

RHEOLOGICAL PROPERTIES OF SOME KETCHUPS
ON THE POLISH MARKET

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Abstract. The paper presents the results of rheological measurements of five selected ketchups available on the Polish market. Rheological identification was carried out in rotary shear conditions and using forced oscillation. The equilibrium flow curves (shear at constant and stepwise increasing values of shear rate) were determined, and the thixotropic effect in the form of shear hysteresis loop under conditions of shear at increasing and then decreasing shear rates. The values of the dynamic storage modulus, the loss modulus and the complex viscosity modulus were determined in dynamic measurements. The water content was also measured, and qualitative characterisation of the structure was made on the basis of photographs taken under conditions of shear interferometry. The research revealed significant differences in rheological properties and structure of the ketchups examined. All the media showed a significant thixotropic effect. The values of apparent viscosity of the ketchups did not depend on water content but primarily on the consistency stabiliser used. The presence of modified starch had a significant impact on the flow curves, and thus on the rheological properties. The presence of tomato cell walls in ketchup structure caused the appearance of discontinuity in the flow curves at low shear rates and lower storage modulus values. It was also demonstrated that the ketchups studied did not meet the Cox-Merz equation.

Keywords: rheological properties of ketchup, apparent viscosity, thixotropic effect

INTRODUCTION

Ketchup is a popular condiment with the consistency of a sauce, made from tomato products enriched with a variety of seasonings and spices (Sharoba *et al.* 2005). It is one of the most important products made of fresh tomatoes or from tomato concentrates, pomace and pastes (Sahin and Özdemir 2004). It is a non-homogeneous product, being a suspension of insoluble components in a solution of components soluble in water (Koocheki *et al.* 2009). Ketchup is one of the

products that are known world-wide, but data on its properties and methods of production are relatively scarce in the world literature (Sharoba *et al.* 2005, Yilmaz *et al.* 2008). Commercial ketchups differ significantly in their raw material composition, spices and seasonings used, and the production technology (Koocheki *et al.* 2009, Sharoba *et al.* 2005).

The basic quality properties of ketchup include the rheological properties. This results from the fact that ketchup is usually used at ambient temperature, being pressed out of plastic tubes or poured from a glass bottle directly onto a plate or dish. Therefore, the rheological properties of the product constitute the basis for consumer acceptance (Bayod *et al.* 2008). Knowledge of the rheological properties is also necessary for designing the technological process, and in particular of the operations of mixing, homogenisation, heating, hydraulic transport, and dosage (Koocheki *et al.* 2009, Sahin and Özdemir 2004). The rheological properties of ketchup depend on a variety of factors, among which we can enumerate the raw material composition and additives used (starch, pectins, protein, water, levels of components soluble and insoluble in water, carboxymethyl cellulose, dry matter content, etc.) (Mazaheri Tehrani and Ghandi 2007, Sahin and Özdemir 2007), the enzymatic degradation of the components (e.g. starch, pectins) (Sahin and Özdemir 2004), the effectiveness of the process of homogenisation (degree of diminution and morphology of the insoluble fraction) (Bayod *et al.* 2008), and the application of special methods of production (Vercet *et al.* 2002). An important additive frequently included in ketchup is starch which is used as a modifier of rheological properties and for counteracting the stratification of the product (Hoover *et al.* 2010, Sharoba *et al.* 2005).

The existing literature reports indicate that ketchup is a non-Newtonian fluid characterised by shear rarefaction, displaying a flow limit (Bayod *et al.* 2008, Koocheki *et al.* 2009). It is generally maintained that it is a rheologically stable fluid (non-dependent on the shear time) or displaying a slight thixotropic effect (Bottiglieri *et al.* 1991, Koocheki *et al.* 2009, Sharoba *et al.* 2005). However, there are studies presenting ketchup and tomato pastes as media whose rheological properties are distinctly related to the shear time and which display either the thixotropic or the anti-thixotropic effect (Bayod *et al.* 2008, Sharoba *et al.* 2005, Tiziani and Vodovotz 2005). It is pointed out that there is a possibility of significantly modifying the rheological properties through the application of various hydrocolloids (Sahin and Özdemir 2004, Koocheki *et al.* 2009). Rheological measurements of ketchup and similar food media are usually realized in rotary rheometers with measuring system of the cylinder-cylinder type (Bayod *et al.* 2008, Juszczak *et al.* 2004, Tiziani and Vodovotz 2005). There are studies which indicate a possibility of using the Bastwick rheometer for the determination of the consistency of ketchup for technological purposes (Mazaheri Tehrani and Ghandi

2007, Probola *et al.* 2011). Most often, rheological tests are conducted under conditions of rotary shear or/and with the use of forced oscillation. Rotary shear is usually realized in the shear rate range of 0-100 s⁻¹ (Bayod *et al.* 2008, Tiziani and Vodovotz 2005). Dynamic measurements are realized usually in the frequency range from 0 to 100 Hz (Sharoba *et al.* 2005, Valencia *et al.* 2003). The model applied most frequently for the characterisation of the rheological behaviour of multiphase food suspensions is the Herschel-Balkley equation (Gamonpilas *et al.* 2011, Jaszczuk *et al.* 2004, Koocheki *et al.* 2009, Sharoba *et al.* 2005). It is emphasised that generally ketchups do not meet the fundamental Cox-Merz equation (Sharoba *et al.* 2005, Tiziani and Vodovotz 2005).

In the study presented here an attempt was made to characterise, qualitatively and quantitatively, five commercial ketchups available on the Polish market, using various methods of rheological identification. The tests were conducted under conditions of rotary shear with shear rates varied stepwise, with adopted shear cycles of increasing and decreasing shear rates, and under conditions of forced oscillation. The results of the tests are complemented with photographs presenting the morphology of particles identified in the media studied.

MATERIAL

The experimental material comprised five selected tomato ketchups of commercial brands commonly available on the Polish market. The products were purchased in a retail grocery shop and were within their shelf life. The ketchups acquired were code-named at random with the letter symbols A, B, C, D, E. According to the producers' declaration, the initial raw material for the production of ketchups A, D and E was tomato concentrate. Ketchups B and C were produced directly from fresh tomatoes. Ketchups C and E had no content of any thickeners, and the composition of the remaining three included modified starch, while ketchup D contained additionally xanthan gum as a thickener.

METHODS

Determinations of water content in the test material were conducted with the use of the method of thermal drying at atmospheric pressure, used for food concentrates in conformance with the standard PN-A-79011-3. The method consisted in the drying of samples at temperature of 105°C for 4 hours, and gravimetric determination of mass loss after the drying. The mass of the samples of the ketchups tested was 5 g. The weighing was made using a balance with an accuracy of 0.001 g. The end result was the arithmetic mean from two parallel determinations W (PN-A-79011-3).

The structure of the ketchups under study was observed under conditions of shear interferometry, in transient light, by means of an interference-polarising microscope Biolar PI. Specimen preparation consisted in placing a drop of the medium between the microscopic slide and cover glass. Observations were made at magnification of ca. 150X. Images were acquired by means of a CEMOS digital camera, OPTA TECH, with resolution of 5MP.

The rheological tests were made with the use of the rheometer HAAKE Rheo-Stress 6000, with Searle type cylinder-cylinder measuring system ZE43 DIN 53019. The outer cylinder had a diameter of $R_z = 23.5$ mm and was fixed, while the rotor was characterised by diameter of $R_w = 21.66$ mm and height of $H = 64.96$ mm. The measuring system was in a thermostatic casing, working in conjunction with a PolyScience ultra-thermostat. The measurements and the registration of results were automatic. In all cases the rheological measurements were made at temperature of 20°C.

The research plan was prepared on the basis of a series of preliminary experiments. Three independent methods of identification of the rheological properties of the media were applied:

1. Determination of equilibrium flow curves;
2. Measurement of the thixotropic effect, through the determination of the hysteresis loop in the shear of the media with repeatable deformation cycle in the CR mode;
3. Identification of rheological behaviour under conditions of oscillation-rotary shear.

The flow curves of the media tested were determined under equilibrium conditions. For that purpose measurements of equilibrium strain τ_{eqi} (Pa) were made at medium shearing for a suitably long time at constant rate of $\dot{\gamma}_i = const$ (s^{-1}). The measurement was programmed so that the reading of the equilibrium strains was automatic. The program took measurements of static strains τ_j (Pa) at every 3 s and computed their relative percentage drop on the basis of the formula:

$$\delta = \frac{\tau_j - \tau_{j+1}}{\tau_{j+1}} 100\% . \quad (1)$$

The measurement of the equilibrium strain τ_{eqi} , at a specific shear rate, lasted until the moment (maximum 120 s) when its relative drop attained values of $\delta \leq 0.5\%$, i.e. when the readings of strain decrease reached the value of:

$$\Delta \tau_{j+1} = \tau_j - \tau_{j+1} \leq 0.005 \tau_{j+1} . \quad (2)$$

Then the last measured value of strain was adopted as the equilibrium value at a given shear rate $\dot{\gamma}_i = const$, i.e.:

$$\tau_{j+1} = \tau_{eq} \dot{\gamma}_i \quad (3)$$

A series of measurements of the same sample was made automatically, from the lowest to the highest values of shear rate, at 46 measurement points according to a programmed algorithm. The shear rate values were as follows:

- within the range from 0 to 2 s⁻¹ they varied with a step of $\Delta\dot{\gamma} = 0.1$ s⁻¹ (20 measurement points),
- within the range from 2 to 10 s⁻¹ the step was $\Delta\dot{\gamma} = 1$ s⁻¹ (8 measurement points),
- within the range from 10 to 100 s⁻¹ the step was $\Delta\dot{\gamma} = 5$ s⁻¹ (18 measurement points).

On the basis of the determined values of equilibrium shear strain $\tau_{eq_i} = f(\dot{\gamma}_i)$ approximation to the Herschel-Bulkley model was performed:

$$\tau_{eq} = \tau_0 + K \cdot \dot{\gamma}^n \quad (4)$$

and the rheological parameters of the model were determined, i.e.: τ_0 (Pa) – flow limit, K (Pa sⁿ) – index of consistency, and n (–) – index of flow.

The effects of rheological instability were studied in an experiment consisting in subjecting the media to shearing in a closed cycle – initially with an increasing and then decreasing shear rates within the range from 0 to 20 s⁻¹. The measurement was made in the CR mode, during 60 s, with sampling at every 0.2 s and automatic recording of results. The rate of increase and then decrease of the shear rates was constant. Next, after taking into account the rheological constant of the measurement system, the area of the hysteresis loops obtained was determined as the difference:

$$A = A_1 - A_2, \quad (5)$$

where: A_1 (Pa s⁻¹) – area beneath the curve obtained at sample shearing at increasing shear rate, A_2 (Pa s⁻¹) – area beneath the curve obtained at sample shearing at decreasing shear rate.

The value of area obtained from the above formula is expressed in pascals per second and can be called the value of thixotropy (Sharoba *et al.* 2005). This is equivalent to the value of energy dissipated in a sample studied, in joules per second and a unit of volume of the sample tested (Schramm 1998). It should be noted that the area determined in this way may also have a negative value. Such a case will appear when the medium tested displays the anti-thixotropic effect, often referred to as rheopexy (Ferguson and Kembłowski 1995, Sharoba *et al.* 2005, Tiziani and Vodovotz 2005).

Identification of rheological behaviour under conditions of oscillation-rotary shear (CD mode of rheotest operation) was conducted within the frequency range from 0 to 50 Hz, “panning” the studied area at every 2 Hz (Schramm 1998). The oscillation angle was 0.05 rad $\approx 3^\circ$. The values measured included the modulus of elasticity G' and modulus of viscosity (loss) G'' , the complex viscosity η^* and the value of the phase shift angle δ . The results of the experiment were expressed, as in other studies, in the form of changes of the modulus of elasticity, loss modulus and phase shift angle in the function of frequency (Sopade *et al.* 2004, Yoo and Rao 1996). The results obtained under dynamic conditions were compared with data obtained in the measurements of equilibrium shear – it was tested whether they meet the Cox-Merz equation:

$$\eta^* = \eta \Big|_{\omega = \dot{\gamma}} \quad (9)$$

η' (Pa s) – value of apparent viscosity at shear rate $\dot{\gamma}$ (s^{-1}), η^* (Pa s) – value of complex viscosity at oscillation angular velocity ω (rad s^{-1}).

All rheological measurements were made in three replicates. Statistical analysis of the results was performed using the programs RheoWin 4 Job Manager and RheoWin 4 Data Manager. These programs are the original software supplied with the rheometer RheoStress 6000. They permit the calculation of rheological parameters appearing in the Herschel-Bulkley model, with the use of methods of optimisation.

RESULTS

At the start of presentation of results photographs are shown, presenting the structure of the ketchups studied. It is made up of particles of two kinds. The first component of the structure are large flat fragments of tomato cell walls, attaining notable sizes, frequently above 500 μm , with characteristic cellulose fibres, shining under conditions of shearing interferometry. On the basis of those shiny fibres we can measure the size of the flat particles present in the ketchups. The remaining part of the structure are small particles (mainly starch granules), filling the space between the flat particles. The structure is revealed particularly well during the observation of flow taking place when the microscopic glasses are pressed together. The objects observed in the structure of the ketchups are analogous to those obtained by other authors (Bayod *et al.* 2008). Even a quick visual analysis of the photos shown permits to note that the largest numbers of the large flat particles are contained in ketchups B and C which are produced directly from tomatoes. Whereas, notable amounts of starch granules can be seen in ketchups A and D. In the structure of ketchup E an absence of visible starch granules was noted,

and a large number of flat structures, but with smaller dimensions than in the case of e.g. ketchup B.

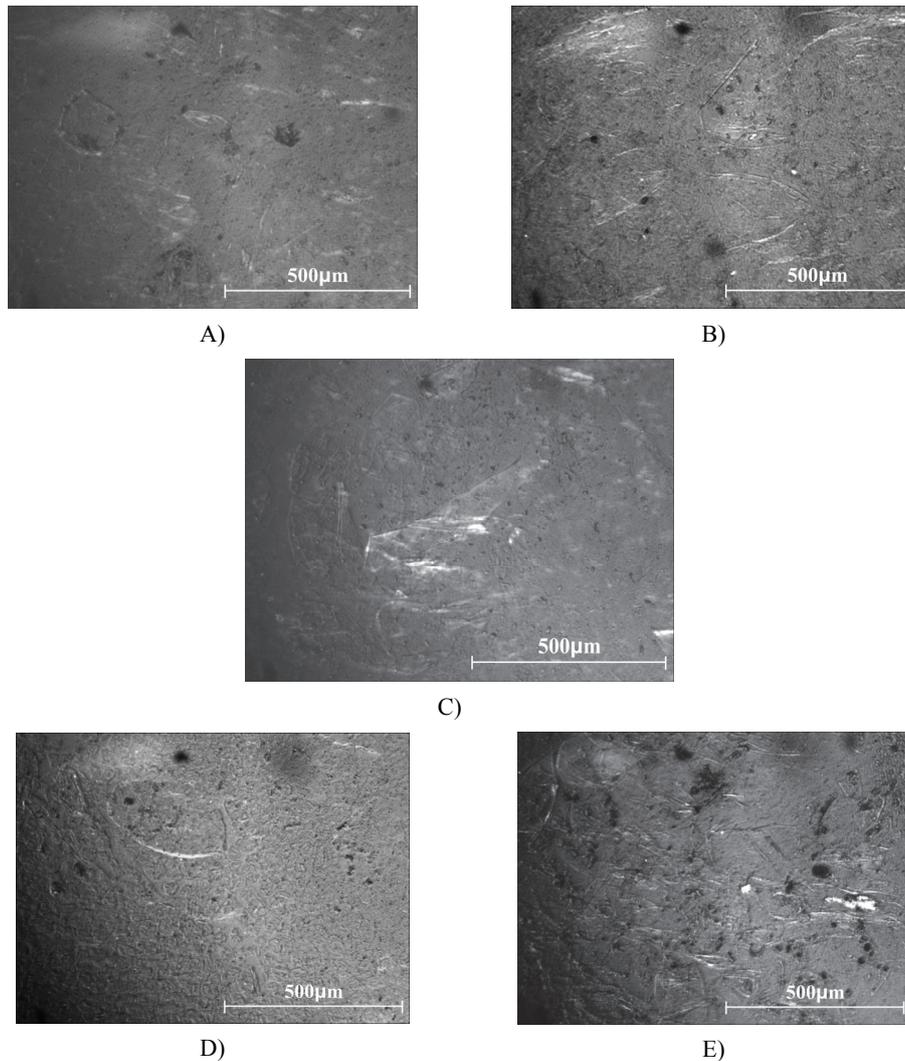


Photo. 1. Photos of the structure of studied ketchups obtained in the conditions of shearing interferometry at magnification of about 150X

The results of water content measurements are presented in Table 1. The ketchup studied differed notable in water content. The lowest water content was characteristic of ketchup B, for which it was 58.2%. The highest water content,

71.6%, was obtained for the ketchup denoted as E. The difference between those two media was as much as 13.4%. The remaining ketchups, A, C, D and E, had similar water content values within the range from 66.3 % to 69.8 %.

Table 1. Water content in the ketchups (PN-A-79011-3)

Ketchup symbol	A	B	C	D	E
Mean water content (%)	69.8	58.2	68.5	66.3	71.6

The results of the first rheological experiment are presented in Figure 1, where flow curves for the studied media within the shear rate range from 0 to 100 s⁻¹ are shown. The results are presented in the form of empirically determined discrete values of $\tau_i = f(\dot{\gamma}_i)$, against the background of which the curves obtained through approximation using the program RheoWin 4 Job Manager are shown.

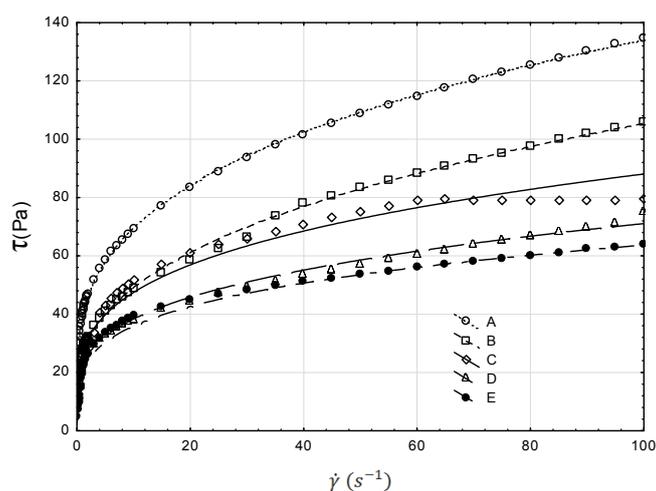


Fig. 1. Equilibrium flow curves for the investigated ketchups within shear rate range from 0 to 100 s⁻¹ (legend in Figure)

The graphic presentation of the results of approximation in Figure 1, as well as the results of statistical analysis (Tab. 2), show that the ketchups studied meet the Herschel-Balkley model relatively well. The only exception, at high share rates of $\dot{\gamma} > 60$ s⁻¹, is ketchup C which, within that area, is characterised by a practically constant value of shear strain. Greater deviations from the model curves appear within the range of low shear rates. Figure 2 presents the same results as in Figure 1, but for the shear rate range from 0 do 1.6 s⁻¹. Here we can see distinct irregularities that appear in particular at shear rates of $\dot{\gamma} < 1$ s⁻¹ in ketch-

ups C and E. It should be noted that both of those media do not have starch in their composition. This supports the conclusion of other authors that starch stabilises the rheological properties of ketchup (Hoover *et al.* 2010, Sharoba *et al.* 2005). Ketchup B was produced from fresh tomatoes, as was ketchup C, but it contains an addition of starch, due to which its empirically determined curve is relatively “smooth”.

Table 2. Results of calculations of values Herschel-Bulkley model parameters using RheoWin Job Manager 4

Ketchup	Flow limit τ_0 (Pa) $\pm\sigma$	Index of consistency K (Pa s ⁿ) $\pm\sigma$	Index of flow $n \pm \sigma$	Coefficient of determination R^2
A	13.06 \pm 0.15	26.48 \pm 0.04	0.33 \pm 0.00	0.99
B	10.56 \pm 0.05	15.74 \pm 0.04	0.39 \pm 0.00	0.99
C	6.66 \pm 0.11	20.34 \pm 0.10	0.23 \pm 0.12	0.98
D	8.29 \pm 0.02	14.38 \pm 0.02	0.32 \pm 0.00	0.99
E	2.10 \pm 0.11	18.60 \pm 0.10	0.26 \pm 0.00	0.97

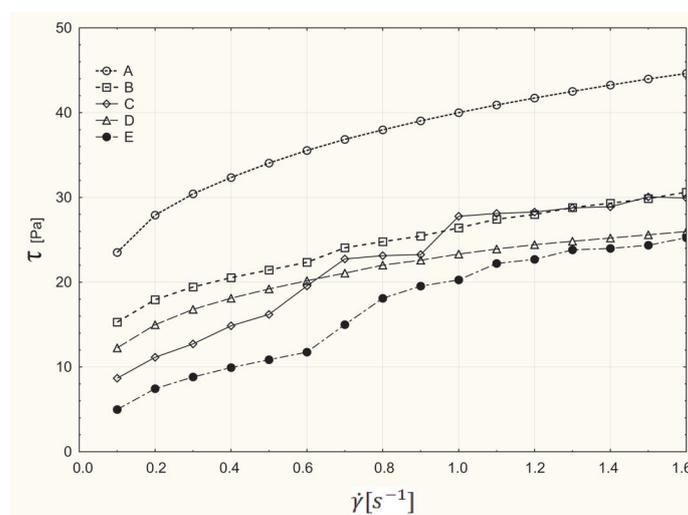


Fig. 2. Equilibrium flow curves for the investigated ketchups within shear rates from 0 to 10 s⁻¹ (legend in Figure)

The obtained results of the index of consistency K and the flow index n are comparable with results obtained by other authors (Sharoba *et al.* 2005, Koocheki *et al.* 2009).

In the course of the second rheological experiment it was demonstrated that all of the ketchups studied displayed a significant thixotropic effect, manifested in the appearance of hysteresis loop, which is shown in Figure 3. The upper curves, obtained at increasing shear rates, in four cases displayed distinct extremes in the shear rate range between 2 and 6 s^{-1} . Only ketchup A displayed a regularly rising upper curve. Particularly high extremes were displayed by ketchups C and E which had no content of modified starch. In this case we can assume that this effect was due to the internal structure of those media which was composed of a large amount of flat particles with considerable dimensions. An addition of starch reduced that effect, but does not eliminate it, which is clearly illustrated by hysteresis loops of ketchups B and D. The values of the area of hysteresis loop were the highest for ketchup A, and the lowest for the medium marked with the symbol D (Tab. 3). The values obtained constituted the central part of the range of hysteresis loop areas of ketchups, obtained by Sharoba *et al.* (2005). Among the samples tested, within the strain ranges examined the anti-thixotropic effect was noted only in the case of ketchup E and that only at shear rates of $\dot{\gamma} < 1 \text{ s}^{-1}$.

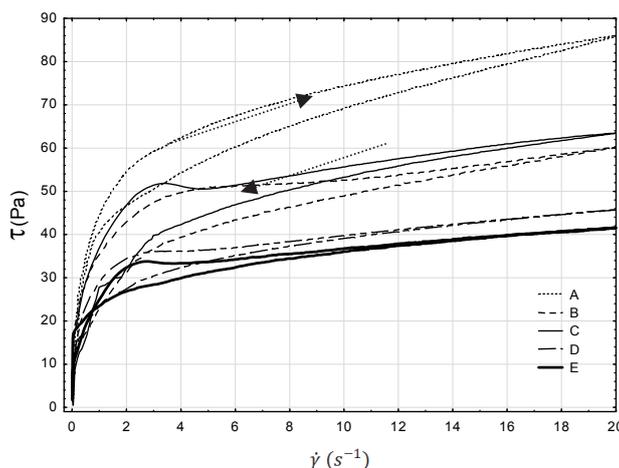


Fig. 3. Hysteresis loops studied ketchups identified during shear with increasing and then decreasing shear rates within the range from 0 to 20 s^{-1} (legend in Figure)

Subsequent Figures present the results of dynamic measurements. Figures 4 and 5 present changes in the values of the storage modulus and loss modulus in relation to the frequency of oscillation. In all cases the values of the storage modulus increased systematically from the frequency of about 6 Hz. The highest values of G' were obtained for ketchups A and B, and the lowest value was that for ketchup E. Both the values and the character of the changes of the storage

modulus are analogous to those obtained by other authors (Sharoba *et al.* 2005, Koocheki *et al.* 2009).

Table 3. Surface area of hysteresis loops in the media tested

Product	A_1 (Pa s ⁻¹) or (W m ⁻³)	A_2 (Pa s ⁻¹) or (W m ⁻³)	$A = A_1 - A_2$ (Pa s ⁻¹) or (W m ⁻³)
A	1413	1284	128.5
B	1027	913	113.9
C	1084	982.2	102.3
D	778.3	726.3	52.02
E	724.1	667.9	56.23

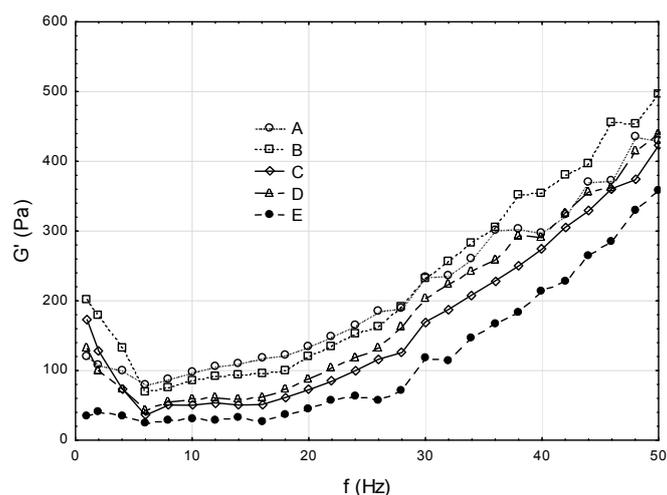


Fig. 4. Storage modulus of investigated ketchups (legend in figure)

In the case of modulus G'' there were no such characteristic behaviours, which can be seen in Figure 5. In the frequency range up to 25 Hz the variation of the loss modulus values was slight. At $f = 30$ Hz there appeared a minimum in the case of ketchups A and D, while in the other ketchups that minimum occurred in the range of $f \in (35 \text{ Hz}, 40 \text{ Hz})$. At higher frequencies in all the cases there was a regular increase in the values of modulus G'' . Comparison of the character of those changes with the results obtained by Sharoba *et al.* (2005) shows that they differ primarily qualitatively. One can assume that the minimum observed in the

range of $f \in (30 \text{ Hz}, 40 \text{ Hz})$ is related with exceeding the range of linear viscoelasticity. This results directly from the applied amplitude of oscillation, i.e. the adopted value of the angle of oscillation which, in the study presented here, was $0.05 \text{ rad} (\approx 3^\circ)$. Analysing the conditions involved in the realization of research by other authors, usually no information is given on the values of the amplitude of oscillation, and emphasis is placed only on the fact that measurements were realized under conditions of linear viscoelasticity (Bayed *et al.* 2008, Yilmaz *et al.* 2008). Therefore, in determinations of this kind, it is recommended to apply a lower amplitude of oscillation and to check whether the range of linear viscoelasticity has not been exceeded (Schramm 1998). Nevertheless, the above results indicate that the minimum appearing at the loss of viscoelasticity can be also used for the rheological differentiation of ketchups, as its occurrence is related with the internal structure of the fluid and with the oscillation amplitude applied.

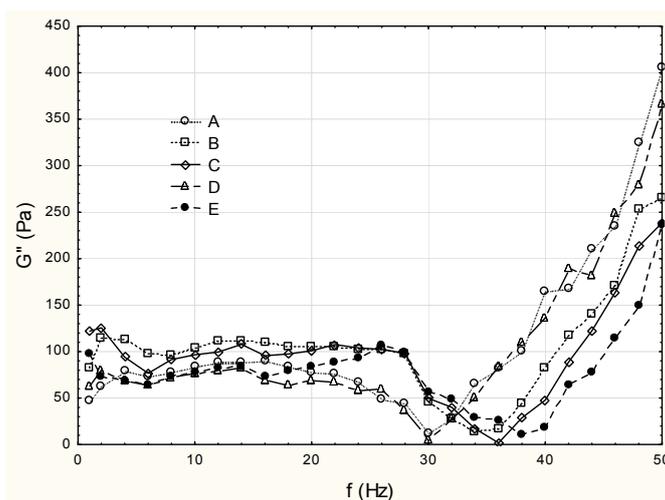


Fig. 5. Changes in the values of the loss modulus (G'') as a function of the frequency of oscillation (legend in Figure)

The values of complex viscosity obtained under dynamic conditions were compared with the values of apparent viscosity obtained in rotary shear tests and under equilibrium conditions. Figure 6 presents, in the form of a double logarithmic graph, a summary of the results of measurements obtained with those two methods. The results of the comparison clearly demonstrate that the Cox-Merz equation is not met over the whole range of shear rates and angular velocities of oscillation. In all the cases the values of complex viscosity obtained for the ketchups studied are higher than those of apparent viscosity. Analogous results were

obtained by Yilmaz *et al.* (2011). In addition, it should be noted that the results obtained in rotary shear differ not only quantitatively but also qualitatively from the results obtained in oscillation shear. The highest values of apparent viscosity in rotary shear were obtained for ketchup A, followed successively by ketchups B, C, D and E. In oscillation shear (at $\omega > 30 \text{ s}^{-1}$) the highest values were obtained for B, followed by ketchups A, C, E and D, respectively. The differences are the result of the effect of the internal structure of the ketchups on the changing conditions of shearing in the rotary and the oscillating flows.

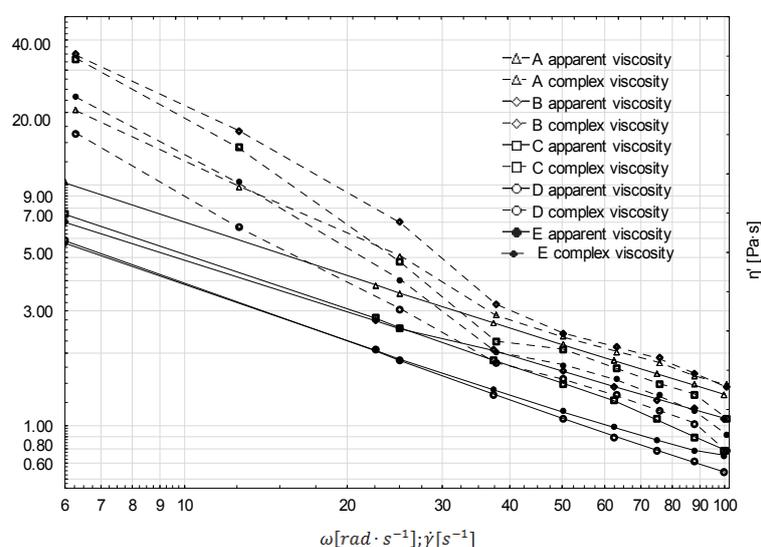


Fig. 6. Summary of the apparent and complex viscosity of the ketchups tested

CONCLUSIONS

1. The ketchups tested displayed significant differences in their rheological properties. They differed in the values of the flow limit, index of consistency, flow index, and the apparent and complex viscosity.

2. All the ketchups used in the experiment can be classified as thixotropic fluids. They displayed the strongest thixotropic effect at shear rates of $\dot{\gamma} < 6 \text{ s}^{-1}$.

3. An addition of starch in the composition of ketchup stabilises the rheological properties (smooth flow curves) and “masks” its water content. Ketchup A, which was characterised by water content at the level of 69.8% and had the highest content of starch, displayed the highest values of apparent viscosity. Ketchup B, although it contained 58.2% of water, was characterised by significantly lower values of apparent viscosity.

4. The results of rheological tests of ketchups are affected by the method of their measurement. Results obtained under conditions of rotary shear differ qualitatively and quantitatively from those obtained under the conditions of oscillating shear. The ketchups do not meet the Cox-Merz equation. This is surely a result of the presence of particles with irregular shapes in their structure.

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WŁAŚCIWOŚCI REOLOGICZNE WYBRANYCH KETCHUPÓW NA RYNKU POLSKIM

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Streszczenie. W pracy przedstawiono wyniki pomiarów reologicznych pięciu wybranych ketchupów dostępnych na rynku polskim. Identyfikację reologiczną prowadzono w warunkach ścinania rotacyjnego i za pomocą oscylacji wymuszonych. Wyznaczano równowagowe krzywe płynięcia (ścinanie przy stałych i skokowo rosnących wartościach szybkości ścinania) i efekt tiksotropowy w postaci pętli histerezy przy ścinaniu w warunkach rosnących, a następnie malejących szybkości ścinania. W pomiarach dynamicznych wyznaczono wartości modułu magazynowania, modułu strat i lepkości zespolonej. Mierzono również zawartość wody i jakościowo charakteryzowano strukturę na podstawie fotografii wykonanych w warunkach interferometrii birefrakcyjnej. W wyniku badań wykazano, że występują znaczące różnice we właściwościach reologicznych oraz strukturze ketchupów poddanych badaniom. Wszystkie media wykazywały znaczący efekt tiksotropowy. Wartości lepkości pozornej ketchupów nie zależały od zawartości wody, ale głównie od użytego stabilizatora konsystencji. Obecność skrobi modyfikowanej wywierała znaczący wpływ na przebieg krzywych płynięcia, a tym samym właściwości reologiczne. Obecność ścian komórkowych pomidorów w strukturze ketchupu wpływała na wystąpienie nieciągłości w krzywych płynięcia przy niskich szybkościach ścinania i niższe wartości modułu magazynowania. Wykazano również, że badane ketchupy nie spełniały równania Coxa-Merza.

Słowa kluczowe: właściwości reologiczne ketchupu, lepkość pozorna, efekt tiksotropowy