micrometric NOVA touch 1LX apparatus, employing the Brunauer-Emmett-Teller (BET) method. The surface characteristics of the OPEFB and OPKS were determined through an analysis of more than six multiple points after preconditioning by drying at 105 °C under vacuum.

2.5. Bio-composites characterization

2.5.1. Tensile mechanical characterization

Tensile mechanical performance evaluation, including elongation at break, modulus of elasticity, tensile strength, and toughness, was conducted using the INSTRON universal testing machine, model 3365 (Norwood, USA). For this purpose, and in accordance with standard ASTM D638-22 [26], 20 specimens type IV of each formulation were used. The crosshead speed was set at 20 mm/min with a load cell of 50 N.

The mechanical properties of bio-composites could exhibit significant variations among different specimens, even when manufactured under similar conditions. To address this variability, and identify the factors influencing these properties, a statistical analysis was performed. This analysis ensures the validity of experiments, supporting the acquisition of reliable results [27]. The statistical analysis of mechanical property data for bio-composites followed a sequence that included: (a) correlation analysis between variables, (b) assessment of data distribution, (c) identification of outliers, (d) determination of means and standard deviation, and (e) analysis of variance, as illustrated in Fig. 2.

Table 1
Formulation details of bio-composites with different flour types.

Flour	Bio-composite name	Matrix (35 w/w %)	Reinforcement (40 w/w %)
		Flour:PVAc	OPKS:OPEFB
Barley	B1	20:80	10:90
	B2	20:80	30:70
	B3	30:70	10:90
	B4	30:70	30:70
Wheat	W1	20:80	10:90
	W2	20:80	30:70
	W3	30:70	10:90
	W4	30:70	30:70
Cassava	C1	20:80	10:90
	C2	20:80	30:70
	C3	30:70	10:90
	C4	30:70	30:70

*The proportion of glycerol was kept constant at 25 %.

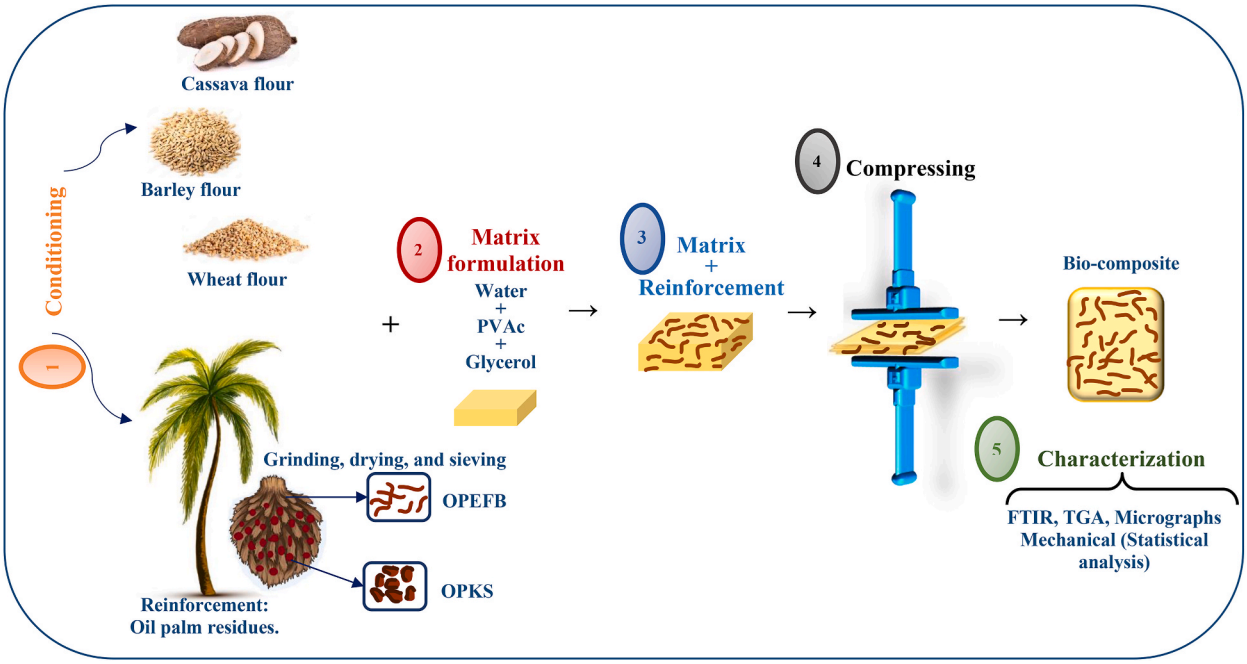

Fig. 1. Experimental procedure for the bio-composites fabrication.

2.5.2. *Instrumental characterization*

The identification of functional groups was conducted using Fourier Transform Infrared Spectroscopy (FTIR) with a JASCO spectrometer, model FT/IR-C800 (Tokyo, Japan). The range of the spectrum was from 450 to 4000 cm^{-1}, with a resolution of 4 cm^{-1}.

The morphology of the bio-composites was examined using Scanning Electron Microscopy (SEM) with an ASPEX electron microscope, model PSEM eXpress, based in Billerica, United States, operating at an accelerating voltage of 25 kV. Microscopic analysis of the surface (10×) and cross-section (20×) of the bio-composites using a MEIJI TECHNO stereomicroscope, model EMZ-13TR (Saitama, Japan). Additionally, thermal behavior was evaluated through Thermogravimetric Analysis (TGA) using a METTLER TOLEDO thermobalance model TGA-2. The analysis covered a temperature range of 25–650 °C, with a heating rate of 10 °C/min and a nitrogen flow of 50 mL/min.

3. Results and discussion

3.1. *Flour and reinforcement characterization*

The comprehensive characterization of raw materials (Table 2) is pivotal in discerning the physicochemical and mechanical properties of bio-composites. The protein, crude fiber, and ash content of barley flour is significantly higher than that of wheat and cassava flours, with values of 11.11 %, 5.64 %, and 2.80 %, respectively. This rich composition of barley flour suggests the potential for enhancing the compatibility between the matrix and reinforcements, as well as facilitating load distribution within the bio-composite. The protein composition of flours has a direct impact on the mechanical properties of bio-composites, influencing their cohesion, strength, and ductility. When proteins are integrated into the bio-composite matrix, they can enhance the internal structure and load-bearing capacity of the material, resulting in improved cohesion between components and enhanced performance under tensile stress [15].

In contrast, while barley and wheat flours share similar carbohydrate contents (around 74 %), cassava flour presents a notably higher carbohydrate concentration (≈97.8 % w/w% on a dry basis), with minimal other components (≈2.2 % on a dry basis). The carbohydrates found in these flours encompass various compounds, with starch being the most predominant. Cassava flour boasts a significantly high starch content, often exceeding 80 % [3], whereas wheat and barley flours typically range between 70 and 75 % in starch content [28,29].

Starch is a fundamental polysaccharide that is composed primarily of amylose and amylopectin, with proportions of these two components varying depending on the source material [29]. The amylose:amylopectin ratio in barley and wheat is approximately 30:70, whereas cassava exhibits a ratio of approximately 20:80 [28,29]. Amylose and amylopectin could form gels when starch is mixed with hot water. Amylose, with its linear chain, yields strong and rigid structures, whereas amylopectin, which is characterized by its branched chain, produces weaker and more flexible structures compared to amylose [30]. Therefore, the higher amylopectin content in cassava starch suggests enhanced a more elastic and flexible three-dimensional network compared to wheat and barley starches [31]. These distinctive properties could lead to increased flexibility in bio-composites. However, the molecular structure of

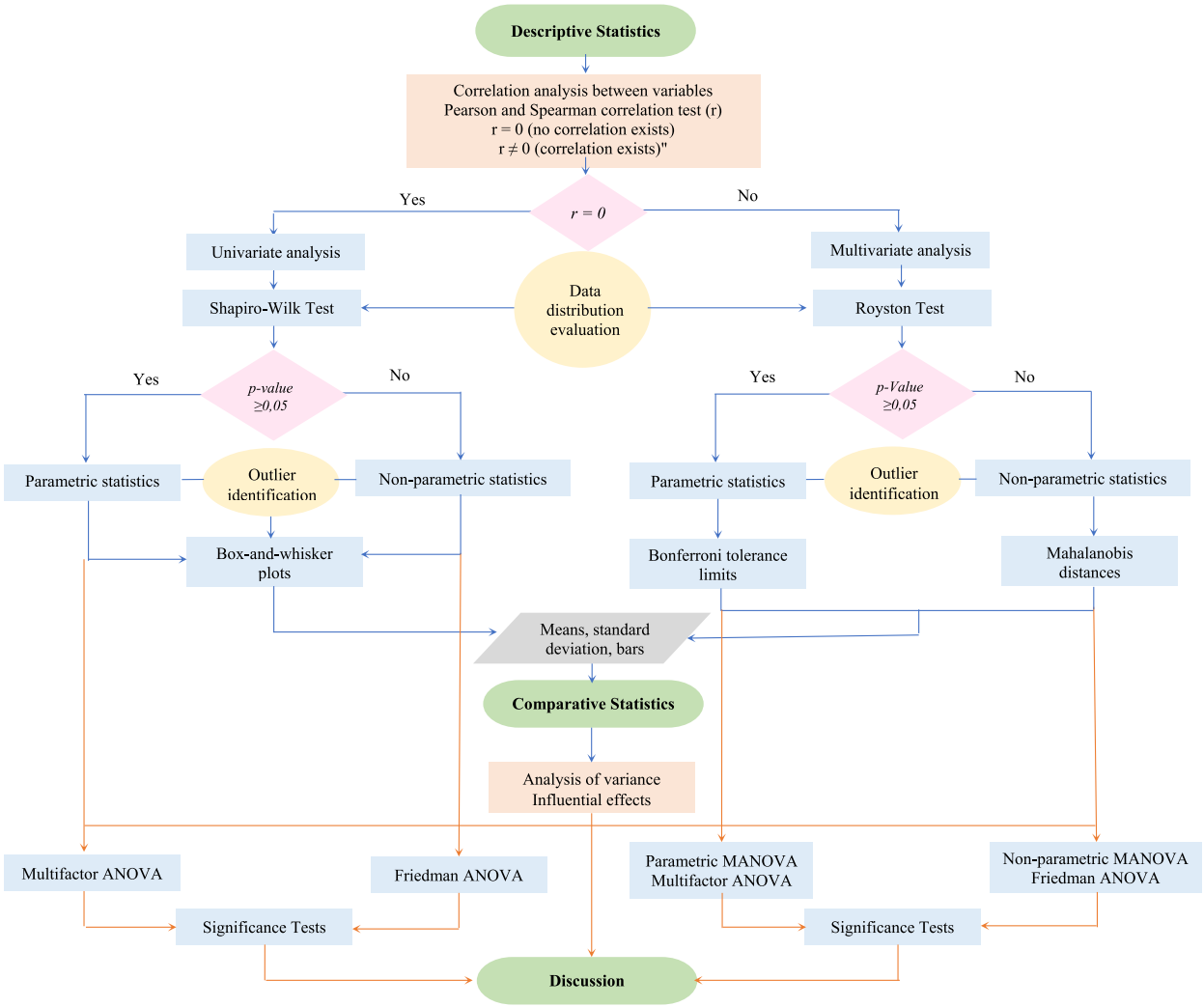

Fig. 2. Flowchart for selection of statistical test to evaluate mechanical properties of bio-composites.

Table 2
Properties and composition of flours and reinforcement materials.

Flour						
Type	**Moisture (w/w %)**	**Ash (w/w%)**	**Ether extract (w/w%)**	**Protein (w/w%)**	**Carbohydrates (w/w %)**	**Crude fiber (w/w%)**
Barley	10.23	2.80	1.55	11.11	74.31	5.64
Wheat	12.94	1.61	1.49	9.33	74.62	1.34
Cassava	13.94	0.15	0.2	0.73	85.01	0.85
Reinforcement[a]						
Type	**Lignin (w/w%)**	**Cellulose (w/w %)**	**Hemicellulose (w/w %)**	**Extractives (w/w %)**	**Surface área (m^2/g)**	
OPEFB	25.64	46.06	25.41	2.89	0.47	
OPKS	48.94	24.96	23.13	2.97	0.66	

[a] The composition of the reinforcements was determined on a dry basis.

amylopectin varies among different starches, leading to specific performance [29].

Micrographs taken at 400× and 1000× magnifications reveal distinct characteristics of flour granules (see Fig. 3). Cassava flour granules arenotably smaller in size anddisplay an oval or spherical shape with a smooth or slightly rough texture, offering greater uniformity compared to other flours [32]. Conversely, wheat flour granules are rougher and larger, exhibiting diverse and irregular

shapes such as spherical, lenticular, and angular [30,33]. Meanwhile, barley flour granules exhibit the greatest heterogeneity in size and shape, presenting polyhedral, angular, and lenticular forms [34].

Regarding reinforcement materials, OPEFB demonstrates significantly higher levels of extracts (11.6 times), and proteins (2.6 times) compared to OPKS, whereas OPKS boasts nearly double the crude fiber content. However, both reinforcements exhibit similar levels of lignin, cellulose (OPEFB: 71.7 % and OPKS: 73.9 %), and hemicellulose. These biopolymers are important in shaping the mechanical characteristics of bio-composites [35]. Additionally, matrix-reinforcement compatibility significantly influences this behavior, with the porosity of the reinforcement material playing a pivotal role in matrix infiltration [15]. BET analysis reveals OPEFB has a specific surface area of 0.467 m^2/g, while OPKS exhibits 0.662 m^2/g, suggesting a higher surface area may facilitate improved matrix penetration into the reinforcement material [36].

3.2. Bio-composites characterization

3.2.1. Morphological analysis

In Fig. 4, SEM images depicting the fractured surface morphologies (magnification: 25×) of the bio-composites are presented, accompanied by microphotographs of the surface and cross-section at 10× and 20× magnifications, respectively. The images of the surface and cross-sectional areas reveal improved adhesion between reinforcements when cassava flour was (Fig. 4), likely attributable to the amylose and amylopectin content/type of its starch, as previously discussed [31]. It has been observed that this type of starch tends to form more viscous and sticky gels compared to barley and wheat starch, enhancing its adhesive capability [32,37]. Generally, there is a strong chemical affinity between the reinforcements and the matrix in composite materials. However, the adhesion values may be influenced by the diversity of the components and the starch content [30,33].

SEM images of the fracture zones (Fig. 4) reveal moderately ductile fracture in the bio-composites, where surfaces separate with deformation perpendicular to the fracture surface. Differences in density and appearance of faults in areas adjacent to fractures are also observed [38]. The bio-composite of cassava flour exhibits low fault density and fine, nearly superficial cracks, which is associated to its more elastic behavior, facilitating stress redistribution and uniform dissipation [31]. Conversely, bio-composites made with wheat and barley flour display higher fault density, with deeper and fragmented cracks. This difference can primarily be attributed to their greater rigidity, making them more brittle and prone to fault formation [30]. It is likely that this increased fragility is due to the specific compositions of the flours as well as greater heterogeneity in particle size and flour shape [34].

3.2.2. FTIR spectroscopy analysis

Fig. 5 shows the FTIR spectra of the bio-composites. FTIR analysis was performed to examine the impact of varying both the matrix and reinforcement proportions, as well as to analyze the interactions among the flour, fiber, and plasticizer.

The FTIR analysis revealed a broad band in the range of 3600 to 3000 cm^{-1}, indicating the stretching vibration of the O-H bond related to the composition of the flours (starch), glycerol, lignocellulosic reinforcement, and water [39]. The bands within the range of 2960 to 2850 cm^{-1} correspond to stretching vibrations of the C-H bonds in alkyl groups (-CH_2 and -CH_3) present in all components of the bio-composite [40,41]. The band observed around 1700 cm^{-1} indicates the stretching vibration of the C=O bond present in the

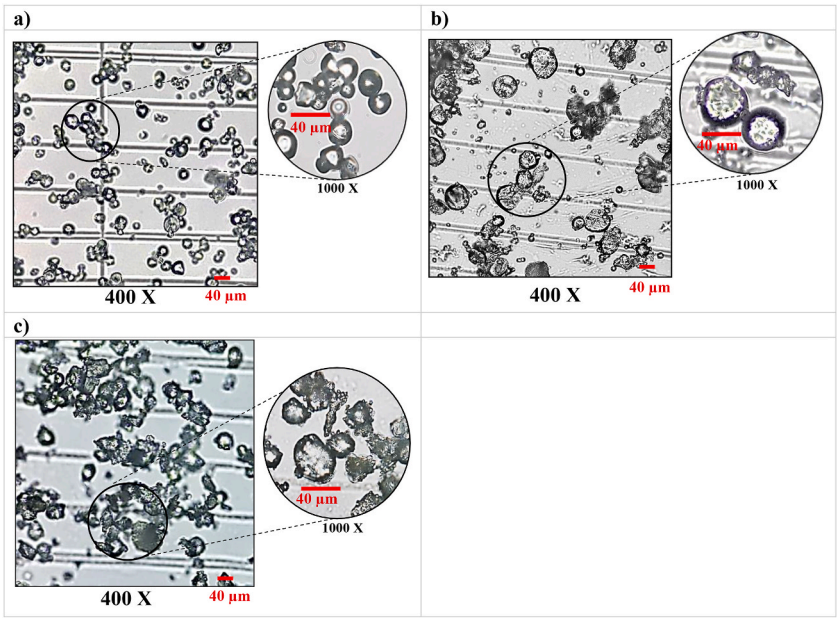

Fig. 3. Morphological analysis of flours: a) Cassava, b) Wheat, and c) Barley at 100× and 400× magnification.

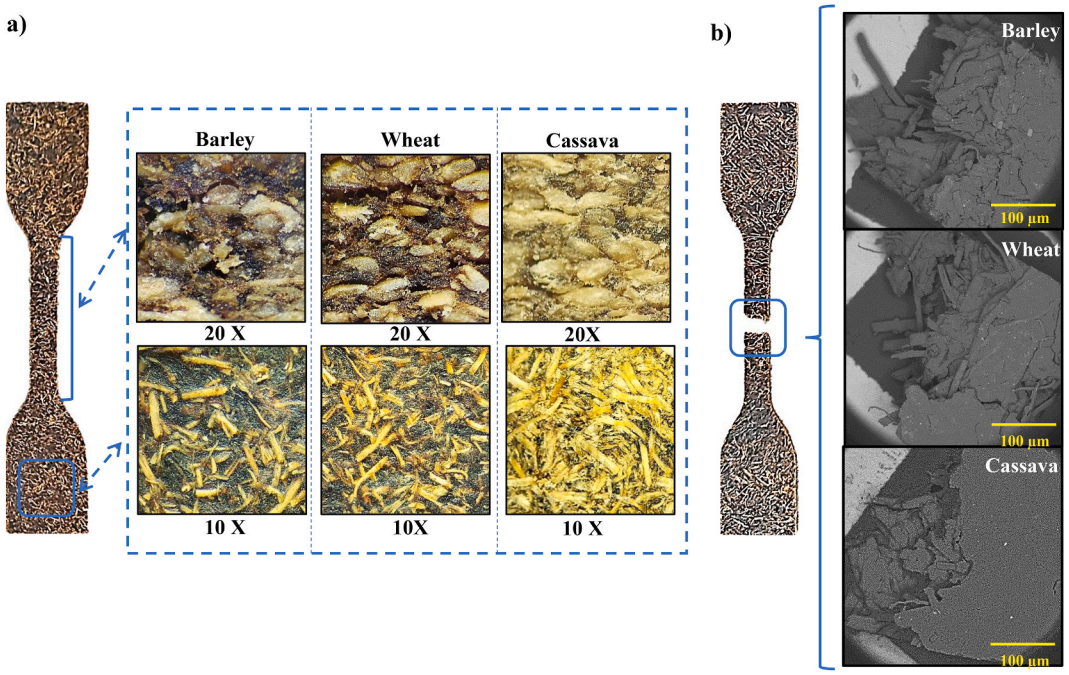

Fig. 4. Morphological analysis of bio-composites: a) Pre-mechanical testing: surface zone at 20× magnification, cross section at 10× magnification; b) Post-mechanical testing: Scanning electron microscopy images at 25× magnification.

lipid compounds of the flours and reinforcements, as well as in the PVAc [40,42]. The band in the range of 1650 to 1540 cm^{-1} could be connected to combinations of stretching and bending vibrational modes of the C=O, N-H, C-N bonds present in the amino acids of the flours' proteins and the bending vibration of the O-H bond in water [40]. The bands in the range of 1500 to 1295 cm^{-1} correspond to bending vibrations of the C-H bonds in alkyl groups (-CH_2 and -CH_3), the aromatic groups present in lignin, and to the stretching vibration of the C-O bond of the crystalline cellulose in the OPEFB/OPKS [43]. The band observed around 1250 cm^{-1} corresponds to the stretching vibration of the C-O bond of the ester group belonging to the PVAc [44]. Bands in the range between 1170 and 1000 cm^{-1} correspond to the combination of bending and stretching vibrations of the C-O bonds (glycosidic bond) present in the polysaccharides of the flours and reinforcements, as well as of the ester group of the PVAc [45]. Finally, a small band around 840 cm^{-1} is presented, corresponding to the stretching vibration of the C-O bond of the amorphous cellulose present in the reinforcements [35,43].

3.2.3. *Thermogravimetric behavior*

Fig. 6 depicts the thermogravimetric analysis of the bio-composites, revealing five distinct stages of thermal degradation. The first stage, extending up to 120 °C, shows a mass loss ranging from 6.2 % to 11.2 %. This initial phase is mainly attributed to the release of highly volatile compounds, presumably associated with the evaporation of water contained in the bio-composites [46].

In the second stage, between 120 and 290 °C, there are mass losses ranging from 24.9 % to 33.0 %. This suggests the evaporation of glycerol present in the matrix of the bio-composites [47]. The third stage, from 290 °C to 350 °C, records a mass loss between 35.2 % and 48.0 %. This phase involves the decomposition of various components such as carbohydrates, proteins, carboxylic acids, fiber, lignin, and PVAc. During this stage, the breaking of bonds and polymer chains occurs, leading to the formation of carbon dioxide, water, and molecules such as levoglucosan and furfural, along with fragments of lower molecular weight products derived from plant-based components [15]. Additionally, aromatic products such as benzene, toluene, and naphthalene volatilize, and polyenes are generated from PVAc [42].

The fourth stage, spanning from 400 °C to 500 °C, exhibits a mass loss between 1.5 % and 6.3 %. This phase is characterized by the degradation of products generated from the decomposition of PVAc, especially polyenes formed in earlier stages [42]. Finally, at temperatures exceeding 500 °C, a residue comprising carbon and minerals (ashes) is observed, representing between 15.0 % and 18.0 % of the overall composition of the analyzed bio-composites. The solid residue indicates the presence of inorganic components that remain undegraded during the thermal process [48].

3.2.4. *Tensile mechanical characterization*

The stress-strain behavior of the bio-composites is depicted in Fig. 7. Initially, all bio-composites display elastic behavior, with the modulus varying according to material composition. The modulus of elasticity is observed to be higher in compounds with a greater proportion of wheat and barley. Subsequently, a moderately ductile plastic behavior is observed. Compounds containing higher proportions of wheat and barley flour (B2, B4, W2, W4) demonstrate lower ductility compared to cassava-based compounds. This reduced ductility can be attributed to the presence of more rigid structures that are less capable of accommodating extensive plastic

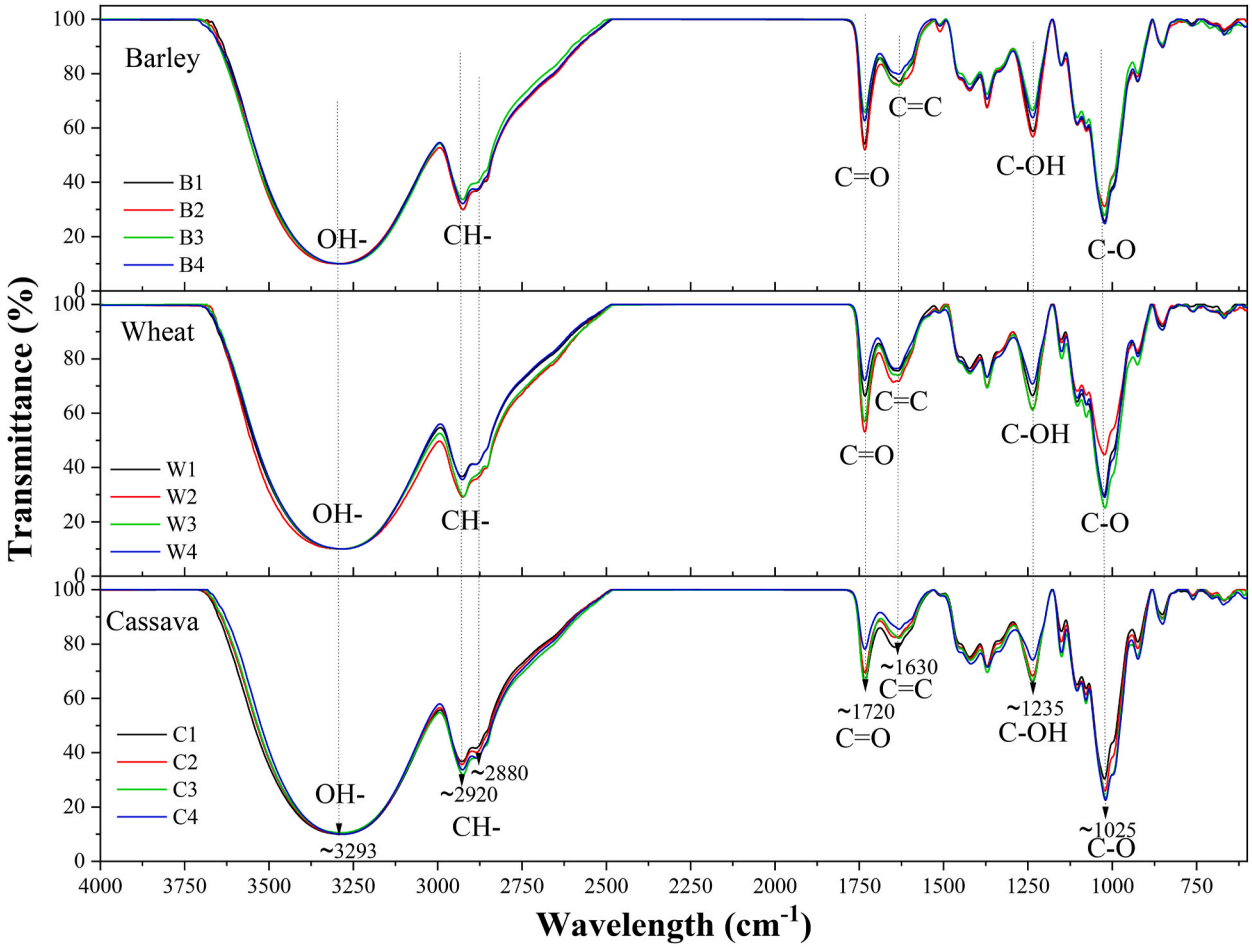

Fig. 5. Fourier transform infrared spectra of the bio-composites. **B1, W1, C1**: Flour:PVAc = 20:80 and OPKS:OPEFBF = 10:90; **B2, W2, C2:** Flour:PVAc = 20:80 and OPKS:OPEFBF = 30:70; **B3, W3, C3:** Flour:PVAc = 30:70 and OPKS:OPEFBF = 10:90; **B4, W4, C4:** Flour:PVAc = 30:70 and OPKS:OPEFBF = 30:70.

deformations, resulting in increased brittleness. This effect is primarily due to the higher likelihood of defect or discontinuity formation caused by the various components in these flours. These defects act as stress concentrators, weakening the structure and diminishing its ability to undergo plastic deformation. Consequently, the ability to absorb energy before fracture is limited [49].

Based on the statistical analysis conducted, Pearson and Spearman test coefficients ranged between −0.75 and 0.61, indicating a correlation between variables. Values of $p < 0.05$ suggested a significant interrelation between elongation at break and toughness. Results from the Royston test confirmed a normal distribution of data (p-values >0.05), allowing for parametric statistical analysis. Bonferroni tolerance limits were applied to identify and eliminate outliers in each experiment, enhancing the calculation of mean and standard deviation for mechanical properties. The aforementioned outcomes are detailed in Fig. 8.

Bio-composites with a higher modulus of elasticity (Fig. 8a) incorporated barley flour (970.5 MPa), followed by wheat (549.7 MPa) and cassava (319.7 MPa). This behavior was attributed to the higher crude fiber (5.64 %) and protein content (9.33 %) in barley flour. The structure of these molecules enables them to act as additives or bonding agents between components, facilitating permanent interfacial adhesion through van der Waals forces and covalent bonds. Additionally, certain proteins (e.g., albumins and globulins) and crude fiber can act as mechanical reinforcements within the polymer matrix, preventing flow and deformation of the thermoplastic phase by helping to distribute applied loads more uniformly throughout the bio-composite, thus improving its stiffness [33]. Fig. 8b shows higher tensile strength (1.7–2.1 MPa) in bio-composites containing 12 % OPKS in their formulation (W4, B4, C4). This phenomenon could be attributed to the smaller particle size and larger surface area (1.4 times) of the OPKS compared to OPEFB, which facilitates matrix penetration and adhesion to the reinforcement. This results in the creation of a mechanical interlocking support system and a reduction in defect formation in the bio-composite. Bio-composites incorporating cassava flour exhibit higher elongation at break (1.2 %) and toughness (≈13.3 kJ/m^3), see Fig. 8c and d. These characteristics could be attributed to the quantity and structure of amylopectin present in the starch, which provides the material with greater elasticity, ductility, and energy absorption capacity before fracture.

Fig. 8. To ascertain the impact of variables on the mechanical behavior of bio-composites, a multivariate analysis of variance

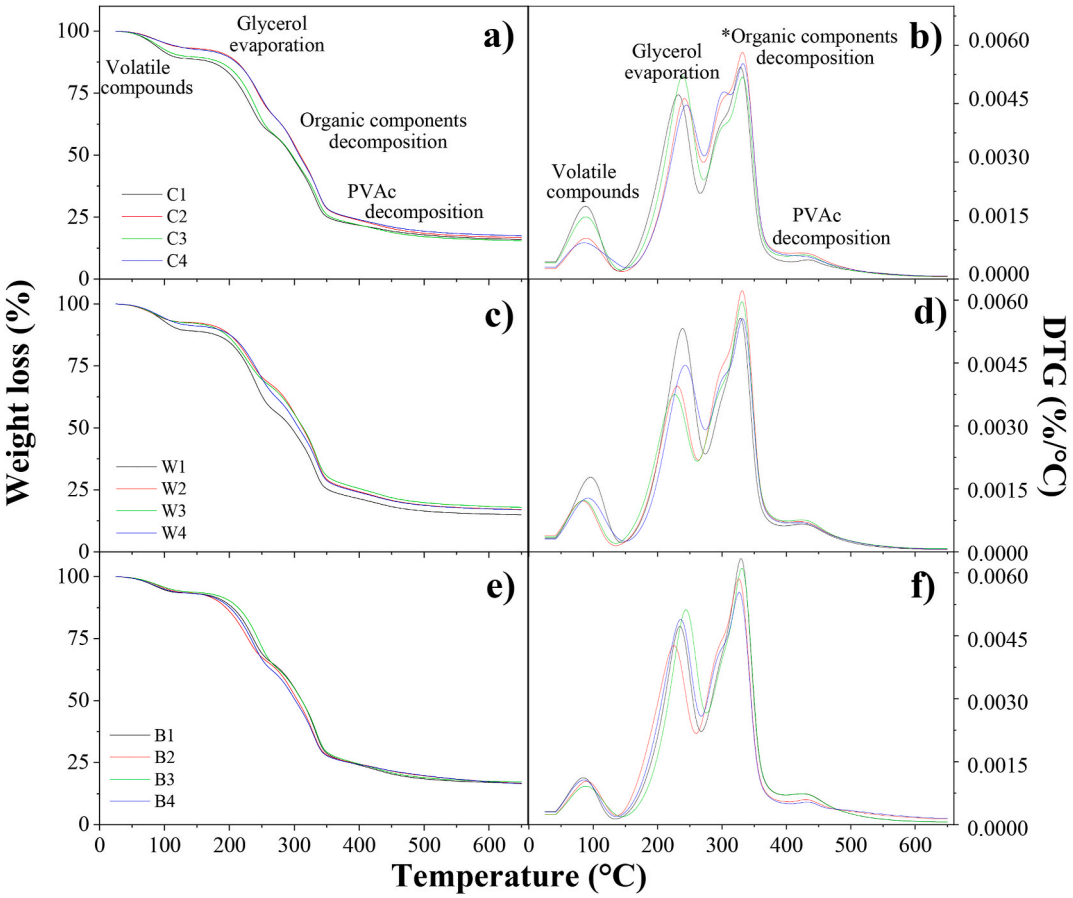

Fig. 6. Thermogravimetric analysis and derivative thermogravimetric analysis of the bio-composites a), b) Cassava = C; c), d) Wheat = W; e), f) Barley = B. **C1, W1, B1**: Flour:PVAc = 20:80 and OPKS:OPEFBF = 10:90; **C2, W2, B2:** Flour:PVAc = 20:80 and OPKS:OPEFBF = 30:70; **C3, W3, B3:** Flour:PVAc = 30:70 and OPKS:OPEFBF = 10:90; **C4, W4, B4:** Flour:PVAc = 30:70 and OPKS:OPEFBF = 30:70.

(MANOVA) was conducted. Seven effects of interest were identified, comprising three main effects (flour, matrix, reinforcement) and interactions between factors (flour-matrix, flour-reinforcement, matrix-reinforcement, and flour-matrix-reinforcement). The findings disclosed that all factors exert an influence on the mechanical behavior of bio-composites, with the flour-matrix-reinforcement interaction being the most significant, exhibiting a higher Wilks' Lambda statistic (0.78). Additionally, a significant interaction was observed between flour-reinforcement factors in each property studied. This suggests that the effect of flour on the response is conditioned by reinforcement level, indicating that the relationship between variables is not uniform, and specific conditions play an important role in the observed results. However, the effect of the matrix (flour:PVAc) was not influential, probably because the difference between the proportions studied (20:80 and 30:70) was not significant. Nevertheless, the relationship between these factors also endows the bio-composite with specific characteristics. The presence of starch within the matrix serves to reinforce the PVAc, forming a more robust network that enhances the material's strength. This is achieved by enabling a more uniform distribution of mechanical stresses, which in turn prevents stress concentration and improves flexibility [42].

After identifying the significant influences of factors, the Fisher LSD (Least Significant Difference) multiple comparison test at 95 % was performed, with homogeneous groups detailed in Table 3. This analysis confirmed that all three factors significantly influence all variables. However, the interactions between these factors are of greater consequence, as evidenced by the analysis of variance. Thus, the influence of flour/reinforcement composition and structure on mechanical properties is supported. Nonetheless, other reinforcement characteristics could also be associated with this interaction. For instance, the crystalline structure of cellulose and the three-dimensional polymeric nature of lignin serve as pivotal determinants of stiffness and strength. Consequently, OPEFB and OPKS, which possess approximately 70 % of these biopolymers between them, may confer superior mechanical properties to the composites. Additionally, hemicellulose can improve adhesion between reinforcement and polymer matrix since it could form hydrogen bonds with the matrix, which can also increase the strength of the composite material. The presence of extractives in reinforcements (palmitic and oleic acids) is also worthy of note, as their presence is conducive to adhesion/compatibility and load transfer between the matrix and the reinforcement. This is due to the fact that carboxyl groups can interact with the matrix, or esterification reactions can occur in the thermal process of composite production [3].

Moreover, the shape and distribution of reinforcements influence the mechanical behavior of the composite. The proper alignment

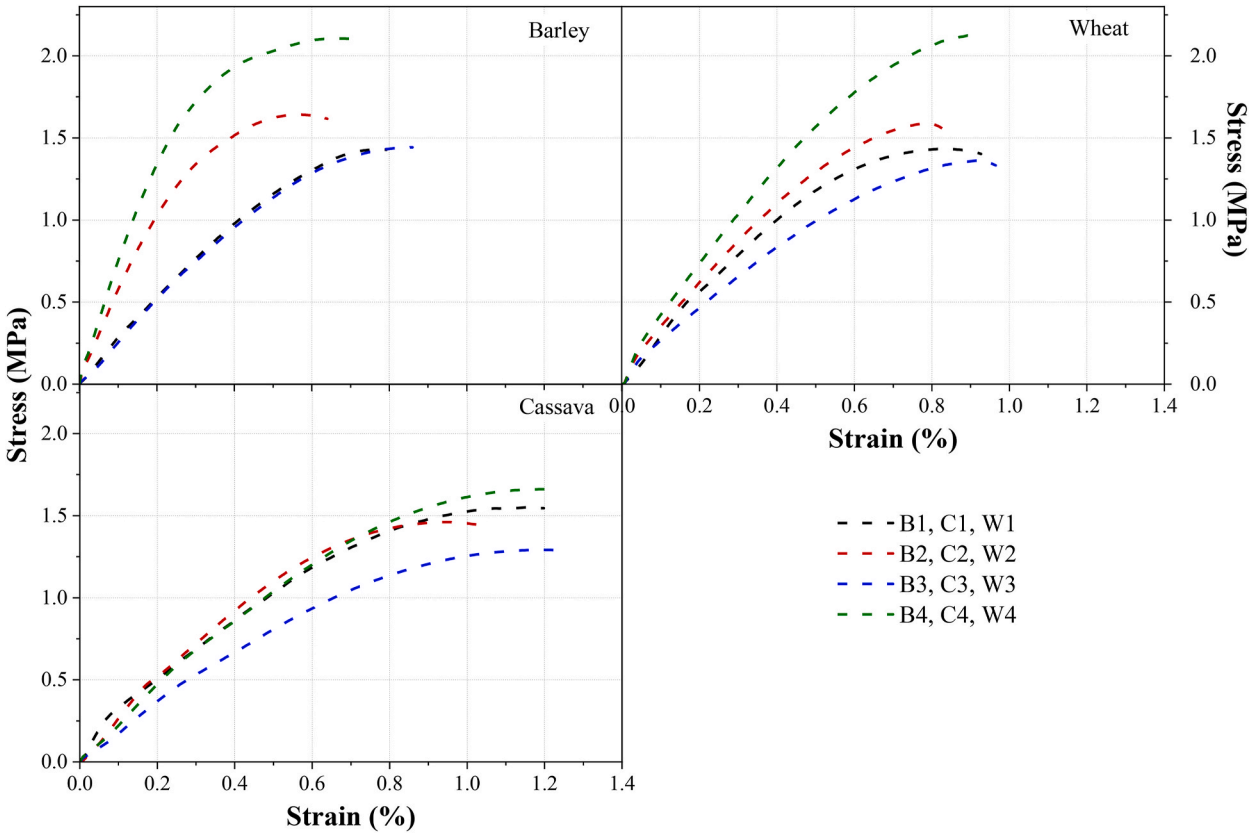

Fig. 7. Stress-strain curves of bio-composites. **B1, W1, C1**: Flour:PVAc = 20:80 and OPKS:OPEFBF = 10:90; **B2, W2, C2:** Flour:PVAc = 20:80 and OPKS:OPEFBF = 30:70; **B3, W3, C3:** Flour:PVAc = 30:70 and OPKS:OPEFBF = 10:90; **B4, W4, C4:** Flour:PVAc = 30:70 and OPKS:OPEFBF = 30:70.

and distribution of OPEFB fibers within the polymer matrix can significantly improve its stiffness and strength, maintaining consistency with the values obtained from the statistical analysis conducted on each flour group. Additionally, the longitudinal and tubular structure of the fibers contribute to greater ductility, improving flexibility, elasticity, and toughness of the composite material. However, particle size exerts an even more pronounced influence, highlighting the superior properties of the endocarp in this aspect, as mentioned earlier.

4. Conclusions

The study conducted a characterization of raw materials, including barley, wheat, and cassava flour, as well as oil palm residues (OPEFB and OPKS), to comprehend their physicochemical and mechanical properties in bio-composite development. Barley flour showed higher protein, crude fiber, and ash content, while cassava flour exhibited a higher concentration of carbohydrates and starch content. SEM analysis evidenced differences in the fracture surfaces. As regard FTIR, spectra demonstrated the presence of different functional groups associated with the matrix and the reinforcement in all bio-composites. Thermogravimetric analysis identified distinct stages of thermal degradation. Mechanical characterization indicated that bio-composites with higher barley flour content had a higher modulus of elasticity, while those with 12 % OPKS showed greater tensile strength. The bio-composites comprising cassava flour exhibited higher elongation at break and toughness. Multivariate analysis confirmed s that the mechanical behavior of the bio-composites was significantly influenced by the type of flour, the matrix, and the reinforcement used. Overall, the shape, distribution, and composition of the reinforcements significantly influenced the mechanical behavior of the bio-composites. Overall, this comprehensive characterization provides valuable insights for the development of high-performance bio-composite materials.

CRediT authorship contribution statement

Katherine Tenemaza: Writing – review & editing, Writing – original draft, Validation, Resources, Methodology, Investigation, Data curation, Conceptualization. **Cristina E. Almeida-Naranjo:** Writing – original draft, Resources, Investigation, Formal analysis. **Paola Gutiérrez:** Writing – original draft, Investigation, Formal analysis, Data curation. **Alex Darío Aguilar:** Methodology. **Vladimir Valle:** Writing – review & editing, Supervision, Resources, Project administration, Funding acquisition. **Francisco Cadena:** Writing – review & editing.

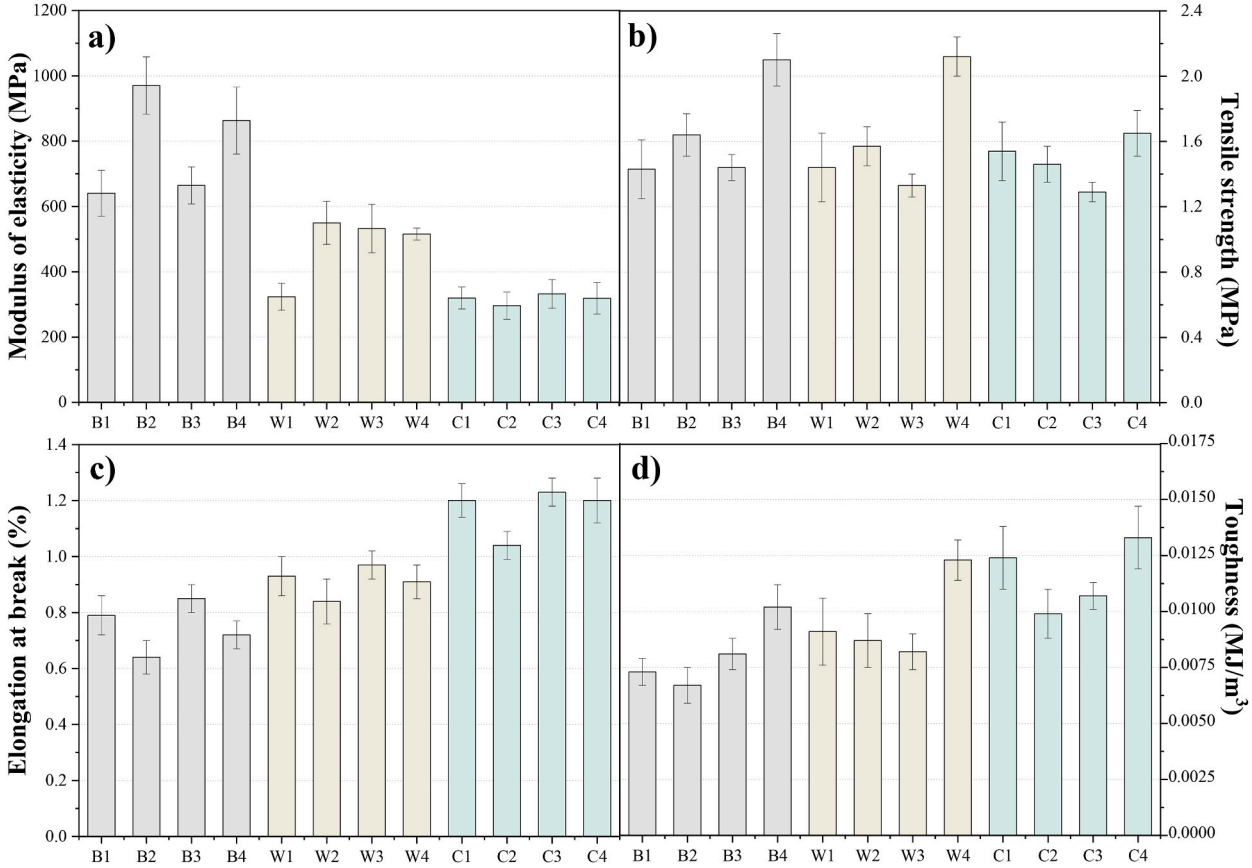

Fig. 8. Tensile mechanical behavior of bio-composites. **B1, W1, C1**: Flour:PVAc = 20:80 and OPKS:OPEFBF = 10:90; **B2, W2, C2:** Flour:PVAc = 20:80 and OPKS:OPEFBF = 30:70; **B3, W3, C3:** Flour:PVAc = 30:70 and OPKS:OPEFBF = 10:90; **B4, W4, C4:** Flour:PVAc = 30:70 and OPKS: OPEFBF = 30:70.

Table 3
Fisher's LSD multiple comparison: homogeneous groups for tensile properties.

Factor	Elastic Modulus	Tensile Strength	Elongation at Break	Toughness
Flour				
Barley	C	B	A	A
Wheat	B	B	B	B
Cassava	A	A	C	C
Matrix				
Fluor/PVAc = 20:80	A	A	A	A
Fluor/PVAc = 30:70	A	B	B	B
Reinforcement				
OPKS:OPEFB = 10:90	A	A	B	A
OPKS:OPEFB = 30:70	B	B	A	B

Research data for this article

The data obtained in this research are presented in this article.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors gratefully acknowledge the support provided by the Escuela Politécnica Nacional for the development of the project PIS-22-23: “Composites bio-basados pro-venientes de residuos lignocelulósicos empleados en la remoción de metales pesados”.

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