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Gelled Emulsions based on Amaranth Flour with Hemp and Sesame Oils †

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Abstract: Gelled emulsion (GE) systems are one of the novel proposals for reformulation of meat products with healthier profiles. The aim of this research was to obtain a better understanding of the impact of different oils in physicochemical properties, emulsion stability and TBARs level for two gelled emulsions based on amaranth flour with hemp oil (GAH) and amaranth flour with sesame oil (GAS). The characterization of these GE was carried out after 24 h in cooling of 4 °C (t0) and 15 days in freezing at −23 °C (t15). The spreadability was measured only at t0 and this revealed that the GAH sample had greater firmness and greater work of shear than GAS sample. The GAS sample had a higher value of emulsion instability at t0, with an increase after freezing of 10% more. For the TBARs, the initial oxidation was higher for GAH with 1.230 ± 0.074 mg ma/Kg sample and after 15 days in freezing increased to 12% this amount. Between the emulsions studied, GAS has less consistence and emulsion stability than GAH, so it could be undesirable for some meat products. Thus, GE could be a potential alternative for their application in the development of functional foods.

Keywords: hemp; emulsion stability; amaranth flour; spreadability

1. Introduction

Nowadays the consumer is more and more interesting in healthier foods, between this there are meat products. There for, the food industry is shifting to make low-fat or fat-free products [1]. The reason why the consumer requires meat products healthier is because meat products contain a high amount of saturated fat and salt. An association has been seen between the consumption of saturated fats with diseases such as obesity and hypertension, which leads to cardiovascular problems. So, the reformulation of meat products is necessary [2]. There are several alternatives to formulate healthier meat products, in particular one of them is to use fat substitutes, but it would be desirable to imitate the appearance, sensory, technological and rheological properties of animal fat [3,4]. Although sometimes the use of fat replacers causes technological problems specially in texture and flavor of foods. The new fat may affect some desired quality attributes in the reformulated product. Thus, the fat replacement is a difficult task [5]. One way to make healthier meat products is replacing animal fat by vegetable oil sources and this can be done, among other strategies, with the generation of gelled emulsions. The gelled emulsions (GE) can be formulated in different ways with the use of protein together heat, acidification or enzyme action. On the other hand, these processes could be carried out with cold gelling agents which are able to create a network with protein bond to polysaccharides to generate polymers [6,7]. To form a GE, firstly forming a liquid emulsion for generate a small droplets pf the dispersed phase suspended in the continuous phase [8]. The GE properties depend mainly of the type or number of hydrocolloids and oil added [5]. About the oils used, both hemp oil and sesame oil offer interesting possibilities. Hemp (*Cannabis sativa* L.) oil is rich of polyunsaturated (PUFA) fatty acids in fact in linoleic acid and alpha-linoleic acid with a ratio 2.1:1 to 3:1 of this PUFAS. Sesame oil make up about 50% of the sesame seeds (*Sesamum indicum* L.). Sesame oil is used in many processed products, as a lubricants, cream, insecticides, pharmaceuticals, soap and salad oil. The main fatty acid composition of sesame oil is about 38–47% linoleic acid and 38–44.3% oleic acid [9]. The aim of this study was to develop oil-in-water (O/W) gelled emulsions formulated with hemp oil, sesame oil, amaranth flour and different gelling agents.

2. Materials and Methods

2.1. Materials

Amaranth flour was obtained from Tentorium Energy S.L. (Tarragona, Spain). Their composition was 11.97% protein, 6.29% fat, 2,73% ash. The hemp oil was available from Laboratorios Almond, S.L., Spain. Their composition was saturated fatty acids 9%, mono-unsaturated fatty acids 11% and polyunsaturated fatty acids 80%, the main fatty acids was linoleic acid (54%) and α-linoleic acid (16%). The sesame oil was obtained from Laboratorios Almond, S.L., Spain. Their composition was saturated fatty acids 14%, mono-unsaturated fatty acids 40% and polyunsaturated fatty acids 46%, the main fatty acids was oleic acid (46%) and linoleic acid (44%). Gellan gum and gel instant was available from Sosa Ingredients S.L., Spain.

2.2. Gelled Emulsion Preparation

Two different types of O/W gelled emulsion were formulated as shown in Table 1. One type of gelled emulsion was prepared by mixing amaranth flour, hemp oil and gelling agents (gellan gum and gel instant. The other was prepared by mixing amaranth flour sesame oil and gelling agents. The O/W gelled emulsions were prepared by mixing instant gel with the water for 2 min at 60 °C at high speed, using a homogenizer (Thermomix 31, VorwerkEspaña M.S.L., S.C, Spain). There for, the amaranth flour was added and mixing for 1 min at medium speed. Then the temperature was turned down to 37 °C and gellan gum was added and mixed for 2.5 min at 250 rpm. The different oils were added until they were perfectly integrated, then the ingredients were mixed for 5 min, at 37 °C at 1100 rpm. The gelled emulsion were subsequently cooler at 4 °C during 24 h after that the parameters were measured and then samples were kept at −23 °C during 15 days.

Table 1. Formulation of hemp and sesame oils-in-water emulsion gels.

Samples [1]	Water	Flour	Gel Instant	Gellan Gum	Hemp Oil	Sesame Oil
GAH	47	10	1.5	1.5	40	-
GAS	47	10	1.5	1.5	-	40

[1] GAH: Gelled emulsion of amaranth flour and hemp oil. GAS: gelled emulsion of amaranth flour and sesame oil. The results are expressed in g/100 g.

2.3. Instrumental Color Analysis

The instrumental color parameters of gelled emulsions were measured in the CIEL*a*b* color space using a Minolta CM-700 (Minolta Camera Co., Osaka, Japan), with illuminat D65, SCI mode and an observer angle of 10°. Low reflectance glass (Minolta CR-A51/1829-752) was placed between the samples and the equipment.

2.4. Texture Profile Analysis

The texture of each sample was evaluated using a TA-XT2i texturometer (Stable Micro Systems, Surrey, UK). The spreadability of samples was analyzed with the accessory TTC spreadability rig (HDP/ SR, Stable Micro Systems), which was composed of a 90° male cone probe and five coneshaped product holders precisely matched female. Both cones were at 25 mm of distance and the gelled emulsions were forced to flow out at 45° with a test speed of 3 mm/s.

2.5. Gelled Emulsion Stability

The stability of the emulsion was determined by procedure from [10]. The determinations were made in triplicate for each GE. The results are expressed in g/100 g of sample and were calculated using the following expression:

$$\% \text{ TEF} = (\text{Weight of tube with sample-Weight of tube with pellet})/(\text{Weight of sample}) \times 100 \qquad (1)$$

2.6. Lipid Oxidation

Oxidative stability of GE was evaluated by measuring change in thiobarbituric acid reactive substances (TBARs). TBAR determination for each sample were performed in triplicate by the method described by [11]. TBARS values were calculated from a malonaldehyde (MDA) standard curve and were expressed as mg MDA/kg sample.

2.7. Statistical Analysis

To determine if there were statistical differences between samples, an one-way analyses of variance (ANOVA) was used. It was ascertained whether there were statistically significant differences by means of Tukey's multiple range test with a confidence level of 95%. The data analysis was performed with the statistical package Statistic data editor (SPSS 24).

3. Results and Discussion

3.1. Color Measurement

The instrument color values of gelled emulsions were affected by the different oil sources and the storage conditions. In Table 2, values for L* were different for all types. It is also observed that after freezing the luminosity decreases for both samples, the decrease of this being more pronounced in the GAH sample with an 11% of reduction.

Table 2. Color parameters at t_0 and t_{15} of the gelled emulsions.

Samples [1]	Day	L*	a*	b*
GAH	0	69.45 ± 1.91 ^{ab}	−1.03 ± 0.21 ^{d}	23.52 ± 0.54 ^{a}
	15	61.83 ± 2.30 ^{c}	−0.52 ± 0.28 ^{c}	23.22 ± 1.62 ^{a}
GAS	0	71.47 ± 0.95 ^{a}	0.71 ± 0.08 ^{b}	12.72 ± 0.22 ^{b}
	15	67.37 ± 0.65 ^{b}	0.75 ± 0.09 ^{a}	13.04 ± 0.44 ^{b}

[1] GAH: gelled emulsion amaranth flour and hemp oil. GAS: gelled emulsion amaranth flour and sesame oil. L*: luminosity; a*: red/green coordinate; b*: yellow/blue coordinate. Values followed by the same lowercase letter within the same column indicate that there are no statistically significant differences ($p > 0.05$) according to the Tukey multiple range test.

About the coordinate a*, the sample GAH at time 0 and time 15, present more greenish color than the GAS sample. In both samples after freezing the sample becomes more red. The samples were not affected in the b* coordinate during their storage period. However, they showed statistically significant differences ($p < 0.05$) between both emulsions, the GAH being the one with the highest yellow coloration. These color differences could be due to the color of the oil itself. The color is a essential property for fat analogs as it is one of the characteristics that determines consumers choice of foods [12].

3.2. Textural Properties

The results of adding hemp or sesame oil in the texture of gelled emulsions, is shown in Table 3. A significant reduction of firmness ($p < 0.05$) and work of shear ($p < 0.05$) presented the GAS sample. From the physical point of view, spreadability is the ability of elastoviscoplastic materials to deform [18]. So, these results translate into greater spreadability by the sample GAS with significant differences with the sample GAH.

Table 3. Texture parameters at t_0 to mesure the spreadability of samples.

Samples [1]	**Firmness (g)**	**Work of Shear (g.s)**
GAH	536.67 ± 21.28 ^{a}	460.00 ± 8.17 ^{a}
GAS	466.67 ± 11.45 ^{b}	366.67 ± 13.42 ^{b}

[1] GAH: gelled emulsion amaranth flour and hemp oil. GAS: gelled emulsion amaranth flour and sesame oil. Values followed by the same lowercase letter within the same column indicate that there are no statistically significant differences ($p > 0.05$) according to the Tukey multiple range test.

3.3. Gelled Emulsions Stability

The results of the stability of the emulsion are calculated by determining the total exudate fluids (TEF), the results obtained for the different samples of gelled emulsions are shown below in Figure 1. The lower the TEF, the greater the stability of the emulsion. It is observed in Figure 1 that there are statistically significant differences ($p < 0.05$) for both samples. At time 0, the sample that presented the greatest stability of the emulsion was GAH (11.32 ± 0.66), followed by the GAS sample at time 0 (29.16 ± 1.87). After freezing, the most stable is GAH, but its instability increased by 22.9% and for GAS the instability is less pronounced with an increase of 10%. Several previous studies have published that the addition of dietary fiber to meat products helps to improve the stability of the emulsion and the rheological properties [13–15]. So the addition of these emulsions could benefit the stability of the meat product for which they are intended.

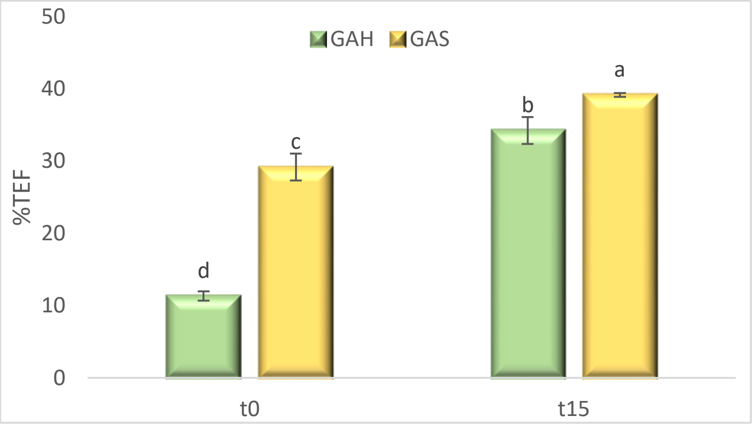

Figure 1. Emulsion stability measured as g of total liquid expelled/100 g sample. Values followed by the same lowercase letter there are no statistically significant differences ($p > 0.05$) according to the Tukey multiple range test.

3.4. Lipid Oxidation

Lipid oxidation can have negative effects on the quality of meat products, causing changes in sensory attributes such as smell, taste, color and texture. Their nutritional quality is also affected [16]. Figure 2, shows the results of the stability to lipid oxidation (TBARs) of gelled emulsions samples. The stability of the samples was evaluated by determining the amount of malonaldehyde, since it is one of the main secondary products of the lipid oxidation process carried out by the decomposition of hydrogen peroxide [17]. There are significant differences between the samples at 0 time, GAS are the least oxidized sample initially with a value of 0.501 ± 0.167 mg MDA/ kg of sample. During the storage the GAS sample maintains the oxidation levels showing no significant differences ($p > 0.05$). However, for the GAH sample, an increase in lipid oxidation of 11% is observed after conservation, going from values of 1.230 to 1.379 mg MDA/Kg of sample. This could be due to the initial lipid oxidation that oils present during their production, as well as their composition, since hemp oil contains 80% polyunsaturated fatty acids while sesame oil only 46%.Even so, the malonaldehyde concentration values obtained for the different samples would not be sensory detected by the consumer, since according to [19] from concentrations of 2 mg/kg of sample, it is believed that the samples may mean loss of sensory quality and oxidation be perceived by the consumer. This is in accordance with other authors [20,21] who reported that the use of vegetable oils as functional ingredients in food lipid emulsions might be complex due to the high oxidation susceptibility of these unsaturated oils.

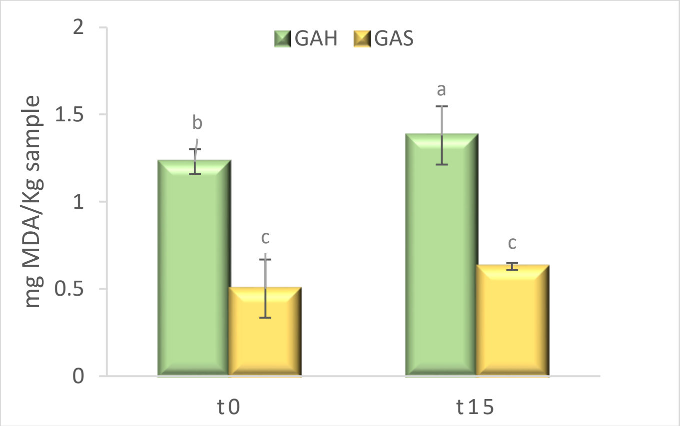

Figure 2. Lipid oxidation by measuring change in TBARs. Values followed by the same lowercase letter there are no statistically significant differences ($p > 0.05$) according to the Tukey multiple range test.

4. Conclusions

In view of the results obtained, the GAH emulsion showed the highest stability, the best firmness values, although GAS has a higher initial lipid oxidation than GAS and a more greenish color. The color could be a small inconvenience when the gelled emulsion is introduced in meat products to replace the fat. The both emulsions are not viable after freezing because their stability is lost and their lipid oxidation values are triggered. Despite this, gelled emulsions could be a potential alternative for their application in the development of functional foods. So, in future studies could investigate the use of oil in water gelled emulsion prepared with healthier combinations of pseudo-cereal flour with seed oils as possible future fat replacer.

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