

# Probing Hydrogen Bond Interactions in a Shear Thickening Polysaccharide using Nonlinear Shear and Extensional Rheology

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## Abstract

Mamaku gum is a polysaccharide extracted from the fronds of the black tree fern found in New Zealand. The cooked pith has traditionally been used for various medicinal purposes and as a food source by the Māori people of New Zealand. It has potential applications as a thickener in the food industry and as a palliative for patients with dysphagia. Studies on the shear rheology of Mamaku gum have revealed that the gum exhibits shear thickening at a critical shear rate due to a transition from intra- to inter-molecular chain interactions upon shear-induced chain elongation. In this paper we demonstrate that these interactions are primarily due to hydrogen bonding. We perform extensional rheology on mixtures of Mamaku gum and urea (a known disruptor of hydrogen bonds) to quantify the nature of these interactions. Capillary Breakup Extensional Rheometry (CaBER) performed on the pure Mamaku gum solutions yield plateau values of the Trouton ratio as high as  $\sim 10^4$ , showing that the viscoelasticity of the gum in uniaxial elongation is much higher than in shear. For all Mamaku concentrations tested, the extensional viscosity decreases upon increasing urea concentration. Furthermore, the relaxation time decreases exponentially with increasing urea concentration. This exponential relationship is

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independent of the Mamaku concentration, and is identical to the relationships between urea concentration and characteristic timescales measured in nonlinear shear rheology. We show using the sticky reptation model for polymers with multiple sticker groups along the backbone how such a relationship is consistent with a linear decrease in the free energy for hydrogen bond dissociation. We then demonstrate that a time-concentration superposition principle can be used to collapse the viscoelastic properties of the Mamaku-gum urea mixtures.

*Keywords:* CaBER; Polysaccharide; Extensional Rheology; Shear Thickening

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## 1. Introduction

Polysaccharides play critical roles in a number of industrial and biological applications [24]. They provide structural reinforcement in plants and animals [19, 3, 50], are the chief component of the lubricating synovial fluid found in mammalian joints [61, 17], are the main source of energy in [many](#) foods [54],  
5 and are found in various biological slimes and mucus [6, 12]. Furthermore, the widespread availability, biocompatibility and biodegradability, plus the ability of polysaccharides to form swollen gels has stimulated much research in using them in controlled drug release systems [22, 35]. Perhaps one of the most important  
10 applications of polysaccharides is in the foods industry. Precise control of the organoleptic characteristics of foodstuffs such as texture, thickness, chewiness, tackiness and mouth-feel is crucial for the shelf-life, consumer perception and overall quality of the food [24]. Polysaccharides such as Xanthan gum, Guar gum and Locust Bean gum have enjoyed particular success in this area [51].

15 Recently, a new plant polysaccharide called Mamaku gum, obtained from the fronds of the black tree fern, has been discovered and its shear rheology has been characterized [14, 15]. The Māori people of New Zealand have traditionally used Mamaku gum for treating boils, burns, wounds, rashes and diarrhea [29]. A large number of plant mucins and gums exhibit such healing and curative  
20 properties [38]. Plant gums such as Mamaku also control the rate of flow of food through the digestive tract due to their ability to swell and retain water. This

leads to longer transit times in the digestive tract and higher nutrient uptake [24]. It is also hypothesized that some classes of polysaccharides provide bulk to ingested foods, thus helping in smoother peristalsis and healthier bowel movements [13]. Given these myriad uses of polysaccharide containing mixtures, and indeed polysaccharides themselves, an extensive rheological study of Mamaku gum and the understanding of the nature of inter- and intra-molecular interactions will aid in promoting commercial scale applications of Mamaku gum in food thickeners and as a digestive emollient.

It has been shown in previous viscometric studies [14] that in steady simple shear flow, Mamaku gum exhibits shear-thickening behavior, i.e., the steady shear viscosity  $\eta(\dot{\gamma})$  increases as a function of shear rate  $\dot{\gamma}$  for a certain range of shear rates. This is an exceptional occurrence for polysaccharide solutions [24], which very frequently display shear-thinning, i.e.,  $\eta(\dot{\gamma})$  decreases as a function of shear rate  $\dot{\gamma}$ . This shear-thickening behavior arises from the appearance of increased inter-molecular interactions at a critical shear rate. Matia-Merino et al. [29] have shown that the shear thickening behavior of Mamaku gum is insensitive to changes in salt composition as well as salt concentration. The rheology of Mamaku gum is also unchanged over a wide range of pH values. By contrast, the rheology of Xanthan gum, which is currently one of the most widely used food thickeners, is sensitive to both salt content as well as pH [53]. This presents the possibility of using Mamaku gum as a rheology modifier for foods with low pH in which other frequently-used modifiers are ineffective. Moreover, the unique shear-thickening behavior of the gum (as opposed to the shear-thinning that characterizes the majority of other food thickeners) may itself have potential applications. For example, thickening agents are added to foods as a treatment for dysphagia; this retards the process of bolus swallowing and hence provides more time for muscular control of the swallowing process [43]. With this application in mind, it is important to understand the rheology and the nature of the supramolecular interactions present in Mamaku gum that lead to the shear-thickening behavior. The peristaltic swallowing and digestive processes involve extensional deformations [60, 46], and fluid elements are intermittently stretched

or elongated as the food bolus moves from the mouth and through the digestive tract. Moreover, the dynamical response of a complex fluid to extensional flows is a more sensitive probe of the composition, morphology and structure of the fluid [20, 32, 48], than a shearing deformation of comparable strength. Therefore, use of polysaccharides such as Mamaku gum as a digestive emollient requires a characterization of their viscoelastic response under extensional deformation. However, a brief review of the literature indicates that such data is relatively sparse for polysaccharide solutions and self-associating polymeric fluids in general.

In this paper, we use a combination of nonlinear shear rheology, and Capillary Breakup Extensional Rheometry (CaBER) [1] to probe the nature of the intermolecular interactions in Mamaku gum. We validate the hypothesis that hydrogen bonding interactions lead to the unusual viscoelastic response of Mamaku gum, using mixtures of Mamaku gum and urea. The remainder of the paper is organized as follows. The next section details the extraction and preparation of the fluids and describes the various experimental techniques used. In the third section we describe and interpret the experimental results. We comprehensively characterize the extensional rheology of Mamaku gum using CaBER measurements and extract relaxation times and extensional viscosities of both pure Mamaku gum solutions as well as Mamaku-urea mixtures. Urea is known to be an effective disrupter of hydrogen bonding in proteins [41] and polysaccharides [34]. We document the rheological changes induced upon the addition of urea to Mamaku gum, and demonstrate that the source of the unusual nonlinear rheology of the solution arises from intra-molecular hydrogen bonds. We demonstrate the existence of a quantitative ‘time-concentration superposition’ and interpret the underlying physics of this superposition principle in terms of the lifetime of hydrogen bond formation and the changes induced in the activation energy landscape upon the addition of urea.

## 2. Experimental

### 2.1. Materials

The freeze-dried aqueous extract of Mamaku gum was obtained from the stem pith of the fronds of the New Zealand black tree fern (*Cyathea medullaris*)  
85 in Palmerston North, New Zealand, in August 2011 according to the procedure outlined by Goh et al. [14] The freeze-dried native extract was prepared by hydrating in deionized water overnight under gentle stirring at 25°C. Solutions that were not used immediately were stored under refrigeration at 4°C. In all cases, experiments were performed with solutions less than 72 hours old.

### 90 2.2. Methods

The shear rheology presented in this paper was performed using a TA Instruments (New Castle, DE, USA) stress-controlled ARG2 rheometer with a 40 mm, 2° cone-and-plate fixture. For all experiments, the temperature was held fixed at 25°C using a Peltier plate. Extensional rheology was performed using a  
95 Capillary Breakup Extensional Rheometer (CaBER). The CaBER device consists of two parallel plates of diameter  $D_0$  separated by an initial gap of length  $L_0$ . The test fluid is loaded between this gap and the top plate is pulled apart rapidly ( $t_{\text{open}} \approx 50$  ms) using a stepper motor to a final gap  $L_f$  to impose an extensional deformation on the fluid sample and form a liquid bridge between  
100 the plates. The resulting filament then thins under the action of viscous, elastic and capillary forces, and the mid-plane diameter of the fluid  $D(t)$  varies as a function of time [1]. In our CaBER setup, this diameter is measured using a laser micrometer (resolution 5  $\mu\text{m}$ ), and is also independently monitored using a macro lens with a focal length of 100 mm attached to a DSLR camera. For  
105 sufficiently viscous Newtonian fluids, in the absence of inertial or gravitational effects, the mid-plane diameter  $D(t)$  decays linearly with time until eventual breakup [33]. However, in the present study, there is a point in the thinning process of the filament at which the capillary pressure arising from surface tension is balanced purely by the stress arising from fluid elasticity. Such a balance  
110 of stresses is known as an elasto-capillary balance [8].

The Hencky strain  $\varepsilon(t)$  experienced by the fluid element at the mid-plane of the thinning filament is given by

$$\varepsilon(t) = 2 \ln \left( \frac{D_0}{D(t)} \right) \quad (1)$$

Under the conditions of elasto-capillary balance, Entov and Hinch [8] have shown that the mid-plane diameter  $D(t)$  decays exponentially, and is given by

$$\frac{D(t)}{D_0} = \left( \frac{GD_0}{2\sigma} \right)^{1/3} \exp[-t/(3\tau)] \quad (2)$$

in which  $G$  and  $\tau$  are the modulus and relaxation time, respectively, of the longest relaxation mode of the fluid, and  $\sigma$  is the surface tension. Therefore, the CaBER experiment yields a measure of the characteristic relaxation time  $\tau$  of the fluid in elongation. Note that the strain rate imposed on the fluid filament in a CaBER device is chosen by the fluid according to the balance of elastic and capillary forces, and cannot be independently controlled in the experiment. The strain rate  $\dot{\varepsilon}(t)$  in the *elasto-capillary regime* can be calculated from equations (1) and (2) and is given by

$$\dot{\varepsilon}(t) = \frac{2}{3\tau} \quad (3)$$

which is a constant. In our experiments,  $D_0 = 6$  mm,  $L_0 = 2$  mm and  $L_f = 7$  mm, and the step from  $L_0$  to  $L_f$  is performed over a controlled time step of 50 ms. The transient extensional viscosity of the fluid may then be calculated as [1]

$$\eta_E^+ = -\frac{\sigma}{dD_{\text{mid}}(t)/dt} \quad (4)$$

Note that in a CaBER measurement, we do not independently measure the tensile stress difference; instead, we obtain it from balancing the elastic stress difference and the capillary pressure arising from surface tension in the thinning filament. The surface tension of the fluids was measured independently with a

115 platinum Wilhelmy plate (Krüss K-10 tensiometer).

### 3. Results and discussion

#### 3.1. Shear Rheology

We begin with a discussion of the shear rheology of the Mamaku gum solutions. In figure 1a we show the zero shear rate viscosity of Mamaku gum as a  
120 function of concentration, which has been replotted from Goh et al. [14]. The dilute and the semidilute regimes are clearly demarcated by the two different power-laws ( $\eta_0 \sim c^{1.25}$  and  $\eta_0 \sim c^{4.64}$  respectively). The concentration at which the two power-laws intersect gives us a coil overlap concentration  $c^* \approx 2.2$  wt.%. The two distinct power-laws observed in the scaling of zero shear viscosity with  
125 concentration has also been widely observed in a number of synthetic polymers [26]. The change in the scaling occurs from increased interactions between polymer molecules upon coil overlap. The observed exponent is consistent with scaling arguments for an entangled flexible chain in a  $\theta$ -solvent [52]. This exponent is higher than what has been observed in the majority of polysaccharide  
130 solutions with the notable exception of Xanthan gum [4] — in this case the semidilute regime exhibits a scaling of  $\eta_0 \sim c^{4.2}$ . This anomalous scaling has been attributed to the presence of intermolecular interactions in addition to those arising due to physical entanglements of overlapping coils [37, 40]. [Recently, the large exponent observed in some polysaccharides in the scaling law for zero-shear viscosity as a function of concentration has been explained by the molecular weight dependent partial solubility of the polymer molecules \[49\].](#) In  
135 this paper, it is our goal to explore the nature of the intermolecular interactions in Mamaku gum solutions, using the amplified molecular deformation resulting from extensional flow.

140 These intermolecular interactions are even more dramatically visible at higher shear rates. In Figure 1(b), we replot the nonlinear shear rheology results of Goh et al. [14]. For all concentrations larger than  $c^* \approx 2.2$  wt.%, pronounced shear thickening is present in the flow curve over a certain range of shear rates

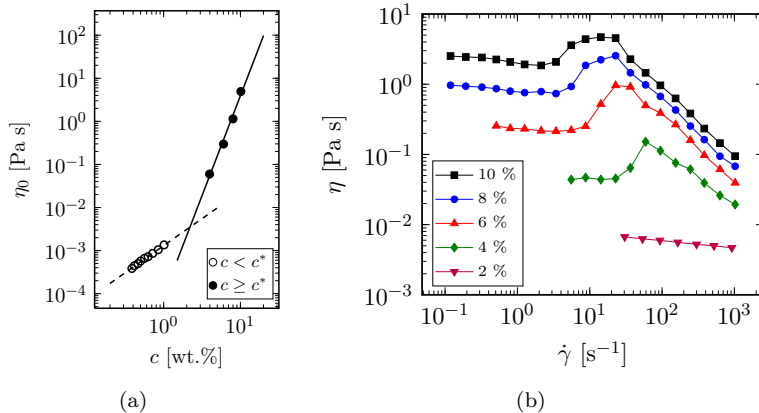


Figure 1: **(a)** The zero shear viscosity  $\eta_0$  of Mamaku gum solutions as a function of concentration showing the different power law scalings characteristic of the dilute and semidilute regimes. In the semi-dilute regime,  $\eta_0 \sim c^{4.64}$ . **(b)** The shear rheology of different concentrations of Mamaku gum in the absence of urea, reproduced with permission from Goh et al. [14] For Mamaku gum,  $c^* \approx 2.2$  wt. %. At some critical shear rate  $\dot{\gamma}_p$ , which depends on the Mamaku gum concentration, a shear thickening regime appears for  $c > c^*$ , followed by strong shear thinning.

$\dot{\gamma}$ . Such shear thickening has been observed in many associative polymer solu-  
 145 tions, suspensions and worm-like micelles, [59] but has rarely been observed in  
 polysaccharide biopolymers [63, 21]. The proposed mechanism of shear thicken-  
 ing in Mamaku gum is the conversion of *intra*-molecular interactions to *in-*  
*ter*-molecular interactions; upon the imposition of high shear rates (compared  
 to the characteristic relaxation time of the polymer), the polymer chains are  
 150 partially elongated due to the extensional component of the shear deformation  
 (because any shear flow can be decomposed into a combination of pure exten-  
 sion plus pure rotation). This elongation exposes additional ‘sticker’ groups that  
 locally interact between different molecules [14]. The physical crosslinks thus  
 formed lead to an increase in the effective hydrodynamic size of the polymer  
 155 chains, thus leading to an increase in viscosity [62]. The strong shear-thinning  
 observed at higher shear rates occurs when the stress in the fluid exceeds the  
 value needed to break the intermolecular associations, and the physically asso-  
 ciated chains are then pulled apart. This is effectively a constant stress process,  
 and this can be validated by plotting the shear stress  $\sigma(\dot{\gamma})$  as a function of shear



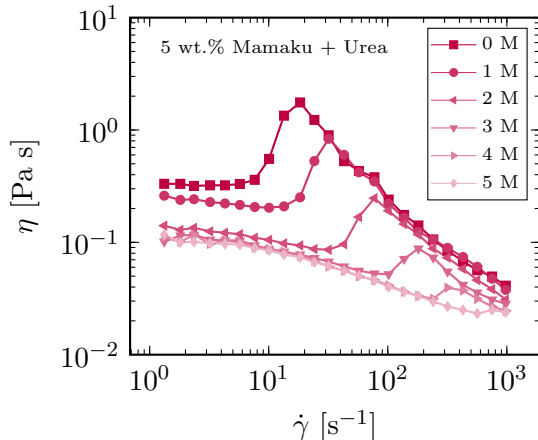


Figure 2: Effect of the addition of urea on the viscosity of a 5 wt.% Mamaku gum solution. Upon the addition of urea, three changes are observed, namely, the zero shear viscosity plateau drops, the onset of shear thickening is pushed to higher shear rates, and the extent of shear thickening also drops.

160 rate  $\dot{\gamma}$  (see supporting information). Previous studies have demonstrated that it is unlikely that the interactions which lead to the shear-thickening behavior arise from electrostatic or hydrophobic effects [29]. Intra- and intermolecular hydrogen bonding is present in many polysaccharide systems [55, 23] making it a likely candidate for the origin of the observed physical entanglements.

To test this hypothesis we measure the rheology of Mamaku gum solutions with different concentrations of urea added. Urea is known to be a strong disruptor of macromolecular hydrogen bonds [36], in the sense that it competes for the hydrogen bonding sites along the chain, and prevents Mamaku-Mamaku intermolecular hydrogen bonding. In figure 2, we show the effect that the addition of urea has on the shear rheology of Mamaku gum. There are three changes induced in the shear rheology of the solutions upon the progressive increase in urea concentration: (1) The zero-shear viscosity  $\eta_0$  drops, (2) the shear rate  $\dot{\gamma}_p$  at which the peak viscosity is observed is shifted out to larger shear rates and (3) the peak viscosity  $\eta_p$  drops. This shows that the intermolecular interactions in Mamaku gum are strongly decreased in the presence of urea, and it is hydrogen bonding that leads to the shear-thickening behavior seen in these solutions.

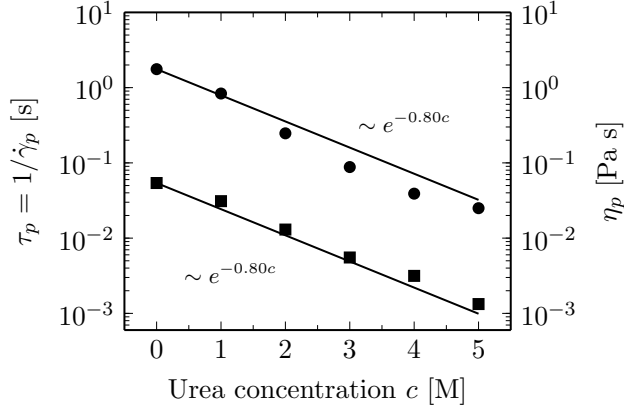


Figure 3: Dependence of the characteristic timescale  $\tau_p$  (squares) and the peak viscosity  $\eta_p$  (circles) on the concentration of added urea for a 5 wt. % Mamaku gum solution. An identical exponential dependence (differing only by a constant pre-factor) is observed in the variation of  $\eta_p$  as well as  $\tau_p$  with urea concentration. We measure the same exponential sensitivities for 2.5 wt. % and 5.0 wt. % Mamaku gum solutions.

Defining a time constant  $\tau_p = 1/\dot{\gamma}_p$  yields a characteristic timescale for the lifetimes of the hydrogen bond associations between Mamaku gum molecules in solution. In figure 3 we plot the value of  $\tau_p$  as a function of the urea concentration  $c$  on a log-linear scale. We observe that the characteristic timescale  $\tau_p$  decreases exponentially with urea concentration as  $\tau_p \sim \exp(-mc)$  where  $m$  is a constant. Linear regression gives us

$$\tau_p = \tau_p^0 e^{-0.80c}. \quad (5)$$

165 where  $c$  is the molar concentration of urea ( $M_0 = 60.06$  g/mol) and  $\tau_p^0$  is the characteristic timescale for the onset of shear-thickening with no urea addition.

Moreover, when we plot the peak shear viscosity  $\eta_p$  as a function of urea concentration  $c$  (also shown in Figure 3), we observe that  $\eta_p$  varies with  $c$  in an identical exponential fashion, i.e.  $\eta_p = \eta_p^0 e^{-0.80c}$ . The stress  $\sigma_p$  at which this peak viscosity occurs is given by

$$\sigma_p = \eta_p \dot{\gamma}_p \quad (6)$$

$$= \eta_p^0 e^{-0.80c} \cdot \dot{\gamma}_p^0 e^{0.80c} = \eta_p^0 \dot{\gamma}_p^0 \quad (7)$$

in which  $\eta_p^0$  and  $\dot{\gamma}_p^0$  are the peak viscosity and the value of the shear rate at which the peak viscosity is attained for the Mamaku gum solution with zero added urea ( $c = 0$ ). This quantity  $\sigma_p$  is independent of urea concentration, 170 indicating that the onset shear thinning appears at a constant value of stress. Our measurements give  $\sigma_p \approx 28$  Pa for the 5 wt.% Mamaku gum solution.

These observations suggest that the addition of urea does not change the average number of association junctions per chain, or the strength of each hydrogen bond, but only modifies the average lifetimes of the associations. We 175 explore this hypothesis further with the help of the extensional rheology experiments described below.

### 3.2. Capillary Breakup Extensional Rheometry

Because shear thickening behavior can arise from the partial extension of polymer chains leading to increased intermolecular interactions [14, 62], we directly 180 study the behavior of Mamaku gum solutions in extensional flow. We use the CaBER device to quantitatively measure the changes in the extensional rheology of Mamaku gum upon increasing the urea concentration. Although limited in number, CaBER experiments performed on other polysaccharide systems, such as cellulose/ionic liquid solutions [18], Sundew plant mucilage [9], 185 guar gum solutions [57, 7] and Schizophyllan solutions [5], have revealed that capillary breakup rheometry is an accurate technique for quantifying the elongational properties of these fluids. Moreover, the potential application of Mamaku gum solutions as a food thickener necessitates an understanding of its elongational properties; the biomechanics of swallowing is such that a food bolus en- 190 counters a squeeze flow [42, 46], whose kinematics has elongational deformation components.

In figure 4, we show images of CaBER experiments as a function of time for both 2.5 wt.% (top row) and 5 wt.% (bottom row) Mamaku gum solutions.

We have scaled time by the breakup time  $t_b$  of the fluid filament for each concentration (the values of  $t/t_b$  are given in the figure caption). The shape of the liquid bridge helps us determine the onset of the elasto-capillary regime, in which equations (2) - (4) hold. At very early times  $t/t_b \ll 1$ , the liquid bridge

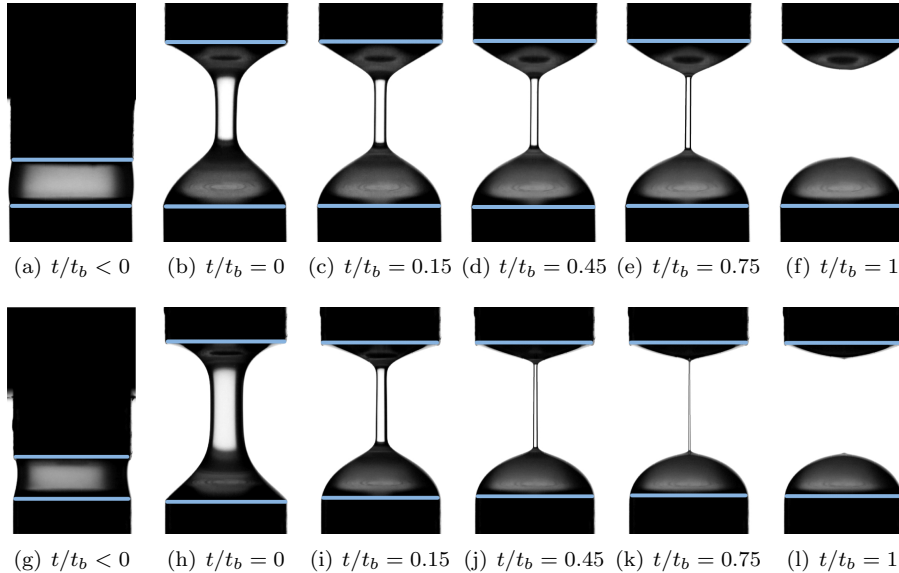


Figure 4: Snapshots of CaBER experiments for 2.5 wt. % (top row) and 5.0 wt. % (bottom row) Mamaku gum solutions. In both cases, it can be seen that the onset of the elasto-capillary regime, characterized by a uniform cylindrical fluid filament, occurs at around  $t/t_b \approx 0.15$ . For the 2.5 wt.% solution, the break-up time  $t_b = 0.80$  s, while for the 5 wt.% solution,  $t_b = 55.30$  s. The initial gap is  $L_0 = 2$  mm, the final gap  $L_f = 8$  mm, and the plate diameter  $D_0 = 6$  mm. This yields an initial aspect ratio of  $\Lambda_0 = 0.33$  and a final aspect ratio of  $\Lambda_f = 1.33$ .

has just been formed and inertial stresses generated during the step deformation are dominant. Immediately following this inertial regime there is a viscocapillary regime, where capillary forces are balanced by the viscosity of the fluid. In this regime, the midplane diameter of the fluid filament decreases linearly with time and is given by [33]

$$D(t) = D_0 - \frac{2x-1}{6} \frac{\sigma}{\eta_0} t \quad (8)$$

where  $x = 0.7127$  for the viscocapillary similarity solution [33]. The linear viscous thinning regime is followed by an exponential elasto-capillary regime

in which the filament diameter decays as  $D \sim \exp(-t/3\tau)$ . Because the fluid filament formed after the step deformation in a CaBER device experiences the deformation kinematics of a uniaxial elongational flow, the polymeric chains of Mamaku gum are constantly accumulating strain, and elastic stresses in the filament increase with time. At one particular instant of time, the elastic stress contribution exceeds that of the viscous stresses, and the capillary forces are predominantly balanced by the elastic stresses [1]; the breakup dynamics now enters the elasto-capillary regime which is characterized by the formation of a uniform cylindrical liquid bridge of constant diameter between two filament ‘feet’ attached at each endplate. In this regime, the evolution of the diameter as a function of time is given by equation (2). From figure 4, we see that for both the 2.5 wt% and 5 wt. % solutions, the elasto-capillary regime is established for  $t/t_b \gtrsim 0.15$ . Anna and McKinley [1] have shown that during a CaBER experiment, the diameter evolution as a function of time can generally be fit by a function of the form

$$D(t) = ae^{-bt} - ct + d \quad (9)$$

where  $a$ ,  $b$ ,  $c$  and  $d$  are constants, and this functional form captures both the early time viscous regime as well as the subsequent elasto-capillary regime. The coefficient  $b$  is related to the relaxation time of the fluid, and the value of  $c$  is related to the steady state extensional viscosity plateau at large Hencky strains.

We show the midplane diameter of the liquid bridge  $D_{\text{mid}}(t)$  as a function of time for 2.5 wt.%, 5.0 wt.% and 7.0 wt.% Mamaku gum solutions respectively. As the Mamaku gum concentration is increased, breakup of the fluid filament occurs at larger times; we measure the breakup time  $t_b$  as being 0.80 s, 55.3 s and 89.2 s for the 2.5 wt.%, 5.0 wt.% and 7.0 wt.% solutions respectively. From the  $D_{\text{mid}}(t)$  vs.  $t$  data, we can now use equation (2) in the elasto-capillary regime of the experiment to determine the relaxation time of the fluids, and these are  $\tau = 0.16$  s,  $\tau = 4.55$  s and  $\tau = 6.28$  s for the 2.5 wt.%, 5.0 wt.% and 7.0 wt.% solutions respectively. We can also use the midplane diameter

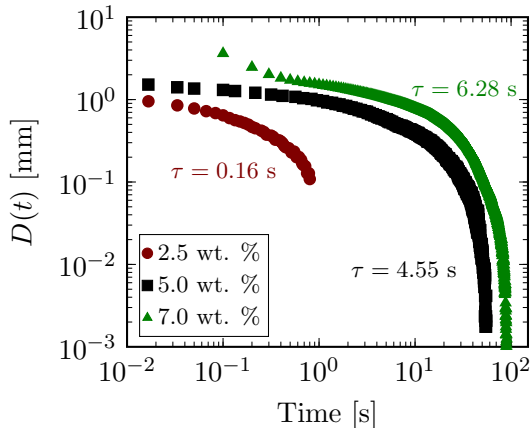


Figure 5: Diameter of the fluid filament as a function of time for CaBER experiments performed on different concentrations of Mamaku gum. The relaxation times shown in the figure is determined by fitting equation (2) to the elasto-capillary regime of the experiment. The relaxation time  $\tau$  increases with increasing Mamaku concentration.

data to calculate the transient extensional viscosities  $\eta_E^+$  of the Mamaku gum solutions using equation (4). In figure 6a, we show the variation of  $\eta_E^+$  as a function of the Hencky strain at the filament midplane  $\varepsilon_H(t)$ ; the latter was calculated using equation (1). To find the derivative of the midplane diameter  $dD(t)/dt$ , rather than fitting a function of the form given in equation (9), we directly differentiate the measured data for the diameter (shown in figure 5) and apply a minimal amount of smoothing (3 point moving average). The surface tensions for the 2.5 wt. %, 5.0 wt.% and 7.0 wt.% was measured to be  $\sigma = 44.6$  mN m,  $\sigma = 33.7$  mN m and  $\sigma = 33.5$  mN m respectively. We observe that at large values of Hencky strain  $\varepsilon_H$ , the transient extensional viscosity  $\eta_E^+$  for the 5.0 wt.% and 7.0 wt.% solutions are both of the order  $\mathcal{O}(10^3 \text{ Pa s})$ .

For the Mamaku gum solutions used in this study, the coil overlap ratio ranges between  $1.27 < c/c^* < 3.18$ , based on the value of  $c^* = 2.2$  wt. % determined by Goh et al. [14] and the macromolecules in solution are semi-dilute and entangled. The measured value of the steady extensional viscosity are an order of magnitude higher than the steady state extensional viscosities of other polysaccharide systems with the same values of  $c/c^*$  used in this study, for ex-

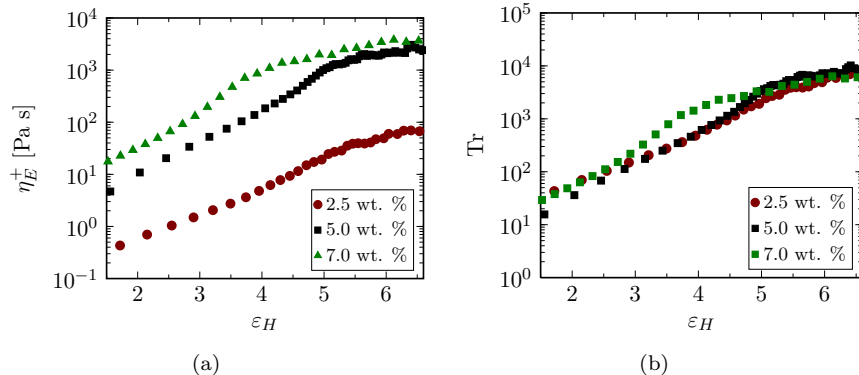


Figure 6: **(a)** Transient extensional viscosity of different concentrations of Mamaku gum calculated using equation (4). **(b)** Trouton ratio  $Tr = \eta_E^+/\eta_0$  for the same concentrations of Mamaku gum shown in (a). Whereas the extensional viscosity increases with increasing Mamaku gum concentration  $c$ , the Trouton ratio is nearly independent of  $c$ .

ample, hydroxypropyl guar gum solutions and sodium hyaluronate [2]. This indicates that intermolecular interactions during extension are significantly higher for Mamaku gum as compared to many other polysaccharide systems. We have already noted from Figure 1 that the shear viscosities of the Mamaku gum solutions increase as the concentration is increased. In the elasto-capillary regime, the flow field in the CaBER device is well described by uniaxial elongational kinematics and hence is shear-free. Therefore, to separate out the effect of increasing shear viscosity with concentration (cf. Figure 1), we define a transient Trouton ratio  $Tr$  as

$$Tr = \frac{\eta_E^+}{\eta_0} \quad (10)$$

in which  $\eta_E^+$  is the transient extensional viscosity of the fluid, and  $\eta_0$  is the zero shear viscosity. For a Newtonian fluid [25], the Trouton ratio is a constant, and  $Tr = 3$ . We show the values of the Trouton ratio  $Tr$  for Mamaku gum solutions in Figure 6b. We observe that the Trouton ratio remains relatively unchanged upon changing the Mamaku gum concentration, indicating that increasing the concentration of Mamaku gum affects the shear properties of the gum more than the form of the extensional response.

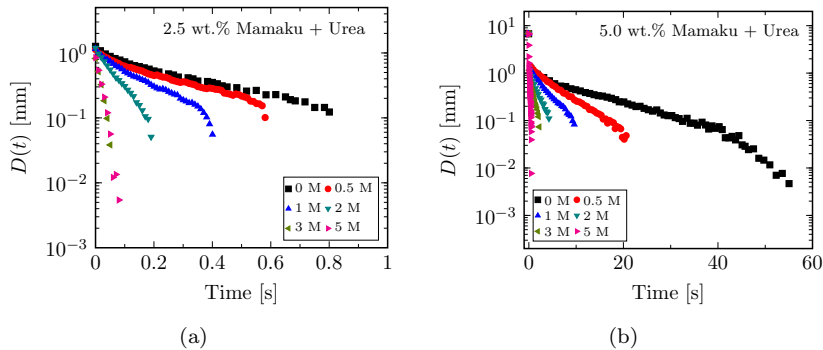


Figure 7: The midplane diameter  $D(t)$  of the thinning filament as a function of time  $t$  of 2.5 wt. % (a) and 5.0 wt. % (b) Mamaku gum solutions measured during CaBER experiments, plotted on a log-linear scale. Increasing the urea concentration leads to earlier breakup and a drop in viscoelasticity. The magnitude of the slope of the  $D(t)$  vs.  $t$  curves is inversely related to the relaxation time  $\tau$ ; for both Mamaku concentrations, the relaxation time decreases upon increasing urea concentration.

Having characterized the extensional rheology of urea-free Mamaku gum  
 235 solutions, we next study the changes induced in the rheological response of Ma-  
 maku gum solutions when hydrogen bonding interactions are suppressed, by  
 studying Mamaku-urea mixtures in the CaBER device. We first observe the  
 breakup dynamics of the Mamaku gum solutions in the presence of urea. We  
 show the evolution of the midplane diameter  $D(t)$  as a function of time  $t$   
 240 2.5 wt. % and 5 wt. % solutions with varying concentrations of added urea in  
 Figures 7a and 7b respectively. We immediately observe that for both concen-  
 trations of Mamaku gum solutions, the breakup time  $t_b$  strongly decreases with  
 increasing urea concentration. This indicates that the elastic stresses gener-  
 ated in the fluid filament formed upon imposition of the step extensional de-  
 245 formation are greatly reduced in comparison to the capillary stresses. This is again a con-  
 sequence of the Mamaku macromolecules in solution preferentially forming hy-  
 drogen bonds with urea molecules rather than intermolecular Mamaku-Mamaku  
 hydrogen bonds.

In figure 8a we show the transient extensional viscosity  $\eta_E^+$  of 2.5 wt. % Ma-  
 250 maku gum solutions with various molar concentrations of urea added. Figure 8b  
 shows the corresponding values of  $\eta_E^+$  for 5 wt.% Mamaku gum solution with



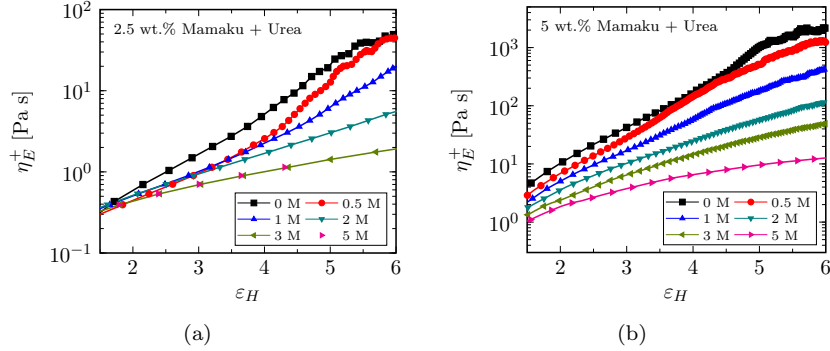


Figure 8: The transient extensional viscosity  $\eta_E^+$  of 2.5 wt. % (a) and 5.0 wt. % (b) Mamaku gum solutions measured in a CaBER device. In both solutions,  $\eta_E^+$  drops by nearly two orders of magnitude when the urea concentration is increased from 0 M to 5 M.

added urea of varying molar concentrations. We observe the expected trend of a substantial decrease in  $\eta_E^+$  and Tr with increasing urea concentration in both cases, indicating that once again the addition of urea interferes with the intermolecular hydrogen bonds formed by Mamaku gum in solution. With 5 M  
 255 added urea the extensional viscosity of the wt. % gum decreases by a factor of over two hundred. The data also allows us to conjecture that a concentration of 0.5 M of added urea is enough to disrupt all the hydrogen bonding sites along the chain when it is coiled, but not as it stretches out; there is an upturn in the  
 260 transient extensional viscosity  $\eta_E^+$  for  $\varepsilon_H > 4$ . This could arise from access to new sites for hydrogen bonding that are exposed during the unraveling process.

From the data showing the evolution of the midplane diameter as a function of time (figure 7), we can also calculate the characteristic relaxation time for each specific Mamaku-urea mixture from the midplane diameter vs. time curves  
 265 by fitting an exponential of the form given by equation (2) in the elasto-capillary regime. We show the values of the relaxation times thus extracted on a log-linear scale in Figure 9 as a function of the urea concentration in the mixture. **Although we do not explicitly show the evolution of the midplane diameter as a function of time for 7.0 wt.% Mamaku gum solutions, we have also performed CaBER**  
 270

experiments on these solutions with the same concentrations of urea added as in the 2.5 wt.% and 5.0 wt.% solutions. The relaxation times of these solutions are also shown in Figure 9. Note that the relaxation time is a function of the

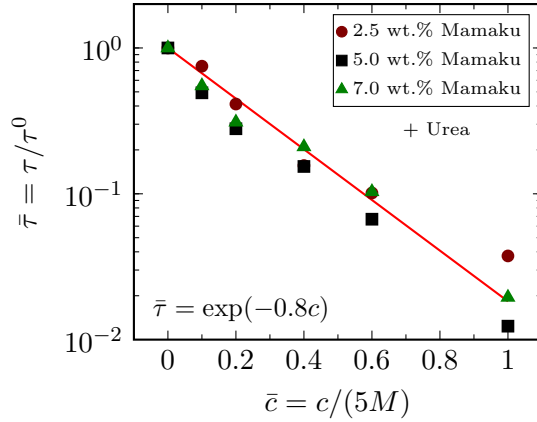


Figure 9: **(a)** The normalized relaxation time  $\bar{\tau} = \tau/\tau^0$  for Mamaku/urea mixtures calculated from CaBER experiments, where  $\tau^0$  is the relaxation time of the pure Mamaku solution (0 M urea). The relaxation times fall onto a master curve given by  $\bar{\tau} = \exp(-0.80c)$ , independent of the Mamaku concentration. **(b)** An identical exponential dependence is observed in the variation of the peak shear viscosity with urea concentration, as well as the reciprocal of the critical shear rate at which the peak shear viscosity is observed, shown here for a 5 wt.% solution of Mamaku. These exponential relationships are related to the lifetimes and the free energy of the hydrogen bond interactions.

concentrations of two different components present in the mixture: the Mamaku  
275 gum concentration as well as the urea concentration present in the mixture,  
i.e.,  $\tau \equiv \tau(c_{\text{Mamaku}}, c_{\text{urea}})$ . In figure 9 the relaxation time of each Mamaku-  
urea mixture has been non-dimensionalized by the value of the relaxation time  
 $\tau^0 = \tau(c_{\text{Mamaku}}, 0)$  obtained for the Mamaku gum solution of concentration  
 $c_{\text{Mamaku}}$  with zero added urea ( $c_{\text{urea}} = 0$ ). We denote this non-dimensionalized  
280 relaxation time by the notation  $\bar{\tau} = \tau(c_{\text{Mamaku}}, c_{\text{urea}})/\tau^0$ . Moreover, we scale  
the horizontal axis by 5 M, which is the maximum urea concentration used in  
the mixtures, and hence, the lower and upper bounds of the abscissa are 0 and 1  
respectively. We find that for all the Mamaku concentrations tested in this study  
(2.5, 5.0 and 7.0 wt.%), the relaxation time varies exponentially with increasing  
285 Mamaku concentration (i.e. we observe linear decay on a log-linear scale), and  
 $\bar{\tau} = \exp[-0.80c]$ . Comparing this result with what we obtain from figure 3, we

find that this exponential form is identical to that obtained for the dependence of the characteristic shear thickening timescale  $\tau_p$  on the concentration of urea (Equation (5)). The presence of the identical exponential forms across Mamaku  
 290 gum concentrations in both shear and extensional rheology experiments suggests a common origin which can be rationalized by examining the influence that the addition of urea has on the lifetime of the intermolecular hydrogen bond associations present in Mamaku gum.

The rheological response and strong shear-thickening behavior of Mamaku gum is reminiscent of other physically crosslinked networks that form temporary, reversible associations [27]. These associations can arise from a number of physical mechanisms, for example hydrophobic interactions [58], ion complexation [62] and, most relevant to this study, hydrogen bonding [47]. Leibler et al. have developed a theory for soft reversible networks called sticky reptation [28], which applies to networks formed by linear chains with multiple temporary cross-links along the chain (For example the modified polybutadienes studied by Freitas and Stadler [11]). The relaxation time of a system that relaxes through sticky reptation is given by [28, 27]

$$\tau \approx \left( \frac{N}{N_e} \right)^{1.5} \frac{2S^2\tau_d}{1 - 9/p + 12/p^2} \quad (11)$$

in which  $N$  is the number of monomers per chain,  $N_e$  is the number of monomers in an entanglement segment,  $S$  is the number of stickers per chain and  $p$  is the average fraction of stickers that are associated at any given time. The timescale  $\tau_d$  is the average time a sticker spends in the associated state, and is given by [56, 27]

$$\tau_d = \omega_0^{-1} e^{\Delta G/k_B T} \quad (12)$$

in which  $\Delta G$  is the free energy barrier for disassociation,  $k_B$  is Boltzmann's constant,  $T$  is the absolute temperature and  $\omega_0$  is a vibration frequency that determines the average number of times per second the sticker tries to climb the

energy barrier for dissociation as a result of thermal fluctuations [56]. Substituting Equation (12) into Equation (11), we obtain

$$\tau \approx \omega_0^{-1} \left( \frac{N}{N_e} \right)^{1.5} \frac{2S^2}{1 - 9/p + 12/p^2} e^{\Delta G/k_B T} \quad (13)$$

It is evident from the above equation that the relaxation timescale  $\tau$  of a particular system depends exponentially on the free energy for disassociation  $\Delta G$ , all other parameters being held constant. Our experimental observations in Figure 9 show that the relaxation time  $\tau$  decreases exponentially with increasing concentration of urea. This is only possible if adding urea to the Mamaku gum solutions modifies the free energy  $\Delta G$  in such a way that

$$\Delta G = \Delta G^0 - mc \quad (14)$$

Here  $\Delta G^0$  is the free energy for disassociation in the absence of any urea,  $c$  is the concentration of urea added and  $m$  is a constant. Substituting Equation (14) into Equation (13) we obtain

$$\tau = \tau^0 e^{-mc/k_B T} \quad (15)$$

where  $\tau^0$  is the relaxation time of the hydrogen-bonded temporary network in the absence of urea and is given by

$$\tau^0 = \omega_0^{-1} \left( \frac{N}{N_e} \right)^{1.5} \frac{2S^2}{1 - 9/p + 12/p^2} e^{\Delta G^0/k_B T} \quad (16)$$

The linear dependence of the free energy  $\Delta G$  on the urea concentration  $c$  given  
 295 in Equation (14) has been experimentally observed in the context of protein  
 solutions. Greene and Pace have observed that adding denaturants such as  
 urea or guanidine hydrochloride (GmHCl) to various protein solutions results  
 in a linear decrease of the free energy for denaturation with denaturant con-  
 300 centration [16]. Similar observations have been made by many other studies of  
 protein denaturation [39, 30, 64]. In fact, the denaturation energies  $\Delta G^0$  for

protein solutions are routinely determined by linearly interpolating the  $\Delta G$  vs  $c$  curve to zero denaturant concentration [31]. Our results show that this linear relationship also holds for solutions of Mamaku gum polysaccharide, and may also be applicable to other polysaccharide systems as well. From our experimental result of  $\tau = \tau^0 e^{-0.80c}$ , we calculate a value of  $m = 471.9$  cal/mol  $\cdot$  M ( $m = 1982$  J/mol  $\cdot$  M), where units of M stand for molarity of urea in moles/liter. The value of  $m$  quantifies the strength of the interaction of a hydrogen bond-disruptor such as urea with the Mamaku gum polysaccharide; the larger the value of  $m$ , the stronger the interaction between the bond-breaker and the polysaccharide, and the more pronounced is the ability of the bond-disruptor to decrease the free energy barrier for disassociation. The value of  $m$  will vary not only with the specific chemical used, but also the polysaccharide system [39]. Myers et al. have listed the  $m$  values of various proteins-denaturant combinations, and the  $m$  values obtained on urea addition range from 250 cal/mol  $\cdot$  M to as high as 7800 cal/mol  $\cdot$  M. [39]

Note that our experimental observation of an exponential dependence of the viscoelastic time constant  $\tau$  on urea concentration  $c$  (at fixed Mamaku concentration) indicates that the addition of urea does not modify the other network parameters such as the number of stickers per chain  $S$  or the average fraction of stickers that are associated at any given time  $p$ ; it is only the dissociation lifetime  $\tau_d$  that is modified through the variation in the free energy barrier for disassociation. This implies that there are no fundamental structural changes induced in the Mamaku gum polysaccharide upon the addition of urea and suggests the possibility of a *time-concentration* superposition principle. Time-temperature superposition is widely used in rheology to predict the relaxation spectra of polymeric systems at frequencies that are experimentally inaccessible [10]. It has been observed that for complex fluids that obey time-temperature superposition, small amplitude oscillatory shear experiments may be performed at different temperatures and then shifted along the frequency axis using a shift factor  $a_T$  to obtain a master curve of the relaxation spectrum of the fluid over many decades of frequency. Such fluids are said to be thermorheologically

simple, and time-temperature superposition holds for polymeric systems that do not undergo microstructural changes or phase transitions upon a change in temperature [10]. As discussed above, we observe no structural changes in Mamaku gum polysaccharide molecules upon the addition of urea, and we expect a time-concentration superposition principle to exist in this case.

In figure 10(a) we show the values of the reduced storage and loss moduli,  $G'_r(\omega)$  and  $G''_r(\omega) - \eta_s(\omega_r)$  respectively, of a 5 wt.% Mamaku gum solution with a range of different molar concentrations of added urea. After subtract-

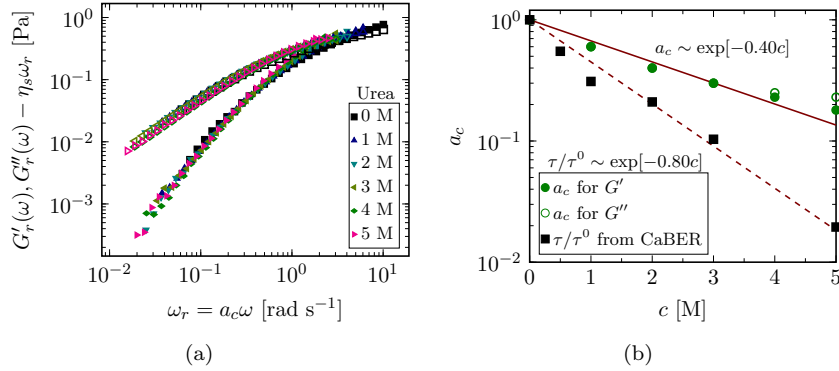


Figure 10: (a) The values of reduced storage and loss moduli measured in an SAOS experiment for a 5 wt. % Mamaku gum solution with different concentrations of added urea. The curves have been shifted along the frequency axis using a shift factor  $a_c$  to generate a master curve. (b) The values of the shift factor  $a_c$  as a function of urea concentration required to generate the master curves of  $G'_r(\omega)$  and  $G''_r(\omega)$ . There is an exponential relationship between  $a_c$  and urea concentration  $c$ . However, the dependence of the shift factor on urea concentration is stronger in the nonlinear experiments (black squares) as compared to the linear SAOS experiments.

ing the purely viscous contribution of the solvent to the loss modulus, we have shifted these curves along the frequency axis using a shift factor  $a_c$  to construct a reduced frequency  $\omega_r = a_c \omega$ . The subscript  $c$  denotes that this shift factor is a function of the urea concentration  $c$ . We note that the values of  $G'_r(\omega)$  and  $G''_r(\omega)$  for each of the different Mamaku gum-urea mixtures fall on a master curve over nearly three decades of frequency. Again, this confirms the fact that there are no major microstructural changes introduced in this gum upon the addition of urea, and it is only the timescale of hydrogen bond association and dissociation that is altered. Figure 10(b) shows the values of the

shift factors  $a_c$  used to construct the master curve as a function of the urea  
 concentration  $c$ . The concentration shift factor  $a_c$  varies exponentially, with  
 350  $a_c \sim e^{-0.40c}$ . The co-efficient 0.40 in the exponential yields a urea sensitivity  
 of  $m = 235.9$  cal/mol · M ( $m = 991$  J/mol · M). Interestingly, this value is  
 much lower than the value  $m = 471.9$  cal/mol · M we obtained previously from  
 nonlinear shear and extensional rheology experiments. The latter dependence  
 355 is shown as black squares in Figure 10.

The differing sensitivities to urea measured in linear and nonlinear de-  
 formations (which we quantify in terms of the magnitude of the shift factors)  
 indicates that the Mamaku gum solutions show time-concentration rheological  
 complexity. This complexity can be explained in terms of the increased chain  
 360 extension of Mamaku gum solutions under the action of a nonlinear flow. In the  
 case of proteins, the sensitivity to denaturants has been found to be larger for  
 proteins that are in more extended or unfolded conformations [39], and this effect  
 has been studied by controlling the amount of unfolding of the protein molecule  
 by varying the pH [45, 44]. Previous rheological studies have shown that Ma-  
 365 maku gum solutions are relatively insensitive to change in pH [29]. However a  
 steady shear flow at high shear rates or extensional flows such as that produced  
 in the CaBER device can elongate the Mamaku gum polysaccharide chains and  
 this appears to lead to much larger concentration shifts as compared to those  
 found from a linear viscoelastic experiment. Upon the imposition of a nonlinear  
 370 deformation (say steady shearing flow at a shear rate  $\dot{\gamma} \approx \dot{\gamma}_p$ ), the elongated  
 chain now has additional exposed sites for hydrogen bonding i.e. the value of  
 $S$  in Equation (13) is modified. The hydrogen bonding at these additional ex-  
 posed sites will also be influenced by the addition of urea. In fact, we note that  
 the shift factor obtained from nonlinear rheology is almost exactly a factor of  
 375 two larger than the linear viscoelastic shift. This suggests that nonlinear effects  
 arise predominantly from pairwise interactions i.e.  $a_c(\tau) \sim [a_c(G^*)]^2$ . Detailed  
 investigation of the microstructural origins of these urea different sensitivities  
 we have documented in weak and strong flows requires further experimental and  
 computational studies, for example, kinetic theory simulations of sticky polymer

380 networks under flow.

#### 4. Conclusions

Measurements of the steady shear flow curves of Mamaku gum solutions exhibit a pronounced shear-thickening response, which is very unusual for polysaccharide systems [24]. At a critical shear rate  $\dot{\gamma}_p$ , the shear-thickening is arrested and there is an onset of extreme shear-thinning, which occurs at an approximately constant shear stress  $\sigma_p$  for all experimentally imposed shear-rates  $\dot{\gamma} > \dot{\gamma}_p$ . In this paper, we have explored the origin and consequence of this shear thickening behavior; through a combination of shear and extensional rheology experiments performed on Mamaku gum-urea mixtures, we have determined the source of the shear-thickening to be intermolecular hydrogen bonding.

Nonlinear steady shear experiments reveal that when we increase the amount of urea in the mixture (while holding the Mamaku gum concentration constant), both the zero shear viscosity  $\eta_0$  as well as the peak viscosity in the shear-thickening regime  $\eta_p$  progressively decrease. The reciprocal of the shear rate  $\dot{\gamma}_p$  at which the peak viscosity appears provides a characteristic timescale of the fluid in nonlinear deformation and also becomes smaller; in fact both  $\eta_p$  and  $\tau_p = \dot{\gamma}_p^{-1}$  decrease exponentially with increasing urea concentration.

Transient extensional rheometry performed using a CaBER device demonstrate that the relaxation time in extension also follows an exponentially decreasing relationship with increasing urea concentration. Moreover, this exponential dependence on relaxation time with urea concentration is identical to that obtained from nonlinear shear experiments. We interpret this in terms of the modification of the free-energy barrier for hydrogen bond dissociation, leading to an exponential relationship between the dissociation timescale of hydrogen bonds with urea concentration. Our experiments are consistent with the expected relaxation dynamics of Mamaku gum-urea mixtures predicted by the sticky reptation theory for reversible networks of polymers with multiple associative groups along the backbone. We show that this leads to the concept



of a time-concentration superposition principle, akin to the more familiar time-  
410 temperature superposition used for concentrated polymer solutions or polymer  
melts. However we find that the linear and nonlinear rheology of the Mamaku  
gum-urea mixtures shift by different extents upon addition of urea. By anal-  
ogy with other polymeric systems which are described as thermorheologically  
complex, we may refer to Mamaku gum solutions as *urheologically* complex.

415 This rheological study improves our understanding of Mamaku gum solu-  
tions in particular and shear thickening polysaccharides in general. Mamaku  
gum has traditionally been used as a food source by the native Māori of New  
Zealand [14]. The shear thickening properties and the pH insensitivity make it  
an excellent potential food thickener to aid patients with dysphagia. The ability  
420 to independently control the linear and nonlinear rheological characteristics via  
the different sensitivities to hydrogen bond disruptors offers an additional level  
of formulation control. Additional controlled trials on the safety and the efficacy  
of Mamaku gum, as well as the behavior of the gum in mammalian digestive  
tracts would greatly help towards realizing this possibility.

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