EFFECT OF POTATO STARCH AND AGAR ON THE RHEOLOGICAL BEHAVIOUR OF TOMATO KETCHUP

Mircea-Adrian OROIAN¹, Gheorghe GUTT¹

¹Ștefan cel Mare University of Suceava, Faculty of Food Engineering, 13 Universității Street, 720229, Suceava, Romania, e-mail: <u>m.oroian@usv.ro</u>, <u>g.gutt@usv.ro</u>

Abstract: Two different type of hydrocolloids (potato starch and agar) were added, at different levels (for agar 0, 0,25, 0,5 and 1 g/100 g (w/w), and for potato starch 0, 0,5, 1, 2, 4g/100 g (w/w)), to a tomato ketchup which was a homemade one, having total soluble solid (TSS) content of 10 g/100 g (w/w). The intrinsic viscosity of the tomato ketchup is leading from the pectic substances which normal occurs in fruits. The effect of these two hydrocolloids used, was investigated by a rotational viscometer, Brookfield viscometer (Brookfield Engineering Inc, Model RV- DV I Prime) at 6 rpm with RV spindles. The Brookfield viscometer DV I Prime with disk spindles represents an easily and cheap method for rheological characterization of non-Newtonian fluids, in this case of tomato ketchup. Both biopolymers increased the viscosity of tomato sausage. The highest viscosity was obtained for the sample where 1 g agar / 100 g tomato ketchup was added. The tomato ketchup viscosity of the samples with potato starch has a linear evolution with the increasing of the concentration, while the viscosity of the sample with agar increases exponentially with the increasing of agar concentration.

Keywords: *hydrocolloids, pseudo-plastic, viscosity, viscometer*

Introduction:

Rheology is now well established as the science of the deformation and flow of matter: It is the study of the manner in which materials respond to applied stress or strain. [1]

Food rheology is the study of the manner in which food materials respond to an applied stress and strain. The food rheology has many applications in the fields food acceptability, of food handling. processing food and Determination of rheological properties of foodstuffs provides an instrumental quality control of raw material prior to processing, of intermediate products during manufacturing, and on finished goods after production. [2]

A gel is a solid-in-liquid colloid in which the solid phase forms a network structure that immobilizes the liquid and produces solid-like properties. Gelation arises either from chemical cross-linking through polvmer-polvmer interactions. The macromolecular substances responsible for network formation in food systems are primarily polysaccharides and proteins. [3] Hydrocolloids are water-soluble, high molecular weight polysaccharides that serve a variety of functions in food systems, such as enhancing viscosity, creating gel-structures, formation of a film, control of crystallization, inhibition of syneresis, improving texture, encapsulation of flavours and lengthening the physical stability, etc. [4]

Agar is a cell wall component of seaweeds such as *Gelidiaceae* or *Gracilariadeae* belonging to the red algae family, and is extracted with boiling water and dried. This extract is composed of two kinds of straight chain polysaccharides with galactose as the basic skeleton; one is based on the neutral polysaccharide "agarose" which governs the gelling ability of agar, the other is the acidic polysaccharide "agaropectin" which includes ionic groups such as sulfate, pyruvate and methoxy groups.

Agar swells in cold water but is not soluble. The agar dissolves in boiling water to become an aqueous solution, and forms a gel when it is cooled. It is widely accepted that agarose molecules take a random coil conformation in aqueous solution at higher temperatures while they form double helices at lower temperatures, and the aggregation of helices leads to the gel formation. [5]

Starch is a common place material of great nutritional and industrial importance. Starch occurs in most green plants as minute granules in the leaves, stems, roots, fruits and seeds [6]. In these plants, starch traditionally has been considered as a reserve material, stored for the future use of the plant. Starch Chain Structure: Chemical and Amylose. biochemical evidence indicated that the main chains of starch are composed of D glucose units, linked by α -1,4 bonds. Amylose consists entirely of α -l,4-1 inked glucose units. Most commercial starches (e.g., potato, corn) contain about 25% amylose, the remainder being amylopectin. Molecular-weight measurements indicate that amylose contains several hundreds or thousands of glucose units. Branching in Starch: Arnylopectin. It is well established that a-1,6-1inks constitute the major, if not exclusive, branching linkages. These α -1,6 branch links comprise about 4 to 5% of the total number of linkages in amylopectin.[7] Tomato is one of the most important vegetable products and is mainly marketed as a processed product, i.e. pastes, concentrates ketchup, salsa, etc. Viscosity is one of the most important quality parameters of such tomato products. Knowledge of the rheological properties of fluid and semisolid foodstuffs is important in the design of flow processes in quality control, in storage and processing stability measurements. [4]

Consistency/viscosity of ketchup is an important attribute from the engineering and consumer viewpoints. Therefore, reliable and accurate rheological data are necessary for designing and optimization of various unit operations (pumping, mixing, heating, etc.), and ensuring product acceptability since the products with improper consistency may be graded as unacceptable, or sold at lower price.[4]

2. Materials and methods

2.1. Materials

The tomato ketchup with 10% TSS was obtained using a homemade recipe, with ingredients typically used in ketchup preparation (salt, sugar, onion, garlic and spices). Agar and potato starch were provided from Romanian market.

 Table 1

 Recipe used for tomato ketchup preparation

 (for 1 kg)

(101 1 Kg)	
Ingredients	
Tomato paste, g	794
Sugar, g	50
Salt, g	10
Onion, g	50
Garlic, g	5
Spices, g	1

2.2. Preparation of tomato ketchup

To the tomato ketchup, obtained using a homemade recipe, was added agar (0,25, 0,5, 1 g/ 100g) and potato starch (0,5, 1, 4g/ 100 g). The samples were stirred for 5 min at 200 rpm with a stirrer with paddle impeller. The samples were heated at the gel formation temperature ($35^{\circ}C$ for agar, and $63^{\circ}C$ for starch) for 10 minutes on a water bath.

Agar characteristics		
Moisture %	7.5	
pH 1,5% solution	6.6	
Gelation point, ⁰ C	35	
Melting point, ⁰ C	87	

3.14

Table 3

Table 2

Potato starch characteristics	
Moisture, %	18-20%
pH solution	5-8
Ash, %	0-0.5
Gel formation temperature, ⁰ C	63

Ash, %

Each ketchup sample was then immediately poured into the glass jar, while still hot, sealed with screw caps, and then stored at room temperature $(20-22^{\circ}C)$ for 24 h before being analyzed.

2.3. Determination of rheological properties of ketchup

Viscosity measurements were carried out on the ketchup samples at room temperature (20⁰C), with a Brookfield viscometer (Brookfield Engineering Inc, Model RV- DV I Prime) at 6 rpm with RV spindles (RV2, RV3, RV4, RV5, RV6, RV7).



The samples in 300 ml of beaker with a 8,56 cm diameter (according to the Brookfield requests) were kept in a thermostatically controlled water bath for about 10 min before measurements in order to attain the desirable temperature of 25^{0} C. First measurements were taken 2 min after the spindle was immersed into each sample, so as to allow thermal equilibrium in the sample, and to eliminate

the effect of immediate time dependence.

All data were then taken after 40 s in each sample. Each measurement was duplicated on the sample.

3. Results and discussion

The pectins present in tomato have the ability to form gel and they influence the rheological properties of tomato ketchups.

According to Mitschka, P., Steffe, J.& Daubert, C. [8, 9] the Brookfield viscometer with disk spindles represents a good method to determine non-Newtonian fluid properties.

The gel formation is caused by the galacturonic acid chains associations obtained and stabilized by the non-covalent bonds: hydrogen bounds and ionic bounds.[2]

The agar has a gel formation temperature lower than the other gums. The agarose is responsible for the gel formation because of the changes in the agarose conformation from the initial linear structure to a double helices formed from left-handed threefold helices.[2]

Starch gelatinization is a process that breaks down the intermolecular bonds of good method to determine non-Newtonian fluid properties.

The intrinsic viscosity of the tomato ketchup is leading from the pectic substances which normal occurs in fruits. Pectins are complex carbohydrate molecules, used especially as gelling agents in food industry.



Fig.2. Tomato ketchup viscosity

Viscosity functions data showed that all ketchups under examination were non-Newtonian fluids, (the tomato ketchup without any hydrocolloids has a flow behaviour index n = 0,32) which was indicative of the pseudo-plastic shear thinning nature of tomato ketchups.

The two hydrocolloids increased the apparent viscosity of the tomato ketchup. The agar added to the sample obtained the higher apparent viscosity of the sample at small concentration.

Table 4.Tomato ketchup viscosity

Sample	Apparent viscosity Pa s
Tomato ketchup	4,43
Tomato ketchup 0,25% agar	11,38
Tomato ketchup 0,5% agar	61,51
Tomato ketchup 0,1% agar	326,02
Tomato ketchup 0,5% potato starch	7,47
Tomato ketchup 1% potato starch	11,17
Tomato ketchup 4% potato starch	18,01



Fig.3. Tomato ketchup viscosity with 0,5% potato starch



Fig.4. Tomato ketchup viscosity with 1% potato starch



Fig.5. Tomato ketchup viscosity with 4 % potato starch



Fig.6. Tomato ketchup viscosity with 0,25% agar



Fig.7. Tomato ketchup viscosity with 0,5% agar



Fig.8. Tomato ketchup viscosity with 1% agar



Fig.9. Influence of potato starch concentration on the tomato ketchup viscosity

The tomato ketchup viscosity of the samples with potato starch have a linear evolution with the increasing of the concentration (fig.9), while the viscosity of the sample with agar increased exponentially with the increasing of agar concentration (fig.10).

All samples with agar or with potato starch decrease their viscosity with the shear time, having a pseudo-plastic shear thinning behaviour, characteristic for the tomato ketchup (fig.3-7), the sample with 1% agar seems to have a pseudo-plastic shear thickening behaviour (fig.8).

The influence of agar is quite different from the potato starch, at 0,25% agar the consistency is like a paste, at 0,5% agar the tomato ketchup appears like a gel, and at 1% agar the tomato ketchup appears like a firm gel which rives in slices.

All the samples with potato starch appear like a paste, the sample with 4% potato starch has the highest viscosity of all the samples with potato starch.

Conclusions

The present study showed that all tested hydrocolloids (agar and potato starch) can be used to improve viscosity of tomato ketchups.

The Brookfield viscometer DV I Prime with disk spindles represents an easily and cheap method for rheological characterization of non-Newtonian fluids, in this case of tomato ketchup.

The addition of agar generated the highest

viscosity range (at 1% agar added to tomato ketchup) but the tomato ketchup structure appears like a gel and not like a



Fig. 10. Influence of agar concentration on the tomato ketchup viscosity

paste. For the industrial obtaining of tomato ketchup the addition of 0,25% agar will lead to a good consistency of tomato ketchup, the sample with 1% agar has an unpleasant aspect and it rives in slices. On the other hand, the addition of potato starch do not generate the same viscosity (the sample with 1% potato ketchup has the same viscosity with the sample with 0,25% agar), all the samples (with 0,5%, 1%, 4%) appear like a paste (having the structure of a tomato ketchup but with different consistency). The potato starch represents a cheap method of improving the rheology behaviour of tomato ketchup.

Acknowledgment

This paper was supported by the project "Knowledge provocation and development through doctoral research PRO-DOCT -Contract no. POSDRU/88/1.5/S/52946 ", project co-funded by the European Social Fund through Sectorial Operational Program Human Resources 2007-2013.

References

1. STEFFE, J., DAUBERT, C., Bioprocessing pipelines: Rgeology and Analysis, Freeman Press. USA, 2006

2. BANU, C. Aditivi și ingrediente pentru industria alimentară, Editura Tehnică, București, 2000

3. TABILO-MUNIZAGA,G, BARBOSA-CÁNOVAS, G. Rheology for the food industry, Journal of Food Engineering, 67, 147-156, Elsevier, 2004 4. SAHIN, H., OZDEMIR, F., Effect of some hydrocolloids on the rheological properties of different formulated ketchups, Food Hydrocolloids, 18, Elsevier, 2004

5. UZUHASHI, Y., NISHINARI, K., Physicschemical Properties of Agar and its Utilization in Food and Related Industry Foods & Food Ingredients Journal of Japan., Vol. 208, No.10, Japan, 2003

6. BADEN-HUIZEN, N. P. The Biogenesis of Starch Granules in Higher Plants. Appleton-Century-Crofts, New York. p. 27-37, 1969 7. FRENCH, D., Journal of animal Science Chemical and physical properties of starch, vol. 3, no. 4, Standford University Libraries Highwire Press, USA, 1973

 MITSCHKA, P. A simple conversion of Brookfield R.V.T. readings into viscosity functions, Rheologica Acta, 21, 207-209, SpringerLink, 1982
 STEFFE, J., DAUBERT, C., Bioprocessing pipelines: Rgeology and Analysis, Freeman Press. USA, 2006