Food Hydrocolloids 150 (2024) 109683

Contents lists available at ScienceDirect

Food Hydrocolloids

journal homepage: www.elsevier.com/locate/foodhyd

Process-structure-function relationship for mamaku suspension: Effect of drying methods on powder functionality

Akshay Bisht, Kelvin K.T. Goh, Lara Matia-Merino *

School of Food and Advanced Technology, Massey University, Palmerston North, New Zealand

ARTICLE INFO

Keywords:
Mamaku tree fern pith
Shear-thickening polymer
Freeze-drying and oven-drying
Powder rehydration behaviour
In vitro digestion

ABSTRACT

The pith from mamaku tree fern entraps a unique shear-thickening biomacromolecule called mamaku polysaccharide (MP) that may alter the rheological profile in the gut. Here we examined the potential of using the whole pith—natural entrapment of MP in the tissue of pith—to develop a food ingredient with shear-thickening behaviour as an alternative to MP extract. In this study, fresh mamaku pith was collected and dried using an oven-dryer or freeze-dryer, and ground into a powder (ODP: oven-dried powder; FDP: freeze-dried powder). Both the ODP and FDP were characterised for their physical properties (colour, densities, surface morphology), rehydration in water, rheological behaviour and *in vitro* starch digestion. Freeze-drying resulted in a porous structure, while after oven-drying, the structure collapsed and an increase in density was observed. Upon rehydration with water, both FDP and ODP absorbed water, causing the powder particles to swell and release the water-soluble compounds into the continuous phase. The ability of FDP to release water-soluble MP into the continuous phase resulted in a rheological behaviour of a suspension similar to MP extract solution (shear-thickening behaviour). No shear-thickening was observed in ODP suspension because not enough MP was available in the continuous phase to form polymer-polymer interactions. *In-vitro* digestion of wheat biscuits mixed with rehydrated FDP suspension reduced starch digestion by ~35% after 10 min, but starch digestion was unaffected by ODP suspension. This was due to the changes in the rheological behaviour resulting from the alteration in structural characteristics of the powder samples by the different drying methods.

1. Introduction

Cyathea medullaris (commonly known as mamaku) is one of the world's tallest ferns, indigenous to New Zealand and the Pacific Islands, and can grow up to 20 m high in warm and humid conditions (Crowe, 2004). The pith from the fronds and trunk of the mamaku fern has been traditionally used for treating skin conditions such as wounds and bruises, swollen feet and eyes, and to treat boils and facilitate pus eruptions. The boiled pith has also been administrated orally to treat gastric conditions such as sore stomach; used in the removal of the placenta after childbirth; and consumed as a food product (Crowe, 2004; Foster, 2008; McGowan, 2014; Riley, 1994). Many of the therapeutic benefits of mamaku fern can be attributed to a water-soluble biomacromolecule called mamaku polysaccharide (MP) entrapped within the pith.

MP has been reported to be a glucuronomannan with a repeating backbone of methylesterified glucopyranosyl uronic acid and mannopyranosyl residues. The mannopyranosyl residues are branched at O-3 and at both O-3 and O-4 with sidechains made of galactose, arabinose, non-methylesterified glucuronic acid and other simple sugars (Wee, Matia-Merino, Carnachan, Sims, & Goh, 2014). MP exhibits a distinctive rheological profile comprising Newtonian, shear-thickening and shear-thinning behaviours, depending on applied shear (Goh, Matia-Merino, Hall, Moughan, & Singh, 2007; Matia-Merino, Goh, & Singh, 2012), which is uncommon in nature. Furthermore, MP has shown strong extensional properties when stretched using a capillary thinning extensional rheometer (Bisht et al., submitted; Jaishankar, Wee, Matia-Merino, Goh, & McKinley, 2015). The unique rheological behaviour of MP has been shown to alter the peristalsis contractions in an *ex-vivo* rat stomach model when compared with guar gum at a similar viscosity (Lentle, Janssen, Goh, Chambers, & Hulls, 2010). In a subsequent *in vivo* study, food consumption was reduced in rats gavaged with MP (Wee, Lentle, Goh, & Matia-Merino, 2017). The weight of the stomach content, retrieved after 2 h of final gavage, was significantly higher in the MP-treated group. In both of these studies, MP was directly administrated into the stomach, but in reality, MP needs to travel from

* Corresponding author. School of Food and Advanced Technology, Massey University, Palmerston North, 4442, New Zealand.
E-mail addresses: A.Bisht@massey.ac.nz (A. Bisht), K.T.Goh@massey.ac.nz (K.K.T. Goh), l.matia-merino@massey.ac.nz (L. Matia-Merino).

https://doi.org/10.1016/j.foodhyd.2023.109683
Received 23 October 2023; Received in revised form 3 December 2023; Accepted 21 December 2023
Available online 27 December 2023

the mouth *via* the oesophagus before it reaches the stomach; and in this case, the shear-thickening may develop in the oesophagus, which may pose an undesirable swallowing experience and choking hazard. Additionally, the physiological effects observed in these studies were at a high concentration of MP (more than ~15% w/w), which may not be a realistic concentration to deliver to humans if used in food systems. Lastly, MP is sensitive to shear and temperature treatment (Bisht, Goh, Sims, Edwards, & Matia-Merino, 2023), which may render its rheological properties ineffective in food products.

In this study, we explored the potential of using the whole pith from mamaku fronds as an alternative to extracted MP for developing a food ingredient. Using the whole pith is a more sustainable way of utilising mamaku fern that will generate less waste, as opposed to the additional processing steps involved in extracting MP. Furthermore, the pith contains a high amount of fibres that will have additional physiological benefits (Monro, Bisht, Mishra, Goh, & Matia-Merino, unpublished).

Fresh mamaku pith has a high moisture content, which makes it susceptible to microbial spoilage. However, drying can hinder microbial spoilage and prolong its shelf-life. Drying is a widely employed technology for the processing and preservation of high-moisture foods. Oven-drying is a commonly used low-cost method, where a continuous flow of hot air is used to heat the product causing moisture to migrate within the matrix toward the surface by diffusion and/or hydrostatic pressure gradient (Karam, Petit, Zimmer, Djantou, & Scher, 2016). Freeze-drying is another method, used mostly for high-value products such as coffee, spices and herbs, where dehydration is achieved by sublimation of frozen products (Verma & Sharma, 2018). It is well established that the drying process can significantly affect the physicochemical properties of the product. For example, freeze-dried sea buckthorn berries retained more carotenoids, vitamin C and phenolics than oven-dried (Araya-Farias, Makhlouf, & Ratti, 2011). It has also been reported that chokeberries had a higher porosity after freeze-drying than after oven-drying (Calín-Sánchez et al., 2015). The drying method also may cause deformation that can alter the structural matrix of food products and consequently affect their functionality. These dried products can be milled into powders for ease of transportation, storage and application.

Food powders are generally rehydrated in water before consumption. Several studies have reported the dynamic hydration process for milk powders (Crowley, Kelly, Schuck, Jeantet, & O'mahony, 2016; Ji, Cronin, Fitzpatrick, Fenelon, & Miao, 2015; Ji et al., 2016) and hydrocolloids (Premathasan & Taylor, 2018; Wangler & Kohlus, 2017; Wangler, Teichmann, Konstanz, & Kohlus, 2019). However, there are limited studies on rehydration of powdered plant materials. The rehydration process for powders can be divided into four sequential steps: (i) wetting, (ii) sinking, (iii) dispersion and (iv) particle solubilisation into solutions, if soluble (Fig. 1) (Crowley et al., 2016; Fang, Selomulya, & Chen, 2007; Schubert, 1993; Wangler & Kohlus, 2018). Wetting refers to replacing the gaseous phase on the powder surface with water. Sinking refers to the submerging of powder below the surface of the water. Dispersion refers to the disintegration of wetted bulk powder particles and their dispersion throughout the bulk liquid. Solubilisation refers to the dissolution of the powder particles into the water to form a solution. These steps tend to overlap with each other and thus are difficult to study in isolation. An ideal food powder should be able to wet thoroughly, sink into the water rather than float on the surface, disperse and dissolve within a short time without forming any lumps. The rate of rehydration of powders *i.e.,* how quickly each step can be completed, mainly depends on the composition and physical properties (such as size, charge, porosity and morphology) of the powder, among others, which in turn may be affected by the drying method used (Gaiani et al., 2011; Li, Jin, & Sheng, 2020). The surface composition will influence the hydrophilicity which will affect the wetting behaviour. Particles with high porosity enable water to penetrate easily into their structure. The morphology (size and shape) of particles can also impact how water penetrates the bulk powder (Yekeler, Ulusoy, & Hiçyılmaz, 2004).

With the motivation of developing a natural shear-thickening food ingredient using the whole mamaku pith, we investigated the process-structure-function relationship for the mamaku pith powder. It is hypothesised that, with an appropriate drying method, dried ground mamaku pith can confer similar shear-thickening properties as the extracted MP. The whole mamaku pith was firstly dried (oven- and freeze-drying) and then ground to powder using a pin mill. The resulting powders were characterised for changes in their physiochemical properties, rehydration behaviour in water, rheological behaviour and *in vitro* starch digestion.

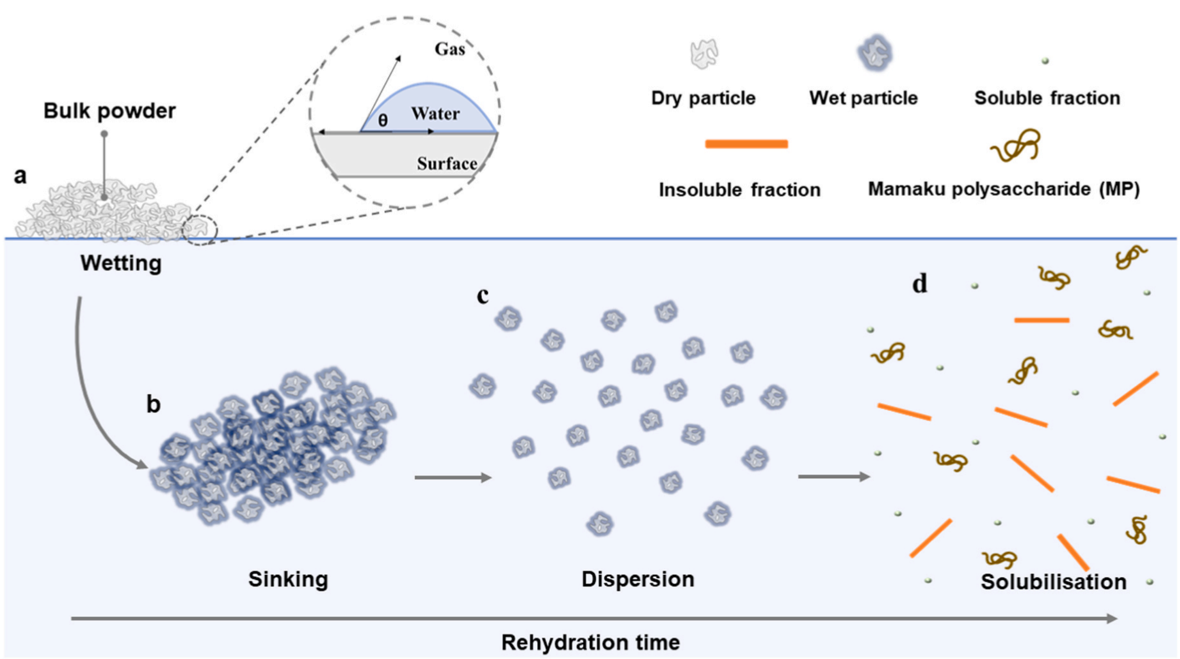


Fig. 1. Schematic representation of powder rehydration behaviour, showing (a) wetting, (b) sinking, (c) dispersion and (d) solubilisation steps.

2. Material and methods

2.1. Processing of mamaku fronds

The fully grown mamaku fronds were harvested from a farm in the Taranaki region of New Zealand between the 10th and 30th of October 2020 following local practices. The harvested fronds were peeled to remove the external rind. This yielded ~40% (w/w) of pith, which was cut into slices (~1 cm in thickness). The sliced pith was dried using either a freeze-dryer (FD18ISLA, Cuddon Freeze Dry, Blenheim, New Zealand) or an oven-dryer (Inoxtrend, Treviso, Italy). The freeze-drying was performed at 1.8 mbar pressure in the chamber and 20 °C shelf temperature, while oven-drying was performed with a continuous circulation of air at ~50 °C. Both freeze-drying and oven-drying were terminated once the final moisture content of the pith was reduced to ~5% w/w, yielding ~9.5% (w/w) (dried pith from sliced peeled, fresh pith). The dried pith was ground using a pin mill (Grain Tech Engineering Ltd., Auckland, New Zealand, sieve size 650 μm), and the powder was stored in sealed aluminium bags until use. The freeze-dried pith powder (FDP) and oven-dried pith powder (ODP) have particles of size, D(50), 105.5 ± 0.5 μm and 104.75 ± 9.7 μm, respectively (Fig. A1) and water activity (a_w) of 0.21 ± 0.01 and 0.27 ± 0.01, respectively.

2.2. Powder characterisation

2.2.1. Chemical composition

Moisture, protein, lipid and ash contents were determined using AOAC 950.46B, AOAC 968.06, AOAC 991.36 and AOAC 920.153 methods, respectively. Starch and dietary fibres were determined using Megazyme kits based on AOAC 996.11 and AOAC 991.43 methods, respectively. The mineral composition was determined using an inductively coupled plasma (ICP)-optical emission spectrometer and sugar composition was analysed using gas chromatography. Uronic acid content was quantified spectrophotometrically using the *m*-hydroxydiphenyl method with glucuronic acid as the standard (Blumenkrantz & Asboe-Hansen, 1973). The chemical analyses were conducted by an accredited Nutrition Laboratory, Massey University, Palmerston North, New Zealand.

2.2.2. Colour

The surface colour was measured with a digital chroma meter (CR-400, Konica Minolta, Tokyo, Japan) in the CIE system (L*: lightness, a*: + redness, - greenness and b*: + yellowness, - blueness). The browning index (BI, defined as brown colour purity) for each powder sample was calculated using:

$$BI = \frac{(x - 0.31)}{0.17} \times 100 \qquad \text{Eq. 1}$$

where, $x = \frac{(a^* + 1.75 \times L^*)}{(5.645 \times L^* + a^* - 3.012 \times b^*)}$, while the total difference in powder samples (ΔE) was calculated using:

$$\Delta E = \left[\left(a^* - a_o^*\right)^2 + \left(b^* - b_o^*\right)^2 + \left(L^* - L_o^*\right)^2\right]^{1\backslash 2} \qquad \text{Eq. 2}$$

where, a*, b* and L* correspond to ODP and a_o*, b_o* and L_o* correspond to FDP.

2.2.3. Density of powder

Powder samples were accurately weighed (5.0 g) into a 25 ml measuring cylinder (15 × 1.8 cm) and without disturbing the cylinder the volume was read to give the bulk volume of the powder. The cylinder with powder was then manually tapped until there was no further change in volume, giving the tapped volume of the powders. The bulk (ρ_b) or tapped density (ρ_t) were calculated as the ratio of the weight of powder to the bulk or tapped volume, respectively (Ermis & Özkan, 2021).

Particle density (ρ_s) was measured using the gas pycnometer (Ultrapycnometer 1000, Quantachrome Instruments, Boynton Beach, Florida, USA), where mamaku powders (~1 g) were placed in a sample cell and purged with Nitrogen to degas the cell by ten pressurisation cycles to obtain the volume occupied by powders (Stange, Scherf-Clavel, & Gieseler, 2013). The ratio of weight to volume was used to calculate ρ_s. Furthermore, porosity (φ) defined as the ratio of the volume occupied by voids to total volume, was calculated using:

$$\varphi = \frac{\rho_s - \rho_b}{\rho_s} \text{ x } 100 \qquad \text{Eq. 3}$$

2.2.4. Powder flow behaviour

The density of the ground mamaku powder samples was also used to characterise the flow behaviour. Based on the change in volume after tapping the bulk sample, compressibility or Carr index (CI) and Hausner ratio (H_R) were calculated using the following equations (4) and (5):

$$CI = \left(1 - \frac{\rho_b}{\rho_t}\right) \times 100 \qquad \text{Eq. 4}$$

$$H_R = \frac{\rho_t}{\rho_b} \qquad \text{Eq. 5}$$

In addition, the angle of repose measurement was carried out for FDP and ODP by freely flowing the powders (3 g) through a funnel clamped 10 cm from a paper surface (Nep & Conway, 2011). The height, *h*, and the radius, *r*, of the cone formed after the complete flow of powder were measured and θ was calculated using:

$$tan(\theta) = \frac{h}{r} \qquad \text{Eq. 6}$$

2.2.5. Scanning electron microscopy (SEM)

The surface of the freeze-dried and oven-dried pith and their respective powders was analysed using SEM. The dried pith was cut into cubes (~0.5x0.5 × 0.5 cm) and mounted on aluminium stubs using double-sided tape, while the powder samples were uniformly spread on the double-sided tape adhered to the aluminium stub. The samples were then sputter coated with gold (~100 nm thickness) using Baltec SCD 050 sputter coater and viewed under FEI Quanta 200 Environmental Scanning Electron Microscope (Field Electron and Ion Company, Hillsboro, Oregon, United States) at an accelerating voltage of 20 kV.

2.2.6. X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy

XRD (MiniFlex600-C, Rigaku Corporation, Tokyo, Japan) and FTIR (Thermo-Fisher Scientific, Waltham, Massachusetts, USA) analysis of powders were performed as described by Bisht, Goyal, Sachdev, and Pasricha (2019) and Salleh et al. (2022), respectively.

2.3. Powder rehydration

2.3.1. Wetting: contact angle

The contact angle between FDP or ODP and water was analysed using the sessile drop technique as described by Ji et al. (2016). Briefly, powder samples were compressed to form the smooth disk under 281 bar pressure using a powder press (Vaneox Pressing Technology, Kleve, Germany). A 10 μl droplet of milli-Q water (at ~20 °C) was placed on the disk surface using the auto-injector control system of the optical tensiometer (Biolin Scientific Attention theta flex, ATA Scientific Instruments, Sydney, Australia). The dynamic contact angle was measured every second, till the droplet disappeared.

2.3.2. Sinking time

The time taken by FDP and ODP to immerse in water spontaneously without agitation was measured as described by Ji et al. (2016), with modifications. Briefly, 0.5 g of powder sample was placed evenly on the surface of the milli-Q water in a 400 ml beaker (~10 × 8 cm, containing 200 ml of water at ~20 °C) and the time when all the powder immersed in water was recorded using a timer.

2.3.3. Dispersion: particle size measurements

Dispersion of FDP and ODP was studied by monitoring the change in particle size as a function of time. Powder samples were dispersed in milli-Q water (1% w/w, ~20 °C) and stirred at 150 rpm in a water bath (~20 °C). The samples at different time points (0–1440 min) were added to the dispersion unit of Mastersizer 2000 (Malvern Instruments Ltd, Malvern, England) until a laser obscuration of ~10% was achieved. A general-purpose analysis model with a refractive index of 1.5 and 1.33 for powder particles and water, respectively, was used to calculate the particle size distributions.

2.3.4. Solubilisation

FDP and ODP samples (0.5 g) were dispersed in 50 ml of milli-Q water (1% w/w, ~20 °C) in a beaker (~10 × 8 cm) and placed in a water bath (~20 °C) with constant stirring at 150 rpm for different mixing times (0–1440 min). After mixing, the suspensions were transferred to 50 ml centrifuge tubes and centrifuged at 13,000 *g* for 30 min. The supernatant was collected, and the amount of solids was determined by drying in a hot-air oven at 105 °C. Solubilisation (%) was calculated as the ratio of the amount of solids in the supernatant to the initial sample dry weight (Boucheham, Galet, Patry, & Zidoune, 2019).

2.4. Rheology measurements

FDP and ODP samples were hydrated in milli-Q water at different concentrations ranging from 0.5 to 8% (w/w) for ~15 h at ~20 °C. Rheological measurements were performed in rotational mode using a Paar Physica MCR 302 rheometer (Anton-Paar, Graz, Austria) in a controlled shear rate (CSR) mode with a log-ramp profile from 15 s to 2 s (initial to final) at 20.0 ± 0.1 °C. Viscosity curves were measured using the cup-and-bob geometry (CC27 and C-PTD 200) or parallel plate (PP-40/Q1 and P-PTD200, gap = 1.5 mm) or double gap geometry (DG-26-7 and C-PTD 200), depending on the viscosity of the sample and data was recorded using Rheoplus/32 software (Version 3.62).

2.5. Release behaviour of mamaku polysaccharide

FDP and ODP samples were weighed (0.5 g) and poured into 50 ml milli-Q water in a beaker (~9 × 4.5 cm, 1% w/w) at ~20 °C. The samples were stirred using a magnetic stirrer initially at 600 rpm for 15 s to create a vortex to disperse the powder and thereafter, stirred at 150 rpm for different rehydration times (0–1440 min). After a specific rehydration time, the samples were centrifuged at 13,000 *g* for 30 min to collect the supernatant. The whole suspension before centrifugation and the supernatant after centrifugation (*i.e.,* continuous phase) were characterised for viscosity and uronic acid content.

2.6. *In vitro* digestion of wheat biscuit starch

The effect of FDP and ODP on the digestion of starch from WeetBix™ flaked wheat biscuit was studied as described previously (Monro, Mishra, & Venn, 2010). Briefly, FDP and ODP suspensions (5% w/v) were prepared by hydrating the samples in water for ~18 h. WeetBix (WB; 2.5 g) was weighed into 70 ml specimen pots and mixed with 20 ml gastrointestinal salt solution (7 g/L of a stock mixture of 50 g NaCl, 4 g $CaCl_2$, 1 g $NaHPO_4$, 0.1 g $MgCl_2$), maleate buffer (5 ml, 0.1 M, pH 6.0) and powder suspension (25 ml) and volume adjusted to the 53 ml mark. A control pot of WeetBix alone (WB + water + buffer) was also prepared. Digestion was initiated by adding pancreatin (1 ml, 1% w/v, Sigma P1750, 4 x USP specifications) and amyloglucosidase (0.1 ml, Megazyme EAMG) to the reaction pots, which were then installed in a rotary mixer (Heidolph REAX 2, Schwabach, Germany) placed in a heated cabinet (Heidolph INKUBATOR 1000 air heater, 37 °C) for end-over-end rotation at 12 rpm to simulate physiological mixing. Digestion was timed from the start of the rotation. An aliquot (1 ml) was removed from each pot at 0, 10, 20 and 40 min and mixed with ethanol (4 ml) to stop digestion and precipitate undigested starch. After centrifuging a 0.5 ml sub-sample of supernatant was removed for secondary amyloglucosidase digestion and subsequent analysis of reducing sugars by dinitrosalicylic acid (DNS) method (Englyst & Hudson, 1987).

2.7. Statistical analysis

All the experiments were performed at least in triplicate. The data are reported as mean ± standard deviation. The data were checked for normality using the Shapiro-Wilk test. Statistical analysis was performed using a one-way analysis of variance (ANOVA) with Tukey HSD post-hoc test at a 95% confidence level using SPSS software (IBM SPSS Statistics, Version 28.0.1.1(15)).

3. Results and discussion

3.1. Chemical composition

The fresh mamaku pith had high moisture content (~94%), which was sufficiently reduced to ~5% dry weight using a freeze-dryer or oven-dryer, followed by grinding of the samples using a pin mill. The resulting mamaku pith powders contained a large proportion of dietary fibres (~36–40%) with the majority being insoluble dietary fibres (~23–27% of pith dry weight) (Table A1). About 32–36% of the dietary fibre was soluble and of that about 32% was uronic acid (~4% of the dry weight of both powders), reflecting the large contribution of glucuronomannan to the soluble fibre fraction. The amount of sugar was also high (~36–40%)—fructose (~17–19%) and glucose (~19–20%) were dominant sugars. The powder samples were relatively high in minerals (~8%), especially potassium, aluminium, sodium and calcium. Small amounts of fat (~1%) and protein (~2%) were present.

3.2. Powder characterisation

3.2.1. Colour

Colour is a critical quality attribute that is significantly affected by processing conditions. ODP had higher red and yellow Hue values and lower Lightness than FDP (low L*, high a* and b* for ODP), giving ODP a more brownish appearance (higher BI for ODP) (Table 1). The total colour difference (ΔE) between ODP and FDP was calculated as ~8. $\Delta E > 3$ suggests that the difference between samples is perceptibly different (Pathare, Opara, & Al-Said, 2013). The development of a darker colour for ODP could be a result of enzymatic and non-enzymatic browning reactions: oxidation of phenolic compounds by polyphenol oxidase and Maillard reaction between sugars and proteins at high temperature, respectively (Silva, Abreu, Silva, & Cardoso, 2019). On the contrary, the relatively low temperature involved during freeze-drying did not result in the browning of the mamaku powder. A similar observation that a darker colour was obtained after oven-drying as compared to freeze-drying, has been reported for black mulberries (Chen et al., 2017), chokeberries (Samoticha, Wojdyło, & Lech, 2016), sugar beetroot (Ermis & Özkan, 2021), soy okara (Muliterno, Rodrigues, de Lima, Ida, & Kurozawa, 2017) and mushrooms (Argyropoulos, Heindl, & Müller, 2011).

3.2.2. Density and flow behaviour

Higher density (ρ_b, ρ_t and ρ_s) values were observed for ODP than for FDP (Table 1), which is in agreement with previous studies on mango (Caparino et al., 2012) and sugar beetroot (Ermis & Özkan, 2021) powders. The high particle density of ODP—and lower porosity—indicates the shrinkage and collapse of the pith structure during oven-drying. In addition to shrinkage, the difference in particle size distribution, surface structure and irregular shape may also affect the close packing of particles and therefore, the bulk and/or tapped packing density. Furthermore, the flow properties of the powders were predicted. A higher value of the angle of repose for FDP suggests that it is more cohesive than ODP. A similar trend was observed for CI and H_R, indicating relatively poor flow for FDP. Generally, from both CI and H_R data, ODP was categorised as a poor flowing powder (CI: 26–31, H_R: 1.35–1.45), while FDP was categorised as a very, very poor flowing powder (CI: >38, H_R: >1.60) (Amidon, Meyer, & Mudie, 2017). The relatively poor flow behaviour for FDP and ODP could be attributed to the high sugar content, which makes the powder highly hygroscopic rendering a greater tendency to stick and form clumps.

3.2.3. Powder microstructure

The micrographs for freeze-dried and oven-dried whole pith and their respective powder surfaces are shown in Fig. 2. Freeze-dried pith exhibited a more porous structure, while in oven-dried pith the porous structure appeared to collapse (pore size diminishes) somewhat resulting in a more compact and denser structure (pores within dotted circles). In addition, the surface of FDP appeared smooth and flake-like while the ODP surface appeared thicker and wrinkled. The collapse in structure could be a result of heating the pith above its glass transition temperature (T_g) leading to a soft and rubbery state where the solid food matrix can no longer support its own weight (Ratti, 2001). Izli and Polat (2019) reported a similar structural collapse on drying quince (45–75 °C), and the degree of collapse of the tissue matrix increased with an increase in drying time. Air drying Kiwifruit (at 60 °C) has also been reported to result in a tightly shrunken, thicker cellular structure and flattened surface when compared to freeze-dried samples (Zhang et al., 2019). The shrinkage and collapse in structure led to lower porosity for ODP (~8% lower than FDP) which is mainly responsible for the higher density of ODP compared to that of FDP (Table 1). Higher porosity after freeze-drying relative to oven-drying has also been reported for other plant materials (Calín-Sánchez et al., 2015; Ermis & Özkan, 2021; Michalska, Wojdyło, Lech, Łysiak, & Figiel, 2017).

3.3. Rehydration behaviour of powders

3.3.1. Wetting

The wettability of powders is generally determined by measuring the contact angle formed by a droplet of water on the powder surface after spreading and reaching equilibrium by the balance of interfacial tensions between the solid (powder), the liquid (water droplet) and the gas (air). However, the contact angle measured on FDP and ODP using the current method changes over time as the water droplet once placed on

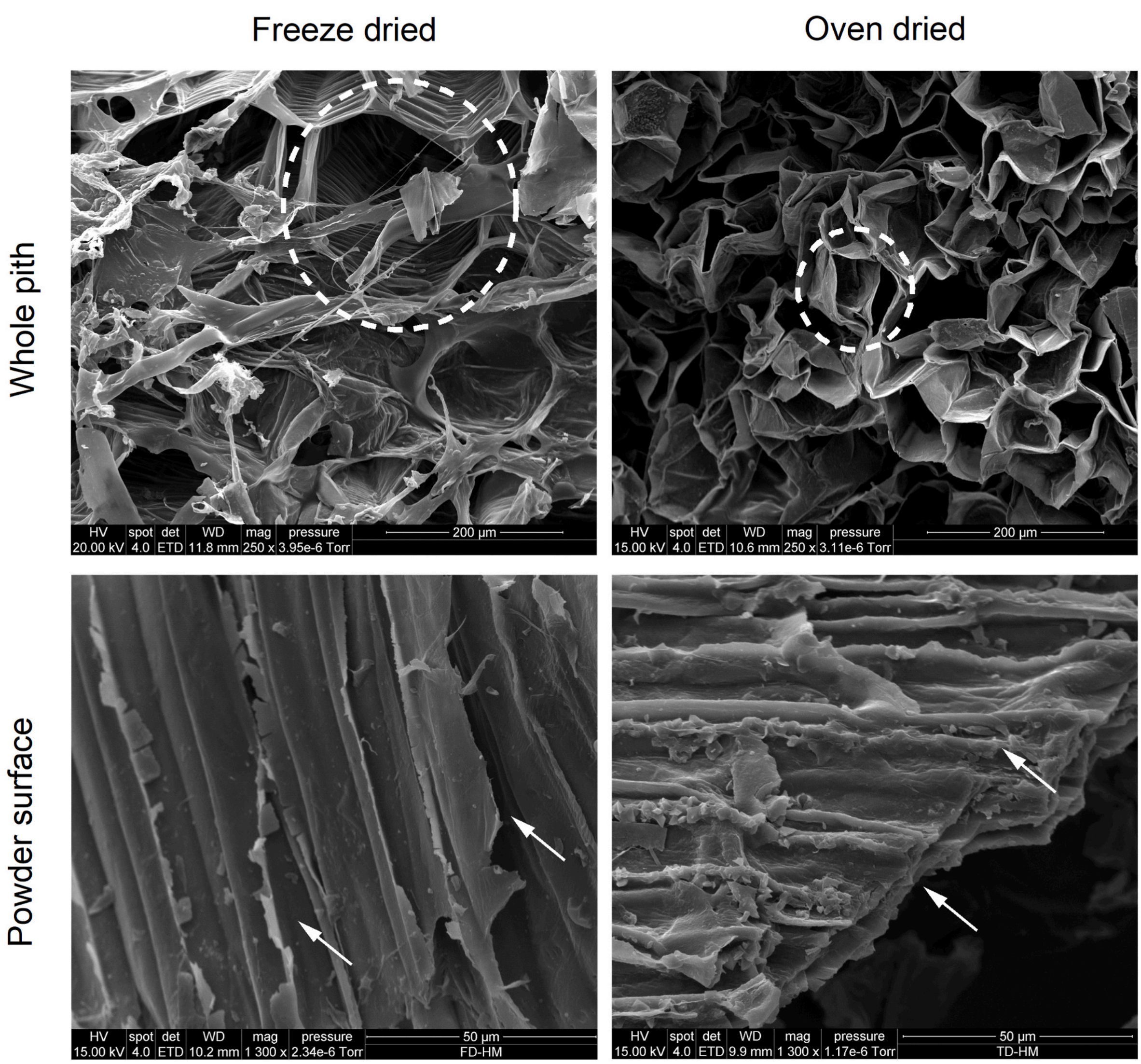


Fig. 2. Micrographs of freeze-dried and oven-dried mamaku whole pith and their respective powder surfaces, showing the difference in structure highlighted using dotted circles (pores) and arrows (flakes in the freeze-dried powder and wrinkles in the oven-dried powder).

Table 1
Characterisation of freeze-dried (FDP) and oven-dried (ODP) mamaku pith powders.

	FDP	ODP
		
L*	89.27 ± 0.28[a]	84.43 ± 0.37[b]
a*	0.98 ± 0.06[b]	2.22 ± 0.05[a]
b*	14.49 ± 0.05[b]	20.76 ± 0.15[a]
Browning index (BI)	18.12 ± 0.06[b]	29.65 ± 0.24[a]
Bulk density (ρ_b, g/cm^3)	0.14 ± 0.01[b]	0.26 ± 0.01[a]
Tapped density (ρ_t, g/cm^3)	0.25 ± 0.01[b]	0.38 ± 0.01[a]
Particle density (ρ_s, g/cm^3)	1.48 ± 0.001[b]	1.52 ± 0.004[a]
Porosity (φ, %)	90.95 ± 0.03[a]	82.40 ± 0.01[b]
Angle of repose (°)	38°±3[a]	32°±2[b]
Carr's index (CI)	44.53 ± 3.47[a]	31.05 ± 1.89[b]
Hausner ratio (H_R)	1.81 ± 0.12[a]	1.45 ± 0.04[b]

Values are expressed as means ± standard deviation (n = 10). Values in the same row denoted with the different superscript letters are significantly different ($p \leq 0.05$).

the powder disk penetrates and gets absorbed into the powder bulk. A contact angle of 0–90° represents good wetting, whereas a contact angle above 90° represents poor wetting behaviour. Fig. 3a shows the penetration of a water droplet into FDP and ODP at different time intervals. The contact angles for FDP and ODP were similar (~70°) at the start of the experiment, and they significantly reduced to ~20° within 5 s and 12 s, respectively (Fig. 3b). A drastic decrease in contact angle suggests the hydrophilic nature of both powders. In the case of FDP, the presence of larger voids between particles generally facilitate easier movement of water into the powder bulk (Freudig, Hogekamp, & Schubert, 1999; Hogekamp & Pohl, 2003). Powders are commonly engineered to develop a porous agglomerated structure that improves the wetting behaviour (Forny, Marabi, & Palzer, 2011; Ji et al., 2015). The compression of powders when filling the disk may cause some changes in the surface roughness, the structure of the bulk powder and the compaction pressure, thus, the contact angle should be treated as an apparent contact angle (Wangler & Kohlus, 2018). Furthermore, the contact angle measured using a powder disk may differ from the contact angle formed on individual powder particles.

3.3.2. *Sinking*

Once the gaseous phase around the powder is replaced by water, the water penetrates the powder particles, which will increase the particle density. As soon as the powder particles overcome the buoyant force exerted by the fluid, the powder will sink. It has been reported that food particles of size ≥100 μm and $\rho_s \approx 1.5$ g/cm^3 could easily sink into water (Freudig et al., 1999). In the current study, both FDP and ODP are close

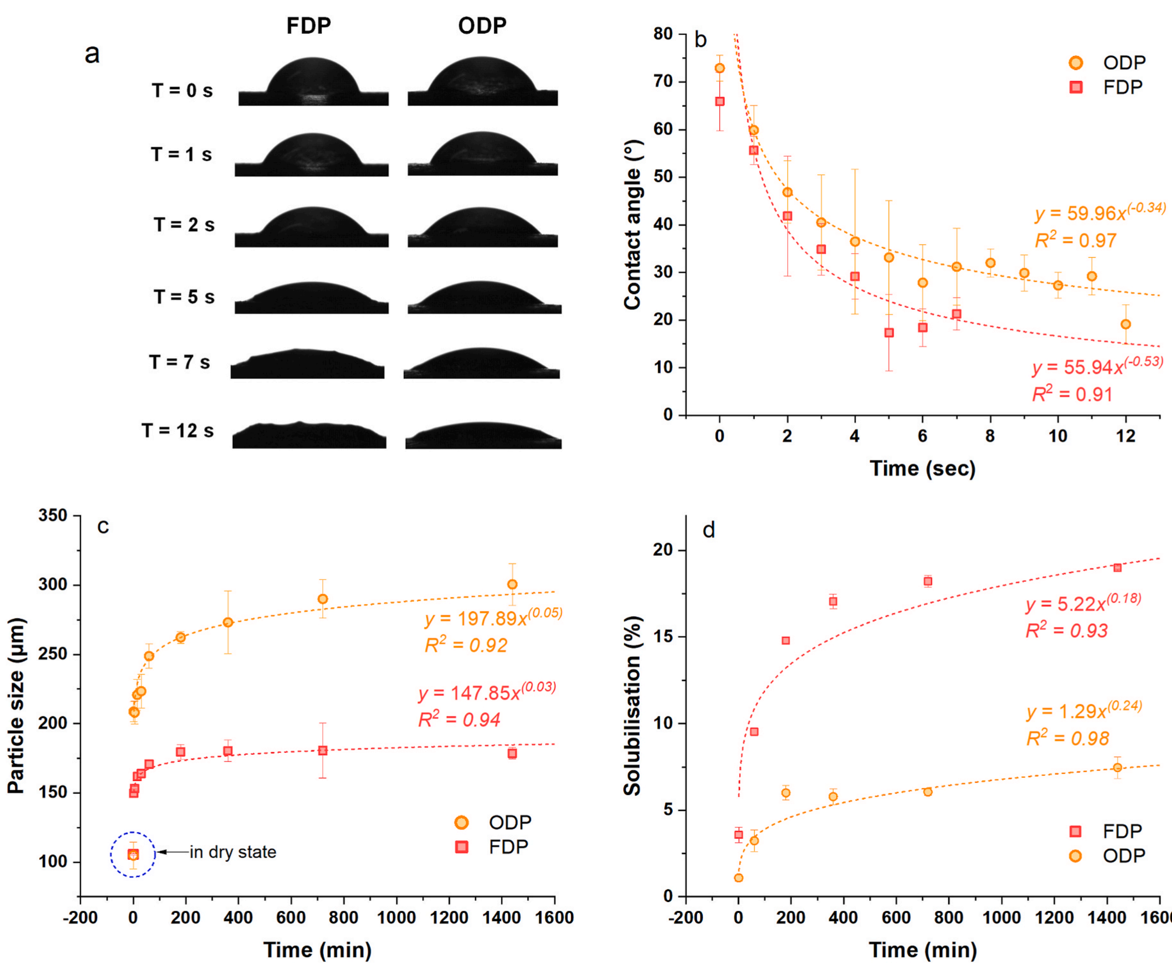


Fig. 3. Rehydration behaviour of freeze-dried (FDP) and oven-dried (ODP) mamaku pith powders in water at ~20 °C: (a) Images showing the penetration of water droplet into powder at different time intervals. Change in (b) contact angle (c) particle size (D50) and (d) % solubilisation as a function of time. Values are plotted as means ± standard deviation (n = 6).

to these generally accepted conditions, however, marked differences in the sinking behaviour were observed. The ODP submerged into the water in ~2 min, while FDP continued to float on the surface (for the entire observation period of 60 min). Furthermore, a gelatinous layer around some aggregates of powder particles was observed for the FDP (Fig. A2). It is possible that due to the high porosity, water quickly penetrates the FDP particle surface (Forny et al., 2011; Hedenus, Mattsson, Niklasson, Camber, & Ek, 2000), and initiates the dissolution process before the particles sink and disperse (*i.e.,* a faster rate of water uptake than powder dissolution). This could lead to a poorly wetted centre, incomplete dissolution and formation of the viscous surface layer on the particle surface (Premathasan & Taylor, 2018; Wangler et al., 2019). The longer the FDP float on water, the polysaccharides (such as MP and cellulose) present in the wet surface layer of the powder particle may continue to interact with water and develop a viscous gelatinous layer, which could further delay the uptake of water (and the escape of entrapped air) and cause the formation of particle aggregates (Wangler et al., 2019; Wangler & Kohlus, 2018). On the other hand, ODP has a higher density and a lower porosity, which led to more rapid water uptake, thus enabling the particles to be wetted sufficiently and sink more easily than the FDP.

3.3.3. Dispersion and solubilisation

In order to circumvent the poor sinking of the FDP powder, shear was applied (to both FDP and ODP) to facilitate a more effective dispersion. The change in particle size under the applied shearing conditions was monitored. Generally, as food powders are dispersed during reconstitution, the particle size reduces due to the breakdown of particles and the dissolution of water-soluble components such as sugars and polysaccharides into the bulk water phase (Ji et al., 2015). However, for FDP and ODP, the particle size was found to increase with time, suggesting swelling of the particle structure (Fig. 3c). The increase in particle size was highest during the first 180 min for both FDP and ODP. FDP had a smaller particle size than ODP throughout the entire experiment. Similar swelling behaviour has been observed for different cereal and legume powders that contained fibrous materials (Boucheham et al., 2019). The swelling is related to the insoluble fraction within the particle structure which appears to occur simultaneously with the solubilisation of the water-soluble fraction of the particles (Fig. 3d). The increase in solubilisation was also the most significant in the first 180 min of the experiment. The data show that the FDP was more soluble than ODP which could explain the lower particle size of FDP compared to ODP.

The swelling of powder particles starts as soon as the particles are brought in contact with the water and may have contributed to the poor sinking behaviour of FDP (Freudig et al., 1999; Hogekamp & Schubert, 2003). The swelling causes an increase in particle size that may lead to a drop in ρ_s, thus, impeding sinking (Wangler & Kohlus, 2017). The swelling of particles may also block the pores, which will hinder the ease with which water penetrates inside (Wangler & Kohlus, 2018), and as a result, powder particles will take longer to overcome the buoyant forces. The delay in the sinking may promote the diffusion of water-soluble compounds from the wet surface layer of the particles into the water phase (*i.e.,* solubilisation) before completing intermediate steps (*i.e.,* sinking and dispersion). The dissolution of compounds into bulk water will further reduce the density and delay sinking. Though the swelling was also observed for ODP, its impact on sinking was not as drastic as for FDP. This could be due to higher density (Table 1) and a lower solubilised fraction observed for the ODP (Fig. 3d) with also a clear greater powder particle size during sweeling which could easily contribute to a faster sinking.

3.4. Rheological characterisation

The FDP and ODP samples were hydrated overnight at a concentration ranging from 0.5 to 8% (w/w total solids) prior to viscosity measurements which are shown in Fig. 4. The FDP suspension (which

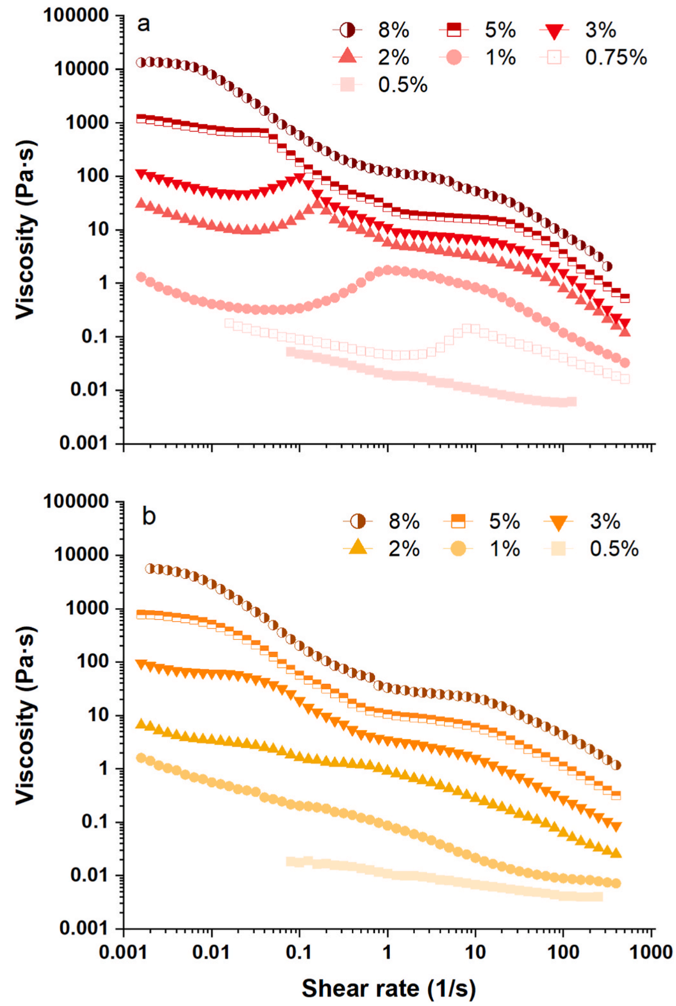


Fig. 4. Viscosity profiles of (a) freeze-dried (FDP) and (b) oven-dried (ODP) mamaku pith powder suspensions (after 15h hydration) as a function of shear rate. Values are plotted as means of triplicates (n = 3). Measurements were taken using cup-and-bob geometry at 20 °C. 8% (w/w) sample was measured using parallel plate geometry.

consisted of the insoluble particle fraction + soluble MP) exhibited three distinctive regions: Newtonian behaviour at a low shear rate, shear-thickening at an intermediate shear rate, and shear-thinning at a higher shear rate, which is the typical rheological profile of MP extracted from the pith (Goh et al., 2007). The ability of the FDP suspension to show similar viscosity profiles to MP indicates the strong contribution of the soluble MP in the continuous phase without marked interference from the insoluble particle fraction. As expected, the viscosity of FDP suspension increased with an increase in powder concentration. As the concentration of the powder increases, the volume fraction of the particles also increases correspondingly which leads to decreasing proximity, closer packing of particles and increasing particle-particle collisions. In addition to the particle concentration, MP concentration in the continuous phase also increases, which increases the viscosity of the continuous phase. The swollen insoluble fraction in the dispersed phase and the complex rheological behaviour of the continuous phase from the MP contributed to the overall unique rheological properties of the dispersion. Interestingly, at higher concentrations (5% and 8% w/w) the shear-thickening behaviour was lost.

The particle polymer suspension can give rise to three types of interactions: polymer-polymer, polymer-particle and particle-particle. The polymer-polymer interactions are dominant at dilute particle concentration, while particle-particle interactions become important with increasing concentration becoming dominant at very high concentrations. Intermediate to polymer-polymer and particle-particle interactions lies the polymer-particle interactions (Mazzanti & Mollica, 2020; Pryamitsyn & Ganesan, 2006). A concentrated suspension of hard particles, when particle-particle interactions are strong, can exhibit shear-thickening behaviour due to the formation of transient particle aggregates, called hydroclusters, as particles come in close proximity during shearing (Gürgen, Li, & Kuşhan, 2016; Park, Rathee, Blair, & Conrad, 2019; Warren et al., 2015). However, the shear-thickening behaviour of the FDP suspension cannot be attributed to particle clustering because, at the higher concentrations of FDP (5% and 8% w/w), the shear-thickening behaviour was lost. The loss of shear-thickening behaviour could be due to several possible explanations including limited hydration of FDP that reduce the solubility of MP; reduced

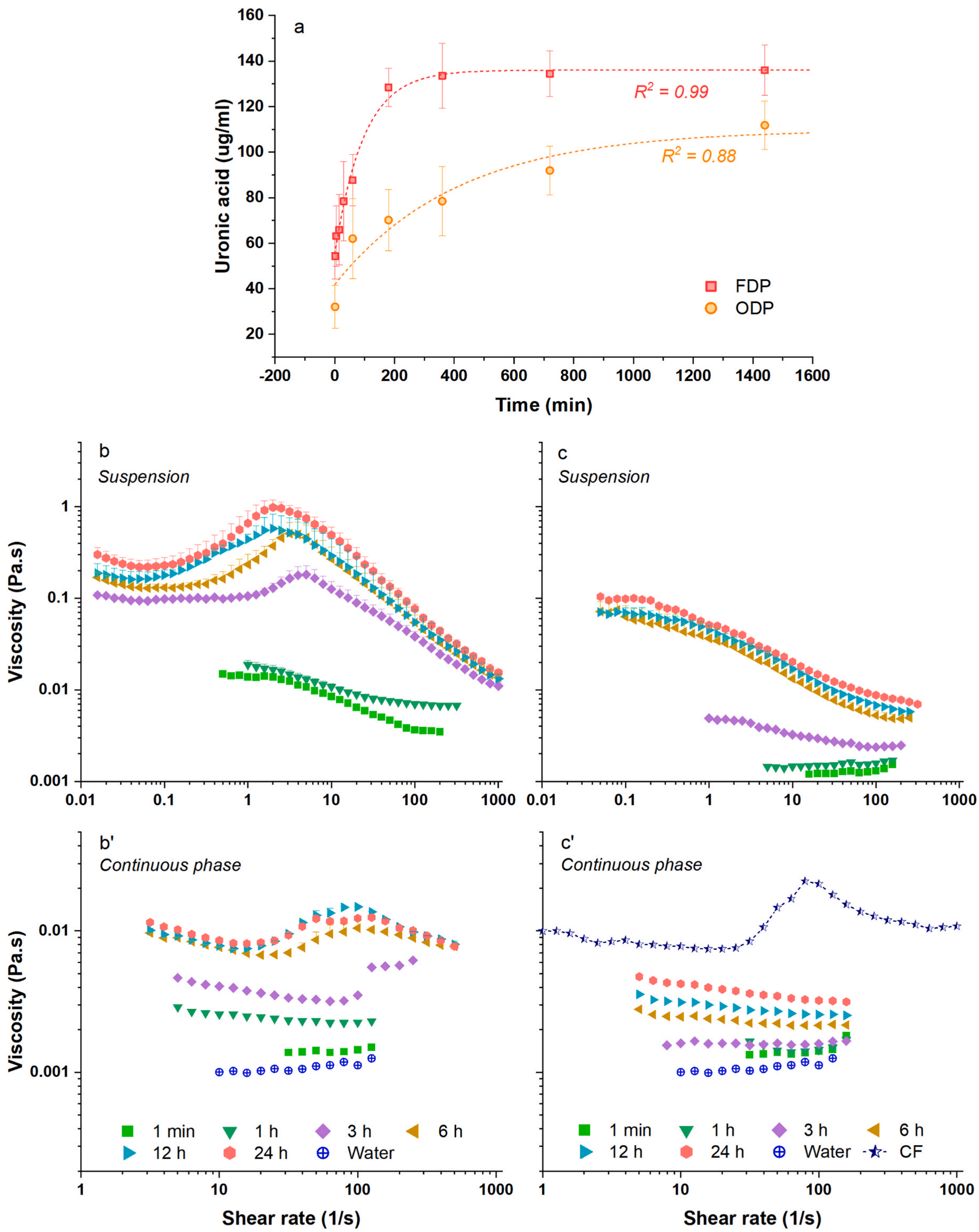


Fig. 5. (a) Amount of uronic acid in the continuous phase of freeze-dried (FDP) and oven-dried (ODP) mamaku pith powder suspension (1% w/w) as a function of hydration time. Time-dependent viscosity profiles of (b) FDP and (c) ODP suspension (1% w/w) and their respective continuous phases (b': FDP; c': ODP). ODP continuous phase collected after 24 h of rehydration was concentrated using a vacuum evaporator: CF, concentrated fraction. Values are plotted as means ± standard deviation (n = 3). Rheological measurements were taken using cup-and-bob (for suspension) or double gap geometry (for continuous phase) at 20 °C.

available space for the polymer chains to stretch upon shear (Goh et al., 2007; Bisht et al., submitted) and the interference from the insoluble powder fractions which disrupts the intermolecular interactions among the MP during shear.

The ODP suspension, on the other hand, did not exhibit any shear-thickening region; rather a shear-thinning behaviour was observed (Fig. 4b) at all concentrations. This further affirms that the shear-thickening behaviour in the FDP suspension is not because of particle clustering. The reason for the loss of shear-thickening behaviour in the ODP suspension was investigated by heating mamaku gum extract (2% w/w total solids) in the oven at ~50 °C for 40 h (similar conditions used for preparing the ODP). However, the rheological profile of mamaku gum was unaffected (Fig. A3), indicating that the drying regime used did not affect the shear-thickening properties of the MP. A plausible explanation for the loss of shear-thickening behaviour could be due to the entrapment of the MP within the dense structure of ODP resulting in insufficient MP being released in the continuous phase to exhibit the typical shear-thickening behaviour of the MP.

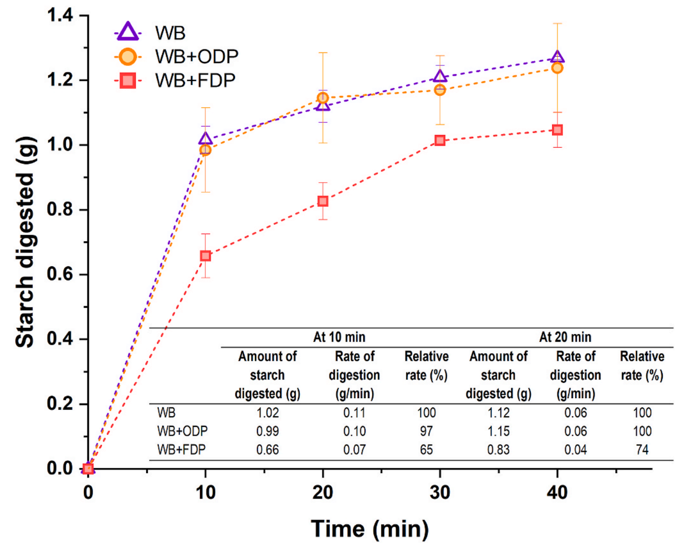
3.5. Release of mamaku polysaccharide from powder particles

The release of MP from FDP and ODP was studied by quantifying the amount of uronic acid in the continuous phase and monitoring the viscosity of suspension (1% w/w) and continuous phase over 1440 min of hydration (Fig. 5). The amount of uronic acid released into the continuous phase increased with time for both powders; however, the amount released by FDP was significantly higher than for ODP at all time points (Fig. 5a). The amount of uronic acid increased exponentially in the continuous phase of FDP for the first 180 min, which then plateaued (as no marked increase was observed). On the contrary, the amount of uronic acid released by ODP, even after 1440 min of rehydration, was markedly lower than that released by FDP at 180 min.

The continuous phase of the reconstituted FDP exhibited shear-thinning behaviour at the beginning of the rehydration process. The shear-thickening behaviour only appeared at 180 min and became more prominent as the rehydration time increased (Fig. 5b'). A similar trend in viscosity was observed for the FDP suspension (Fig. 5b). On comparing the suspensions with their continuous phases, it can be observed that MP contributed to the rheological profile of the suspension while the particles increased the overall viscosity without altering the trend of the rheological properties. No shear-thickening behaviour was observed for the ODP suspensions and their continuous phases (Fig. 5c, c'). However, on concentrating the continuous phase of the ODP collected after 1440 min of rehydration, the shear-thickening behaviour was observed (Fig. 5c'). This demonstrates that the lack of shear-thickening is just a MP concentration effect as not enough gum was released from the ODP powder particles. However, when the gum in the continuous phase is concentrated, the shear-thickening is recovered, proving that the gum was not damaged during heat treatment.

For both FDP and ODP, the viscosity of the suspensions increased with rehydration time. This development of viscosity could be a net result of multiple events happening simultaneously such as the increasing release of MP in the continuous phase, the solubilisation of powder particles, the increase in particle size and possible changes in the size distribution and shape of particles. Once the MP is released in the continuous phase, MP may continue to interact with water to develop an interfacial hydrogen bond network *i.e.,* hydration of the individual polysaccharide chains (Grossutti & Dutcher, 2020) (Fig. 7b), which may further contribute to viscosity enhancement. Although the understanding of the hydration of individual chains at the molecular level is limited, an increase in viscosity with polymer hydration time has been reported previously (Premathasan & Taylor, 2018; Wang, Ellis, & Ross-Murphy, 2002; Wangler & Kohlus, 2018), which may be due to an increasing hydrodynamic volume and conformational changes.

One should be cautious while interpreting the true values of the amount of uronic acid and viscosity of the continuous phase because the loss of MP during centrifugation cannot be discounted. MP release behaviour was also studied for FDP and ODP of different particle sizes (bigger >105 μm > smaller), and similar trends in the amount of uronic acid and viscosity of the continuous phase were observed (Figs. A4 and A.5). The consistency of these trends indicates that the results are reliable.



	At 10 min			At 20 min		
	Amount of starch digested (g)	Rate of digestion (g/min)	Relative rate (%)	Amount of starch digested (g)	Rate of digestion (g/min)	Relative rate (%)
WB	1.02	0.11	100	1.12	0.06	100
WB+ODP	0.99	0.10	97	1.15	0.06	100
WB+FDP	0.66	0.07	65	0.83	0.04	74

Fig. 6. *In vitro* digestion profiles for wheat biscuit alone (WB), and in the presence of 2.5% (w/v) freeze-dried (FDP) and oven-dried (ODP) mamaku pith powder. Values are plotted as means ± standard deviation (n = 3).

3.6. Effect of hydrated powders on in vitro starch digestion

The digestion curves for WB in presence of FDP and ODP suspension are shown in Fig. 6. FDP suspension decreased the digestion of WB by ~35% after 10 min, whereas the rate of digestion was hardly affected by the presence of the ODP suspension. A plausible reason for the difference in digestion rate could be the high viscosity and shear-thickening behaviour of FDP suspension (Fig. 4), which may hinder the mixing of enzyme and substrate and/or delay the movement of the enzyme to substrate, leading to lower enzymatic activity (Brownlee, 2011; Edwards & Garcia, 2009). Similar retardation in the digestion of WB in the presence of mamaku pith suspension was observed by Monro et al. (unpublished). The authors suggest that mamaku pith suspension (with shear-thickening behaviour) can significantly reduce the rate of mixing and diffusion, and thus, the rate of digestion, as compared to guar gum and psyllium husk (no shear-thickening behaviour). Furthermore, the MP released into the continuous phase from FDP may interact with the enzymes and may inhibit the enzyme activity by altering the enzyme conformation due to bonding or competing with the substrate for the enzyme's active site (Bisht, Goh, & Matia-Merino, 2023; Capuano, 2017).

3.7. General discussion

Drying is a frequently used industrial operation for the preservation of perishable foods. The type of drying method used can affect the quality of the final product (process-structure relation), which consequently can limit the application of the product (structure-function relation). Here, we compared the effect of the drying method (freeze-drying and oven-drying) on the structure and functionality of the mamaku pith powders.

Process-structure: The fresh plant tissues have a very low T_g, [broccoli: 29 °C (Xin, Zhang, & Adhikari, 2013); peas puree: 20 to −26 °C (Lim, Wu, Breckell, & Birch, 2006); carrots: 50 °C (Xu, Li, & Yu,

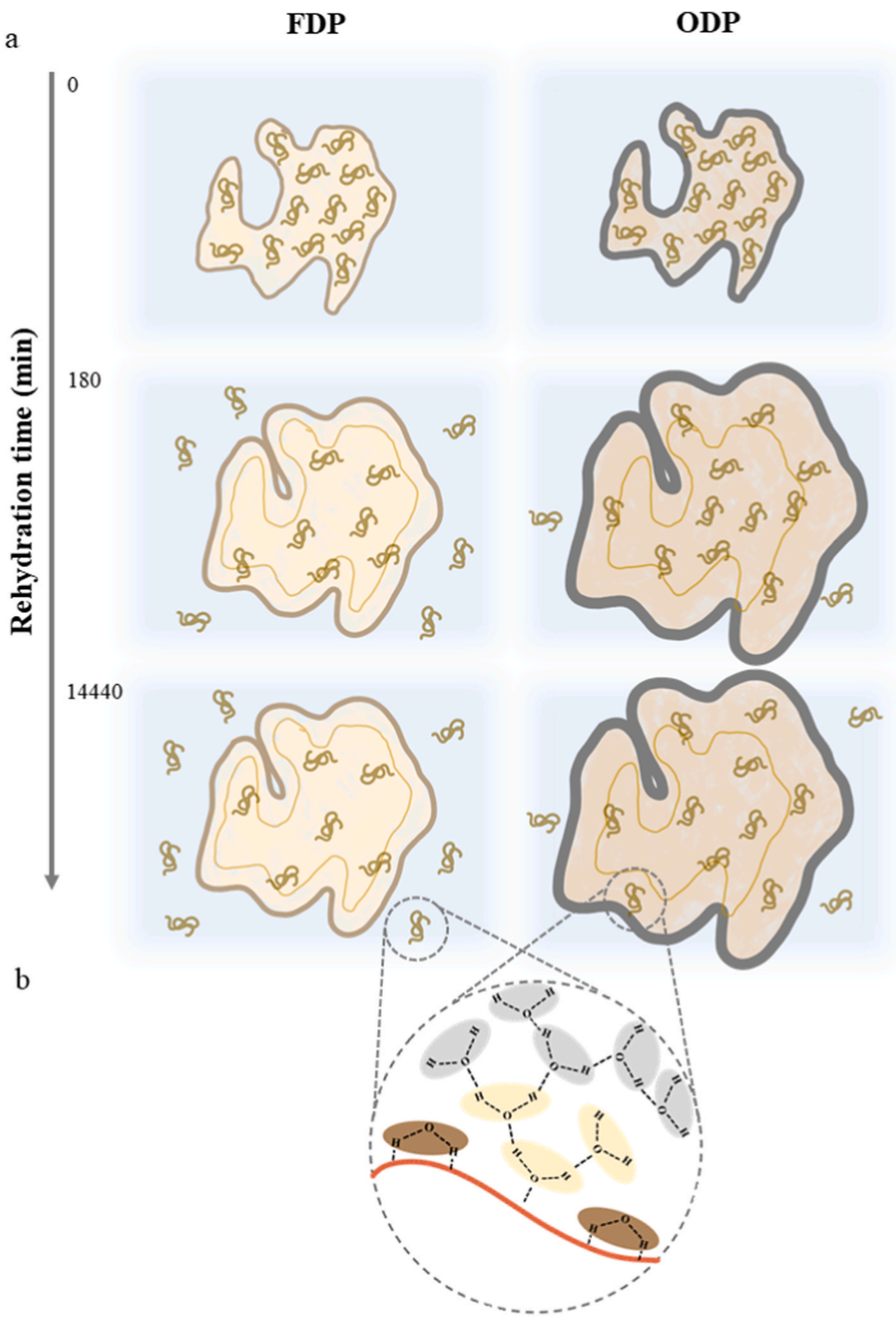


Fig. 7. (a) Rehydration of freeze-dried (FDP) and oven-dried (ODP) mamaku pith powder and release of mamaku polysaccharide (MP). (b) Interaction of MP with water in and outside the powder particle.

2014); potato: 47 to −53 °C (Anglea, Karathanos, & Karel, 1993)] below which the high viscosity of the matrix limits the movements of molecules. On heating above T_g, as during oven-drying, the glassy matrix changes to a soft and rubbery state, which allows molecules to move more freely (Bhatta, Stevanovic Janezic, & Ratti, 2020). The rubbery state reduces the mechanical properties of the plant cellular matrix, which as a result cannot develop stress to balance the capillary stresses, leading to shrinkage (*i.e.,* structural collapse) (Achanta, Okos, Cushman, & Kessler, 1997), as observed for mamaku pith. T_g is dependent on the moisture content of the plant product, and as drying continues, the moisture is removed, and subsequently, the plant cellular matrix transforms from a soft, rubbery state to a hard, glassy state (due to an increase in T_g) (Gulati & Datta, 2015). As the surface of the mamaku pith is exposed to heat during oven-drying, the surface temperature is higher than the inner temperature. Consequently, the rate of evaporation on the surface will be higher than the migration of the moisture from the inside of the matrix, leading to a faster transformation of the surface to a rigid glassy state, resulting in a stiff and denser structure on the surface (*i.e.,* causing case hardening) (Zhao et al., 2019). The phenomenon of collapse and case hardening during oven-drying leads to irreversible structural changes with shrunken capillaries; making the plant cellular matrix and subsequently ground powder denser, compact and rigid (Table 1, Fig. 2). On the other hand, during freeze-drying, the majority of water is frozen to ice, and only a small amount of unfrozen water will contribute to the T_g of the mamaku pith (Roos, 1998). Thus, the T_g of the frozen mamaku pith will elevate, which helps prevent the structure of the food matrix during sublimation, leading to a porous structure with lower density (Table 1, Fig. 2).

Structure-function: The changes in structure affect the interaction of powder particles with the environment (water). In the initial stage of hydration, the transfer of water from out to inside the powder is driven by capillary forces (Hedenus et al., 2000). Capillary forces depend on the porosity of the powder; thus, the porous FDP absorbs water faster than the denser ODP (Fig. 3a and b). Over time, the capillary forces will decrease, and water will transfer *via* diffusion. Inside the particle, different constituents of the particle interact with water molecules causing the particles to swell and increase in particle size (Figs. 3c and 7b). MP and other macromolecules present in the swollen (wet) layer of the particles formed a gelatinous layer around the particles (Fig. A2). The swelling of particles and the formation of a gelatinous layer is known to delay the rate of rehydration (Wangler et al., 2019; Wangler & Kohlus, 2018). For FDP and ODP, the rehydration process was long, and most considerable changes happened over the first 180 min of rehydration (Fig. 3c and d, 5, and 7a). Simultaneously, the water-soluble compounds will diffuse from the wet layer of the powder into the bulk water as the driving force for diffusion is the concentration difference between these two. The concentration of soluble materials in bulk water will increase with time, which will reduce the rate of diffusion of MP (Fig. 5) and other water-soluble compounds; as a result, the rate of solubilisation decreased with time, after 180 min (Fig. 3d). The diffusion of MP into the continuous phase and solubilisation of water-soluble compounds, in general, was significantly slower for ODP than for FDP (Fig. 3d, 5 and 7a). This difference could be due to the dense and hard structure (due to structural collapse and case hardening) formed during oven-drying. The inability of ODP to release enough MP in the continuous phase impaired its ability to form sufficient polymer-polymer interactions to exhibit shear-thickening behaviour (Fig. 4) and therefore did not have any effect on starch digestion (Fig. 6). In general, crystallinity and surface properties of the powders can affect the rehydration process, however, no striking difference was observed in XRD and FTIR for FDP and ODP (Fig. A6). Thus, the changes in functionality of ODP are most likely due to the formation of a hard and compact powder structure.

4. Conclusion

This study shows the effect of freeze-drying and oven-drying methods on the physical and functional properties of mamaku pith powder. Oven-drying resulted in a dense powder that trapped the MP tightly within the matrix, limiting the release of MP in the continuous phase. Thus, no shear-thickening behaviour was observed for ODP suspension. Freeze-drying, on the other hand, resulted in a porous structure that led to the rapid rehydration of powder and easy diffusion of MP into the continuous phase. The release of MP from FDP is a time-dependent process, and after sufficient MP is available in the continuous phase the shear-thickening behaviour is observed. These findings suggest that freeze-dried whole mamaku pith powder with retained shear-thickening behaviour can be used as an effective method for mamaku fronds to be made into a functional food ingredient as opposed to MP extract. Further work on improving the rehydration behaviour of powders, the stability of powders during storage and their incorporation into food systems is needed. Freeze-drying is a costly technique, so combining it with other drying methods such as microwave drying and atmospheric freeze-drying may be advantageous but need further investigation.

Funding

The research was funded by the High-Value Nutrition programme of The New Zealand National Science Challenges in the program *Mamaku whakaoraora* (Contract no. AUAX1902). The New Zealand Institute for Plant and Food Research Limited funded Akshay's PhD studies (PFR Contract no. 38041).

CRediT authorship contribution statement

Akshay Bisht: Conceptualization, Formal analysis, Investigation, Methodology, Validation, Visualization, Writing – original draft. **Kelvin K.T. Goh:** Conceptualization, Methodology, Supervision, Writing – review & editing. **Lara Matia-Merino:** Conceptualization, Methodology, Project administration, Supervision, Writing – review & editing.

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.

Data availability

Data will be made available on request.

Acknowledgements

The project was consulted with Prof. Dr. Nicholas Rahiri Roskruge (from the Māori leadership team, College of Science at Massey University) for cultural review and Mātuaranga Māori.

We thank Prof. Dr Anthony Paterson and Dr Qun (Jim) Chen for their valuable discussions and for proofreading the manuscript. We thank Dr. John Monro and Dr. Suman Mishra for their contribution to the *in vitro* analysis of the powders.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.foodhyd.2023.109683.

References

Achanta, S., Okos, M. R., Cushman, J. H., & Kessler, D. P. (1997). Moisture transport in shrinking gels during saturated drying. *AIChE Journal, 43*(8), 2112–2122.

Amidon, G. E., Meyer, P. J., & Mudie, D. M. (2017). Particle, powder, and compact characterization. In *Developing solid oral dosage forms* (pp. 271–293). Academic press.

Anglea, S. A., Karathanos, V., & Karel, M. (1993). Low-temperature transitions in fresh and osmotically dehydrated plant materials. *Biotechnology Progress, 9*(2), 204–209.

Araya-Farias, M., Makhlouf, J., & Ratti, C. (2011). Drying of seabuckthorn (Hippophae rhamnoides L.) berry: Impact of dehydration methods on kinetics and quality. *Drying Technology, 29*(3), 351–359.

Argyropoulos, D., Heindl, A., & Müller, J. (2011). Assessment of convection, hot-air combined with microwave-vacuum and freeze-drying methods for mushrooms with regard to product quality. *International Journal of Food Science and Technology, 46*(2), 333–342.

Bhatta, S., Stevanovic Janezic, T., & Ratti, C. (2020). Freeze-drying of plant-based foods. *Foods, 9*(1), 87.

Bisht, A., Goh, K. K., & Matia-Merino, L. (2023). The fate of mamaku gum in the gut: Effect on in vitro gastrointestinal function and colon fermentation by human faecal microbiota. *Food & Function, 14*(15), 7024–7039.

Bisht, A., Goh, K. K., Sims, I. M., Edwards, P. J., & Matia-Merino, L. (2023). Shear and temperature sensitivity of a shear-thickening biopolymer from the New Zealand black tree fern. *Food Hydrocolloids, 145*, Article 109075.

Bisht, A., Goh, K. K. T., Sims, I. M., Edwards, P. J. B., Monro, J. A., Mishra, S., & Matia-Merino, L. (submitted). Does harvesting age matter? Changes in structure and rheology of a shear-thickening polysaccharide from Cyathea medullaris as a function of age.

Bisht, A., Goyal, A., Sachdev, D., & Pasricha, R. (2019). Aminopropyl functionalized ordered mesoporous silica as an efficient adsorbent for separation of widely used acidulant citric acid from expired juices. *Separation Science and Technology, 54*(17), 2853–2862.

Blumenkrantz, N., & Asboe-Hansen, G. (1973). New method for quantitative determination of uronic acids. *Analytical Biochemistry, 54*(2), 484–489.

Boucheham, N., Galet, L., Patry, S., & Zidoune, M. N. (2019). Physicochemical and hydration properties of different cereal and legume gluten-free powders. *Food Science and Nutrition, 7*(9), 3081–3092.

Brownlee, I. A. (2011). The physiological roles of dietary fibre. *Food Hydrocolloids, 25*(2), 238–250.

Calín-Sánchez, Á., Kharaghani, A., Lech, K., Figiel, A., Carbonell-Barrachina, Á. A., & Tsotsas, E. (2015). Drying kinetics and microstructural and Sensory properties of black chokeberry (aronia melanocarpa) as affected by drying method. *Food and Bioprocess Technology, 8*(1), 63–74.

Caparino, O., Tang, J., Nindo, C., Sablani, S., Powers, J., & Fellman, J. (2012). Effect of drying methods on the physical properties and microstructures of mango (Philippine 'Carabao'var.) powder. *Journal of Food Engineering, 111*(1), 135–148.

Capuano, E. (2017). The behavior of dietary fiber in the gastrointestinal tract determines its physiological effect. *Critical Reviews in Food Science and Nutrition, 57*(16), 3543–3564.

Chen, Q., Li, Z., Bi, J., Zhou, L., Yi, J., & Wu, X. (2017). Effect of hybrid drying methods on physicochemical, nutritional and antioxidant properties of dried black mulberry. *Lebensmittel-Wissenschaft und -Technologie, 80*, 178–184.

Crowe, A. (2004). *A field guide to the native edible plants of New Zealand*. Auckland: Godwit.

Crowley, S., Kelly, A., Schuck, P., Jeantet, R., & O'mahony, J. (2016). Rehydration and solubility characteristics of high-protein dairy powders. *Advanced dairy chemistry*, 99–131.

Edwards, C. A., & Garcia, A. L. (2009). The health aspects of hydrocolloids. In G. O. Phillips, & P. A. Williams (Eds.), *Handbook of hydrocolloids* (2 ed., pp. 50–81). Cambrridge: CRC Press.

Englyst, H., & Hudson, G. (1987). Colorimetric method for routine measurement of dietary fibre as non-starch polysaccharides. A comparison with gas-liquid chromatography. *Food Chemistry, 24*(1), 63–76.

Ermis, E., & Özkan, M. (2021). Sugar beet powder production using different drying methods, characterization and influence on sensory quality of cocoa-hazelnut cream. *Journal of Food Science and Technology, 58*(6), 2068–2077.

Fang, Y., Selomulya, C., & Chen, X. D. (2007). On measurement of food powder reconstitution properties. *Drying Technology, 26*(1), 3–14.

Forny, L., Marabi, A., & Palzer, S. (2011). Wetting, disintegration and dissolution of agglomerated water soluble powders. *Powder Technology, 206*(1–2), 72–78.

Foster, T. (2008). *Plant heritage New Zealand: Te whakapapa o nga rakau: Interpreting the special features of native plants*. North Shore: Raupo.

Freudig, B., Hogekamp, S., & Schubert, H. (1999). Dispersion of powders in liquids in a stirred vessel. *Chemical Engineering and Processing: Process Intensification, 38*(4–6), 525–532.

Gaiani, C., Boyanova, P., Hussain, R., Pazos, I. M., Karam, M., Burgain, J., et al. (2011). Morphological descriptors and colour as a tool to better understand rehydration properties of dairy powders. *International Dairy Journal, 21*(7), 462–469.

Goh, K. K. T., Matia-Merino, L., Hall, C. E., Moughan, P. J., & Singh, H. (2007). Complex rheological properties of a water-soluble extract from the fronds of the black tree fern, Cyathea medullaris. *Biomacromolecules, 8*(11), 3414–3421.

Grossutti, M., & Dutcher, J. R. (2020). Hydration water structure, hydration forces, and mechanical properties of polysaccharide films. *Biomacromolecules, 21*(12), 4871–4877.

Gulati, T., & Datta, A. K. (2015). Mechanistic understanding of case-hardening and texture development during drying of food materials. *Journal of Food Engineering, 166*, 119–138.

Gürgen, S., Li, W., & Kuşhan, M. C. (2016). The rheology of shear thickening fluids with various ceramic particle additives. *Materials & Design, 104*, 312–319.

Hedenus, P., Mattsson, M. S., Niklasson, G., Camber, O., & Ek, R. (2000). Characterisation of instantaneous water absorption properties of pharmaceutical excipients. *International Journal of Pharmaceutics, 202*(1–2), 141–149.

Hogekamp, S., & Pohl, M. (2003). Porosity measurement of fragile agglomerates. *Powder Technology, 130*(1–3), 385–392.

Hogekamp, S., & Schubert, H. (2003). Rehydration of food powders. *Food Science and Technology International, 9*(3), 223–235.

Izli, N., & Polat, A. (2019). Freeze and convective drying of quince (Cydonia oblonga Miller.): Effects on drying kinetics and quality attributes. *Heat and Mass Transfer, 55*(5), 1317–1326.

Jaishankar, A., Wee, M. S. M., Matia-Merino, L., Goh, K. K. T., & McKinley, G. H. (2015). Probing hydrogen bond interactions in a shear thickening polysaccharide using nonlinear shear and extensional rheology. *Carbohydrate Polymers, 123*, 136–145.

Ji, J., Cronin, K., Fitzpatrick, J., Fenelon, M., & Miao, S. (2015). Effects of fluid bed agglomeration on the structure modification and reconstitution behaviour of milk protein isolate powders. *Journal of Food Engineering, 167*, 175–182.

Ji, J., Fitzpatrick, J., Cronin, K., Maguire, P., Zhang, H., & Miao, S. (2016). Rehydration behaviours of high protein dairy powders: The influence of agglomeration on wettability, dispersibility and solubility. *Food Hydrocolloids, 58*, 194–203.

Karam, M. C., Petit, J., Zimmer, D., Djantou, E. B., & Scher, J. (2016). Effects of drying and grinding in production of fruit and vegetable powders: A review. *Journal of Food Engineering, 188*, 32–49.

Lentle, R. G., Janssen, P. W. M., Goh, K. K. T., Chambers, P., & Hulls, C. (2010). Quantification of the effects of the volume and viscosity of gastric contents on antral and fundic activity in the rat stomach maintained ex vivo. *Digestive Diseases and Sciences, 55*(12), 3349–3360.

Li, P., Jin, Y., & Sheng, L. (2020). Impact of microwave assisted phosphorylation on the physicochemistry and rehydration behaviour of egg white powder. *Food Hydrocolloids, 100*, Article 105380.

Lim, M., Wu, H., Breckell, M., & Birch, J. (2006). Influence of the glass transition and storage temperature of frozen peas on the loss of quality attributes. *International Journal of Food Science and Technology, 41*(5), 507–512.

Matia-Merino, L., Goh, K. K. T., & Singh, H. (2012). A natural shear-thickening water-soluble polymer from the fronds of the black tree fern, Cyathea medullaris: Influence of salt, pH and temperature. *Carbohydrate Polymers, 87*(1), 131–138.

Mazzanti, V., & Mollica, F. (2020). A review of wood polymer composites rheology and its implications for processing. *Polymers, 12*(10), 2304.

McGowan, R. E. (2014). *Rongoa maori: A practical guide to traditional maori medicine*. Robert McGowan.

Michalska, A., Wojdyło, A., Lech, K., Łysiak, G. P., & Figiel, A. (2017). Effect of different drying techniques on physical properties, total polyphenols and antioxidant capacity of blackcurrant pomace powders. *Lebensmittel-Wissenschaft und -Technologie, 78*, 114–121.

Monro, J. A., Bisht, A., Mishra, S., Goh, K. K. T., & Matia-Merino, L. (unpublished). Cyathea medullaris (Mamaku) pith has functional attributes of potential importance to human health.

Monro, J. A., Mishra, S., & Venn, B. (2010). Baselines representing blood glucose clearance improve in vitro prediction of the glycaemic impact of customarily consumed food quantities. *British Journal of Nutrition, 103*(2), 295–305.

Muliterno, M. M., Rodrigues, D., de Lima, F. S., Ida, E. I., & Kurozawa, L. E. (2017). Conversion/degradation of isoflavones and color alterations during the drying of okara. *Lebensmittel-Wissenschaft und -Technologie, 75*, 512–519.

Nep, E. I., & Conway, B. R. (2011). Physicochemical characterization of grewia polysaccharide gum: Effect of drying method. *Carbohydrate Polymers, 84*(1), 446–453.

Park, N., Rathee, V., Blair, D. L., & Conrad, J. C. (2019). Contact networks enhance shear thickening in attractive colloid-polymer mixtures. *Physical Review Letters, 122*(22), Article 228003.

Pathare, P. B., Opara, U. L., & Al-Said, F. A.-J. (2013). Colour measurement and analysis in fresh and processed foods: A review. *Food and Bioprocess Technology, 6*(1), 36–60.

Premathasan, N., & Taylor, S. E. (2018). Viscometric analysis of the hydration of a surface cross-linked EM-HEC polymer. *European Polymer Journal, 102*, 111–119.

Pryamitsyn, V., & Ganesan, V. (2006). Mechanisms of steady-shear rheology in polymer-nanoparticle composites. *Journal of Rheology, 50*(5), 655–683.

Ratti, C. (2001). Hot air and freeze-drying of high-value foods: A review. *Journal of Food Engineering, 49*(4), 311–319.

Riley, M. (1994). *Māori healing and herbal: New Zealand ethnobotanical sourcebook*. Auckland: Viking Sevenseas N.Z.

Roos, Y. H. (1998). Role of water in phase-transition phenomena in foods. In M. A. Rao, & R. W. Hartel (Eds.), *Phase/state transitions in foods: Chemical, structural and rheological changes* (pp. 57–86). New York: Marcel Dekker, Inc.

Salleh, N., Goh, K. K. T., Waterland, M. R., Huffman, L. M., Weeks, M., & Matia-Merino, L. (2022). Complexation of anthocyanin-bound blackcurrant pectin and whey protein: Effect of pH and heat treatment. *Molecules, 27*(13), 4202.

Samoticha, J., Wojdyło, A., & Lech, K. (2016). The influence of different the drying methods on chemical composition and antioxidant activity in chokeberries. *LWT-Food Science & Technology, 66*, 484–489.

Schubert, H. (1993). Instantization of powdered food products. *International Chemical Engineering, 33*(1), 28–45.

Silva, A. F., Abreu, H., Silva, A. M., & Cardoso, S. M. (2019). Effect of oven-drying on the recovery of valuable compounds from ulva rigida, gracilaria sp. and fucus vesiculosus. *Marine Drugs, 17*(2), 90.

Stange, U., Scherf-Clavel, M., & Gieseler, H. (2013). Application of gas pycnometry for the density measurement of freeze-dried products. *Journal of Pharmaceutical Sciences, 102*(11), 4087–4099.

Verma, R. C., & Sharma, G. P. (2018). Freeze drying. In P. K. Nema, B. P. Kaur, & A. S. Mujumdar (Eds.), *Drying technology for foods: Fundamentals and applications* (pp. 57–70). Boca Raton: CRC Press, Taylor & Francis Group.

Wang, Q., Ellis, P. R., & Ross-Murphy, S. B. (2002). Dissolution kinetics of guar gum powders. I. Methods for commercial polydisperse samples. *Carbohydrate Polymers, 49*(2), 131–137.

Wangler, J., & Kohlus, R. (2017). Dynamics of capillary wetting of biopolymer powders. *Chemical Engineering & Technology, 40*(9), 1552–1560.

Wangler, J., & Kohlus, R. (2018). Development and validation of methods to characterize rehydration behavior of food hydrocolloids. *Food Hydrocolloids, 82*, 500–509.

Wangler, J., Teichmann, H., Konstanz, E., & Kohlus, R. (2019). Experimental investigation and simulation of rehydration dynamics of biopolymer powders. *Powder Technology, 355*, 461–473.

Warren, J., Offenberger, S., Toghiani, H., Pittman, C. U., Jr., Lacy, T. E., & Kundu, S. (2015). Effect of temperature on the shear-thickening behavior of fumed silica suspensions. *ACS Applied Materials & Interfaces, 7*(33), 18650–18661.

Wee, M. S. M., Lentle, R. G., Goh, K. K. T., & Matia-Merino, L. (2017). The first of the viscoceuticals? A shear thickening gum induces gastric satiety in rats. *Food & Function, 8*(1), 96–102.

Wee, M. S. M., Matia-Merino, L., Carnachan, S. M., Sims, I. M., & Goh, K. K. T. (2014). Structure of a shear-thickening polysaccharide extracted from the New Zealand black tree fern, Cyathea medullaris. *International Journal of Biological Macromolecules, 70*, 86–91.

Xin, Y., Zhang, M., & Adhikari, B. (2013). Effect of trehalose and ultrasound-assisted osmotic dehydration on the state of water and glass transition temperature of broccoli (Brassica oleracea L. var. botrytis L.). *Journal of Food Engineering, 119*(3), 640–647.

Xu, C., Li, Y., & Yu, H. (2014). Effect of far-infrared drying on the water state and glass transition temperature in carrots. *Journal of Food Engineering, 136*, 42–47.

Yekeler, M., Ulusoy, U., & Hiçyılmaz, C. (2004). Effect of particle shape and roughness of talc mineral ground by different mills on the wettability and floatability. *Powder Technology, 140*(1–2), 68–78.

Zhang, L., Qiao, Y., Wang, C., Liao, L., Liu, L., Shi, D., … Xu, Q. (2019). Effects of freeze vacuum drying combined with hot air drying on the sensory quality, active components, moisture mobility, odors, and microstructure of kiwifruits. *Journal of Food Quality, 2019*.

Zhao, Y., Bi, J., Yi, J., Njoroge, D. M., Peng, J., & Hou, C. (2019). Comparison of dynamic water distribution and microstructure formation of shiitake mushrooms during hot air and far infrared radiation drying by low-field nuclear magnetic resonance and scanning electron microscopy. *Journal of the Science of Food and Agriculture, 99*(6), 2826–2834.