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The Quantification of Fatty Acids, Color, and Textural Properties of Locally Produced Bakery Margarine

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Abstract: This study focused on the analysis of bakery margarine samples divided into three groups according to physical-chemical analyses of their fat and water content. A Gas Chromatograph-Mass Spectrometer (GC-MS) was used for the evaluation of fatty acids, and from 37 fatty acids studied, only 18 were quantified. The highest concentration was occupied by the long-chain saturated fatty acids category (C14:0–C20:0), ranging between 85.61 µg/mg and 127.30 µg/mg. The dominant fatty acid was palmitic acid for all margarine samples. The texture parameters (hardness, mechanical work of plastic deformation, and fracturability) analyzed in this study with three different penetrometers and a puncture test showed that bakery margarine is a hard plastic material with a pronounced fracturability. The margarine's fracturability varied from 0.35 N to 8.23 N. The highest values were measured using the 10 mm diameter spherical penetrometer. Of the outside and inside evaluated color parameters, only the b* color parameter indicated an influence on the principal component analysis samples' projections; its values are also positively correlated with polyunsaturated fatty acids (PN).

Keywords: bakery margarine; fatty acids; fracturability; color; PCA

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1. Introduction

Food emulsion represents a mixture of two non-miscible phases, with one of the phases being dispersed as small spherical drops in the other one [1].

In food technologies, emulsions take place partially or totally in the structures of various natural (milk, cream, butter) and processed (ice cream, mayonnaise, margarine, cake batters) food products. Certain foods are already emulsified in some phases of production; emulsion science has an important role in quality assurance and improving food quality or production techniques benefiting from emulsion principles [2].

Margarine was produced for the first time in 1869 by Hippolyte Mège Mouriès as a spreadable butter substitute and is a much cheaper water-in-oil (W/O) emulsion than butter. In addition to water, the aqueous phase also contains preservatives and salt, while the fatty phase represents a mixture of liquid oil and crystalline fat that confers texture and consistency to the margarine [3,4]. The solid or semisolid structure of margarine is attained by the fat crystal aggregate matrix, in which small drops of water are entrapped. The most commonly used emulsifiers are represented by lecithin, mono-and diglycerides of fatty acids, diacylglycerol, and distilled monoacylglycerol, to which are added antioxidants, dyes, vitamins, and flavorings [5].

According to the Codex Alimentarius [6], margarine is defined as a food in the form of a plastic or fluid emulsion that is mainly composed of a minimum of 80% m/m fat phase and a maximum of 16% m/m aqueous phase. In addition to this type of margarine, there are also variants with a lower fat content (less than 80% fat), whose role is to reduce caloric intake and reduce heart disease risk.

Since its invention, margarine has been modified and improved, resulting in the development of the range of products now available on the market that can be used for spreading, baking, or cooking. The physical characteristics of margarine are influenced largely by the physical properties of oil triacylglycerols, the total solid fat content, the fat's polymorphic state, and also the distribution of these solid fats [7]. The properties of triacylglycerols that are of great importance for margarine include the number of carbons in the fatty acid chain, the degree of unsaturation, and the main fatty acid [3].

Generally, to obtain margarine, vegetable oil is subject to technological operations to become semisolid or solid, depending on the desired final functionalities. Hydrogenation, interesterification (enzymatic and chemical), fractionation, and blending are the main technological operations used by the margarine industry to harden oils to desirable degrees [8].

Initially, the non-selective hydrogenation process led to products with a high concentration of saturated fatty acids (the most abundant fatty acid was stearic acid) and disagreeable textural characteristics, but the selective hydrogenation technique reduced the fatty acids' saturation. Thus, the most abundant fatty acid was oleic acid, which contributes to the softness and spreadability of margarine. Selective hydrogenation has the disadvantage of producing trans-fatty acids, which are known to have a negative effect on human health [9,10].

Recently, the European Union regulated the content of trans fats (other than trans-fat naturally occurring in the fat of animal sources) in food intended for the final consumer and food intended for supply to retail, at a limit of a maximum of 2% [11].

Depending on fat hardness and the melting point, margarine can be classified into hard and medium plastic margarine used for cooking or baking (bakery margarine) and medium plastic and soft margarine, known as table margarine (spreadable margarine) [3].

Both the textural and rheological properties of emulsions and margarine, respectively, are very important for consumers and also for industry. The rheological properties are important practical properties during processing, whereas in the final product, the textural properties represent the significant factor of mouthfeel. Good margarine should not present with oil separation, discoloration, hardening, sandiness, graininess, or water separation [12].

Taking into account the above, when it comes to margarine, its quality is influenced by the type, quantity, and mixture of oils and also by the technology applied. Therefore, the purpose of this study was to investigate the chemical composition and the fatty acid concentration of locally produced margarine used by bakery manufacturers in close correlation with textural properties like hardness, fracturability, and plasticity measured with different penetrometers; additionally, color parameters were evaluated.

2. Materials and Methods

The materials used in this study were represented by locally (Romania) produced margarine (n = 9) used by bakery manufacturers. The margarine was from the same producer and, based on the fat/water content, was classified into 3 categories (M1, M2, M3). The margarine samples were stored in refrigerated conditions at 8–10 °C until further analysis.

2.1. Physicochemical and Color Analysis

The fat content of margarine samples was conducted according to Toma et al. [13] using the Soxhlet method and petroleum ether as extraction solvent. The results were expressed as percentages by mass. The moisture content was evaluated by heating 5 g of margarine sample at 103 °C ± 2 °C until a constant weight was achieved [14,15].

Both outside and inside color parameters of margarine samples were evaluated using a ChromaMeter CR-400 from Konica Minolta (Konica Minolta, Japan) based on the CIE L*a*b* (Commission Internationale de l'Eclairage) uniform color space method and using the C illuminant [16]. The measured and calculated parameters were: L*—brightness, a*—red-green parameters, b*—yellow–blue parameters, h^0—hue angles, WI—whiteness indexes, C*—color intensities, YI—yellowness indexes, and ΔE*—color differences [17].

2.2. Fatty Acid Composition Analysis

The fat was extracted from the margarine samples at 50 °C, and the resulting fat phase was filtered through filter paper with anhydrous Na_2SO_4 [18]. The fatty acid methyl ester (FAME) preparation assumed the solubilization of margarine's fat in n-hexane. Then, 0.2 mL methanolic potassium hydroxide (2 mol/L) was added as a transesterification agent, following the method described by Jirarattanarangsri [19]. The standard used contained a FAME mix of 37 components (FAME Mix, Restek, Bellefonte, PA, USA), and the identification of margarine FAME was made by comparing their retention time with those of the FAME mix standard. Additionally, the resulting mass spectra were confronted with the ones from the GC-MS database (NIST MSSearch 2.0). The GC-MS (GC MS QP 2010 Plus, Shimadzu, Kyoto, Japan) following the method described by Oroian et al. [20], using a SUPELCOWAX10 capillary column (60 m length, 0.25 mm in diameter, with 0.25 µm film thickness, Supelco Inc., Bellefonte, PA, USA) and helium gas with a flow rate of 0.8 mL/min and a split ratio of 1/24; the injection volume was set at 0.001 mL.

2.3. Textural Evaluation

The texture parameters of margarine samples were evaluated with a Mark 10-ESM 301 (Mark 10 Corporation, Copiague, NY, USA) texturometer using three penetrometers of different geometries (120° conical penetrometer—4 mm penetration, 5 mm diameter spherical penetrometer—2 mm penetration, and 10 mm diameter spherical penetrometer—4 mm penetration). The MESUREgauge software was used for data collection at a reading rate of 5 points per second, and the curves were represented as force (expressed in Newtons) versus travel (expressed in millimeters). The cubic (side of 30 mm) margarine samples were tested at a speed of 10 mm/min. The measured texture parameters were: hardness, plasticity, and fracturability. Hardness (H) was calculated as the maximum force recorded at the end of the penetration. Plasticity (P) was calculated as the positive area/work under the penetration curve and was expressed as (N·mm or mJ). The margarine fracturability (F) was quantified as the height of the peaks of the force-penetration curves and expressed in Newtons [21,22].

All reagents used for physicochemical and fatty acid composition analysis were of analytical grade (Sigma Aldrich, Darmstadt, Germany).

2.4. Statistical Analysis

The results were expressed as the mean of three measurements, and the difference between the analyzed margarine samples was studied by one-way ANOVA; variance analysis was executed with STATGRAPHICS CENTURION XVI software (Trial Version). The OriginPro software was used to perform principal component analysis, while the Pearson correlation matrix was obtained by SPSS 13.0 software (Chicago, IL, USA).

3. Results and Discussion

Margarine is commonly consumed in various diets because it is cheaper than butter, contains no cholesterol, and many consumers consider that margarine has a lower atherogenic index than butter [23]. In Romania, according to the Population Consumption Availability report from recent years (2017–2019), the consumption per capita of margarine varies between 3.4–4.1 kg per year. This is a much larger amount than butter, which has an annual average consumption per capita of 0.7–0.8 kg [24,25].

3.1. Physicochemical and Color Analysis

Figure 1 shows the average fat and moisture results of margarine samples, and it can be noticed that fat content ranged between 58.96% and 76.16%, while moisture content ranged between 22.93% and 39.66%. The M1 margarine samples presented a lower amount of fat, while the moisture content had high values. In contrast, the M3 samples presented a high fat content and a low moisture content. The M2 margarine samples had an average fat content of 69.63% and a moisture content of 29.50%. The determined protein content was insignificant.

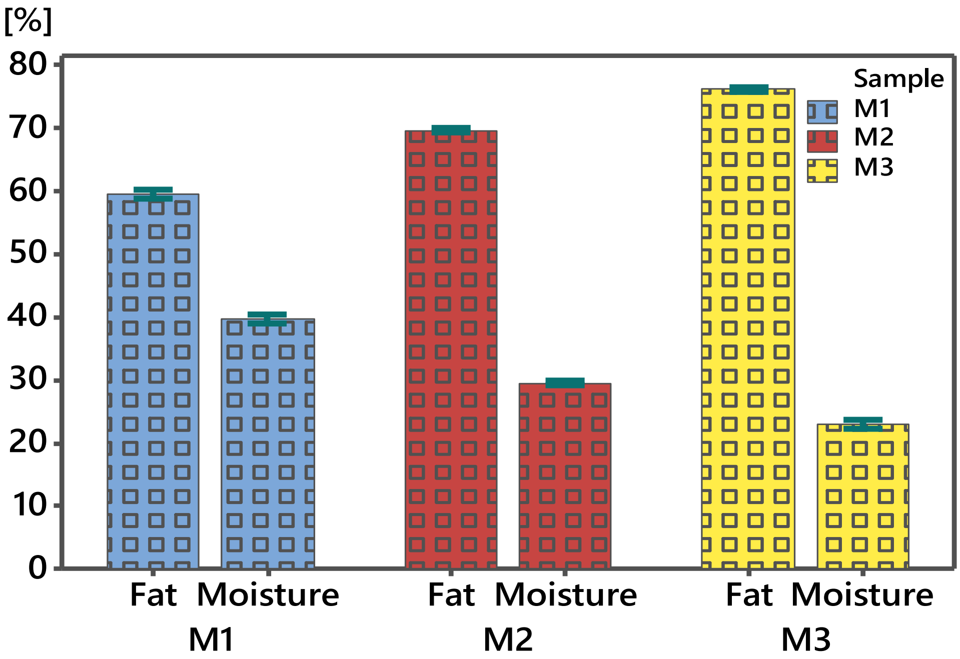

Figure 1. Chemical composition of margarine samples.

For consumers, the color of food represents a major quality attribute, being related to food freshness, nutritional value, and sensory properties. Thus, it is critically important to consumers. The instrumental or physical color evaluation represents a rapid and objective non-destructive method and uses analytical tools that offer rigorous data for quality control [26].

The measured and calculated color parameters of analyzed margarine samples are shown in Table 1. The color properties such as L* (brightness or luminosity), a* (+red/−green), and b* (+yellow/−blue) were the measured properties, while the h^0 (hue angle or tone), WI (whiteness), C* (color intensities), YI (yellowness), and ΔE* (color differences) were the calculated color parameters for both inside and outside color evaluation. The samples' brightness ranged from 95.67 to 91.54, with the highest value being recorded for the M1 inside evaluation. The ANOVA statistical analysis divided the luminosity results into five groups. For M2 samples, there was no difference between inside and outside measurements, with the results belonging to the same statistical group (c). The values of the a* color parameter were in the negative region for all analyzed margarine samples, revealing that this color parameter is more green. Between the outside measurements of the M1 and M2 samples, the ANOVA analysis showed no differences. In the case of margarine samples, the positive b* color parameter represents the degree of yellow, and as can be seen, the b* results varied from 35.74 to 22.22; the lowest value was measured for outside M1 samples, while the highest value was recorded for outside M3 samples. A higher value of the b* color parameter means more yellowness in the margarine sample. Additionally, the outside results presented higher values than the inside ones; the ANOVA highlighted these differences at a level of $p < 0.001$, dividing the measurements into six statistical groups. Furthermore, the measured color parameters were in the same range as the results discussed by Smetana et al. [12].

Table 1. The CIE L*a*b* color parameters of margarine samples.

Sample	**Outside Color Parameters—Mean (SD)**						
	L*	**a***	**b***	**C**	**h^0**	**YI**	**WI**
M1	95.41 ^{b} (0.16)	−6.46 ^{e} (0.07)	22.22 ^{d} (0.16)	23.14 ^{d} (0.17)	106.21 ^{b} (0.07)	33.27 ^{d} (0.30)	76.40 ^{b} (0.20)
M2	94.99 ^{c} (0.16)	−6.51 ^{e} (0.05)	23.94 ^{c} (0.53)	24.81 ^{c} (0.52)	105.21 ^{d} (0.19)	36.01 ^{c} (0.85)	74.68 ^{c} (0.54)
M3	91.81 ^{d} (0.02)	−5.82 ^{b} (0.07)	35.74 ^{a} (0.55)	36.21 ^{a} (0.55)	99.25 ^{f} (0.02)	55.61 ^{a} (0.87)	62.87 ^{e} (0.54)
	Inside Color Parameters—Mean (SD)						
M1	95.67 ^{a} (0.07)	−6.39 ^{d} (0.01)	21.68 ^{e} (0.05)	22.60 ^{e} (0.05)	106.42 ^{a} (0.04)	32.37 ^{e} (0.11)	76.98 ^{a} (0.06)
M2	95.14 ^{c} (0.06)	−6.21 ^{c} (0.01)	22.50 ^{d} (0.16)	23.34 ^{d} (0.15)	105.43 ^{c} (0.09)	33.79 ^{d} (0.26)	76.15 ^{b} (0.16)
M3	91.54 ^{e} (0.25)	−5.51 ^{a} (0.05)	32.33 ^{b} (0.22)	32.79 ^{b} (0.21)	99.67 ^{e} (0.16)	50.45 ^{b} (0.49)	66.13 ^{d} (0.27)
F	1002	312.78	1905	1773	4937	1913	1785
p	$p < 0.001$	$p < 0.001$	$p < 0.001$	$p < 0.001$	$p < 0.001$	$p < 0.001$	$p < 0.001$

SD—standard deviation. Different lowercase letters (a–f) between columns (L*, a*, b*, C, h^0, YI, WI) indicate a significant difference of mean values ($p < 0.05$) tested with one-way ANOVA.

The chroma values (C*) represent the color saturation, and in this study, the chroma results ranged between 36.21 and 22.60. Higher values were measured for outside color evaluations. The whiteness (WI) and yellowness (YI) indexes of margarine, butter, and spreadable fats can be considered a critical color parameter. The whiteness indexes indicate the degree of sample whiteness and mathematically combine three color parameters (brightness, red-green, and yellow-blue) in a single color parameter, whereas the yellowness indexes indicate the degree of sample yellowness, combining two color parameters (brightness and yellow-blue) in a single term [17]. The highest yellowness index was registered for M3 outside measurements (55.61 ^{a}), while the highest whiteness index was registered for M1 inside measurements (76.98 ^{a}). The hue angle values (h^0) varies between 0 and 360 and describes the main spectral component, like red for 0° or 360°, yellow for 90°, green for 180°, or blue for angles of 270° [27]. The margarine hue angle values were higher than 99.25 and lower than 106.42, presenting a yellow main spectral component with some green interferences and also presenting variations in the margarine's chemical composition. Regarding the chemical composition, it can be observed that the margarine samples with a high fat content (M3 samples) also present high values for b*, C*, and yellowness index color parameters.

The total color difference represents the magnitude of color variation between any two samples [28]; the human perception of total color difference is influenced by the observed color and eye sensitivity. If the total color difference is smaller than 1, the differences cannot be distinguished by the human eye. If the total color difference is between 1 and 3, minor color differences can be distinguished. If the total color difference is greater than 3, the color differences can be easily perceived by the human eye [29].

Table 2 shows the results of margarine color differences calculated between samples and between outside and inside color measurements. As we can see, the highest color differences were obtained for M1 inside and M3 outside margarine samples (14.59), followed by M1 outside and M3 outside color differences (14.00). Smaller color differences were calculated for M1 inside and M1 outside (0.60) and for M2 inside and M1 outside (0.46); these samples showed close color parameters. It can be observed that the color difference is especially greater between the samples with the minimum and maximum fat content; the fat content is an important factor in assessing color differences of margarine samples. In addition, the results of total color differences were also assessed by ANOVA statistical analysis, resulting in a significant difference at a level of $p < 0.05$ between the margarine samples. The evaluated margarine color parameters are of great importance in the classification of the analyzed samples. The total color differences present different values influenced by the fat content of the compared samples.

Table 2. The CIE L*a*b* color differences of margarine samples.

Sample		Outside			Inside		
		M1	M2	M3	M1	M2	M3
M1	outside	-	1.77	14.00	0.60	0.46	10.86
M2			-	12.23	2.36	1.47	9.12
M3				-	14.59	13.65	3.43
M1	inside				-	0.99	11.45
M2						-	10.48
M3							-

3.2. Fatty Acids Analysis

Table 3 presents the concentration of the fatty acids of analyzed margarine samples, and as can be seen from 37 fatty acids investigated, only 18 were quantified. The 18 quantified fatty acids were grouped depending on the chain length and according to the degree of unsaturation into 4 groups as follows: short- and middle-chain saturated, long-chain saturated, monounsaturated, and polyunsaturated. Of the 4 categories mentioned, the highest amount was the long-chain saturated fatty acids category (C14:0–C20:0), ranging between 85.61 µg/mg for M1 samples and 127.30 µg/mg for M3 samples, while the short and middle-chain saturated fatty acids (C8:0–C12:0) were present in a small amount (from 12.95 µg/mg to 19.22 µg/mg). The monounsaturated fatty acid methyl esters (C14:1–C20:1) also represent an important category of the chemical composition, varying from 53.50 µg/mg (M1) to 65.64 µg/mg (M3). The polyunsaturated fatty acid methyl esters (C18:2–C18:3) of margarine samples ranged between 31.16 µg/mg and 46.10 µg/mg. All analyzed margarine samples contained a significant quantity of lauric, myristic, palmitic, and stearic saturated fatty acids and considerable quantities of oleic and linoleic unsaturated fatty acids.

From the saturated fatty acids quantified, it can be seen that the dominant fatty acid was palmitic acid for all margarine samples; the M1 margarine samples presented a lower concentration of 60.01 µg/mg, whereas the highest concentration of 94.76 µg/mg was recorded for M3 margarine samples. Similar results were also reported by Anwar et al. [30] and Karabulut & Turan [31] on both margarines and shortenings. According to Kandhro et al. [32], the palmitic acid results designate the greater influence of palm oil in the margarine production process. Furthermore, the most abundant monounsaturated fatty acid was oleic acid, ranging from 50.28 µg/mg for M1 samples to 55.89 µg/mg for M2 and 62.81 µg/mg for M3 samples. From the polyunsaturated category, only linoleic, γ-linolenic, and linolenic acids were identified; significant concentrations of linoleic acid were present.

Of the three groups of samples analyzed, the M3 group presented the highest values of fatty acid concentration, whereas the M1 group presented lower levels of fatty acid concentration; Pearson correlation highlighted the positive connection between a sample's fat content and the concentration of fatty acids at a level of $p < 0.05$ ($r = 0.986$).

Taking into account that the maragarines analyzed contain between 53.79% and 56.73% saturated fatty acids (SFAs) and between 43.26% and 46.20% unsaturated fatty acids (UFAs), and considering the World Health Organization recommendation, the ratio of UFAs and SFAs was also calculated. The results for margarine samples varied from 0.76 to 0.85, which are smaller than 1.6; the World Health Organization recommends a ratio of UFAs and SFAs higher than 1.6 [33].

Table 3. Fatty acids concentration (µg/mg) of margarine samples.

Name	Abbreviation	RT ± 0.5 min	Margarine Samples—Mean (SD)		
			M1	M2	M3
Caprylic	C8:0	10.82	1.68 (0.12)	1.81 (0.11)	2.40 (0.01)
Capric	C10:0	14.25	1.54 (0.11)	1.69 (0.12)	2.44 (0.01)
Lauric	C12:0	17.63	9.72 (0.72)	10.72 (0.05)	14.37 (0.22)
Short- and middle-chain saturated			12.95	14.23	19.22
Myristic	C14:0	20.48	6.12 (0.20)	7.21 (0.46)	10.18 (0.30)
Pentadecanoic	C15:0	22.31	0.25 (0.02)	0.34 (0.01)	0.46 (0.02)
Palmitic	C16:0	23.96	60.01 (2.53)	74.48 (2.45)	94.76 (1.82)
Heptadecanoic	C17:0	25.77	1.87 (0.23)	0.54 (0.03)	0.68 (0.01)
Stearic	C18:0	27.91	17.34 (0.56)	16.66 (0.57)	20.78 (0.01)
Arachidic	C20:0	30.82	0.00	0.95 (0.11)	0.41 (0.01)
Long-chain saturated			85.61	100.20	127.30
Tetradecenoic	C14:1	21.42	0.40 (0.02)	0.41 (0.01)	0.71 (0.01)
cis-10-pentadecenoic	C15:1	23.00	0.28 (0.03)	0.19 (0.02)	0.27 (0.01)
Palmitoleic	C16:1	24.51	1.19 (0.22)	0.92 (0.12)	0.97 (0.02)
cis-10 Heptadecanoic	C17:1	26.43	1.27 (0.08)	0.91 (0.03)	0.84 (0.02)
Oleic	C18:1 cis (n9)	28.56	50.28 (1.89)	55.89 (2.53)	62.813 (1.78)
cis-11 Eicosenoic	C20:1 (n9)	33.66	0.06 (0.01)	0.03 (0.01)	0.02 (0.01)
Monounsaturated			53.509	58.37	65.64
Linoleic	C18:2 cis (n6)	29.85	30.97 (1.23)	34.15 (1.98)	45.86 (2.45)
γ-Linolenic	C18:3 (n3)	31.84	0.00	0.28 (0.02)	0.12 (0.02)
Linolenic	C18:3 (n6)	34.61	0.19 (0.01)	0.10 (0.01)	0.12 (0.01)
Polyunsaturated			31.16	34.55	46.10
Unsaturated/saturated fatty acids			0.85	0.81	0.76
Atherogenicity index			1.11	1.22	1.35

SD—standard deviation.

Regarding the fatty acids with atherogenic potential, it is well known that lauric acid (12:0), myristic acid (14:0), and palmitic acid (16:0) have this effect. The quantity of those acids found in the analyzed margarine samples ranged from 75.86 µg/mg for M1 samples to 119.33 µg/mg for M3 samples; the obtained results were much smaller than those reported by Vučić et al. [23] for Serbian margarines, but closer to those reported by Alonso et al. [34] for Spanish margarines. In contrast to the ratio of UFAs and SFAs, the atherogenicity index is a more complex indicator that evaluates the potential effects of fatty acids on the incidence of pathogenic phenomena. The atherogenicity index (IA) has been calculated as follows: IA = [C12:0 + (4 × C14:0) + C16:0]/UFA. For the analyzed margarine samples, this index ranged between 1.11 for M1 group samples and 1.22 for M2 and 1.35 for M3 margarine samples. The obtained results were greater than those reported for soft margarines (0.42), [35] but close to the ones of hard margarines (1.17–1.67) [23]. Regarding the atherogenicity index of margarine compared to butter (1.78–1.85), we can observe that the former is 27% to 36% smaller, being influenced also by the fat content of the sample [36]. Therefore, the consumption of low-atherogenicity index foods can decrease the total cholesterol of the blood.

3.3. Textural Evaluation

Texture properties represent one of the most important attributes of food products [37], and when it comes to margarine, butter, or shortening, the main textural parameter is hardness (firmness) [38]. The most commonly used instrumental assays include major deformations such as puncture, extrusion, and compression, which lead to the destruction of the material's structure under analysis. Given the fact that the analyzed samples fall into the plastics materials category, another very important parameter is the mechanical work of plastic deformation (or plasticity).

The evolution of force (N) versus deformation (mm) of margarine samples determined using the 10 mm diameter spherical penetrometer is displayed in Figure 2. The profile of the margarine test curves shows that it is a material with a pronounced fracturability. The margarine's fracturability varied from 0.35 N to 8.23 N; the highest values were measured using the 10 mm diameter spherical penetrometer, and from the point of view of the analyzed samples, the M2 margarine group presented the highest values of fracturability.

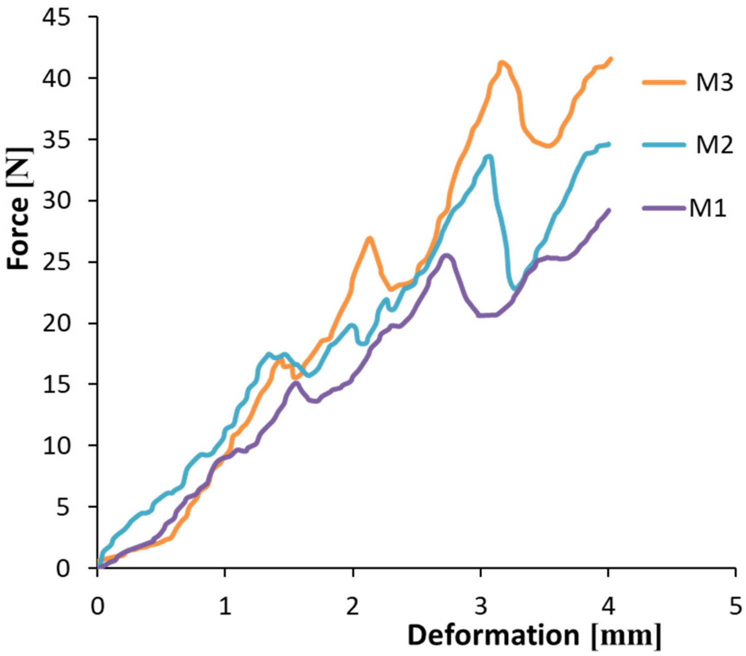

Figure 2. Force versus deformation curves of margarine samples.

The textural parameters of margarine samples analyzed in this study using three different penetrometers and a puncture test are displayed in Table 4. As in the case of butter and corresponding to ISO 16305 [39], the margarine hardness was also expressed in newtons (N) and ranged between 4.76 N and 52.28 N. The 5 mm diameter spherical penetrometer hardness measurements showed the smallest values, varying from 8 N for M3 samples to 4.76 N for M1 samples; by comparison, the 10 mm diameter spherical penetrometer and conical penetrometer presented close values varying from 41.56 N to 29.18 N and from 52.28 N to 19.02 N, respectively. The mechanical work of plastic deformation (plasticity) was calculated as the area under the deformation curve and ranged between 6.12 and 82.84 mJ (millijoules), with the greatest value being recorded for M3 margarine samples. In contrast, the lowest plasticity was measured for M1 samples. Of the three probes used to test the margarine samples, the 10 mm diameter spherical penetrometer presented the highest values (82.84–63.48 mJ).

Table 4. The textural parameters of margarine samples.

Probe	**PS$_5$**			**PS$_{10}$**			**PC**		
Sample	**H (N)**	**P (mJ)**	**F (N)**	**H (N)**	**P (mJ)**	**F (N)**	**H (N)**	**P (mJ)**	**F (N)**
M1	4.76 (0.40)	6.12 (0.62)	0.68 (0.02)	29.18 (1.85)	63.48 (2.25)	4.25 (0.92)	19.02 (2.78)	38.93 (3.54)	1.36 (0.28)
M2	7.26 (0.25)	7.76 (0.32)	0.35 (0.10)	34.66 (1.22)	73.37 (1.87)	8.23 (1.20)	30.06 (2.42)	53.55 (5.10)	2.66 (0.54)
M3	8 (0.30)	7.79 (0.43)	0.74 (0.12)	41.56 (1.89)	82.84 (2.02)	5.39 (0.33)	52.28 (3.25)	70.76 (4.83)	0.42 (0.08)

SD—standard deviation, PS$_5$—5 mm diameter spherical penetrometer, PS$_{10}$—10 mm diameter spherical penetrometer, PC—120° conical penetrometer, H—hardness, P—plasticity, F—fracturability, SD—standard deviation.

Both the hardness and the plasticity values of the margarine samples were influenced by their chemical composition, especially by the fat content and by the saturated and unsaturated fatty acids. Pearson correlation showed a positive influence ($p < 0.05$) of palmitic fatty acid content on the cone ($p < 0.05$; $r = 0.995$), the 10 mm spherical hardness ($p < 0.01$; $r = 0.998$) and on plasticity values ($p < 0.05$; $r = 0.994$; $r = 0.999$). Another consideration is that the hardness and plasticity of the 10 mm spherical penetrometer and cone penetrometer are positively correlated ($p < 0.01$; $r = 0.992$; $r = 0.997$). Furthermore, the content of cis-10 heptadecanoic and cis-11 eicosenoic fatty acids have a negative influence ($p < 0.05$; $r = -0.998$; $r= 0.991$; $r = -0.990$) on margarine plasticity and hardness evaluated with 5 and 10 mm spherical penetrometers.

In addition, to highlight the differences between analyzed margarine samples, emphasize the significant information obtained from the evaluated parameters, and diminish the amount of the variables, a PCA analysis (principal component analysis) was performed. The PCA results are represented by the biplot (score and loading) from Figure 3. PCA analysis was accomplished on physicochemical properties, fatty acid groups, measured color properties, and texture parameters of analyzed margarine samples. The two principal components, PC1 and PC2 cover 98.37% of data variation: the first component, PC1, describes 96.34% of the variation, while the second component, PC2, describes 2.03% of the variation. According to these PCA scores, it can be observed that the margarine samples are distributed into diverse quadrants according to chemical composition and evaluated textural parameters. The first component (PC1) separates the M1 and M2 margarine group samples from M3 margarine samples based on monounsaturated fatty acids (MN), 10 mm spherical penetrometer hardness, cone plasticity, and the long-chain saturated fatty acid (LCS) content. The second component (PC2) separated the M2 group from the other samples based on the cone and 10 mm spherical fracturability values, with a smaller contribution having the 5 mm hardness and plasticity. From the loadings plot, it can be observed that the projection of M3 margarine samples was significantly influenced by the long-chain saturated fatty acids (LCS) and by the cone hardness values and polyunsaturated fatty acids (PN), which have a smaller influence. Of the outside and inside measured color parameters, only the b* color parameter indicates an influence in the M3 sample distribution; its values are also positively correlated with polyunsaturated fatty acids (PN). Regarding the projection of the M1 samples, it can be observed that moisture content has a strong influence on their positioning in the PCA diagram.

The high value achieved in the dispersal of data variation highlights the utility of PCA in margarine classification using chemical composition, color parameters, and textural properties.

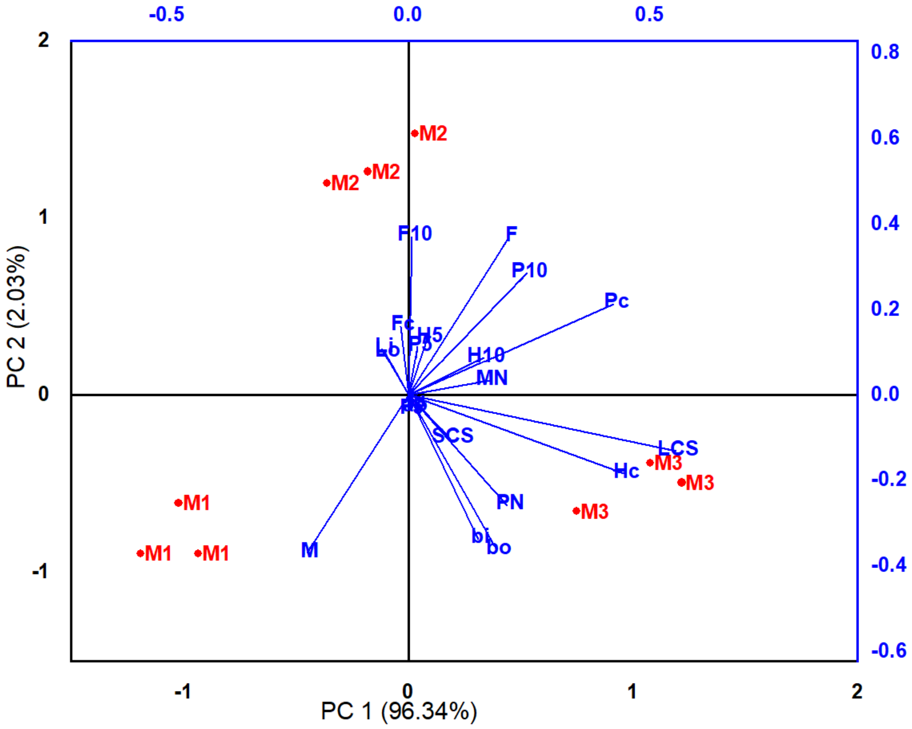

Figure 3. Principal component analysis (score and loading) of margarine samples: Lo, ao, bo-outside color parameters, Li, ai, bi-inside color parameters, F-fat content, M–moisture content, SCS-short- and middle-chain saturated fatty acids, LCS-long-chain saturated fatty acids, MN-monounsaturated fatty acids, PN-polyunsaturated fatty acids, Hc-cone penetrometer hardness, Pc-cone penetrometer plasticity, Fc-cone fracturability, H5-5 mm spherical penetrometer hardness, P5-5 mm spherical penetrometer plasticity, F5-5 mm spherical fracturability, H10-10 mm spherical penetrometer hardness, P10-10 mm spherical penetrometer plasticity, F10-10 mm spherical fracturability.

4. Conclusions

In this study on bakery margarines with different chemical compositions, it was observed that from the saturated fatty acids quantified, the dominant fatty acid was palmitic acid, whereas the most abundant unsaturated fatty acid was oleic. The atherogenicity index of margarine samples, calculated based on fatty acid concentration, was smaller than that of butter but close to hard margarine, being also influenced by the fat content of the sample. Regarding the penetrometer's geometry used for margarine texture evaluation, the cone and 10 mm diameter spherical penetrometer registered high values for both hardness and plasticity, which have been influenced by the sample's chemical composition, especially by the fat content and the saturated and unsaturated fatty acids. Bakery margarine is a plastic material with a pronounced fracturability, and the 10 mm diameter spherical penetrometer is recommended for evaluating this texture parameter. In terms of color parameters, both the outside and inside b* color parameter influence the differentiation of the analyzed samples. The ANOVA highlighted these differences at a level of $p < 0.001$, dividing the measurements into six statistical groups, whereas the PCA analysis indicates an influence in the fattest margarine samples' projection.

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