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RHEOLOGICAL PROPERTIES OF ULTRAFILTRATED HERBY WHITE CHEESE

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ABSTRACT

Herby white cheese is considered as a new product in the Egyptian markets. Buffalo's milk retentate was used with dried spearmint or its essential oil to study the rheological characteristics of herby white cheese. Prepared cheese samples were subjected to rotational concentric rheometer to determine the shear stress, dynamic viscosity, power law model, yield stress and apparent viscosity of fresh and stored herby cheese.

Obtained results showed that all cheese samples behave as a pseudoplastic non-Newtonian paste where the shear stress values increased with increasing the shear rate. Stored herby cheese for four weeks reached the lowest shear stress which indicated that the presence of essential oil enhanced the enzymatic activity during ripening and produced cheese with softer structure than the control. Also, white cheese with dried spearmint showed higher shear stress values than control samples which indicated the effect of dried herbs on binding water in the cheese matrix and increasing the resistance of cheese curd to flow.

INTRODUTION

Herby cheese, called "Otlu peynir" in Turkish, traditionally produced from raw sheep's milk on the farms. Nowadays, it is produced from a mixture of sheep and cow or sheep and goat milk. About 25 kinds of herbs can be used to make herby cheese e.g. *Allium spp., Thymus spp*., *Ferula spp., Anthriscus nemorosa*, etc. (Tarakci *et al.,* (2004).

Little information was found about herby white cheese in Egypt. So, previous researches by the authors were done to introduce this type of cheese to the Egyptian markets. Buffalo's milk retentate was used with green celery or thyme to prolong the shelf life of white cheese (Foda *et al.,* 2006 and 2008 a). Also, dried or essential oil of spearmint, which is the most common herb in the Mediterranean region, was used to manufacture the herby white cheeses. Chemical composition, microbiology and sensory analysis of ultrafiltrated spearmint herby white cheese were done (Foda *et al.,* 2008 b, 2009 a, and 2009 b).

Cheese is a viscoelastic material and all texture characteristics are a weighted combination of measurable rheological and fracture (mechanical) properties. As cheese is a viscoelastic material, time plays an important role in its mechanical behavior influencing the results obtained in rheological tests as well as sensory attributes. The time scale of an experiment is the time that a stress of certain magnitude and direction acts on a material (Van Vliet and Walstra, 1999). Different cheese varieties have a wide range of textural characteristics and these greatly change with aging due to proteolysis, moisture loss, salt uptake, pH change and the slow dissolution of residual Ca associated with CN particles (Lucey, *et al.,* 2003). Cheese composition (i.e., moisture, protein, fat, NaCl, milk salts and pH) has a major impact on the body and texture of cheese. Cheese composition is mainly controlled by the initial composition of cheese milk and the manufacturing protocols (Lucey, *et al.,* 2003).

The objective of this work was to study the effect of dried spearmint or its essential oil on the rheological properties of ultrafiltrated white cheese either fresh or during cold storage for four weeks.

MATERIALS AND METHODS

Dried spearmint (*Mentha spicata*) was obtained from Medicinal and Aromatic Plant Research Dept., Agriculture Research Center, Giza, Egypt. Buffalo's milk retentate was obtained from Dairy Industry Unit, Animal Production Research Institute, Ministry of Agriculture, Cairo, Egypt. The milk retentate contained 29.2% total solids; 15.5 % fat; 10.5% total protein and 0.09% titratable acidity. Microbial rennet (*Mucor mehiei)* was obtained from Novo, Denmark.

Essential oil was extracted from dried spearmint by hydro distillation using a Clevengar-type apparatus according to Tepe *et al.,* (2005). The obtained essential oil was dried over anhydrous sodium sulfate, decanted and stored at -18 C in dark glass vials until use.

Preparation of herby white cheese

Ultrafiltrated white cheese with essential oil:

White cheese was prepared according to Foda *et al.,* (2006). Milk retentate was divided into 7 portions; each portion was salted to a concentration of 3%, well mixed and pasteurized at 73 °C for 15 sec. First portion was served as control and for the other six portions different concentrations of spearmint essential oil (0.5, 0.75, 1.0, 1.5, 2.0 and 2.5 ml/kg retentate} were added at 40°C. Curds were hold at 40°C for 30 min., in plastic containers after adding the rennet.

Ultrafiltrated white cheese with dried spearmint:

Three different levels of dried spearmint (0.25, 0.5 and 0.75 %) were added to milk retentate before pasteurization. Further steps were done as mentioned with spearmint essential oil cheese.

All cheese samples were stored under refrigerator temperature (5°C±2) for 4 weeks. Samples were taken fresh, after two and four weeks for analysis. Three replicates were prepared for each cheese to determine its rheological properties.

Rheological properties of white herby cheese

Prepared cheese samples were subjected to rheological examination using rotational concentric rheometer type Rheotest II (Pruefgeraetewerk, Medingen, Germany). Cheese samples were loaded into the cup cylinder (H) and subjected to different shearing rates by using appropriate rotating spindle. Each sample was subjected to twelve levels of shear rates ranging from 0.33 to 145.8 (S^{-1}). The corresponding deflection of the torque devise (α readings) were converted to shear stress values (dynes/m^2) using manufacturer standard tables following this formula according to Toledo, (1991).

$\tau_r = Z.\ \alpha$ ----------------------- (1)

where:

τ_r = shear stress
Z = cylinder constant (dyne/cm^2. skt)
α = scale reading (skt)

For each run, shear stress values were recorded for the ascending shear rate increase (up shearing). Values of shear rate and shear stress as well as those of dynamic viscosity obtained from experimental runs were plotted in appropriate curves for better demonstration of the results according to Toledo, (1991) using the following equation:.

$\eta_{dyn} = \tau_r / D_r$ ------------------- (2)

where:

η_{dyn} = dynamic viscosity (Poise)
τ_r = shear stress (dynes/cm^2)
D_r = shear rate (S^{-1})

Rheological modeling:

Shear rate (γ) and shear stress (τ) data were evaluated according to the rheological Power law model (Toledo, 1991) of non-Newtonian fluids as follows:

$\tau = K.\ \gamma^n$ ----------------------- (3)

where:

γ = shear rate (S^{-1})
τ = shear stress (dyne/cm^2)
n = flow behavior index of non-Newtonian fluids
K = consistency coefficient (dyne/cm^2.S^n)

Apparent viscosity

Apparent viscosity was calculated only at shear rate of (48 S^{-1} and 81 S^{-1}) according the following formula:

$\eta_{app} = K.\ \gamma^{n-1}$

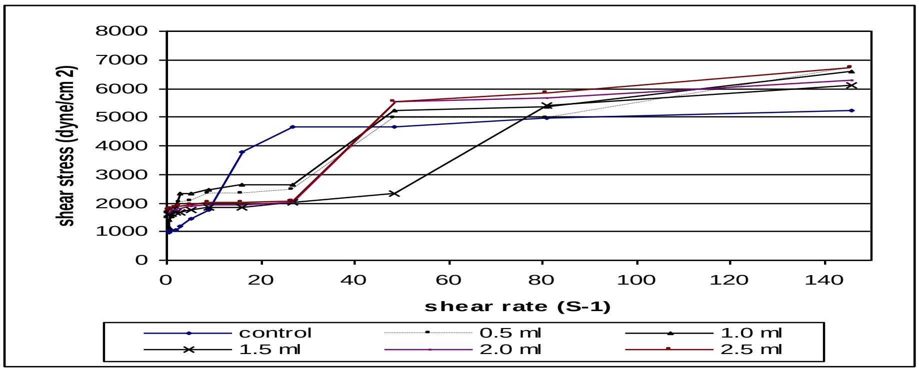
RESULTS AND DISCUSSION

Rheological characteristics of ultrafiltrated white cheese with essential oil:

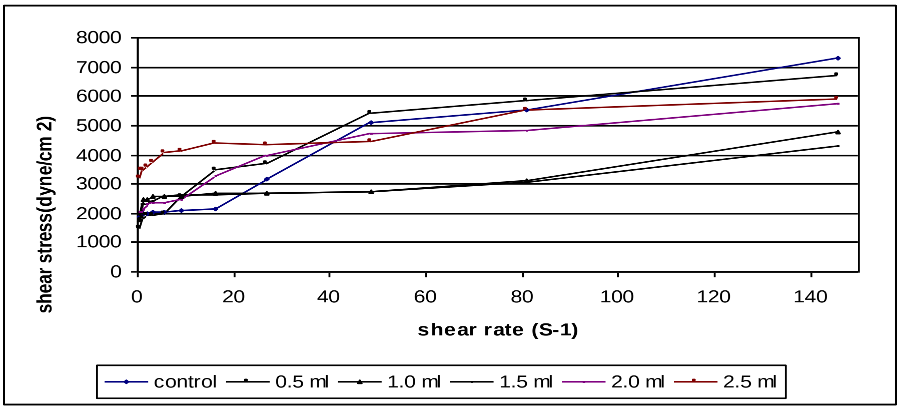
a) Flow curves

The relationship between shear rate and shear stress is related to structure and depends on the manner in which material responds to force or to an imposed deformation (Finney, 1972).

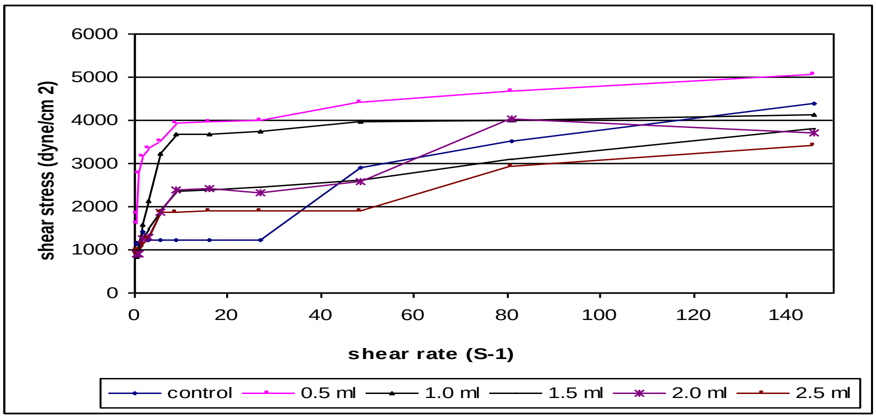
Fig.1 (a, b and c) shows the course for ascending flow curves of the fresh white cheese prepared with different concentrations of spearmint essential oil and during cold storage period for four weeks.



(a) Fresh herby white cheese



(b): Herby white cheese after two weeks of cold storage



(c): Herby white cheese after four weeks of cold storage

Fig. 1: (a, b and c): Flow curves of herby white cheese prepared with different concentrations of spearmint essential oil

It could be noticed that all cheese samples behave as a pseudoplastic non-Newtonian paste where the shear stress values were non-linearity increased with increasing shear rate until the maximum value of shear stress has been achieved. The level of the maximum shear stress value as well as the magnitudes of their corresponding shear rate values depend on added amount of essential oil. Fresh samples of herby cheese showed higher shear stress values (6000 -7000 dynes/cm^2) than control sample (5000 dynes/cm^2) at shear rate 145.8 S^{-1}. This could be due to the addition of essential oil which emulgate with the cheese components and may increase the volume fraction of gel fragments. The latter is larger than the volume fraction of casein particles because the fragments may contain a lot of interstitial solvent (more swollen) which lead to intermolecular bond, hence increase the shear stress response (El-Sayed, 2003). Previous study showed that spearmint essential oil contained twenty two components with different amounts, the main component was carvone (68.58 %) and limonene (16.42 %), followed by β- Pinene (2.29%) and β-bourbonene (2.08 %), the others ranged from 0.09-1.51%. Foda *et al.,*(2009 a). Also, Dimandja *et al.,* (2000) and Marongiu *et al.,* (2001), found that carvone and limonene were the main components of spearmint essential oil. After two weeks of cold storage (Fig-1b), the shear stress of control sample was higher (>7000 dynes/cm^2) than herby cheese at γ = 145.8 S^{-1}. It means that herby white cheese had more aggregation of casein gel compared with control sample.

All cheese samples after four weeks (Fig-1c), reached the lowest shear stress (3000-4000 dynes/cm^2) at the same shear rate, where control and 0.5 ml oil addition having higher shear stress values than other samples, these results could be referred to enzymatic proteolysis. Foda *et al.,* (2008 b) reported that the presence of herbs essential oils in the cheese matrix enhanced the enzymatic activity during ripening and produce cheese with softer structure than control cheese sample. Herby cheese had less aggregation especially at high oil levels (>1.5 ml), which soften the surfaces of casein aggregates (conjunction) of casein aggregates.

Also, the results of Foda *et al.,* (2008 b) showed that sensory evaluation scores of (body & texture) of spearmint essential oil white cheese were decreased significantly (P<0.05) after four weeks of cold storage.

b) Dynamic viscosity:

Fig. (2 a, b and c) shows the dynamic viscosity values of herby white cheese with different concentrations of spearmint essential oil during cold storage as a function of shear rate. It could be noticed that the viscosity curves tended to flatten to the equilibrium dynamic viscosity values (the lowest η-value) at shear rates higher than 3.0 S^{-1}. Therefore, the viscosity curves include only values of lower shear rates (γ < 3.0 S^{-1}), where the η-values are strongly dependent on the applied shear rate. As seen, the dynamic viscosity values of all cheese samples strongly decreased with increasing the applied shear rate indicating the pseudoplastic flow pattern of the cheese samples. Referring to shear rate region between 0.33 and 3.0 S^{-1}, (low rotation of measuring spindle or mechanical mixers in industrial apparatus), the dynamic viscosity values of cheese samples at zero time were lower than after two weeks and slightly higher than after four weeks of cold storage, indicating the aggregation behaviour or the enzymatic activity which discussed before. Dynamic viscosity values at low shear rate (0.6 S^{-1}) ranged between 1043 to 1777 (Poise), at zero time, increased to the level of 1776 to 3472 (Poise), after two weeks and then decreased to the level of 902 to 1825 (Poise), after four weeks of cold storage.

On other side, the average equilibrium dynamic viscosity at (γ =145.4 S^{-1}) of all cheese samples were 43, 40 and 28 (Poise) at zero time, after two weeks and four weeks of cold storage respectively.

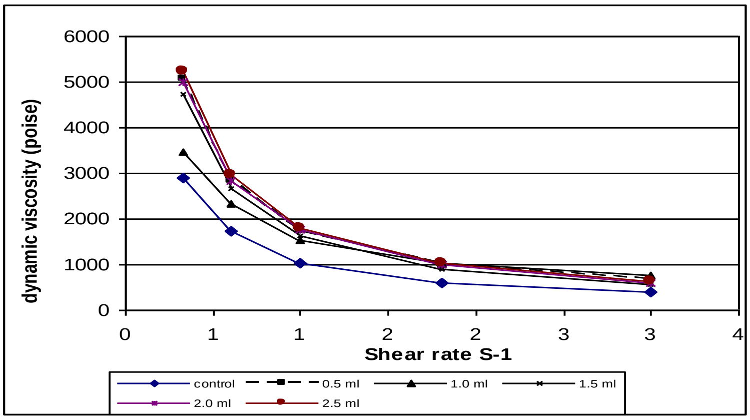
c) Rheological parameters:

The shear stress/ shear rate data of tested cheese samples were fitted to the power law model of non-Newtonian fluids (eq. 3) and the calculated rheological parameters were given in Table (1). As seen, the power law model proved to be suitable for representing the shear data of tested cheese samples since the R^2-values of the estimation were almost higher than 0.8. On other side, the flow behaviour index (N-values) were very low (lower than 0.35), indicating the strong pseudoplasticity of the tested cheese samples. However, the N-values of cheese samples stored for two weeks were much lower than those of fresh or four weeks stored samples, indicating the aggregation process of cheese matrix during the first two weeks of cold storage, before the effect of hydrolytic enzymes becomes obvious. The average value of consistency coefficient of the herby cheese samples were in the range of 1600 (dynes/cm^2. S^n) at zero time**,** then it was increased to 2324 (dynes/cm^2. S^n) after two weeks and reached a level of 1420 (dynes/cm^2. S^n) after four weeks of cold storage.

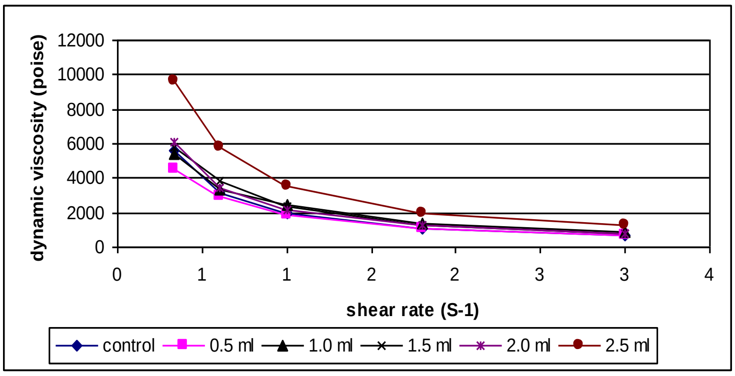
Table (1): Rheological parameters of white cheese prepared with different concentrations of spearmint essential oil during cold storage period

Oil concentrations (%)	Rheological parameters								
	Fresh			After two weeks			After four weeks		
	N	K	R^2	N	K	R^2	N	K	R^2
0	0.343	1029.9	0.905	0.226	1898.7	0.87	0.234	1138.2	0.844
0.5	0.247	1590	0.867	0.254	1725	0.926	0.168	2430	0.855
1.0	0.294	1506	0.952	0.103	2160	0.734	0.276	1379	0.834
1.5	0.237	1552	0.823	0.094	2170	0.779	0.237	1158	0.971
2.0	0.216	1629	0.734	0.181	2100	0.903	0.265	1076	0.945
2.5	0.248	1720	0.839	0.899	3467	0.918	0.214	1055	0.949

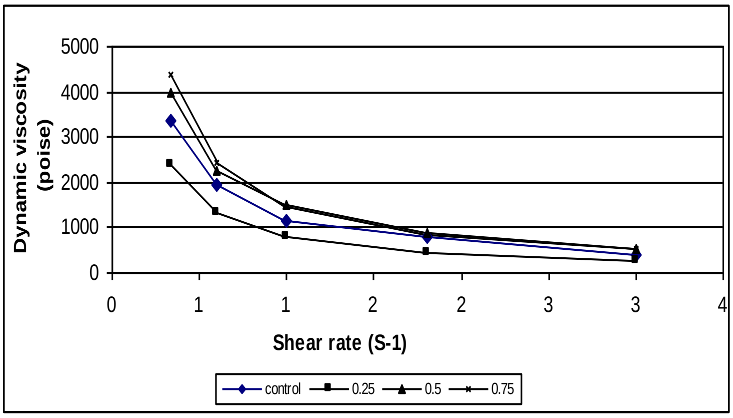
K: Consistency coefficient
R^2 : Power law
N: Flow behaviour index



(a) Fresh herby white cheese



(b) Herby white cheese after two weeks of cold storage



(c) Herby white cheese after four weeks of cold storage

Fig. 2: (a, b and c): Dynamic viscosity values of herby white cheese prepared with different concentrations of spearmint essential oil as function of shear rate

d) Yield stress and apparent viscosity:

Yield stress (τ_o) is an important rheological parameter for non-Newtonian fluids (such cheese) as it represent the initial stress required to start the flow of a fluid. Its calculation is important for proper designing of cheese handling machines (mixing, pumping and filling). Table (2) gives the yield stress values as well as the apparent viscosities of cheese samples. As seen, all oil supplemented samples showed higher yield stress values than that of the control samples indicating the role of essential oil in changing the binding forces in the cheese matrix. This effect was more obvious after two and four weeks of storage than at zero time. However, the magnitude of apparent viscosities measured at 48 S^{-1} and 81 S^{-1} show that the oil supplement samples were almost more viscous than the control sample at zero time and after four weeks, with the magnitude of apparent viscosity values being lower than at zero and after two weeks as a sequence of ripening activity.

Table (2): Yield stress and apparent viscosity of herby cheese prepared with different concentrations of spearmint essential oil during cold storage period

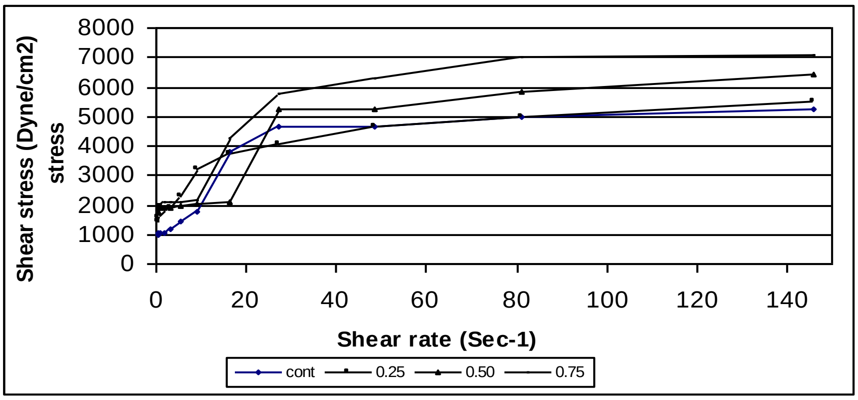
Oil concentrations (%)	Rheological parameters								
	Fresh			After two weeks			After four weeks		
	τ_o (Poise)	η 48 (S^{-1})	η 81 (S^{-1})	τ_o (Poise)	η 48 (S^{-1})	η 81 (S^{-1})	τ_o (Poise)	η 48 (S^{-1})	η 81 (S^{-1})
0	560	80.99	57.40	796	94.88	63.28	799	58.67	39.29
0.5	1169	86.18	58.12	1229	85.54	56.99	3201	97.01	62.77
1.0	1408	97.92	67.66	2347	67.05	41.93	3018	83.63	57.26
1.5	545	80.93	54.29	2354	65.05	40.49	1602	60.38	40.51
2.0	795	78.31	51.96	1693	66.46	41.67	1185	62.53	42.57
2.5	886	93.59	63.15	3350	102.33	63.56	1159	50.33	33.36

Rheological characteristics of ultrafiltrated white cheese with dried spearmint:

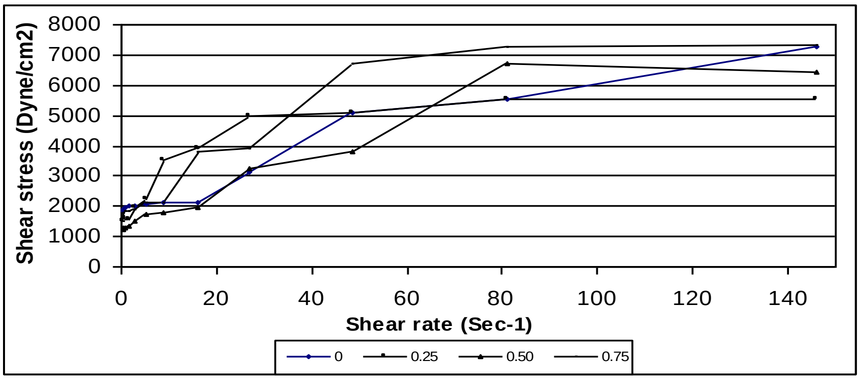
a) Flow curves

Fig. 3 (a, b and c) show the flow curves of the fresh herby white cheese samples. As seen, all cheese samples behave as a pseudoplastic non-Newtonian fluid similar to those supplemented with essential oil. However the magnitude of shear stress responses were slightly higher than those recorded for the essential oil supplemented cheese. All herbs supplemented cheese showed higher shear stress values than the control samples indicating the effect of dried herbs on binding water in the cheese matrix and increasing the resistance of the cheese curd to flow.

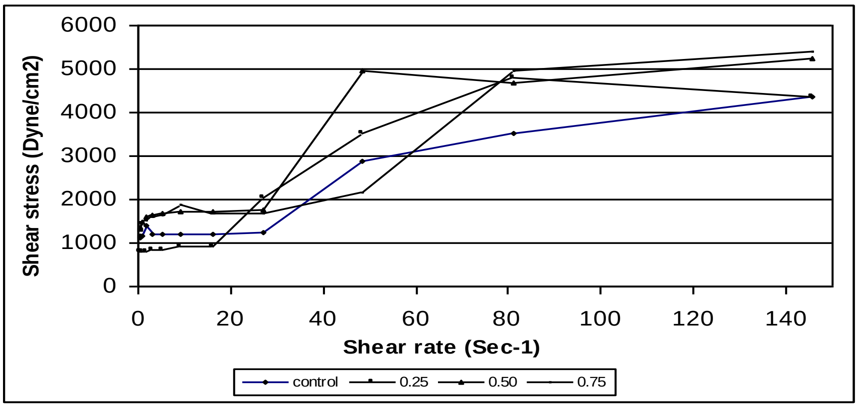
Walstra & Van Vliet (1982) reported that increasing the moisture content or increasing the ratio of moisture to protein (nonfat substances) in cheese weakens the rigidity as the volume fraction of protein decreases, and this influences a wide range of textural characteristics e.g. softness shreddability and meltability (Lucey *et al.,* 2003). Also, Foda *et al.,* (2009 b) found that increasing dried spearmint concentration from 0.25 to 0.75 % increased the moisture contents of white cheese insignificantly, and prolonging the cold storage for 2 weeks decreased the moisture content significantly.



(a): Fresh herby cheese



(b): Herby cheese after two weeks of cold storage



(c) Herby cheese after four weeks of cold storage

Fig. 3: (a, b and c): Flow curves of herby white cheese with different concentrations of dried spearmint

The shear stress value of tested cheese samples ranged between 5000 to 7000 dynes/cm^2 at (γ =145.4 S^{-1}). This magnitude was not affected after two weeks of cold storage unless the control sample showed higher shear stress values at (γ =145.4 S^{-1}), may be due to a faster moisture loss than these of the herbs supplemented cheese. After four weeks of cold storage, the magnitude of maximum shear stress values was decreased by 25 % to reach a range of 4300 to 5300 dynes/cm^2. This loss in flow resistance could be referred to the proteolytic and lypolytic enzyme activity during ripening. Park, (2007) found that cheese samples became more elastic cohesive, meltable viscous and softer after 4 weeks of aging presumably due to proteolysis. However herby cheese samples showed lower structure degradation than that of oil supplemented samples (Fig.3).

b): Dynamic viscosity

Fig (4 a, b and c) shows the change in the dynamic viscosity of the dried herbs supplement cheese samples in the low shear rate region (γ =0.33 to 3.0 S^{-1}), which is the region of importance for soft cheese handling equipment. In this region, the dynamic viscosity values were rapidly decreased with increasing the applied shear rate. The dynamic viscosity values were rapidly decreased from a high level at (γ = 0.33 S^{-1}) of 3000 to 6000 (Poise) to a level lower than 300 (Poise) at (γ = 3.0 S^{-1}), which express the high torque power required by mixing, pumping and filling machines to force the cheese to start flow. In most cases cheese samples supplemented with dried spearmint showed higher dynamic viscosity values than the control samples.

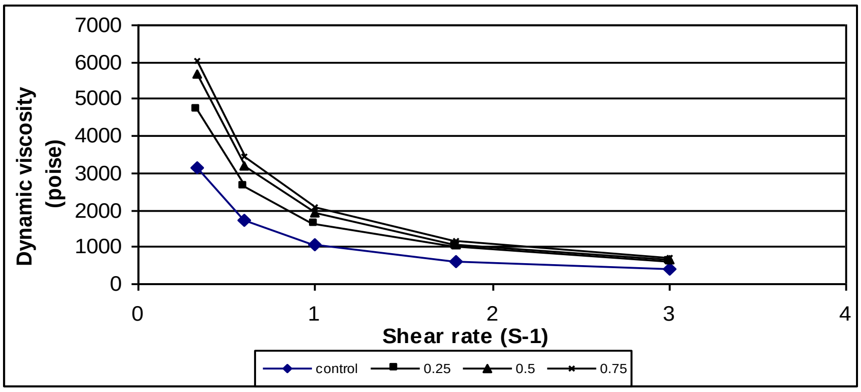
c): Rheological parameters:

Table (3) gives the Flow parameters of dried spearmint white cheese samples. As seen, the values of flow behavior index (N-values) were lower than the unity magnifying the non-Newtonian behaviour of the cheese samples. However no remarkable differences in the flow behaviour index have been observed between cheese samples supplemented with essential oil or dried spearmint, but both were different than control cheese. The values of consistency coefficient (K-values) of the dried spearmint supplemented cheese exceeded that of control cheese by 67 to 100 %, indicating the role of herbs in thickening the consistency of the cheese samples. This magnitude has been buffered after two weeks of cold storage and became obvious again after four weeks, but with little intensity (23 to 24 %) as a result of the onset of proteolysis and lipolysis reactions. Values of K and N are necessary for proper designing of flow operations of cheese during processing.

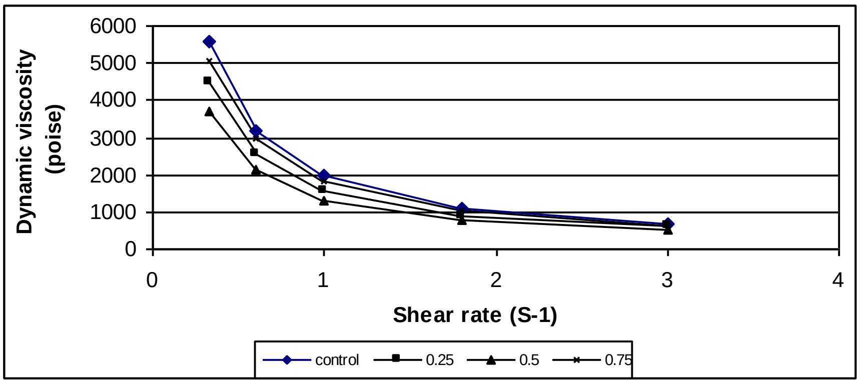
Table (3): Rheological parameters of white cheese prepared with different concentrations of dried spearmint during cold storage period

Dried concentrations (%)	Rheological parameters								
	Fresh			After two weeks			After four weeks		
	N	K	R^2	N	K	R^2	N	K	R^2
0	0.343	1029.9	0.905	0.226	1898.7	0.87	0.234	1138.2	0.844
0.25	0.238	1730.2	0.950	0.263	1730.4	0.931	0.345	752.1	0.85
0.5	0.231	1866.8	0.846	0.226	1898.7	0.87	0.254	1412.1	0.882
0.75	0.254	2061.3	0.828	0.277	1823.8	0.903	0.245	1396.6	0.857

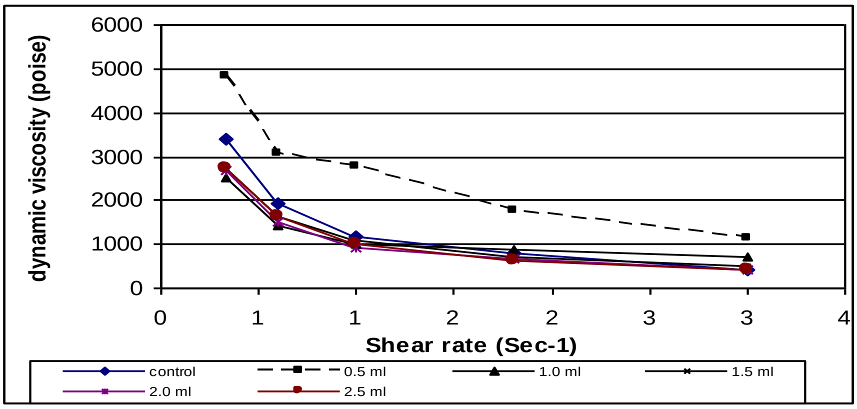
K: Consistency coefficient R^2 : Power law N: Flow behaviour index



(a) Fresh herby cheese



(b) Herby cheese after two weeks of cold storage



(c) Herby cheese after four weeks of cold storage

Fig. 4 (a, b and c): Dynamic viscosity values of herby white cheese prepared with different concentrations of dried spearmint as function of shear rate

d) Yield stress values and dynamic viscosity:

Table (4) gives the yield stress and apparent viscosity values of the dried spearmint white cheese. As seen, supplementation of white cheese with dried spearmint resulted in higher yield stress and apparent viscosity values at zero time and to some extent after two weeks of cold storage. However, after four weeks of storage the herby cheese became softer and more able to start flow (to spread as example) than the control one, since the yield stress and apparent viscosity values of these samples became lower. Such effect could be referred to the role of dried spearmint in promoting ripening processes during storage.

Table (4): Yield stress and apparent viscosity of herby cheese prepared with different concentrations of dried spearmint during cold storage period

Dried concentrations (%)	Rheological parameters								
	Fresh			After two weeks			After four weeks		
	τ_o (Poise)	η 48 (S^{-1})	η 81 (S^{-1})	τ_o (Poise)	η 48 (S^{-1})	η 81 (S^{-1})	τ_o (Poise)	η 48 (S^{-1})	η 81 (S^{-1})
0	973	80.95	57.42	1073	94.88	63.28	798	58.66	39.29
0.25	1785	90.57	60.79	1614	99.78	67.86	812	59.57	42.28
0.5	577	95.99	63.60	453	94.88	63.28	530	78.64	53.23
0.75	1251	114.8	77.70	1120	113.03	76.06	547	73.96	49.72

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الخواص الريولوجية للجبن الأبيض بالاعشاب الطبية المصنع بنظام الترشيح الفائق

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١- قسم الألبان – المركز القومي للبحوث – القاهرة,
٢- قسم علوم الأغذية – كلية الزراعة – جامعة عين شمس – القاهرة

يعتبر الجبن الأبيض بالاعشاب الطبية من المنتجات اللبنية الجديدة علي السوق المصري، ولتصنيع هذا النوع من الجبن تم استخدام اللبن الجاموسي المركز بالترشيح الفائق مع النعناع البلدي الجاف او الزيت العطري له ودراسة الخواص الريولوجية للجبن الناتج باستخدم جهاز (Rotational concentric rheometer) مثل جهد التدفق الابتدائي، اللزوجة الديناميكية، معامل القوام و اللزوجة الظاهرية.

وأظهرت النتائج المتحصل عليها أن كل عينات الجبن تحت الدراسة لها سلوك لانيوتوني من نوع شبيه البلاستيك pseudoplastic non-Newtonian وذلك لتزايد جهد التدفق الابتدائي مع معدل التدفق وكان للجبن الابيض المصنع باضافة زيت النعناع العطري المخزن لمدة ٤ اسابيع تركيب طري مقارنة بعينات الجبن الكنترول، ويرجع هذا لتأثير اضافة الزيت العطري في اسراع النشاط الانزيمي المصاحب لتسوية الجبن الابيض. كما ادي اضافة النعناع الجاف الي زيادة قدرة الخثرة علي الارتباط بالماء وبالتالي زيادة المقاومة علي التدفق.