Effect of different molecular characteristics on the lubrication behavior of polysaccharide solutions

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ARTICLE INFO

ABSTRACT

Polysaccharides strongly affect the sensorial properties of foods, which is partly related to the lubrication they provide. We investigated the lubrication performance of polysaccharides with different characteristics (i.e. molecular weight, conformation, stiffness, and charge density) to identify the most relevant structural features related to lubrication ability. The effect of viscosity was excluded using isoviscous systems. Conformation resulted to be a key factor in determining lubrication. Rigid rod-like polysaccharides (xanthan) showed higher lubricating capacity and better resistance to changes in pH and ionic strength compared to semi-flexible (pectin and carboxymethyl cellulose) and flexible polysaccharide (guar gum). The friction behavior of flexible polysaccharides was highly dependent on concentration and sliding speed, for which a model including parameters of friction, concentration, and speed was developed. The concentration-dependency of the lubrication was related to the shear-thinning behavior, and possible mechanisms to explain these differences in terms of molecular properties of the polysaccharides are proposed.

1. Introduction

Polysaccharides are widely used in the food industry as thickeners, stabilizers, or gelling agents (Nishinari et al., 2016; Zhu et al., 2018; Zhu et al., 2019). The role of molecular characteristics of polysaccharides in determining rheological properties has been extensively studied, but the contribution to lubrication behavior is still lacking understanding. Lubrication properties of foods have aroused enormous interest among food scientists as they are potentially linked with complex sensorial attributes such as creaminess, smoothness, and slipperiness (Chojnicka-Paszun et al., 2014; Fan et al., 2021; Kokini et al., 1977; Ng et al., 2018; Shewan et al., 2020; Upadhyay & Chen, 2019), which are important drivers for food palatability. As lubrication aspects are important factors for the textural perception of foods, gaining insight into the lubrication properties of different food systems is expected to make a great contribution to designing foods with engineered sensory properties.

In many of these studies, real foods or multicomponent systems were used. However, is it often not known what the contribution of individual components is to the lubrication properties. Up to now, only a few studies have focused on individual polysaccharides acting as a lubricant (Garrec & Norton, 2012; Stokes et al., 2011; Taira & McNamee, 2014). As reported in these studies, characteristics such as molecular weight, conformation, and charge density have been shown to be important to the lubrication properties of polysaccharides. Taira et.al, for example, studied the effect of molecular weight and showed that chitosan-derived compounds with a lower molecular weight showed better lubrication than those with a higher molecular weight (Taira and McNamee, 2014). However, opposite results were found for inulin, as inulin with a higher molecular weight provided more efficient lubrication than one with a lower molecular weight (Meyer et al., 2011). With respect to conformation, it has been reported that polysaccharides that are stiff and charged provide good lubrication. For example, the stiff molecule scleroglucan gave lower friction coefficients than a random coil polysaccharide guar gum (Garrec & Norton, 2012). However, other studies have shown that differences in conformation did not show a significant effect on lubrication (de Vicente et al., 2006). The effect of conformation on lubrication properties is thus not fully understood yet. As the conformation of polysaccharides is related to the structure, also the

charge density can affect lubrication. The anionic polysaccharide pectin has already been shown to be more effective as a lubricant than the non-ionic locust bean gum, which may be related to the charged group that pectin contains (Chojnicka-Paszun & de Jongh, 2014; Stokes et al., 2011). As charge density is also influenced by pH and ionic strength, these factors should also be considered to understand the lubrication profiles. Both pH and salt ions can influence intramolecular and intermolecular electrostatic interactions and change the conformation of polysaccharides (Carneiro-da-Cunha et al., 2011). Since many polysaccharides are naturally charged and have a certain buffering capacity, it becomes even more complicated to relate lubrication properties to specific characteristics of the polysaccharides.

Currently, limited studies have been reported that discuss the effect of charge density and ionic strength on lubrication, and it is not completely understood yet how specific characteristics of polysaccharides influence the lubrication performance. Our work aimed to get more insight into the effect of separate characteristics of the polysaccharides on lubrication by studying a set of polysaccharides systematically varying in molecular properties, i.e. molecular weight, conformation, charge density, and vary conditions such as pH and ionic strength. To limit the effect of viscosity on lubrication, isoviscous model systems of commercially available polysaccharides were used to be able to isolate the effect of the molecular properties. We hypothesized that the molecular weight of polysaccharides influences their ability to spread and cover the contacting surfaces, thereby influencing the polysaccharide film formation on the surfaces. This was investigated using maltodextrins (Newtonian fluids) and carboxymethyl cellulose (CMC, non-Newtonian fluids) with varying molecular weight. We also hypothesized that for larger polysaccharides, the stiffness of the molecule can increase the ability of the fluid to be entrained into the contact area and increase lubrication, because stiffer polysaccharides align easier with the flow of the fluid. This was examined using xanthan gum, guar gum and locust bean gum. With respect to environmental conditions, we hypothesized that pH has a large influence, as this parameter affects the charge density and further influences the conformation of polysaccharides. To be able to investigate the various effects separately, we varied the pH of pectin, CMC and xanthan gum samples, which have a different sensitivity toward pH. In addition, as the conformation and electrostatic interactions can also be varied by ionic strength, we hypothesized that the specific effect of pH and ionic strength depends on the conformation.

2. Materials and methods

2.1. Materials

Maltodextrins with dextrose equivalent (DE) of 4.0–7.0 and 16.5–19.5, carboxymethyl cellulose (CMC) with molecular weights (Mw) of ~90 kDa and ~700 kDa, guar gum (GG, ~4000 kDa), xanthan gum (XG, ~4000 kDa) and locust bean gum (LBG, ~310 kDa) were purchased from Sigma-Aldrich Chemie GmbH (Steinheim, Germany). Pectin with two different esterification degrees (38 % and 71 %) were kindly provided by Herbstreith & Fox Corp. (Herbstreith & Fox, Neuenburg, Germany). Polydimethylsiloxane (PDMS 184 silicone elastomer kit) was purchased from Dow (Dow silicones, Dow Europe GmbH, Wiesbaden, Germany).

2.2. Methods

2.2.1. Preparation of polysaccharide solutions

Polysaccharide solutions were made by dispersing sample powders in Milli-Q® water and stirring for 3 h at room temperature (20 ± 0.1 °C). Afterwards, the solutions were heated at 80 °C for 1 h to further hydrate the polysaccharides and then cooled down to room temperature (20 ± 0.1 °C) after complete dissolution. NaOH or HCl (0.1 and 1 M) were used to adjust the pH when necessary. Concentration was determined as

described in Section 3.1.

2.2.2. Molecular weight distribution determination with HPSEC

The molecular weight distribution of polysaccharides was determined by High Pressure Size Exclusion Chromatography (HPSEC) on an Ultimate 3000 HPLC (Dionex, Sunnyvale, CA, USA) equipped with a Shodex RI-101 refractive index detector (Showa Denko, Tokyo, Japan), according to the method described by Rösch (Rösch et al., 2017). The prepared polysaccharide solutions were diluted to a concentration of 2.5 mg/ml and centrifuged (18,000g) for 10 min at 20 °C. The supernatant was collected and analyzed with three TSK-Gel columns connected in series (4000-3000-2500 SuperAW; 150 × 6 mm; Tosoh Bioscience, Tokyo, Japan). A sample volume of 20 µl was injected and eluted with 0.2 M NaNO$_3$ at 40 °C with a flow rate of 0.6 ml/min. Standards with molecular weight of 342, 6100, 21,102, 19,400 and 708,000 Da were used for calibration and calculation.

2.2.3. Zeta-potential measurement

The ζ-potential of the polysaccharide solutions was determined at room temperature (20 ± 0.1 °C) by dynamic light scattering using a Zetasizer Nano ZS (Malvern Instruments, Worcestershire, UK). Samples were diluted 10 times with Milli-Q water. The refractive index (RI) of samples was set at 1.45 for all polysaccharides. All the measurements were performed in triplicate and ζ-potential is presented as mean ± standard deviation (SD).

2.2.4. Conductivity measurement

Conductivity was determined at room temperature (20 ± 0.1 °C) by a conductivity meter (pHenomenal® CO 3100 L, VWR, USA). All the measurements were performed in triplicate and the results are presented as mean ± standard deviation (SD).

2.2.5. Adsorption measurement

Adsorption of polysaccharide was measured using a quartz crystal microbalance with dissipation monitoring (QCM-D, Biolin Scientific, Sweden) equipped with silicon dioxide Qsensors (QSX-303, Biolin Scientific, Sweden) at room temperature (20 ± 0.1 °C). Polysaccharide solutions were diluted to a concentration of 0.1 % (w/w). Milli-Q water was initially injected with a flow rate of 50 µl/min to wet the surface and obtain a stable baseline. Afterward, polysaccharide solutions were injected with a flow rate of 50 µl/min for 14,000 s and then Milli-Q was injected again with a flow rate of 50 µl/min to rinse the surface. The signals of 3rd, 5th, 7th and 11th overtones for frequency (f) and dissipation (D) were recorded and taken into account for data analysis and only the 7th overtone is shown in the results.

2.2.6. Rheological measurements

The viscosity of samples was measured using a stress-controlled rheometer (MCR 302, Anton Paar, Austria) with a double gap geometry (probe DG.26.7/Ti; cup DG 26.7/T200/Ti) or a concentric cylinder geometry (probe CC17/Ti; cup CC17/Ti). A sample of 3.8 ml (double gap) or 4.7 ml (cylinder) was poured into the cup and kept at 20 °C. The samples were equilibrated in the cup for 5 min before the measurement started. The shear rate was increased in logarithmic steps from 0.1 s^{-1} to 1000 s^{-1} in 5 min and then decreased from 1000 s^{-1} to 0.1 s^{-1} in 5 min. All measurements were performed in triplicate and the average value of the viscosity was plotted as a function of shear rate.

2.2.7. Tribological measurements

Tribological measurements were performed on a TriboLab (UMT, Bruker, Billerica USA) with an oscillation linear movement to determine lubrication properties of polysaccharide solutions. The tribo-pair consisted of a spherical glass ball (d = 12.7 mm) as probe and a PDMS substrate (L × W × H = 60 × 45 × 4 mm). The PDMS substrate (SYLGARDTM 184, Silicone Elastomer Kit, Dow Inc., USA) was made by mixing the base and curing agent, i.e. dimethyl vinylated and

trimethylated silica, respectively, at a ratio of 10:1. The well stirred mixture was poured onto a plastic plate that has a sandpaper (180, CAMI-standard) glued on the bottom of the plate to create a rough surface on the PDMS substrate. The PDMS mixture was de-aired with a vacuum pump and afterwards was put into an oven overnight at 60 °C to solidify. Afterwards, the PDMS substrate was cut to be fitted into a metal container that is connected to a motor able to apply an oscillating movement in a linear direction. The spherical glass ball was inserted into a holder connected to a force sensor. A schematic representation of the set-up is shown in Fig. 1.

For each measurement, a sample with a volume of 10 ml was added on top of the PDMS substrate to fully cover the surface. The temperature was kept at 20 ± 0.1 °C and a normal force, F_N, of 0.5 N was applied. The friction coefficient (μ) was measured as a function of sliding speed in a range from 0.1 to 120 mm/s, which was recorded as one cycle, over a moving distance of 5 cm. One measurement consisted of 3 cycles. The data were processed with the software UMT Test Viewer (UMT, Bruker, Billerica USA), and "zero" values obtained by limitations of sensor sensitivity were considered invalid and excluded from data analysis. The data of the second and third runs were selected for further analysis, as the data obtained from the first run were less repeatable and thus less reliable. Each sample was analyzed in triplicate, and the averaged value of 6 measured values of the friction coefficient (μ) was determined as a function of sliding speed.

3. Results and discussion

3.1. Overview of molecular weight (Mw) determination and concentration selection

The Mw of the studied polysaccharides was determined by HPSEC, and the obtained results are shown in Table 1. The molecular weight has a large effect on viscosity, which is known to influence lubrication to large extent. To gain more insights into the role of polysaccharide properties itself and to compare different types of polysaccharides, it is more appropriate to use isoviscous systems, to exclude effects of viscosity. We prepared polysaccharide solutions in a range of concentrations to vary their viscosity. To select isoviscous systems, polysaccharide solutions with similar viscosity were selected in pairs or trios at different viscosity regimes.

An overview of all polysaccharide solutions with selected concentrations for the present study are summarized in Table 1.
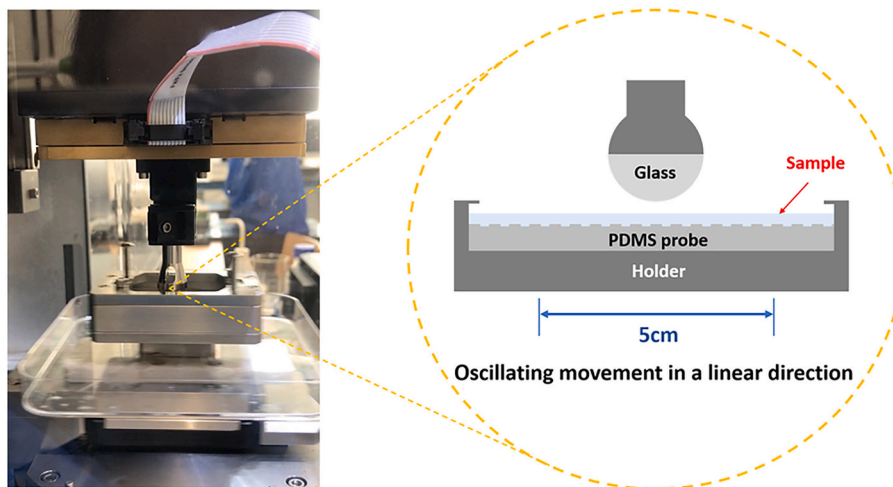
Table 1

Polysaccharides selected for the present study with their respective molecular weight and with the concentrations used to prepare isoviscous samples.

Polysaccharides	Molecular weight (Mw, Da)	Concentration (w/w %)
Maltodextrin (DE = 16.5–19.5) (LMD)	~800	10, 25
Maltodextrin (DE = 4.0–7.0) (HMD)	~13,000	5, 16
Pectin (esterification degree = 38 %, HCP)[a]	~63,500	0.52
Pectin (esterification degree = 71 %, LCP)	~78,900	0.45
Locust bean gum (LBG)	~310,000	0.25, 0.5, 1, 2
Guar gum (GG)	~4000,000	0.25, 0.5, 1, 2
Xanthan gum (XG)	~4000,000	0.1, 0.25, 0.5, 1, 2
Low Mw carboxymethyl cellulose (LCMC)	~90,000	1
High Mw carboxymethyl cellulose (HCMC)	~700,000	0.01

[a] Pectin with a low esterification degree has a high charge density and thus is abbreviated to HCP.

3.2. Effect of polysaccharide molecular weight (Mw) on lubrication

Since the Mw of polysaccharides has been recognized to be an important characteristic for lubrication, to investigate this point, two maltodextrins with different averaged Mw, one with a high Mw of 13,000 Da (HMD), and one with a low MW of ~800 Da (LMD), were selected (Table 1). Maltodextrin consists of D-glucose units and is a non-charged polysaccharide with flexible conformation. LMD is assumed to consist of 5 units of glucose, while HMD contains >80 units (BeMiller, 2019; Castro et al., 2016). The viscosity of 10 % LMD and 5 % HMD were matched at 1.4 mPa·s, and were considered as low viscosity systems in the present study. The viscosity of solutions with 25 % LMD and 16 % HMD was matched at 4 mPa·s, and were considered as high viscosity systems in the present study. All solutions showed Newtonian behavior at the measured shear rate range and the viscosity curves are shown in Fig. 2 (the insert figure). The measured friction coefficients of these samples are shown in Fig. 2.

The lubrication behavior of both maltodextrin types showed a concentration dependence: higher concentrations led to lower friction coefficients. This was not surprising as high concentration leads to high viscosity and high viscosity provides better lubrication due to better separation of the surfaces. The concentration-dependence of lubrication for large polymers was also reported in other studies (Cassin et al., 2001; de Vicente et al., 2006). A study with polysaccharides like polyethylene oxide, xanthan gum and guar gum also showed lower friction
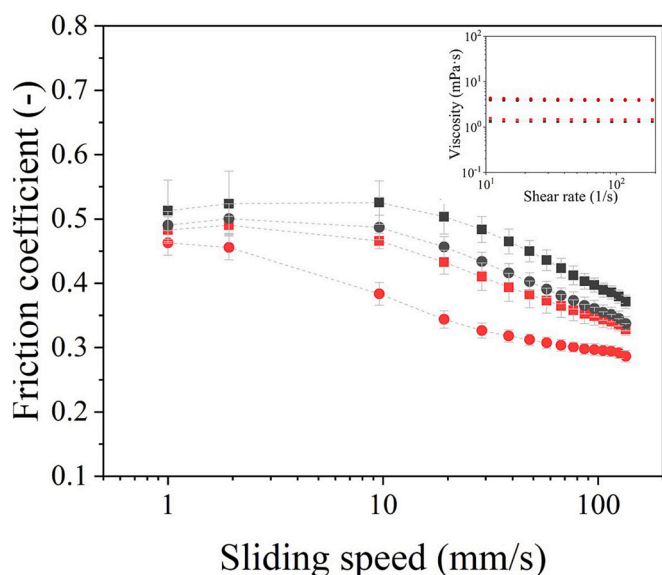

Fig. 1. Schematic representation of the tribological set-up used for the present study: glass ball sliding over a PDMS surface with an oscillating movement in a linear direction. The sliding distance was 5 cm.

Fig. 2. Friction coefficient as a function of sliding speed for maltodextrin solutions. Low viscosity group (1.4 mPa·s): 10 % LMD (red square) and 5 % HMD (dark grey square); high viscosity group (4 mPa·s): 25 % LMD (red circle) and 16 % HMD (dark grey circle). Dotted lines are shown to guide the eye. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
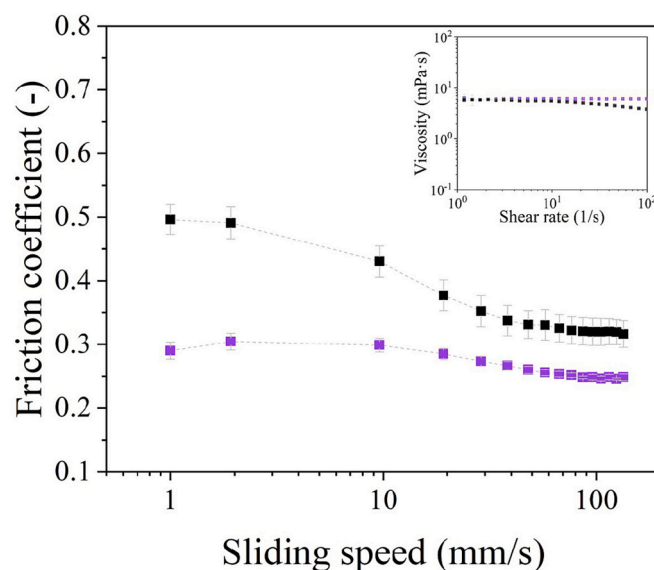

Fig. 3. Friction coefficient as a function of sliding speed for 1 % LCMC (purple square) and 0.01 % HCMC (black square) solutions with similar viscosity. Dotted lines are shown to guide the eye. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

coefficients for higher concentrations (de Vicente et al., 2006). We discovered that maltodextrin solutions with comparable viscosity had different lubrication depending on the Mw (Fig. 2). To be more specific, in the case of the low viscosity group (1.4 mPa·s), a 10 % LMD solution showed a lower friction coefficient than the 5 % HMD solution, indicating that small polysaccharides exhibited better lubrication properties at a comparable viscosity than larger polysaccharides. The difference in friction became more evident in the high viscosity group of 4 mPa·s, where the 25 % LMD solution showed much lower friction coefficients than the 16 % HMD solution. Besides lower friction coefficients, the 25 % LMD solution also provided a faster transition from the boundary regime (i.e. where the friction coefficient is independent on sliding speed) to the mixed regime (i.e. where the friction coefficient decreases with increasing sliding speed) at a speed of 1.5 mm/s, compared to 10 mm/s for the other three samples. This showed that a higher concentration of LMD was better able to limit the contact between the rotating glass ball and PDMS surface. The superior lubrication properties could be due to the better occupation on the PDMS surface. To achieve the same viscosity, higher concentrations were required for polysaccharides of lower Mw, and, therefore, there was a higher number of polysaccharide molecules in the LMD solution. With respect to space occupation/utilization, a high number of small molecules led to a more effective spreading on the surface and a higher utilization of surface space, compared with the larger ones, which better assisted in separating the two surfaces.

To investigate whether this observation was valid for other polysaccharides, carboxymethyl cellulose (CMC) with two different MW were also used. CMC is a negatively charged polysaccharide and its solutions can be characterized as non-Newtonian fluids. To eliminate possible viscosity effects, we aimed to obtain samples with the same viscosities. However, the solution with a high Mw CMC (HCMC, 700 kDa) showed shear-thinning behavior at very low concentration (0.01 %), while the solution with a low Mw CMC (LCMC, 90 kDa) showed Newtonian behavior. Therefore, their viscosities could not be matched over the entire shear rate range. The viscosities of the 1 % LCMC and 0.01 % HCMC solutions were mostly matched until a shear rate of $10 \, \mathrm{s}^{-1}$ and started to differ more at higher shear rates (the insert figure in

Fig. 3). The frictional profile of the two CMC samples is shown in Fig. 3. The 1 % LCMC solution showed better lubrication than the HCMC solution, which is in line with the results of the maltodextrin solutions, confirming that a larger number of smaller polysaccharide molecules contribute positively to lubrication at a fixed viscosity.

3.3. Effect of polysaccharide conformation on lubrication

Besides molecular weight, the effect of polysaccharide conformation was evaluated in isoviscous systems. Xanthan gum (XG) and guar gum (GG) were selected as they differ in conformation. XG has a rigid-rod conformation, due to the formation of interchain double helices leading to considerable chain stiffness and high persistence length (i.e. length that determines the rigidity of a polymer chain by their segments) of 100–150 nm (Harding, 2013). GG has a random coil conformation with a persistence length of 3–8 nm and is therefore considered a flexible polysaccharide (Bocchinfuso et al., 2010; Picout et al., 2001). For this study, XG and GG with a comparable molecular weight (Mw ~ 4000 kDa) were chosen. The concentrations were adjusted to obtain a similar viscosity to decouple the effect of conformation from that of viscosity on lubrication. The viscosity of the solutions was matched at 2 % for XG and 1 % for GG. Both solutions exhibited non-Newtonian behavior, and in spite of differences in conformation, their shear-thinning behavior was comparable, resulting in a comparable viscosity over a large shear rate range (the insert figure in Fig. 4). However, at low sliding speeds (<20 mm/s, boundary regime), the 2 % XG solution generated much lower friction coefficients than the 1 % GG solution, as shown in Fig. 4. The differences in lubrication could not be attributed to viscosity or Mw and were thus related to differences in molecule flexibility. A possible explanation for the higher boundary lubrication of XG could be that XG showed a slightly higher shear stress at low shear strain compared to GG (data shown in Fig. A.1 in Supplementary information), which may provide better resistance to the applied load at low sliding speeds, leading to a better separation of the opposing surfaces and a reduction in friction. In addition, the superior boundary lubrication of XG could be attributed to a better film formation capacity. In a previous study, charged XG was reported to form a thicker film on PDMS surfaces than the non-charged flexible polysaccharide locust bean gum (LBG) (Stokes et al., 2011). As LBG has a similar structure as the GG in our study, our
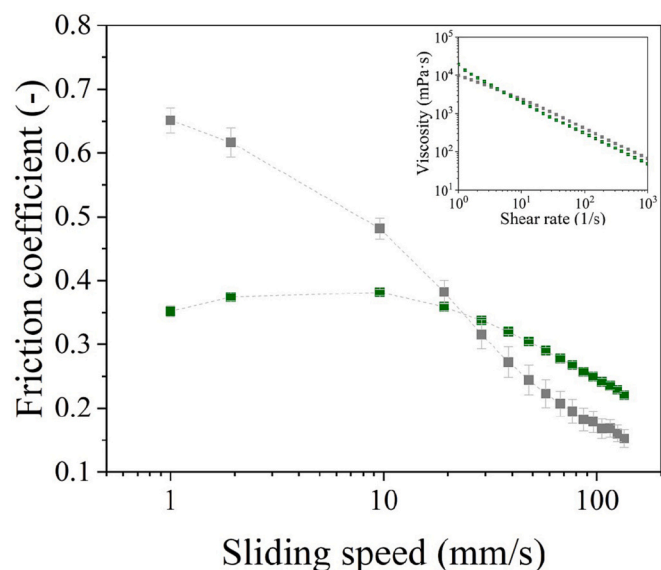
Fig. 4. Friction coefficient as a function of sliding speed for 1 % GG (grey square) and 2 % XG (green square) solutions. Dotted lines are shown to guide the eye. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

initial friction coefficients at low speeds, its friction coefficients decreased fast with increasing sliding speed, and at higher speeds (>30 mm/s), they were even lower than those for the XG solution. This is in line with the fact that the stress of GG was higher than that of XG under high shear strain (>6000 %, data shown in Fig. A.1 in Supplementary information). Thus, the stress-strain behavior could influence lubrication. These results confirm that the conformation plays an important role in the lubrication behavior.

Besides conformation, also the number of molecules may play a role here, as discussed before. The MW of the two polysaccharides was similar, but the concentration of XG (2 %) was twice that of GG (1 %). Therefore, XG has a higher number of molecules, which may partly explain the lower friction coefficient at lower speeds.

To investigate the effect of concentration (number of molecules) further, the lubrication behavior of XG and GG solutions at different concentrations (0.25, 0.5, 1 and 2 %) was also characterized (Fig. 5). For GG, higher concentrations gave lower friction coefficients, in agreement with our previous observations on the relation between higher number of molecules and better lubrication. However, the friction curves for XG at 4 different concentrations were very similar and overlapped with each other. This was not fully in line with the findings of a previous study (de Vicente et al., 2006), in which lubrication of xanthan showed clear concentration dependence. This could be due to several reasons. First, de Vicente et al. investigated a XG concentration range from 0.005 to 0.2 %, which was much lower than the concentration range (0.25–2 %) of our study. The fact that a 0.25 % XG solution was able to provide sufficient film formation to lubricate the surfaces and that the friction coefficient did not further decrease with additional XG suggests that the concentration of 0.25 % was (beyond) a critical concentration. Also, the material used for the tribo pair could matter. In the study in question, a stainless-steel ball and silicone elastomer were used as tribo-pair, while we used a glass ball and PDMS in our study. Though both glass and stainless steel are considered hydrophilic surfaces, the wetting efficiency of the polysaccharides can still be different for the different materials. The difference in the used hydrophobic surface, i.e. silicone elastomer and roughed PDMS surface, could also play a role. These results also confirm that the high lubricating capacity of XG could be better attributed to the conformation than to the number of molecules in the system.

The effect of shear-thinning behavior has already been discussed for hydrodynamic friction, (Marx et al., 2018), however, a potential link between shear-thinning behavior and boundary and mixed regime lubrication has not yet been proposed. Since the shear-thinning degree is affected by conformation of molecules under shear stress, we believe that the shear-thinning behavior could also affect boundary and mixed regime lubrication. We quantified the shear-thinning degree of the studied polysaccharide solutions to correlate the shear-thinning behavior and lubrication properties in the boundary and mixed
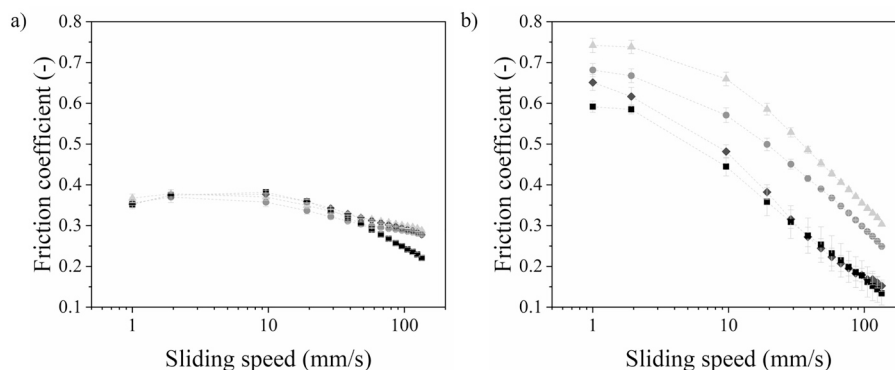
results thus confirm that XG provided better lubrication, probably through better film formation. To confirm differences in film formation, the adsorption of the polysaccharides on a hydrophobic surface was characterized by QCM-D measurements (data shown in Fig. A.2 in Supplementary information). For both XG and GG, the dissipation (D7) was recorded as a measure of the viscoelastic properties of the film, which has been discussed in other studies (Dunér et al., 2013; Molino et al., 2012). The higher energy dissipation (D7) for XG suggests that XG formed a more viscoelastic layer than GG on the surface, indeed confirming that XG provides better film formation, generating low friction coefficients between the two interacting surfaces under relative sliding. The results of our isoviscous systems provide strong evidence that the good lubricating ability of polysaccharides is due to the molecular characteristics and not by viscosity. These results were consistent with those reported in a published study in which random coil polysaccharides (i.e. guar gum and locust bean gum) were shown to have a lower ability in reducing friction than extended-coil (i.e. l-carrageenan) and rigid-rod (i.e. scleroglucan) polysaccharides (Garrec & Norton, 2012). In the above mentioned study, however, the samples were not isoviscous, which makes a direct comparison more difficult. Our results therefore provide more evidence for the role of polysaccharide conformation. It should be noted that although the GG solution had higher

Fig. 5. Friction coefficient as a function of sliding speed for solutions of a) XG b) GG at concentrations of 0.25 % (light grey triangle), 0.5 % (grey circle), 1 % (dark grey diamond) and 2 % (black square). Dotted lines are shown to guide the eye.

regimes. The degree of shear-thinning, n, was extracted from the power-law relationship

$$\eta = K \cdot \dot{\gamma}^{n-1} \qquad (1)$$

where η is the viscosity, K is the consistency index, $\dot{\gamma}$ is the shear rate, and n is the flow behavior index. For GG, LBG, and XG at different concentrations (0.25, 0.5, 1 and 2 %), the correlation between shear-thinning degree and concentration was quantified as

$$n \sim C^a \qquad (2)$$

where n is the flow behavior index, C is the concentration, and a is a power law exponent describing the concentration dependence of shear-thinning degree. Values for the exponent a for the different polysaccharides are shown in Table 2.

Since the frictional behavior of GG showed concentration- and speed-dependency, we also used a power-law model to quantify the frictional behavior with respect to concentration as:

$$\mu \sim C^q \qquad (3)$$

in which μ is the friction coefficient, C is the concentration, and q is a power law exponent describing the concentration dependence. For GG, values for q were estimated by taking the best fit through the experimental data points at different sliding speeds. In addition, we used a power-law model to relate the absolute values of q to sliding speed, as

$$|q| = M \cdot v^b \qquad (4)$$

in which M is a proportionality constant, v is sliding speed, and b is a power-law exponent describing the speed dependence. These results are shown in Fig. 6. Only speed ranges for which the friction coefficients varied with sliding speeds and concentrations were taken into account.

Merging Eqs. (3) and (4) provides a description of the friction coefficient, μ, as a function of sliding speed, v, and concentration, C as:

$$ln\mu = H \cdot v^b \cdot lnC \qquad (5)$$

in which H is a proportionality constant. These equations allow us to predict the friction coefficients of polysaccharides for a selected concentration range and a specific range of sliding speeds. To confirm the validity of the equations for other polysaccharides, we selected LBG as a third polysaccharide (Fig. 6, blue triangle). The extracted exponent b and proportionality constant H for the different polysaccharides are shown in Table 2.

A higher absolute value for the proportionality constant H indicates a higher concentration dependency and a greater b refers to a lower dependency of friction coefficient (μ) with speed. For instance, the absolute value of H, $|H|$, is higher for GG than for XG, indicating that the lubrication of GG has a higher concentration dependence (Table 2, Fig. 5). The lower exponent b of GG shows that the friction coefficient is more influenced by speed (Fig. 5). LBG has values of H and b between those of GG and XG, indicating that the lubrication properties of LBG has a relatively lower concentration dependence (lower $|H|$,) than GG, and the friction coefficient is less affected by sliding speed (higher b). The exponent, a, related to the concentration dependence of the shear-thinning behavior, is related to both the proportionality constant H and exponent b. A larger absolute value of a, $|a|$, is related to a larger absolute value of H, $|H|$, and a smaller value of b. A greater
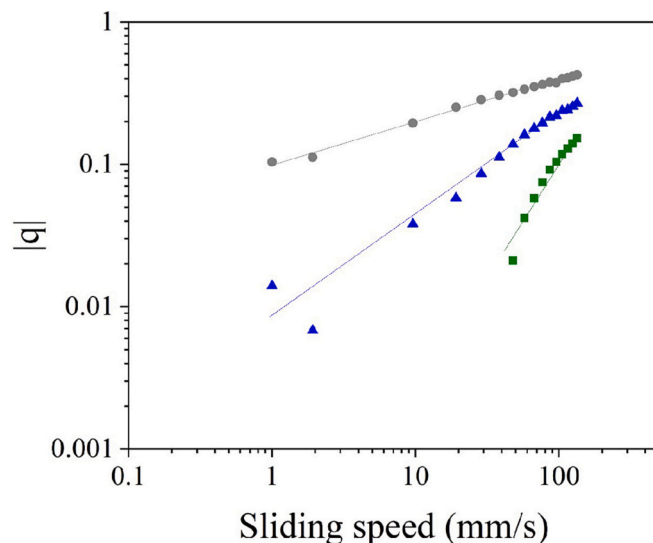

Fig. 6. Absolute value of q ($|q|$) as a function of sliding speed for GG (grey circle, $R^2 = 0.9954$), XG (green square, $R^2 = 0.9588$), and LBG (blue triangle, $R^2 = 0.9919$). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

concentration dependence of the shear-thinning behavior, represented by high absolute values of exponent a, such as for GG, leads to greater concentration dependence of the lubrication behavior, (high $|H|$), and higher dependency with speed (low b). On the other hand, when shear-thinning behavior is less affected by concentration (low $|a|$), this leads to less concentration dependence and less speed dependence in the frictional behavior.

3.4. Effect of charge density and conductivity of polysaccharide on lubrication

The results presented above show that the lubrication properties of polysaccharides depend on their conformation. As the conformation also depends on the charge density of the molecules, the pH of a specific system may have a large effect on lubrication. To gain more insights into the effect of charge and at the same time minimize the effect of molecular characteristics, such as Mw and conformation, two types of pectin with different esterification groups were used. Their charge density, i.e., zeta potential values, were adjusted by changing the pH. Pectin with a high esterification level (esterification degree = 71 %, Table 1) was used as a low charge density (LCP) polysaccharide, and pectin with a low esterification level (esterification degree = 38 %) was used as high charge density one (HCP). Concentrations were again adjusted (Table 2) to obtain similar viscosity in a range between 7 and 9 mPa·s at a natural pH of 3.5. To increase charge density, the pH was adjusted from 3.5 to 7 by adding NaOH. The measured zeta potential of the different pectin solutions is shown in Supplementary information Table A.1.

The zeta potential of HCP was consistently higher (-29.2 or -57.9) than that of LCP (-22.9 or -32.6) at both pH 3.5 and 7. However, no difference in lubrication properties between the two types of pectin solutions was observed, independently of pH (Fig. 7). This was unexpected, as it has been described in the literature that charge can affect

Table 2

Extracted exponents a and b, and proportionality constants M and H for GG, LBG and XG. Regression coefficients, R^2 are provided for the best fit of Eq. (2) to obtain exponent a, and for the best fit of Eq. (4) to obtain the proportionality constant M and exponent b.

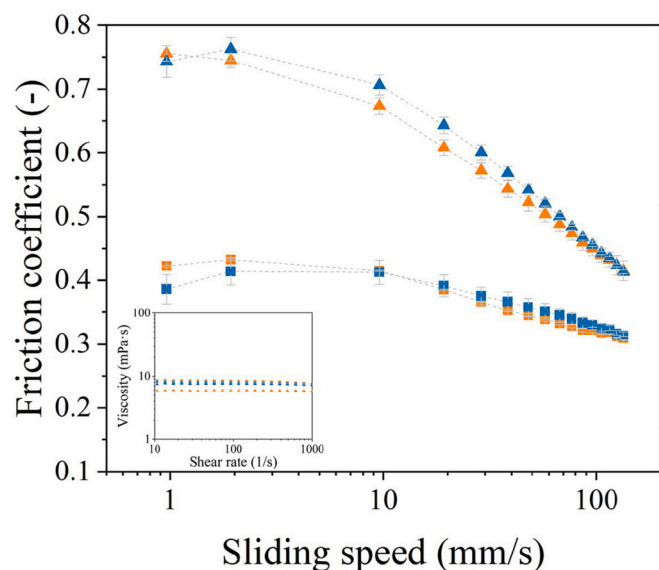| Polysaccharides	a	R^2	M	b	R^2	H
GG	−0.743	0.8511	0.10010	0.298	0.9954	−0.10010
LBG	−0.556	0.9277	0.00780	0.729	0.9919	−0.00780
XG	−0.460	0.9826	0.00003	1.777	0.9588	−0.00003

Fig. 7. Friction coefficient as a function of sliding speed for a 0.52 % HCP solution at pH 3.5 (orange square) and 7 (orange triangle), and a 0.45 % LCP solution at pH 3.5 (blue square) and 7 (blue triangle). Dotted lines are shown to guide the eye. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

lubrication (Stokes et al., 2011; Wong & Ho, 2009). The zeta potential of HCP was consistently higher (−29.2 or −57.9) than that of LCP (−22.9 or −32.6) at both pH 3.5 and 7. Although for both types of pectin the friction coefficient increased when the charge density increased (as a consequence of increased pH), no difference in lubrication properties between the two types of pectin solutions was observed, even though the charge of the two types of pectin was different (Fig. 7). The increase in friction with increasing charge contradicts studies that proposed that a higher charge density would lead to lower friction coefficients (better lubrication) (Kampf et al., 2004; Stokes et al., 2011). These results suggest that charge density alone cannot explain why higher friction coefficients were observed for pectin with increasing charge, and other factors must be responsible for the differences. It must be noted that only small changes in viscosity were detected when the pH, i.e. charge density, was changed (the insert figure in Fig. 7). Therefore, viscosity was not considered to influence lubrication in this case. Differences in frictional behavior must be attributed to variation in the physical properties of the polysaccharides.

Pectin is a semi-flexible polysaccharide, and, therefore, the conformation will change when the charge density is altered. For higher charge density, pectin would have a higher degree of intramolecular repulsion among charged groups, resulting in a more stretched and stiffer chain, which is expected to provide lower friction coefficients. However, the opposite was observed in our experiments.

To better understand the effect of charge on lubrication, we included two other polysaccharides, XG and LCMC. Stiffer polysaccharides, such as XG, would be expected to be less influenced by changes in charge density. On the other hand, LCMC, a semi-flexible polymer, is expected to be more influenced by changes in charge density. For both polysaccharides, solutions at their natural pH (unadjusted) were measured, and the pH was also varied by adding HCl. The natural pH of the XG solution was around 6 and by decreasing the pH from 6 to 3, the charge density decreased from −80 to −40 mV (Table A.1). In the case of LCMC, by decreasing the pH from 7 (the unadjusted pH value) to 3, the charge density decreased from −18.3 to −1.4 mV (Table A.1). The friction coefficients of the XG, LCMC, and HCP solutions at different pH values were measured to evaluate the lubrication performance as affected by charge density. We plotted the friction coefficients of the different polysaccharides at a sliding speed of 1 mm/s

as a function of the respective charge density, i.e. zeta potential (Fig. 8). For XG, we observed that the friction coefficient slightly increased with decreasing charge density and showed less charge dependence (Fig. 8a). The lubrication behavior of stiffer polysaccharides was thus less influenced by variations in charge density. In the case of LCMC, the friction coefficients increased with decreasing charge density, confirming a larger effect of charge density on lubrication for the less stiff polysaccharide. However, although the lubrication of both LCMC and pectin solutions showed a greater dependence on charge, the trend observed for the two polysaccharides was the opposite. This inconsistency shows that the charge density and its impact on the conformation are insufficient to explain changes in lubrication. Thus, additional factors must be involved.

It is worth noting that the friction coefficient always increased when the initial pH (labeled with red circles in Fig. 8) of the solutions was adjusted to other pH values. The natural pH of the polysaccharides seems to play a large role, and thus, the specific nature of the polysaccharide in this cannot be ignored. The initial pH of the different polysaccharide solutions was very different, which may help to explain the differences in the observations. When adjusting the charge density, we added either HCl or NaOH, which also increased the ionic strength of the polysaccharide solutions. Therefore, the results discussed above may also be related to changes in ionic strength.

To verify this, the friction coefficients of samples of XG, HCP and LCMC with varying pH and charge density were plotted as a function of their conductivity (Fig. 8b). The trends were consistent for all polysaccharides: an increase in conductivity (i.e. ionic strength) led to an increase in the friction coefficient. We noticed that the lubrication of stiffer XG was less influenced by the ionic strength compared to the more flexible polysaccharide, similarly to what we observed for charge density. For the more flexible molecules HCP and LCMC (Fig. 8b), the change in friction was dependent on conductivity. This effect of ionic strength has also been seen by other researchers, who showed that the friction coefficients of chitosan solutions were higher in buffers than in water (Taira & McNamee, 2014). The presence of salt may change the lubricating performance in different manners. Salt can screen the charges on the polysaccharides, and thereby reduce intramolecular electrostatic repulsion, decreasing the conformational extension, and interfere with the film formation on the PDMS surface (Carneiro-da-Cunha et al., 2011; Mantelli et al., 2011; Turkoz et al., 2018).

In the case of LCMC, an increase in ionic strength corresponded to a decrease in charge density (Fig. 8). Both the increase in ionic strength and decrease in charge will lead to less expansion of the molecule. In contrast, for pectin, the increase in ionic strength corresponded to an increase in the charge density. Thus, a competition between ionic strength and charge density on the effect on conformation could occur. Based on our results, for pectin, the high charge density accompanied by high ionic strength seems detrimental to lubrication, suggesting that the effect of ionic strength on lubrication seemed to be more important than that of charge density. The increase in friction caused by increased ionic strength cannot be compensated by the increase in charge density. The reason for this could be that the higher exposure of negative charges of pectin at a high pH and the presence of positively charged sodium forced the chains of pectin into a more coiled conformation, possibly due to the counterion condensation effect (Alba et al., 2018; Wang et al., 2011; Yu et al., 2017). The more folded conformation was confirmed by a slight decrease in viscosity (from 8.5 to 6 mPa·s) for increasing pH (Fig. 7). This decrease in viscosity could also partly have contributed to the increase in friction coefficients, as a lower viscosity provides less pressure to separate the surfaces. However, the small decrease in viscosity cannot explain the large difference in friction. In addition, at pH 3.5, the dissipation (D7), as measured with QCM-D, for the formed pectin layer on the silicon dioxide sensor surface was higher than that at pH 7 (data shown in Fig. A.3 in Supplementary information), suggesting that pectin at pH 3.5 has a more viscoelastic layer even though the charge density was lower. These results explain why friction decreased with decreased
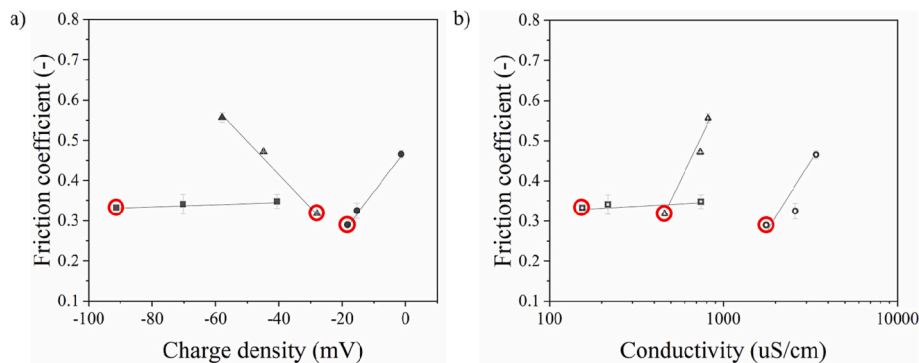
Fig. 8. Friction coefficient obtained at 1 mm/s as a function of a) charge density, and b) conductivity for 0.1 % XG (square/open square), 0.52 % HCP (triangle/open triangle), and 1 % LCMC (circle/open circle) solutions. Dotted lines are shown to guide the eye. Red circles indicate friction coefficients at the natural pH value. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

charge density (pH 3.5) in the case of pectin. The natural pH and charge of the polysaccharides thus seem to have a large effect on lubrication.

In addition, the formation of a lubricant film on PDMS could be affected by changes in ionic strength. Naturally charged polysaccharides were reported to form a thicker film on PDMS, (Pradal et al., 2019; Stokes et al., 2011). However, as ionic strength affects the hydration and swelling of the polysaccharide layer, film formation and thus lubrication may be affected. An increasing amount of NaCl has been found to decrease film lubrication of pre-adsorbed mucin on PDMS, which was attributed to conformation changes and dehydration of the mucin layer (Song et al., 2019). To evaluate the effect of salt itself, we measured the friction coefficients of salt solutions (NaCl) with different ionic strengths within a range in conductivity of 604–23,300 μS/cm. No significant difference in frictional behavior was found among salt solutions with different ionic strengths (data not shown), indicating that salt deposition on PDMS did not have a direct effect on friction on its own. Therefore, we could conclude that the phenomena discussed above were due to changes in the molecular characteristics of polysaccharides in presence of salt.

Our work shows that polysaccharides with a natural high charge density tend to have good lubrication ability. The lubrication of naturally stiff polysaccharides seems affected by changes in charge density, ionic strength, and concentration only to a limited extent. For semi-flexible charged polysaccharides, the effect of charge depends on the natural pH of the polysaccharide solution. In case the change in pH leads to a decrease in the charge density, friction increases due to a decrease in polysaccharide stiffness as a result of reduced intramolecular electrostatic repulsion. In case the change in pH leads to an increase in the charge density accompanied by an increase in ionic strength, the most important of the two opposing effects will determine whether lubrication will increase or decrease.

4. Conclusion

We evaluated the frictional behavior of solutions containing commercial polysaccharides varying in size, conformation, and charge density. We confirmed our hypothesis that several characteristics of the polysaccharides and the conditions are important: 1) the size and number of polysaccharide molecules, 2) the conformation of the polysaccharides, 3) the charge density of the polysaccharides, and 4) the ionic strength of the polysaccharide solution.

Our results confirm our hypothesis that at a fixed viscosity, with a high number of small molecules, i.e. lower molecular weight, better film formation is obtained, which increases the lubrication ability. This was confirmed for both maltodextrin (small) and carboxymethylcellulose (large). This film forming ability was also increased with stiffer polysaccharides, indicating that the conformation also plays a crucial role. In addition, the effect of conformation appears indeed influenced by both

pH and ionic strength. However, the effect of these factors depends on the type of the polysaccharides and its natural change upon dilution. Polysaccharides with a high natural charge and a rigid-rod conformation, such as xanthan generated low friction. In this case, changes in pH and ionic strength lead to limited differences in lubrication properties. However, the lubrication behavior of ionic polysaccharides with a semi-flexible conformation, such as pectin and carboxymethylcellulose, was much more affected by pH and ionic strength. These polysaccharides were less efficient in providing film formation than rigid polysaccharides. However, depending on the natural pH of the polysaccharides, pH and ionic strength had a synergistic or counteracting effect. In the case of non-charged flexible polysaccharides, such as guar gum, high initial friction coefficients (boundary regime) were observed. For such polysaccharides, the frictional behavior depended highly on concentration and sliding speed, which could be related to the shear-thinning behavior of the samples. The relation among the different parameters was integrated into a new descriptive model. Overall, the results highlight the role of the different factors that influence polysaccharide lubrication, and show that the effect of the different conditions are mostly related to changes in the conformation of the polysaccharides.

CRediT authorship contribution statement

Lei Ji: Investigation, Data curation, Methodology, Visualization, Writing – original draft. **Antonia Orthmann:** Investigation, Data curation. **Leonardo Cornacchia:** Methodology. **Jinfeng Peng:** Methodology. **Guido Sala:** Methodology, Validation, Supervision, Writing – review & editing. **Elke Scholten:** Conceptualization, Methodology, Validation, Writing – review & editing, Supervision, Funding acquisition.

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

The data that has been used is confidential.

the method.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.carbpol.2022.120000.

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