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# Design of freeze-dried microstructured powders from coffee husk: Linking wall material chemistry, molecular interactions, and functional performance

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ABSTRACT

Coffee husk (CH), a major agro-industrial byproduct, represents a promising source of biopolymers and polyphenol-rich compounds; however, the application of these bioactives is limited by their low stability during processing and storage. In this study, freeze-drying was employed as a structure-forming process to develop microstructured powders using CH-derived polyphenols and different wall materials— CH-derived powder pectin (PP), maltodextrin (MD), and a PP/MD blend—to elucidate how matrix chemistry governs stabilization and delivery. The results demonstrate that wall material chemistry controls intermolecular interactions during processing, which in turn determine microstructure and functional performance. The pectin-based system (FD-PP) formed an interaction-driven network through hydrogen bonding between polyphenols and carboxyl groups of low-methoxyl pectin, combined with electrostatic interactions. This structure reduced molecular mobility, resulting in enhanced thermal stability, higher polyphenol retention (i.e. antioxidant activity), and improved bioaccessibility through controlled release under simulated gastrointestinal conditions. In contrast, maltodextrin (FD-MD) acted as a weakly interactive carrier, stabilizing polyphenols primarily via physical entrapment in a glassy matrix, leading to lower retention and rapid release. The hybrid system (FD-PP/MD) exhibited reduced performance due to disruption of the pectin network and dilution of interaction sites. These findings establish that the balance between protection and release is governed by the interplay between molecular interactions and microstructure generated during freeze-drying, providing a mechanistic basis for designing functional microstructured powders from agro-industrial byproducts.

## 1. Introduction

The global coffee industry generates substantial quantities of agro-industrial residues, among which coffee husk (CH) is a major by-product obtained during the processing of coffee berries. Within a bio-circular economy framework, CH represents a promising feedstock for biorefinery applications due to its complex composition, including carbohydrates (35–85%), soluble fibers (≈31%), and proteins (5–11%) (del Castillo et al., 2019). Notably, pectin—a heteropolysaccharide with emulsifying and gelling capacity—constitutes a significant fraction of this biomass (up to ≈19%, depending on extraction conditions) (Ali and Bhowmik, 2025; Chamyuang et al., 2021, p. 34; Divyashri et al., 2023; Tran et al., 2025). This polymer contains carboxyl (C(O)OR) and hydroxyl (OH) functional groups that enable intermolecular interactions, making it a suitable candidate as a structuring matrix in dehydrated systems. In parallel, CH contains polyphenolic compounds (≈1.2%), including tannins and phenolic acids such as gallic, protocatechuic, and caffeic acids, which can act as functional solutes in food and bioproduct formulations (Castaldo et al., 2018; del Castillo et al., 2019).

However, the incorporation of these polyphenols into processable materials is limited by their high sensitivity to environmental conditions. Exposure to oxygen, light, temperature, and pH variations

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promotes degradation reactions that reduce their stability and functionality during processing and storage (Zhang et al., 2022). From a process engineering standpoint, this instability highlights the need for structuring strategies capable of restricting molecular mobility and protecting reactive compounds during transformation.

Freeze-drying (FD) is a dehydration unit operation that involves freezing, sublimation, and desorption stages, resulting in highly porous, amorphous solids (Abla and Mehanna, 2025). Beyond water removal, FD governs the formation of microstructure, as ice crystal growth during freezing and subsequent sublimation define pore architecture and matrix organization. In this context, formulation variables—particularly the nature of the matrix-forming biopolymer—act as key design parameters that determine intermolecular interactions during processing and ultimately control the resulting structure.

Biopolymers differ significantly in their interaction capacity with polyphenols. Pectin, especially in its low-methoxyl form, contains ionizable carboxyl groups and hydroxyl functionalities that enable hydrogen bonding and electrostatic interactions with phenolic compounds (Rosales and Fabi, 2023). These interactions can reduce molecular mobility during freeze-drying, promoting the formation of cohesive amorphous matrices with enhanced retention and controlled release behavior. In contrast, maltodextrin (MD), a widely used matrix former, exhibits limited interaction potential and primarily stabilizes solutes through physical entrapment within a glassy matrix (Li et al., 2020). This fundamental difference suggests that matrix chemistry governs not only solute retention but also the development of microstructure during drying (Otálora et al., 2024).

Despite increasing interest in the valorization of coffee-derived materials, there remains a lack of mechanistic understanding linking matrix composition, intermolecular interactions, and microstructure formation during freeze-drying. In particular, predictive relationships that connect molecular-scale interactions to structural organization and functional outcomes—such as thermal stability, compound retention, and release behavior—are still underdeveloped. This gap limits the rational design of microstructured powders derived from agro-industrial by-products.

The co-extraction of pectin and polyphenols from the same raw material offers a unique opportunity to develop intrinsically compatible systems, in which matrix–solute interactions are maximized due to chemical affinity. Such systems may enable more efficient structure formation during drying and improved functional performance, while contributing to integrated and sustainable processing strategies. However, the extent to which these intrinsic interactions govern microstructure development and functionality has not been systematically elucidated.

Therefore, the aim of this study was to develop freeze-dried microstructured powders using coffee husk polyphenols as functional solutes and CH-derived pectin as a structuring matrix, in comparison with maltodextrin and a combined system. This work evaluates how matrix chemistry governs intermolecular interactions, how these interactions determine microstructure formation during freeze-drying, and how the resulting structures control thermal stability, polyphenol retention, and *In vitro* bioaccessibility. By establishing this process–structure–function relationship, the study provides a mechanistic framework for the rational design of microstructured powders from agro-industrial residues within food and bioproduct processing systems.

## 2. Materials and method

### 2.1. Vegetal material

Coffee husk (CH) derived from *Coffea arabica* L. var. Castillo, generated during wet coffee processing, was obtained from a coffee-producing farm located in the central region of Santander, Colombia (6°06′07″N, 73°26′26″W). The biomass was considered a representative agro-industrial residue suitable for bioprocessing applications.

To preserve its native chemical composition and minimize enzymatic and oxidative degradation, freshly collected CH was immediately frozen at −80 °C using an ultra-low temperature freezer (Buzzer MDF-86V188E, Shanghai, China). This pre-treatment stabilizes thermolabile components, including pectic polysaccharides and polyphenols.

The frozen material was subsequently dehydrated by freeze-drying (Labconco FreeZone 4.5, Kansas City, MO, USA) under controlled conditions (−84 °C condenser temperature, 0.133 mbar) for 48 h, yielding a porous dry matrix. The dried CH was milled into a homogeneous powder to enhance mass transfer during extraction and ensure reproducibility. The powder was stored at −2 °C in airtight containers until further use.

### 2.2. Co-extraction of pectin and polyphenols from coffee husk

Pectin and polyphenols were co-extracted from freeze-dried CH powder using a modified hot acid–water extraction method (Otálora et al., 2025; Santos Silva et al. 2024). This approach enables the simultaneous recovery of a structuring biopolymer (pectin) and functional solutes (polyphenols), facilitating the development of intrinsically compatible systems.

Briefly, 4 g of CH powder were dispersed in 100 mL of acidified distilled water (pH 2, adjusted with citric acid) and heated at 80 °C for 4 h under continuous agitation. Under these conditions, acid-mediated hydrolysis promotes the solubilization of protopectin, while temperature enhances the release of bound phenolic compounds. Thus, pH and temperature act as key process variables governing extraction efficiency and chemical integrity.

The extract was centrifuged (3000 rpm, 15 min) to remove insoluble material. The supernatant was subjected to ethanol precipitation by adding ethanol (≥ 99.5% purity, Merck, Darmstadt, Germany) at a 1:2 (v/v) ratio, reducing solvent polarity and inducing polysaccharide aggregation. The recovered pectin was dried at 40 °C, ground, and its yield calculated as 3.54 ± 0.72% (w/w, dry basis).

The remaining ethanolic–aqueous phase, enriched in polyphenols, was centrifuged again (3000 rpm, 15 min) and concentrated at 40 °C under light protection to minimize degradation, yielding a pigment powder with a recovery yield of 13.73 ± 1.75%. Both fractions were stored in amber airtight containers at −2 °C.

### 2.3. Pigment powder characterization

The chemical composition and reactivity of the pigment powder were evaluated to determine its potential for intermolecular interactions with structuring matrices.

Total phenolic content (TPC) was determined using the Folin–Ciocalteu method (Sigma-Aldrich, St. Louis, MO, USA), with absorbance measured at 760 nm and results expressed as mg gallic acid equivalents per gram (mg GAE/g). This parameter reflects the availability of hydroxyl groups capable of forming hydrogen bonds.

Antioxidant activity was assessed using the oxygen radical absorbance capacity (ORAC) assay following the protocol described by Otálora et al. (2025). The assay used AAPH (2,2′-azobis(2-methylpropionamidine) dihydrochloride) as the peroxyl radical generator, with fluorescence measured spectrofluorometrically over time. Quantification was performed using a Trolox (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid, Sigma-Aldrich, St. Louis, MO, USA) standard curve, with results expressed as μmol Trolox equivalents per gram of sample (μmol TE/g).

Polyphenolic profiling was performed by UPLC-MS/MS using an ACQUITY UPLC H-Class system coupled to a Xevo TQD mass spectrometer (Waters, Milford, USA). Extracts were prepared in acetonitrile: water (50:50, v/v), filtered (0.22 μm), and injected (2 μL) into a C18 column. Separation was achieved using a gradient of 0.1% formic acid in water and acetonitrile at 0.4 mL/min. Identification and quantification were performed by comparison with reference standards (Zouari Ayadi et al., 2025; Grassino et al., 2024). This analysis provides insight into the functional group distribution governing interaction potential.

### 2.4. Preparation of freeze-dried microstructured powders

Microstructured powders were prepared following a formulation-driven approach (Otálora et al., 2024), in which matrix composition was treated as a key variable controlling intermolecular interactions and structure formation.

Powder pectin (PP) and maltodextrin (MD; DE 20, Cimpa, Bogotá, Colombia) were dissolved separately in distilled water (1.0 g/100 mL) under stirring (300 rpm, 18–20 °C) until complete hydration (2 h for PP, 30 min for MD). A combined system (PP/MD) was prepared by mixing both solutions at a 1:1 (v/v) ratio.

Pigment powder (1.0 g) was incorporated into 100 mL of each solution and homogenized (300 rpm, 5 min). Matrix composition at this stage governs intermolecular interactions: pectin enables hydrogen bonding and electrostatic interactions, whereas maltodextrin promotes physical entrapment.

Samples were frozen at −80 °C for 48 h, where ice crystal formation defines pore architecture. Freeze-drying was then performed (−50 °C, 0.1 mbar, 40 h), preserving the frozen structure and yielding porous amorphous solids. Powders were milled and stored at 4 °C.

Samples were designated as:

- FD-PP: pigment microstructured powder formulated with PP,
- FD-MD: pigment microstructured powder formulated with MD,
- FD-PP/MD: pigment microstructured powder formulated with a 1:1 (v/v) PP:MD mixture.

Fig. 1 presents a schematic overview of the main stages involved in the freeze-drying microencapsulation process of pigment rich polyphenols using PP, MD, and the PP/MD blend as wall materials.

### 2.5. Characterization of microstructured powders

A multi-scale approach was used to relate intermolecular interactions, microstructure, and functional performance.

#### 2.5.1. Structural analysis

The structural characteristics of the freeze-dried microstructured powders (FD-PP, FD-MD, and FD-PP/MD) were evaluated by Fourier Transform Infrared (FTIR) spectroscopy and zeta potential analysis.

FTIR spectra were recorded on a PerkinElmer Spectrumday IR spectrophotometer (Version

10.7.2) from 4000 to 450 $cm^{-1}$, at 2 $cm^{-1}$ resolution with 32 scans (Otálora et al., 2025). IR

peaks were analyzed to identify characteristic functional groups of the wall materials and the

encapsulated pigment, as well as potential molecular interactions formed during the freeze

drying process.

The surface charge of the microstructured powders, expressed as Zeta (ζ) potential, was determined using a ZetaSizer Nano ZS90 (Malvern Instruments, Malvern, UK). Measurements were carried out at 25 °C after dispersing the powders in distilled water under gentle stirring. The ζ-potential values provided additional information on the electrostatic behavior and colloidal stability of the microstructured systems.

#### 2.5.2. Morphological analysis

The surface morphology of the freeze-dried microstructured powders (FD-PP, FD-MD, and FD-PP/MD) was examined using scanning electron microscopy (SEM) with an EVO MA 10-Carl Zeiss instrument (Oberkochen, Germany). Samples were fixed on aluminum stubs with conductive carbon tape and sputter-coated with gold. Micrographs were obtained at 60 ×, 500 ×, and 1000 × magnifications using a 20 kV accelerating voltage (Otálora et al., 2025).

Particle size (PS) distribution and polydispersity index (PI) of the powders were measured with a NanoPlus-3 analyzer (Micromeritics, Particulate Systems, USA) following the procedure described by Monton et al. (2022). Measurements were conducted after dispersing the powders in distilled water under controlled agitation to ensure homogeneous suspension.

#### 2.5.3. Thermal analysis

Thermal behavior and stability of the FD-PP, FD-MD, and FD-PP/MD samples were evaluated by simultaneous thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).). Analyses were performed using an SDT Q600 V20.9 Build 20 system (Universal V4.7 A, TA Instruments). Approximately 5–10 mg of sample were heated from 20 to 1200 °C at a heating rate of 10 °C/min under a constant nitrogen flow. The DSC thermograms were used to identify thermal transitions such as glass transition or melting-like events, while TGA curves revealed mass-loss steps associated with moisture evaporation, polymer degradation, and pigment thermal decomposition.

#### 2.5.4. Colorimetric analysis

The colorimetric properties of the freeze-dried microstructured powders (FD-PP, FD-MD, and FD-PP/MD) were evaluated using a Minolta colorimeter (CR-20; Konica Minolta Sensing Inc., Tokyo, Japan) operating in the CIEL*ab* color space. The parameters measured were L* (lightness, ranging from black at L* = 0 to white at L* = 100), $a^*$ (negative values indicating green and positive values indicating red), and $b^*$ (negative values indicating blue and positive values indicating yellow).

From these primary coordinates, chroma ($C^*_{ab}$), representing color saturation, and hue angle (h°), representing the dominant color tone, were calculated using Eqs. 1 and 2, respectively:

$$C^*_{ab} = \left[(a^*)^2 + (b^*)^2\right]^{1/2} \quad (1)$$

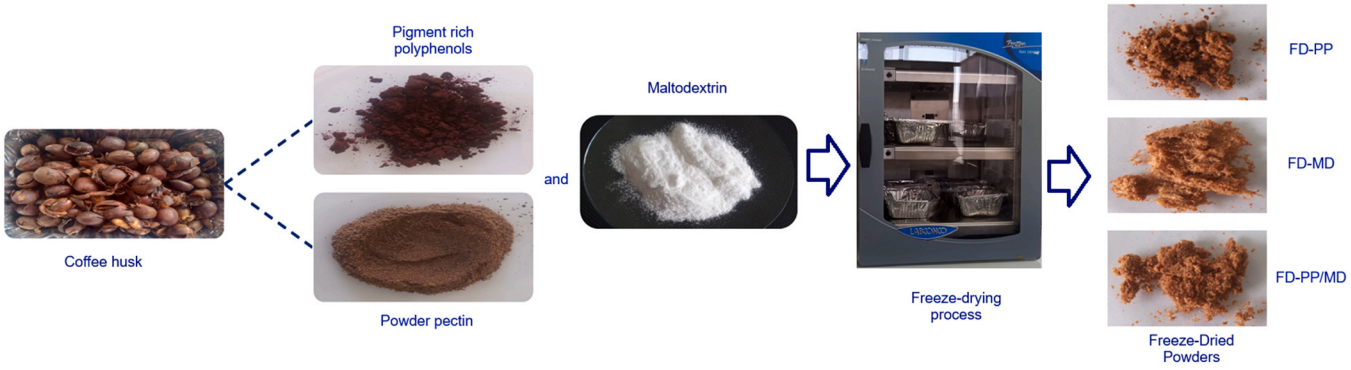


**Fig. 1.** Schematic representation of the microencapsulation process of pigment rich polyphenols using powder pectin (PP), maltodextrin (MD), and a powder pectin–maltodextrin (PP/MD) mixture as wall materials.

$$h^{\circ} = \arctan(b^*/a^*) \quad (2)$$

#### 2.5.5. Bioactive characterization

The bioactive properties of the freeze-dried microstructured powders (FD-PP, FD-MD, and FD-PP/MD) were evaluated based on the release of polyphenolic compounds into aqueous medium. For this purpose, each powder was dispersed in distilled water under magnetic stirring to promote pigment release. The resulting aqueous extracts were analyzed for total phenolic content (TPC) and antioxidant activity the AAPH-based ORAC assay, following the methodology described in 2.3.

Additionally, the identify and quantify of the polyphenolic compounds released of the freeze-dried microstructured powders (FD-PP, FD-MD, and FD-PP/MD) was characterized by UPLC-MS/MS, following the methodology described in 2.3.

#### 2.5.6. In vitro digestion of microstructured powders

The *in vitro* digestion of the FD-PP, FD-MD, and FD-PP/MD microstructured powders was evaluated by simulating the salivary (oral), gastric, and intestinal phases of the human gastrointestinal tract following the standardized static INFOGEST protocol (Brodkorb et al., 2019). During each digestion stage, the corresponding simulated fluids were prepared at their prescribed ionic strengths, pH values, and enzyme activities, with pH adjustments made to reproduce the physiological conditions of each gastrointestinal compartment.

Polyphenols compunds is known as a powerful antioxidant agent. Thus, to provide more evidence for this claim, was determine polyphenols microencapsulated capacity to scavenge AAPH radicals (Hussain et al., 2024), therefore, antioxidant activity of the microstructured powders was determined both before digestion and after the intestinal phase, using the analytical procedures described in 2.3. The bioaccessibility of antioxidant compounds (%) was calculated using the following Equation (Andrade et al., 2022):

$$\text{Bioaccessibility of antioxidant compounds}(\%) = \frac{\text{Antioxidant activity after } \textit{in vitro} \text{ intestinal digestion}}{\text{Antioxidant activity before } \textit{in vitro} \text{ intestinal digestion}} \times 100$$

### 2.6. Statistical analysis

All experiments, except for FT-IR, SEM, and DSC/TGA analyses, were conducted in triplicate (n = 3). The results are expressed as the mean ± standard deviation. Statistical analyses were performed using a one-way analysis of variance (ANOVA), followed by Fisher's least significant difference (LSD) post-hoc test to determine significant differences among sample means. A confidence level of 95% ($p < 0.05$) was considered to indicate statistical significance.

## 3. Results and discussion

### 3.1. Pigment characterization

The polyphenol-rich pigment extracted from coffee husk exhibited a high total phenolic content (TPC) of 78.36 ± 0.12 mg GAE/g, indicating a significant concentration of hydroxyl-bearing compounds capable of participating in intermolecular interactions with structuring biopolymers. From a process perspective, this high density of reactive functional groups is expected to enhance hydrogen bonding with pectin matrices, thereby influencing molecular mobility during freeze-drying and contributing to the formation of more cohesive amorphous structures.

UPLC-MS/MS analysis revealed a complex polyphenolic profile dominated by alkaloids and phenolic compounds, including caffeine (288.474 mg/100 g), theophylline (7.850 mg/100 g), ferulic acid (2.962 mg/100 g), and quercetin (4.799 mg/100 g). The presence of hydroxylated phenolic acids (e.g., ferulic acid) and flavonoids (e.g., quercetin) is particularly relevant, as these compounds contain multiple hydroxyl groups capable of forming hydrogen bonds with the carboxyl groups of low-methoxyl pectin. Such interactions are expected to promote the formation of interaction-driven matrices, in contrast to systems based on maltodextrin, where molecular association is limited.

In addition, the relatively high concentration of caffeine, a less hydroxylated molecule, suggests the coexistence of compounds with different interaction potentials within the system. This compositional heterogeneity may lead to differential incorporation within the matrix, where strongly interacting polyphenols contribute to structural stabilization, while weakly interacting compounds remain more mobile and are more readily released during rehydration or digestion.

Consistent with its compositional profile, the pigment exhibited a high antioxidant capacity (ORAC value of 552.8 ± 7.95 μmol TE/g), reflecting the ability of the system to scavenge peroxyl radicals. This functional property provides a baseline for evaluating the effectiveness of the structuring matrices in preserving polyphenol activity during freeze-drying and subsequent processing. In particular, systems with stronger matrix–polyphenol interactions are expected to better retain this antioxidant capacity by limiting oxidative degradation and molecular mobility.

The identified polyphenolic composition is consistent with previous reports on coffee husk extracts, where caffeine, theophylline, quercetin, and hydroxycinnamic acids have been described as major constituents (Pua et al., 2021). However, beyond compositional agreement, the present results highlight the relevance of functional group distribution and molecular structure in determining interaction potential with biopolymer matrices, which is a key factor governing microstructure formation and functional performance in freeze-dried systems.

### 3.2. Microstructured powders characterization

#### 3.2.1. Structural analysis

The FTIR spectra of the pigment (core material), the structuring matrices—pectin (PP) and maltodextrin (MD)—and the resulting freeze-dried microstructured powders (FD-PP, FD-MD, and FD-PP/MD) are presented in Fig. 2. The spectra of the raw materials exhibited characteristic absorption bands consistent with their chemical structures, including hydroxyl (O–H), aliphatic (C–H), carbonyl (C═O), and aromatic (C═C) functionalities associated with polyphenols and polysaccharides (Geng et al., 2024; Resende et al., 2023; Tripathi et al., 2025; Otálora et al., 2026).

Following freeze-drying, systematic shifts in peak positions and variations in band intensities were observed in all microstructured systems, indicating the establishment of non-covalent interactions between polyphenols and the matrix-forming biopolymers. However, the extent and nature of these interactions were strongly dependent on matrix composition.

In the FD-PP system, the O–H stretching band shifted to lower wavenumbers (3278 $cm^{-1}$) compared to both the pigment (3315 $cm^{-1}$) and pectin (3285 $cm^{-1}$), reflecting the formation of strong hydrogen bonding between hydroxyl groups of polyphenols and the hydroxyl and carboxyl groups of pectin. This shift indicates increased intermolecular association and reduced vibrational freedom, consistent with the formation of a dense hydrogen-bonding network. Additionally, modifications in the region near 1596 $cm^{-1}$ , relative to the carboxylate band of pectin (1610 $cm^{-1}$), suggest the involvement of electrostatic interactions between dissociated carboxyl groups ($COO^-$) and polar functionalities of the polyphenols. These combined interactions support the formation of a cohesive and highly interconnected matrix, in which polyphenols are strongly associated with the pectin network.

In contrast, the FD-MD system exhibited only minor shifts in the O–H stretching region (3294 $cm^{-1}$), closely resembling the spectra of the individual components. This indicates limited specific interactions, consistent with the non-ionic nature of maltodextrin, which lacks functional groups capable of strong electrostatic association (Kong et al.,

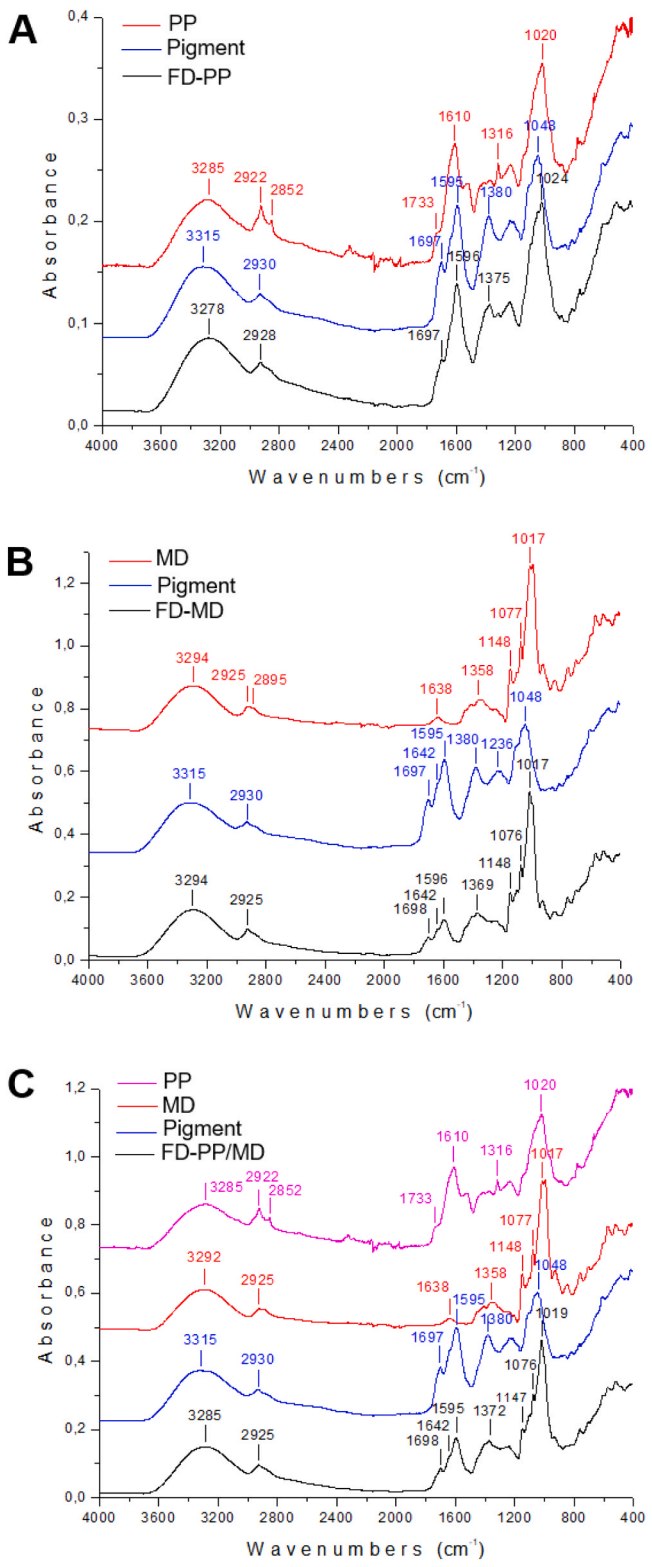


**Fig. 2.** Comparison of the FTIR spectra of the microstructured powders FD-PP (A), FD-MD (B), and FD-PP/MD (C) with the corresponding constitutive wall materials (powder pectin (PP) and maltodextrin (MD)) and core material (pigment rich polyphenols). FTIR spectra of FD-PP (A), FD-MD (B), and FD-PP/MD (C) microstructured powders.

2026). The observed spectral changes are therefore attributed primarily to weak hydrogen bonding and physical entrapment within a glassy matrix, rather than the formation of an interaction-driven network. As a result, polyphenols in MD-based systems remain relatively mobile within the amorphous structure.

The FD-PP/MD system displayed intermediate behavior, with attenuated shifts in the O–H and carboxylate regions. This suggests that the presence of MD reduces the density of available interaction sites, effectively diluting the pectin network and limiting both hydrogen bonding and electrostatic interactions. The persistence of characteristic MD bands (e.g., C–O stretching in the 1147–1017 $cm^{-1}$ region) confirms its structural contribution within the hybrid matrix (Hay et al., 2025; Mansour et al., 2020).

The disappearance of the band at 1048 $cm^{-1}$ , previously associated with chlorogenic acids, further indicates that these compounds are no longer present in a free state but are embedded within the polymeric matrix, supporting the occurrence of matrix–polyphenol interactions.

From a structural perspective, these results establish a clear hierarchy: pectin promotes the formation of an interaction-driven, cohesive microstructure; maltodextrin leads to a weakly associated amorphous matrix dominated by physical entrapment; and the combined system results in a partially disrupted network due to reduced interaction density. This hierarchy is expected to directly influence molecular mobility within the matrix and, consequently, functional properties such as thermal stability, retention, and release behavior.

Zeta potential measurements further support these structural differences. The ζ-potential values of FD-MD (−19.85 ± 0.88 mV), FD-PP (−17.94 ± 0.26 mV), and FD-PP/MD (−17.71 ± 0.15 mV) indicate that MD-based systems exhibit a higher surface charge density, which enhances electrostatic repulsion and improves dispersion stability in aqueous media. In contrast, the lower absolute values observed for pectin-containing systems suggest reduced electrostatic stabilization and a greater tendency toward aggregation (Rigolon et al., 2024).

Importantly, these results demonstrate that electrostatic stability and intermolecular interaction strength represent distinct but complementary factors. While maltodextrin enhances colloidal dispersion through surface charge effects, pectin promotes stronger polyphenol retention through hydrogen bonding and electrostatic interactions. The balance between these mechanisms governs the structural organization of the microstructured powders and ultimately determines their functional performance.

### 3.2.2. *Morphological analysis*

SEM micrographs of the freeze-dried microstructured powders at 60 × , 500 × , and 1000 × magnifications are presented in Fig. 3. The observed morphological features reflect the influence of matrix composition and intermolecular interactions on structure formation during freezing and sublimation.

At low magnification (60 ×), all samples exhibited irregular, glass-like fragmented structures, characteristic of freeze-dried materials subjected to post-drying grinding. The absence of macroscopic collapse suggests that the structural framework generated during freezing was preserved throughout sublimation. However, clear differences in particle organization were observed as a function of matrix composition.

FD-PP displayed pronounced agglomeration, forming large, interconnected clusters. This behavior is consistent with the strong intermolecular interactions identified by FTIR, where hydrogen bonding and electrostatic interactions between polyphenols and the partially ionized carboxyl groups of pectin promote interparticle adhesion. As a result, the system forms a continuous interaction-driven network, which reduces dispersibility upon rehydration due to increased cohesion between particles.

In contrast, FD-MD exhibited a lower degree of agglomeration, with more discrete and separated particles. This reflects the limited interaction capacity of maltodextrin, whose non-ionic structure restricts the formation of strong intermolecular associations. Consequently, particles

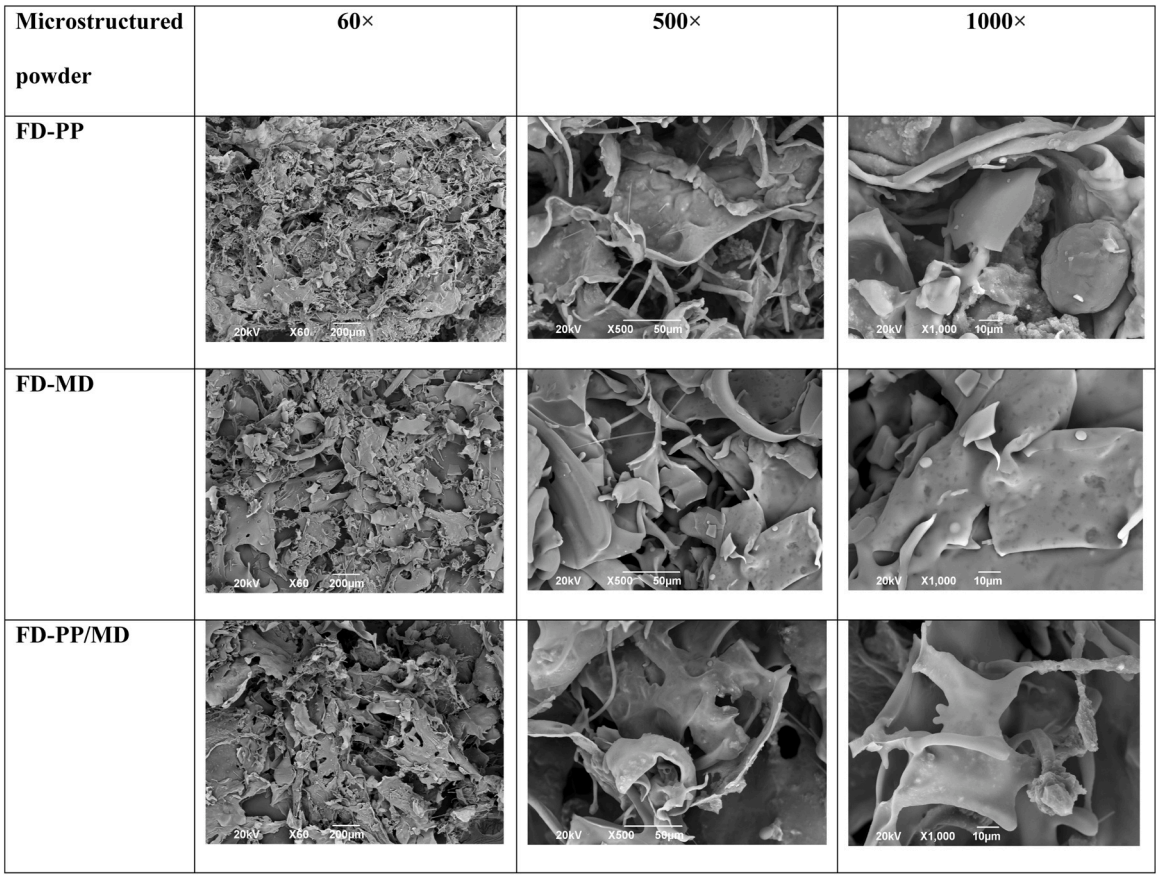


**Fig. 3.** SEM micrographs of FD-PP, FD-MD, and FD-PP/MD microstructured powders at magnifications of 60 × , 500 × , and 1000 × , with a scale bars of 200 µm, 50 µm and 10 µm, respectively.

remain more independent, favoring improved dispersion and solubility in aqueous systems (Alves et al., 2023).

At higher magnification (1000 ×), all samples showed laminar, flake-like morphologies with interconnected pore networks formed during ice sublimation, typical of freeze-dried matrices (Groult and Budtova, 2018). Nevertheless, distinct differences in pore structure and surface organization were observed.

FD-PP exhibited a compact and heterogeneous porous structure, characterized by thicker lamellae and smaller, less uniform pores. This morphology is indicative of a highly interconnected matrix in which strong polymer–polyphenol interactions restrict molecular rearrangement during freezing, limiting ice crystal growth and reducing pore coalescence (Liang et al., 2021). The resulting structure is expected to decrease effective diffusivity within the matrix, contributing to enhanced retention and slower release of polyphenolic compounds.

Conversely, FD-MD presented smoother surfaces and a more homogeneous pore distribution. The absence of strong intermolecular interactions allows greater molecular mobility during freezing, facilitating more uniform ice crystal formation and resulting in a more regular porous network (Aksoylu Ozbek and P. Günç Ergonül, 2020). This structure is associated with increased diffusivity and faster release behavior due to less restricted transport pathways.

The FD-PP/MD system exhibited intermediate characteristics, with partial preservation of the pectin-derived network but increased structural discontinuities. This indicates that maltodextrin disrupts the continuity of the interaction-driven pectin matrix, reducing interaction density and leading to a less cohesive microstructure. Consequently, this hybrid system represents a compromise between structural rigidity and diffusional accessibility.

Particle size (PS) and polydispersity index (PI) values (Table 1) further support these observations. FD-MD exhibited lower PS and PI values, indicating a narrower and more homogeneous particle size distribution, consistent with reduced aggregation. In contrast, FD-PP showed larger particle sizes and broader distributions, reflecting aggregation driven by strong intermolecular interactions. The FD-PP/MD system displayed intermediate values, confirming that the incorporation of maltodextrin partially mitigates aggregation while maintaining

**Table 1**
Structural, morphological, bioactive, and colorimetric parameters of freeze-dried microstructured powders containing polyphenols rich pigment.

| Parameters* | Microstructured powder sample | | |
|---|---|---|---|
| | FD-PP | FD-MD | FD-PP/MD |
| Zeta potential (mW) | $-17.94 \pm 0.26^{B}$ | $-19.85 \pm 0.88^{A}$ | $-17.71 \pm 0.15^{B}$ |
| PS[a] (µm) | $1.69 \pm 0.08^{A}$ | $0.91 \pm 0.01^{B}$ | $1.15 \pm 0.02^{B}$ |
| PI[b] | $0.56 \pm 0.03^{B}$ | $0.46 \pm 0.00^{C}$ | $0.69 \pm 0.00^{A}$ |
| TPC[c] | $73.74 \pm 3.45^{A}$ | $65.17 \pm 4.36^{B}$ | $72.80 \pm 1.93^{A}$ |
| AAPH[d] | $1372.71 \pm 111.43^{A}$ | $700.82 \pm 11.51^{C}$ | $935.77 \pm 65.33^{B}$ |
| L | $38.49 \pm 0.64^{A}$ | $40.86 \pm 0.51^{A}$ | $26.97 \pm 1.23^{B}$ |
| $a^*$ | $11.99 \pm 0.90^{A}$ | $11.00 \pm 0.16^{A}$ | $12.85 \pm 0.13^{A}$ |
| $b^*$ | $14.75 \pm 1.80^{A}$ | $15.06 \pm 0.24^{A}$ | $15.28 \pm 0.40^{A}$ |
| $C^*_{ab}$ | $19.02 \pm 1.96^{A}$ | $18.65 \pm 0.27^{A}$ | $19.97 \pm 0.35^{A}$ |
| $h_{ab}$ | $50.82 \pm 1.27^{A}$ | $53.85 \pm 0.32^{A}$ | $49.92 \pm 0.66^{A}$ |

* Different superscript letters within the same row indicate statistically significant differences between samples ($p < 0.05$).
[a] PS: Particle Size.
[b] PI: Polydispersity Index.
[c] TPC: Total polyphenol content; expressed as mg GAE/g of dry sample.
[d] AAPH: Antioxidant activity, expressed as µmol TE/g of sample.

some degree of interaction-driven structuring.

Overall, these results demonstrate that matrix composition governs microstructure formation during freeze-drying through its effect on intermolecular interactions. Pectin promotes the formation of dense, cohesive networks with restricted transport pathways, whereas maltodextrin favors more homogeneous, weakly associated structures with higher diffusivity. The hybrid system exhibits intermediate behavior, reflecting a balance between interaction strength and structural continuity. These differences provide a structural basis for the variations in stability, retention, and release behavior observed in subsequent analyses.

### 3.2.3. Thermal analysis

The thermal behavior of the freeze-dried microstructured powders (FD-PP, FD-MD, and FD-PP/MD) was evaluated by combined DSC/TGA analysis (Fig. 4a–c), enabling the assessment of mass loss profiles and thermal transitions associated with matrix organization and molecular mobility. These results provide insight into how matrix composition governs stabilization mechanisms through its effect on structure formation during freeze-drying.

All systems exhibited two main thermal events. The first transition, occurring between approximately 25 and 200 °C, is attributed to the removal of physically adsorbed and weakly bound water. FD-PP showed a lower mass loss (22.4%) compared to FD-MD (28.0%) and FD-PP/MD (26.3%), along with a broader temperature range. This behavior suggests a more structured water-binding environment in the pectin-based system, where hydrogen bonding between water molecules, polyphenols, and the pectin network leads to stronger water retention and reduced volatility. In contrast, the higher mass loss observed for FD-MD indicates the presence of more loosely bound water, consistent with a less interactive amorphous matrix.

The second thermal event, observed above 200 °C, corresponds to the degradation of the polysaccharide matrices and associated polyphenolic compounds. Importantly, differences in degradation profiles should not be interpreted solely in terms of onset temperature or total mass loss, but rather in relation to the underlying structural organization and stabilization mechanisms.

In the FD-PP system, the degradation behavior is consistent with an interaction-driven network, where hydrogen bonding and electrostatic interactions between polyphenols and partially ionized pectin chains restrict molecular mobility. This reduced mobility delays the volatilization and degradation of polyphenolic compounds, resulting in a more controlled decomposition process.

In contrast, FD-MD exhibits a relatively extended degradation range, which reflects the formation of a glassy amorphous matrix rather than strong intermolecular interactions. In this system, maltodextrin stabilizes polyphenols primarily through physical entrapment within a vitrified structure. The glassy state limits molecular diffusion and reduces oxygen accessibility, thereby delaying thermal degradation. Thus, the apparent thermal resistance of FD-MD arises from physical stabilization rather than interaction-driven mechanisms (Rigolon et al., 2024).

The FD-PP/MD system displayed an earlier onset of degradation (≈164 °C) and the highest overall mass loss (66.3%), indicating a less cohesive and less stable microstructure (Wang et al., 2025; Bassetto Carra et al. 2022). This behavior suggests that the incorporation of maltodextrin disrupts the pectin–polyphenol interaction network, reducing interaction density and facilitating earlier structural breakdown. Consequently, the hybrid system exhibits a compromise between interaction-driven and physically driven stabilization mechanisms, without fully benefiting from either.

Differential scanning calorimetry further supports these interpretations through the determination of glass transition temperatures (Tg). The Tg values of FD-PP (44.06 °C), FD-MD (35.71 °C), and FD-PP/MD (34.59 °C) reflect differences in molecular mobility within the matrices (Bashir et al., 2025). The higher Tg observed for FD-PP indicates a more rigid structure, where strong intermolecular interactions

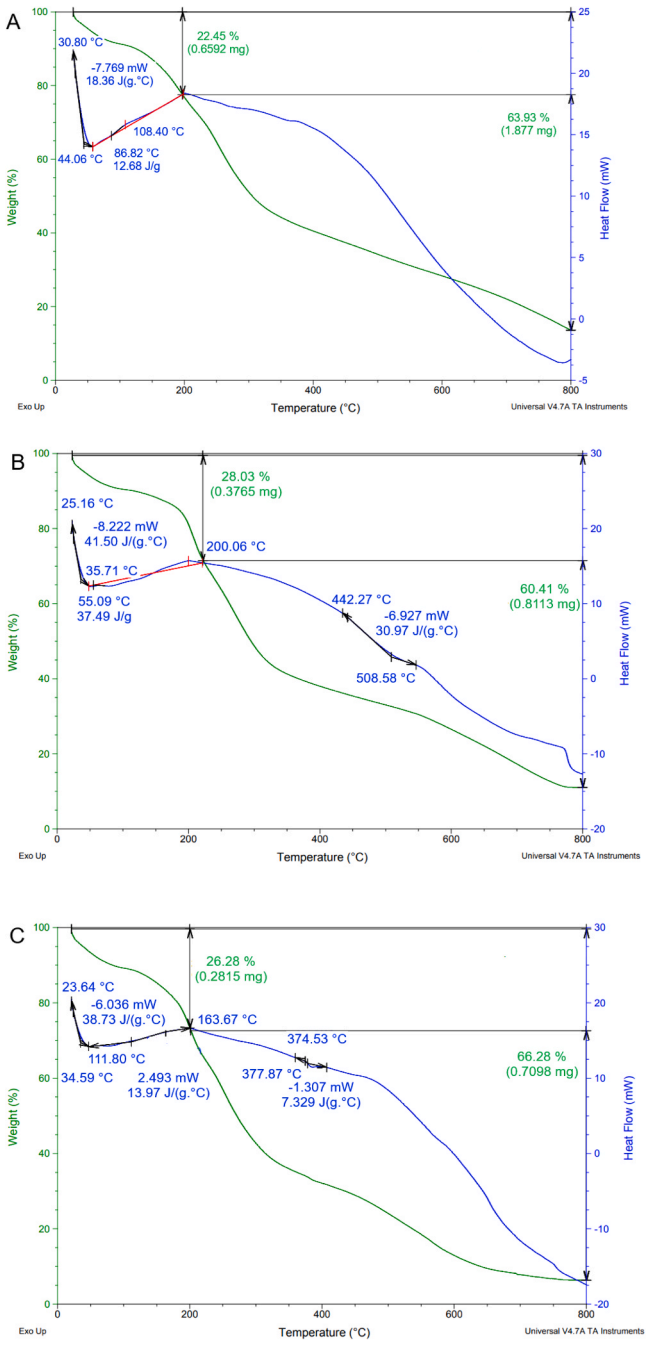


**Fig. 4.** DSC/TGA thermograms of FD-PP (A), FD-MD (B), and FD-PP/MD (C) microstructured powders. DSC red curves and TGA blue curves.

restrict polymer chain mobility. In contrast, the lower Tg values of MD-containing systems are indicative of increased molecular mobility and a less structured matrix.

From a functional perspective, Tg is a critical parameter governing storage stability. Systems with higher Tg remain in the glassy state under typical storage conditions, limiting molecular mobility and reducing degradation reactions. Therefore, the FD-PP system is expected to exhibit enhanced stability, whereas the lower Tg values of FD-MD and FD-PP/MD increase the likelihood of transitioning to a rubbery state, promoting moisture uptake and polyphenol degradation.

Overall, the thermal analysis demonstrates that matrix composition determines the dominant stabilization mechanism: pectin promotes interaction-driven stabilization through hydrogen bonding and electrostatic interactions, while maltodextrin provides physical stabilization

via glass formation. The combined system results in a partial loss of both mechanisms due to reduced interaction density and structural discontinuity. These findings are consistent with the interaction patterns identified by FTIR and the microstructural organization observed by SEM, confirming the central role of matrix chemistry in governing the structure–function relationship of the microstructured powders.

### 3.2.4. Colorimetric analysis

Table 2 presents the colorimetric parameters (L*, $a^*$, $b^*$, $C^*_{ab}$, and h°) of the freeze-dried microstructured powders (FD-PP, FD-MD, and FD-PP/MD). These parameters provide indirect insight into the physical state and stability of polyphenolic compounds within the matrix, as color is strongly influenced by pigment dispersion, oxidation, and molecular interactions.

The FD-MD system exhibited the highest lightness (L*) values, indicating a brighter and more visually uniform powder. This behavior is associated with the formation of a homogeneous amorphous matrix in which polyphenols are physically dispersed within maltodextrin. The absence of strong intermolecular interactions limits pigment clustering, enhancing light scattering and resulting in a lighter appearance.

In contrast, FD-PP and FD-PP/MD showed lower L* values, corresponding to darker powders. This reduction in lightness can be attributed to the formation of interaction-driven networks in pectin-containing systems, where hydrogen bonding and electrostatic interactions promote closer association between polyphenols and the polymer matrix. Such interactions may lead to localized pigment aggregation or reduced dispersion uniformity, decreasing reflectance and producing a darker appearance (Yang et al., 2022).

The higher $a^*$ and $b^*$ values observed in FD-PP and FD-PP/MD indicate increased red and yellow color intensities compared to FD-MD. This behavior suggests a greater retention of chromophoric polyphenolic structures within the pectin-based matrices. Stronger matrix–polyphenol interactions can limit oxidative degradation and structural transformation of these compounds, preserving their optical properties. In contrast, the lower chromatic intensity observed in FD-MD may reflect partial pigment dilution and/or increased susceptibility to structural changes due to weaker matrix interactions.

Chroma ($C^*_{ab}$) values further support this interpretation, with higher saturation observed in pectin-containing systems, indicating more intense coloration. The hue angle (h°), ranging from 49 to 54°, confirms that all powders fall within a yellow–reddish tonal region, consistent with the polyphenolic composition of coffee husk extracts.

From a structure–function perspective, these results indicate that matrix composition influences not only microstructure and thermal behavior but also the optical properties of the powders through its effect on pigment stabilization and dispersion. Pectin-based systems, characterized by stronger intermolecular interactions, tend to preserve chromatic intensity at the expense of brightness, whereas maltodextrin-based systems favor optical uniformity but may provide less protection of chromophoric structures. The hybrid system exhibits intermediate behavior, reflecting the balance between these mechanisms.

### 3.2.5. Bioactive characterization

The total phenolic content (TPC) and antioxidant capacity of the microstructured powders (Table 1) showed significant differences among formulations, demonstrating that matrix composition governs both polyphenol retention during processing and their functional expression.

FD-PP exhibited the highest TPC (73.74 ± 3.45 mg GAE/g), followed by FD-PP/MD and FD-MD. This trend reflects the formation of an interaction-driven matrix in the pectin-based system, where hydrogen bonding between hydroxyl groups of polyphenols and carboxyl groups of low-methoxyl pectin, together with electrostatic interactions involving partially ionized carboxylate groups, reduces molecular mobility and limits diffusion during freeze-drying. As a result, polyphenols remain more effectively retained within the matrix, minimizing exposure to oxidative and thermal degradation (Hu et al., 2025).

In contrast, the lower TPC observed in FD-MD is consistent with a weakly interactive amorphous matrix, where maltodextrin acts primarily as a physical carrier. The absence of strong binding interactions increases polyphenol mobility, facilitating diffusion and degradation during processing, which reduces overall retention (Abdel-Aty et al., 2023; Alam et al., 2025).

The FD-PP/MD system exhibited intermediate TPC values, reflecting a reduction in effective interaction sites due to dilution of the pectin network. This leads to a partially disrupted structure with reduced capacity to immobilize polyphenols, consistent with the interaction and structural trends observed in FTIR and SEM analyses.

UPLC-MS/MS profiling (Table 2) further supports these findings. All systems showed reduced concentrations of individual phenolics relative to the initial pigment, indicating processing-induced transformations such as oxidation and hydrolysis (Silva et al., 2024). However, selective retention patterns were observed. FD-PP and FD-PP/MD exhibited relatively higher levels of compounds such as quercetin and theophylline, suggesting preferential stabilization of molecules capable of stronger hydrogen bonding or electrostatic interactions with pectin (Aktaş et al., 2024).

The appearance of caffeic acid in all microstructured systems, despite its absence in the initial extract, indicates the hydrolysis of chlorogenic acid during processing. This transformation highlights that polyphenol composition is dynamic and that TPC reflects not only retention but also structural modifications of the compounds (Aung Moon et al., 2025).

Antioxidant activity followed a different trend from TPC: FD-PP showed the highest ORAC value (1372.71 ± 111.43 μmol TE/g), followed by FD-MD and FD-PP/MD. This divergence demonstrates that antioxidant performance is not solely governed by total phenolic concentration but also by the accessibility and structural state of the compounds.

In FD-PP, strong polyphenol–matrix interactions not only enhance retention but also preserve the structural integrity of antioxidant-active moieties, contributing to high functional activity. In FD-MD, although retention is lower, the weaker interactions allow greater accessibility of polyphenols during the assay, enabling effective radical scavenging despite reduced total content.

In contrast, FD-PP/MD exhibited the lowest antioxidant capacity despite intermediate TPC. This behavior reflects a structurally heterogeneous matrix in which reduced interaction strength compromises protection, while irregular microstructure limits uniform accessibility during the assay. Consequently, neither retention nor accessibility is optimized, leading to reduced functional performance.

Overall, these results demonstrate that bioactive performance is governed by the interplay between interaction-driven retention and matrix-controlled accessibility. Pectin-based systems favor stabilization through strong molecular interactions, maltodextrin promotes accessibility through a weakly interactive matrix, and the hybrid system represents a suboptimal balance between these mechanisms.

**Table 2**
Identification and quantification of phenolic compounds in freeze-dried microstructured powders by UPLC–MS/MS analysis.

| Microstructured powder sample | Caffeine (mg/100 g) | Quercetin (mg/100 g) | Caffeic acid (mg/100 g) | Theophylline (mg/100 g) | Ferulic acid (mg/100 g) |
|---|---|---|---|---|---|
| FD-PP | 210.824 | 6.116 | 4.366 | 4.858 | — |
| FD-MD | 193.906 | 5.918 | 6.618 | 4.808 | 4.590 |
| FD-PP/MD | 173.902 | 4.960 | 7.130 | 5.250 | 3.907 |

### 3.2.6. In vitro digestion and bioaccessibility

The bioaccessibility of antioxidant compounds, expressed as the percentage of ORAC activity retained after simulated gastrointestinal digestion (Table 3), revealed clear differences among formulations, confirming that matrix composition governs release behavior under physiological conditions.

FD-PP exhibited the highest bioaccessibility, which can be attributed to the formation of a pH-responsive, interaction-driven network. As demonstrated by FTIR and SEM analyses, polyphenols are strongly associated with the pectin matrix through hydrogen bonding and electrostatic interactions. During digestion, the increase in pH from gastric to intestinal conditions promotes deprotonation of pectin carboxyl groups, increasing electrostatic repulsion within the network. This induces controlled swelling and gradual matrix relaxation, enabling a sustained release of polyphenols.

This controlled release mechanism is critical: it limits premature exposure of polyphenols to the acidic gastric environment, reducing degradation, while promoting release in the intestinal phase, where absorption is more favorable (Khotimchenko, 2020; Rosales, Fabi, 2023; Hu et al., 2025). Thus, FD-PP achieves an optimal balance between protection and availability.

In contrast, FD-MD exhibited lower bioaccessibility, despite its more homogeneous structure. The absence of strong matrix–polyphenol interactions results in rapid release during early digestion stages. This immediate release exposes polyphenols to acidic and oxidative conditions in the gastric phase, promoting degradation before reaching the intestinal stage. Therefore, although accessibility is initially high, the lack of temporal control over release reduces effective bioaccessibility.

The FD-PP/MD system showed the lowest bioaccessibility, despite its intermediate structural characteristics. This behavior results from disruption of the pectin interaction network by maltodextrin, which reduces both protective capacity and controlled release functionality. The resulting heterogeneous matrix likely undergoes non-uniform swelling and premature disintegration, leading to early release combined with insufficient protection. This provides a mechanistic explanation for the observed "$1 + 1 < 1$" effect, where combining wall materials yields inferior performance compared to the pectin-only system.

It is important to note that bioaccessibility was assessed using ORAC as a functional proxy, reflecting both the concentration and activity of bioaccessible compounds. While this approach captures overall antioxidant performance, it does not directly quantify individual phenolics after digestion. Therefore, future studies incorporating post-digestion compositional analysis would provide complementary insight.

These results demonstrate that bioaccessibility is governed by matrix-controlled release kinetics, which are in turn dictated by molecular interactions and microstructure responsiveness to pH. Pectin-based systems enable controlled, site-specific release through interaction-driven networks, whereas maltodextrin promotes rapid but poorly protected release. The hybrid system compromises both mechanisms, resulting in reduced functional efficiency.

**Table 3**
ORAC values of microstructured powder samples before and after *In vitro* gastrointestinal digestion, and corresponding bioaccessibility percentages.

| Microcapsules sample | Undigested* | Digested* | Bioaccessibility (%) |
|---|---|---|---|
| FD-PP | 343.614 ± 3.873 $^{A}$ | 330.702 ± 6.423 $^{A}$ | 104.65 |
| FD-MD | 219.575 ± 11.741 $^{C}$ | 229.806 ± 6.837$^{B}$ | 96.24 |
| PD-PP/MD | 285.342 ± 1.279$^{B}$ | 184.033 ± 4.891 $^{C}$ | 64.49 |

* ORAC: oxygen radical absorbance capacity (μmol Trolox equivalents/g). The data were reported as mean ± standard deviation (n = 3). Different letters in the same column for each parameter indicate statistically significant differences ($p < 0.05$) between samples.

## 4. Conclusions

This study demonstrates that the functional performance of coffee husk-derived microstructured powders is governed by a process–structure–function relationship in which the chemical nature of the wall material controls molecular interactions with polyphenols, thereby determining microstructure formation and, ultimately, stability and bioaccessibility.

Among the evaluated systems, the pectin-based formulation (FD-PP) exhibited superior performance in terms of phenolic retention, antioxidant activity, and bioaccessibility. This behavior arises from the ability of low-methoxyl pectin to establish specific intermolecular interactions with polyphenols, primarily through hydrogen bonding between hydroxyl groups of phenolic compounds and carboxyl groups of the polymer, complemented by electrostatic interactions involving partially ionized carboxylate groups. These interactions generate an interaction-driven network that restricts molecular mobility during freeze-drying, enhances structural cohesion, and enables controlled, pH-responsive release under gastrointestinal conditions.

In contrast, maltodextrin-based systems (FD-MD) behave as physically structured matrices in which polyphenols are stabilized predominantly through vitrification and physical entrapment. While this mechanism favors dispersion and immediate accessibility, it lacks the interaction specificity required to prevent premature release and degradation, resulting in lower effective retention and bioaccessibility.

The combined system (FD-PP/MD) exhibited intermediate but overall inferior performance, demonstrating that the incorporation of a weakly interactive carrier reduces the density of functional interaction sites, disrupts the continuity of the pectin network, and compromises both retention and controlled release. This non-additive behavior highlights that matrix design cannot rely on simple component blending, but must consider interaction compatibility at the molecular level.

Integration of structural (FTIR, SEM) and thermal (DSC/TGA) analyses confirmed that interaction strength governs microstructure formation, which in turn controls molecular mobility, transport properties, and degradation pathways. These results establish that stability and bioaccessibility are not intrinsic properties of the compounds alone, but emergent properties of the structured matrix generated during processing.

Additionally, the formation of caffeic acid during processing, likely via chlorogenic acid hydrolysis, demonstrates that polyphenol functionality is influenced not only by retention but also by chemical transformation, reinforcing the need to consider reaction pathways during process design.

Overall, this work provides a mechanistic basis for the rational design of microstructured powders from agro-industrial byproducts. It establishes that optimal functional performance is achieved when wall materials are selected based on their capacity to form specific interactions that enable the simultaneous control of structure formation, molecular mobility, and release kinetics. These findings support the development of sustainable, high-value bioproducts with tailored stability and delivery properties for food and related applications.

## CRediT authorship contribution statement

**Maria Carolina Otálora:** Conceptualization, Formal analysis, Investigation, Methodology, Project administration, Writing – original draft, Writing – review & editing. **Eliana Rocio Herrera Giraldo:** Formal analysis, Investigation. **Gabriel Ricardo Cifuentes:** Project administration. **Jovanny A. Gómez Castaño:** Formal analysis, Writing – review & editing.

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## Declaration of Competing Interest

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

## Data availability

Data will be made available on request.

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