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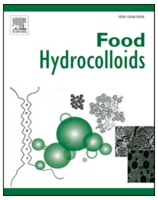

Shear and extensional rheological properties of whole grain rye and oat aqueous suspensions

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ABSTRACT

Whole grain flours contain polysaccharides with techno-functional and nutritional properties which make them good candidates as natural texturisers in foods and beverages, thus reducing the use of highly refined ingredients. However, the use of plant components to develop complex fluids and soft materials, requires an enhanced understanding of the relationship between their physicochemical and rheological properties. Here, we systematically investigated the shear and extensional rheological properties of aqueous suspensions of whole grain rye and oat flours. Our results indicated that both types of suspensions (3.5 wt %) showed similar shear thinning behaviour ($n = 0.4$) however, oat suspensions presented higher viscosity and gel-like behaviour ($G' > G''$) compared to rye. Additionally, the oat suspensions exhibited an apparent extensional viscosity, which was not present in rye suspensions. The rheological properties of the continuous and disperse phases, separated by centrifugation, were investigated before and after starch hydrolysis and protein removal. Our results indicate that the distinct behaviour of oat suspensions is mainly due to the molecular structure of starch in the liquid phase of i.e oat starch had a higher amylose/amylopectin ratio than rye. Whilst the presence of protein and cell wall polysaccharides in the solid phase contribute to the overall rheology of the suspensions. Furthermore, our results show that the systems do not follow the Cox-Merz rule, indicating that they behaved as suspensions of soft particles rather than macromolecules in solution. Aqueous suspensions of whole grain rye and oat flours showed rheological properties that could be of interest to design low-medium viscosity food and beverage products.

1. Introduction

Food rheological properties are directly link to food texture and, determine how food breaks down in the mouth and mixes with saliva until it is swallowed as a bolus. Viscosifiers and gelling agents are added to food formulations to tailor textural properties for specific purposes (Phillips & Williams, 2009). However, many of the thickeners used, such as modified starches and gums, have low nutritional value and are obtained with processes that require large amounts of water and energy. As an alternative, exploiting the natural texturising potential of plant materials could lead to the design of texture modified foods with less refined and more nutritious ingredients.

For people suffering from swallowing disorders such as dysphagia, texture is an important factor in safe swallow of foods. Increasing bolus viscosity, which is usually done with the aid of thickeners, reduces the flow of the food during swallowing, allowing sufficient time for individuals with dysphagia to close the airways before the arrival of the bolus, which they are unable to do with low viscosity boli (Chen & Lolivret, 2011). There is not a consensus with respect to which rheological properties determine ease-to-swallow, especially for complex systems such as particulated foods however, shear rheology data alone is not enough and, other rheological parameters such as extensional

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viscosity, also play an important role (Hanson, Jamshidi, Redfearn, Begley, & Steele, 2019). Whilst shear viscosity is related to food texture and mouthfeel, extensional properties have been proposed to impact food bolus formation and ease of swallow (Ben Tobin et al., 2020; Hadde & Chen, 2019). *In vitro* studies suggested that the extensional properties can affect the transition from the oral to the pharyngeal phase of swallowing (Marconati & Ramaioli, 2020). Furthermore, friction and lubrication of oral surfaces could also be of importance, although these properties have been less investigated (Sharma, Pondicherry, & Duizer, 2022).

Different techniques and devices have been developed for measuring extensional viscosity, mainly for uniaxial extension. Among these devices are tensile rheometers (Meissner, Stephenson, Demarmels, & Portman, 1982), and their modified versions (Bach, Rasmussen, & Hassager, 2003; Schweizer, 2000). As an alternative to those rheometers, fluid flow can also be studied through a contraction to calculate the uniaxial extensional viscosity from entrance pressure (Cogswell, 1972). Among others, Wikström and Bohlin (Wikström & Bohlin, 1999), used a hyperbolically shaped nozzle to minimize the effect of shear at the walls of the contraction. The Hyperbolic Contraction Flow (HFC) method, which consists in forcing a fluid through an HCF geometry and to monitor the resulting forces, has been previously used for different systems, including studies on suspensions of plant materials (Ben Tobin et al., 2020; Malafronte et al., 2021). Recently, an hyperbolic slit contraction has been designed for online monitoring of polymeric materials (Köpplmayr et al., 2016; Luger, Low-Baselli, Neunhauserer, Friesenbichler, & Miethlinger, 2019).

Whole grains are cereal kernels from i.e. wheat, rye, oat, barley and rice including all parts of the naked seed (endosperm, bran and germ) (Van Der Kamp, Poutanen, Seal, & Richardson, 2014). Their starchy endosperm (the main part of the grain) is a good source of energy, and their bran (the outer layer), and germ (the smallest part of the kernel) are essential sources of vitamins, minerals and dietary fibers (Cui & Wang, 2009; Inglett & Chen, 2012; Kaur & Sharma, 2019). The main component of whole grain rye and oat is starch, being 54 wt % and 62 wt % respectively (Frølich, Åman, & Tetens, 2013). Starch is found as a complex granule structure (diameter 1–100 μm) in the endosperm and consists mainly of two polysaccharides, amylose, and amylopectin. Thermal processing results in the swelling of the granules and leaching of these macromolecules into the surrounding fluid (Taggart & Mitchell, 2009). Depending on the ratio of amylose to amylopectin, the gelatinization temperature will differ because of the different accessibility of the granule to hydration (Taggart & Mitchell, 2009), i.e. the temperature at the onset of gelatinization of rye and oat is 49 °C and 53 °C measured by microscopy, respectively (Hoseney, Finney, Pomeranz, & Shogren, 1971). Furthermore, whole grain cereals have health-promoting components such as soluble and insoluble dietary fiber i.e non-starch polysaccharides, which are present in the cereal bran and endosperm as cell wall structural components. Whilst high contents of arabinoxylans (AX) are predominant in rye, (1,3; 1,4)-β-glucans are found in oats (Izydorczyk & Biliaderis, 1995; Lazaridou, Biliaderis, & Izydorczyk, 2006). Rye and oat also contain proteins in concentrations that varied between 8 and 18 wt % (Poutanen et al., 2022).

The rheology of whole grain flours has been mainly studied at low water contents in relation to dough properties. For oat whole grain the dough knitting ad baking ability has been found to depend greatly on the particle size of the bran (Londono, Smulders, Visser, Gilissen, & Hamer, 2015; Sammalisto, Laitinen, & Sontag-Strohm, 2021) and, the water hydration capacity determined by small flour particle size, damaged starch granules and high protein content (Hüttner, Dal Bello, & Arendt, 2010). For rye, the presence of non-starch polysaccharides from bran led to higher water-holding capacity and, in consequence higher viscosity of the dough (Girhammar & Nair, 1995; Gómez, Pardo, Oliete, & Caballero, 2009). However, the rheology of whole grain flours at high water contents i.e in aqueous suspensions, has not been investigated.

Dispersions of plant materials can be considered as colloidal and non-colloidal suspensions. The rheological properties of a suspension are determined by the viscosity of the continuous phase, and the volume fraction occupied by the particles in the dispersed phase. The maximum volume fraction, i.e the amount of particles which can be packed in a certain volume, depends on several factors such as particle size distribution, particle morphology (for example aspect ratio), hardness of the particles and interparticle forces, among others (Macosko, 1994). Studies regarding suspension rheology have been of interest for many decades, ranging from the simple case of non-interacting spherical hard particles (Einstein, 1906) to complex polydisperse suspensions of soft particles including starch granules (Evans & Haisman, 1980), agar microgels (Adams, Frith, & Stokes, 2004) and Sephadex (cross-linked dextran) particles (Evans & Lips, 1990). Considering food systems, and in particular for plant materials, complexity due to heterogeneity and polydispersity in size, shape and softness of particles has to be taken into account (Boehm et al., 2014; Lopez-Sanchez, Chapara, Schumm, & Farr, 2012; Lopez-Sanchez & Farr, 2012).

Using whole grains instead of highly refined cereal ingredients could aid the transition towards a more sustainable food production by reducing processing by-products. Here, the rheological properties of suspensions of whole grain rye and oat flours were studied, specifically the shear viscosity, extensional viscosity and viscoelastic properties were investigated in relation to polysaccharide composition and starch molecular features, with the goal to use such flours as natural texturisers in low viscosity products with specific requirements, such as beverages for populations suffering from dysphagia.

2. Materials and methods

2.1. Raw materials

Whole grain rye (*Secale cereale*) and oat (*Avena sativa*) flours from crops cultivated in Sweden were purchased from a local store. The milling and grinding processes lead to commercial flours with broad particle size distribution. Therefore, the flours were sieved to standardize their particle size with the help of a sieve with a mesh size of 250 μm using an Analysette 3 Model Pro Vibratory Sieve Shaker (FRITSCH GmbH; Germany) with an amplitude setting of 1.5 mm, interval time of 10 s and sieving time of 3 min. Sieved flours were used for all chemical and rheological analysis.

2.2. Preparation of rye and oat suspensions

Suspensions were prepared by adding 20 g of sieved flour to 500 mL of deionised water, while mixing with an electric hand mixer (RG 28s Elram, Germany, DDR). The concentration of the suspension was adjusted to 3.5 wt % with deionised water and transferred into a 1000 mL borosilicate glass beaker and heated in a heating bath (JULABO ED GmbH, Germany). All suspensions were heated at 95 °C for 20 min with constant stirring using a double propeller stirrer. After 20 min, the suspension was immediately cooled down to room temperature in a water bath. Temperature profiles during heating were recorded using a thermometer (model 735-2, Testo AG, Germany).

A subset of the suspension was centrifuged using a Heraeus Megafuge 16R centrifuge (Thermo Fisher, Germany) equipped with a HIGHConic II rotor. Centrifugation was performed at 6573 g (7000 rpm) for 30 min at 25 °C, this is a lower g force than that previously used to separate liquor from dough (Salt et al., 2006; Turbin-Orger et al., 2015). After centrifugation three phases were clearly differentiated, they were carefully collected with a pipette. After treatment to hydrolyse starch and remove proteins only two phases were visible, a liquid supernatant and a pellet.

The heated suspensions and the related phases obtained after centrifugation were stored at 5 °C for 24 h prior to rheological measurements. A subset of the samples was freeze dried (Alpha 1–2 LDplus freeze dryer, Martin Christ, Germany) and used for chemical analysis.

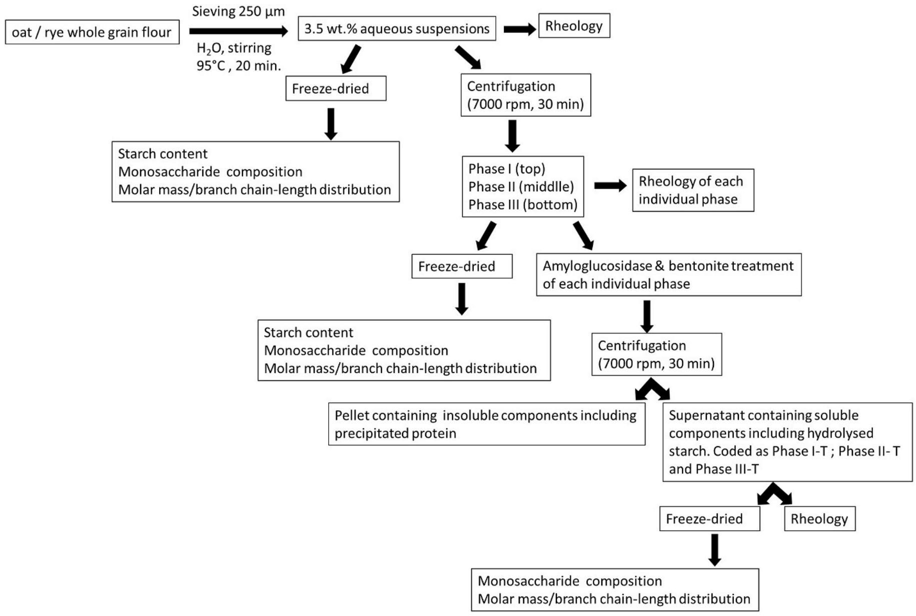

Fig. 1. Schematic overview of preparation and analysis of rye and oat wholegrain aqueous suspensions and phases.

A schematic overview of the sample preparation and the different treatments applied is depicted in Fig. 1.

2.3. *Dry matter content*

The solid content of the samples was measured by drying in an oven ULE 400 (Memmert, Germany) at 115 °C for 12 h. Samples were measured in duplicates.

2.4. *Starch hydrolysis and protein removal*

The liquid and solid phases obtained after centrifugation were treated to hydrolyse starch and remove proteins with a procedure based on that suggested by Comino et al. with minor modifications (Comino, Shelat, Collins, Lahnstein, & Gidley, 2013). In brief, the pH was adjusted to 4.5 using 0.1 M HCl solution. Then, amyloglucosidase (Megazyme, Ireland) was added at a concentration of 20 U/ml and incubation was performed at 55 °C and 80 rpm for 14 h in a shaking water bath (VWR, USA). After, the solution was heated in boiling water for 30 min to inactivate the enzyme and precipitate soluble proteins. The supernatant was separated by centrifugation at 3200*g* for 10 min, and it was further treated to remove remaining proteins using bentonite (Acros Organics, Belgium). In this case, the pH was adjusted to 5 using 0.1 M NaOH solution and 2 wt % bentonite solution was added at a concentration of 1 ml/100 ml and stirred for 30 min. The supernatant was separated by centrifugation at 3200*g* for 10 min, stored at 5 °C and used for analysis of rheological properties. A subset of the supernatant was freeze dried for chemical analysis (see Fig. 1).

2.5. *Monosaccharide composition and starch content*

The monosaccharide composition of suspensions and phases before and after treatment was determined using high-performance anion exchange chromatography with pulsed amperometric detection (HPAEC-PAD) system (Dionex ICS 3000, Sunnyvale, CA, USA) after a sulfuric acid (H_2SO_4) hydrolysis (Saeman, Moore, Mitchell, & Millett, 1954). Approximately 2 mg of the samples were incubated with 72% H_2SO_4 at room temperature for 3 h and then hydrolysed in diluted H_2SO_4 at 100 °C for 3 h. The hydrolysates were filtered (0.2 µm Nylon filters) and injected into the HPAEC-PAD equipped with a CarboPac PA1 column (4 × 250 mm, Dionex) maintained at 30 °C with a flow rate of 1 mL/min. Standard solutions of fucose, arabinose, rhamnose, galactose, glucose, mannose and xylose at concentrations between 0.005 and 0.1 g/L were employed for calibration. The measurements were done in triplicate.

The starch content of the samples was determined using the Megazyme total starch assay kit (Megazyme International, Wicklow, Ireland) in duplicate.

2.6. *Molar mass and branch chain-length distribution*

The molar mass distributions of suspensions and phases before and after treatment were analysed using size exclusion chromatography (SEC) coupled to a multiple-angle laser light scattering detector (MALLS; BIC-MwA7000, Brookhaven Instrument Corp., New York) and a refractive index detector (SECcurity 1260, Polymer Standard Services, Mainz, Germany) thermostatted at 45 °C. SEC analyses were performed using a column set consisting of a GRAM PreColumn, 30 and 10000 analytical columns (Polymer Standard Services, Mainz, Germany) with a flow rate of 0.5 mL/min at 60 °C. The samples were dissolved (3 mg/mL) in DMSO supplemented with 0.5 wt % LiBr at 60 °C and filtered through a 0.2 µm Nylon filters. Standard calibration was performed using pullulan standards between 342 and 708 000 Da (Polymer Standard Services, Mainz, Germany). The calibration of the elution volume to the hydrodynamic radius (R_h) was performed using the Mark-Houwink parameters for pullulan in DMSO/LiBr (0.5 wt %) ($K = 2.427 \times 10\text{-}4$ dL g^{-1} and $a = 0.6804$), using a procedure described in detail in Vilaplana et al. (Vilaplana & Gilbert, 2010a). The absolute molar mass distributions (Mw (Vh)) and the average number-average (Mn) and weight-average (Mw) molecular weights were obtained from the MALLS detector using WinGPC software (Polymer Standards Services, Mainz, Germany) and Berry extrapolation.

The branch chain-length distributions of the starch fractions in the rye and oat flours and their suspensions were also determined by SEC after enzymatic debranching of starch. Approximately 50 mg of the samples were wetted with 0.5 mL distilled water and then 4.5 mL DMSO was added. The dispersions were heated in a boiling water bath for 1 h and then left under constant stirring at room temperature overnight. 0.5 mL aliquots of the samples were precipitated with 2.5 mL EtOH followed by centrifugation (3000 g, 10 min) and then the pellet was dissolved in 4.5 mL distilled water in a boiling water bath for 15 min. The dispersions were cooled down and 0.5 mL of 0.1 N acetate buffer and 25 µL isoamylase (EC 3.2.1.68, Megazyme, Wicklow, Ireland) was added. The

Table 1

Total Starch, monosaccharide composition (in % dry weight), and total solids content of the rye and oat suspensions, and the corresponding Phase I, Phase II and Phase III before and after treatment (T) to hydrolyse starch and remove proteins. Notice that after treatment only the supernatants were measured. The total starch and monosaccharide composition are reported as percentage of the total carbohydrate content on a dry weight basis (% dw). The total solid content is express as percentage on a total weight basis (wt. %). The standard deviation was less than 0.1 for all the measurements. n.d. Not detected; n.a. Not applicable.

		Starch %dw	Arabinose % dw	Galactose % dw	Glucose% dw	Xylose % dw	Total solids wt. %
Rye	Flour	72.2 ± 3.4	1.20	n.d	97.78	1.02	n.a
	Suspension	67.2 ± 1.6	1.40	0.15	97.04	1.40	3.5
	Phase I	64.6 ± 3.2	1.24	n.d.	97.64	1.12	2.2
	Phase II	78.6 ± 5.9	0.37	n.d.	99.63	0.00	5.1
	Phase III	52.5 ± 1.4	2.76	n.d.	94.52	2.72	9.5
	Phase I - T	n.a	0.98	n.d.	98.12	0.90	2.1
	Phase II -T	n.a	n.d.	n.d.	100.00	n.d.	4.9
	Phase III - T	n.a	n.d.	n.d.	100.00	n.d.	6.1
Oat	Flour	77.1 ± 1.7	0.50	0.63	98.88	n.d.	n.a
	Suspension	78.5 ± 4.5	0.40	0.40	99.20	n.d.	3.5
	Phase I	62.9 ± 2.8	0.58	0.85	97.85	0.72	0.4
	Phase II	89.5 ± 3.0	n.d.	n.d.	100.00	n.d.	7.2
	Phase III	63.9 ± 3.3	1.42	0.42	96.40	1.77	11.4
	Phase I - T	n.a	1.22	1.22	96.66	0.90	0.5
	Phase II - T	n.a	n.d.	n.d.	100.00	n.d.	6.8
	Phase III - T	n.a	n.d.	n.d.	100.00	n.d.	6.5

samples were incubated at 37 °C for 4 h and the debranched starch was precipitated with 25 mL EtOH. The samples were then centrifuged (4000 g, 10 min) and the pellet was dissolved in DMSO supplemented with 0.5 wt % LiBr at 80 °C for 2 h. The debranched starch samples were injected into the SEC system. The SEC weight distribution $w(\log V_h)$, the branch chain-length distributions $w(\log X_{de})$ and the size dependence of the weight-average molecular weight $Mw(V_h)$ were obtained using the same size exclusion parameters as described in Vilaplana, Meng, Hasjim, & Gilbert, 2014 (Vilaplana et al., 2014).

2.7. Shear viscosity and viscoelastic properties

The shear viscosity and the viscoelastic properties of the rye and oat solutions as well as the phases separated by centrifugation were determined using a strain-controlled rheometer (ARG2; TA Instruments, USA). with a40 mm parallel plate geometry. A 1 mm gap was used. All the measurements were performed at 25 °C. A solvent trap was used to prevent drying of the samples during the measurements. No sedimentation was observed during the time of the measurements. After the treatment for starch hydrolysis and protein removal, due to the low viscosity of the samples, the geometry used was a concentric cylinder with a cup diameter of 30 mm and inner cylinder of 27.7 mm. The shear viscosity, η_s, was determined at increasing shear rate from 1 to 100 s^{-1}. The viscoelastic properties were measured in the linear viscoelastic region determined by applying a strain sweep from 0.1 to 100% at a constant frequency of 6.28 rad s^{-1}. The storage modulus, G′, and the loss modulus, G’’, were obtained by applying a frequency sweep from 0.6 to 50 rad s^{-1} at 1% strain within the linear viscoelastic region. All the measurements were performed in duplicates.

2.8. Extensional viscosity

The extensional viscosity, η_E, was measured using a Hyperbolic Contraction Flow (HFC) method (Stading & Bohlin, 2001; Wikström & Bohlin, 1999). The HCF geometry had a height (H) of 15 mm, an inlet radius (r0) of 10 mm and an exit radius (r_1) of 0.83 mm. The forces were monitored and recorded on the Instron instrument (Instron 5542, Instron, USA) equipped with a 10 N load cell. Measurements were performed at 25 °C in triplicate. The HCF method forces a fluid through a hyperbolic contraction nozzle to extend it to a maximum Hencky strain (εH) given by the specific nozzle and, the shear thinning index of the fluid. The resulting stress on the nozzle is monitored through the force recorded on the Instron instrument. During contraction flow the fluid experiences extension and shear, the shear contribution was subtracted from the total measured stress by calculating the shear contribution as a function of the shear thinning index (n) and the flow consistence index (k). The parameters n and k were obtained from shear viscosity measurements assuming a power-law (Equation (1)), as described in Wikström et al. (Wikström & Bohlin, 1999).

$$\sigma_{shear} = k\dot{\gamma}^n \tag{Eq. 1}$$

where σ_{shear} is the shear stress and $\dot{\gamma}$ the shear rate. When the shear rate equals the extensional strain rate, the elastic contribution is determined by calculating the Trouton ratio at an extensional rate, $\dot{\varepsilon}$, equal to the shear rate, $\dot{\gamma}$, as:

$$T_r = \frac{\eta_E(\dot{\varepsilon})}{\eta_s(\dot{\gamma})} \tag{Eq. 2}$$

The maximum fluid deformation was assessed using the Hencky strain (ε_H) given by the specific nozzle (H, r_0, r_1) and the shear thinning index of the fluid (n), as:

$$\varepsilon_H = \frac{3n+1}{n+1}\ln\left(\frac{r_0^2}{r_1^2}\right) \tag{Eq. 3}$$

3. Results and discussion

3.1. Chemical composition of the flours and suspensions

The crude composition of rye and oat whole grain flours has been previously assessed, rye whole grain flour consists on average of 76.3 wt % carbohydrates, 12.9 wt % protein, 2.4 wt % fat and 1.4 wt % ash (Nordlund et al., 2013). For oat whole grain the average composition is 71 wt % carbohydrates, 12 wt % protein, 5.7 wt % fat (Gu et al., 2022) and 1.98 wt % ash (Doehlert & Moore, 1997). Based on suppliers' specifications the flours used contained 9.2 wt% and 12 wt% protein for rye and oat respectively. In Table 1 it is displayed the starch content of the whole grain flours used in our study. After sieving, the starch content in the rye flour was 72.2 ± 3.4 wt % whilst for oat was 77.1 ± 1.7 wt %, respectively, these values are somehow higher than data reported in the literature with values of 54 wt % for rye and 62 wt % for oat (Frølich et al., 2013), these differences in starch content could be due to the natural variation between raw materials, but also to the enrichment of starch after sieving, as these are relative amounts and large bran pieces were removed during sieving. The monosaccharide analysis showed that the main component in the whole grain flours was glucose, attributed to mixed linkage β-glucans and cellulose. Furthermore, the rye flour contained minor amounts of arabinose and xylose, which could be

Table 2
Molecular properties of starch from the branched and debranched distributions. Number-average molecular weight Mn, weight-average molecular weight Mw and dispersity D for branched starches using light scattering. Percentage of AP, AM, and peak maximum of degree of polymerization X_{de} of debranched samples and height ratio of AM/AP (AP-amylopectin, AM-amylose) using DRI calibration. n.a. Not applicable.

		Branched starch			Debranched starch						
		M_n(x 10^6 Da)	M_w(x 10^6 Da)	D	AP(%)	AM(%)	X_{de}(AP1)	X_{de}(AP2)	AP2/AP1	X_{de}(AM1)	X_{de}(AM2)
Rye	Flour	n.a.	n.a.	n.a.	59.38	40.62	27	49	0.56	680	4000
	Suspension	1.41	10.53	7.49	59.70	40.30	27	49	0.59	400	2200
	Phase I	1.53	13.90	9.07	57.40	42.60	27	48	0.65	340	2285
	Phase II	1.14	7.94	6.94	63.50	36.50	27	49	0.63	500	1860
	Phase III	1.15	10.10	8.82	54.00	46.00	27	50	0.70	300	2170
Oat	Flour	n.a.	n.a.	n.a.	55.00	45.00	27	53	0.56	640	4540
	Suspension	3.29	23.47	7.13	58.93	41.07	27	51	0.56	615	4300
	Phase I	n.a.	n.a.	n.a.	13.50	86.50	27	50	0.69	265	2470
	Phase II	6.15	39.09	6.36	63.26	36.77	27	51	0.61	680	4300
	Phase III	18.57	54.93	2.96	n.a.	n.a.	n.a.	n.a.	n.a.	617	4530

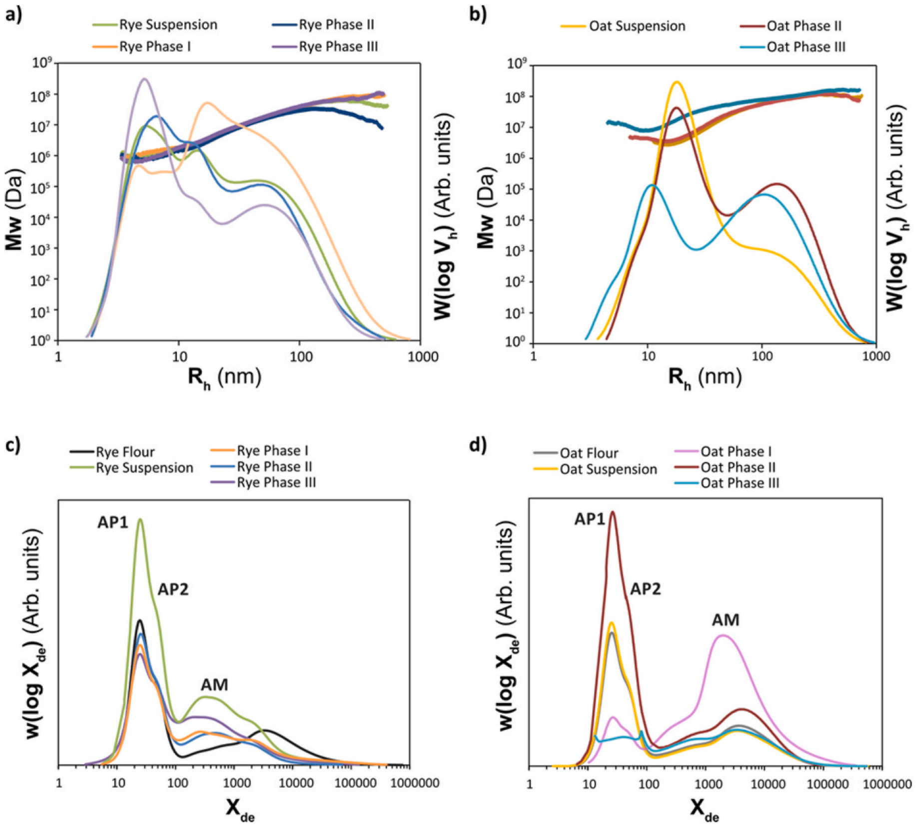

Fig. 2. SEC weight distribution and weight-average molecular weight as a function of hydrodynamic radius Rh for (a) rye suspension and phases, (b) oat suspension and phases. SEC weight distribution of debranched starches as a function of degree of polymerization (Xde) for (c) rye flour, suspension and phases and (d) oat flour, suspension and phases.

collectively attributed to the presence of arabinoxylan (AX) that consists of a linear backbone of xylose residues with arabinose substitutions. The oat flour contained minor amounts of arabinose and galactose suggesting the presence of arabinogalactan proteins (AGP), a type of proteoglycans that are commonly found in most plant species (Table 1). Mannose and fucose were also measured but not detected neither in rye nor in oat suspensions.

The starch and the monosaccharide composition of the aqueous suspensions (3.5 wt %) was similar to that one of the flours (Table 1). A higher amount of arabinose and xylose was found in rye compared to oat suspensions, whilst higher galactose content was detected in the oat suspensions.

3.2. *Chemical composition of the different phases before and after starch hydrolysis*

Three phases were obtained after centrifugation of the rye and oat suspensions namely Phase I (top phase), Phase II (middle phase) and Phase III (bottom phase/sediment). In case of rye, Phase I accounted for 70 wt % of the total initial suspension, Phase II for 20 wt % and Phase III for 10 wt %. For oat, the yields of Phase I, Phase II and Phase III were 58 wt %, 35 wt % and 7 wt% respectively. The total solid content increased from the Phase I to Phase III (Table 1).

The content of starch in Phase I, II and III of the rye suspensions was 64.6 ± 3.25% dw, 78.6 ± 5.94% dw and 52.5 ± 1.45% dw. respectively (Table 1). In the case of oat, the starch content was 62.9 ± 2.82% dw, 89.5 ± 3.04% dw. and 63.9 ± 3.29% dw. respectively in Phase I, Phase

II and Phase III. For both rye and oat, arabinose and xylose accumulated in Phase I and Phase III. For oat galactose was present in Phase I and Phase III. These results indicate that starch was present in all three phases, whilst non-starch polysaccharides, were mainly present in phase I (soluble polysaccharides) and III (insoluble polysaccharides). Strong association of starch and proteins has been previously reported for oat endosperms (Autio & Eliasson, 2009; Saldivar, 2014). After the treatment to hydrolyse starch and remove proteins, the samples were centrifuged, the supernatants analysed, and the pellets discarded. The monosaccharides composition remained similar in Phase I-T of both rye and oat compared to Phase I. In Phase III, a reduction of arabinose and xylose was measured after treatment (Phase III-T), indicating that the insoluble polysaccharides remained in the pellet.

3.3. Molecular structure of starch

The molecular structure of starch was determined in terms of the molar mass distribution of the starch macromolecules and the branch chain-length distribution after debranching (Table 2 and Fig. 2). The rye suspension exhibited a multimodal size distribution (Fig. 2a) with three populations that can be mainly attributed to small molecules (e.g. dextrins and other low molecular weight compounds with R_h 2–10 nm), amylose and potential amylopectin fragments induced by the treatments (R_h 8–20 nm) and intact amylopectin (R_h 20–600 nm). For oat suspensions (Fig. 2b), the three populations can still be observed, but with a main contribution of the amylose (R_h 10–30 nm) and amylopectin (R_h 60–800 nm) macromolecules. Comparing rye and oat suspensions, the distinct amylose and amylopectin populations appear larger for oat compared to rye, which is also correlated with an increased molecular weight for oat (Table 2), evidencing the distinct branched structures of the intact starch from both sources. The occurrence of scission of the amylopectin populations due to the treatments cannot be excluded; however, we consider that this effect is minor, as the AP populations coelute at similar hydrodynamic radius regions in the original suspensions and the derived phases.

As for the rye phases, the size distributions displayed multimodal patterns corresponding to the three populations already discussed, albeit with distinct enrichment in the different phases (Fig. 2a). Phase I is largely enriched in the larger amylopectin and amylose populations, whereas Phase II and III had a larger proportion of the low molar mass fraction. With regards to oat, Phase II and III exhibited bimodal distributions with similar sizes to that of the oat suspension, showing a distinct enrichment in the amylopectin population compared to the oat suspension. After the selective treatments, the typical SEC distributions attributed to starch macromolecular populations were not observed, which demonstrated the successful hydrolysis of starch.

The amylose (AM) and amylopectin (AP) populations were further investigated after enzymatic debranching of starch in all the samples providing their branch chain-length distributions. The range of the degree of polymerization (X_{de}) for each branch population (AP1, AP2, and AM branches) and the peak height ratio of the longer to shorter AP branches (AP2/AP1) were obtained from the branch chain-length distributions as structural parameters. These results for each sample are presented in Table 2 and the size distributions are shown in Fig. 2c–d. The chain-length distribution of debranched starches exhibited two distinct peaks of AP and AM. The distribution of the AP branches was associated with the branching pattern of single lamellar branches (X_{de} ~5 to 35) and lamellae spanning branches (X_{de} ~35 to 100) and the AM branches were multimodal ($X_{de} > 100$) (Vilaplana & Gilbert, 2010b). The AP fractions were mainly composed of short-branched populations. All AM fractions exhibited a shoulder between X_{de} ~100 and 1000 corresponding with short AM branches (Takeda, Shitaozono, & Hizukuri, 1990).

A shift in the peak of the long-chain AM fraction was observed for the rye suspension compared to the flour (Fig. 2c). This may suggest that the long-branch fractions were sensitive to hydrolytic cleavage during heat

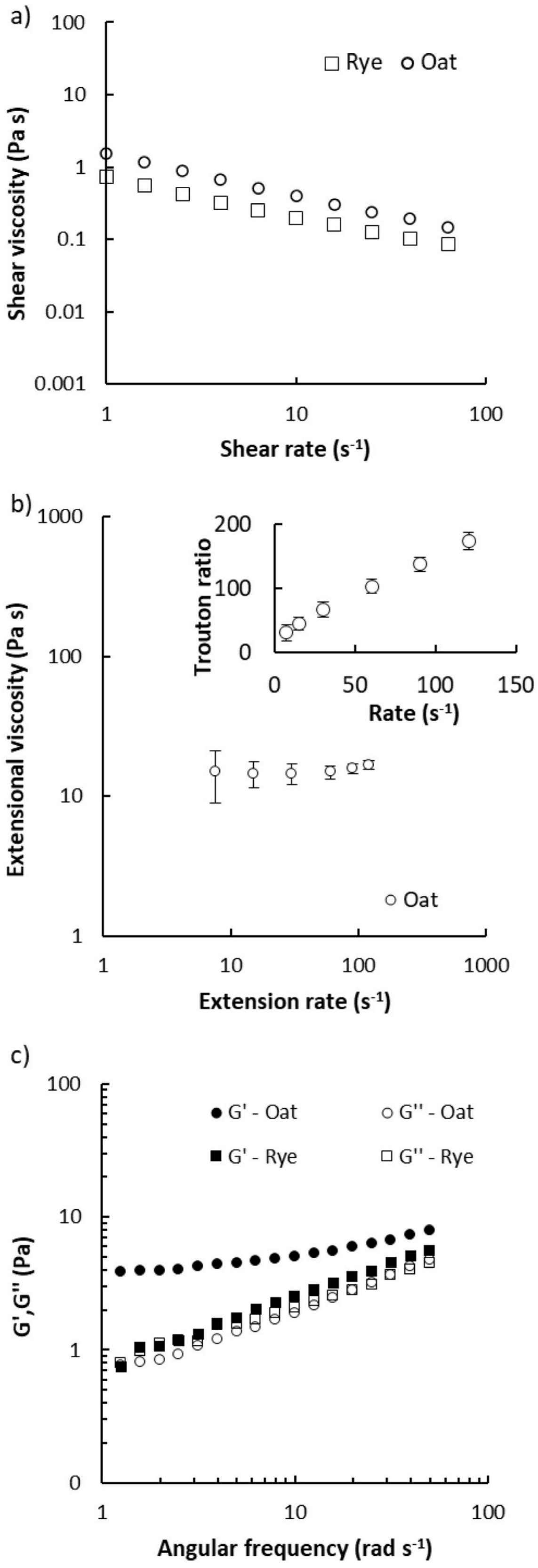

Fig. 3. Rheological properties of rye and oat suspensions (3.5 % wt): (a) shear viscosity as a function of the shear rate; (b) Extensional viscosity as a function of the extension rate. Rye suspensions did not show any extensional behavior. The insert represents the Trouton ratio of the oat suspensions. The error bars indicate the standard deviation of three measurements. (c) Elastic modulus G′ and viscous modulus G′′ as a function of the angular frequency.

Table 3
Flow behaviour index (n), consistency coefficient (k) and Hencky strain (ε_H) of the rye and oat suspensions and the corresponding Phase I, Phase II and Phase III before and after treatments to hydrolyse starch and remove proteins (T). n.a. Not applicable.

		n (–)	k(mPa s^n)	ε_H
Rye	Suspension	0.48 ± 0.01	721.1 ± 20.7	n.a.
	Phase I	0.49 ± 0.02	174.5 ± 19.7	n.a.
	Phase II	0.35 ± 0.00	3255 ± 34	7.6
	Phase III	0.28 ± 0.00	37 420 ± 78	7.1
	Suspension - T	0.99 ± 0.01	3.20 ± 0.03	n.a.
	Phase I - T	1.00 ± 0.00	2.84 ± 0.06	n.a.
	Phase II - T	0.98 ± 0.01	1.79 ± 0.32	n.a.
	Phase III - T	0.97 ± 0.01	7.05 ± 0.10	n.a.
Oat	Suspension	0.42 ± 0.01	1562.7 ± 66.4	7.9
	Phase I	1.00 ± 0.00	4.00 ± 0.00	n.a.
	Phase II	0.27 ± 0.00	48 556 ± 772	7.1
	Phase III	0.39 ± 0.01	66 240 ± 359	7.8
	Suspension - T	0.99 ± 0.01	1.21 ± 0.05	n.a.
	Phase I - T	0.98 ± 0.00	1.20 ± 0.01	n.a.
	Phase II - T	1.00 ± 0.00	1.20 ± 0.03	n.a.
	Phase III - T	1.00 ± 0.00	1.75 ± 0.07	n.a.

treatment (Liu, Halley, & Gilbert, 2010) or that the suspension process caused retrogradation of the long amylose branches, making them inaccessible to the debranching enzyme. The rye phases displayed similar AP and AM fractions compared to the suspension. As for the content of AM and AP, the rye flour contained higher AM than the previously reported values (Buksa, 2018). This difference was explained using different methods for the determination of AM and AP populations. The peak height ratio (AP2/AP1) remained relatively constant when the rye flour was heat treated to prepare the suspension (Table 2). The phases exhibited higher AP2/AP1, indicating a larger proportion of longer lamellae-spanning AP branches.

Interestingly, with regards to oat, the starch in the suspension showed a similar branch chain-length distribution to that of the flour (Fig. 2d). Regarding AM and AP in oat flour, a higher AM content was measured compared to previous observations (Zhou, Robards, Glennie-Holmes, & Helliwell, 1998). This was again attributed to the different measurement methods or the variety of oat, as different varieties have been shown to contain highly different amylose contents varying from 18% to 34% (Zhou et al., 1998). The peak height ratio (AP2/AP1) for the oat suspension was similar to the flour, and increased for the phases, implying that the phases were enriched in longer lamellae spanning branches (AP2) similar to the rye phases. The oat phases showed distinct relative composition of the AM and AP populations; oat Phase I showed an enrichment in the AM populations compared with the AP, whereas Oat Phase II showed the opposite trend with an enrichment of the AP versus the AM populations.

Comparing rye and oat, similar peak maxima for the AP1 and AP2 branches were observed for all the samples with X_{de} of between 27-28 and 49–53, respectively. Both rye and oat flours exhibited similar peak maxima for AM branches between 650 (AM1) and 4500 (AM2), indicating similar branch chain-length of AM in these flours. Interestingly, the AM branches for the oat suspension and phases had higher X_{de} (between 600 and 4500) than those for the rye suspension and phases (between 300 and 2400). This indicated that the suspension and phases of oat were composed of longer amylose branches compared to the rye phases. These results could be attributed to a larger resistance of the oat starch to hydrolytic cleavage by heat, under the conditions studied here, compared to the rye starch, resulting in longer amylose chains.

Taken together, the SEC results demonstrated that amylose and amylopectin fractions of rye and oat starches were influenced differently by the treatments applied, as presented by the changes in the size distribution of the starch macromolecules and the branch chain-length distributions. We cannot exclude the occurrence of hydrolytic cleavage of the amylopectin populations during the heat treatments, but we believe these are minor as inferred from the SEC data.

3.4. Shear viscosity, extensional viscosity and viscoelastic properties

3.4.1. Whole grain rye and oat suspensions

The shear viscosity of the rye suspensions was half of that one of oat suspensions, being 0.20 Pa s and 0.41 Pa s at 10 s^{-1} for rye and oat respectively. The suspensions exhibit shear thinning behaviour (Fig. 3a), i.e the viscosity decreased with shear rate; and follow a power law (Eq. (1)), which allow determining the shear thinning index (n) and flow consistency (k) (Table 3). Both suspensions exhibited similar shear thinning behaviour ($n_{rye} \sim n_{oat} \sim 0.4$) however, rye consistency index was half of the consistency index of the oat.

The oat suspensions presented an apparent extensional viscosity of about 15 Pa s, independent of the extension rate (Fig. 3b). The elastic contribution is noticeable, as indicated by the Trouton ratio (Tr) greater than 30, which is higher than the Newtonian limit of Tr = 3. For rye suspensions the extensional viscosity was not detected, indicating that if present, it was below 10 Pa s which is the threshold value of the set up used in this study (Malafronte et al., 2021).

The viscoelastic properties of the suspensions are reported in Fig. 3c in terms of storage modulus (G′) and loss modulus (G’’) as a function of the angular frequency. Rye showed frequency dependence, with similar values of G′ and G’’ and $\tan\delta_{rye}$ ($\tan\delta = G''/G'$) equals to 0.82 at 10 rad s^{-1}. In the case of oat, the suspensions also showed frequency dependence however, G′ was greater than G’’. $\tan\delta_{oat}$ was 0.38 at 10 rad s^{-1} indicating that oat suspensions presented a higher elastic behaviour than rye suspensions.

The content of starch (wet weight) was similar in rye and oat suspensions, with values of 2.35 ± 0.05% for rye and 2.75 ± 0.16% for oat therefore, the higher shear viscosity, presence of extensional viscosity and the higher elasticity of the oat suspension might be attributed to the starch molecular structure, i.e. the occurrence of longer amylose chains in oat, compared to small molecules (e.g. dextrins and other low molecular weight compounds) in the rye samples, (Fig. 2 and Table 2); and a higher swelling factor, which is 28 for oat starch at 95 °C and 14 for rye starch at 90 °C (Collins et al., 2010). The presence of non-starch polysaccharides in the suspensions could also contribute to the overall rheological properties, therefore removal of starch and proteins was carried out. The rheological properties were investigated before and after treatment and are presented in the following section.

3.4.2. Rheological properties of liquid and solid phases in rye suspensions

All the phases of the rye suspension exhibited a shear thinning flow behavior ($n < 1$), with shear viscosity increasing from Phase I to Phase III (Fig. 4a), their shear viscosity at 10 s^{-1} was 0.05 Pa s, 0.67 Pa s and 7.09 Pa s, from Phase I to Phase III respectively. Phase II and III of the rye suspensions exhibit a significant extensional viscosity (Tr > 3) with a slight extensional thinning behavior (Fig. 4c). They had a close value of deformation, indicated by the Hencky strain, meaning that the samples could be compared (Table 3). The extensional viscosity of Phase II was 71.1 ± 5.03 Pa s at approximately 10 s^{-1}, whilst for Phase III was 485.2 ± 15.7 Pa. No extensional viscosity was detected for Phase I. All rye phases, Phase I, II and III exhibit viscoelastic properties (Fig. 4e) and frequency dependence. The G′ values increased from Phase I to Phase III, and tanδ were 0.96, 0.51 and 0.29 at 10 rad s^{-1} for Phase I, Phase II and Phase III, respectively. The solid content between the phases, was 2.2 % wt., 5.1 wt % and 9.5 wt % from Phase I to Phase III respectively, in particular Phase I and Phase II were rich in starch, with values of 1.48% ± 0.07%, and 4.01% ± 0.30 for Phase I and Phase II respectively. Phase III contained 4.98% ± 0.14% starch, suggesting that other components such as proteins and non-starch polysaccharides accounted for almost 50% of phase III, and could also contribute to the rheological properties.

After treatment all the phases of the rye suspension show Newtonian behavior (ñ1), and a significant reduction in shear viscosity, as shown in Fig. 4a. The shear viscosity of Phase I decreases from 0.05 to 0.003 Pa s,

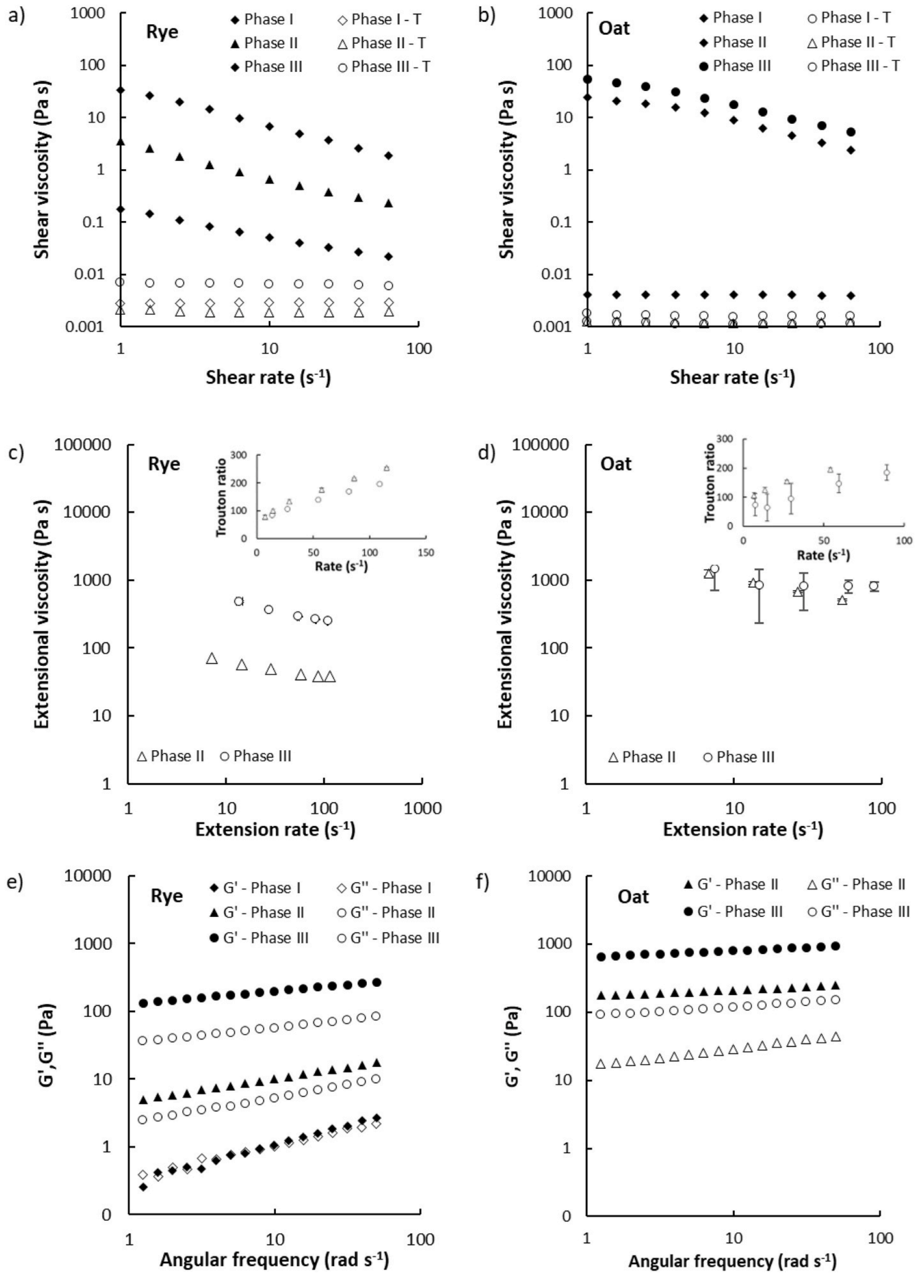

Fig. 4. Representative shear viscosity as a function of the shear rate of phases before and after treatment to hydrolize starch and remove proteins (T) for (a) rye and (b) oat. Extensional viscosity as a function of the extension rate of phases before treatment for (c) rye and (d) oat. No extensional viscosity was detected for the rye Phase I and oat Phase I. Due to their Newtonian behavior it was not possible to measure the extensional viscosity of the phases after treatment. The insert represents the Trouton ratio of the oat suspensions. The error bars indicate the standard deviation of three measurements. Representative elastic modulus G′ and viscous modulus G'' as a function of the angular frequency of (e) rye and (f) oat suspensions and their related phases before treatment. Due to their Newtonian behaviour, the viscoelastic properties were not measured after treatment.

Phase II from 0.67 to 0.002 Pa s and Phase III from 7.09 to 0.007 Pa s at the shear rate of 10 s^{-1}. Moreover, after treatment either extensional viscosity or viscoelastic properties could be detected in any of the phases.

In Phase I and Phase II the total solids content did not significantly change after treatment to hydrolyse starch and remove proteins (Phase I-T and Phase II-T in Table 1). This indicated that proteins were not removed during treatment, because either they were not present, or they did not precipitate with bentonite. On the other hand, starch was successfully hydrolysed (as shown by SEC in Fig. 2 and Table 2) and would still contribute to total solids content as glucose molecules. These results suggested that starch was the main contributor to the rheological properties, hydrolysis of starch led to a drastic change in shear viscosity, extensional viscosity and viscoelastic properties. The results also showed that the presence of minor amounts of soluble non-starch polysaccharides (Table 1) had a minimal contribution to the rheological properties. The shear viscosity of Phase III-T was very low compared to Phase III, it should be noted that Phase III corresponded to the insoluble solids in the suspensions, and those remained in the pellet after treatment.

3.4.3. Rheological properties of the liquid and solid phases in oat suspensions

In case of oat suspensions (Fig. 4b), Phase I showed Newtonian behaviour ($n_{PhaseI,oat} = 1$),whilst Phase II and III exhibited shear thinning behaviour and higher viscosities and consistency index than Phase I ($k_{PhaseI,oat} < k_{PhaseII,oat} < k_{PhaseIII,oat}$). The shear viscosity at 10 s^{-1} was 0.004 Pa s, 9.30 Pa s and 18.27 Pa s for Phase I, Phase II and Phase III, respectively.

Phase II and III exhibited close apparent extensional viscosity (Fig. 4d), with values of around 1000 Pa s, the elastic contribution in these phases was noticeable, with a Trouton ratio greater than 74. The Hencky strains, ε_H range from 7.1 to 7.9, indicating that all samples were subjected to a similar deformation, hence comparable (Table 3). Furthermore, Phase II and Phase III showed similar linear viscoelastic behaviour, with G′ larger than G'' and tanδ equal to 0.14 and 0.15 at 10

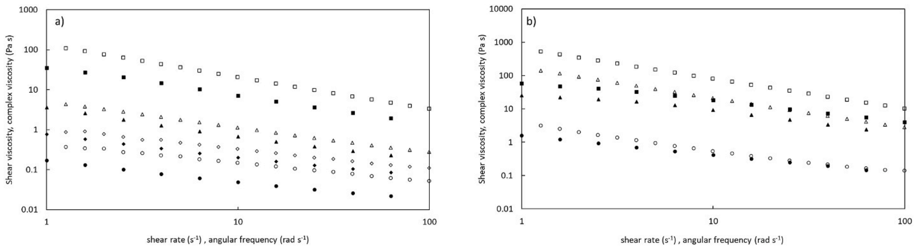

Fig. 5. Cox−Merz rule comparison of shear viscosity η (full symbols) and complex viscosity η* (empty symbols) as a function of shear rate and frequency, respectively, for rye suspensions and phases (a) and oat suspensions and phases (b).

rad s^{-1}, respectively. Neither extensional viscosity nor viscoelastic moduli were present in Phase I.

After the treatment to hydrolyse starch and remove proteins all the phases showed Newtonian behaviour and a significant decrease in shear viscosity. Phase I decreased from 0.004 Pa s to 0.001 Pa s, Phase II from 9.30 Pa s to 0.001 Pa s and Phase III from 18.27 Pa s to 0.002 Pa s at 10 s^{-1}. In addition, the treatment caused the loss of the extensional viscosity and viscoelastic properties in Phase II and Phase III.

Phase I had the lowest total solid content (0.4 % wt.), followed by Phase II (7.9 % wt.) and Phase III (11.4 wt %). Phase I and II were rich in starch and, once the starch was hydrolysed, (Phase I-T and Phase II-T) there was a drastic change in the rheological properties. The presence of non-starch polysaccharides had a very small contribution to the rheological properties of these phases. Regarding Phase III-T, as previously described for rye, the insoluble solids i.e including protein and non-starch polysaccharides, were removed during treatment, leading to a decrease in shear viscosity and loss of elastic properties.

The flours we used contained 9.2 wt% and 12 wt% protein for rye and oat respectively, in agreement with previously reported values (Poutanen et al., 2022). Our results suggest that although proteins might contribute to the overall rheological properties of these type of aqueous suspensions, under the processing conditions used in this study, it is mainly the starch that determines the viscosity and viscoelastic properties.

3.4.4. Cox Merz rule

The suspensions and phases were further studied by application of the Cox–Merz rule (Cox & Merz, 1958), stating that shear and complex viscosity match when plotted as a function of shear rate and frequency, respectively. All suspensions and phases violated the Cox–Merz rule at the concentrations investigated (Fig. 5). The shear viscosity was lower than complex viscosity allowing to conclude that they behave as suspension of soft particles rather than macromolecules in solution. Fig. 5 depicts the Cox–Merz rule comparison for the samples presented in Fig. 3. The Cox–Merz rule has been confirmed experimentally for several biopolymers, but not for macromolecule dispersions with either hyperentanglements or aggregates (Chamberlain & Rao, 1999; Lopes da Silva & Rao, 1992). This is the case of starch of modified waxy corn starch (Chamberlain & Rao, 1999), corn starch (Park, Chung, & Yoo, 2004) and rice flour (Chun & Yoo, 2004). Furthermore, in the whole grain flours, other components such as proteins and non-starch polysaccharides would contribute to their distinct rheological behaviour.

4. Conclusions

This paper has reported on the relationship between polysaccharide composition and starch molecular structure on the rheological properties of whole grain rye and oat aqueous suspensions. The extensional viscosity of such systems has been reported for the first time, which could potentially contribute to the design of the mouthfeel and ease-to-swallow properties of low to medium viscosity products making use of these cereals. We conclude that at the same total solids, oat aqueous suspensions present higher shear viscosity and higher elastic modulus that rye suspensions. Furthermore, oat suspensions have an apparent extensional viscosity which is not present in rye. A systematic investigation of the liquid and solid phases before and after starch hydrolysis and protein removal indicated that starch is the main responsible for the distinct rheological behaviour of the continuous phase of both rye and oat suspensions, whilst protein and cell wall polysaccharides contributed to a lesser extent. Regarding the solid phase, the results indicate that protein and cell wall polysaccharides would also contribute to the rheology. The continuous phase differences between rye and oat were mainly attributed to starch molecular features i.e oat starch showed higher amylose/amylopectin ratio and longer amylose branches, compared to rye starch Furthermore, our results show that the systems do not follow the Cox-Merz rule indicating that they behaved as suspensions of soft particles rather than macromolecules in solution. Studying the role of polysaccharide composition and starch molecular features on the rheological properties of suspensions of whole grain rye and oat flours is key for promoting their utilization as natural texturisers in food systems.

Authors contribution

Loredana Malafronte: Investigation, Formal Analysis, Data curation, Visualisation, Writing – original draft, Writing – review & editing. Secil Yilmaz-Turan: Investigation, Formal Analysis, Visualisation, Data curation, Writing – original draft. Leyla Dahl: Investigation, Formal Analysis, Visualisation, Writing – original draft. Francisco Vilaplana: Formal Analysis, Writing – review & editing. Funding acquisition. Patricia Lopez-Sanchez: Conceptualization, Methodology, Formal analysis, Writing – original draft, Writing - review & editing, Funding acquisition, Project administration.

Declaration of competing interest

The authors have declared that no competing interests exist.

Data availability

Data will be made available on request.

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