

Roasted Sunflower Kernel Paste (Tahini) Stability: Storage Conditions and Particle Size Influence

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Abstract Sunflower tahini faces quality problems due to the tendency of oil to exudate, causing accelerated rancidity and low marketability. In this study, the colloidal and oxidative stability of different trimodal particle size distributions of sunflower tahini (cumulative volume percentages of small, middle and large class populations of 9.61–16.67, 43.03–55.03 and 47.36–28.3) was evaluated during storage at three different temperatures. Decreasing sample particle size decreased the sunflower tahini colloidal stability. The coarsest prototype, being the most stable tahini in terms of oil separation, was included in the oxidative stability storage test together with a commercial tahini. The peroxide values of the studied sunflower tahini samples increased significantly ($p < 0.05$) with storage time, irrespective of storage temperature, while the p-anisidine values showed an irregular pattern. Considering 30-meq O₂/kg as a PV limit, the commercial tahini showed good oxidative stability as it was under this when stored 3 months at 4 °C, 2 months at room temperature and 1 month at

40 °C. The coarsest tahini sample was under the limit when stored 2 months at 4 °C, 1 month at room temperature and 2 weeks at 40 °C. Particle size was shown to be an essential parameter for controlling sunflower tahini's overall stability.

Keywords Tahini · Nut spread · Sunflower paste · Storage test · Stability

Introduction

Tahini is a food product that is usually produced by milling hulled, roasted sesame seeds into a paste. The resulting product can be used as a condiment, dressing, spread, sauce and mixture with different fruits syrups. Several tahini varieties and combinations of tahini with various types of food have been described, such as a tahini-pine honey blend [1]; pekmez, a blend of tahini with either grape or mulberry juice [2, 3]; low-fat sesame paste blended with date syrup [4, 5] and bozkir, which is tahini obtained from unhulled roasted sesame seeds [6]. Tahini is also the major ingredient in halva (a confection that includes nougat), hummus (mashed chickpeas, flavored with lemon juice and garlic) and baba ghanoush (a purée of eggplant, lemon juice, garlic and oil) [7].

Tahini is mainly used in the Middle Eastern, North African [8] and South Eastern European cuisines [9], but it also has a notable presence in Asia, especially in India, China and Japan [10]. Although the term tahini was first assigned specifically to sesame paste, for decades in Central Eastern Europe sesame seeds have been fully replaced by sunflower kernels, resulting a cheaper product—roasted sunflower kernel paste (sunflower tahini) [11].

Sunflower tahini may be a viable global alternative to other nut pastes obtained from more expensive oleaginous

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kernels (e.g., peanut, pistachio, hazelnut, almond, etc.), which are used in the production of different nut butters, spreads, chocolate (hazelnut paste) or other typical confectionery products (e.g., Xixona turrón, a typical Spanish product based on almond paste). When comparing sesame and sunflower tahini, Damir [12] concluded that their chemical composition and sensory properties showed a close similarity. Sunflower kernels have a high nutritional value, containing (% dry weight basis) 20.4–40 % proteins, 47–65 % lipids (fatty acid composition mainly unsaturated with 51–73 % linoleic, 15–37 % oleic and low levels of saturated 5–7 % palmitic, 2–6 % stearic), 4–10 % carbohydrates, 0.07 % tocopherol, 0.01–0.02 % carotenoids, 0.002 % vitamin B1, 0.67–0.75 % potassium, 0.60–0.94 % phosphorus and 0.35–0.41 % magnesium [13]. Sunflower kernels are allergen free, pointing to another possible advantage as an allergen-free alternative in confectionery products. Given the chemical similarities between sesame and sunflower kernels, the high nutritional value and low allergen levels of sunflower seeds and the relative cost effectiveness, sunflower tahini may be of future interest for the food industry on a global scale.

The two main quality problems facing the tahini industry derive from the tendency of the oil to separate at the top of containers: first, it causes negative effects on consumer acceptability, since it is very difficult to re-disperse the sediment cake for further processing or consumption. Second, when free separated oil is exposed to air and light, it leads to rancidity. This holds true for both the well-known and studied sesame tahini as well as for sunflower tahini or other nut pastes. Ahmad et al. [14] recently published a study emphasizing the oxidative stability and oil separation problems of nut spreads (tahini similar products). Mureşan et al. [15] stressed the importance of research on sunflower halva technology in order to solve the identified storage problems of oil separation and rancidity. This study also highlighted that sunflower tahini is the single fat-containing ingredient added to halva, making it the main contributor to sunflower halva instability.

Many studies have been conducted on sesame tahini colloidal stability (CS) [1, 6, 16] as well as on similar products, such as sesame halva [17–19], pistachio butter [20] and peanut butter [21–25]. Unfortunately, limited information regarding sunflower tahini [12] or sunflower butter [26, 27] CS is available. After 90 days of storage at room temperature, Damir [12] reported that the amount of oil separated reached 7.6 % (sesame tahini), 11.8 % (sunflower tahini) and 6.25 % (sunflower tahini containing 1 % glycerol monostearate), concluding that the addition of glycerol monostearate to tahini-like sunflower butter had a pronounced stabilizing action. However, even if the reduction of separated oil was significant, the problem was not totally solved, with more studies being required. To prevent

oil separation of sunflower butters by the development of a network of fat crystal structures that immobilize the free oil, MacDonald et al. [26] included 2–4 % hydrogenated vegetable oil in all three formulations obtained. Two of these also contained 2 % mono- and diglycerides. In order to solve the same issue, Lima and Guraya [27] considered two stabilizers for the formulation of sunflower butters (i.e., hydrogenated palm oil and a hydrogenated blend of rapeseed/cottonseed oil). Both of the above-mentioned studies [26, 27] concluded that oil separation decreased with the amount of stabilizer added. However, it was noted that excessive stabilizer in the product resulted in a hard butter that was difficult to spread.

Due to their high oil content, and accentuated by the exuded oil phase on the surface, tahini and tahini-related products are susceptible to oxidation. Studies have been undertaken on the oxidative stability (OS) of sesame tahini [8, 28, 29] and peanut butter [30]. There is limited literature related to the OS of sunflower tahini [12] and value-added products from sunflower kernels [31, 32]. Damir [12] reported a much lower OS of sunflower tahini compared with sesame tahini, the former showing a rancid taste after reaching the maximum peroxide value. However, the same study mentioned that the addition of antioxidants (i.e., BHA, BHT) postponed peroxide formation in sunflower tahini and increased its stability from 18 to 47 days. In another study a level of 200 µg/g, raisin extract proved to be an effective natural antioxidant in sunflower butter [31]. Muttagi et al. [32] showed that plastic jars were slightly more efficient than glass jars in terms of oilseed butter OS: Peroxide values were initially 7.37–8.58 meq/kg, and upon 60-day storage at 37 °C, rose to 18.26–23.41 meq/kg and 18.26–22.87 meq/kg in plastic and glass jars, respectively. All products were highly acceptable at the end of the storage period.

Despite the fact that research has been done to solve the oil separation and rancidity problems of sunflower tahini and similar products, the issues have not been completely solved and understood. Our group recently showed that sunflower tahini particle size had an impact on the product's rheological behavior and structure [33]. Thus, the objective of this study was to assess the influence of the particle size distribution and storage conditions on sunflower tahini colloidal and oxidative stability. It has already been demonstrated [33] that utilizing different milling strategies in order to prepare different particle sizes of sunflower tahini, but starting from the same raw material, with the same chemical composition, leads to prototypes with very different rheological properties (e.g., prototypes that were highly viscous and thixotropic with high volume fractions to slightly viscous and thixotropic with low volume fractions, the industrial reference being intermediate). Consequently, from a practical point of view, controlling the milling stage of sunflower kernels might be an important and “in place

tool” for food researchers and technologists to improve sunflower tahini stability, without adding hydrogenated fats or chemical antioxidants or emulsifiers. The current article is an essential continuation of this previously published work [33] in order to assess the colloidal and oxidative stability of the same, varied-particle-size sunflower tahini sample set. Moreover, in addition to the extensive storage test, for the first time, a rapid rheological method was used for the prediction of sunflower tahini CS. While sunflower seeds may be of interest as a food crop, for sunflower tahini to be used properly as an ingredient (e.g., sunflower halva, hummus, spread, butter, etc.) or develop new creamy products (e.g., dressings, sunflower tahini-fruit juice blends), it is essential to improve its colloidal and oxidative stability.

Materials and Methods

Roasted Sunflower Kernel Production and Chemical Characterization

The roasted sunflower kernels were produced industrially by Feleacul Plant Cluj-Napoca (S.C. AMYLON S.A., Sibiu, Romania) from an industrial mix of sunflower seeds, the roasting temperature being 120 °C. Detailed process operations, technical means and technological regimes used during roasted sunflower kernel manufacturing were revised by Mureșan et al. [15]. The protein content of roasted sunflower kernels was measured by the Kjeldahl method [34] using a Tecator Digestor and KJELTEC 2100 apparatus. Oil content was determined by extraction with n-hexane on SOXTHERM equipment [35]. Ash was determined as the residue remaining after incineration at 600 °C [36]. Moisture and volatile matter contents were determined by drying at 130 ± 2 °C, until a constant mass was reached [37]. All measurements were performed in triplicate.

Commercial Sunflower Tahini Production

Commercial sunflower tahini (THC) was derived industrially at Feleacul Plant Cluj-Napoca from the roasted sunflower kernel batch via a two-step process that is currently used for sunflower tahini production, as described by Mureșan et al. [15]: the roasted sunflower kernels are milled to a flour by a three-roll refiner and then further processed on a continuous beating machine in order to obtain a paste.

Pilot Plant Production of Sunflower Tahini Prototypes

It was impossible to adjust the industrial sunflower tahini production process for the manufacturing of

different particle size tahini samples. Thus, roasted sunflower kernels from the same batch were ground at a pilot plant scale using a Microcut MCV 12B colloidal mill. The mill is a versatile fine-grinding and dispersing system, working on the rotor-stator principle. As described by Muresan et al. [33], by increasing the number of passes through the colloidal mill, eight prototypes were obtained, ranging from the coarsest sample (TH1, one pass through the colloidal mill) to the finest sample (TH8, eight passes through the colloidal mill). Tahini prototypes were obtained by a different technology than the one currently used by the food industry, but the study allowed assessing the stability of different sizes of sunflower tahini, thus providing future alternatives for the industry.

Particle Size Distribution Determination

Particle size distributions of each tahini sample were determined by a laser diffraction instrument, Malvern Mastersizer 2000, connected to the sample handling unit, Hydro 2000S, as reported previously by Muresan et al. [33]. In order to obtain an average value and avoid unreliable results caused by the high sample heterogeneity, three subsamples were sampled from the commercial tahini, as well as from each prototype. Each subsample was measured ten times. Subsamples were transferred to the equipment sample unit and dispersed in hexane. The resulting scattering pattern was analyzed according to the Mie theory using hexane and sunflower tahini particle refractive indexes of 1.38 and 1.47, respectively. The software Mastersizer 2000, version 5.22, was used. Results are provided as histograms of sizes, cumulative volume percentages (CVPs) and coordinates of the modes (CMs).

Rheological Measurements

Flow behavior measurements of sunflower tahini samples at 4, 25 and 40 °C were performed by a CVO 120 high-resolution controlled stress rheometer, equipped with SP 25 serrated plate system (25 mm diameter; gap set to 1250 μm) for sample TH1, with cup (27.5 mm diameter and 50 mm height) and bob (25 mm diameter and 37.5 mm height) C25 system for samples THC, TH2 $\rightarrow$ TH8. All the samples were vigorously manually sheared for 1 min in order to suppress the previous rheological history of the sample tested. They were then allowed to equilibrate for 5 min before starting the experiment. The shear stress and apparent viscosity were recorded as a function of the shear rate. Shear rates were adapted according to the sample characteristics. Viscosimetry measurements were carried out in duplicate. The experimental data obtained for each sample were fitted to the Bingham model:

$$\sigma = \sigma_0 + \eta' \dot{\gamma} \quad (1)$$

where σ is the shear stress, σ_0 the Bingham yield stress, η' the Bingham viscosity and $\dot{\gamma}$ the shear rate.

Vertical Scan Macroscopic Analysis

The physical stability of sunflower tahini was monitored by a Vertical Scan Macroscopic Analyzer Turbiscan MA 2000 instrument, which detects and measures modifications of concentrated and opaque suspensions. Immediately after preparation, the sunflower tahini samples (5 ml) were placed into flat-bottomed cylindrical glass tubes (140 mm height, 16 mm diameter), and the first measure of the transmission and backscattering profiles as a function of height (70 mm) was made. Stability measurements were made in duplicate. For each sample, the percent colloidal stability [38] was determined at randomly chosen time intervals over 375 days using the equation below:

$$CS [\%] = \left(\frac{H_t - H_o}{H_t} \right) \times 100 \quad (2)$$

where H_o is the height of oil phase determined at 2, 7, 23, 35, 50, 84, 127, 168, 273, 301 and 375 days from transmission Turbiscan profile, and H_t is the total height of sunflower paste in the test tubes assessed from the initial backscattering Turbiscan profile.

Fat Extraction

For all samples, oil was extracted according to a slightly modified method described by Folch et al. [39]: 15 g of sunflower tahini was placed in a 250-ml centrifuge tube and homogenized with 100 ml of solvent mix (chloroform–methanol 2:1, v/v) for 30 min on a Velp Multiposition Magnetic Stirrer. Subsequently, each sample was centrifuged 5 min at 3,000 rpm (900×g) and the supernatant filtered and transferred to a separating funnel. Samples left in the centrifugation tube were washed with 25 ml of chloroform–methanol 2:1, homogenized for another 10 min, centrifuged (under the same conditions as above), filtered and added to the corresponding separating funnel. A final rinse was done with 25 ml of solvent mix. The filtrate from the separating funnel was homogenized for 1 min with 50 ml of 1 mM CaCl_2 solution and allowed to separate into two phases overnight. The next day, the lower phase was taken and the solvent evaporated at 40 °C using a rotary evaporator Büchi RE121. The extracted oil was brought to dryness by flushing with nitrogen. The extracted oil was used for the analysis of the peroxide, p-anisidine and oil stability indexes. The chloroform used was analytical grade from VWR (Leuven, Belgium), while calcium chloride and methanol (analytical grade) were from Merck (Darmstadt, Germany).

Peroxide Value

The primary oxidation products were measured using the peroxide value, according to a small-scale modified method of the AOCS Official Method Cd 8-53 described by Crowe and White [40]. Automatic titration was done by Metrohm 785 DMP Titrino. The sodium thiosulfate 0.1 N Titrisol, glacial acetic acid and potassium iodide were from Merck (Darmstadt, Germany), while the chloroform used was from VWR (Leuven, Belgium). Peroxide values were determined in duplicate.

p-Anisidine Value

Secondary oxidation products were assessed by measuring the p-anisidine value, which was determined according to the AOCS Official Method Cd 18-90 [41]. The spectrophotometric reading was done by a Shimadzu UV-2401PC. Isooctane used was for spectroscopy from Sigma Aldrich (Bornem, Belgium). The p-anisidine analytical reagent and glacial acetic acid were from Merck (Darmstadt, Germany). p-Anisidine values were determined in duplicate.

Oil Stability Index

The Oil Stability Index (OSI) is defined as the point of maximum change of the rate of oxidation. The method used was AOCS Cd 12b-92 [42] and the test performed by Metrohm 679 Rancimat. The sample (2.5 g) was weighed and air was bubbled through at a rate of 15 l/h, while the temperature was held constant at 100 °C. Measurements were done in duplicate.

Storage Tests

For the CS measurements, two individual tubes from each tahini prototype (TH1 → TH8) and the commercial tahini (THC) were stored at 4 °C, room temperature (25 ± 3 °C) or 40 °C, and measurements were done at randomly chosen time intervals over 375 days (i.e., 2, 7, 23, 35, 50, 84, 127, 168, 273, 301 and 375 days).

For the OS assessment, the most stable prototype in terms of oil separation and the commercial tahini were selected for the storage test. Reference sunflower oil from commerce (SOC) was used for the oxidation storage test as a control sample. Sunflower tahini samples (~30 g) were placed in 50-ml Falcon tubes (BD Biosciences, Erembodegem, Belgium), while sunflower oil samples (~10 g) were placed in 15-ml Falcon tubes and stored at 4 °C, room temperature (25 ± 3 °C) or 40 °C for 3 months. Samples were removed for analysis after different time intervals. Separate sample containers were used for each day of analysis.

Statistical Methods

In order to show the effect of particle size distribution, storage time and temperature on sunflower tahini colloidal and oxidative stability, a three-way ANOVA general linear model as well as one-way ANOVA and Tukey's comparison statistical tests (significance level $\alpha = 0.05$) was performed on Minitab 16.1.0.

Results and Discussions

A high level of similarity was found between the chemical composition of sunflower and sesame tahini reported in previous studies [7, 12, 16, 43] and the chemical composition of the roasted sunflower kernel batch (total fat 60.07 %; crude protein 20.55 %; ash 3.87 %; moisture 0.73 %) used in the current study for the production of different particle size sunflower tahini prototypes as well as for the commercial type sunflower tahini sample. Given this high level of chemical composition similarity, the research results from this study can be expected to be representative of and pertinent to industrial applications.

Particle Size Distributions

The particle size histograms of TH1, TH8 and THC are outlined in Fig. 1. The other samples fell in between extreme tahini particle sizes TH1 and TH8, following the same trimodal distribution. All samples were characterized by the following particle size populations: small ($\sim 0.2 \rightarrow \sim 2 \mu\text{m}$), middle ($\sim 2 \rightarrow \sim 60 \mu\text{m}$) and large ($> \sim 60 \mu\text{m}$). As distribution is more important than mean particle size, when more than one peak is identified, a mean

value should not be used [22]. Thus, in order to characterize sunflower tahini particle size distributions, the CVP and CM of each peak of sunflower tahini samples were assessed. As Table 1 shows, the higher the number of passes through the mill, the smaller the resulting particle sizes were (the commercial sample being intermediate).

Colloidal Stability

Tubes prepared for periodical scanning, filled with the finest sunflower tahini sample and stored at 4 °C, room temperature or 40 °C for 127 days, are shown in Fig. 2 for exemplification. As expected, for all temperatures and samples, oil separation occurred at the top of the tahini vessels during storage. Vertical scan macroscopic analysis proved to be a suitable technique, with Turbiscan scanning profiles enabling destabilization phenomenon characterization as well as a precise quantification of sunflower tahini samples' colloidal stability. The detection head moves up and down along a flat-bottomed glass cylindrical cell, acquiring transmission and backscattering data each 40 μm [44]. By scanning the full length of the samples, it detects the destabilization with high accuracy, more than four times faster than visual detection [45]. For each sample, on the bottom and median portions of the tubes, the backscattering profiles showed higher relative values with increasing storage time. This phenomenon is explained by the increase of particle concentration in the median and lower part of the tube, creating the shorter path for light inside the product at higher particle concentrations (i.e., little energy absorbed). This leads to the higher values of backscattering. The relatively high values of backscattering profiles coinciding with the upper region of the tube should be ignored, being due to secondary glass reflection correspondent to the increase

Fig. 1 Sunflower tahini particle size distributions: coarsest (TH1), finest (TH8) and commercial (THC) samples

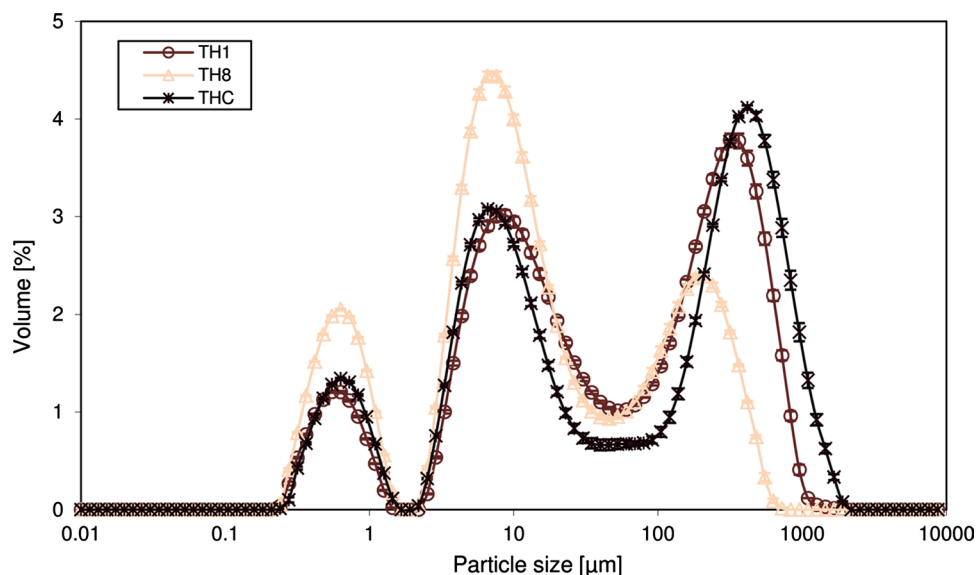


Table 1 Particle size distributions of sunflower tahini samples—cumulative volume percentages (CVPs) and coordinates of modes (CMs) (x;y)^a

Sunflower tahini samples	Particle size populations intervals					
	A: 0.2–2 μm		B: 2–60 μm		C: >60 μm	
	CVP (%)	CM (μm);(%)	CVP (%)	CM (μm);(%)	CVP (%)	CM (μm);(%)
TH1	9.61	A1(0.59;1.21)	43.03	B1(8.14;3.01)	47.36	C1(295.82;3.78)
TH2	10.84	A2(0.59;1.37)	46.33	B2(7.09;3.35)	42.83	C2(295.82;3.47)
TH3	12.43	A3(0.59;1.53)	46.43	B3(7.09;3.48)	41.14	C3(295.82;3.38)
TH4	14.75	A4(0.59;1.81)	49.73	B4(7.09;3.96)	35.52	C4(224.40;2.89)
TH5	15.19	A5(0.59;1.88)	50.79	B5(7.09;4.08)	34.02	C5(224.40;2.78)
TH6	15.53	A6(0.59;1.91)	52.22	B6(7.09;4.29)	32.25	C6(195.44;2.60)
TH7	16.48	A7(0.59;2.02)	52.95	B7(7.09;4.32)	30.57	C7(195.44;2.55)
TH8	16.67	A8(0.59;2.05)	55.03	B8(6.18;4.44)	28.3	C8(195.44;2.39)
THC	10.51	A9(0.59;1.34)	36.9	B9(6.18;3.08)	52.59	C9(389.97;4.12)

TH1 coarsest; TH8 finest; THC commercial

^a Modes of distributions are defined by abscissa value 'x' (μm)—the mean of the particle size band with the highest frequency in the population—and ordinate value 'y' (%) representing the volume corresponding to the size band

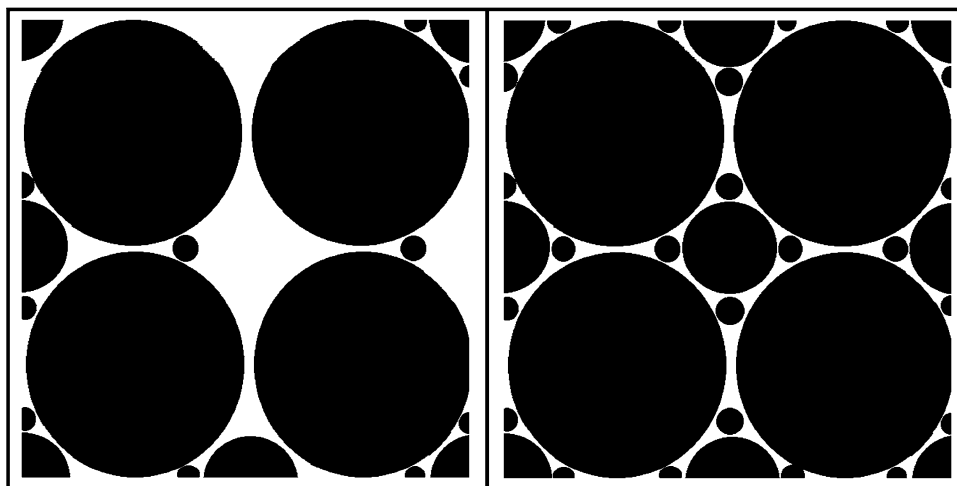
**Fig. 2** Photograph showing Turbiscan tubes filled with finest sunflower tahini sample TH8 (repetition 1 and 2) at time 127 days, stored at: 4 °C (image left side), room temperature (center) and 40 °C (image right side)

in transmission (Lefevre, Y. EMEA Manager Formulation, L'Union, France, Personal communication 2011). The increase of transmission values in the upper part of the Turbiscan tubes corresponds to the separation of the lipid layer. This process is caused by uniaxial compression of the particle network under its own weight [46], coupled with the motion of small particle solids, which slowly sediment and pack efficiently at the median and bottom part of the tube [43]. Figure 3 is a schematic representation developed from combining Lindner and Kinsella's [43] pack efficiency sediment reasoning and Beckett's [47] packing of spheres representation. It emphasizes the particles' efficient sediment formation, as influenced by trimodal

particle size distribution: smaller particles sediment and fill the spaces in between larger particles, replacing the oil continuous phase, which accumulates at the top of containers. The particle size distribution measurements conducted on the studied samples corroborated the sediment packing efficiency theory proposed above: the higher the CVPs of small particle size population (Table 1), the lower the CS was. Even though the THC sample had a low CVP of small particle size population, the sample showed a relatively low CS. This apparent contradiction is explained by its CMs. The middle size THC particle population had a similar particle size band with the highest frequency (6.18 μm) to TH8 (CMs from Table 1), thus creating a shift to smaller particles in the particle distribution second peak (Fig. 1).

The variations in CS of different particle size sunflower tahini stored at 4 °C, room temperature and 40 °C during 375 days are presented in Table 2. Increasing the number of passes through the colloidal mill, thus decreasing particle size, increased the oil separation at the top of the tube. Lindner and Kinsella [43] noticed that sesame tahini is also a concentrated suspension of hydrophilic particles in oil, and despite the high concentration of suspended solids, a layer of oil separates above a dense cake of solids after prolonged standing. They had obtained the distribution of sizes of the solid particles from free sedimentation in hexane, expressing it as percent weight distribution with respect to the equivalent Stokes diameter: 6 % smaller than 1 μm , 76 % of particles between 1 and 10 μm , 3 % between 10 and 100 μm , 14 % between 100 and 500 μm and less than 1 % higher than 500 μm . In this study, during the 375 days of storage, the finest sunflower tahini sample (i.e., TH8), obtained by eight passes through the colloidal mill, having CVPs of 16.67, 55.03 and 28.3 % for particle size

Fig. 3 Efficiently packing sedimentation theory—vertical section schematic representations of the lower and/or median part of a vessel filled with a fine sample of sunflower tahini (for ease of representation, particles are shown as spheres; trimodal distribution as measured by laser diffraction). *Left* initial state. *Right* sediment formation (adapted after Lindner and Kinsella [43]; Beckett [47])



populations of 0.2–2 μm , 2–60 μm and >60 μm , respectively, showed the highest oil separation among the analyzed sunflower tahini samples. Considering the high proportion of smaller particle population in sample TH8, and applying Lindner and Kinsella's [43] reasoning, these findings proved consistent with the earlier study.

When Çiftçi et al. [16] assessed the CS of different particle size sesame tahini samples, it was noted that decreasing the particle size improved the CS. They concluded that decreasing particle size improved dispersion of the solid phase particle in the oil phase, improving the interaction of solid and oil phases and increasing cohesiveness. However, the most stable sesame tahini samples in Çiftçi et al.'s [16] study had considerably lower particle sizes (i.e., 43.3, 53 and 3.7 % for particle classes of ~0.1–2 μm , ~2–100 μm and ~100–300 μm , respectively) than the sesame tahini from Lindner and Kinsella [43] or the finest sunflower tahini from the current study. Product research has found that the coarser sunflower tahini is more appreciated by consumers [15]. Furthermore, the typical commercial derivation of sunflower tahini results in an inherently coarser consistency. Consequently, obtaining very fine sunflower tahini, similar to that in Çiftçi et al. [16], was not the aim of this work.

A three-way general linear model ANOVA for CS [%] revealed highly significant differences ($p < 0.0001$) for particle size, storage time and temperature, as well as for their first and second order interactions. Consequently, three-way interactions Sample $\times$ Temperature $\times$ Time were analyzed by several one-way ANOVA tests and compared by Tukey's method (Table 2).

When the storage temperature increased, the CS of samples decreased (Table 2), as expected. This CS reduction is due to the low viscosities of oil (suspension continuous phase) at high temperatures, which facilitates the sedimentation of solids. Overall, samples showed a decrease of

CS with the increase of storage time (Table 2). Moreover, there was a higher oil separation in all analyzed samples in the first 3 months of storage at all temperatures. After this time period, a slowly descending trend was observed. After 375 days of storage at 4 $^{\circ}\text{C}$, tahini samples TH2 $\rightarrow$ TH8 and THC showed no statistical difference ($p > 0.05$) (Table 2) and registered only slight differences at room temperature. Samples of different particle size can be classified with respect to their oil separation level at 40 $^{\circ}\text{C}$. After 375 days of storage at 40 $^{\circ}\text{C}$, sample TH8 showed the highest level of oil separation, followed by $\leq$ TH7 $\leq$ THC $\leq$ TH6 $\leq$ TH5 $\leq$ TH4 $<$ TH3 $\leq$ TH2 $<$ TH1 (Table 2). The lower stability of THC is justified by its above-mentioned CMs similarities with the finest sunflower tahini [i.e., only THC and TH8 had, for the middle size particle population, the smallest (6.18 μm) particle size band with the highest frequency; see CMs in Table 1]. Overall, the lower stability of the finest sunflower tahini might be explained by both the packing efficiency theory of sedimentation and the uniaxial compression of the particles network [43, 46]. As shown by Muresan et al. [33] finer samples lead to smaller volume fractions. This in turn leads to a higher availability of oil prone to exudation in between particles.

Application of Rheology for Assessment and Prediction of Sunflower Tahini Colloidal Stability

With the intent to distill the CS testing timeline down to a process that can be more easily adapted to industrial applications, the attempt was made to predict the CS of sunflower tahini samples from rheological measurements. A simple rheological measurement, which usually takes a few minutes, could be enough to predict sunflower tahini CS, similarly to the full process of measured storage tests over a few months. It is known that food structure stability can be observed

Table 2 Colloidal stability of sunflower tahini during 375 days of storage at 4 °C, room temperature and 40 °C

Storage temperature	Sample	Storage time										
		2d ^b	7d	23d	35d	50d	84d	127d	168d	273d	301d	375d
		Colloidal Stability (%)										
4 °C	TH1	99.67 ^{aA}	97.71 ^{bA}	97.39 ^{bcA}	96.33 ^{cdA}	95.26 ^{deAB}	94.12 ^{efA}	93.71 ^{fA}	92.90 ^{fgA}	91.67 ^{ghA}	91.51 ^{hA}	90.94 ^{hA}
	TH2	99.34 ^{aAB}	97.85 ^{abA}	97.52 ^{abA}	96.20 ^{bcA}	94.88 ^{cdAB}	93.64 ^{deA}	92.48 ^{efAB}	91.33 ^{fgAB}	90.01 ^{gAB}	89.68 ^{gB}	89.35 ^{gAB}
	TH3	98.51 ^{aB}	97.77 ^{aA}	97.19 ^{abA}	95.61 ^{abcA}	94.37 ^{bcdB}	93.13 ^{cdeA}	92.14 ^{defB}	91.23 ^{efgB}	89.33 ^{fgB}	89.16 ^{fgB}	88.91 ^{gB}
	TH4	98.84 ^{aAB}	97.85 ^{bA}	96.94 ^{cA}	96.03 ^{dA}	95.20 ^{eAB}	94.21 ^{fA}	92.80 ^{gAB}	91.56 ^{hAB}	89.41 ^{iB}	89.08 ^{iB}	88.67 ^{iB}
	TH5	99.03 ^{aAB}	98.13 ^{abA}	97.32 ^{bcA}	96.19 ^{cdA}	95.38 ^{deAB}	94.40 ^{efA}	93.10 ^{fgAB}	92.13 ^{gAB}	89.85 ^{hB}	89.37 ^{hB}	88.80 ^{hB}
	TH6	98.94 ^{aAB}	98.13 ^{bA}	97.48 ^{bA}	96.17 ^{cA}	95.60 ^{cA}	94.54 ^{dA}	93.16 ^{eAB}	92.18 ^{fAB}	89.74 ^{gB}	89.25 ^{gB}	88.44 ^{hB}
	TH7	98.44 ^{aB}	97.95 ^{aA}	96.96 ^{bA}	96.14 ^{cA}	95.40 ^{dAB}	94.42 ^{eA}	93.19 ^{fAB}	92.04 ^{gAB}	89.33 ^{hB}	88.84 ^{hB}	87.77 ^{iB}
	TH8	98.77 ^{aAB}	97.87 ^{bA}	97.05 ^{bA}	96.06 ^{cA}	95.33 ^{cAB}	94.34 ^{dA}	93.28 ^{eAB}	92.21 ^{fAB}	89.67 ^{gB}	89.09 ^{gB}	87.86 ^{hB}
	THC	98.71 ^{aAB}	97.74 ^{bA}	96.84 ^{cA}	96.04 ^{dA}	95.15 ^{eAB}	94.09 ^{fA}	92.88 ^{gAB}	91.83 ^{hAB}	89.73 ^{iB}	89.24 ^{ijB}	88.76 ^{jB}
RT ^a	TH1	98.76 ^{aA}	98.43 ^{abA}	97.11 ^{bcA}	95.86 ^{cdA}	95.53 ^{deA}	94.78 ^{defA}	94.20 ^{efgA}	93.96 ^{fgA}	93.79 ^{fgA}	93.71 ^{fgA}	92.96 ^{gA}
	TH2	98.87 ^{aA}	97.58 ^{aAB}	96.53 ^{abA}	94.68 ^{bcA}	93.87 ^{cdB}	92.74 ^{cdeBC}	91.85 ^{defB}	91.53 ^{defB}	91.13 ^{efB}	90.88 ^{efB}	90.00 ^{fB}
	TH3	98.86 ^{aA}	98.53 ^{aA}	96.99 ^{bA}	95.20 ^{cA}	94.38 ^{cAB}	93.00 ^{dB}	92.02 ^{deB}	91.61 ^{efB}	90.88 ^{efB}	90.39 ^{fB}	88.93 ^{gB}
	TH4	98.46 ^{aA}	97.81 ^{aAB}	95.70 ^{bA}	94.57 ^{bA}	93.35 ^{cB}	91.57 ^{dBC}	90.27 ^{eC}	89.62 ^{efCD}	88.98 ^{fC}	88.73 ^{fC}	87.44 ^{gC}
	TH5	98.78 ^{aA}	97.89 ^{bAB}	96.02 ^{cA}	94.88 ^{dA}	93.66 ^{eB}	92.04 ^{fBC}	90.58 ^{gC}	89.93 ^{gC}	89.03 ^{hC}	88.46 ^{hC}	86.76 ^{iCD}
	TH6	98.79 ^{aA}	97.99 ^{aAB}	95.98 ^{bA}	94.77 ^{cA}	93.48 ^{dB}	91.79 ^{eBC}	90.10 ^{fC}	89.38 ^{fCDE}	88.17 ^{gCD}	87.77 ^{gCD}	86.16 ^{hDE}
	TH7	98.85 ^{aA}	97.71 ^{bAB}	95.74 ^{cA}	94.76 ^{dA}	93.21 ^{eB}	91.33 ^{fC}	89.45 ^{gC}	88.47 ^{hE}	87.24 ^{iD}	86.75 ^{iD}	85.03 ^{jE}
	TH8	98.69 ^{aA}	97.87 ^{aAB}	96.15 ^{bA}	94.85 ^{cA}	93.95 ^{cAB}	91.98 ^{dBC}	90.10 ^{eC}	88.71 ^{fDE}	87.48 ^{gD}	86.83 ^{gD}	85.27 ^{hE}
	THC	98.54 ^{aA}	97.24 ^{bB}	96.03 ^{cA}	94.73 ^{dA}	93.59 ^{eB}	91.89 ^{fBC}	90.59 ^{gC}	89.78 ^{hCD}	88.89 ^{iC}	88.32 ^{iC}	87.19 ^{jCD}
40 °C	TH1	98.51 ^{aA}	97.60 ^{bA}	95.11 ^{cA}	94.78 ^{cA}	93.62 ^{dA}	93.12 ^{deA}	92.46 ^{efA}	92.12 ^{fA}	91.88 ^{fgA}	91.63 ^{fgA}	91.05 ^{gA}
	TH2	97.62 ^{aB}	97.13 ^{aAB}	93.76 ^{bBC}	93.11 ^{cBC}	91.80 ^{dB}	90.73 ^{eB}	89.99 ^{fB}	89.41 ^{fgB}	89.00 ^{ghB}	88.59 ^{hB}	87.86 ^{iB}
	TH3	98.45 ^{aA}	96.73 ^{aB}	93.86 ^{bAB}	93.13 ^{bcB}	91.41 ^{cdB}	89.94 ^{deB}	88.63 ^{efC}	88.05 ^{efgC}	87.56 ^{fgB}	86.99 ^{fgB}	86.17 ^{gB}
	TH4	98.30 ^{aAB}	95.80 ^{bC}	92.97 ^{cBC}	91.84 ^{cBCD}	89.82 ^{dC}	87.96 ^{deC}	86.67 ^{efD}	85.78 ^{fgD}	84.97 ^{fghC}	84.33 ^{ghC}	83.44 ^{hC}
	TH5	98.29 ^{aAB}	95.61 ^{bC}	93.01 ^{cBC}	91.71 ^{dBCD}	89.85 ^{eC}	87.73 ^{fC}	86.35 ^{gDE}	85.38 ^{hDE}	84.40 ^{iCD}	83.92 ^{iC}	83.02 ^{jC}
	TH6	98.39 ^{aA}	95.58 ^{bC}	92.93 ^{cBC}	91.57 ^{dCD}	89.96 ^{eC}	87.71 ^{fC}	86.35 ^{gDE}	85.14 ^{hDE}	84.26 ^{iCD}	83.54 ^{jC}	82.73 ^{kCD}
	TH7	98.30 ^{aAB}	95.39 ^{bC}	92.88 ^{cBC}	91.66 ^{dBCD}	89.88 ^{eC}	87.45 ^{fC}	85.67 ^{gDEF}	84.54 ^{hEF}	83.25 ^{iDE}	82.52 ^{jCD}	81.30 ^{kDE}
	TH8	97.87 ^{aAB}	95.32 ^{bC}	92.53 ^{cC}	91.13 ^{cdD}	89.57 ^{dCD}	86.78 ^{eC}	84.65 ^{efF}	83.58 ^{fgF}	81.85 ^{ghE}	80.87 ^{hD}	80.05 ^{hE}
	THC	98.53 ^{aA}	95.76 ^{bC}	92.58 ^{cBC}	90.87 ^{dD}	88.58 ^{eD}	86.71 ^{fC}	85.40 ^{gEF}	84.59 ^{hDEF}	83.61 ^{iCD}	83.12 ^{ijC}	82.47 ^{jCD}

Like capital superscripts within columns for each storage temperature group and lower-case superscripts within rows indicate no significant difference ($p > 0.05$)

Particle size distributions corresponding to each sample are presented in Table 1

TH1 coarsest, TH8 finest, THC commercial

^a Room temperature

^b Days

through yield stress analysis [48]. As determined previously by rheological measurements [33], sunflower tahini showed a behavior typical of weak gels, which was explained by the existence of a weak network formed by particle aggregates. When this weak network structure is destroyed, flow occurs. Thus, the attempt was made to correlate the yield stress value relative to the level of internal structure in the material that must be destroyed before flow can occur [48] with CS. The CS values were measured by vertical scan macroscopic analysis on the conventional storage test. Quantifying yield stress, however, must be done carefully because the value obtained depends on the analytical technique used. As

suggested by Steffe [49], one common method of obtaining a yield stress value is to extrapolate the shear stress versus shear rate curve back to the shear stress intercept at zero shear rate. Thus, when fitting experimental data obtained for different particle size sunflower tahini samples to the Bingham model (Eq. 1), high coefficients of determination (R^2) were obtained (Table 3). The obtained Bingham yield stresses (σ_0) of each sunflower tahini sample (Table 3) at 4, 25 and 40 °C were considered predictors in a simple linear regression (Eq. 3), and CS values, measured conventionally (Table 2) at each storage time [i.e., 2, 7, 23, 35, 50, 84, 127, 168, 273, 301 and 375 days] for each storage temperature

Table 3 Sunflower tahini prototype rheological properties—Bingham model ($\sigma = \sigma_0 + \eta'\gamma$) parameters (η' and σ_0) and coefficients of determination (R^2)

Sample code	η' [Pa s ^a]			σ_0 [Pa]			R^2		
	4 °C	25 °C	40 °C	4 °C	25 °C	40 °C	4 °C	25 °C	40 °C
TH1	2650.00	1067.70	741.56	342.38	242.73	90.08	0.91	0.94	0.88
TH2	76.52	24.82	14.56	146.01	51.33	28.18	0.97	0.98	0.99
TH3	48.10	16.58	9.45	100.33	46.11	31.05	0.98	0.98	0.99
TH4	17.54	5.69	2.90	43.85	22.03	13.71	0.98	0.99	0.99
TH5	13.83	4.06	2.09	30.53	16.33	10.54	0.99	0.99	0.99
TH6	11.12	3.22	1.67	24.54	12.73	8.30	0.99	0.99	0.99
TH7	9.20	2.63	1.40	19.36	10.15	7.00	0.99	0.99	0.99
TH8	7.96	2.30	1.28	16.24	8.32	6.41	0.99	0.99	0.99
THC	24.73	8.12	4.27	48.83	25.49	13.91	0.98	0.99	0.99

TH1 coarsest, TH8 finest, THC commercial, σ shear stress, σ_0 Bingham yield stress, η' Bingham viscosity, γ shear rate

Table 4 Regression coefficients, R^2 and P values for colloidal stability values at each storage time, for each storage temperature measured conventionally (response variable) versus correspondent Bingham yield stresses (predictors)

Storage time	Regression ^b											
	Storage temperature											
	4 °C				RT ^c				40 °C			
	β_0	β_1	R^2	P value	β_0	β_1	R^2	P value	β_0	β_1	R^2	P value
2d ^a	98.7	2.90E-03	0.41	0.130	98.7	2.41E-04	0.01	0.751	98.2	2.78E-03	0.05	0.533
7d	98.0	-8.29E-04	0.31	0.113	97.8	2.79E-03	0.27	0.150	95.5	2.74E-02	0.76	0.002
23d	97.1	1.07E-03	0.19	0.229	96.0	5.10E-03	0.54	0.023	92.6	2.94E-02	0.90	<0.001
35d	96.0	6.07E-04	0.10	0.406	94.7	4.74E-03	0.81	0.001	91.2	4.28E-02	0.84	<0.001
50d	95.2	-8.00E-04	0.05	0.546	93.5	8.66E-03	0.83	0.001	89.3	5.10E-02	0.80	0.001
84d	94.2	-1.38E-03	0.10	0.395	91.7	1.32E-02	0.87	<0.001	87.0	7.43E-02	0.84	<0.001
127d	92.9	1.17E-03	0.07	0.489	90.2	1.78E-02	0.83	0.001	85.3	8.65E-02	0.82	0.001
168d	91.8	1.90E-03	0.15	0.303	89.3	2.07E-02	0.78	0.001	84.3	9.58E-02	0.83	0.001
273d	89.3	6.14E-03	0.81	0.001	88.3	2.46E-02	0.77	0.002	83.1	1.08E-01	0.80	0.001
301d	88.8	7.24E-03	0.91	<0.001	87.8	2.65E-02	0.78	0.002	82.4	1.14E-01	0.80	0.001
375d	88.1	8.40E-03	0.89	<0.001	86.3	3.00E-02	0.78	0.002	81.5	1.18E-01	0.81	0.001

^a Days

^b $y = \beta_0 + \beta_1 x$, where 'y' is the response (dependent) variable, colloidal stability at each storage time (i.e., 2, 7, 23, 35, 50, 84, 127, 168, 273, 301 and 375 days) for each storage temperature (i.e., 4 °C, room temperature and 40 °C); 'x' is the predictor (independent) variable, Bingham yield stress; β_0 is a constant that is equal to the value of 'y' when the value of 'x' = 0; β_1 is the coefficient of 'x'

^c RT room temperature; $p < 0.05$ significant; $p < 0.01$ very significant; $p < 0.001$ highly significant; *italics* not significant ($p > 0.05$)

(i.e., 4 °C, room temperature and 40 °C), were considered the response variable.

$$y = \beta_0 + \beta_1 x \quad (3)$$

where 'y' is the response (dependent) variable, colloidal stability (%);

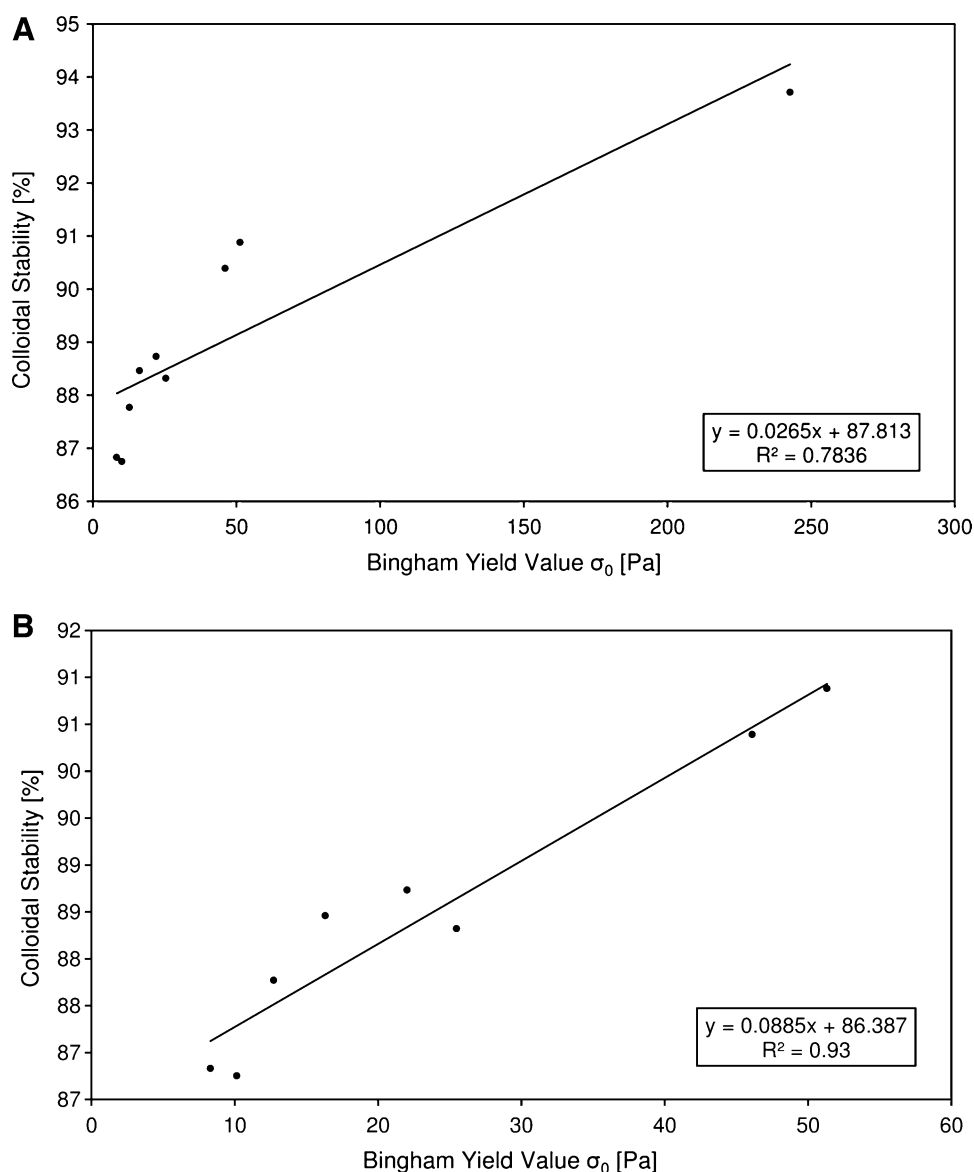
'x' is the predictor (independent) variable, Bingham yield stress (σ_0);

β_0 is a constant that is equal to the value of 'y' when the value of 'x' = 0;

β_1 is the coefficient of 'x'.

It should be noted from Table 4 that statistically significant tests ($p < 0.05$) are observed when samples showed a higher degree of instability (i.e., after 168 days of storage at 4 °C, after 7 days storage at room temperature and after 2 days storage at 40 °C), indicating, as expected, a relationship between yield stress and CS after advanced destabilization occurred. In the last periods of storage at 4 °C, all samples were considered statistically similar for CS with the exception of TH1 (Table 2). In these cases, the linear relationship was derived because of the one single data point for TH1 (Table 4). However, at 25 and 40 °C, this effect was reduced.

Fig. 4 Linear regression between colloidal stability of sunflower tahini (after 301 days of storage at 25 °C) (response variable) and Bingham yield stresses at 25 °C (predictors): **a** including sample TH1 (coarsest sunflower tahini); **b** excluding sample TH1



As an example, Fig. 4 presents the linear regressions between CS (after 301 days of storage at 25 °C) (response variable) and Bingham yield stresses at 25 °C (predictors) including (Fig. 4a) and excluding TH1 (Fig. 4b). Overall satisfactory R^2 (~0.5–0.9) was obtained for all statistically significant tests ($p < 0.05$). R^2 values were found to fluctuate among the different storage time samples, controlled for the same storage temperature, indicating the inability of Bingham yield stress to accurately predict sunflower tahini CS. However, for screening purposes of sunflower tahini CS, Bingham yield stress analysis is recommended as a faster measurement.

Oxidative Stability

As sample TH1 was the most stable prototype in terms of oil separation, together with THC, it was chosen for further

oxidative stability assessment during a 3-month storage test.

Sunflower Tahini and Oil Peroxide Values During Storage

PV is a measure of the concentration of peroxides and hydroperoxides formed in the initial stages of lipid oxidation, being one of the most widely used tests for the measurement of oxidative status in food. For tahini samples TH1 and THC, the initial PV was measured after the production. Values of 25.17 and 8.42 meq/kg oil were recorded (Table 5). The PV of sample THC was similar to other values reported in the literature for freshly roasted sunflower seeds, 4.01–6.93 meq O_2 /kg fat after 5–15 min of microwave roasting [50], 6.97 meq O_2 /kg fat for conventional

Table 5 Mean peroxide and p-anisidine values ($\pm$ standard deviations) of sunflower tahini and commercial oil stored for 3 months at 4 °C, room temperature and 40 °C

Sample	Storage temperature	Storage time					
		T1 Initial state	T2 5 days	T3 2 weeks	T4 1 month	T5 2 months	T6 3 months
		Peroxide value (meq O ₂ /kg oil)					
TH1	4 °C	25.17 ^{Af} ± 0.21	26.80 ^{Ce} ± 0.04	27.73 ^{Cd} ± 0.06	28.45 ^{Bc} ± 0.16	30.61 ^{Cb} ± 0.33	36.29 ^{Ca} ± 0.09
	RT ^a	25.17 ^{Ad} ± 0.21	24.61 ^{Bd} ± 0.34	28.65 ^{Bc} ± 0.20	28.22 ^{Bc} ± 0.52	40.16 ^{Bb} ± 0.28	50.18 ^{Ba} ± 0.18
	40 °C	25.17 ^{Af} ± 0.21	21.34 ^{Ae} ± 0.00	29.60 ^{Ad} ± 0.03	41.97 ^{Ac} ± 0.36	80.37 ^{Ab} ± 0.55	100.12 ^{Aa} ± 0.04
THC	4 °C	8.42 ^{Ae} ± 0.31	10.92 ^{Cd} ± 0.02	14.08 ^{Cc} ± 0.11	14.57 ^{Cc} ± 0.27	19.24 ^{Cb} ± 0.40	27.42 ^{Ca} ± 0.02
	RT	8.42 ^{Af} ± 0.31	11.91 ^{Be} ± 0.03	17.44 ^{Bd} ± 0.05	20.22 ^{Bc} ± 0.03	27.73 ^{Bb} ± 0.56	39.90 ^{Ba} ± 0.63
	40 °C	8.42 ^{Af} ± 0.31	15.63 ^{Ae} ± 0.17	20.28 ^{Ad} ± 0.01	29.88 ^{Ac} ± 0.01	61.56 ^{Ab} ± 0.22	81.84 ^{Aa} ± 0.13
SOC	4 °C	1.45 ^{Ac} ± 0.01	1.78 ^{Bbc} ± 0.01	1.84 ^{Cbc} ± 0.01	1.75 ^{Cbc} ± 0.10	2.39 ^{Cab} ± 0.14	2.95 ^{Ca} ± 0.52
	RT	1.45 ^{Af} ± 0.01	2.64 ^{Ae} ± 0.03	10.02 ^{Bd} ± 0.19	20.86 ^{Bc} ± 0.25	39.07 ^{Bb} ± 0.20	55.31 ^{Ba} ± 0.12
	40 °C	1.45 ^{Af} ± 0.01	3.37 ^{Ae} ± 0.32	14.19 ^{Ad} ± 0.05	50.42 ^{Ac} ± 0.19	94.29 ^{Ab} ± 0.32	136.09 ^{Aa} ± 0.22
p-Anisidine value							
TH1	4 °C	5.51 ^{Ab} ± 0.03	5.62 ^{Bab} ± 0.10	6.15 ^{Ca} ± 0.02	6.07 ^{Ca} ± 0.10	5.35 ^{Cb} ± 0.28	5.34 ^{Bb} ± 0.10
	RT	5.51 ^{Ab} ± 0.03	4.90 ^{Bc} ± 0.25	6.60 ^{Ba} ± 0.03	6.47 ^{Ba} ± 0.03	6.25 ^{Ba} ± 0.10	5.69 ^{Bb} ± 0.12
	40 °C	5.51 ^{Ac} ± 0.03	7.81 ^{Ab} ± 0.34	8.89 ^{Aa} ± 0.01	8.53 ^{Aa} ± 0.02	8.35 ^{Aab} ± 0.00	8.90 ^{Aa} ± 0.25
THC	4 °C	4.12 ^{Abc} ± 0.04	3.87 ^{Bc} ± 0.01	4.74 ^{Ca} ± 0.07	4.42 ^{Cab} ± 0.04	4.23 ^{Babc} ± 0.17	4.30 ^{Babc} ± 0.27
	RT	4.12 ^{Ab} ± 0.04	3.78 ^{Bb} ± 0.25	5.38 ^{Ba} ± 0.09	5.51 ^{Ba} ± 0.03	4.99 ^{Ba} ± 0.06	5.04 ^{Ba} ± 0.28
	40 °C	4.12 ^{Ad} ± 0.04	4.73 ^{Ac} ± 0.11	6.48 ^{Ab} ± 0.06	7.42 ^{Aa} ± 0.03	7.47 ^{Aa} ± 0.28	6.90 ^{Ab} ± 0.01
SOC	4 °C	6.88 ^{Aa} ± 0.04	6.67 ^{Bab} ± 0.05	6.90 ^{Aa} ± 0.04	6.80 ^{Ba} ± 0.03	6.83 ^{Aa} ± 0.10	6.47 ^{Bb} ± 0.10
	RT	6.88 ^{Aa} ± 0.04	7.10 ^{ABa} ± 0.16	6.96 ^{Aa} ± 0.05	6.77 ^{Ba} ± 0.05	5.97 ^{Bb} ± 0.11	4.95 ^{Cc} ± 0.26
	40 °C	6.88 ^{Ab} ± 0.04	7.23 ^{Ab} ± 0.07	7.05 ^{Ab} ± 0.03	7.18 ^{Ab} ± 0.02	7.19 ^{Ab} ± 0.17	7.82 ^{Aa} ± 0.17

Like capital superscripts within columns for each sample group and lower-case superscripts within rows indicate no significant difference ($p > 0.05$)

TH1 coarsest sunflower tahini, THC commercial sunflower tahini, SOC commercial sunflower oil

^a Room temperature

roasting [51] and 7.37–8.58 meq/kg for fresh produced sunflower butter from pan-roasted kernels [32]. Given the assumption that the oxidation level would be homogeneous within the same batch of roasted sunflower kernels, the PVs of TH1 were unexpected. The same batch as for THC was also used for TH1 production, yet both samples showed different oxidation levels. However, this could be explained by the fact that milling technology may influence the oxidative status of foods [52]. Upon testing the initial PV of sample TH1 and THC, this explanation was supported. Tahini obtained by one pass through the colloidal mill was more oxidized than industrial tahini obtained traditionally in a two-step process—a three-roll refiner and a beating machine. This might be caused by the high temperatures achieved in the colloidal mill (~50 °C) and high amount of oxygen incorporated during this type of milling [26] relative to the three-roll refiner and beating machine technology. It must be stressed that the colloidal mill was chosen for this study because the current industrial process for producing sunflower tahini was impossible to adjust in order to obtain different particle sizes of tahini. Although

sunflower tahini prototypes were obtained for this study by a different milling technology from the one used currently in the industry, the study brings knowledge of different particle size prototype stabilities, thus giving future alternatives to research and industry.

Significant differences were detected ($p < 0.05$) between the PV of each sample stored for the same period at different temperatures (Table 5), confirming that the extent of oxidation increases with storage temperature. The literature shows that autooxidation proceeds slowly at low temperature, and the rate increases as the temperature increases [53–55]. TH1 stored for 3 months at 40 °C had a PV about three times higher than the ones stored at 4 °C, and about two times higher than those stored at room temperature. The marked effect of temperature on peroxide development was explained by List et al. [54] who mentioned that peroxides developed very slowly at 21.1 °C but increased markedly at 37.8 and 48.9 °C, probably because oxygen diffuses more rapidly into the reaction interface at higher temperatures. To our knowledge, there are no specifications regarding the maximum allowable limit for the PV of sunflower paste. For

similar products, such as nut butters, pastes and oils, maximum PVs of 10–30 meq/kg are specified, depending on the product, as subsequently detailed. FAO [56] stated a maximum of 15 meq/kg for cold-pressed and virgin vegetable oils and 10 meq/kg for refined oils, while in a study regarding the quality of macadamia nuts, Borompichaichartkul et al. [57] specified the 30 meq/kg limit according to Thai Industrial Standards. Taking into consideration the above-mentioned limit of 30 meq/kg, which is used for similar products, it is strongly recommended also to set a criterion of ~30 meq/kg for sunflower tahini PV. However, more research is needed to implement this for sunflower tahini/halva/nut pastes, including toxicological studies. As a starting point, Gotoh et al. [58] concluded that deteriorated fats and oils with PV values of at least 100 meq O₂/kg revealed neurotoxic effects in animal studies. Of the tahini samples in this study, only sample THC was under the aforementioned limit of 30 meq/kg PV during the 3 months of storage at 4 °C. This sample showed good oxidative stability when stored for 2 months at room temperature and for 1 month at 40 °C, as it was under the limit of 30 meq/kg. TH1 was under the limit when stored 2 months at 4 °C, 1 month at room temperature and 2 weeks at 40 °C.

For the studied samples at all temperatures, the PV increased significantly ($p < 0.05$) with storage time (Table 5). However, for the oil sample (SOC), the PV, initially 1.45 meq/kg oil, rose very slowly, reaching 2.95 meq/kg oil after 3 months of storage at 4 °C (Table 5); during the first month of storage at 4 °C, this sample showed no significant changes ($p > 0.05$) in the peroxide value, thus confirming the high oxidative stability of the commercially refined sunflower oil. The initial PV of sample SOC—1.45 meq/kg—agrees with values reported for sunflower oils in other studies: 1.7–2.5 meq/kg for commercial oils [55, 59], 2.45–3.92 meq/kg for pressed oil [53] and 2.6–3.77 meq/kg for extracted oil [50]. The SOC sample was included in the storage test as a control and proved the conformity of chemical tests and conditions during storage. The PVs of sample SOC stored at 4 °C were under the limit accepted for refined oils—10 meq O₂/kg fat [56]—during the 3 months of storage, but at room temperature, it exceeded this limit after 2 weeks. Eidhin and O’Beirne [59] reported a PV of 17.8 meq/kg for sunflower oil after 105 days of storage at room temperature, which is three times lower than the PV obtained in this study for commercial sunflower oil stored 3 months at room temperature (55.31 meq/kg). Differences between oxidative stabilities of commercial oils may exist and might be caused by different raw material qualities, varieties and different processing technologies. Overall, the sample SOC showed a classical oxidation pattern (Table 5), highly influenced by storage temperatures. For example, when stored 3 months at 4 °C, it attained only 2.95 meq/kg, while at room temperature it

reached 55.31 meq/kg and at 40 °C 136.09 meq/kg, respectively. Lee et al. [55] obtained a PV of ~90 meq/kg when storing commercial sunflower oil at 40 °C for ~45 days. The current study supports these findings.

Sunflower Tahini and Oil p-Anisidine Values During Storage

The pAV is commonly used to follow the formation of aldehydic compounds in edible oils and correlates well with the development of off-flavors in lipids undergoing oxidation [60]. For TH1 and THC, the initial pAV was measured after the production, with values of 5.51 and 4.12 being found (Table 5). pAV of samples stored at 40 °C were significantly ($p < 0.05$) higher compared to samples stored at 4 °C or RT for the same period (Table 5). For each type of tahini, with little exception, the pAVs of samples stored at 4 °C were significantly lower ($p < 0.05$) than those in samples stored at 40 °C or room temperature for the same period. This phenomenon is due to the known instability of secondary oxidation products. These findings corroborate that the extent of sunflower tahini oxidation increases with storage temperature. This has also been shown by PV determinations. It is already known that breakdown of hydroperoxides to carbonyl compounds is affected by the storage temperatures [55], but the aim of this work was to determine the extent of sunflower tahini oxidation, dependent on storage time and temperatures. Abou-Gharbia et al. [28] also reported that sesame tahini kept at 22 °C attained a much lower pAV than that stored at 65 °C, but they found an ascending pAV-by-time trend for sesame that is different from the one found in the current sunflower tahini study. Sunflower tahini and oil pAVs during storage showed a more or less irregular pattern. Similar results were reported by Eidhin and O’Beirne [59] for sunflower oil stored at 4 °C or room temperature and by Lee et al. [55] for soybean, sunflower and olive oils stored at 25 °C or 40 °C. The same pAV vs. time pattern was revealed by Hung and Slinger [61] when storing different oils (salmon, canola and soybean) at room temperature. Other investigators have found that the total amount of carbonyls present in an oil changes in an erratic manner, or decreases, during refrigeration and frozen storage of food [62]. Sun-Waterhouse et al. [63] explained that fluctuation in the pAV readings of avocado and coconut oils with added phenolics might be due to the involvement of the phenolic carboxyl acid group and C = C bond structure in the formation of carbonyls (in addition to hydroxyl groups on the aromatic ring). Laguerre et al. [64] mentioned that the pAV results are, however, interpreted in a relatively empirical manner, since each of the many aldehydes produced during oxidation generates a specific signal. It is well known that the colorimetric response with p-anisidine varies according to the extent of

aldehyde unsaturation. Hence, at identical concentrations, the response is more intense with di-unsaturated aldehydes than with mono-unsaturated aldehydes, which in turn are more sensitive than saturated aldehydes. As reported also by Sun et al. [65], aldehydes do not break up rapidly, thus allowing the history of an oil to be determined with the pAV. Scrutinizing the results for SOC, one can observe that this sample showed the lowest PV and the highest pAV during the 3 months of storage at 4 °C, no rancid flavor being detected. These inconsistencies noted during the analysis of some products are explained by nonvolatile aldehydes, or core aldehydes, which also form during lipid oxidation processes and are measured by pAV [64]. Oils obtained by refining a highly oxidized raw material could thus have a high pAV, a low PV and an undetectable rancid odor, simply because of the presence of nonvolatile aldehydes, which are hard to remove by refining. Caution is thus required when interpreting the pAV index. According to Man et al. [66], as a rule of thumb, the pAV should be less than 10 for a good quality oil. The pAV of the analyzed sunflower tahini and oil samples are under this threshold.

As sunflower is to be promoted as an alternative to sesame in tahini production, a useful comparison between current sunflower tahini oxidative stability and published results on commercial sesame tahini is further provided. Damir [12] measured a PV of ~2 meq/kg for sesame tahini stored 30 days at room temperature, revealing the high oxidative stability of this product. Similar results, pAVs of 1.1–2.6 and PVs of 0.6–2.9 meq/kg for sesame tahini stored up to 120 days at 22 °C, were also reported [28]. At 65 °C, when stored 35 days, sesame tahini attained a pAV of 10.1 and PV of 86.2 meq/kg [28]. In another study Borchani et al. [29], when storing sesame tahini ~38 days at 65 °C, reported a PV of ~150 meq/kg, no pAV being provided. The oxidative stability indexes of sunflower tahini obtained during this work (Table 5), especially at higher storage temperature, are comparable to sesame. However, it is known that sesame contains more antioxidant compounds (phenolic, tocopherols) than sunflower [12]. In order to improve sunflower tahini's oxidative stability, alongside particle size control, the addition of different exogenous antioxidants is worth including in further research.

Oxidative Stability Index

The OSIs of the analyzed sunflower tahini and oil in their initial state were 5.72, 8.07 and 11.55 h for TH1, THC and SOC, respectively. The OSI results corroborate the PV and pAV, sample THC having also the smallest PV and pAV among studied the tahnins. Merrill et al. [67], when studying the oxidative stability of different oils, reported an OSI of 5.2 h for conventional sunflower oil with no antioxidants. This is supported by the current study results.

However, the higher OSI (11.55 h) found in this study for SOC was attributed to the added antioxidants, as this is a usual practice within the oil industry [68].

Conclusions

The CS of sunflower tahini decreased as the storage time and temperature increased, reaching 91.05, 80.05 and 82.47 % for TH1, TH8 and THC, respectively, after 375 days at 40 °C. For the particle size range studied, decreasing the particle size decreased the sunflower tahini CS. This phenomenon was attributed to uniaxial compression of the particles network [46] as well as to the particle efficient packing sedimentation theory [43]. Significant regression equations ($p < 0.05$) between the Bingham yield stress values and CS values, conventionally measured in the storage test, were established when samples showed a higher degree of instability. This allows the prediction of sunflower tahini CS via a faster rheology measurement; at this time the technique is recommended only for screening purposes and not for quality control. The most stable tahini prototype in terms of oil separation was TH1, which was further included on the oxidative stability storage test together with the THC and SOC. The PVs of the studied sunflower tahini and oil samples increased significantly ($p < 0.05$) with storage time, irrespective of storage temperature. Included as a control in the storage test, as expected, the SOC showed an oxidation pattern characteristic of vegetable oils. Given a suggested 30 meq O₂/kg PV limit, the THC showed good oxidative stability when stored 3 months at 4 °C, 2 months at room temperature and 1 month at 40 °C. The TH1 was under the limit when stored 2 months at 4 °C, 1 month at room temperature and 2 weeks at 40 °C. Overall, it is strongly recommended to monitor the storage temperature of tahini, and the sunflower tahini particle size must be controlled in order to improve the tahini stability.

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