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Structuring Vegetable Oils Through the Formation of Capillary Suspensions: Comparison of Wheat Middlings and Pure Cellulose Processed by High-Pressure Homogenization

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Reducing the intake of harmful trans-fats and saturated fats in the diet, by replacing detrimental fats with healthier oils, without affecting the organoleptic properties of the food product, represent a formidable challenge for the scientific community. In this scenario, this work explores a possible strategy for structuring sunflower oil by investigating the formation of capillary suspensions using wheat middlings (WM) and pure cellulose (CL) as a structuring solid fraction. High-pressure homogenization (HPH), a purely mechanical cell disruption technology, was directly applied to oil suspensions of WM or CL. Subsequently, the addition under high-shear mixing (HSM) of different amounts of an immiscible secondary fluid, water, to the oil suspensions, led to WM and CL particles bridging and network formation, through the development of attractive capillary forces among the particles. The effect of water and particles characteristics on the rheological behavior of the oil suspensions was investigated. The presence of water caused initially an increase in viscosity and then a decrease, as water concentration exceeded a critical value, with an inversion from a continuous oil phase to a continuous aqueous phase. Moreover, the oxidative stability of the capillary suspensions was evaluated, during accelerated aging. The proposed approach not only does not suffer the presence of water, but significantly improves the oxidation stability with respect to the pure oil

1. Introduction

In the last decade, oil structuring has gathered increasing interest because of its potential use in the food, pharmaceutical, and biotechnology industries for replacing unhealthy saturated fats. More specifically, oleogels have been proposed as novel systems in food preparations incorporating vegetable oils, to enhance their techno-functional properties and nutritional value, without penalizing taste and mouthfeel (Le Révérend et al., 2010). Oleogels are systems characterized by a continuous liquid phase physically immobilized by a self-assembled network of gelators, such as waxes, monoglycerides, fatty acids, plant sterols, and esters. A heating step is generally applied to melt the gelator in the liquid oil phase under gentle stirring for its full dissolution. By cooling below the gelation transition temperature, the gelator self-assembles into a thermoreversible three-dimensional network that entraps the surrounding oil phase (Blake et al., 2018; Zhao et al., 2021). Oleogelators should typically feature (i) the presence of lipophilic and interacting parts, (ii) surface activity, and (iii) thermoreversible characteristics. However, for food use, the gelators should be of natural origin and considered as GRAS, hence severely reducing the available options. For this reason, capillary suspensions have emerged as a promising potential alternative for oil structuring. The addition of small amounts of a secondary immiscible fluid (generally water) to a suspension (such as particles in oil) triggers attractive capillary forces, leading to particle bridging and the formation of a 3D network (Koos, 2014; Mustafa et al., 2018). In this way, a transition from a fluid-like to a gel-like state is promoted. The rheological properties can be tuned by controlling the attractive capillary forces (e.g. particle size or water fraction), with an increase in yield stress and shear viscosity by several orders of magnitude (Koos and Willenbacher, 2011), increasing also suspension stability. Depending on how primary and secondary fluid wet the particles, capillary suspensions can be classified in the pendular state, spherical agglomerates, bi-continuous, Pickering emulsion, and capillary state (Bossler et al., 2016).

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This work aims at structuring sunflower oil by high-pressure homogenization treatment applied to wheat middlings (WM) or cellulose (CL) particles directly suspended in oil, with the final goal of obtaining a gel-like product without the use of unhealthy fats or undesired additives, but only with the use of water as secondary fluid. The use of WM enables also the reduction of the caloric content of the oil, while sustainably valorizing an agri-food residue (AFR) of the wheat milling process, hence contributing to implementing the circular economy across the food chain. Moreover, the antioxidant content of WM could also contribute to slowing down oil oxidation processes. The use of pure cellulose, which is especially challenging when considering the hydrophilic nature of the sugar monosaccharides building blocks, enables the exploitation of a natural biopolymer with high biocompatibility, ecological acceptability, renewability, and low toxicity. By advancing the understanding of the mechanism of network formation of oil suspensions using high-pressure homogenization (HPH), a contribution will be given to developing new applications in oil structuring.

2. Materials and methods

2.1 Raw materials

Wheat middlings (WM) was kindly supplied by a local milling industry (Albanella, Salerno, Italy), and stored at room temperature until used. Commercial cellulose (CL) Arbocel® BWW40, with a declared average length of the cellulose fibers of 200 µm, was kindly supplied by Rettenmaier Italia (Brescia, Italy). Sunflower oil was purchased from a local market (Olio di Semi di Girasole Basso, San Michele di Serino (AV), Italy). Its composition (on a weight basis) comprises 10.3% wt of saturated fatty acids, 19.5% wt of monounsaturated fatty acids, and 65.7% wt of polyunsaturated fatty acids. All water used throughout this work was purified by the Milli-Q water purification system (Barnstead™ Pacific TII Water, Thermo Scientific, Waltham, MA, USA).

2.2 Formulation of oil suspensions

WM was suspended in sunflower oil at 30% w/w and cellulose fibers at 5%, which correspond to the cellulose content in WM particles (data not shown). The solid particles were firstly dispersed using a high-shear mixer (HSM) (Ultra Turrax T25, IKA Labortechnik, Germany) at 20,000 rpm for 5 min within an ice bath. The obtained suspensions were then subjected to high-pressure homogenization (HPH) treatment (80 MPa for 20 equivalent passes) using an in-house developed system, using cooling water at 10 °C.

2.3 Characterization of oil suspensions

The particle size distribution of the samples micronized in oil by HSM or HPH was measured by laser diffraction using a Malvern Mastersizer 2000 (Malvern Instruments Ltd., UK). The oil phase of oil dispersions was substituted by water by washing them three times with saponin from quillaja bark (Sigma-Aldrich, St. Louis, MO, USA)) at 0.5% w/v in water, followed by centrifugation at 6,500 rpm. The diameters corresponding to the 10^{th}, 50^{th}, and 90^{th} percentile of the cumulative distribution (d(0.1), d(0.5), and d(0.9), respectively), the volume-based and surface-based mean diameter (D[4,3] and D[3,2], respectively), were calculated as previously described (Pirozzi et al., 2021). The mean value of three replicates was determined.

2.4 Capillary suspensions formulation

The capillary suspensions were obtained by adding a secondary fluid (distilled water) at 0.05, 0.30, and 0.50 values of saturation ratio SR (Equation 1) to the HPH-treated oil suspensions under HSM (20,000 rpm for 10 min) within an ice bath (Bossler et al., 2017).

$$\mathrm{SR} = \frac{V_{water}}{V_{oil} + V_{water}} \tag{1}$$

2.5 Capillary suspensions characterization

The suspension morphologies were observed with an optical microscope (Nikon Eclipse TE 2000S, Nikon Instruments Europe B.V., Amsterdam, The Netherlands), coupled to a DS Camera Control Unit (DS-5M-L1, Nikon Instruments Europe B.V, Amsterdam, The Netherlands) for image acquisition and analysis.
Rheological analyses of capillary suspensions were performed in a rotational rheometer (AR 2000 rheometer, TA instruments, Newcastle, DE, USA), equipped with a concentric cylinder (15 mm stator inner diameter, 28 mm rotor outer diameter, 42 mm cylinder immersed height, 2° cone angle) and plate-cone geometry (40 mm diameter, 2° cone angle and 1 mm fixed gap width). The apparent yield stress was evaluated using a shear rate ramping. Flow curves were obtained by continuously varying the shear rate from 0.1 s^{-1} up to a rate of 200 s^{-1} at 20 °C. Measurements were repeated five times on two independently prepared samples and were reported as means ± standard deviations for apparent yield stress.

2.6 Accelerated oxidation stability test

The primary oxidation compounds analysis is always carried out by the peroxide value (PV) to assess the quality of oil at its stability. For the Schaal oven accelerated stability test, approximately 1 g of each sample was put in vials and stored in an oven at 65 ± 2 °C in absence of light after 15-days of storage (Lužaić et al., 2022). The PV value was determined iodometrically (visually) with a starch indicator and a sodium thiosulfate standard solution according to ISO 3960:2007 (International Organization for Standardization).

2.7 Statistical analysis

All experiments and analyses were performed in triplicate unless differently specified and the results were reported as means ± standard deviations. Statistically significant differences among mean values were analyzed by one-way variance (ANOVA and Tukey test ($p < 0.05$), performed with SPSS 20 (SPSS IBM., Chicago, USA) statistical package.

3. Results and discussions

3.1 Oil suspensions

The size distribution is a crucial analysis that affects the physical properties of oil suspensions. The particle size distributions for WM and CL-based oil suspensions treated by HSM and HPH (Figure 1) give information on the effect of the two different mechanical treatments. For the WM-based oil suspensions treated by HPH, the distribution was narrower and more uniform than for HSM-treated samples, as already observed in the case of tomato peels, because of the disruption of individual plant cells into fibrous debris (Jurić et al., 2019). In contrast, HPH treatment applied on cellulose-based oil distribution induced only a slight decrease in the particle size with respect to the HSM-treated samples, likely because of the initial finer size of the used cellulose, limiting the capability of HPH treatment to further break down the cellulose fibrils.

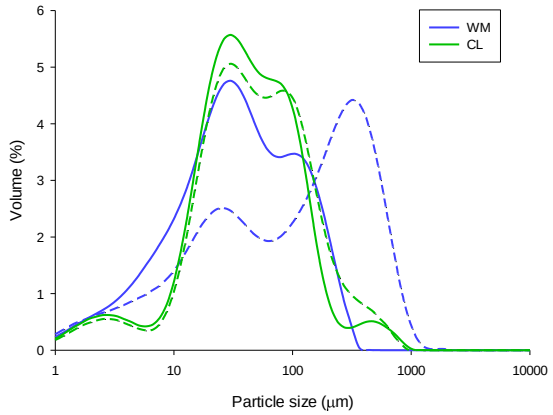

Figure 1: Particle size distribution of oil suspensions treated with high-shear mixing (dashed lines) and high-pressure homogenization (solid lines).

Table 1: Effect of different mechanical treatments on WM and cellulose-based oil dispersed on particle size distribution expressed as the main characteristic diameters.

Component	WM		CL	
	HSM	HPH	HSM	HPH
d(0.1)	6.4 ± 0.3	5.5 ± 0.2	11.6 ± 0.4	10.2 ± 0.5
d(0.5)	101.3 ± 1.8	30.9 ± 1.9	43.2 ± 1.9	36.9 ± 2.7
d(0.9)	461.3 ± 23.5	136.9 ± 7.3	168.0 ± 3.0	124.5 ± 7.5
D[3,2]	15.1 ± 1.2	12.4 ± 0.7	17.5 ± 0.5	15.7 ± 1.0
D[4,3]	177.8 ± 10.7	53.3 ± 2.7	76.3 ± 2.4	63.7 ± 2.5

Table 1 reports the characteristic diameters of WM and CL oil suspensions, treated by HSM and HPH. As shown also in Figure 1, the mean particle size of WM was significantly reduced after HPH treatment: D[4,3] decreased by ~70%, D[3,2] by ~17%, and significant decreases were observed for both d(0.5) and d(0.9). In contrast, HPH treatment on cellulose-based oil suspension did not significantly change the size distribution with respect to HSM treatment: D[4,3] and d(0.5) decreased by ~15%, and D[3,2] by ~10%, whereas only the larger particles were effectively reduced in size, as shown by the decrease of d(0.9) of ~10% upon HPH processing.

3.2 Capillary suspensions characterization

The addition of water into the oil suspensions caused a drastic change in the system structure, due to the formation of capillary bridges and the development of a gel-like network, with higher consistency as the SR increased, as shown in Figure 2. At SR = 0.05 and 0.30, both WM and CL suspensions exhibited a weak gel-like behavior, with no interconnected water-rich aggregates. With the increase in water concentration, an increase in aggregates was observed (the dark area in the microscopic images). Therefore, a compact and homogeneous 3D structure was developed for SR = 0.50, suggesting the formation of a capillary bridge network.

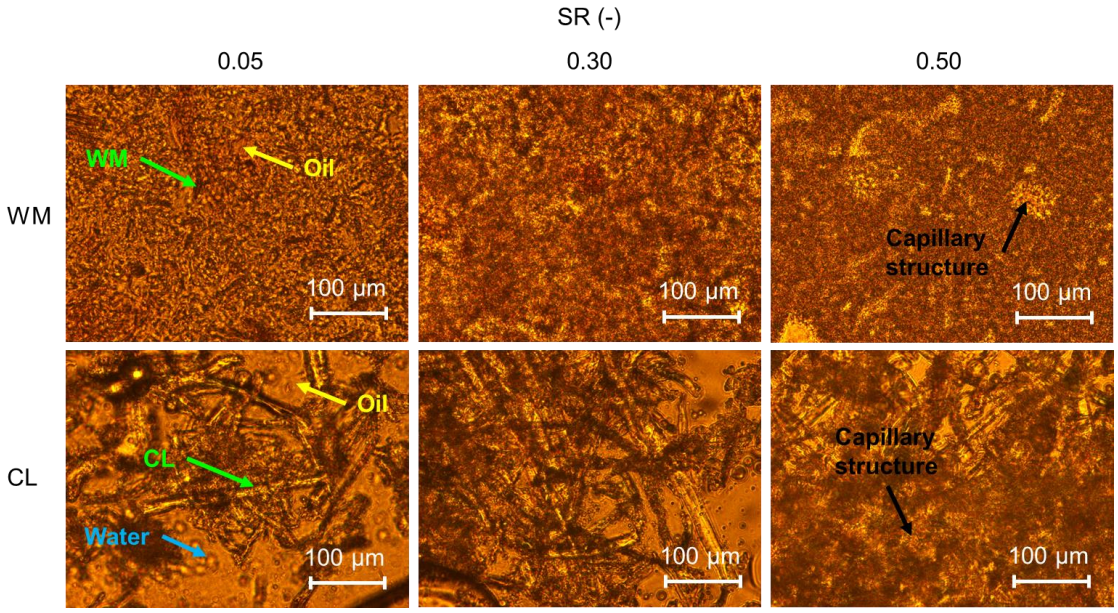

Figure 2: Microscopic observations of capillary suspensions prepared from WM (first raw) and CL (second raw) oil suspensions adding water at different saturation ratios (SR = 0.05 in the first column, 0.30 in the second column, and 0.50 in the third column).

The rheological behavior of WM and CL stabilized capillary suspensions is shown in Figure 3. In agreement with the results of the microscopic analysis in Figure 2, the formation of a 3D network structure was observed upon water addition, which became stronger with the increase of SR value, with a corresponding increase in apparent viscosity. Remarkably, for WM-stabilized capillary suspensions, higher apparent viscosity values than for CL-stabilized suspensions were observed, at a low shear rate, for SR = 0.30 and SR = 0.50, whereas higher values were recorded for CL at SR = 0.05. Moreover, due to the gel-like structure of the suspensions, at all SRs, as the shear rate increased, the network broke down, and the viscosity decreased rapidly.

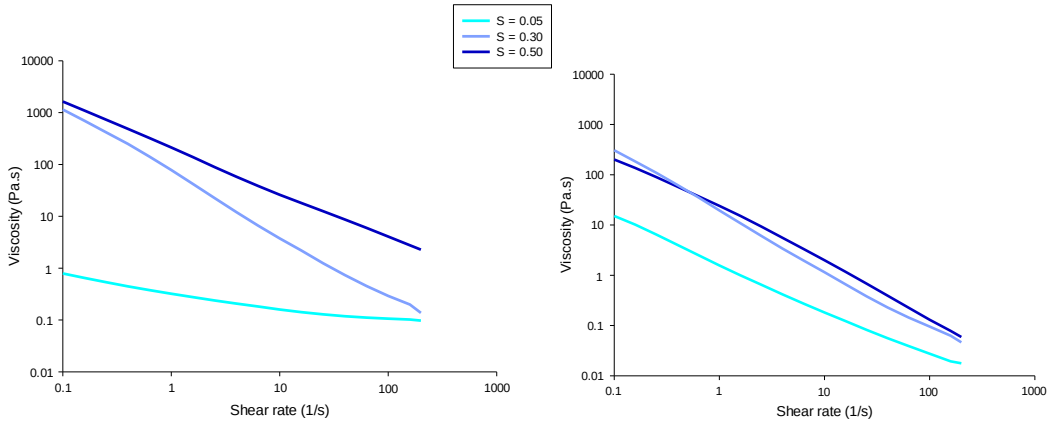

Figure 2: Flow curves of capillary suspensions stabilized by WM (left) and CL (right) particles as a function of the saturation ratio SR.

Table 2 summarizes the results of the apparent yield stress values, derived from the flow curves, calculated as previously reported (Mustafa et al., 2018). The capillary suspensions exhibited an increase in apparent yield stress with increasing water concentration (SR) in the oil suspensions. This trend can be explained by the increase in network strength. However, when SR is increased above a critical value (SR > 0.5), a phase inversion was observed, with a switch from a continuous oil phase to a continuous water phase (data not reported). Moreover, using different types of solid particles (e.g. WM or CL) greatly affected the network formation in the capillary suspensions, and the deriving rheological properties: the apparent yield stress of CL-based capillary suspension was significantly higher (one order of magnitude) than for WM at SR = 0.05, but it was significantly lower (one order of magnitude) at SR of 0.50. The differences in the rheological behavior of the different particles can be assumed to be related to the shape of the particles, affecting the capillary bridges formed in the suspensions (Maurath et al., 2016).

Table 2: Apparent yield stress for WM and CL-in-oil suspensions at 30% and 5% w/w, respectively, as a function of saturation ratio SR.

SR (-)	Apparent yield stress (Pa)	
	WM	CL
0.05	1.10 ± 0.32^{aA}	11.70 ± 2.24^{aB}
0.30	33.26 ± 7.01^{bA}	25.14 ± 4.98^{bA}
0.50	322.23 ± 22.30^{cB}	31.20 ± 0.34^{cA}

Different lowercase letters denote statistically significant ($p < 0.05$) differences in the same column.
Different capital letters denote statistically significant ($p < 0.05$) differences in the same raw.

3.3 Capillary suspensions' oxidative stability

The 15-day period of storage in the accelerated Schaal oven test conditions (65 °C) correspond to 15 equivalent months at room temperature (Lužaić et al., 2022). A remarkable increase in peroxide values, which are the indicator of primary lipid oxidation, was noticed both in pure sunflower oil and CL-based capillary suspensions for all tested SRs, with higher values in CL-based capillary suspension because of the presence of water, which enhanced the oxidation process. In contrast, WM-based capillary suspensions ensured always the lowest PV in the oil: the phenolic bioactive compounds with high antioxidant activity, contained in the WM particles, but not present in the CL capillary suspensions, enabled to significantly slow down the oil oxidation phenomena during the entire period of storage, despite the presence of water, demonstrating that the proposed approach not only does not suffer the presence of water, but significantly improves the oxidation stability with respect to the pure oil.

Table 3: Peroxide value (PV) of capillary suspensions after a 15-day storage period at 65 °C.

SR (-)	PV (mEq kg^{-1}_{oil})	
	WM	CL
0.00*	62.41	
0.05	16.01	104.55
0.50	13.02	99.52

* pure sunflower oil, without suspended particles

4. Conclusions

The present work showed the feasibility of a novel approach proposed for oil structuring, based on direct processing via high-pressure homogenization of oil suspension of fibrous particles, such as wheat middlings, and subsequent addition of water to form a 3D network stabilized by interparticle capillary forces.
This approach offers many advantages in comparison with more conventional approaches based on oleogelation, namely: (1) a facile and versatile process, based only on physical processing, without the addition of undesired ingredients to the formulation (e.g. gelators), (2) the replacement of part of the oil with the fibrous material and water, hence reducing the caloric intake, while ensuring the desired mouthfeel, as the oil will still constitute the continuous phase, (3) the delivery of bioactive molecules, associated with the fibours particles, when obtained from agri-food residues or other biomass, still rich in valuable compounds, with an antioxidant effect on the oil and expected health-beneficial effects also on consumers, and (4) the high transferability of the proposed approach, enabling to tune color, flavor, and taste of the structured oil, depending on the desired application. Currently, the main limitation of the proposed approach is the reduced temperature dependence of

the rheological behavior, which could affect the organoleptic properties in some applications (e.g. when the solid fat are expected to melt in the mouth), and which needs to be addressed by future studies.

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