

Stress relaxation characteristics of low-fat chicken sausages made in Argentina

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Abstract

Low-fat sausages were prepared with fresh chicken breast meat and formulated with different levels of added fat, whey protein concentrate, and hydrocolloids (xanthan and guar gums) to study the effect of composition on the stress relaxation behavior of the products. Stress relaxation experiments were conducted on precooked sausages at 25 °C. Generalized Maxwell and empirical Peleg models were used to predict the stress relaxation behavior of the material. A model with seven maxwellian elements in parallel with a pure elastic element showed a very good agreement with experimental data. Results show that the proposed model satisfactorily fits the experimental data better than Peleg's model or Maxwell models with less elements. The relaxation time distribution functions were obtained. The characteristic relaxation time was shorter (2500 s) for the formulations with no added fat which produced a less elastic product while the sausages with added fat showed longer characteristic relaxation time (5000 s). The stress relaxation experiment differentiated the viscoelastic nature of different formulations due to reduction of fat content.

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1. Introduction

Consumer demand for low-fat products has been increasing. Fat content in processed meat products, such as sausages, can be readily reduced through formulation with leaner meats and/or by adding less fat to the formulation. However, lowering the fat content without increasing water content in frankfurters increases toughness and changes product quality (Decker, Conley, & Richert, 1986; Hand, Hollingsworth, Calkins, & Mandigo, 1987), while replacing fat with water has been reported to increase cooking and purge losses (Claus, Hunt, Kastner, & Kropf, 1990; Gregg, Claus, Hackney, & Marriott, 1993); besides, increasing water may affect the texture and juiciness of the product (Matulis, McKeith, Sutherland, & Brewer, 1995). The combined total fat and added water content cannot exceed 40%, whereas the traditional level was 30%

fat and 10% added water (USDA-FSIS, 1990). Proteins and other extenders have also been used in frankfurters-type products to improve their water-holding capacity (WHC) and textural properties (Whiting, 1984; Su, Bowlers, & Zayas, 2002). Besides the ability of some macromolecular hydrocolloids, or gums, to physically bind water has also been investigated (Andrés, Zaritzky, & Califano, 2007; Foegeding & Ramsey, 1986; Wallingford & Labuza, 1983). Phosphates have also been added to meat products to improve their binding and water-holding properties (Andrés, García, Zaritzky, & Califano, 2006; Whiting, 1984).

One of the fundamental tests to study viscoelastic response is stress relaxation. In stress relaxation tests, a constant strain is applied and the stress required to maintain the deformation is measured as a function of time (Steffe, 1996). The stress–relaxation test is widely used in rheological studies of food products (Mitchell, 1976, 1980). Stress–relaxation response permits a rapid characterization of the material behavior (Gunasekaran & Ak,

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2002; Tabilo-Munizaga & Barbosa-Cánovas, 2005) and it may provide information on permanent cross-linking of the polymers (Hsieh & Regenstein, 1992; Ziegler & Rizvi, 1989). Del Nobile, Chillo, Mentana, and Baiano (2007) used the generalized Maxwell model for describing the stress relaxation behavior of solid-like foods (agar gel, meat, ripened cheese, Mozzarella cheese, and white pan bread).

The objectives of this study were: (1) to characterize the stress relaxation behavior of low-fat chicken sausages using a mechanical model (generalized Maxwell) and an empirical model (Peleg, 1980); (2) to determine the effects of fat reduction and the addition of whey protein and hydrocolloids on the stress relaxation behavior.

2. Materials and methods

2.1. Materials

Fresh breast chicken meat and beef tallow were obtained from local processors (pH values 5.7–5.9). Whey protein concentrate (WPC) containing 40% protein (42% lactose, 4.5% water, and 4% fat) (Milkaut, Santa Fe, Argentina), food-grade commercial preparation of xanthan and guar gums (Sigma Chemical Co., St. Louis, MO) and analytical grade NaCl, NaNO₂, and sodium hexametaphosphate (HMP) were used. Cold distilled water was used in all formulations (4 °C).

Two different type of commercial sausages made of beef and pork meat were used for comparison, type A corresponded to regular frankfurter sausages (Bells, Buenos Aires, Argentina) and type B to light frankfurter sausages (Molinos, Buenos Aires, Argentina).

2.2. Product manufacture and experimental design

Breast chicken meat (500 g per batch) was ground with a commercial food processor (Universo, Rowenta, Germany) equipped with a 14 cm blade for 10 min at the highest speed and storage overnight at 4 °C. Dry ingredients were slowly added to the ground chicken meat as powders while processing. Afterwards cold water was incorporated and finally ground fat (beef tallow) at room temperature was added. The addition of ingredients took less than 5 min and final temperature of the chicken paste varied between 12 and 15 °C. Plastic tubes (3 cm diameter) were stuffed with chicken paste, and weighted before further heat processing. Two batches of six tubes per replicate were heat-processed in a temperature- controlled water-bath (Haake L, Haake Buchler Instruments, Karlsruhe, Germany) maintained at 80 °C until a final internal temperature of 73 °C was reached. Then, samples were cooled immediately in an ice water-bath. One extra tube was loaded, and type-T (copper constantan) thermocouple was inserted in the centre of the sausage and sealed in to serve as the temperature monitoring tube; time/temperature data were recorded (Servoger 102, Omni Instruments,

Dundee, UK). Afterwards, these precooked sausages were removed from the tubes, weighed again to assess weight losses, and stored in covered plastic lugs at 4 °C for 24 h.

Three independent variables: added fat (F), whey proteins (WPC), and gums (G) were considered in the formulation of the chicken sausages. A full 3 × 2 × 2 × 2 factorial design using three levels of added fat (0, 1.98 and 4.96% beef tallow), two levels of whey proteins concentrate (0.64 and 1.94%) and two levels of hydrocolloids (0.13 and 0.32%) was used for 12 different formulations. Perceptual contents were expressed as g/100 g raw batter.

In all formulations a 3:7 ratio guar/xanthan was used (Andrés et al., 2006, 2007). Water was added to the formulations to maintain constant the quantity of added fat + water content. The keys used for each formulation are shown in Table 1.

All formulations were prepared with the same common ingredients (% = g/100 g raw batter) 31.76% added fat + water, 0.2% HMP, 2.48% NaCl, 0.2% white pepper, 0.05% ground nutmeg, and 0.015% NaNO₂. The process was replicated twice.

2.3. Analysis

The moisture, ash, and protein contents were determined according to AOAC methods 24.003, 24.009 and 24.027, respectively (AOAC, 1980) in triplicates. Fat content was determined on previously dried samples by Soxhlet method, using ethyl ether and petroleum ether (Bp: 35–60 °C) in a 1:1 relationship as extraction solvent. Chemical composition was analyzed on raw chicken meat and precooked sausages for all the treatments.

2.4. Stress relaxation test

The stress relaxation tests were performed on precooked sausages (cylinders 1.5 in thickness and 1.7 cm in diameter)

Table 1
Formulations expressed as g/100 g of raw sausage (%)

Composition	Gums	Added fat	WPC	Chicken meat	Added water
LL1	0.13	0	0.64	64.52	31.76
LL2	0.13		1.94	63.23	31.76
HL1	0.32		0.64	64.33	31.76
HL2	0.32		1.94	63.04	31.76
LM1	0.13	1.98	0.64	64.52	29.78
LM2	0.13		1.94	63.23	29.78
HM1	0.32		0.64	64.33	29.78
HM2	0.32		1.94	63.04	29.78
LH1	0.13	4.96	0.64	64.52	26.80
LH2	0.13		1.94	63.23	26.80
HH1	0.32		0.64	64.33	26.80
HH2	0.32		1.94	63.04	26.80

First position in the code notation corresponds to hydrocolloids, second position to fat content, and third position to whey protein concentrate (WPC) content.

Codes for hydrocolloids: L = low and H = high.

Codes for fat levels: L = low, M = medium, and H = high.

Codes for WPC: 1 = low, 2 = high.

Gums: guar gum/xanthan gum = 3:7.

at room temperature using a TAXT2i Texture Analyser (Stable Micro Systems, Surrey, UK) with the Texture Expert Exceed software. Samples were compressed to the maximum relative strain for linear elastic behavior (20%) between flat plates at a crosshead speed of 0.5 mm/s. At this point the crosshead was stopped and the force as a function of time was recorded for 600 s, every 0.25 s, while the applied deformation was maintained. Six measurements were performed on each formulation. The same procedure was used for the commercial sausages which were already pasteurized.

2.5. Data analysis

The mechanical properties appear in constitutive equations (or rheological equations of state) in which they form the link between an excitation and a response. For a linear viscoelastic material subjected to an instantaneous constant strain, ε the initial stress will be proportional to the applied strain and will decrease with time. The decaying stress, $\sigma(t)$, and the applied strain are related according to:

$$\sigma(t) = G(t) \cdot \varepsilon \quad (1)$$

where $G(t)$ is the relaxation modulus, a material function, and t is the experimental decay time.

Although food products like sausages are complex matrices, they could be described with a certain approximation on the base of simplified models. Massless mechanical models, composed of springs and dashpots, combined in different ways, are useful in conceptualizing rheological behavior (Steffe, 1996).

Time dependent mechanical properties are therefore characterized by *response times*, in fact, almost always by distributions of such times. If the stress relaxes, the response times are *relaxation times* λ_i . Each response time is associated with a *spectral strength* G_i . The time dependence of a material is thus revealed in a finite, discrete set of response times and their associated spectral strengths. When the excitation is a strain, this set is $\{G_i, \lambda_i\}$ (Tschoegel, 1997).

The mechanical model most suitable for quantification of relaxation behavior of foods and a variety of polymeric materials has traditionally been the generalized Maxwell mechanical model with a discrete number of elements (Ak & Gunasekaran, 1996; Gunasekaran & Ak, 2002; Singh, Lakes, & Gunasekaran, 2006; Sherman, 1970; Steffe, 1996). A Maxwell element contains a Hookean spring in series with a Newtonian dashpot. The Maxwell model considering only a single Maxwell element is suitable for understanding stress relaxation data, but does not consider the equilibrium stress. For this reason, the viscoelastic behavior of food can be better described by using a generalized Maxwell model. The generalized Maxwell model considered in this work consisted in several Maxwell elements in parallel with an independent spring:

$$G(t) = G_e + \sum_{i=1}^n G_i \exp\left(-\frac{t}{\lambda_i}\right) \quad (2)$$

where G_i and λ_i are the elastic modulus and the relaxation time of the i th Maxwell element, respectively, and G_e represents the equilibrium or residual modulus at the fully decayed state. Viscoelastic materials would relax gradually with the end point depending on the molecular structure of the material being tested (Kfoury, Mpagana, & Hardy, 1989).

From Eqs. (1) and (2):

$$\sigma(t) = G(t) \cdot \varepsilon = \left(G_e + \sum_{i=1}^n G_i \exp\left(-\frac{t}{\lambda_i}\right) \right) \cdot \varepsilon \quad (3)$$

Since each element may have a different relaxation time (λ_i), a relaxation spectrum can be obtained for a viscoelastic material. The spectrum itself is not accessible by direct experiment, but it can often be calculated exactly from a mathematical model of a response curve (Tschoegel, 1989). However, from experimental data the spectrum is necessarily obtained as an approximation to the unknown “true” spectrum whose existence is but assumed. Then the discrete relaxation time distribution may be obtained as:

$$H(\lambda) = (\lambda_i \cdot G_i) \quad (4)$$

The relaxation curve has also been modeled by much simpler models. Peleg and Normand (1983) suggested that stress relaxation data be calculated as a normalized stress and fit to the following linear equation:

$$\frac{\sigma_0 \cdot t}{\sigma_0 - \sigma} = k_1 + k_2 \cdot t \quad (5)$$

where σ_0 is the initial stress, σ is the decreasing stress at time t , and k_1 and k_2 are constants. The reciprocal of k_1 depicts the initial decay rate and k_2 is a hypothetical value of the asymptotic normalized force (Steffe, 1996). Eq. (5) can be rearranged as:

$$\sigma = \sigma_0 \left(1 - \frac{t}{k_1 + k_2 \cdot t} \right) \quad (6)$$

Experimental relaxation curves were fitted by non-linear regression to the Maxwell generalized model described by Eq. (3) (Mao, Tang, & Swansson, 2000) and to the Peleg's model, Eq. (6).

2.6. Statistical analysis

Analysis of variance and pairwise comparisons were computed using the SYSTAT software (SYSTAT, Inc., Evanston, IL). Differences in means and F -tests were considered significant when $P < 0.05$. Non-linear regressions were calculated using Microcal Origin software (OriginLab, Natick, MA). Mean square errors due to regression were compared by an F -test to choose among different models tested by non-linear regression statistics. (Brandt, 1976).

3. Results and discussion

Chemical composition data for precooked chicken sausages are shown in Table 2; total protein content depended

Table 2
Proximate analysis values of the formulated and commercial sausages (% = g/100 g sausage)

Code	Moisture (%)	Protein (%)	Total fat (%)	Ash (%)
LL1	79.9 (0.13)	14.0 (0.01)	0.31 (0.004)	3.25 (0.004)
LL2	79.2 (0.02)	14.5 (0.13)	0.51 (0.003)	3.34 (0.03)
HL1	79.4 (0.11)	13.7 (0.03)	0.22 (0.05)	3.29 (0.03)
HL2	79.5 (0.01)	13.2 (0.06)	0.37 (0.01)	3.27(0.003)
LM1	77.8 (0.19)	12.7 (0.11)	2.44 (0.004)	3.34 (0.04)
LM2	77.2 (0.16)	13.6 (0.02)	2.60 (0.23)	3.38 (0.02)
HM1	77.9 (0.06)	12.6 (0.04)	2.30 (0.29)	3.26(0.004)
HM2	77.6 (0.11)	12.7 (0.01)	2.88 (0.03)	3.09 (0.04)
LH1	75.4 (0.01)	12.3 (0.19)	6.09 (0.12)	3.16 (0.09)
LH2	74.0 (0.05)	12.2 (0.16)	6.07 (0.06)	3.09 (0.02)
HH1	74.5 (0.03)	12.9 (0.08)	5.59 (0.04)	3.32 (0.01)
HH2	75.3 (0.14)	12.3 (0.35)	5.04 (0.05)	3.22 (0.02)
“A”	62.8 (0.16)	12.8 (0.14)	21.2 (1.7)	2.88 (0.3)
“B” light	69.4 (0.18)	12.9 (0.02)	4.9 (0.01)	3.47 (0.07)

Standard errors of the means are given within parenthesis. Codes are given in Table 1.

strongly on the corresponding values of the raw chicken meat, without skin, used, and they were not affected by treatments. Mean values of moisture, protein, fat, and ash contents of the raw breast chicken meat, without skin, were 74.3 (0.02), 19.7 (0.2), 1.05 (0.01), and 1.18 (0.02) g/100 g raw meat, respectively. Values between parentheses correspond to standard errors of the means. Experimentally determined chemical composition of the sausages fairly agrees with the theoretical values calculated from raw chicken meat contents and the different ingredients added. Table 2 also shows the average chemical composition of the commercial products.

Fig. 1 shows a typical relaxation curve (formulation HL2). There is first a sharp decrease in the stress after which the stress levels off to constant value. This behavior was in accord with that found by several authors working with disparate food systems (Bertola, Califano, Bevilacqua,

& Zaritzky, 1996; Del Nobile et al., 2007; Gunasekaran & Ak, 2002; Singh, Rockall, Martin, Chung, & Lookhart, 2006; Tabilo-Munizaga & Barbosa-Cánovas, 2005). The relaxation curves were analyzed with two fitting models, the generalized Maxwell model and Peleg's model, in order to choose the one that provided the best fit. Fig. 1 also shows the curves obtained by fitting both models to experimental data. It can be seen that Peleg's model was totally inadequate to predict the relaxation response. When Maxwell model was used, the number of necessary terms for a satisfactory fit was determined, obtaining seven maxwellian elements in parallel with a pure elastic element. The λ_i values proposed were: 1, 10, 100, 1000, 2500, 5000, and 10,000 s. As can be inferred from Fig. 1 the generalized Maxwell model excellently fits experimental data ($R^2 > 0.994$) suggesting that it can be advantageously used to determine the viscoelastic behavior of these systems. In this material, when it is subjected to a constant strain, the total stress is the sum of the stress of each element (Eq. (3)). In order to calculate the spectra for the different formulations tested from our stress relaxation curves, average values of the elastic moduli (G_i) were calculated for each formulation to obtain the discrete relaxation time distribution (Eq. (4)). The obtained relaxation time distribution functions for the precooked sausages are shown in Fig. 2 ($\lambda_i \cdot G_i$ vs. λ_i); plotted in logarithmic coordinates in dashed (formulations with no added fat) and solid lines (1.98 and 4.96% fat added), the continuous spectra assume the appearance of bell shaped curves. One main peak is observed, which represents the major relaxation process. Only one peak was also found when the relaxation spectra for the commercial sausages (Fig. 3) was calculated. The dominant relaxation moduli which define the peaks are shown in Table 3. The shape of the discrete relaxation time distribution is often correlated with specific molecular architectures. Fast dynamics is associated with small scale relaxation processes (small molecules, molecular strands, subunits of molecules) and, vice versa, slow dynamics (long relaxation times) belongs to macromolecular motions or

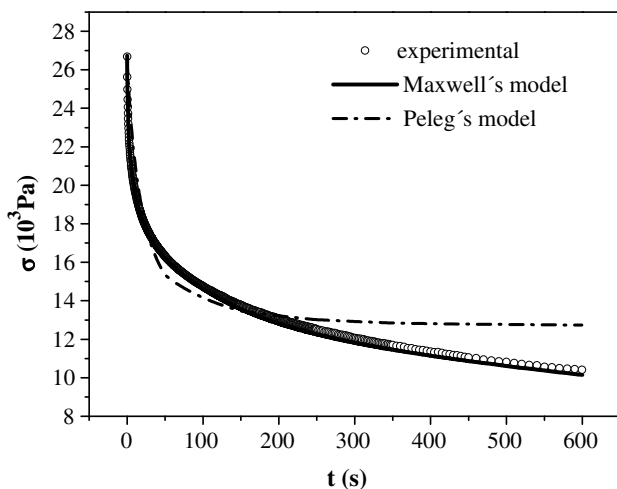


Fig. 1. Experimental stress relaxation curves (○) and values fitted with: (a) Peleg model (---); (b) an eight term Maxwell model (—) for precooked formulation HL2 (0.32% gums, 0% fat, 1.94% WPC).

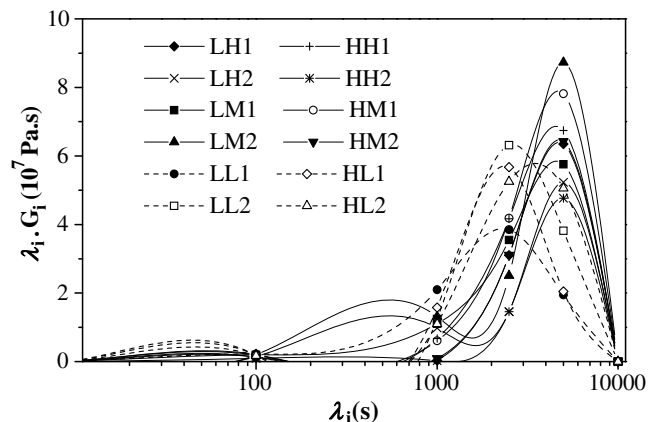


Fig. 2. Obtained relaxation time distribution functions ($\lambda_i \cdot G_i$ vs. λ_i) for the precooked sausages.

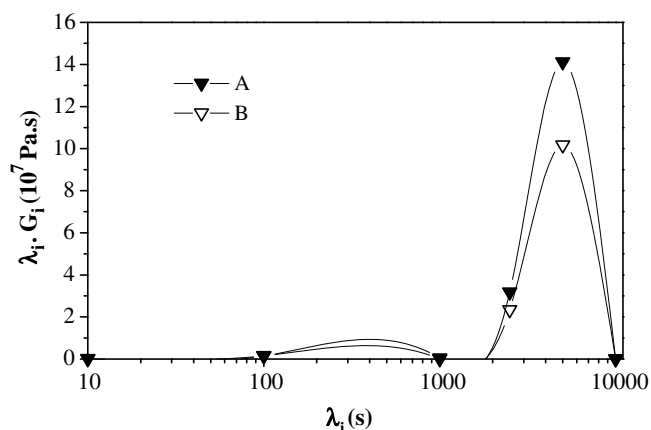


Fig. 3. Obtained relaxation time distribution functions ($\lambda_i \cdot G_i$ vs. λ_i) for the commercial products: \blacktriangledown “A” commercial regular frankfurter, ∇ “B” commercial light frankfurter.

Table 3
Generalized Maxwell relaxation moduli (G_i) that define the main peak observed in Fig. 2 for the tested formulations

Code	G_i (kPa)		
	$\lambda_5 = 1000$ s	$\lambda_6 = 2500$ s	$\lambda_7 = 5000$ s
LL1	21.0 ^a	15.4 ^c	3.9 ^d
LL2	12.5 ^{abc}	25.3 ^a	7.6 ^{cd}
HL1	15.8 ^{ab}	22.7 ^a	4.1 ^d
HL2	11.0 ^{abc}	21.0 ^{ab}	10.1 ^{bc}
LM1	11.0 ^{abc}	14.2 ^c	11.5 ^{abc}
LM2	13.2 ^{abc}	10.0 ^d	17.5 ^{ae}
HM1	6.1 ^{bcd}	16.7 ^{bc}	15.6 ^{abe}
HM2	0.9 ^d	12.4 ^{cd}	12.8 ^{abc}
LH1	0.3 ^d	12.4 ^{cd}	12.7 ^{ab}
LH2	9.8 ^{bcd}	6.3 ^d	10.5 ^{bc}
HH1	6.8 ^{bcd}	16.7 ^{bc}	13.5 ^{abc}
HH2	0.3 ^d	5.8 ^d	9.5 ^{bcd}
“A” light	1×10^{-11} ^d	9.3 ^d	20.3 ^c
“B”	4.7 ^{cd}	12.2 ^{cd}	26.0

* Different superscripts within the same column indicate that the average values differ significantly ($P < 0.05$).

Codes are given in Table 1.

long range correlation of supermolecular motions (physical aggregation, for instance). Besides, a wide range of stress relaxation time spectra suggests a broad range of junction zone strengths (Mao et al., 2000).

When a stress is applied to a macromolecular system, a finite time of the order of λ is required for the stored energy to build up to its steady-state value (Ferry, 1959). The changes during this transient period are determined by characteristic relaxation times, and the corresponding relaxation time at peak position may be considered as a characteristic relaxation time λ_c , which corresponds to the relaxation of the crosslinked polymers. λ_c describes the tendency of the flow properties of the material; as λ_c increases the relative importance of the elastic component also increases (Steffe, 1996). Relaxation processes in polymers occur on a wide range of time scales (Mours & Win-

ter, 2000). Fig. 2 shows the relaxation time distribution obtained for the products prepared in the present work while Fig. 3 corresponds to the commercial formulations. The time needed to reach the fully decayed state (λ_c) was shorter and the range of stress relaxation time spectra was wider for the formulations with no added fat (LL1, LL2, and HL1) where the peak appeared around 2500 s (Fig. 2, dashed lines). The characteristic relaxation times for the formulations with 1.98 and 4.96% fat added were displaced to longer times (5000 s), similar to the characteristic times observed for the commercial sausages (Fig. 3). No added fat corresponded to higher water contents (Table 2), thus the concentration of hydrocolloids in the aqueous phase was smaller and more water was available to facilitate the movement of macromolecules. This resulted in a material with less elastic characteristics than the rest of the formulations which contained higher hydrocolloid concentration in the aqueous phase. The HL2 formulation (no added fat, high levels of both gums and WPC) showed an intermediate characteristic relaxation time (between 2500 and 5000 s). Rayment, Ross-Murphy, and Ellis (1998) performed creep tests in guar gum-rice starch mixtures, reporting that as galactomannan concentration decreased, the stress relaxation time also decreased, which is in agreement with the tendency found in the present study.

The relaxation spectrum of a material characterizes its mechanical behavior, which is represented by the linear viscoelastic functions. Once the relaxation time spectrum is known other material functions can be calculated; as an example, equilibrium stress ($\sigma_e = \varepsilon \cdot G_e$), glassy (or instantaneous) shear modulus ($G_g = G_e + \Sigma G_i$), zero-shear viscosity ($\eta_0 = \Sigma(G_i \lambda_i)$), and steady-state compliance ($J_e^0 = (\Sigma G_i \lambda_i^2) / (\Sigma G_i \lambda_i)^2$) were calculated. σ_e , G_g , and η_0 values were not significantly affected by the different formulations, obtaining average values of $\sigma_e = 1.4$ kPa, $G_g = 8.3$ kPa, and $\eta_0 = 10.4 \times 10^4$ kPa s. J_e^0 is a measure of the stored energy in steady flow under small stresses and can be attributed to the elastic components of the material. An analysis of variance showed that only fat content affected J_e^0 values ($P < 0.03$). Mean steady-state compliance showed no significant difference between medium and low-fat contents (3.5 and 2.7×10^{-2} kPa⁻¹), while formulations with the highest fat content presented the highest J_e^0 values (4.8×10^{-2} kPa⁻¹) indicating that the increasing fat produced a more elastic network. As a comparison, the steady-state compliance for the commercial products ranged between 3.6×10^{-2} kPa⁻¹ for the regular products and 2.5×10^{-2} kPa⁻¹ for “light” ones, similar to the values found for the sausages formulated with 1.98 and 4.96% added fat.

4. Conclusions

Chicken sausages with a total lipid content ranging from 0.22% to 6.09% were formulated and their stress relaxation behavior was studied. It was found that the relaxation times distribution curves of low-fat chicken sausage formu-

lations were adequately predicted by the generalized Maxwell model, considering the superposition of eight distinct contributions. The stress relaxation experiments differentiated the viscoelastic nature of different formulations. Changes in fat content strongly modified the viscoelastic response while WPC and gums content were in general not reflected in the viscoelastic behavior at the assayed levels. Formulations with less than 1% fat showed characteristic relaxation times (λ_c) around 2500 s while fat contents above 2% shifted λ_c to 5000 s. The analysis of characteristic relaxation times and steady-state compliances (J_e^0) showed that increasing added fat (decreasing water content) produced a more elastic product.

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