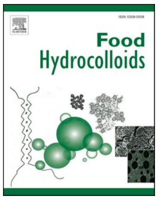
Food Hydrocolloids 145 (2023) 109075

Contents lists available at ScienceDirect

Food Hydrocolloids

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



Shear and temperature sensitivity of a shear-thickening biopolymer from the New Zealand black tree fern

Akshay Bisht [a], Kelvin K.T. Goh [a], Ian M. Sims [b], Patrick J.B. Edwards [c], Lara Matia-Merino [a,*]

[a] *School of Food and Advanced Technology, Massey University, Palmerston North, New Zealand*
[b] *The Ferrier Research Institute, Victoria University of Wellington, New Zealand*
[c] *School of Natural Sciences, Massey University, Palmerston North, New Zealand*

ARTICLE INFO

Keywords:
Mamaku polysaccharide
Shear-thickening
Shear sensitivity
Temperature sensitivity
Shear rheology
Molecular structure

ABSTRACT

Mamaku polysaccharide (MP) is a water-soluble shear-thickening biopolymer that has shown potential to be used in the design of novel food products targeting satiety management and weight loss. During the processing of MP at industrial scale, the polymer may be exposed to high temperature and shear, which could affect its rheological behaviour. Thus, herein we subjected extracted MP to high shear (between 1000–8000 rpm at various times, using a lab-scale high-shear mixer) and temperature treatment (between 65 and 115 °C, for 30 min) and investigated the changes in molecular structure and rheological properties. The temperature treatment disintegrated the backbone of MP into smaller fragments (molecular weight-M_w, reduced from $\sim 3.9 \times 10^6$ Da with no heat, to $\sim 0.6 \times 10^6$ Da at 115 °C), which caused a reduction in viscosity and in the extent of shear-thickening as well as an increase in the damping factor (G''/G'). Similar rheological trends were observed post-shear treatment, however, there was no evidence of depolymerisation, with the M_w, constituent sugar composition and NMR spectra (^{1}H and ^{13}C) being unaffected. It is suggested that the changes in rheological behaviour after shear treatment could be due to changes in the re-arrangement of MP molecules, which led to a compact and folded structure due to increased intra-molecular interactions. The results, therefore, indicate that modification of MP molecules during the industrial process such as shearing and heating should be considered as it may adversely affect the rheological properties of the product where MP is incorporated and the expected physiological benefits in the gastrointestinal tract.

1. Introduction

The New Zealand black tree fern (*Cyathea medullaris*), commonly known as mamaku, is a native fern grown across the Pacific Islands. Mucilage from mamaku fern has been used for treating wounds, bruises and boils and as a remedy for sore stomach and diarrhoea (Crowe, 2004; Foster, 2008; McGowan, 2014; Riley, 1994). Some of these physiological effects could be attributed to a non-starch biomacromolecule, mamaku polysaccharide (MP), mainly present in the fronds of the tree fern. The MP is an anionic glucuronomannan polymer comprising of a repeating backbone of β-1,4-linked methylesterified glucopyranosyl uronic acid and α-1,2-linked mannopyranosyl residues, branched at O-3 of 45% and at both O-3 and O-4 of 53% of the mannopyranosyl residues and side chain made of galactose, arabinose, non-methylesterified glucuronic acid and other simple sugars (Wee, Matia-Merino, Carnachan, Sims, & Goh, 2014). Investigation into the rheological properties revealed that MP can exhibit Newtonian, shear-thickening and shear-thinning behaviour depending on concentration and applied shear rate (Goh, Matia-Merino, Hall, Moughan, & Singh, 2007; Matia-Merino, Goh, & Singh, 2012).

Shear-thickening behaviour is uncommon for natural polysaccharides. This novel rheological behaviour of MP can potentially be used to develop food products that possess functionality suitable for satiety management to curb obesity epidemic (Wee, Lentle, Goh, & Matia-Merino, 2017); possibly reduce the glycaemic response for individuals suffering from diabetes or as a fibre to improve colon health (Bisht, Goh, & Matia-Merino, 2023). However, during manufacturing, MP may be subjected to treatments such as high shear and temperature which could adversely affect the structural and rheological properties, thereby limiting the use of MP as a potential natural active ingredient in

---

* Corresponding author. School of Food and Advanced Technology, Massey University, Private Bag 11222, 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), Ian.Sims@vuw.ac.nz (I.M. Sims), P.J.Edwards@massey.ac.nz (P.J.B. Edwards), l.matia-merino@massey.ac.nz (L. Matia-Merino).

https://doi.org/10.1016/j.foodhyd.2023.109075
Received 24 April 2023; Received in revised form 28 June 2023; Accepted 7 July 2023

food products. Thus, from both technological and physiological perspectives, understanding the effects of processing on MP is essential.

High shear equipment such as high-speed mixers, colloid mills, high-pressure homogenisers and microfluidizers are commonly used in the food industry for emulsification, particle size reduction and modify textural properties of food products. Kivelä, Pitkänen, Laine, Aseyev, and Sontag-Strohm (2010) investigated the effect of the use of a colloid mill, a homogeniser and a microfluidizer on the structure and rheology of oat β-glucan and reported a permanent decrease in viscosity with a simultaneous reduction in molecular weight (M_w), depending on the energy input. Several authors have reported shear- (from mechanical action) induced degradation of various polysaccharides, including flaxseed gum (Wang, Li, Wang, & Xue, 2011), cashew tree gum (Porto, Augusto, Terekhov, Hamaker, & Cristianini, 2015), acacia gum (Al-Assaf, Sakata, McKenna, Aoki, & Phillips, 2009), pectin (Corredig & Wicker, 2001; Shpigelman, Kyomugasho, Christiaens, Van Loey, & Hendrickx, 2015; Xie et al., 2018), xanthan (Eren, Santos, & Campanella, 2015; Harte & Venegas, 2010; Laneuville, Turgeon, & Paquin, 2013), tragacanth gum (Farzi, Yarmand, Safari, Emam-Djomeh, & Mohammadifar, 2015; Keivanfard, Nasirpour, Barekat, & Keramat, 2022), methylcellulose (Floury, Desrumaux, Axelos, & Legrand, 2002), *k*-carrageenan (Harte & Venegas, 2010), tamarind seed polysaccharide (Xie et al., 2021), scleroglucan (Zeng, Wang, Shan, Yu, & Zhou, 2021) and exopolysaccharide from lactic acid bacteria (Nachtigall et al., 2019).

The shear sensitivity of a polysaccharide is not solely dependent on the imposed shear but is simultaneously governed by the structural features of the polymer. According to Pohl's equation, a polymer is affected by shear treatment if the threshold ($\eta \times \gamma \times M_W^2$) is $\geq 1 \times 10^{14}$, highlighting the strong dependence on the molecular weight of the polysaccharide (Mackenzie & Jemmett, 1971). This equation was first reported in 1943 for polymer blend oils, however the threshold value needs to be further examined and validated for a variety of polymers. Nevertheless, the molecular weight dependence of shear is confirmed by many other authors (Kasaai, Charlet, Paquin, & Arul, 2003; Nilsson, Leeman, Wahlund, & Bergenståhl, 2006; Villay et al., 2012; Zaitoun et al., 2012), suggesting the frictional force experienced by the polymer is proportional to the macromolecule length. Furthermore, globular branched structures, such as that of gum Arabic, were reported to be largely unaffected by shear treatment, while linear flexible polymers, such as guar gum, underwent depolymerisation (Villay et al., 2012). Likewise, apple pectin with a greater proportion of neutral sugars in the side chains—giving it a more compact structure than citrus pectin—was reported to resist depolymerisation on shearing (Shpigelman et al., 2015). The presence of large monomer units, the use of poor solvents and the specific pH of the system, all affect the flexibility of the polymer which can make it less sensitive to shear (Shpigelman et al., 2015; Zaitoun et al., 2012). Shear sensitivity is also affected by the inherent strength of the backbone molecules, for example, Si–O bonds (bond energy = 89.3 kcal/mol) are more resistant to shear than C–C bonds (58.6 kcal/mol) (Mackenzie & Jemmett, 1971).

High temperature treatments, such as those used during pasteurisation, sterilisation, blanching and drying for making food products microbiologically safe, inactivating enzymes, and cooking the product, may alter the structure and functionality of polysaccharides and, as a result, impact their functionality when used in food products (Keivanfard et al., 2022; Owen, Tung, & Paulson, 1992). Temperature-induced depolymerisation is has been reported in literature *e.g.*, for β-glucan, detarium gum and dextran (Wang, Wood, Cui, & Ross-Murphy, 2001), diutan gum, xanthan, scleroglucan (Liang, Han, Chen, Su, & Feng, 2019) and exopolysaccharides from lactic acid bacteria (Nachtigall, Rohm, & Jaros, 2021). However, the extent of thermal degradation of the polymer chain varies between different polymers. Robal, Truus, Volobujeva, Mellikov, and Tuvikene (2017) studied six different polysaccharides and observed that degradation at high-temperature decreases in the order of agaro > funoran > furcellaran > *k*-carrageenan > λ-carrageenan > *L*-carrageenan attributing the greater stability to the presence of methoxy groups which stabilises the polymer chains.

Shear and temperature sensitivity for some macromolecules has been reported but cannot be generalised because of differences in the polymer structure. To the best of our knowledge, there is no literature systematically describing the shear and temperature sensitivity of MP. It is hypothesised that shear and temperature treatment might degrade MP molecules causing fragmentation of the polymer chain and affecting rheological functionality. Therefore, the present work aims to investigate the sensitivity of MP towards high shear and temperature, by characterizing the rheological properties, M_w, size and structural changes at the molecular level after various treatments.

2. Material and methods

2.1. Mamaku gum extraction

The mamaku fronds were harvested from a farm at Waverley, Taranaki, in New Zealand, between the 10th and 30th of October 2020 following local practices. Gum extraction was carried out as described by Goh et al. (2007) with some modifications. Briefly, the fronds were chopped, disintegrated, and heated (~55 °C, 5 min) with continuous stirring. The heated mixture was transferred into a mesh bag and crude gum was separated. The crude gum extract was left undisturbed overnight at 4 °C for the remains of pulp to sediment by gravity followed by separating the clearer top layer using a siphon. The collected 'crude gum extract' was concentrated using a vacuum evaporator (BÜCHI Labortechnik AG, Flawil, Switzerland) and stored at −18 °C until use. The crude mamaku gum consists of sugar (~35% - using gas chromatography), fibre (~16% - using AOAC 991.43), ash (~14% - using AOAC 942.05), uronic acid (~6% - using *m*-hydroxydiphenyl spectrophotometric method), protein (~5% - using AOAC 968.06) and starch (~2% - using AOAC 996.11) on a dry weight basis.

2.2. Shear and temperature treatments

For the shear treatment, 300 ml of crude mamaku gum (2% w/w, total solids) was transferred into a beaker (17.5 × 8.7 cm) and subjected to different rotational speeds (1000–8000 rpm) for 1 min or at 5000 rpm from 30 s to 20 min using a bench-top high-shear mixer (Silverson, L4RT, Chesham, England—attached with emulsor screen of perforation ~1 mm and internal diameter ~3 cm). The temperature did not exceed 50 °C during the shear treatment. The shear developed between the high-shear mixer shaft and the beaker was calculated to be about 240–2000 s^{-1} using the Magules equation:

$$\dot{\gamma} = \frac{2\omega}{1 - \frac{r_1^2}{r_2^2}} \qquad \text{Eq. 1}$$

where, ω is the angular velocity and r_1 and r_2 are the radius of the shaft and beaker respectively (Anton Paar). However, the calculated value may not be a true representation of the shear experienced by the polysaccharides, as the flow of the fluid is non-uniformly distributed and there is additional shear developed within the hollow emulsor screen attached (Sisodia, Rajak, Pathak, & Guria, 2015). Additionally to shear, centrifugal forces, suction, turbulence, and cavitation may also affect the polysaccharide—using one value of shear will not reflect all the events. Thus, in this article, shear treatment is represented in terms of the rotational speed of the instrument (*i.e.*, 1k-8k rpm) and not the true shear experienced by the polysaccharide. Shear-treated samples are labelled as rotational speed-treatment time, for example, 2k-1 min and 5k-20 min. Though efforts were made to study the effect of 'shear only' on the crude mamaku gum using a rheometer, the rod-climbing effect made it difficult as prolonged shearing caused the expulsion of the gum from the gap between the geometries. An in-house built capillary viscometer was also used to apply high shear, but the limited duration of the applied shear (fractions of a second) and the incorporation of air bubbles into the gum after shearing, hindered an accurate sample analysis.

For the temperature treatment, crude mamaku gum (100 ml, 2% w/w, total solids) was heated in a water bath at different temperatures (65–95 °C) for a period of 30 min each, and in the retort at 115 °C for 30 min, followed by cooling to room temperature using an ice bath. This range of temperatures is commonly used in the food industry for food safety reasons. The untreated crude mamaku gum was used as a control.

The samples post shear or temperature treatment were immediately characterized in terms of their rheological properties and were further purified ('purified gum fraction') for molecular and structural analysis. The purification process involved ultra-centrifugation (Sorvall WX Ultra 100, T-865 motor, Thermo-Fisher Scientific Inc., Waltham, Massachusetts, USA) at 250,000 *g* for 1 h, followed by dialysis (molecular weight cut-off: 12,000–14,000 Da) in reducing NaCl concentrations (0.01M, 0.001M and milli-Q water only) for ~42 h at 4 °C, then freeze-dried.

2.3. Rheology

Rheological measurements were performed using a Paar Physica MCR 302 rheometer (Anton-Paar, Graz, Austria) in controlled shear rate (CSR) mode at 20.0 ± 0.1 °C. Viscosity profiles were measured using a cup-and-bob geometry (CC27 and C-PTD 200) and data was recorded using Rheoplus/32 software (Version 3.62) using a log-ramp profile from 30 s to 2 s (initial to final). The relative change (%) in viscosity at a specific shear rate, with respect to the control, was calculated using:

$$Relative\ change = \frac{\eta_{control} - \eta_{treated}}{\eta_{control}} \times 100 \qquad \text{Eq. 2}$$

where, $\eta_{control}$ is the viscosity of the control sample and $\eta_{treated}$ is the viscosity of each sample after the shear or temperature treatment.

Oscillatory measurements (frequency sweep) were performed in the range of 0.01–20 Hz at constant 5% strain (within the linear viscoelastic region) using the double gap geometry (DG- 26-7 and C-PTD 200). Samples were allowed to rest for 5 min after being loaded, before the start of the experiment, reducing any shear history effect and allowing for temperature equilibration.

2.4. Size-exclusion chromatography coupled with multi-angle laser light scattering (SEC-MALLS)

Molecular weight analysis of temperature and shear-treated gum samples was performed using a high-performance liquid chromatography (HPLC) system (Shimadzu, Kyoto, Japan) coupled with multi-angle laser light scattering (Dawn Heleos 8+, Wyatt Technology Corp., Goleta, California, USA), as described by Goh, Matia-Merino, Pinder, Saavedra, and Singh (2011). The purified gum samples were centrifuged at 30,000 *g* for 1 h, followed by injection (20 μl) into the HPLC system with 0.1 M NaCl mobile phase at a flow rate of 0.5 ml/min. Separation was achieved using two size-exclusion columns in series with a guard column (OHpak SB-G, SB-804 HQ and SB-806M HQ columns, Shodex, Tokyo, Japan) at 25 °C. The Astra software (Version 6.1.1.17, Wyatt Technology) was used to analyse the light scattering peak using the Zimm plot with an incremental refractive index (*dn/dc*) of 0.178 ml/g.

2.5. Dynamic light scattering

The z-average radius of purified mamaku gum (0.5% w/w redispersed in 0.1 M NaCl overnight) was determined *via* dynamic light scattering using a Zetasizer Pro (Malvern Instruments Ltd., Malvern, England). Each sample was filled in low-volume polystyrene disposable cuvettes (ZEN0040) and the z-average readings were taken at 90° scattering light using a refractive index of 1.55 for MP. The reflective index of the dispersant (water) used was 1.33. The temperature of the samples was controlled at 20 ± 0.1 °C during the measurement. The zeta potential of MP was unaltered after a change in M_w (data not published).

2.6. Constituent sugar analysis and NMR

The constituent sugar composition of purified gum was determined using high-performance anion-exchange chromatography (HPAEC) after hydrolysis to its component monosaccharides, as described by De Ruiter, Schols, Voragen, and Rombouts (1992) with modifications (Wee et al., 2014). Briefly, duplicate samples (400 μg) were hydrolysed with methanolic HCl (3 M, 500 μl, 80 °C, 18 h), followed by aqueous trifluoroacetic acid (TFA, 2.5 M, 500 μl, 120 °C, 1 h). The resulting hydrolysates were dried, diluted with Type 1 water (to 80 μg/ml) and analysed on a CarboPac PA-1 (4 × 250 mm) column equilibrated in 20 mM NaOH and eluted with a simultaneous gradient of NaOH and NaOAc at 30 °C and a flow rate of 1 ml/min.

The purified mamaku gum samples were deuterium exchanged by freeze-drying twice with D_2O and dissolved in D_2O at 6.7 mg/ml, with the addition of acetone (0.4% v/v) as an internal standard, set at 31.45 ppm (^{13}C) and 2.225 ppm (^{1}H). NMR data were collected on a Bruker Avance Neo 700 MHz NMR spectrometer (Bruker BioSpin, Rheinstetten, Germany), equipped with a 5 mm TCI cryoprobe (fitted with a Z-gradient coil), at 65 °C. Spectra were analysed and processed in Mestranova (Version 14.1.2).

2.7. Urea treatment

The crude mamaku gum sample (4% w/w) was shear-treated and mixed with an equal volume of 10 M urea (to give a final concentration of 2% gum and 5 M urea) for 15 min at 200 rpm at 20 °C, followed by rheological analysis.

2.8. Statistical analysis

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

3. Results and discussion

3.1. Rheological analysis

The effects of shear and temperature treatments on the rheological profile of crude mamaku gum (2% w/w, total solids) are shown in Figs. 1 and 2. The control sample (no treatment) displayed the typical three-phase rheological behaviour of mamaku gum, namely Newtonian at a low shear rate (<2 s^{-1}), shear-thickening at an intermediate shear rate (2-5 s^{-1}) and shear-thinning at higher shear rate (>5 s^{-1}). This distinctive behaviour of MP has been attributed to transient molecular bonds being formed at specific shear rates. At low shear, the rate of formation of intermolecular linkages will be equal to the rate of bond disruption, thus, a constant viscosity is observed. As the shear rate increases, MP chains start to unfold and stretch, exposing sites for intermolecular interactions, and promoting the shear-thickening effect. Finally, at a higher shear rate, intermolecular interactions start to break much faster than they are formed again, leading to shear-thinning behaviour (Goh et al., 2007; Matia-Merino et al., 2012; Wee, Matia-Merino, & Goh, 2015).

Upon shear treatment, the rheological profile—including shear-thickening behaviour—of mamaku gum was retained but the following general trends (relative to the control) were observed with an increasing intensity of the shear (Fig. 1 and Table A.1, A.2): (i) viscosity decreased after MP was subjected to shear—the higher the intensity or

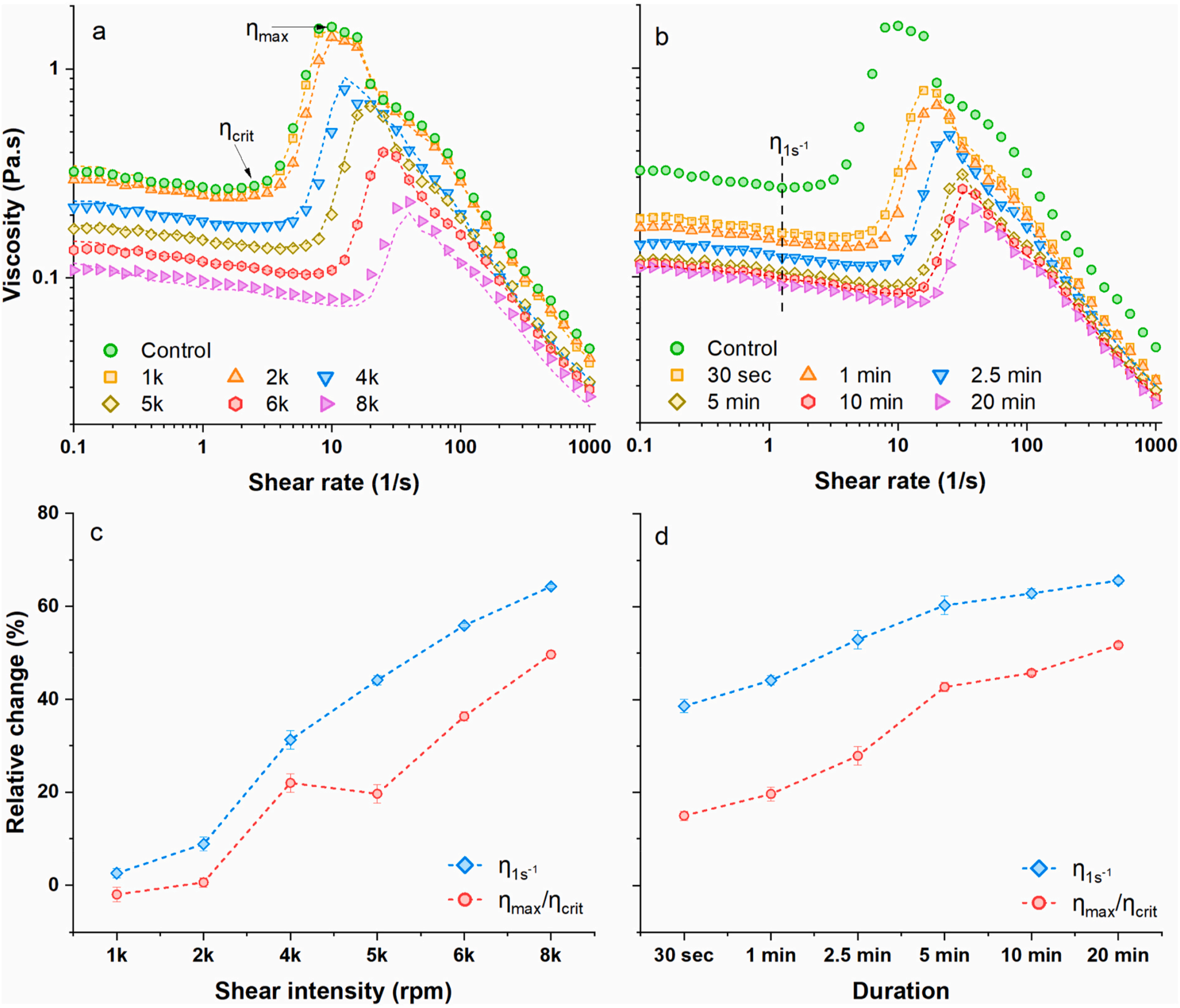


Fig. 1. Viscosity profiles of crude mamaku gum (2% w/w total solids) after shear treatment at (a) 1k-8k rpm for 1 min and (b) 5k rpm for 30 sec-20 min. Dash lines (in a, b) represent the viscosity profile after 48 h storage at 4 °C. Relative change (%) in viscosity at 1 s^{-1}, $\eta_{(1s-1)}$, and extent of shear-thickening, η_{max}/η_{crit}, after shear treatment at (c) 1k-8k rpm for 1 min and (d) 5k rpm for 30 sec-20 min. Values are plotted as means ± standard deviation (n = 3). Measurements were taken using cup-and-bob geometry at 20 °C. η_{max}, maximum viscosity (Pa.s); η_{crit}, critical viscosity (Pa.s).

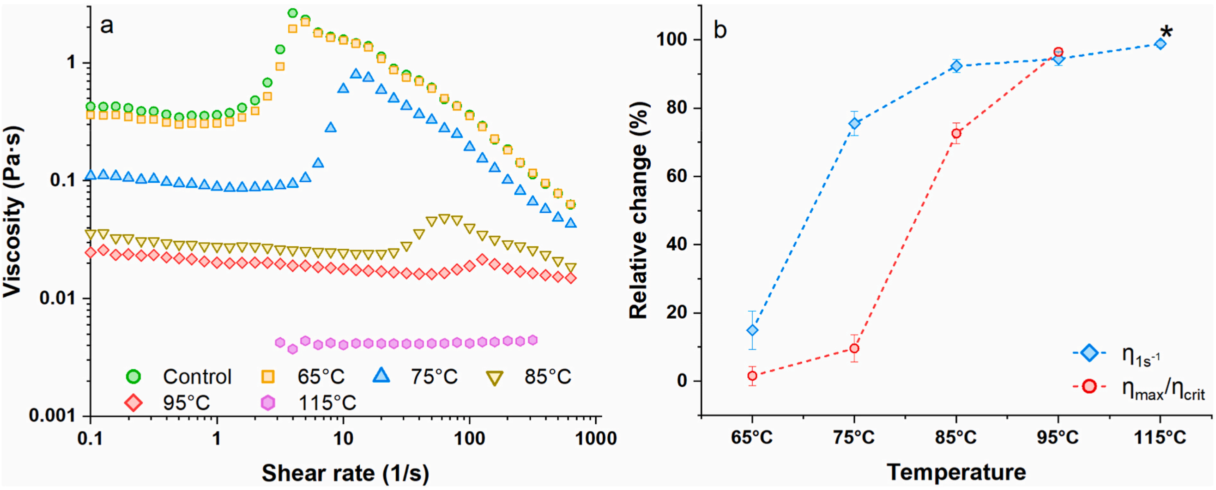


Fig. 2. (a) Viscosity profiles of crude mamaku gum (2% w/w total solids) after temperature treatment between 65 and 115 °C for 30 min. (b) Relative change (%) in viscosity at 1 s^{-1}, $\eta_{(1s-1)}$, and extent of shear-thickening, η_{max}/η_{crit}, after temperature treatment. (*): Newtonian behaviour at 115 °C treatment. Values are plotted as means ± standard deviation (n = 3). Measurements were taken using cup-and-bob geometry at 20 °C.

time of shear, the lower is the viscosity of the MP. For example, at 1 s^{-1}, viscosity was reduced by ~56% and ~60% after treatment at 6k-1 min and 5k-5 min, respectively; (ii) the extent of shear-thickening, η_{max}/η_{crit} (defined as the ratio of maximum viscosity, η_{max}, to viscosity at the onset of shear-thickening, η_{crit}) was reduced by ~50% and ~52% after 8k-1 min and 5k-20 min treatment, respectively; (iii) an increase in the critical shear rate, γ_{crit}, (defined as the shear rate at the onset of shear-thickening) from ~2.51 s^{-1} for control to ~12.6 s^{-1} after 8k-1 min and ~15.8 s^{-1} after 5k-20 min treatments, was observed.

The shear sensitivity of a biopolymer is affected by both the intensity of the applied shear and the duration of exposure. Interestingly, 5k treatment for 30 s caused ~39% reduction in viscosity (measured at 1 s^{-1}) which was only further reduced an additional ~26% after 19 min, whereas 8k treatment, had ~65% reduction after 1 min indicating that the shear sensitivity of MP is influenced by both the applied shear and duration of the shear treatment, with the former having a stronger impact on the viscosity than the latter. These results are in alignment with previous observations by Villay et al. (2012), who reported that for guar gum, sodium alginate, and gum arabica, the first cycle during high-pressure homogenization had a stronger impact on viscosity reduction than the subsequent cycles and the reduction increased with increasing pressure.

In general, large and flexible macromolecules, such as MP, favour random coil conformations and have high entanglement density (Rudin & Schreiber, 1983). On subjecting them to high shear, the polysaccharide chain stretches, and the entanglement density reduces (*i.e.*, breakage of intermolecular interactions) causing a decrease in viscosity (Fig. 1). However, this decrease in viscosity is typically temporary and will revert as the polymer return to the original equilibrium state once the shear forces are removed. The rate of re-entanglement is generally slower, as it depends on diffusion alone, compared to the rate of disentanglement which is favoured by applied shear (Rudin & Schreiber, 1983). Thus, the time-dependent recovery of mamaku gum after shear was tested. Samples were allowed to rest for 48 h at 4 °C, after exposure to shear, and then again examined for rheological behaviour (shown as dash lines in Fig. 1a and b). It is clear that there was no significant recovery in the viscosity for any of the samples after storage (compared to before storage). This indicates that the loss of viscosity in mamaku gum was irreversible and remained somewhat permanent within the duration of our observation (48 h). Depending on the severity of shear treatment, the reduction in viscosity of a polysaccharide solution in general could be the result of one or more factor(s), such as disruption of aggregates or microgels, breakdown of double-strand structures (*e.g.*, for DNA and xanthan gum), reduction in M_w, changes in polydispersity and alteration in secondary structures (Eren et al., 2015; Harrington & Zimm, 1965; Laneuville et al., 2013). A similar reduction in viscosity has been reported for cashew tree gum (Porto et al., 2015), puka gum (Riana, Sims, & Matia-Merino, 2022), pectin (Shpigelman et al., 2015; Xie et al., 2018) and tamarind seed polysaccharide (Xie et al., 2021) when subjected to shear (from mechanical action). These authors collectively suggested shear-led depolymerisation as the primary cause of viscosity reduction. On the contrary, an increase in viscosity for tragacanth gum due to the breakdown of larger aggregates and unfolding of the structures post shear treatment was reported (Farzi et al., 2015).

Similar to shear exposure, temperature treatment caused a reduction in viscosity at all shear rates in a temperature-dependent manner (Fig. 2). The viscosity, at 1 s^{-1}, was reduced by ~15% after heating mamaku gum at 65 °C for 30 min, which drastically decreased by ~75% after heating at 75 °C and ultimately decreased by ~99% after 115 °C treatment. Simultaneously, η_{max}/η_{crit} was reduced by ~10% after heating at 75 °C with a further reduction by ~97% at 95 °C, finally losing the shear thickening behaviour at 115 °C. Furthermore, the γ_{crit} increased from ~1 s^{-1} for the control and 65 °C treated samples, to ~4 s^{-1} and ~63 s^{-1} for 75 °C and 95 °C treated samples, respectively (Table A.3). These changes in the viscosity profiles collectively suggest that there may be thermal degradation of the polysaccharide *i.e.*, breakdown leading to smaller chain fragments in a temperature-dependent manner.

In addition to the viscosity profiles, the viscoelastic behaviour of the shear and temperature-treated samples was also studied within the linear region (Fig A.1). It was observed that for the control, both—storage modulus, G' and loss modulus, G''—increased with increasing frequency, with the 'liquid-like' behaviour ($G'' > G'$) dominating at low frequencies (<0.5 Hz) and both moduli becoming equal above 0.5 Hz. With the shear and temperature treatments, a similar trend of an increase in G' and G'' with increasing frequency was observed, but the values of G' and G'' were reduced with increasing treatment intensity, and the 'liquid-like' behaviour ($G'' >$ G') dominated over the 'weak-gel like' behaviour ($G' > G$") over all the tested frequencies (up to 10 Hz). This is shown by an increase in the damping factor (ratio of G'' to G') (Fig. 3), suggesting a decrease in elastic behaviour. In fact, above 95 °C treatments, the elastic moduli were too weak to be detected by the rheometer, probably due to disruption of weak interactions such as H-bonds and degradation of longer polymer chains to shorter chains, limiting chain-chain interactions. A similar reduction in G' and G'' was observed for tragacanth gum after shear and temperature treatments attributed to polymer degradation (Keivanfard et al., 2022).

3.2. Molecular weight and size of MP

The molecular parameters of MP such as weight-average molar mass (M_w), root-mean-square radius (R_z), polymer conformation and polydispersity were characterised *via* SEC-MALLS, after shear and temperature treatments. Surprisingly, the shear-treated samples did not show any significant changes in M_w after any applied shear (Table 1 and Fig A2). This suggests that the backbone structure of MP was retained after the shear treatment and the decrease in viscosity was not due to shear-induced depolymerisation. However, with increasing treatment intensity, a decreasing trend in R_z was observed which was statistically significant only at extreme conditions (~2.5% reduction at 8k- 1 min and 5k-20 min). These findings contrast with previously reported results where a clear decrease in M_w post-shear treatment was observed for other gums such as acacia gums (Al-Assaf et al., 2009), scleroglucan (Zeng et al., 2021), pectin (Shpigelman et al., 2015), tamarind seed

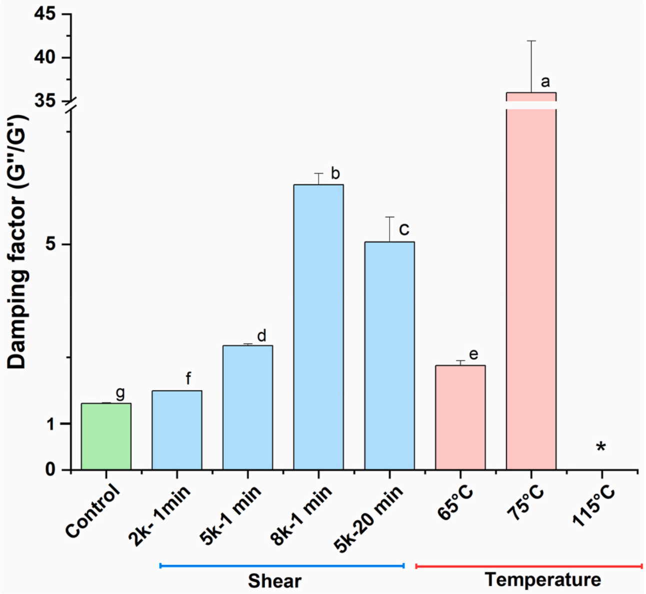


Fig. 3. Damping factor (ratio of G'' to G') of crude mamaku gum (2% w/w total solid) after shear and temperature treatment at 0.1 Hz frequency. (*): G' was not detected. Values are plotted as means ± standard deviation (n = 3). Measurements were taken using double gap geometry at 20 °C. Bars with different letters are significantly different ($p \leq 0.05$).

Table 1
Molecular parameters of purified mamaku gum after shear treatment analysed by size-exclusion chromatography coupled with multi-angle laser light scattering (SEC-MALLS).

	Weight-average molar mass, $M_w \times 10^6$ (Da)	Root mean square radius, R_z (nm)	Slope from the plot of M_w against root-mean-square radius	Polydispersity (M_w/M_n)
Control	3.95 ± 0.05^a	155.8 ± 0.14^a	0.62 ± 0.00^a	1.09 ± 0.00^a
For 1 min				
2k	3.99 ± 0.03^a	155.13 ± 0.46^a	0.61 ± 0.00^a	1.08 ± 0.00^a
4k	3.99 ± 0.03^a	154.4 ± 0.37^b	0.61 ± 0.01^a	1.08 ± 0.01^a
5k	4.05 ± 0.05^a	155.65 ± 0.38^a	0.62 ± 0.01^a	1.08 ± 0.00^a
6k	3.98 ± 0.03^a	154.6 ± 0.79$^{a,\ b}$	0.62 ± 0.01^a	1.08 ± 0.00^a
8k	3.99 ± 0.02^a	151.75 ± 0.96^c	0.62 ± 0.01^a	1.07 ± 0.01^a
At 5k rpm				
1 min	4.05 ± 0.05^a	155.65 ± 0.38^a	0.62 ± 0.01^a	1.08 ± 0.00^a
5 min	4.02 ± 0.06^a	156.125 ± 0.01^a	0.61 ± 0.01^a	1.07 ± 0.00^a
20 min	4.07 ± 0.08^a	152.15 ± 0.35^c	0.6 ± 0.01^a	1.08 ± 0.01^a

Values are expressed as means ± standard deviation (n = 3). Values in the same column denoted with the different superscripts are significantly different ($p \leq 0.05$).

polysaccharide (Xie et al., 2021), chitosan (Kasaai et al., 2003) and methylcellulose (Floury et al., 2002).

In the present study, during sample preparation for molecular analysis, the polymer solutions were subjected to an ultracentrifugation step—to remove large aggregates which otherwise could block the SEC columns and detectors—and therefore some of the polysaccharide chains were lost. Thus, in a separate trial, mamaku gum was first ultracentrifuged and then subjected to shear treatment at 5k-20 min and 8k-1 min followed by directly injecting the samples into the SEC-MALLs—no difference in M_w was observed (Table A.4), confirming that the sample purification steps did not affect the results. Also, a similar change in the relative viscosity at 1 s^{-1} was observed after shear treatment on the crude and purified samples Fig A.3).

Fig. 4 shows the chromatogram for the temperature-treated gum fractions with eluting time. The light scattering profiles clearly shifted to the right, indicating a decrease in M_w with an increase in the treatment temperature. When compared to the control, even at the lowest temperature of 65 °C, a significant decrease in M_w and R_z was observed (from ~3.8 × 10^6 Da to ~3.6 × 10^6 Da and from ~150 nm to 145 nm, respectively) (Table 2). The M_w and R_z continued to significantly decrease as the temperature increased, reaching ~0.6 × 10^6 Da and ~50 nm (~84 and 67% reduction) after heating at 115 °C (Table 2). Furthermore, it can also be observed from Fig. 4, that there was a shift to the right of the chromatogram from a monomodal peak (control and 65 °C) to bimodal/shoulder peaks (75–95 °C) and eventually, a

Table 2
Molecular parameters of purified mamaku gum after temperature treatment analysed by size-exclusion chromatography coupled with multi-angle laser light scattering (SEC-MALLS).

	Weight-average molar mass, $M_w \times 10^6$ (Da)	Root-mean-square radius, R_z (nm)	Slope from the plot of M_w against root-mean-square radius	Polydispersity (M_w/M_n)
Control	3.78 ± 0.04^a	149.53 ± 0.61^a	0.61 ± 0.00^a	1.1 ± 0.00^e
65 °C	3.59 ± 0.01^b	144.85 ± 0.86^b	0.6 ± 0.01^a	1.11 ± 0.00^e
75 °C	2.79 ± 0.06^c	121.95 ± 0.50^c	0.55 ± 0.01^b	1.13 ± 0.00^d
85 °C	2.39 ± 0.02^d	113.05 ± 0.83^d	0.55 ± 0.01^b	1.17 ± 0.01^c
95 °C	1.99 ± 0.03^e	103.93 ± 0.74^e	0.56 ± 0.01^b	1.23 ± 0.01^a
115 °C	0.6 ± 0.00^f	49.65 ± 0.32^f	0.62 ± 0.01^a	1.21 ± 0.00^b

Values are expressed as means ± standard deviation (n = 3). Values in the same column denoted with the different superscripts are significantly different ($p \leq 0.05$).

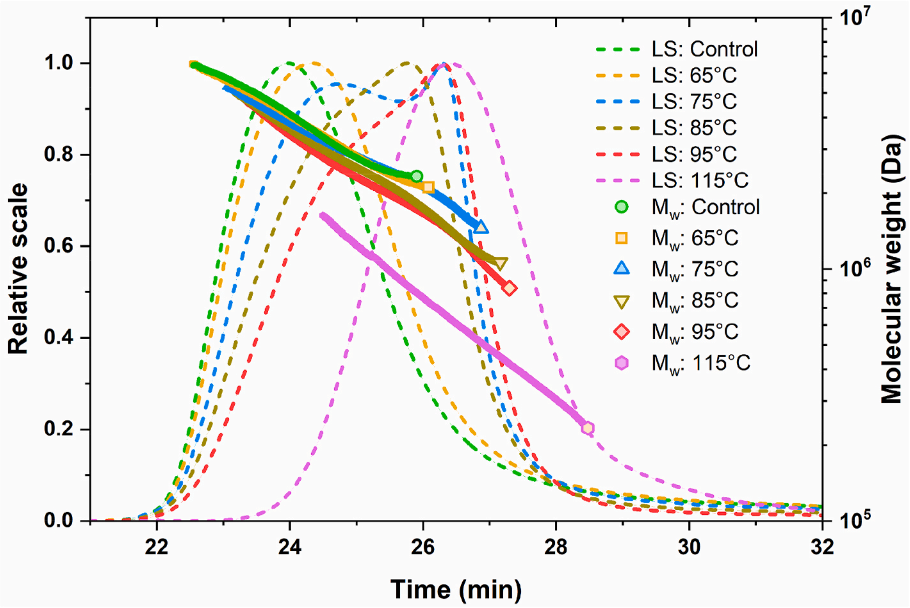


Fig. 4. Light scattering (LS) signal and weight-average molar mass (M_w) analysis by size-exclusion chromatography coupled with multi-angle laser light scattering (SEC-MALLS) of purified mamaku gum after temperature treatment.

monomodal peak at high temperature (115 °C). This shift towards the right-hand side of the light scattering chromatogram is an indication of the degradation of the large native polymer chains to smaller chains as the temperature increases, indicating the high sensitivity of MP when the processing conditions are above 65 °C. A change in molecular conformation (obtained from the slope of log M_w *vs* log R_z plot) was also observed with temperature, where the native polymers transited from an initial value of ~0.6 (implies a linear chain conformation in a good solvent) to ~0.55 (implies a reduction in extended chain conformation as intramolecular interactions dominates over intermolecular interaction, liken to linear random coils in a theta solvent). This temperature-dependent reduction in M_w and R_z could explain the reduction in viscosity (Fig. 2).

Similar to R_z, a decreasing trend was observed for z-average radius with increasing treatment intensity (Fig. 5). A statistically significant decrease in z-average radius (from ~76 nm for control) was only detected at the extreme shear conditions *i.e.*, ~5% reduction at 8k-1 min (to ~72 nm) and 5k-20 min (to ~72.4 nm), while for the temperature-treated samples the decrease in the z-average became significant at 85 °C (~22% reduction, to ~59.6 nm), with a further ~36% reduction (to 48.8 nm), at the highest temperature treatment (115 °C).

3.3. Constituent sugar composition and NMR spectroscopy

Shear treatment (using high-pressure homogenization) has been reported to induce side chain degradation in pectin from potato peel waste, while the main chain composition remained intact (Xie et al., 2018). The removal of some/specific monosaccharide units from the side chain may not significantly affect the M_w, as observed in our case, for the shear-treated MP samples (Table 1), but may impair the hydrogen bonding between chains, thus, causing a reduction in viscosity. Constituent sugar analysis of both temperature and shear treated mamaku samples showed that the overall composition remained similar after all treatments (Fig. 6). No changes in the monosaccharide composition for the temperature-treated samples indicate that the reduction in M_w after heat treatment was purely due to partial hydrolysis of the polysaccharide backbone, rather than the removal of individual monosaccharide units, which would have otherwise been lost *via* dialysis (molecular weight cut-off: 12,000–14,000 Da). Furthermore, NMR spectroscopy showed no discernible changes in the structure of the mamaku samples with either shear or temperature treatment (Fig A.4, A.5).

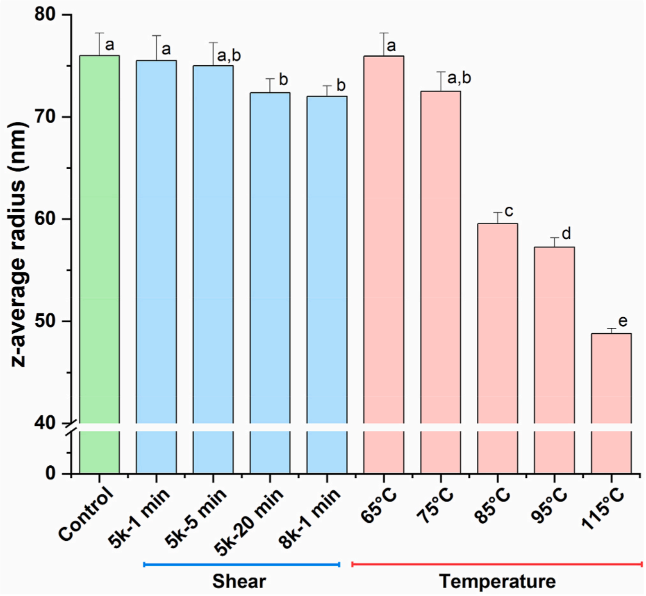


Fig. 5. Effect of shear and temperature treatment on the z-average radius of purified mamaku gum. Values are plotted with mean ± standard deviation (n = 5) obtained at 20 °C. Bars with different letters are significantly different ($p \leq 0.05$).

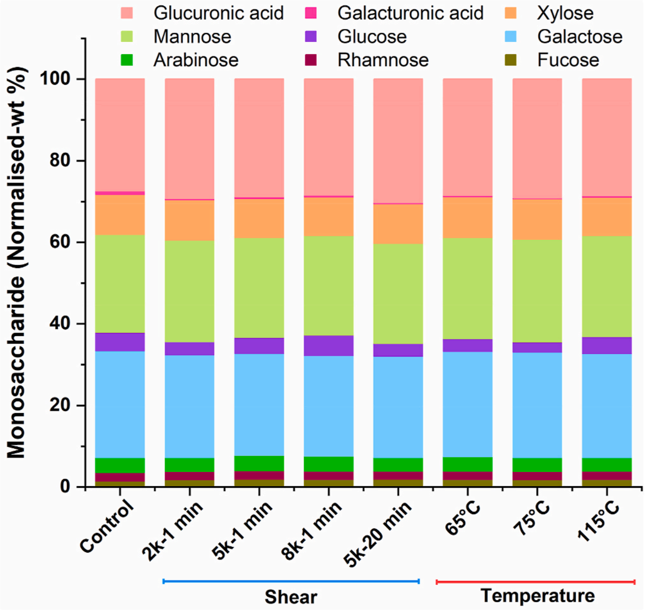


Fig. 6. Constituent sugar composition of purified mamaku gum after shear and temperature treatment.

4. General discussion

Treatment of natural polysaccharides by physical, chemical or enzymatic methods is often used to alter their physicochemical properties and physiological effects (Riaz, Iqbal, Jiang, & Chen, 2021; Wang, Xie, Shen, Nie, & Xie, 2018). The physical modification, by thermal, mechanical, and thermo-mechanical processes is more attractive to the industry, because no chemicals are involved. However, the modification of polysaccharides during processing may have undesirable effects, thereby limiting their use for some applications. Thus, in this study, the sensitivity of MP towards high shear and temperature treatments used during food manufacturing was investigated.

During shearing, the polysaccharide chains stretch and the molecules experience tension. When this tension reaches a critical level, the polymer chains break resulting in the formation of smaller fragments, which cause a reduction in viscosity. The mechanical scission *via* cleavage of strong glycosidic bonds in the backbone chain of a polymer is the primary reason vastly reported for the decrease in viscosity on exposure to shear (from mechanical action) (Belmiro, Tribst, & Cristianini, 2018; Eren et al., 2015; Laneuville et al., 2013). Villay et al. (2012) reported a reduction of ~87% for guar gum, ~60% for alginate and hydroxyethylcellulose and ~50% for CMC in M_w after using a high-pressure homogeniser (200 MPa, 2 cycles). Shearing may also cause changes in the primary structure of the polysaccharide, which could affect the molecular spatial structure and intermolecular interaction, causing a reduction in viscosity (Chen et al., 2012; Porto et al., 2015). However, in the present study, there were no changes detected in the chain length and the composition of the MP (Table 1 and Fig. 6, A.2, A.4, A.5). It is possible that the 'critical level of tension' was not achieved by the shear treatment used in this study, as the forces needed to break the covalent bonds in the main chain were insufficient. A similar resistance to shear-induced depolymerisation has been reported for polysaccharides from *Astragalus* (400 MPa, 10 min) (Zhu et al., 2016) and *Mesona chinensis* Benth (120 MPa, 6 cycles) (Huang et al., 2018). However, these authors reported an improvement in α-glucosidase inhibition and antioxidant activity after shear treatment, and attributed it to changes in exposed groups due to an alteration in the secondary structure (using circular dichroism) (Zhu et al., 2016) and morphology of the polysaccharide (using SEM) (Huang et al., 2018) without any reduction in M_w of the polysaccharide. This could imply conformation changes occurring intramolecularly which resulted in the exposure of side groups that were initially hidden in the polymer chains.

In the case of MP, on subjecting MP to shear treatment, a decrease in $\eta_{(1\ s^{-1})}$ and η_{max}/η_{crit} and an increase in γ_{crit} were observed depending on the severity of the treatment (Fig. 1). The intrinsic viscosity, $[\eta]$, of a polymer (or the volume occupied by an individual polymer chain) is strongly governed by the M_w of the polymer ($[\eta] \propto M_w^a$, where "a" is a conformational factor), where the greater the M_w, the greater the $[\eta]$ and the greater the apparent viscosity of the polymer solution. The M_w of MP was unaffected after shear treatment and therefore, our initial hypothesis of polymer degradation due to shear is proven to be untrue, thus, a new hypothesis must be considered to interpret and explain the results. Based on the results obtained, the decrease in viscosity after shear treatment could be related to several phenomena that relate to chain rearrangements that resulted in a more compact folder chain. These could be the result of changes in the intermolecular, intramolecular, conformation and translational arrangement of MP chains. During shear treatment, MP chains experience shear forces that could disrupt intermolecular interactions among neighbouring chains. The individual chains are then unfolded and stretched by shear which could also disrupt intramolecular interactions (Fig. 7a). Soon after the treatment, chains will continually rearrange into a new favoured state of equilibrium. It is plausible that MP chains, during this translational rearrangement, may undergo some changes in the packing of the three-dimensional units building up the macromolecule, which could consequently result in pockets of stronger intramolecular interactions giving it a more folded and compact structure (Fig. 7b). These changes however are only picked up under extreme shear conditions where the R_z and the z-average radius were slightly reduced compared to the unsheared gum sample. During viscosity measurement, the shear-modified MP structure may resist the stretching of the chains because of the stronger intramolecular interactions and as a result, more energy was needed to unfold the chains to promote sufficient intermolecular hydrogen bonding to initiate the shear-thickening behaviour (thus, the increase in γ_{crit}). Moreover, the chains may not unfold completely due to the stronger intramolecular interactions limiting the sites for the formation of intermolecular interactions (thus, the decrease in η_{max}/η_{crit}) (Fig. 7c).

On the other hand, during thermal treatment, degradation *via* chain scission of the glycosidic linkage caused a reduction in M_w and viscosity in the mamaku gum (Figs. 2 and 4 and Table 2). A similar decrease in M_w and viscosity has been reported for mushroom *Inonotus obliquus* polysaccharide heated at 100 °C for 3 h (Zhang, Chen, Ma, & Zhang, 2013) and waxy potato starch heated at 120–150 °C for 30 min (Ang, Matia-Merino, Lim, & Goh, 2021). Lu, Li, Qiao, Qiu, and Liu (2018) also reported degradation in black garlic polysaccharide during thermal treatment at 70–90 °C for 2–8 days.

Fig. 8 shows the comparison of the rheological profiles for the extreme tested shear treatments *i.e.,* 5k-20 min and 8k-1 min and 75 °C temperature treatment. Though the M_w for the shear-treated samples (~3.99×10^6 Da) was higher than the 75 °C treated sample (~2.79×10^6 Da), three key conflicting observations can be made: (i) the viscosity (at 0.1–2 s^{-1}) was similar for all three samples; (ii) η_{max}/η_{crit} was significantly lower for the shear-treated samples (~2.8) compared to the 75 °C treated sample (~6.6); and (iii) the γ_{crit} was higher for the shear-treated samples (~12-15 s^{-1}) than for the 75 °C treated (~4 s^{-1}) sample. These rheological behaviours of the shear-modified MP could again be explained by the molecular rearrangement and the formation of a more

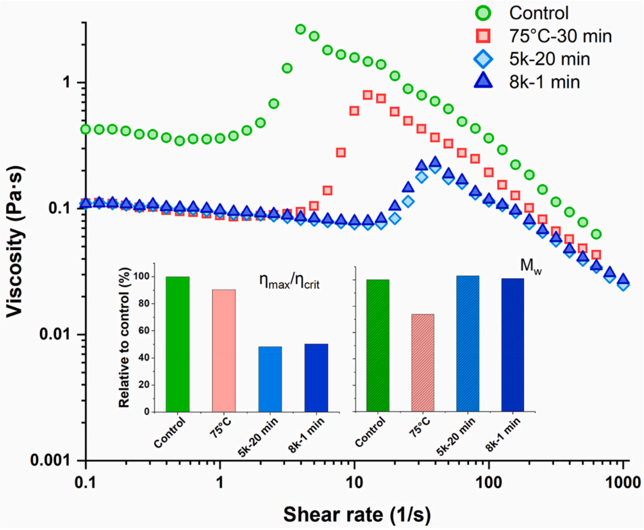


Fig. 8. Comparison between shear (5k- 20 min and 8k-1 min) and temperature (75°C- 30 min) treated mamaku gum samples (2% w/w total solids). η_{max}/η_{crit}, extent of shear-thickening; M_w, weight-average molar mass.

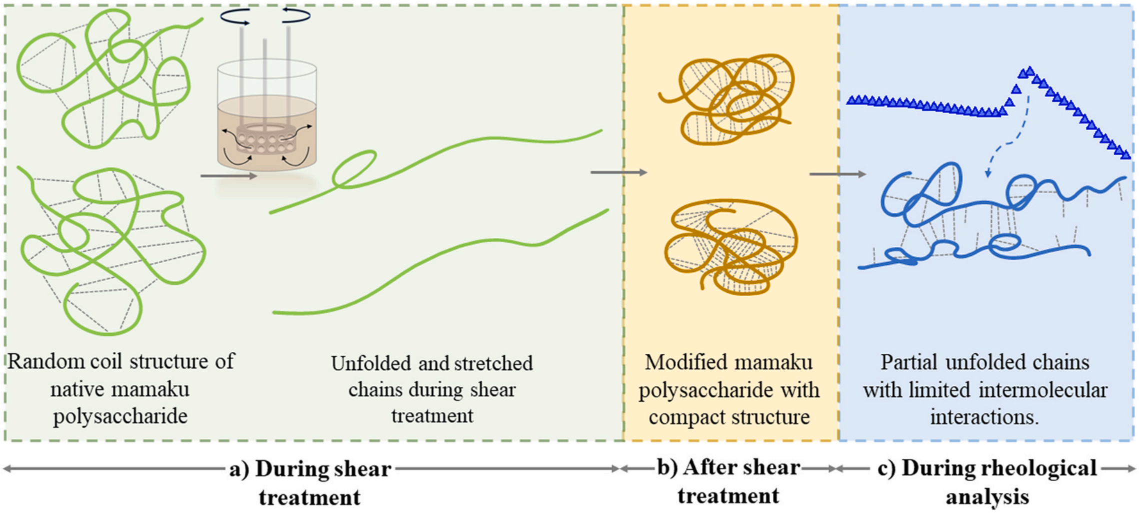


Fig. 7. Schematic illustration showing the effect of (a, b) shear treatment on the packing of mamaku polysaccharide molecules and (c) consequently limiting the unfolding during the rheological analysis.

compact structure (*i.e.,* strong intramolecular interactions leading to partial unfolding during rheological analysis). On the contrary, the smaller chains in the temperature-treated MP may be more easily unfolded due to weaker intramolecular interactions while exposing the sites for intermolecular interactions during the rheological analysis. Furthermore, the similar viscosity at low shear rates suggests that polymer-polymer and polymer-water interactions are comparable between all three samples (5k-20 min, 8k-1 min and 75 °C). This would mean that at low shear rates when polymer molecules largely remain unperturbed, the extent of intermolecular interactions are similar despite the lower molar mass of the temperature treated MP. The rearrangements in shear modified MP may have resulted in a reduced amount of hydrogen bonding groups to be exposed and thereby, impairing the ability of the polymer to interact with neighbouring molecules and thus, reducing the viscosity of the solution. These results are in line with the subtle decrease in the z-average radius of the shear-treated MP mentioned above. The decrease in exposed groups of MP chains will also probably reduce the interaction with the water molecules. As a result, the Brownian motion of the MP-water complex will increase giving lower z-average radius ($\propto \frac{1}{diffusion\ coefficient}$). Changing the interaction between molecules of gum and water will change the rheology properties. Interestingly, the z-average radius for shear-treated (5k-20 min and 8k-1 min) samples was similar to the 75 °C treated sample even though their molar masses differ. It is possible that conformational changes during shear treatment are a subtle intermediate stage between disentanglement and bond rupture, depending on shear intensity. The previous studies might have missed this intermediate stage as in most of them, the polymers were subjected to extreme shear (>5000 s^{-1}) from equipment such as a homogenizer or a microfluidizer. However, this cannot be concluded from the results of the present study.

Additionally, the rheological behaviour of shear-treated mamaku gum was analysed in the presence of urea, a commonly used hydrogen bond disrupter (Fig. 9). If the more compact structure of shear-modified MP is due to increased intramolecular hydrogen bonds alone, then the urea should break them all, bringing the viscosity of the shear-modified MP closer to the control (due to similar M_w). However, this was not the case, as the viscosity of the control was still very different from the shear-treated samples, with the viscosity decreasing with greater treatment intensity. As previously observed for MP (Jaishankar, Wee, Matia-Merino, Goh, & McKinley, 2015), the shear-thickening behaviour was lost in all samples, suggesting that urea interferes with the intermolecular hydrogen bonding between MP chains. The results suggest that the compact structure of the shear-modified MP may not only be due to hydrogen bonds, but possibly other interactions mediated by mono, divalent and trivalent ions—given the presence of the high salt content in the mamaku gum extract.

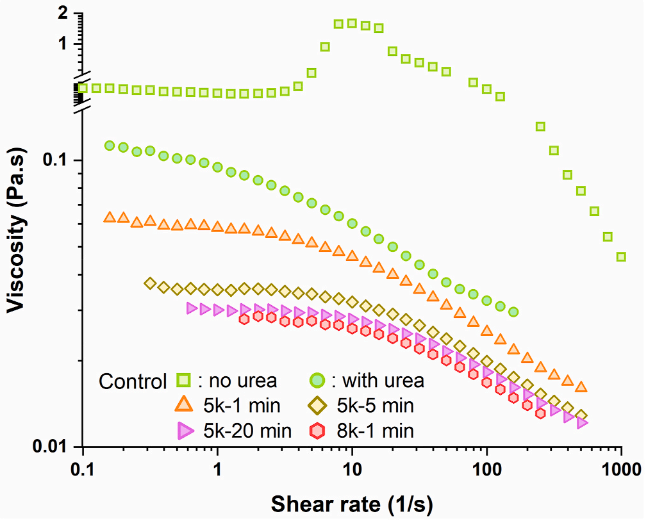


Fig. 9. Effect of urea (5M) on the viscosity profile of shear-treated mamaku gum (2% w/w total solids). Measurements (n = 3) were taken using cup-and-bob geometry at 20 °C.

5. Conclusions

Overall, this study demonstrates the sensitivity of MP towards temperature and shear treatments. Temperature treatment caused thermal degradation of MP depending on the severity of treatment leading to a drastic loss in viscosity. A similar reduction in viscosity was observed after shear treatment without any polymer degradation. It is proposed that the shear-induced viscosity reduction could be related to the rearrangement of MP molecules and the formation of a more folded and compact structure. The results from this study are of high importance to the industry when processing conditions are considered since a decrease in viscosity will lead to texture modification of fluid and semi-solid foods which incorporate the MP. Further work on the effects of industrial treatments such as homogenization and microfluidization is needed to fully understand the sensitivity of MP to shear treatment. Also, further studies on structural changes should be carried out to gain more insights into the behaviour of MP during processing.

Author statement

Akshay Bisht: conceptualization, methodology, validation, investigation, formal analysis, visualization, writing - original draft; **Kelvin K. T. Goh:** conceptualization, methodology, writing - review & editing, supervision; **Ian M. Sims:** investigation, writing - review & editing; **Patrick J. B. Edwards:** investigation, writing - review & editing; **Lara Matia-Merino:** conceptualization; methodology; writing - review & editing; supervision; project administration.

Funding

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

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.

Acknowledgement

The project was consulted with Prof. Dr. Nicholas Rahiri Roskruge for cultural review.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.foodhyd.2023.109075.

References

Al-Assaf, S., Sakata, M., McKenna, C., Aoki, H., & Phillips, G. O. (2009). Molecular associations in acacia gums. *Structural Chemistry, 20*(2), 325–336.

Ang, C. L., Matia-Merino, L., Lim, K., & Goh, K. K. T. (2021). Molecular and physico-chemical characterization of de-structured waxy potato starch. *Food Hydrocolloids, 117*, Article 106667.

Belmiro, R. H., Tribst, A. A. L., & Cristianini, M. (2018). Application of high-pressure homogenization on gums. *Journal of the Science of Food and Agriculture, 98*(6), 2060–2069.

Bisht, A., Goh, K. K. T., & 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*. https://doi.org/10.1039/d3fo01665j

Chen, J., Liang, R.-H., Liu, W., Liu, C.-M., Li, T., Tu, Z.-C., et al. (2012). Degradation of high-methoxyl pectin by dynamic high pressure microfluidization and its mechanism. *Food Hydrocolloids, 28*(1), 121–129.

Corredig, M., & Wicker, L. (2001). Changes in the molecular weight distribution of three commercial pectins after valve homogenization. *Food Hydrocolloids, 15*(1), 17–23.

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

De Ruiter, G. A., Schols, H. A., Voragen, A. G., & Rombouts, F. M. (1992). Carbohydrate analysis of water-soluble uronic acid-containing polysaccharides with high-performance anion-exchange chromatography using methanolysis combined with TFA hydrolysis is superior to four other methods. *Analytical Biochemistry, 207*(1), 176–185.

Eren, N. M., Santos, P. H., & Campanella, O. (2015). Mechanically modified xanthan gum: Rheology and polydispersity aspects. *Carbohydrate Polymers, 134*, 475–484.

Farzi, M., Yarmand, M. S., Safari, M., Emam-Djomeh, Z., & Mohammadifar, M. A. (2015). Gum tragacanth dispersions: Particle size and rheological properties affected by high-shear homogenization. *International Journal of Biological Macromolecules, 79*, 433–439.

Floury, J., Desrumaux, A., Axelos, M. A., & Legrand, J. (2002). Degradation of methylcellulose during ultra-high pressure homogenisation. *Food Hydrocolloids, 16*(1), 47–53.

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

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.

Goh, K. K. T., Matia-Merino, L., Pinder, D. N., Saavedra, C., & Singh, H. (2011). Molecular characteristics of a novel water-soluble polysaccharide from the New Zealand black tree fern (Cyathea medullaris). *Food Hydrocolloids, 25*(3), 286–292.

Harrington, R., & Zimm, B. (1965). Degradation of polymers by controlled hydrodynamic shear. *The Journal of Physical Chemistry, 69*(1), 161–175.

Harte, F., & Venegas, R. (2010). A model for viscosity reduction in polysaccharides subjected to high-pressure homogenization. *Journal of Texture Studies, 41*(1), 49–61.

Huang, L., Shen, M., Zhang, X., Jiang, L., Song, Q., & Xie, J. (2018). Effect of high-pressure microfluidization treatment on the physicochemical properties and antioxidant activities of polysaccharide from Mesona chinensis Benth. *Carbohydrate Polymers, 200*, 191–199.

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.

Kasaai, M. R., Charlet, G., Paquin, P., & Arul, J. (2003). Fragmentation of chitosan by microfluidization process. *Innovative Food Science & Emerging Technologies, 4*(4), 403–413.

Keivanfard, N., Nasirpour, A., Barekat, S., & Keramat, J. (2022). Effects of heat and high-pressure homogenization processes on rheological and functional properties of gum tragacanth. *Food Hydrocolloids, 128*, Article 107593.

Kivelä, R., Pitkänen, L., Laine, P., Aseyev, V., & Sontag-Strohm, T. (2010). Influence of homogenisation on the solution properties of oat β-glucan. *Food Hydrocolloids, 24*(6–7), 611–618.

Laneuville, S. I., Turgeon, S. L., & Paquin, P. (2013). Changes in the physical properties of xanthan gum induced by a dynamic high-pressure treatment. *Carbohydrate Polymers, 92*(2), 2327–2336.

Liang, K., Han, P., Chen, Q., Su, X., & Feng, Y. (2019). Comparative study on enhancing oil recovery under high temperature and high salinity: Polysaccharides versus synthetic polymer. *ACS Omega, 4*(6), 10620–10628.

Lu, X., Li, N., Qiao, X., Qiu, Z., & Liu, P. (2018). Effects of thermal treatment on polysaccharide degradation during black garlic processing. *LWT, 95*, 223–229.

Mackenzie, K., & Jemmett, A. (1971). Polymer shear stability. *Wear, 17*(5–6), 389–398.

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.

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

Nachtigall, C., Berger, C., Kovanović, T., Wefers, D., Jaros, D., & Rohm, H. (2019). Shear induced molecular changes of exopolysaccharides from lactic acid bacteria. *Food Hydrocolloids, 97*, Article 105181.

Nachtigall, C., Rohm, H., & Jaros, D. (2021). Degradation of exopolysaccharides from lactic acid bacteria by thermal, chemical, enzymatic and ultrasound stresses. *Foods, 10*(2), 396.

Nilsson, L., Leeman, M., Wahlund, K.-G., & Bergenståhl, B. (2006). Mechanical degradation and changes in conformation of hydrophobically modified starch. *Biomacromolecules, 7*(9), 2671–2679.

Owen, S. R., Tung, M. A., & Paulson, A. T. (1992). Thermorheological studies of food polymer dispersions. In *Rheology of foods* (pp. 39–53). Elsevier.

A. Paar. Measuring system data sheet CC27-SN5713755104 (CC_ISO3219). In: Anton paar Germany Gmbh.

Porto, B. C., Augusto, P. E. D., Terekhov, A., Hamaker, B. R., & Cristianini, M. (2015). Effect of dynamic high pressure on technological properties of cashew tree gum (Anacardium occidentale L.). *Carbohydrate Polymers, 129*, 187–193.

Riana, L. M., Sims, I. M., & Matia-Merino, L. (2022). Emulsification properties of Puka Gum–An exudate of a native New Zealand tree (Meryta sinclairii): Effect of shear rate and Gum concentration. *Food Hydrocolloids, 124*, Article 107263.

Riaz, T., Iqbal, M. W., Jiang, B., & Chen, J. (2021). A review of the enzymatic, physical, and chemical modification techniques of xanthan gum. *International Journal of Biological Macromolecules, 186*, 472–489.

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

Robal, M., Truus, K., Volobujeva, O., Mellikov, E., & Tuvikene, R. (2017). Thermal stability of red algal galactans: Effect of molecular structure and counterions. *International Journal of Biological Macromolecules, 104*, 213–223.

Rudin, A., & Schreiber, H. P. (1983). Shear modification of polymers. *Polymer Engineering & Science, 23*(8), 422–430.

Shpigelman, A., Kyomugasho, C., Christiaens, S., Van Loey, A. M., & Hendrickx, M. E. (2015). The effect of high pressure homogenization on pectin: Importance of pectin source and pH. *Food Hydrocolloids, 43*, 189–198.

Sisodia, M. S., Rajak, D. K., Pathak, A. K., & Guria, C. (2015). An improved estimation of shear rate for yield stress fluids using rotating concentric cylinder Fann viscometer. *Journal of Petroleum Science and Engineering, 125*, 247–255.

Villay, A., De Filippis, F. L., Picton, L., Le Cerf, D., Vial, C., & Michaud, P. (2012). Comparison of polysaccharide degradations by dynamic high-pressure homogenization. *Food Hydrocolloids, 27*(2), 278–286.

Wang, Y., Li, D., Wang, L.-J., & Xue, J. (2011). Effects of high pressure homogenization on rheological properties of flaxseed gum. *Carbohydrate Polymers, 83*(2), 489–494.

Wang, Q., Wood, P. J., Cui, W., & Ross-Murphy, S. B. (2001). The effect of autoclaving on the dispersibility and stability of three neutral polysaccharides in dilute aqueous solutions. *Carbohydrate Polymers, 45*(4), 355–362.

Wang, Z., Xie, J., Shen, M., Nie, S., & Xie, M. (2018). Sulfated modification of polysaccharides: Synthesis, characterization and bioactivities. *Trends in Food Science & Technology, 74*, 147–157.

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.

Wee, M. S. M., Matia-Merino, L., & Goh, K. K. T. (2015). The cation-controlled and hydrogen bond-mediated shear-thickening behaviour of a tree-fern isolated polysaccharide. *Carbohydrate Polymers, 130*, 57–68.

Xie, F., Zhang, W., Lan, X., Gong, S., Wu, J., & Wang, Z. (2018). Effects of high hydrostatic pressure and high pressure homogenization processing on characteristics of potato peel waste pectin. *Carbohydrate Polymers, 196*, 474–482.

Xie, F., Zhang, H., Nie, C., Zhao, T., Xia, Y., & Ai, L. (2021). Structural characteristics of tamarind seed polysaccharides treated by high-pressure homogenization and their effects on physicochemical properties of corn starch. *Carbohydrate Polymers, 262*, Article 117661.

Zaitoun, A., Makakou, P., Blin, N., Al-Maamari, R. S., Al-Hashmi, A., Abdel-Goad, M., et al. (2012). Shear stability of EOR polymers. *SPE Journal, 17*(2), 335–339.

Zeng, W., Wang, J., Shan, X., Yu, S., & Zhou, J. (2021). Efficient production of scleroglucan by sclerotium rolfsii and insights into molecular weight modification by high-pressure homogenization. *Frontiers in Bioengineering and Biotechnology*, 799.

Zhang, N., Chen, H., Ma, L., & Zhang, Y. (2013). Physical modifications of polysaccharide from Inonotus obliquus and the antioxidant properties. *International Journal of Biological Macromolecules, 54*, 209–215.

Zhu, Z.-Y., Luo, Y., Dong, G.-L., Ren, Y.-Y., Chen, L.-J., Guo, M.-Z., … Zhang, Y. (2016). Effects of the ultra-high pressure on structure and α-glucosidase inhibition of polysaccharide from Astragalus. *International Journal of Biological Macromolecules, 87*, 570–576.