Bulgarian Journal of Agricultural Science, 27 (No 1) 2021, 220–226

Rheological and structural properties of tomato ketchup as affected by the addition of native and modified starches

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Abstract

Dzhivoderova-Zarcheva, M., Nikovska, K. & Dimova, K. (2021). Rheological and structural properties of tomato ketchup as affected by the addition of native and modified starches. *Bulg. J. Agric. Sci., 27 (1)*, 220–226

It was investigated to determine the effect of several modified and/or native starches like a thickening agent, at levels of 5% on the rheological properties, consistency and syneresis of tomato ketchups. Two ketchup model systems: A (without tomato paste) and B (with tomato paste), were analyzed. The model systems A and B were non-Newtonian fluids, and their viscosity variations were closely. In general, corn starches exhibited lower Bostwick values than potato starches, especially when native corn starch was applied. With higher value of Bostwick consistency was the system A with Acetylated distarch phosphate from potato starch – 8.50±0.43 cm and with lower was the system A with Acetylated distarch adipate from waxy maze starch + Native corn starch (1:1) (ADA-WMS+NCS) and Native corn starch (NCS) – 1.00±0.05 cm. Addition of tomato paste significantly affected the consistency and the syneresis resistancy of the systems. The highest value of the separated liquid (in %) for system B was the sample with ADP-PS (13.01±0.65%), and the lowest – the sample with NCS (1.77±0.09%). On the basis of these results, the most suitable for the production of ketchup tomato and in order to reduce also the modified starch, it can be used the acetylated distarch adipate from waxy corn and native corn starch in equal proportions or only native starch.

Key words: starches; tomato ketchup; rheological properties; consistency; syneresis

Introduction

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 (Shatta et al., 2017). 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, and in understanding and designing texture. Tomato ketchup is a heterogeneous, spiced product, produced basically from either cold or hot extracted tomatoes; or directly from concentrates, purees and tomato paste (Koocheki et al., 2009). From the physical point of view, ketchup is two-phase system in which solid particles of tomato pulp and added spices are dispersed in a colloidal continuous phase that consists of sugars, salts, organic acids, a fraction of soluble pectins, and other compounds of extract dissolved in water (Ochmańska, 2006; Koocheki et al., 2009). Tomato ketchup obtains its viscosity from naturally occurring pectic substances in fruits (Lara-Espinoza et al., 2018). The most often used thickening agents are polysaccharide hydrocolloids such as: guar gum, xanthan, tragacanth, sodium alginate and starch (Sahin & Özdemir, 2007; Maity et al., 2018). Starch is one of the most abundant and widely distributed components in food stuffs. After starch granules are gelatinized by cooking in the presence of water, the molecules reassociate during cooling into gel-like structures that affect the functional and sensory properties of foods. During cold storage, the reorganization of starch molecules may result in release of water (or syneresis) to adversely affect functional properties (Papadopoulos, 2008). However, in its native form it shows low rheological stability and low resistance to mechanical, thermal, and chemical agents. Moreover, it undergoes retrogradation and syneresis phenomena that limit the use of native starch in many food products. In order to improve some physicochemical properties of the native starch, it can be modified by chemical, physical, and/or enzymatic methods or their combinations.

The resulting starch preparations exhibit different functional properties and are used as gelling, thickening, stabilizing, and filling agents in food production (Galanakis et al., 2010). Ketchup is a popular product that is used with different foods because it improves their taste. Moreover, it is easy to use and a low-calorie product. Ketchup is Non-Newtonian, shear-thinning fluid, with yield stress. It also shows thixotropy and viscoelastic properties (Koocheki et al., 2009; Hlaváč et al., 2019). Rheological properties of ketchup are essentially affected by the rheological characteristics of tomato concentrate (Bayod et al., 2008; Barbana & El-Omri, 2009). The critical parameters that influence the rheological properties of tomato concentrate and ketchup are tomato variety, the sieve pore sizes, and temperature of the concentration process (Sànchez et al., 2002; Valencia et al., 2004). Bayod et al. (2008) stated that the volume fraction of solids is the most important parameter affecting rheological properties of tomato concentrate and ketchup.

Rheological properties of ketchup depend not only on the amount of tomato paste used and its rheological characteristics but also on the kind and amount of added thickening substances. These substances essentially improve sensory and rheological properties of ketchup. The aim of this work was to evaluate the effect of different modified starches on the rheological properties, consistency and syneresis of tomato ketchups. In order to find out how the kind of modification and a botanical source of starch affect the properties of ketchup, several modified and/or native starches were used in this study.

Materials and Methods

Preparation of ketchup model systems

The A ketchup model system was obtained by mixing sugar, starch (5%), salt and water. The mixture was homogenized and then heated at temperature of 85°C for about 5 minutes before addition of citric acid (50% solution). The samples (25-26°Brix; pH 3.3-3.6) were allowed to cool down and stayed for at least 24 hours before analyzes.

The B ketchup model systems (25-26°Brix; pH 3.4-3.8) were prepared as described above, adding tomato paste (36°Brix) to ensure 6% tomato soluble solids content.

The following native and modified starches were used:

– Hydroxypropyl distarch phosphate from potato starch E 1442 (Farinex BA40), Royal Avebe – HDP-PS;

– Acetylated distarch adipate from waxy maze starch E 1422 (RESISTAMYL 341), Tate & Lyle – ADA-WMS;

– Acetylated distarch phosphate from potato starch E1414 (H-AMILACETAT 75A), Foods Consulting, Ltd – ADP-PS;

– Native corn starch (ADM Native Starch 100), Archer-Daniels Mindland Company – NCS;

Determination of consistency

Flow lengths (after 30 s) of the samples (at 20°C) were measured using a standard Bostwick consistometer (Operating instruction, Bostwick consistometer, Labomat). The results were obtained as the average values of three parallel measurements (McCarthy & McCarthy, 2009).

Rheological measurements

Rheological characteristics were determined using a Rheotest-2 rotational viscometer (RHEOTEST Medingen GmbH, Medingen, Germany), operating at 25°C within the shear rate range from 0.17 to 72.9 s^{-1}.

The dynamic viscosity (η) was calculated using the formula (Rao, 2014):

$$\eta = \frac{\tau}{D} \tag{1}$$

where τ is the shear stress, Pa; D is the shear rate, s^{-1}.

The data were fit to the Herschel–Bulkley model (Juszczak et al., 2013):

$$\tau = \tau_0 + k.D^n, \tag{2}$$

where τ is the shear stress, Pa; D – is the shear rate, s^{-1}; τ_0 – is the yield stress, Pa ; k – is the consistency coefficient, Pa.s; n – is the flow behavior index.

Determination of syneresis resistance

Following centrifugation (Hettich Zentrifugen EBA 200) for 15 min at 3000 min^{-1}, the separated liquid was quantified by weight and expressed as percentage of the sample.

Statistics

All results were expressed as the mean ±standard deviation (SD). The experimental data were subjected to analysis of variance, at the confidence level of p = 0.05, using ANOVA. The test of Tukey was used for determination of the statistically significant differences between values of the samples in the same system.

Results and Discussion

Bostwick consistency

Bostwick consistometer was commonly used in quality control of ketchup, measuring the flow length (in centimeters) of a product sample for 30 s.

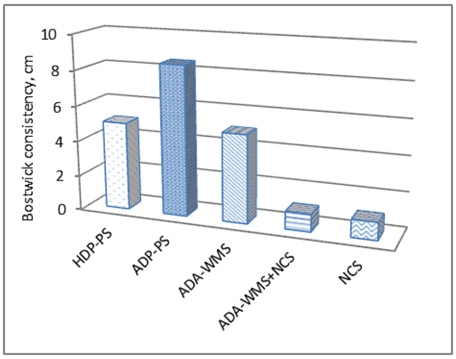
Since the ketchup model systems contained the same amount of starch, the differences observed (Figure 1) could result from the different botanical origin and/or modification pattern of the starch preparations. In general, corn starches exhibited lower Bostwick values than potato starches, especially when native corn starch was applied. The system with acetylated distarch phosphate from potato starch showed thicker consistency (8.50±0.43 cm) than the corresponding hydroxypropyl modification (5.00±0.25 cm). Addition of tomato paste (B system samples) significantly affected the consistency, observing Bostwick values are 1.00±0.05 cm for all samples.

Rheological properties

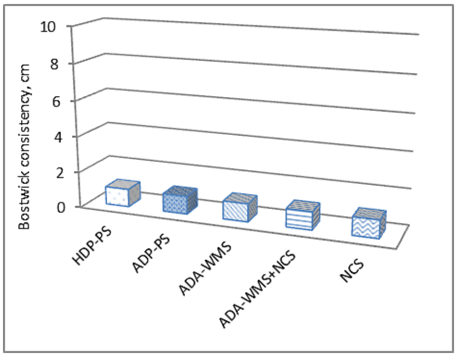
The most important factor determing the quality of tomato ketchup is its viscosity. The flow properties are an important characteristic for all foods products, and it is essential information to the economic design of the most suitable food process equipment and operation that can be selected. Rheological properties of tomato ketchups were studied at 25°C.

The rheograms of the analyzed samples are shown in Figure 2. It was obvious that the samples including 5% starch represents non- Newtonian fluids.

The rheograms of the samples (systems A and B) were given in Figure 2. These rheograms were for samples with 5% starch. The shape of these curves showed non-Newtonian, shear-thinning flow with tendency to yield stress. Non-Newtonian flow behavior of the ketchup was also observed by many authors (Koocheki et al., 2009; Juszczak et al., 2013; Hlaváč et al., 2019). The highest values of shear stress were showed by ketchup samples with ADA-WMS+NCS for system A, whereas the lowest ones were stated for samples with ADP-PS, but for system B the highest values had sample with HDP-PS, and lowest ADP-PS and ADA-WMS+NCS. These results correlated with values of consistency, indicating that ketchup thickened with ADP-PS showed the longest flow length (was the thinnest), whereas this with ADA-WMS+NCS exhibited one of the shortest length flow (was the thickest). Shear-thinning behavior, i.e., decreased in viscosity with increasing shear rate was a common phenomenon. In the case of ketchup, i.e., a product that had the structure of a suspension, shear-thinning phenomena results from orientation of solid particles of the tomato paste along the flow lines. The other factor influencing the viscosity of

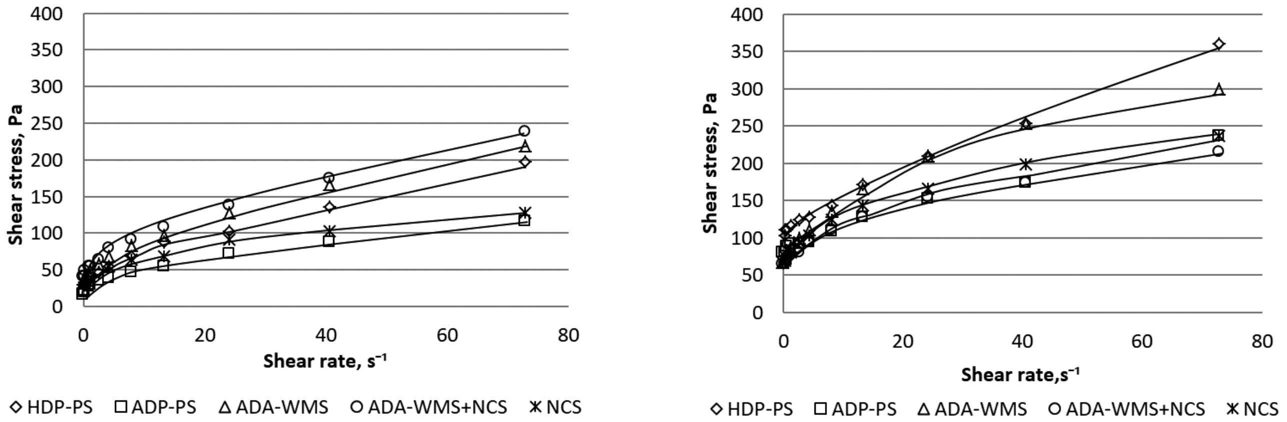


(Systems A)



(Systems B)

Fig. 1. Bostwick consistency of the ketchup model systems (Systems A – without tomato paste; Systems B – with tomato paste) prepared with different starches (5%): HDP-PS – Hydroxypropyl distarch phosphate from potato starch; ADP-PS – Acetylated distarch phosphate from potato starch; ADA-WMS – Acetylated distarch adipate from waxy maze starch; NCS – Native corn starch; ADA-WMS+NCS (1:1)



(Systems A) **(Systems B)**

Fig. 2. Rheograms of the ketchup model systems (Systems A – without tomato paste; Systems B – with tomato paste) prepared with different starches (5%): HDP-PS – Hydroxypropyl distarch phosphate from potato starch; ADP-PS – Acetylated distarch phosphate from potato starch; ADA-WMS – Acetylated distarch adipate from waxy maze starch; NCS – Native corn starch; ADA-WMS+NCS (1:1)

ketchup was presence of swollen and partially gelatinized starch granules or their fragments. At higher shear rates, individual starch granules can be deformed.

The high values of yield stress, $\tau_{0,}$ pointed to a high stability of the structure. All of the samples had closely values of τ_0. This dependence was valid for the two types of system. The consistency coefficient (k) and flow behaviour index (n,) obtained by fitting of the power law and Herschel–Bulkley models to the experimental shear stress-shear rate data, as a function of temperature were given in Table 1.

Consistency coefficient, K, from the Herschel–Bulkley model can also be used as a criterion of viscosity. In terms

Table 1. Parameters of Herschel-Bulkley models for flow curves of systems A and B

System	Sample	τ_0	K	n	R^2	τ_0	K	n	R^2
		Up curve				Down curve			
System A	HDP-PS	26.50± 1.33c	38.48± 1.92a	0.320± 0.032a	0.9532± 0.048a	13.50± 0.68a	39.10± 1.96a	0.384± 0.019a	0.9967± 0.0484a
	ADP-PS	13.70± 0.69d	25.77± 1.29c	0.313± 0.031a	0.9841± 0.049a	10.50± 0.32b	22.12± 1.11b	0.390± 0.020a	0.9934± 0.0497a
	ADA-WMS	30.60± 1.53a	47.30± 2.36b	0.309± 0.031a	0.9651± 0.048a	18.50± 0.93c	42.12± 2.11a	0.339± 0.017b	0.9795± 0.0490a
	ADA-WMS+NCS	37.10± 1.86b	48.97± 2.45b	0.335± 0.034a	0.9761± 0.047a	27.70± 1.39d	55.30± 2.77c	0.288± 0.014c	0.9459± 0.0473a
	NCS	33.30± 1.67ab	33.32± 1.67a	0.305± 0.031a	0.9755± 0.049a	25.30± 1.27d	44.84± 2.24a	0.212± 0.011d	0.9488± 0.0474a
System B	HDP-PS	56.20± 4.56e	99.92± 4.83d	0.246± 0.026abc	0.9352± 0.045b	56.20± 3.59b	106.87± 5.15a	0.224± 0.012b	0.9312± 0.0478b
	ADP-PS	60.40± 3.72e	84.68± 3.10e	0.185± 0.029c	0.9254± 0.045b	51.00± 2.55b	67.20± 3.47c	0.241± 0.011b	0.9358± 0.4503b
	ADA-WMS	58.60± 2.93g	86.99± 4.35ef	0.259± 0.026a	0.9558± 0.048b	47.30± 2.37b	74.12± 4.35c	0.301± 0.013ab	0.9692± 0.4779b
	ADA-WMS+NCS	55.50± 2.78g	74.96± 3.75f	0.212± 0.021ac	0.9465± 0.047b	28.70± 1.44c	55.99± 2.80b	0.271± 0.014a	0.9758± 0.0488b
	NCS	62.70± 3.14g	60,39± 3.02g	0.290± 0.029b	0.9974± 0.048b	32.50± 1.63c	62.71± 3.13cb	0.274± 0.014a	0.9788± 0.0489b

*Parameters between in columns for different systems denoted which have the same letters do not differ statistically at the level of confidence p = 0.05. The comparison was made between the values in the same system.

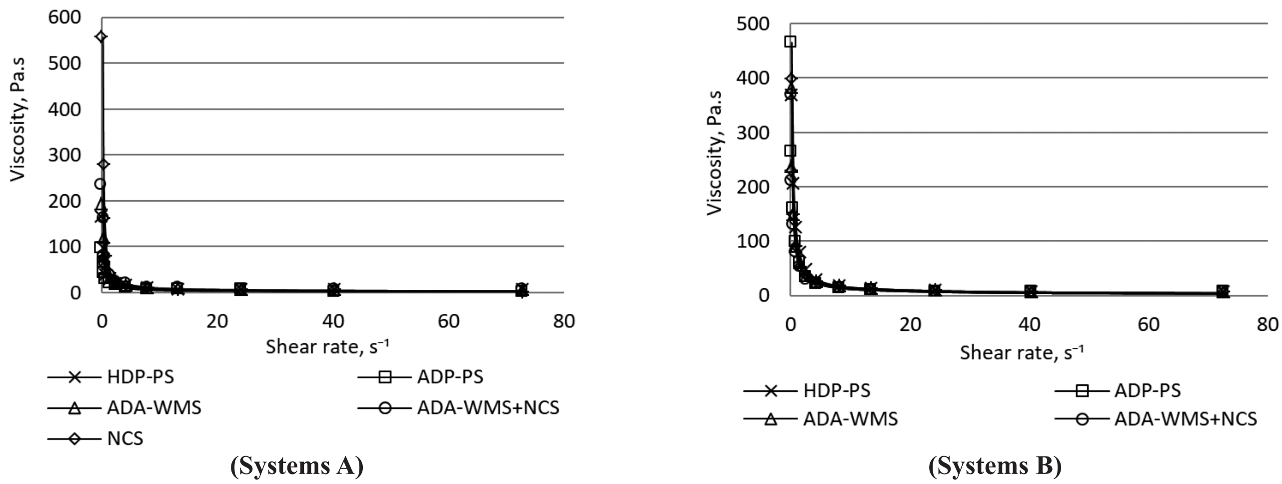


Fig. 3. Changes in the apparent viscosity of the ketchup model systems (systems A and systems B) prepared with different starches (5%): HDP-PS – Hydroxypropyl distarch phosphate from potato starch; ADP-PS – Acetylated distarch phosphate from potato starch; ADA-WMS – Acetylated distarch adipate from waxy maze starch; NCS – Native corn starch; ADA-WMS+NCS (1:1)

of that coefficient, all of the systems had high viscosity except the sample with ADP-PS – System A, which was the least viscous. The power law equation was found to be an adequate model to describe the flow behavior of the samples in this study. Viscosity functions data showed that all ketchups under examination were non-Newtonian fluids, since the values for flow behavior indices, n, were below 1, which was indicative of the pseudoplastic (shear thinning) nature of tomato ketchups (Gujral et al., 2002). The coefficients of determination (R^2) obtained were varied from 0.9967±0.0484 to 0.9254±0.045 for the Herschel–Bulkley models. The flow behavior indices (n) of the models were between 0.185±0.029 and 0.335±0.034 for the Herschel–Bulkley model.

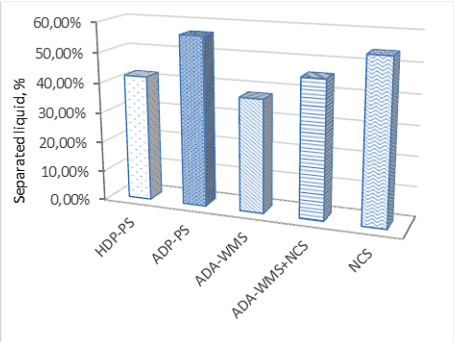
Viscosity is also defined as the main rheological property of ketchup. The viscosity values of the samples as a function of the shear rate (D) in an interval of variation of 0.17 to 72.9 s^{-1} were shown in Figure 3.

The starch amount was the same, and the reasons for the differences of the start viscosity were thickening properties of the used starches. The initial viscosity of the samples was different, and with higher viscosity were the samples with NCS System A and ADP-PS System B. The shear rate increased from 0.17 to 72.9 s^{-1}, and the viscosity decreased. These facts showed that the model systems A and B were non-Newtonian fluids, and there viscosity variations were closely. These samples had pseudoplastic properties because they flow with applying the external impact. With higher initial viscosity was a system A with NCS, which shown, that the quantity of used starch can be reduced, and it will be economical profitable. With higher start viscosity was a system B with ADP-PS, which shown, that the quantity of used starch can be reduced. The results for the Bostwick consistency showed that it had an interconnection with the viscosity.

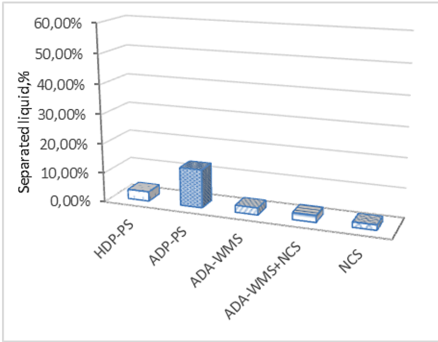
Syneresis resistance

As shown in Figure 4, the presence of tomato paste (system B) resulted in lower liquid medium separation (i.e. a better syneresis resistance) in comparison to the corresponding model systems obtained with starches only (system A). Probably, the interactions between tomato pulp particles, particularly native adsorbed pectin, and starch granules play a major role in determining the structure stability of ketchup. Pectin may retard granule swelling and leaching of starch polymer (primarily amylose) molecules, thus reducing syneresis occurrence due to amylose retrogradation. The later assumption was supported by the lower separated liquid values obtained for ketchups (system B) prepared with maize starches. Potato starches contain more amylose than maize starches, while amylose is missing in waxy corn (Luo et al., 2008; Xie et al., 2012).

Interestingly, the native corn starch, both alone (1.77±0.09%) and combined with modified waxy maize starch (2.38±0.12%), yielded the lowest values of separated liquid for ketchup model systems containing tomato paste (System B). This fact may be worthwhile from technological point of view, considering consumer concerns about the usage of chemically modified starches in foodstuffs. How-



(Systems A)



(Systems B)

Fig. 4.Values of the separated liquid after centrifugation of the ketchup model systems (systems A and systems B) prepared with different starches (5%): HDP-PS – Hydroxypropyl distarch phosphate from potato starch; ADP-PS – Acetylated distarch phosphate from potato starch; ADA-WMS – Acetylated distarch adipate from waxy maze starch; NCS – Native corn starch; ADA-WMS+NCS (1:1)

ever, further studies are needed to verify the system stability during long term storage.

In accordance with the results obtained for Bostwick consistency, the system with acetylated distarch phosphate from potato starch showed lower syneresis resistance (56.44±2.82% for system A and 13.01±0.65 % for system B) than the corresponding hydroxypropyl modification (41.96±2.10% for system A and 3.23±0.16 % for system B).

Conclusions

When in the system A was a tomato concentrate, the concentration of the system B makes higher and the viscosity increase. The highest increase of the concentration had the sample thickened by ADP-PS. An exception was made by the samples with native corn starch. The results of the Bostwick index for the samples of system B were very low, ie. the viscosity was very high. The international requirements for the Bostwick index are between 7.5 and 10 cm so the concentration of starches should be reduced.

The results from the rheological test showed that model systems had closely viscosity values.

The syneresis analyses were shown that for model system A there was more separated liquid than the samples of model system B. It can be concluded that the tomato component increasing viscosity of the samples, except the sample of native starch, also increases the resistance against retrogradation. It has been found that even the ketchup compacted with native corn starch has the lowest percentage of separated water. On the basis of these results, the most suitable for the production of ketchup tomato and in order to reduce also the more expensive modified starch, it can be used with the acetylated distarch adipate from waxy corn and native corn starch in equal proportions. These starches showed high viscosity values, which allowed reducing the amount used, and the syneresis was the lowest. The sample only with native starch also had a high viscosity and high resistance to syneresis.

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Received: November, 22, 2019; *Accepted:* December, 16, 2019; *Published:* February, 28, 2021