VISCOELASTICAL BEHAVIOUR OF SOME FOOD MATERIALS FROM THE SPANISH MARKET

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Abstract: The yogurt presents a weak viscoelastical component due to the presence of the casein in its structure. These casein gels can be clearly distinguished from polymer gels that are formed by long macromolecules with a considerable conformational flexibility between crosslinks. On the macroscopic scale, particle gels are more brittle than polymer gels, and they tend to have a shorter linear elastic region and smaller fracture strain. the measurements of the viscoelastic parameters of weak gels must be done at very small deformations and the stress and the strain involved in the measurements may frequently be below the limits of accuracy of conventional rheological instruments. The purpose of this work is to observe the viscoelastical behavior of some yogurt from the Spanish market. For this study where picked two types of yogurt, simple yogurt and yogurt with fruit, respectively; four samples for each type, each one with different concentration of soluble content, fat content, protein and sugar content. The PCA realised obtained an explanation of the 2 components of 100%, and it was observed that yogurts are divided in two different groups, influenced by the physical chemical composition. The analysis of variance (ANOVA) conducted revealed that considering that a higher value of F-ratio means a more noticeable effect of the factor (type of yogurt) in a variable, G' was the parameters more distinguished by the type of yogurt.

Keywords: yogurt, viscosity, consistency, luminosity, water activity

1. Introduction

Viscoelasticity is the property of materials that exhibit both viscous and elastic characteristics when undergoing deformation. Viscous materials. like honey, resist shear flow and strain linearly with time when a stress is applied. Elastic materials strain instantaneously when stretched and just as quickly return to their original state once the stress is removed. Viscoelastic materials have elements of both of these properties and, as such, exhibit time dependent strain. Whereas elasticity is usually the result of bond stretching along crystallographic planes in

an ordered solid, viscosity is the result of the diffusion of atoms or molecules inside an amorphous material [1]

When a stress is applied to a viscoelastic material such as a polymer, parts of the long polymer chain change position. This movement or rearrangement is called creep. Polymers remain a solid material even when these parts of their chains are rearranging in order to accompany the stress, and as this occurs, it creates a back stress in the material. When the back stress is the same magnitude as the applied stress, the material no longer creeps. When the is taken away. original stress the accumulated back stresses will cause the polymer to return to its original form. The material creeps, which gives the prefix visco-, and the material fully recovers, which gives the suffix –elasticity [2]. Protein particle gels, which consist of a continuous three-dimensional network of flocculated particles, have attracted constantly increasing attention in the last decade. This interest reflects in part, the technological importance of these systems including a variety of soft food colloids (yoghurt, cheese, etc.) [3, 4]. Protein particle gels are normally formed by the generation of crosslinks or other attractive interactions between particles in а suspension induced by a number of different processes (enzyme action, pH lowering, heating, etc.) and followed by the transformation of a liquid suspension to а gel. These gels can be clearly distinguished from polymer gels that are formed by long macromolecules with a considerable conformational flexibility between crosslinks. On the macroscopic scale, particle gels are more brittle than polymer gels, and they tend to have a shorter linear elastic region and smaller fracture strain. The weakness of the gel network is particularly obvious around the point of sol-gel transition, thus creating complications for the application of macroscopic mechanical methods. Therefore, the measurements of the viscoelastic parameters of weak gels must be done at very small deformations and the stress and the strain involved in the measurements may frequently be below the limits of accuracy of conventional rheological instruments [4, 5].

The purpose of this paper is to make a statistical analysis of the yogurt samples from the Spanish market keeping in count the physical chemical and viscoelastical parameters using ANOVA and PCA analysis, and to note which the parameters which distinguish are.

2. Materials and methods

2.1. Materials

For this study were picked 8 samples of yogurt from the Spanish market. The samples were divided in two main categories: natural yogurt (blank samples) and fruit yogurt, respectively. The samples had different physical chemical composition (different concentrations of sugar content, fat content and protein content, respectively).

2.2. Chemical analysis

Yogurts were analyzed for protein by the Kjeldahl method, fat by Gerber method and total solids by oven drying.

2.3. Water activity

The water activity of the yogurt samples was performed using the Fast Lab 2 water activity meter.

2.4. pH measurement

pH measurements were realized with a Metler Toledo pH.-meter, at 20^oC.

2.5. Viscoelastic behaviour

Rheological measurements were carried out in a controlled stress rheometer RS1 (Thermo Haake, Germany), using a parallel cone plate geometry (35 mm diameter; and a angle of 2^0), and a sample temperature of 5^{0} C. A batch of each composition was prepared and at least two measurements were performed on each batch, using a fresh sample for each measurement. After loading the sample, a waiting period of 5 min was used to allow the sample to recover itself and to reach the desired temperature. In order to determine the linear viscoelastic region, stress sweeps were run at 1Hz first at different shear stress. Then, the frequency sweeps were performed over the range f =0.1 -10 Hz, the shear stress was $\tau = 0.05$ Pa and the values of the storage modulus (G'), loss modulus (G"), loss tangent angle (tan

 δ) and complex viscosity (G*) were registered as a function of frequency using the Rheowin Job software.

2.7. Statistical analysis

analysis of variance (ANOVA) An $(\alpha=0.05)$ with least significant difference (LSD) test using Statgraphics Plus 5.1 were performed on the data from physical chemical and viscoelastical parameters. In addition to this, the data were analyzed by using multivariate techniques, applying the software Unscramble version 10.1 (CAMO Process AS, Oslo, Norway, 2005). The variables were weighted with the inverse of the standard deviation of all objects in order to compensate for the different scales of the variables. A Principal Components Analysis (PCA) was applied to describe the relation among the physical chemical and viscoelastical parameters.

3. Results and discussion

The samples submitted to this study presented a level of fats between 0 and 10%, respectively, proteins between 3.3 and 5.2% respectively and sugar 3.90-17.10%. The pH value was in the acid

region, while the water activity was ranged between 0.98-0.99.

Yogurt samples presents a viscoelastical behaviour, but due to the weakness of the gel strength (casein chain macromolecule) the shear stress needed to achieve the linear viscoelastical region is small ($\tau =$ 0.05 Pa). The samples present a phase angle between 13.67 to 20.73 so the yogurt is a viscoelastical fluid but with the elastical component bigger than the viscous component.

The complex viscosity is strongly influenced by the frequency applied (increasing the frequency the viscosity is decreasing due to the pseudo plastic



Fig. 1. Rheogram of yogurt sample (blue line G', red line G", green line η^*

Tab.1

	Yogurt type		E ratio
	Simple	Fruit	r ratio
Physical chemical			
parameters			
Proteins	3.95a	4.5a	4.58ns
Fats	4.1a	1.82a	2.53ns
Sugars	5.8b	12.05a	7.82*
Fruits	0b	7.35a	29.4***
pH	4.21a	4.26a	2.08ns
$a_{ m w}$	0.87a	0.98a	0.9ns
Viscoelastic parameters			
G'	658.4a	261.64a	3.51ns
G"	178.05a	79.95a	2.67ns
G*	682.1a	175.3b	5.05*
η*	108.56a	126.65a	0.11*
δ	15.59a	15.71a	0.01ns

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Note: NS not significant (P<0.05), * P>0.05, ** P>0.01, *** P>0.001

behaviour of the yogurt), while the elastic and viscous component are linear, they increase with the increasing of the frequency but not in the same magnitude with the decreasing of the complex viscosity (fig.1).

A PCA was conducted to evaluate the global effect of the type of yogurt (blank, fruit) on the physical chemical, textural, rheological and color, from a descriptive point of view. Figure 2 shows the sample scores and compound loadings of the PCA analysis performed. It was found, that two principal components (PCs) explained 100% of the variations in the data set.



The PC1 explains 95% of variability, and the PC2 explains 5%. There are two main differentiated groups of samples on the plot, each group have quiet the same physical chemical composition (concentration of fats, fruits, proteins and sugar).

The PC2 differentiate the two groups (fig 2).

The loadings of each parameter on the principal components show that the grouping of the different type is primarily influenced by certain parameters. In the central ellipse could be seen the parameters which influence more the differential of the samples



Fig.3. PCA loadings of the yogurt sample (fruit, fats, proteins, fase angle) while in the outer ellipse the parameters which a lower influence (sugar, complex viscosity, G', G'', G^*).

The viscoelastical parameter which influence more the differential of the two groups in the phase angel (fig3.).In order to know if the observed differences among the different yogurt type for the each parameter are statistically significant, an analysis of variance (ANOVA) with one factor (type) was carried out (Table 1). It is known that if p-value from the ANOVA analysis is equal or superior to 0.05 there are not significant differences among type. Taking this into account differences for the physical chemical and viscoelastical parameters.

Considering that a higher value of F-ratio means a more noticeable effect of the factor (type of yogurt) in a variable, G' is the viscoelastical parameter more affected by the type of yogurt.

4. Conclusion

The yogurt is a weak viscoelastical fluid for which linear viscoelastical behaviour achieving is needed a small shear stress. The elastic component is bigger than the viscous component (confirmed by the phase angle).

The PCA divide the samples in 2 major groups, but they are divided keeping in count the physical composition and not by the type (blank or fruit yogurt). The ANOVA finds that the G' is the parameter which distinguish better the two type of yogurts.

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