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Evaluation of physicochemical, rheological, textural and thermal properties of Mexican manchego-type cheese manufactured from goat's milk

Evaluación de las propiedades fisicoquímicas, reológicas, texturales y térmicas de queso mexicano tipo-manchego producido con leche de cabra

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Abstract
Cheeses made from goat's milk have gained importance in some regions of Mexico, where their diversification of their use beyond traditional sweets has attracted the attention of scientists and food technologists. In this work, Mexican manchego-type cheeses made with goat's milk (GC) at different stages of maturation (60 and 90 days) were subjected to physicochemical, texture (TPA), microstructure, rheological, and thermal characterization analysis. Comparisons with cheeses made with cow's milk (CC, 60 and 90 days) were done. In general, GC showed lower texture values and viscoelastic properties, with higher melting capacity and lower resistance to deformation because of heat treatment, with respect to CC. In addition, differences were observed in the microstructure, texture, and thermal properties with respect to the maturation time and the type of milk used. The characteristics of the cheeses were influenced by the moisture content and the maturation time in the samples, thus decreasing the texture properties and thermal stability, as the moisture decreased and the maturation time increased. After analyzing the cheeses in the maturation time, valuable information can be obtained for the agroindustry, after defining what is the appropriate maturation time for the manchego-type cheese, made with goat's milk, to produce a structure that exhibits the rheological properties, texture and melting of greater acceptance by the consumer, for use in Mexican gastronomy.
Keywords: Goat's milk, Mexican manchego-type cheese, microstructure, rheological properties, thermal analysis, TPA.

Resumen
Los quesos elaborados con leche de cabra han cobrado importancia en algunas regiones de México, donde la diversificación de su uso más allá de los dulces tradicionales, ha atraído la atención de científicos y tecnólogos de alimentos. En este trabajo, quesos mexicanos tipo-manchego elaborados con leche de cabra (GC) a diferentes etapas de maduración (60 y 90 días) se sometieron a análisis fisicoquímico, de textura (TPA), microestructura, reológico y caracterización térmica, y comparados con quesos hechos con leche de vaca (CC, 60 y 90 días). En general, GC mostró valores de textura y propiedades viscoelásticas menores, con mayor capacidad de fundido y menor resistencia a la deformación por efecto del tratamiento térmico, respecto a CC. Además, se observaron diferencias en la microestructura, textura y propiedades térmicas respecto al tiempo de maduración y al tipo de leche utilizada. Las características de los quesos se vieron influenciada por el contenido de humedad y el tiempo de maduración en las muestras, afectando así las propiedades de textura y estabilidad térmica, siendo mayores conforme disminuía la primera y aumentaba la última. Después de analizar los quesos en el tiempo de maduración, puede obtenerse información valiosa para la agroindustria, tras definir cuál es el tiempo adecuado de maduración para que el queso tipo manchego, elaborado con leche de cabra, produzca una estructura que exhiba las propiedades reológicas, textura y fundido de mayor aceptación por parte del consumidor, para su uso en la gastronomía mexicana.
Palabras clave: Leche de cabra, Queso mexicano tipo manchego, microestructura, propiedades reológicas, análisis térmico, TPA.

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1 Introduction

In recent decades, the demand for dairy products around the world has increased with a continuous growing trend (Lara & Alvarado, 2021). The national production of cow's milk represents third place in the national livestock production, accounting for 17.6%, just behind bovine's meat (30%) and poultry meat (23%) (SAGARPA, 2018), while goat's milk represents only 0.2% (SIAP, 2021). In 2020, world milk production grew up to 2% from last year, with a projected increase of 1.6% in the different regions of the world (FAO, 2021). Consumption of goat's milk and its manufactured dairy products has raised attention due to the high nutritive values and sensorial attributes, even superior to those of bovine's milk (Kováčová *et al*., 2021; Turkmen, 2017; Masotti, *et al*., 2012). Goat's milk is composed of 4% lipids (98% triacylglycerols), 3.5% of proteins, 4% of lactose, 1% ashes, and water, with an important content of minerals such as zinc, manganese, calcium, selenium, copper, and vitamins like vitamin A (retinol), vitamin B2 (riboflavin), and vitamin B3 (niacin) (Ferrerira Soares Cabral *et al*., 2020; Lima *et al*., 2016). Most goat's milk is marketed as unpasteurized products like sweets, fresh cheeses, gourmet quality dairy pastes, and hard cheeses especially used in gourmet products, which are mainly manufactured under traditional domestic processes, achieving higher prices per kilogram in the market and seen as refined products with high added value (Ferrerira Soares Cabral *et al*., 2020; Pulina *et al*., 2018; Andrade-Montemayor, 2017).

Cheese is one of the oldest and most popular dairy products, it is dating back several thousands of years, and today, it is found worldwide at the top of the foodstuff's charts due to its valuable nutrients and diversity (Oštarić *et al*., 2022; Vásquez *et al*., 2018). Cheeses are made from different types of milk and production technologies, its production is associated with the chemical and enzyme reactions that lead to the transformation of the curd into cheese products (Darnay *et al*., 2018), also including the ripening process that outcomes in a great number of products with specific characteristics and developed texture, shape, and flavor attributes (Nájera *et al*., 2021). Commonly, the quality of cheese products, fresh or matured, is influenced by the origin of the milk, the chemical and microbiological properties, the type, the concentration of started cultures added, and the time and temperature during the ripening stage, affecting the chemical processes during its production and maturation (Jiménez-Fernández *et al*., 2021; Lei & Sun, 2019; Everett & Auty, 2017; Guerra-Martínez *et al*., 2012). Nowadays, globalization and industrial advancements have led to reducing or losing some dissimilarities between products from specific regions, leading to producers being distinguished based solely on the quality of milk and the selection of dairy cultures and rennet (Oštarić *et al*., 2022; Nieto-Arribas, *et al*., 2009).

In Mexico, there are more than forty varieties of "artisan" cheeses produced under traditional processing (García-Valladares *et al*., 2022), demanding, together with industrialized cheese, just over 25% of the total milk production in the country (Vallejo Córdoba, 2021). These cheeses are produced mostly using cow's milk, whereas a lower amount is produced using sheep and goat's milk (González-Córdova, *et al*., 2016). Mexican manchego-type cheese is known as a semi-hard cheese made with pasteurized cow's milk and matured during 14 to 30 days for developing a mild flavor and texture, similar in taste to Colby or mild cheddar cheese (Lobato-Calleros *et al*., 2002), and consumed preferably in hot dishes such as *quesadillas*, *burritos*, cakes, and snacks.

There are few manufacturers of Mexican manchego-type cheese made with goat's milk (GC), besides the lack of information available in the literature about its characteristics, this work is a pioneer in providing a characterization for GC. Thus, the objective of this work is to evaluate the physicochemical, texture, thermal, and rheological properties of GC at different maturing stages (30, 60, and 90 days) and comparison with those developed by a manchego-type cheese made with cow's milk (CC).

2 Materials and methods

2.1 *Experimental material*

Samples of Mexican manchego-type cheese made with goat's milk (GC) and Mexican manchego-type cheese made with cow's milk (CC) matured for 60 and 90 days were produced and donated by Productos Alimenticios Oly S.P.R. de R.L. company (Apaseo el Grande, Guanajuato, Mexico) following their manufacturing practices and processes. Maturation times for manchego-type cheeses were established based on the common processes handled by the manufacturers. The milk used for the GC and CC production was obtained from milking Saanen, Alpine, and cross goats breeds (fat 38.81±0.02 g/L; protein 36.90±0.1 g/L; solids not fat (SNF) 86.10±0.25 g/L; density 1.03 g/mL and acidity 18 °D), or Holstein's cows (fat 34.50±0.30 g/L; protein 31.24±0.12 g/L; SNF 87.40±0.30 g/L; density 1.029 g/mL and acidity 17 °D) reared in barn conditions, respectively. The GC and CC samples were matured in maturation chambers during the different maturation times. Treatments were labeled by adding the maturation time to each sample abbreviation and stored at 4 °C until use.

2.2 *Proximal chemical analysis of cheeses*

GC and CC samples were pierced with a 1 cm of diameter hole puncher and cut at 1 cm height. The moisture, fat, protein, and ash contents were determined according to the methodologies described by the Standard Association of Official Analytical Chemists (AOAC, 2019). Based on this data, the content of fat in dry matter (FDM) and the moisture in non-fat substance (MNFS) were determined using Equations 1 and 2 (D'Incecco *et al*., 2020). The pH was recorded using a potentiometer (Orion STARA111 Benchtop pH meter, Thermo Scientific Inc, USA) after maceration of cheese sample in distilled water.

$$FDM = \frac{\text{Fat content}}{100 - \text{Moisture content}} \times 100, \tag{1}$$

$$MNFS = \frac{\text{Moisture content}}{100 - \text{Fat content}} \times 100. \tag{2}$$

2.3 Microstructure

Samples taken from the center of each GC and CC piece were cut with a hole puncher in a cylindrical shape with dimensions of 0.5 cm diameter and 0.3 cm height and prepared according to the method described by Sandoval-Castilla *et al*. (2004). For protein binding, the samples were immersed in a 2% glutaraldehyde solution in a phosphate buffer (PBS; 0.2 M, pH 7.2) at room temperature (20 ± 2 °C) for 2 h. Later, samples were subsequently decanted and re-immersed in glutaraldehyde solution for 24 h. The fixed samples were washed with PBS solution and immersed in a 1% osmium tetroxide in PBS for 2 h to fix the lipids. Then, samples were washed with PBS and dehydrated in a gradual series of ethanol solutions (30, 50, 70, 90 % v/v, and absolute ethanol), maintaining them for 1 h doing two changes of solvent at each concentration. Samples were dried at a critical point with carbon dioxide dryer (Critical Point Dryer equipment, Technics CPA II, Tousimis, Rockville, MD). The dried samples were fragmented and mounted in the sample holders. Finally, they were coated with gold under vacuum in a Fine Coat equipment (Jeol Ltd, Jeol JFC-1000, Akishima, Japan). The microstructure of GC and CC samples was examined with a high vacuum scanning electron microscope (Jeol Ltd, Jeol JSM-035, Akishima, Japan) at 20 kV and magnification of 3500X.

2.4 Texture profile analysis (TPA)

The instrumental evaluation of the texture in the GC and CC samples was analyzed by a TPA test, using a Texture Analyzer (Stable Micro Systems, TA-XT2i, U.K.), a 25 kg load cell and a cylindrical aluminum probe of 50 mm diameter. The samples were cut into cylinders (10 mm diameter x 10 mm height) and stored overnight at 4 ºC in closed containers. The analysis was performed by compressing the cheese sample to 40% strain at rate of 5 mm/s during the pre-test, 1 mm/s during the test, and 5 mm/s for the post-test, respectively. The tests were performed immediately after removing the samples from the refrigerator, and carried out at 20 ± 0.5 °C. The textural characteristics obtained from the force-time and force-distance curves were hardness, cohesion, adhesiveness, gumminess, and chewiness (Vyhmeister *et al*., 2019; Lobato-Calleros *et al*., 2002).

2.5 Rheological characterization

The rheological characterization of GC and CC samples was carried out in a rheometer equipment (Anton Paar Messtechnik, Physica MCR 301, Stuttgart, Germany), using a crosshatched plane plate geometry of 50 mm diameter. Disc-shaped samples were taken from the center of each cheese (50 mm diameter x 5 mm thickness), placed in the measurement plate and left rest for 30 min prior testing. All samples were loaded at 20 ± 0.5 ºC and covered with a thin layer of silicone oil to minimize evaporation during tests. Results were analyzed using the software of the equipment (Anton Paar Physica, US200, Germany). Oscillatory strain sweep tests were performed in a strain range from 1-50% to establish the linear viscoelastic zone (LVZ) at a frequency of 1 Hz. The temperature sweep test was performed from 25 to 70 °C at a rate of 5 ± 0.05 °C/min, at a constant frequency of 1 Hz within the LVZ range (Butt *et al*., 2020; Lobato-Calleros *et al*., 2003). Measurements were performed in triplicate for each stage of maturation of the GC and CC and the data were used to determine the change on the storage (G') and loss (G") moduli with temperature.

2.6 Melting test

Meltability in GC and CC was evaluated by using a modified Schreiber test. Manchego-type cheeses were cut into discs (20 mm diameter x 5 mm height) and preconditioned at 4 ± 1 °C for 30 min prior to testing. Samples were placed on a petri dish (10 cm diameter, 1.5 cm height) and covered with wax paper and heated in a microwave oven (800 W) for 1 min (T~ 100 ºC) at 20 % of the power. The samples were cooled for 30 min at room temperature. The diameter of melted samples was measured with a vernier (Steren, HER-411, China) in at least five different positions (45º) and the percentage of extensibility was calculated as the increase in the mean diameter (Ramírez-Navas, 2010), and the area index (AIn) was calculated using the Equation 3, as reported by Schädle *et al*., (2020).

$$AIn = \frac{A_m - A_0}{A_0} \times 100\%, \tag{3}$$

where A_m is the area of melted manchego-type cheeses and A_0 is the area of the original unheated cheeses. All the measurements were determined 5 times for each cheese batch.

2.7 Differential scanning calorimetry (DSC)

The thermal properties of GC and CC samples were analyzed using a differential scanning calorimeter (TA Instruments, DSC Q-1000, New Castle, USA) previously calibrated with Indium (Melting point = 156.6 °C, melting ΔH = 25.8 J/g). The GC or CC samples (~ 30 mg) were placed into aluminum pans, weighed, and hermetically sealed. An empty sealed aluminum tray was used as reference. All the treatments were subjected to heating at a rate of 5 °C/min from 25 °C to 100 °C, and then cooled to 25 °C at a cooling rate of 5 ºC/min (Tomaszewska-Gras *et al*., 2019; Liu *et al*., 2008).

2.8 Statistical analysis

All the tests were done at least by triplicate. TPA analysis was performed by six repetitions. An ANOVA data analysis was performed with Minitab 18.0 statistical software (Minitab Inc., State College, PA, USA). Significant differences between means were established by applying a Tukey's test at a 95% confidence level ($p \leq 0.05$).

3 Results and discussion

3.1 Physicochemical composition

The composition of manchego-type cheeses samples is shown in Table 1. The maturation time did not have a significant ($p > 0.05$) effect on the pH of GC samples, while the CC samples displayed lower pH ($p \leq 0.05$) as the maturation times were longer. According to Van Hekken *et al*. (2017), the imperceptible changes in pH of matured cheeses, such as manchego-type cheeses, can be attributed to the low activity of microorganisms to decompose the lactose substrate, and specifically in GC, closely related to the lower lactose content in the goat's milk *versus* cow's milk (Claeys *et al*., 2014). Moisture shows significant differences ($p \leq 0.05$) between treatments, GC displayed higher ($p \leq 0.05$) moisture content after maturing for 60 days, however, water loss in CC occurred was lesser. Similar behavior has been reported for Swiss cheese (Sapna & Sharmili, 2018), Lighvan cheese made with sheep's milk (Aminifar *et al*., 2010), and in goat's cheese (Burgos *et al*., 2016), where physicochemical characteristics, maturation conditions, and the changes suffered during the cheese matrix formation determined the moisture retention capacity.

Ash content for GC did not exhibit significant differences ($p > 0.05$) during the maturation process, while CC showed a significant decrease with longer maturation time. This behavior may be associated with the lower pH values in CC that led to a greater solubilization of minerals and their expulsion through the cheese whey, this behavior was reported for buffalo's Mozzarella cheese (Gulzar *et al*., 2019). Regarding the total solids content, the GC samples showed higher content of total solids as longer maturation time followed, meanwhile CC samples did not present significant changes. This behavior is attributed to the mineral content in goat milk, which is usually higher than that found in bovine's milk, and to the moisture content found in cheeses at each of the maturation times used (Park, 2011), a similar behavior was reported by Bontinis *et al*. (2008) for Xinotyri, a traditional Greek cheese from raw goat's milk. The fat content in GC was significantly higher (33.33-34.67 g/100g) than that in CC (29.33-31.17 g/100g), the FDM was also higher for the first (48.63-48.97%) with a significant reduction at maturation times longer than 60 days, FDM for CC remained without significant changes. In agreement with D´Incecco *et al*. (2020), cheeses destined to a prolonged maturation process are desirable to retain larger contents of fat to achieve a cheese structure softer, especially when moisture contents are low. Based on the Codex Alimentarius and the International Dairy Federation (2021), MNFS not only allows to exclude the variability of fat content on cheese moisture, but also is used for classifying the firmness designation of cheeses. When MNFS is <51 %, cheeses are designated as extra hard classification, as exhibited by GC and CC maturated during 60 and 90 days.

Table 1. Effect of maturation time on the physicochemical composition of GC and CC.

Physicochemical characteristics	Maturation time (days)			
	60	90	60	90
	GC		CC	
pH	6.18±0.02^a	6.17±0.02^a	5.97±0.03^b	5.85±0.01^c
Moisture content (g/100g)	33.02±0.39^b	28.71±0.68^d	34.60±0.76^a	32.45±0.19^c
Total solids content (g/100g)	66.98±0.39^b	71.95±1.60^a	65.40±0.76^c	67.55±0.19^b
Ashes (g/100g)	5.10±0.22^b	5.70±0.31^a	5.46±0.07^a	4.55±0.47^c
Protein (g/100g)	38.43±0.06^c	38.63±0.20^c	45.20±0.11^b	46.10±0.10^a
Fat (g/100g)	33.33±0.58^b	34.67±0.58^a	29.33±0.58^d	31.17±0.29^c
FDM (%)	49.77±1.16^a	48.63±1.41^a	48.97±1.48^a	46.14±0.56^b
MNFS (%)	49.53±1.02^a	43.95±0.91^c	48.97±1.48^{ab}	47.15±0.47^b

FDM means fat in dry matter; MNFS means moisture in nonfat substance. Different superscripts in the same row represent significant differences among treatments ($p \leq 0.05$).

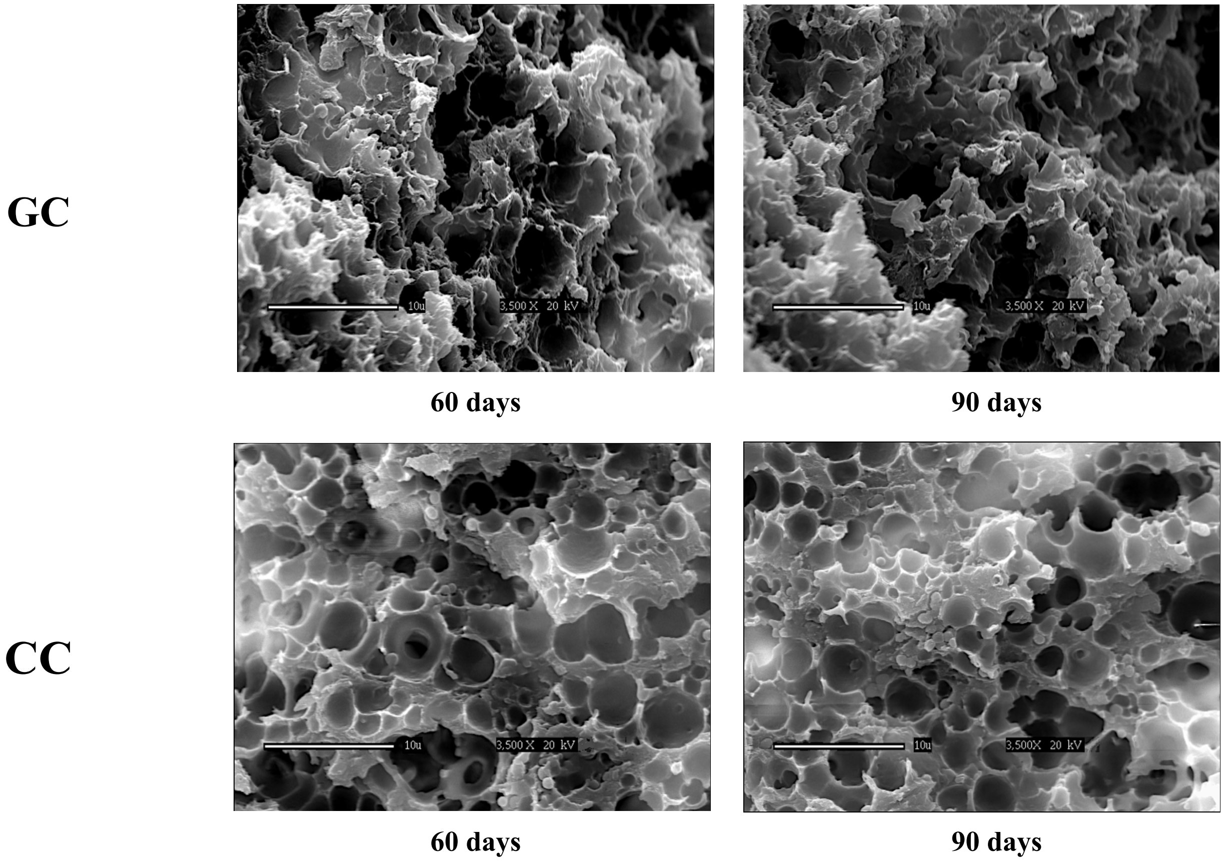


Figure 1. SEM micrographs for manchego-type cheeses made with goat's or cow's milk at different maturation times.

For the protein content, GC displayed contents significantly lower than those of CC, with a decreasing trend for the first and an opposite behavior for the second, as the maturation time increases. These results agree with those reported by Ochoa-Flores *et al*. (2021) for manchego-type cheeses made with cow's milk and by Medina & Nuñez (2017) for cheeses made with goat's milk.

3.2 Microstructure

The microstructure for GC and CC samples, obtained by SEM observations, is shown in Figure 1. Three-dimensional structures were observed for all the samples with uniform and smoother protein matrix with a honeycombing structure (Islam *et al*., 2022), besides the presence of protein aggregates and multiple globular voids (largest diameter ∼ 6 μm) in which fat globules were possibly housed. The formation of channels within the cheese matrix is attributed to the exit of whey during the drying process of samples. Small spherical structures appeared to be attached to the protein matrices in the form of grapes clusters, characteristic of the lactic acid bacteria used during the milk fermentation process. In GC at 60 and 90 days (Figure 1a-b), some whey channels are observed in greater quantity, probably be due to the moisture content, and well-defined globular spaces associated to the fat globules housed within the protein matrix. As maturation time extent, less structured and more fused matrices were observed with closer protein matrices and more irregular geometry enveloping to the fat globules. SEM images for CC (Figure 1c-d) exhibited more open, relaxed, and more compact structure with less fused protein matrix. This behavior is associated to the lower sensitivity to cheddarization in samples made with cow's milk rather than goat's milk (Islam *et al*., 2022; Zady *et al*., 2019; Tunick *et al*., 2012). Regarding the maturation time evaluated in the CC (Figure 1c-d), a more compact protein matrix was found without significant changes on the structure in CC at 60 and 90 days, however, a reduction in the spaces where fat globules were housed can be observed. Soodam *et al*. (2017) mention that the changes that occur in the structure of the protein matrix in cheese are associated with to the proteolytic activities occurred during maturation and storage time.

3.3 Texture profile analysis (TPA)

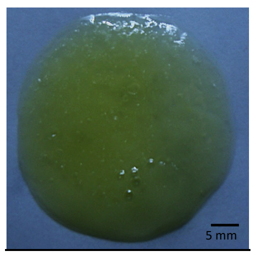
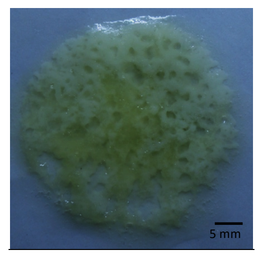
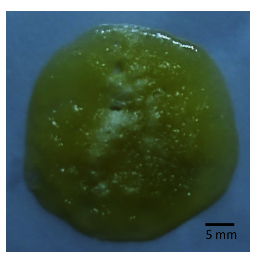
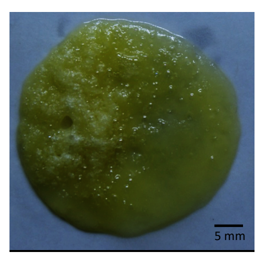
Textural analysis for GC and CC cheeses at different maturation times is shown in Table 2. Hardness represents

Table 2. Textural parameters in GC and CC at different maturation times.

Textural parameter	Maturation time (days)			
	60	90	60	90
	GC		CC	
Hardness (N)	23.81±4.96^{c}	36.53±1.08^{b}	26.82±2.05^{c}	69.84±1.58^{a}
Springiness (-)	0.935±0.008^{b}	0.936±0.004^{ab}	0.888±0.001^{c}	0.948±0.010^{a}
Cohesiveness (-)	0.69±0.03^{a}	0.61±0.02^{b}	0.74±0.02^{a}	0.53±0.03^{c}
Adhesiveness (N·s)	-0.89±0.05^{a}	-0.80±0.07^{ab}	-0.70±0.06^{bc}	-0.67±0.02^{c}
Gumminess (N)	16.29±0.77^{c}	22.36±1.12^{b}	20.17±0.97^{b}	37.11±1.60^{a}
Chewiness (N)	15.24±2.57^{c}	20.93±1.01^{b}	17.62±1.38^{c}	35.21±1.53^{a}

Different superscripts in the same row represent significant differences among treatments ($p \leq 0.05$).

Table 3. Final images, melting and AIn for manchego-type cheeses made with goat's and cow's milk at different maturation times.

GC		
Maturation time (days)	60	90
		
Melting (%)	129.22±6.28^{a}	92.85±2.70^{b}
AIn (%)	425.68±40.72^{a}	271.96±14.73^{b}
CC		
Maturation time (days)	60	90
		
Melting (%)	89.17±2.35^{a}	85.67±2.43^{b}
AIn (%)	257.89±12.57^{a}	244.77±12.76^{a}

Different superscripts in mean values mean significant differences ($p \leq 0.05$) between treatments.

the maximum force needed to achieve a given deformation during the first compression in a food product, similarly to that experienced at the first bite, indicating the crunchiness, crumbliness, or brittleness in food. In manchego-type cheeses samples, the hardness exhibits a dependence with the maturation time, harder cheeses were obtained as longer maturation times were set. This property is closely related to the content of fat, moisture and the acidity reached, where the fat content in cheeses has been inversely correlated to their hardness, because fats disintegrate the protein structure, resulting in a softer texture (Junyusen *et al*., 2017). Regarding the type of milk used for producing manchego-type cheeses samples, CC treatments had significantly higher hardness than those obtained for GC at each maturation time tested. Springiness is related to the recovery of deformation of samples after the compression process, as shown in Table 2, GC did not exhibit significant differences in this parameter despite the different maturation times, nevertheless CC showed the lowest springiness value at 60 days and the highest after 90 days. Cohesiveness is commonly related to the strength of internal bonds such as protein-protein interactions (Aguilar-Raymundo *et al.*, 2022) within the cheese matrix, in both cases the magnitude of this parameter was increased at higher moisture content in the samples and reduced as the maturation time was prolonged. Adhesiveness is the amount of work necessary to overcome attractive forces of the food to a different contact surface and translated to the stickiness sensation. This parameter was significantly higher ($p \leq 0.05$) for GC at 60 days when compared to CC at the same time but remaining without change for the same sample at the rest of maturation times, indicating greater resistance to deformation associated to a more structured protein matrix in the GC. In the case of gumminess and chewiness, these parameters are related to the energy required for disintegrating or chewing a solid-like food until it can be swallowed, in both GC and CC, gumminess and chewiness increase as the maturation time was longer achieving their maximum at 90 days (Table 2). This textural behavior is influenced by the composition of the raw milk used for processing the cheese, depending strongly on the moisture, protein, and fat contents (Fox *et al*., 2017).

3.4 Melting test

Table 3 shows the images of final manchego-type cheeses samples after being melted. GC showed significantly higher melting percentage than CC. GC at 60 days showed significantly higher melting and AIn than those at 90 days. CC showed significant lower melting and AIn for both maturation times than those exhibited by GC. Cais- Sokolińska *et al*. (2017) and Everett & Auty (2017) found that melting in cheeses can be improved by the content of caseins, fat, and moisture, since these components contributes to the proteolysis, further casein-water interactions, and changes in the hardness due to moisture reduction and variations in temperature occurred during the maturation time.

3.5 Rheological characterization

Manchego-type cheese as many other foods is considered as a viscoelastic material, this means that it has both the elastic (solid-like) and viscous (liquid-like) components when submitted to small amplitude or frequency oscillation, these components are defined by means of the storage or elastic modulus (G'), which is proportional to the number and strength of the interactions present in the matrix and measures the rigidity of the sample, and by the loss or viscous modulus (G"), that measures the flow properties of the sample (Kasapis & Bannikova, 2017; Bourne, 2002). In this work, the viscoelastic moduli (G' and G") as function of temperature for both GC and CC, as shown in Figure 2. The G' modulus exhibited higher values than G" modulus with a decrease trend as the temperature raises in both type of manchego-type cheeses and displaying an increase in the $\tan\delta$ profiles despite of the maturation time. This behavior

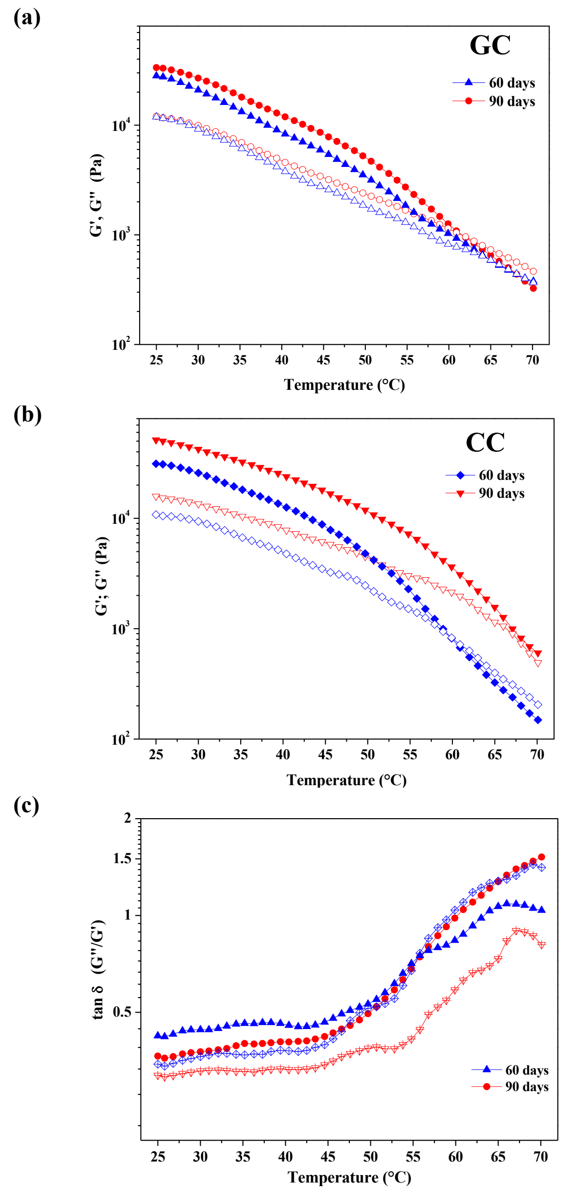


Figure 2. Effect of temperature on the viscoelastic moduli, G' (filled symbols) and G" (empty symbols), for GC (a), CC (b), and c) $\tan\delta$ for GC (filled symbols) and CC (empty symbols) at 60 and 90 days of maturing, respectively.

can be attributed to the restructuring of the protein matrix that is weakened by the effect of the increased temperature. Besides, it can be observed that CC (Figure 2b) samples, have a more elastic structure with a greater capacity for recovery in the face of the application of external stress and thermal treatment compared to that exhibited by the GC treatments (Figure 2a). The maturation time had a significant effect on the viscoelastic properties, for GC at 60 days of maturation showed the lowest G' and G" values, whereas at 90 days of maturation, the manchego-type cheeses achieved the highest elastic behavior. In both GC and CC treatments at 90 days of maturation, higher moduli values were observed, displaying lower magnitude when manchego-type cheeses are matured for 60 days. The viscoelastic properties of samples submitted to thermal treatments are associated to the moisture content in cheese at the different maturation times, while decreasing the moisture in the cheese, an increase in the intermolecular interactions occurred due to the protein content, this means, at higher moisture content the swelling of caseins is stimulated, limiting the molecular interaction within the cheese matrix, and exhibiting a weaker structure and lower G' values (Liu *et al*., 2008). In this sense, GC at 60 days of maturation, showed the lowest values for the G' and the highest moisture content.

Figure 2c shows the evolution of $\tan\delta = G''/G'$ during the temperature swept. This property is used for determining the elastic-dominant ($\tan\delta < 1$), viscous-dominant ($\tan\delta > 1$), or elastic-viscous paired behavior ($\tan\delta = 1$) of materials, signaling the more elastic (solid-like) or more viscous (liquid-like) properties of the materials (Zheng, 2019; Kasapis & Bannikova, 2017). It was observed that approximately at 57.5 °C an abrupt increase in $\tan\delta$ is observed for both GC and CC, suggesting the transition from elastic behavior (more solid-like) to a more viscous-like behavior while raising the temperature, indicating the point where samples start to flow more easily due to the breakdown of the protein structures within the protein matrix, becoming them into a more fluid material. Similar results have been found by Solhi *et al.* (2020), who reported $\tan\delta$ values greater than one in processed cheeses at temperatures between 57.5-59.7 °C, and by Pastorino *et al.* (2002), who attributed these changes to the modifications suffered by the cheese structure with the increase of temperature, causing changes in the scope and nature of the protein interactions. Other works where similar behaviors are reported includes the American processed cheese (Lu *et al*., 2002), Gouda type cheese (Schenkel *et al*., 2013), Gruyere, Raclette, Edam, Brie and Mozzarella cheeses (Schenkel *et al*., 2014), Cheddar cheese (Brickley *et al*., 2007), processed cheese (Hosseini-Parvar *et al*., 2015) and Mexican Manchego cheese (Lobato-Calleros *et al*., 2003).

3.6 Differential scanning calorimetry (DSC)

Thermal properties of manchego-type cheeses obtained by DSC are shown in Figure 3. GC showed lower resistance to heat flow than CC, needing a lower amount of energy for exhibiting their melting, agreeing with the melting index (Table 2). Regarding the maturation time, GC at 60 days of maturation seems to absorb less heat to present the fusion process, increasing the absorption of energy as the maturation time was longer. The CC at 90 days showed the greatest amount of heat flow for reaching the melting point, this behavior agrees with the physicochemical and

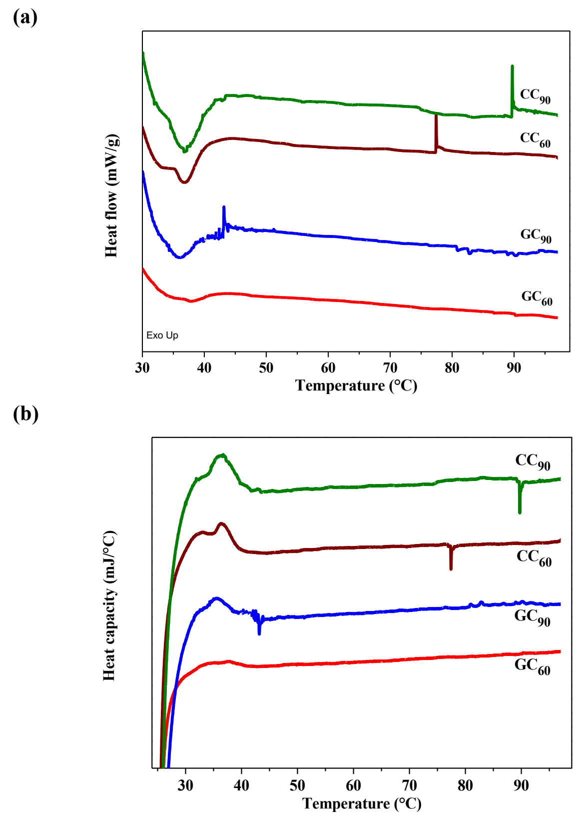


Figure 3. DSC thermograms for a) Hear flow and b) Heat capacity of GC and CC at different maturation times.

structural properties. Mattice & Marangoni (2019) states that the fat content is the component in foods that will display melting in the range of 0-60 °C, nevertheless, cheeses are complex food systems where several casein-casein, casein-fat globule, protein-water interactions are occurred simultaneously, largely affecting their heat capacity. For both GC and CC, endothermic signals were observed at GC60= 37.89 °C, GC90= 36.12 °C, CC60= 36.78 °C and CC90= 36.89 °C, respectively, which are related to the melting process in each sample. These results are comparable with those obtained by Gliguem *et al*. (2011) who reported that the melting temperature range in processed cheese was 32-38.6 °C, whereas Ramel & Maragoni (2017) found this point between 24-40 °C. For CC60 and CC90, an exothermic signal was observed at 77 and 90 °C, respectively. In agreement to Zhu & Damodaran (2011) and Fitzsimons *et al*. (2007), the observation of exothermic signals at relatively high temperatures (>60°C) may be associated to the protein aggregation/denaturation phenomena. While it is known that the protein denaturation results in endothermic signals in the DSC, since heat absorption is required to induce the breaking of intramolecular bonds (non-covalent and disulfide), it is also reported that the aggregation of denatured protein molecules promotes the formation of new bonding interactions, from which exothermic processes are expected to arise. Therefore, the application of heat in cheese samples causes the partial denaturation and reorganization of their components, such as caseins, fatty globules, and whey proteins having a direct influence on their stability and resistance to thermal treatments (Smith *et al*., 2017). In the GC samples, the exothermic signals were not observed.

Conclusions

The textural characteristics conferred by the components of goat's milk to the cheese were reflected in GC products that were less hard, with higher adhesiveness and a higher meltability compared to CC. In turn, the use of goat's milk in the production of manchego-type cheeses generated modifications in the rheological behavior, obtaining products with less viscoelastic character compared to those made with cow's milk during the evaluated maturation time. The micrographs of the GC and CC allowed the observation of the structural components of the cheeses, mainly the behavior of the protein matrix and fat globules during the maturation of the cheeses. The DSC results infer that CC presented a greater structural stability before the application of temperature compared to GC, the latter requiring a lower amount of energy to melt. Components such as moisture, fat content and protein mainly, as well as the maturation time affected to a greater or lesser extent the textural, structural, rheological and thermal characteristics of GC, providing information for its characterization.

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