Iranian Food Science and Technology Research Journal
Vol. 13, No. 3, Aug. Sep. 2017, p. 66-79

نشریه پژوهشهای علوم و صنایع غذایی ایران
جلد 13، شماره 3، مرداد - شهریور 1396، ص. 79-66

Fatty acid composition, rheological and thermal properties of butter from sheep's and omega-3 cow's milks

Morteza Kashaninejad[1], Seyed M. A. Razavi[2*], Mostafa Mazaheri Tehrani[2], Mahdi Kashaninejad[3]

Received: 2015.04.28
Accepted: 2015.12.16

Abstract

In this study, the compositional, rheological, thermal and textural properties of omega-3 cow's butter (OCB), conventional cow's butter (CCB) and sheep's butter (SB) were evaluated. The fatty acid composition of SB showed a relatively high content of the short chain fatty acids (SCFA) compared with that of cow's butters and higher levels of CLA and omega 3 fatty acids in OCB were observed. Regarding to the firmness, at refrigeration temperature (5 °C), SB was much firmer than CCB and OCB, but as a function of temperature, it was softened much quicker. However, at temperatures around 18°C it was already softer than the latter. From dynamic rheological data, it was found that butter samples display solid-like viscoelastic behavior since the values of G′ were much higher than those of G″ with a low dependence on frequency. The values of G′ and G″ also decreased in butters containing more percentage of unsaturated fatty acids. The temperature effect on the viscosity followed an Arrhenius-type relationship and OCB had a less activation energy than others, indicating that the butter containing high SCFA was more sensitive to temperature changes. Through differential scanning calorimetery, the thermal behavior of the butters during melting was analyzed.

Keywords: Butter, DSC, Firmness, GC, Omega-3, Rheology

Introduction

Milk and dairy products contribute considerably the consumption of essential nutrients in human populations (Drewnowski 2011). Health and nutrition professionals advise consumers to limit consumption of saturated fatty acids and increase the consumption of foods rich in polyunsaturated (PUFA) and n-3 fatty acids. An increase in the ratio of saturated to unsaturated fatty acids in milk fat is associated with an increased risk for cardiovascular disease and concentrations of total and low-density lipoprotein (LDL) cholesterol (Sacks and Katan 2002). A higher ratio of saturated fatty acids contributes to the hardness and poor spreadability of butter at refrigeration temperature (Edmondson *et al.* 1974; Taylor and Norris 1977; Ashes *et al.* 1997).

Omega-3 butter produced from milk with elevated PUFA and n-3 fatty acids levels caused by dietary manipulation appears to be improved in texture and nutritional value. Gonzalez *et al.* (2001) observed that Firmness values were lower for the high oleic and high linoleic butter when compared to the control. Oeffner *et al.* (2013) showed that the less saturated fatty acid profile was associated with decreased hardness and adhesiveness of refrigerated butter. Therefore, there has been a great deal of interest in omega-3 milk production containing more SCFA and PUFA in milk fat.

Dairy sheep has an important role in dairy industry of Mediterranean and Middle East region countries (FAO 2003). So far the value of sheep's milk in human nutrition has received very little academic attention and few facts are available (Haenlein 1987; Park 1991). In addition, little literature is available on the thermal, rheological and textural properties of butter from sheep's as well as omega-3 cow's milks.

Rheological measurements are useful in

1 and 2. Former MSc Student and Professor, Department of Food Science and Technology, Faculty of Agriculture, Ferdowsi University of Mashhad, PoBox 91775-1163, Mashhad, Iran.
3. Professor, Faculty of Food Science & Technology, Gorgan University of Agricultural Sciences and Natural Resources, Gorgan, 49138-15739, Iran
(*- Corresponding Author Email: s.razavi@um.ac.ir)
DOI: 10.22067/ifstrj.v1395i0.46869

objectively measuring properties related to texture, functionality, and also providing data for process modeling and quality (Fox and McSweeney 2003). Small amplitude oscillatory shear (SAOS) has been recently considered to predict correct rheological characteristics of semi-solid foods (Ahmed and Ramaswamy 2006) and could be implemented for butter samples. Rheological properties of butter are also influenced by temperature; commonly Arrhenius equation is used to describe temperature dependency of butter samples. Moreover, the viscosity and the melting properties are valuable as quality, process and storage parameters. Although it has long been recognized that the melting properties of butter is a key factor in determining its spreading quality, there have been only a few reports of the liquid fat content of' commercial butter.

Thus, the objective of this study was to compare the properties of omega-3 cow's butter and sheep's butter with conventional cow's butter. An instrumental texture analysis, a strain sweep test, a frequency sweep test and a temperature sweep test were carried out together with the fatty acid composition and melting behavior analysis. All of the tests were performed over a range of temperatures to gain insight into the performance of the materials in storage and consumer usage environments.

Materials and methods

Butter manufacture

For this study, conventional and organic dairy farms (Golshid-Mashhad Co and Shafashir Toos industrial dairy farmer's production and distribution cooperative) located in Northeast of Iran were selected (Mesgaran and Jafarpoor 2012). The sampling took place in January, at the winter for both the cow and sheep.

After pre-pasteurization (78°C for 30 s), the milk was skimmed at 40°C by a centrifugal cream separator (120 L/h, Alfa Pak, Iran). The cream collected was then standardized at 40% fat before being pasteurized (88°C for 1 min 30s). It was then cooled to 6°C using a plate heat exchanger. The cream was physically matured (18°C for 3 h) before being re-cooled and held at 6°C. The cream was then churned at 40 rpm in a 200L industrial churn (Alfa Pak, Iran) until the butter was granulated. After separating the buttermilk, the butter was washed in water at 8°C before being pre-worked in the churn, first at low speed for 15 min then at high speed for 1 min. Butter samples were stored in plastic containers at 5°C until further analysis.

Gas chromatography

Milk fat extraction and fatty acid separation were performed according to a procedure described by Chouinard *et al*. (1999). Fatty acid methyl esters were prepared by trans-methylation, then were quantified using a gas chromatograph (GC ystem 6890 Hewlett-Packard, Wilmington, DE) equipped with a flame-ionization detector and a CP-7489 fused-silica capillary column (100m× 0.25mm with 0.2μm film thickness; Varian, Walnut Creek, CA). Initial oven temperatures (50°C) was held for 1 min then ramped at 5 °C/min to 160°C where it was held for 42 min, and then ramped at 5°C/min to 190°C and held for 22min. Inlet and detector temperatures were maintained at 250°C, and the split ratio was 100:1. Hydrogen carrier gas flow rate through the column was 1 mL/min. Hydrogen flow to the detector was 30 mL/min, airflow was 400mL/min, and nitrogen make-up gas flow was 25mL/min. Peaks in the chromatogram were identified and quantified using pure methyl ester standards. Samples were analyzed in duplicate, and peak identification was accomplished through the analysis of authentic standards.

Differential scanning calorimetry (DSC)

A Perkin-Elmer Pyris-1 (LTI03-USA) differential scanning calorimeter was used to investigate the melting behavior of the samples. Nitrogen gas was used to prevent condensation in the cell and an empty pan was used as the reference. Samples (approximately 10 mg) were weighed in aluminum pans and tightly sealed with an aluminum lid. Measurements were carried out in the temperature range of -40 to 90°C with heating rates of 10°C/min. The endothermic curves of heat flow as a function of temperature were recorded to analyze the non-isothermal melting kinetics. The temperature of each peak (T_{m1}, T_{m2} and T_{m3}) (°C) and enthalpy of melting (ΔH_{m1}, ΔH_{m2} and ΔH_{m3}) (J g^{-1}) were obtained from heating curves, as shown in Fig. 1. All measurements were performed in triplicate for each sample.

Instrumental texture analysis

To determine firmness, the penetration value (P) of the samples were measured at 5, 10 and 20°C, respectively; using a TA-XT2 texture analyzer (Stable Micro Systems, London, UK) with a 45° conical probe was lowered at 0.02 mm/s at a load of 102.5 g. The penetration value (P) is the depth of penetration of the cone into butter sample. Each test was repeated 3 times using fresh samples. The thousand fold value of the reciprocal of the penetration value (F=1000/P) was used for the characterization of the firmness of butter samples. The firmness was characterized by a linear relationship between temperature and firmness.

Dynamic rheological analysis

Small amplitude oscillatory shear (SAOS) measurements were performed using a controlled stress/strain rheometer (Physica MCR 301, Anton Paar GmbH, Stuttgart, Germany) equipped with parallel-plate geometry and a 50mm diameter set to a gap of 2 mm. Data were recorded with the Rheoplus software, version 2.65 (Anton Paar Germany GmbH). For each measurement, a new sample was used. Oscillatory measurements were performed at least in duplicate.

The linear viscoelastic region (LVR) for butter samples was determined by performing an amplitude sweep measurements (0.01-100%) at constant frequency (1 Hz) and two temperatures of 5 and 20°C. Then, frequency sweep tests at a constant strain in the LVE region were carried out to determine the viscoelastic properties of butters. The mechanical spectra were characterized by values of storage modulus (G´, Pa), loss modulus (G″, Pa) and complex viscosity (η*, Pa.s) as a function of frequency in the range of 0.01–100 Hz and two temperatures (5°C and 20°C). Finally, the temperature sweep measurements were performed at the constant strain of 0.01%, which was well within the linear viscoelastic region, while the frequency was fixed at 1 Hz. The experiments were carried out by heating the samples from 5 to 60°C at 5°C/ min $^{-1}$.

Results and discussion

Fatty acid profile

Milk fatty acid composition has been considered to be the main factor influencing nutrition (Palmquist 1991; Jensen 2002) and butter texture (Brunner 1974). Fatty acid compositions of the samples are summarized in Table 1. The SB showed a relatively high content of the SCFA, C4:0 to C10:0, 16.97% by weight, compared with that of cow's butters. Capric acid (C10) was the major SCFA present in SB (9.52% by weight).

Short-chain and medium-chain fatty acids (MCFA) in milk fat have certain interesting characteristics, and they are primarily absorbed through the portal vein during lipid digestion (Christophe and Devriese 2000). In addition, SCFA and, to a lesser extent, MCFA lower the melting point of triacylglycerols and, thus, their presence helps keep milk fat liquid at physiological temperatures.

The degree of saturation ranged between 69.88% by weight in OCB, and 74.17% in SB, in the CCB being relatively higher than that of OCB. The unsaturated fatty acids play an important role in the physical as well as nutritional properties of the milk fat (Marangoni *et al.* 2012). A decreasing degree of saturation of the fatty acid and a decreasing chain length results in a lower melting point compared to saturated fat with a long chain. Such changes in the chemical composition of milk fat are likely to change the rheological properties of produced butter. Of the saturated fatty acids, Stearic (C18) was predominant in both sheep's and cow's butters, while oleic acid was the major unsaturated fatty acid. The oleic acid level was lowest (17.98% by weight) in the CCB and highest (20.14% by weight) in the SB.

26.68% of the fatty acids in OCB are mono-unsaturated (MUFA) with oleic acid (18:1) accounting for 19.19% by weight of the total fatty acids. Poly-unsaturated fatty acids (PUFA) in OCB constituted of 3.44% by weight of the total fatty acids and the main poly-unsaturated fatty acids were linoleic acid (18:2) and α-linolenic acid (18:3) accounting for 1.85 and 1.59% by weight of the total fatty acids. Therefore, it is remarkable that higher levels of CLA and omega 3 fatty acids in OCB were found in this study, which they have been reported before in organic butter (Bergamo *et al*. 2003).

Table 1. Fatty acid profile of different butters from gas chromatographic analysis

Fatty acids (wt %)	SB[1]	CCB[2]	OCB[3]
4:00	2.22	2.01	1.46
6:00	2.4	1.8	1.4
8:00	2.83	1.26	1.04
10:00	9.52	2.94	2.71
12:00	5.52	3.47	3.55
14:00	13.61	12.82	12.77
14:1,cis-9	0.89	1.51	2.19
15:1,cis-9	1.2	1.09	1.49
16:00	26.14	33.56	37.67
16:1,cis-9	1.65	2.19	3.81
17:00	0.67	0.86	0.85
18:00	10.6	15.65	8.32
18:1 Trans	17.42	16.97	18.07
18:1 Trans	2.72	1.01	1.12
18:2cis	1.48	1.75	1.85
18:2 Trans	0	0	0
18: 3	0.47	0.92	1.59
20:00	0.6	0.12	0.07
oleic	20.14	17.98	19.19
MUFA[4]	23.88	22.77	26.68
PUFA[5]	1.95	2.67	3.44
SCFA[6]	16.97	8.08	6.61
MCFA[7]	45.94	50.71	54.84
LCFA[8]	11.2	15.77	8.39
Saturated FA	74.17	74.56	69.88
Unsaturated FA	25.83	25.44	30.12

1. SB: sheep's butter.
2. CCB: conventional cow's butter.
3. OCB: omega-3 cow's butter.
4. MUFA (monounsaturated FA): C10:1, C14:1, C16:1, C17:1, C18:1 trans, C18:1cis, C20:1, C22:1, C24:1.
5. PUFA (polyunsaturated FA): C18:2 Trans, C18:2 cis, C18:3n-3.
6. SCFA (short-chain FA): C4:0 to C10:0.
7. MCFA (medium-chain FA): C11:0 to C17:0.
9. LCFA (long-chain FA): > C18:0.

Today, health authorities normally recommend a higher intake of these fatty acids as they are considered important for normal growth and development and for prevention of a number of diseases like hypertension, diabetes, cancer, and coronary heart disease.

Comparison of fatty acids composition of cow's and sheep's milk has been reviewed by Ramos and Juarez (1986). Their researches involve comparing the ratios of fatty acids. For example, the 12:0/10:0 fatty acid ratio is consistently higher in cow's milk (0.9–1.3) than in sheep's milk (0.4–0.8). Other ratios that have been considered include 14:0/12:0 and 14:0/8:0, and more complex combinations, such as 10:0/ (12:0+ 16:0+ 18:1).

Melting properties

Central to butter sensory character is a continuous-phase lipid composition, which influences melting properties and mouthfeel character. The melting properties of different milk fats give insight into the degree of fluidity at different temperatures as affected by the fatty acids (Osthoff, 2011).

The melting thermograms of SB, CCB and OCB determined by differential scanning calorimetry (DSC) are shown in Fig. 1. It could be seen that the melting profile ranged from −40°C to 90°C. On all melting curves, three endothermic peaks (T_{m1}, T_{m2} and T_{m3}) in accordance with literature data (TenGrotenhuis *et al*. 1999) could be observed. Vasic and DeMan (1968), Shukla and Rizvi (1995) and Chandra *et al*. (2009) also reported three melting zones in melting thermograms of butter. Although, in this study the second peak for OCB was broken down into two peaks.

The shape of the curve as well as height of melting peaks of butter change depending on fatty acid composition (KaisersBerger 1989). The values of peak temperature and melting enthalpy of butters are summarized in Table 2. Between 0ºC and 0.7ºC, an endothermic peak appeared due to the melting of water. The magnitude of these temperature peaks is related to the quantity of water present in the butter (Watson 1975). The lipids in butter samples occur in two groups; one group with high amounts of PUFA and the other more saturated ones. The results showed that these two groups of molecules melt between 11.93ºC to 13.05ºC, and 30.23ºC to 32.97ºC, respectively. Regarding enthalpies, the SB with the lowest level of PUFA showed the highest melting enthalpy of peak 2 (-4.21 Jg_{-1}), while OCB with the lowest saturated fatty acids exhibited the highest melting enthalpy of peak 3 (-3.77 Jg_{-1}). In addition, the melting enthalpy of peaks exhibited the opposite trend with the values of peak temperature.

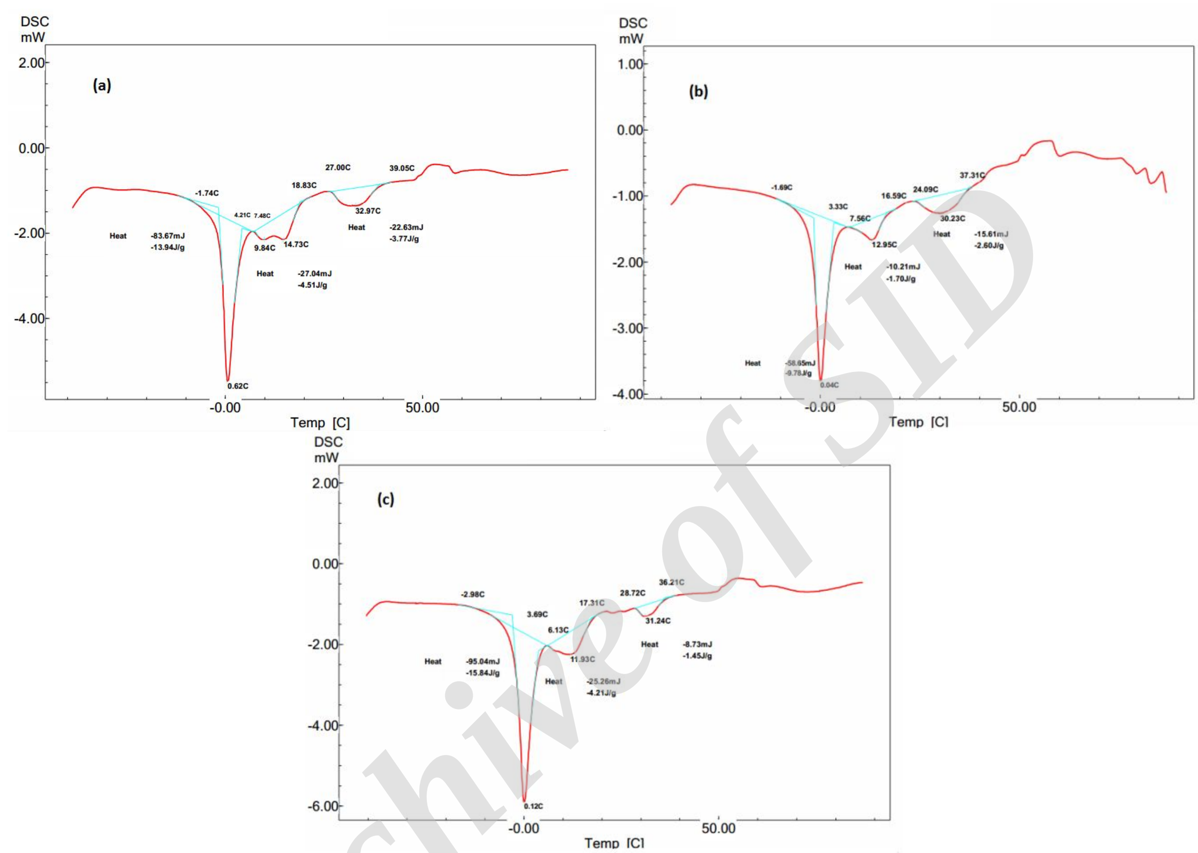

Fig. 1. DSC Curves of melting of omega-3 cow's butter (A), conventional cow's butter (B) and sheep's butter (C).

Table 2. Temperatures and enthalpies of butter melting process measured by DSC

Butter	Temperature (ºC)			Enthalpy (Jg^{-1})		
	T_{m1}	T_{m2}	T_{m3}	ΔH_{m1}	ΔH_{m2}	ΔH_{m3}
CCB[1]	0.04	13.05	30.23	-9.78	-1.70	-2.60
OCB[2]	0.62	9.2/12.9[4]	32.97	-13.94	-1.51/-2.2[4]	-3.77
SB[3]	0.12	11.93	31.24	-15.84	-4.21	-1.45

1. CCB: conventional cow's butter.
2. OCB: omega-3 cow's butter.
3. SB: sheep's butter.
4. The peak is breaking down into two peaks, which indicates the decomposition of this fraction to another two ones.

The most important aspect to be noted is the initial and final melting points. Comparison of the results obtained for SB, showed that fat melting peaks started at a lower temperature than the other samples and also indicated the largest enthalpy of melting and values of peak temperatures. This result is probably because of being richer in SCFA

(Table 1), displayed greater melting in the low temperature range than cow's butters. A high initial, as well as final melting point of CCB is indicative of high amounts of saturated long-chain fatty acids. The second aspect is the different melting peaks observed for the butter samples, which is probably the result of triglycerides composed of different types of fatty acids.

As seen in Table 2, fat melting peaks for CCB were detected as endothermic peaks at 13.05 and 30.23°C, for OCB peaks appeared at 12.09 and 32.97 °C and for SB peaks appeared at 11.93 and 31.24 °C. This means that the butter samples are hard at 5°C and the majority of fat melts at room temperature (25°C).

Firmness

Fig. 2 shows the change of firmness of butters from omega-3 cow's milk, conventional cow's milk and sheep's milk as a function of temperature. It is obvious that at refrigeration temperature (5°C), SB is much firmer than others, but as a function of temperature it softens much quicker and near the 18°C it is already softer than the latter. In addition, the slope of the straight line in the SB is greater than the cow's butters, indicating less temperature stability because of its higher SCFA content. These findings are in agreement with Schaffer *et al*. (2001), who reported the enriched butter with low melting point triglycerides (LMP) versions of traditionally butters are firmer at a low temperature than the samples of butters, and also that the slopes of the straight line are greater.

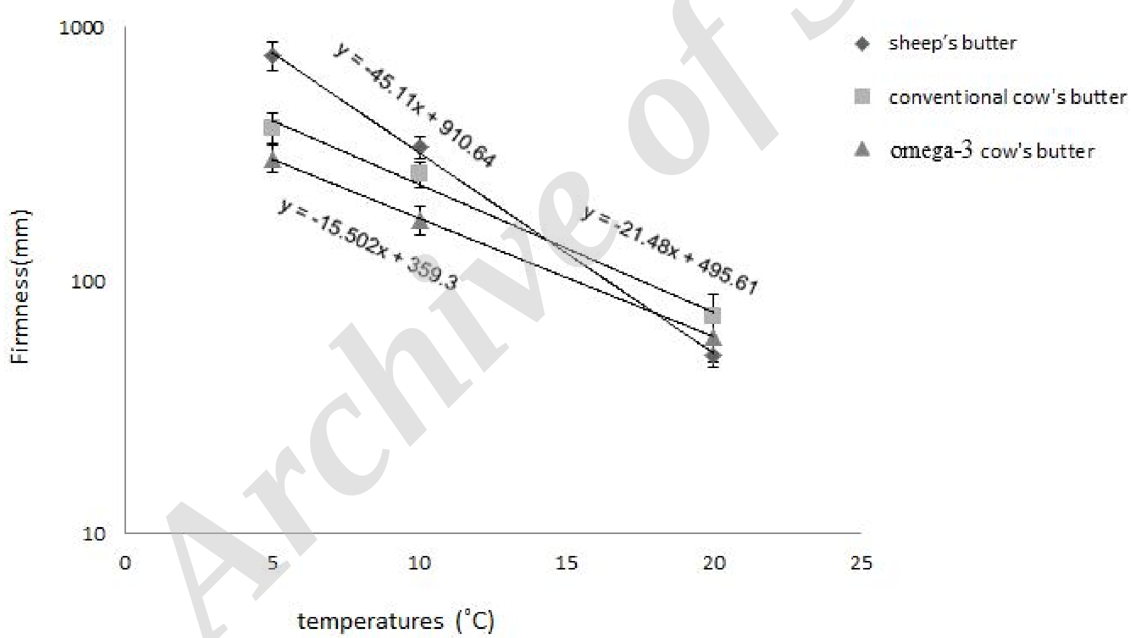

Fig. 2. Firmness of omega-3 cow's butter, conventional cow's butter and sheep's butter as a function of temperature

Generally, OCB with the highest percentage of unsaturated fatty acids had a more depth of penetration (at 5°C and 20°C) than others. Our results for CCB are also consistent with those of Middaugh *et al.* (1988); Lake *et al.* (1996); Lin *et al*. (1996); Baer *et al*. (2001) and Bobe *et al*. (2003).

Rheological properties

Linear viscoelastic domain

Prior to prepare the dynamic measurements of the sample's microstructure, the linear viscoelastic region (LVE) must be defined. Measurement of linear viscoelastic properties is a useful way of gaining information about a foods' microstructure and how it influences the rheological properties (Narine and Marangoni 1999; Gunasekaran and Ak 2002). Fig. 3 shows the strain sweep (G′ and G″ vs strain) determined for SB at 20ºC. It could be seen that the G′ value was almost constant up to a certain strain, and then it began to decrease suddenly when the strain was further increased. The sudden decrease in the G′ may indicate the breaking of fat crystal network and a transition from a linear to a non-linear behavior.

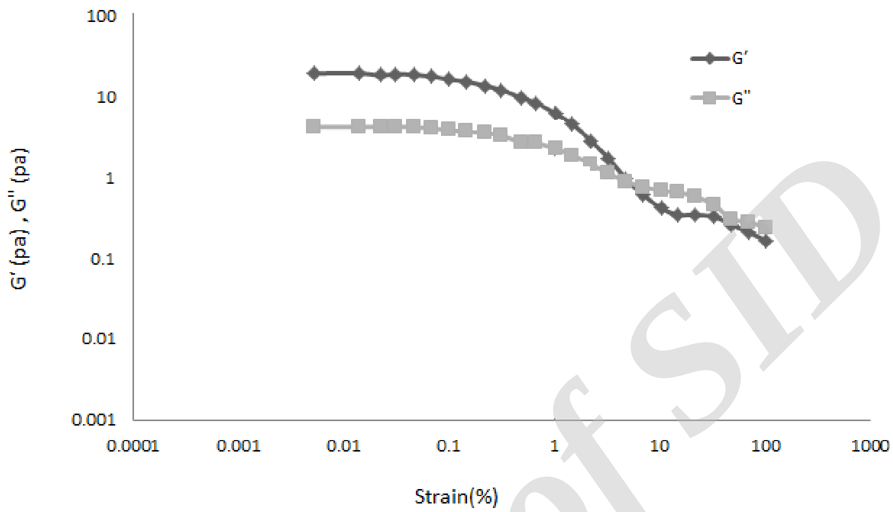

Fig. 3. Strain sweep dependency of storage modulus (G′) and loss modulus (G″) measured for sheep's butter (20 ºC & *f*=1 Hz).

The results indicated that the length of LVE ranged from 0.045% for SB at 20ºC to 0.067% for CCB, depending on the butter, this region lies at a strain of less than 1.0% or even less than 0.1% (Rohm and Weidinger 1993). Chandra *et al*. (2009) proposed that the LVR at 20ºC for butter samples was longer than that at 5ºC. As a result, the strain of 0.01% was selected for frequency sweep and temperature sweep tests since it was well fitted within the linear viscoelastic region for all experimental conditions, where the weak gel network was not damaged by the strain imposed during the measurements.

It was found from strain sweep that the values of G′ and G″ at LVE region increased for the butters with the highest percentage of saturated fatty acids. Furthermore, increasing temperature from 5 to 20ºC decreased the structural strength (G´ at LVE) of samples.

Viscoelastic properties

Fig. 4 shows the changes in storage modulus (G´), loss modulus (G″), and complex viscosity (η^*) as a functions of the frequency (f) for the CCB at 5ºC. It can be seen that the η^* values decreased steeply as the frequency increased, but G´ and G″ showed relatively less frequency dependence, which their G´ and G″ values increased as the frequency increased. The G´ values were greater than G″ values at any given frequency, indicating behavior essentially like that of solids.

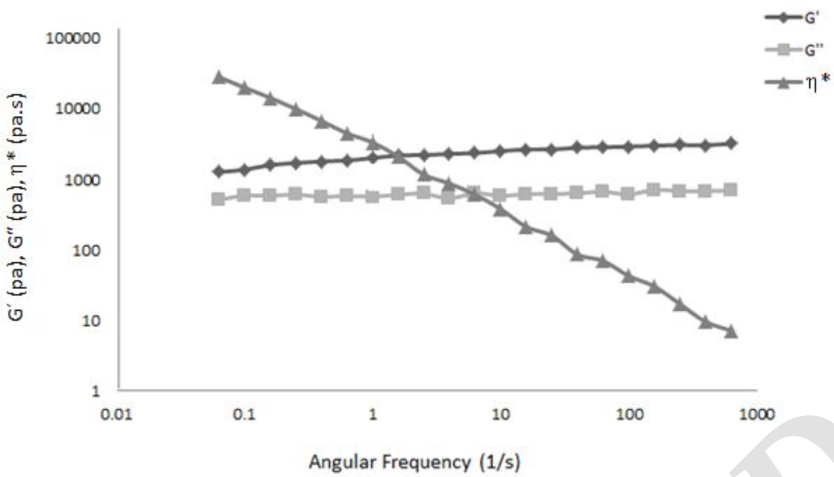

Fig. 4. Storage modulus (G′), loss modulus (G″) and complex viscosity (η*) versus angular frequency of conventional cow's butter (5 °C & γ=0.01%)

The dynamic rheological data of G´, G″ and η* versus angular frequency determined for butters at different temperatures (5–20˚C) were also subjected to power-law type equation, as suggested by Nolan et al. 1989. Table 3 contains the values of slopes (n', n" and n*), intercepts (k', k" and k*), and R^2 for the following equations:

$$G' = k'(\omega)^{n'} \quad (1)$$

$$G'' = k''(\omega)^{n''} \quad (2)$$

$$\eta^* = k^*(\omega)^{n^*} \quad (3)$$

From these dynamic rheological data, it was found that the butter displayed solid-like viscoelastic behavior because the values of k'(0.02– 2.81) are much higher than those of k" (0.002– 0.83) with a low dependence (n'=0.09– 0.12; n"=0.06– 0.17) on frequency.

According to Kokini and Plutchok (1987), for hydrocolloid gels (interwoven network of macromolecules), G' dominates over G" because the network bonding forces prevent translational movement. In a plastic fat, the intertwined crystal aggregates perform a similar function, leading to increased G' and G" values. At higher frequencies, a more solid-like response is observed (Drake *et al.* 1994; Rohm and Weidinger 1993).

Table 3. Storage modulus (G'), loss modulus (G") and complex viscosity (η^*) of butter samples at 5 and 20°C (frequency: 1 Hz).

Type of butters	Temperature (ºC)	G´			G″			η^*		
		n'	k'	R^2	n"	k"	R^2	n*	k*	R^2
CCB[1]	5	0.12	2.81	0.95	0.17	0.83	0.97	-0.80	1.32	0.99
	20	0.10	0.27	0.91	0.06	0.06	0.97	-0.89	0.28	0.99
OCB[2]	5	0.12	2.30	0.92	0.13	0.52	0.97	-0.86	1.25	0.99
	20	0.09	0.18	0.94	0.14	0.02	0.94	-0.91	0.19	0.99
SB[3]	5	0.10	1.16	0.99	0.16	0.22	0.99	-0.90	1.12	0.96
	20	0.09	0.02	0.96	0.13	0.002	0.97	-0.89	0.025	0.99

1. CCB: conventional cow's butter.
2. OCB: omega-3 cow's butter.
3. SB: sheep's butter.

The G' and G" values of butter samples at different temperatures (5–20 °C) showed little frequency dependence, indicative of the presence of a network with low possibility of rupture of junction zones within the low-frequency range used. Similar observations were made by Doubler and Choplin (1989), Rohm and Weidinger (1993), Shukla and Rizvi (1995), and Narine and Marangoni (1999).

The k’ values decreased as temperature increased, indicating greater elastic components at lower temperatures. Trends were similar for k” and k* values, indicating lower loss modulus and complex viscosity at higher temperatures. Diener and Heldman (1968), Rohm and Weidinger (1993), Shukla and Rizvi (1995) and Chandra *et al*. (2009) also reported similar behavior for butter.

These observations could be explained by the crystallization of fat at lower temperatures, which resulted in behavior more like that of solids. Narine and Marangoni (1999) proposed that higher values of the fractal dimension are associated with more ordered systems. At higher temperatures, crystallization proceeds more slowly than at lower temperatures. As a result, crystals will have more time to arrange themselves in more ordered networks.

Compared with CCB and SB, OCB had lower intercept values of k’, k” and k* at similar temperatures, which associated with the highest percentage of unsaturated fatty acids (Table 3). It means that the values of k’ and k” decreased in butters with more percentage of unsaturated fatty acids. The value of G”, which is the viscous response, decreased with increasing the temperature. It is a well-known phenomenon that increasing temperature would decrease the viscosity of many fluid foods due to an increase in kinetic energy (Katsuta and Kinsella 1990).

Temperature dependency

Fig. 5 shows a typical dynamic shear profile of temperature sweep obtained with a CCB. In general, the values of G' and G'' decreased steadily between 5 and 60°C. Below 40°C, the G' values were higher than G'' values, indicating a solid-like behavior, but the two curves of G' and G'' crossed at 38.51°C, indicating a liquid- like behavior above the crossover temperature. The crossing point for CCB and SB were different and detected at 40.50°C and 39.07°C, respectively. Increasing temperature from 5 to 40°C resulted in both G' and G'' decrease, which expressed the melting of butter and fat liquefaction. While decreasing, G' remained over G'', which can be explained by the mechanical resistance of the fat network while butter fat melts progressively. The lipid fraction with high amounts of PUFA has a lower melting point than the other more of saturated ones. Thus it can be assumed that there is a progressive melting of the different lipid fractions in fat up to 30 and 40°C, where the triglycerides of butter are liquids. The decrease in G' indicated a weakening of the butter structure, an effect which might be due in large part to liquefaction of the fat phase, fully liquid at about 40 °C.

The influence of temperature on the complex viscosity of the butters were demonstrated in Fig. 6. In general, for all the butters, the complex viscosity was decreased with increasing temperature from 5 to 60°C

The dependence of viscosity on the temperature can be interpreted by a free volume concept: an increase in temperature allows more thermal motion of macromolecules and greater free volume in the butter, which leads to a decrease in intermolecular or intra-molecular resistances associated with viscosity. The order of the viscosity levels of three butter types was the same as for loss modulus, a fact that confirms the dependence between the G″ and η*. The values of complex viscosity at 5°C ranged from 300004 Pa.s for OCB to 770296 Pa s for SB.

Because of the regular dependence of the viscosity of butter on temperature, a linear relationship between log complex viscosity and the reciprocal of absolute temperature can be obtained. Thus, it is possible to apply the Arrhenius equation;

$$\eta^* = \eta_0 \exp\left(E_a / RT\right) \quad (4)$$

Where η^* is the complex viscosity (Pa.s), η_0 a constant (Pa.s), E_a is the activation energy, R is the universal gas constant (1.987 kcal/mol.K) and T is the absolute temperature (K).

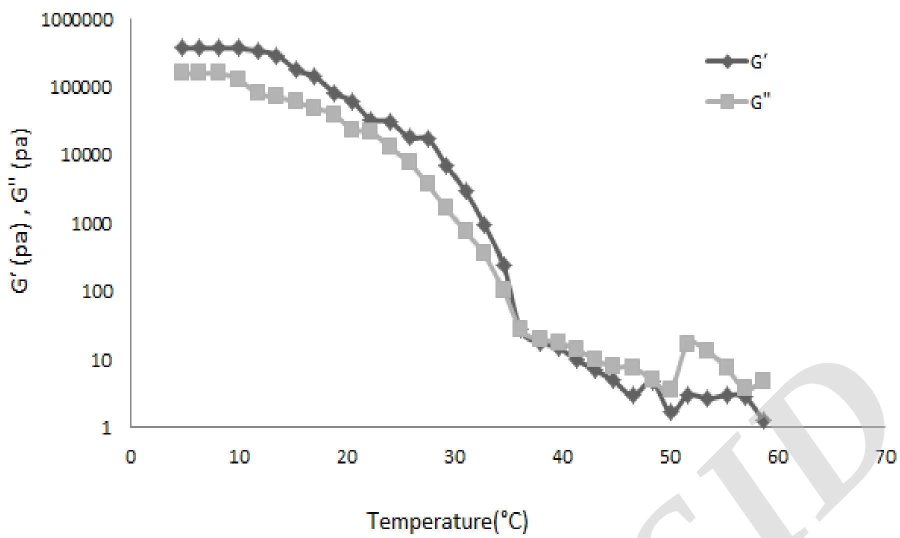

Fig. 5. Temperature dependence of the storage modulus (G′) and loss modulus (G″) of omega-3 cow's butter (*f*=1 Hz, γ=0.01%)

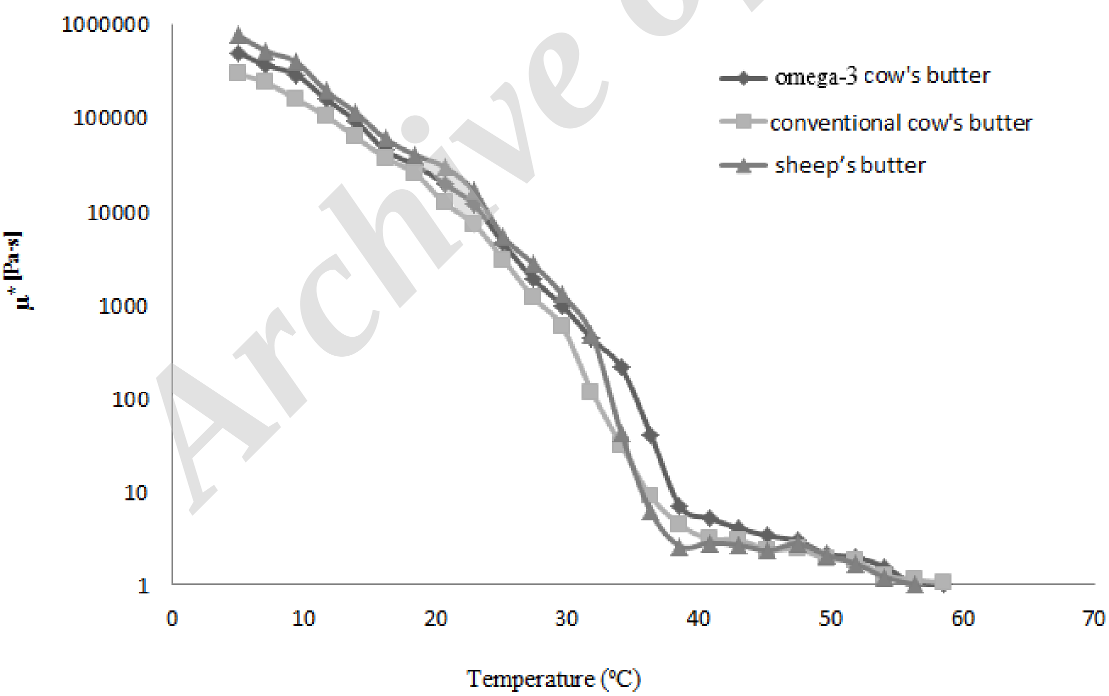

Fig. 6. Complex viscosity changes of butter samples as a function of temperatures (*f*=1 Hz, γ=0.01%)

Activation energy was determined as slope multiplied by R. A linear plot of ln (η^*) versus (1/T) was drawn to obtain the activation energy. The correlation coefficients (R^2) for each butter variety are presented in Table 4. It can be seen that the activation energy (E_a) ranged from 51.55 to 52.63 (kcal/mol). Shukla *et al*. (1994) found activation energy for fractionated high- melting triglyceride (HMT) and anhydrous milk fat (AMF) are 114.47 and 52.68 kcal/mol, respectively. Activation energy levels indicate the sensitivity of the viscosity to the temperature change. Higher E_a means that the butter viscosity is relatively more sensitive to temperature change. Data presented in Table 4 showed that OCB is the least sensitive (lowest E_a value), while SB is the most sensitive (highest E_a value) among the sample examined. The viscosity behavior is a function of composition components present in the butter. Generally, OCB with the lowest percentage of SCFA had a less activation energy than others, indicating that the viscosity is more sensitive to temperature changes at high SCFA contents.

Table 4. The parameters of Arrhenius model determined for different butters

Type of butter	η_0 (Pa.s)	E_a (kcal/mol)	R2
Omega-3 cow's butter	9.45×10^{-40}	51.55	0.95
Conventional cow's butter	6.17×10^{-36}	52.37	0.94
sheep's butter	2.27×10^{-34}	52.63	0.94

R^2 value for the linearied Arrhenius model (lnl vs.1/T)

Conclusions

based on the results obtained in this study, it can be concluded that the OCB with a more levels of CLA and omega 3 fatty acids composition probably have a more health-promoting fatty acid composition and is softer (at 5ºC and 20ºC) than the others. On the other hand, SB with high content of SCFA at the refrigeration temperature (5°C) is much firmer than others, but as a function of temperature, it softens much quicker and near the 18°C, it is already softer than the latter. The melting thermograms of SB displayed fat melting peaks started at a lower temperature than the others. Viscoelastic properties of butter samples were determined using dynamic mechanical analysis, which were dependent upon strain level, frequency, temperature, and chemical composition of samples. From dynamic rheological data, it was found that the butters displayed solid- like viscoelastic behavior, which a more solid- like response is observed at higher frequencies. Compared to CCB and SB; OCB had lower intercept values of k', k" and k* at similar temperatures, which associated with the highest percentage of unsaturated fatty acids. In addition, OCB with the lowest percentage of SCFA had a less activation energy than others, indicating that the complex viscosity is more sensitive to temperature changes at higher SCFA contents.

References

Ahmed J, Ramaswamy HS (2006) Viscoelastic properties of sweet potato puree infant foods. Journal of Food Engineering 74:376-382

Ashes JR, Gulati SK, Scott TW (1997) Potential to alter the content and composition of milk fat through nutrition. Journal of Dairy Science 80:2204-2212

Baer RJ, Ryall J, Schingothe DJ, Kasperon KM, Donovan DC, Hippen AR, Franklin ST (2001) Composition and properties of milk and butter from cows fed fish oil. Journal of Dairy Science 84:345-353

Bergamo P, Fedele E, Lannibelli L, Marzillo G (2003) Fat-soluble vitamin contents and fatty acid composition in omega-3 and conventional Italian dairy products. Food chemistry 82:625-631

Bobe G, Hammond EG, Freeman AE, Lindberg GL, Beitz DC (2003) Texture of butter from cows with different milk fatty acid compositions. Journal of Dairy Science 86:3122-3127

Brunner JR (1974) Physical equilibrium in milk, the lipid phase. In: Webb BH, Johnson JA, Alford eds, Fundamentals of Dairy Chemistry, 2nd edn. AVI, Westport, CT

Chandra RV, Malcolm JG, Bronwen GS (2009) The effect of temperature on the rheology of butter, a spreadable and spreads. Journal of Texture Studies 40:346-369

Chouinard PY, Corneau L, Saebo A, Bauman DE (1999) Milk yield and composition during abomasal infusion of conjugated linoleic acids in dairy cows. Journal of Dairy Science 82:2737-2745

Christophe AB, Devriese S (2000) Fat digestion and absorption. AOCS Press, Champaign

Diener RG, Heldman DR (1968) Methods of determining rheological properties of butter. Transactions of the American Society of Agricultural Engineers 11:444-447

Doubler JL, Choplin L (1989) A rheological description of amylose gelation. Carbohydrate Research 193:215-218

Drake MA, Ma L, Swanson BG, Barbosa C (1994) Rheological characteristics of milk fat and milk fat blend sucrose polyesters. . Food Research International Journal 27:477- 481

Drewnowski A (2011) The contribution of milk and milk products to micronutrient density and affordability of the U.S. diet. Journal of the American College of Nutrition 30:422S-428S

Edmondson LF, Yoncoskie RA, Rainey NH, Douglas JrF W, Bitman J (1974) Feeding encapsulated oils to increase the polyunsaturation in milk and meat fat. Journal of the American Oil Chemists' Society 51:72-76

FAO (2003) Production Yearbook. Food and Agriculture Organization of the United Nations. Rome. Italy

Fox PF, McSweeney PLH (2003) Advanced Dairy Chemistry-1 Proteins, 3rd ed., Kluwer Academic/Plenum. New York

Gonzalez S, Duncan SE, O'Keefe SF, Sumner SS, Herbein JH (2001) Oxidation and textural characteristics of butter and ice cream with modified fatty acid profiles. Journal of Dairy Science 86:70-77

Gunasekaran S, Ak MM (2002) Cheese rheology and texture. CRC Press, Boca Raton FL

Haenlein GFW (1987) Cow and goat milk aren't the same especially in somatic cell content. Dairy Goat Journal 65:806

Jensen RG (2002) The composition of bovine milk lipids. Journal of Dairy Science 85:295-350

Kaisersberger E, GmbH NG, Sbacherstr W (1989) DSC investigations of the thermal Characterization of edible fats and oils. Thermochimica Acta Journal 15:83-90

Katsuta K, Kinsella JE (1990) Effects of temperature on viscoelastic properties and activation energies of whey protein gels. Journal of Food Science 55:1296-1302

Kokini JL, Plutchok GJ (1987) Viscoelastic properties of semi-solid foods and their biopolymeric components. Food Technology 41:89-95

Lake R, Thomson B, Devane G, Scholes P (1996) Trans fatty acids content of selected New Zealand foods. Journal of Food Composition and Analysis 9:365-374

Lin MP, Sims CA, Staples CR, O'Keefe SF (1996) Flavor quality and texture of modified fatty acid high monoene, low saturate butter. Food Research International Journal 29:367-371

Marangoni AG, Acevedo N, Maleky F, Co E, Peyronel F, Mazzanti G, Quinn B, Pink D (2012) Structure and functionality of edible fats, Journal of Soft Matter 8:1275-1300

Mesgaran MD, Jafarpoor MJ (2012) Enhance Omega-3 milk production in Holstein dairy. Journal of Agricultural Science and Technology A2:930-936

Middaugh RP, Baer RJ, Casper DP, Schingoethe DJ, Seas SW (1988) Characteristics of milk and butter from cows fed sunflower seeds. Journal of Dairy Science 71:3179-3187

Narine SS, Marangoni AG (1999) Relating structure of fat crystal networks to mechanical properties-a review. Food Research International Journal 32:227-248

Nicholas PK, Padel S, Cuttle SP, Fowler SM, Hovi M, Lampkin NH, Weller, RF (2004) Omega-3 dairy production-a review Biological Agriculture and Horticulture 22:217-249

Nolan EJ, Holsinger VH, Shieh JJ (1989) Dynamic rheological properties of natural and imitation mozzarella cheese. Journal of Texture Studies 20:179-189

Oeffner SP, Qu Y, Just J, Quezada N, Ramsing E, Keller M, Cherian G, Goddick L, Bobe G (2013) Effect of flaxseed supplementation rate and processing on the production, fatty acid profile, and texture of milk, butter, and cheese. Journal of Dairy Science 96:1177-1188

Osthoff G (2011) In: Fuquay JW, Fox PF, McSweeney PLH (eds) Encyclopedia of Dairy Sciences, Second edn. Elsevier, San Diego

Palmquist DL (1991) Influence of source and amount of dietary fat on digestibility in lactating cows. Journal of Dairy Science 74:1354-1360

Park YW (1991) Relative buffering capacity of goat milk, cow milk, soy-based infant formulae, and commercial nonprescription antacid drugs. Journal of Dairy Science 74:3326-3333

Rohm H, Weidinger KH (1993) Rheological behavior of butter at small deformations. Journal of Texture Studies 24:157-172

Sacks FM, Katan M (2002) Randomized clinical trials on the effects of dietary fat and carbohydrate on plasma lipoproteins and cardiovascular disease. The American Journal of Medicine 113:13-24

Schaffer B, Szakay D, Lorinczy D, SchAffer B (2001) Melting properties of butter fat and the consistency of butter, Effect of modification of cream ripening and fatty acid composition. Journal of Thermal Analysis and Calorimetry 64:659-669

Shukla A, Bhaskar AR, Rizvi SSH, Mulvaney SJ (1994) Physicochemical and rheological properties of butter made from supercritically fractionated milk fat. Journal of Dairy Science 77:45-54

Shukla A, Rizvi SSH (1995) Viscoelastic properties of butter. Journal of Food Science 60:902-905

Taylor MW, Norris R (1977) The physical properties of dairy spreads. New Zealand journal of dairy science and technology 12:166-170

TenGrotenhuis E, van-Aken GA, van-Malssen KF, Schenk H (1999) Polymorphism of milk fat studied by differential scanning calorimetry and real-time X-ray powder diffraction. Journal of the American Oil Chemists' Society 76:1031-1039

Vasic I, deMan JM (1968) Effect of mechanical treatment on some rheological properties of butter. Journal of Texture Studies 27:251- 264

Watson EL (1975). Thermal properties of butter. Canadian Agricultural Engineering 17:68-71

Iranian Food Science and Technology Research Journal
Vol. 13, No. 3, Aug. Sep. 2017, p. 66-79

نشریه پژوهشهای علوم و صنایع غذایی ایران
جلد 13، شماره 3، مرداد - شهریور 1396، ص. 79-66

خصوصیات حرارتی، بافتی و رئولوژیکی کره حاصل از شیر گاوی ارگانیک و شیر گوسفندی

مرتضی کاشانی‌نژاد[1]- سید محمد علی رضوی[2*]- مصطفی مظاهری طهرانی[2]- مهدی کاشانی نژاد[3]

تاریخ دریافت: 1394/02/08
تاریخ پذیرش: 1394/09/25

چکیده

دراین مقاله خصوصیات حرارتی، بافتی و رئولوژیکی کره حاوی آلفالینولنیک ناشی از تغذیه دام، کره گاوی تجاری وکره گوسفندی با پروفایل اسیدهای چرب مختلف مورد بررسی قرارگرفت. نتایج حاصل از اندازه‌گیری پروفایل اسید های چرب نشان داد که کره گوسفندی دارای مقادیر نسبتا بالاتری از اسیدهای چرب کوتاه زنجیر درمقایسه با کره‌های گاوی می باشد در حالی که کره گاو آلفالینولنیک دارای سطوح بالای CLA و اسید چرب آلفالینولنیک (امگا 3) است. همچنین با توجه به نتایج حاصل از آزمون نفوذ بالاترین میزان سختی در دمای 5 درجه سانتی‌گراد به نمونه کره گوسفندی و کمترین آن به نمونه کره آلفالینولنیک اختصاص داشت. در آزمون‌های رئولوژیکی دینامیک درآزمون کرنش متغیر برای نمونه‌های مختلف کره نشان داد که طول ناحیه ویسکوالاستیک خطی (LVE) برای کره با درصد بالاتر اسیدهای چرب اشباع شده بالاتر است و افزایش دما از 5 تا 20 درجه سانتی‌گراد نیز باعث کاهش LVE می‌شود. در آزمون فرکانس متغیر، وابستگی مدول‌های الاستیک و ویسکوز با فرکانس به‌صورت معادله قانون توان نشان داد نمونه‌های کره رفتار ویسکوالاستیک شبه جامدات با وابستگی اندک به فرکانس را دارند زیرا مقادیر 'K (0/02-2/78) بالاتر از مقادیر (0/002-0/83) "K بودند. در آزمون دما متغیر نیز مقادیر 'G و "G به‌طور پیوسته بین 5 تا 60 درجه سانتی‌گراد کاسته می‌شد و در کمتر از 40 درجه سانتی‌گراد، 'G بالاتر از "G بود که این امر رفتار شبه جامدات کره را در این بازه دمایی نشان می داد. همچنین در آزمون حرارتی DSC در منحنی ذوب چربی، سه پیک گرماگیر درنمونه های کره وجود داشت که پیک اول به میزان آب نمونه‌ها، پیک دوم به اسیدهای چرب غیراشباع و پیک سوم به اسیدهای چرب اشباع ارتباط داشت.

واژه‌های کلیدی: کره، DSC، GC، امگا 3، رئولوژیکی

---

1 و 2- دانش‌آموخته کارشناسی ارشد و استاد، گروه علوم و مهندسی صنایع غذایی، دانشکده کشاورزی، دانشگاه فردوسی مشهد
3- استاد، دانشکده علوم و صنایع غذایی، دانشگاه علوم کشاورزی و منابع طبیعی گرگان
(*- نویسنده مسئول : Email: s.razavi@um.ac.ir)