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MODELLING OF EMULSION PROPERTIES BASED ON THE THE RHEOLOGICAL PROPERTIES

MODELOWANIE WŁAŚCIWOŚCI EMULSJI Z WYKORZYSTANIEM WYNIKÓW BADAŃ REOLOGICZNYCH

Key words: rheological properties, paraffin emulsions, flow curves, modelling.

Abstract The article presents the research results of paraffin emulsion properties. The emulsions were developed for use in food packaging. The issue of modelling the rheological properties of these emulsions was presented. In the scope of the article, the analysis of the results of the impact of the production method on the variability of the rheological characteristics of emulsion is presented. In the research results, it has been shown that the use of the twofold homogenization process significantly improves the important properties due to the planned application of applying emulsion on packing paper. Modelling of this type of emulsion was carried out to describe the curves of their flow. In the modelling process, commonly used rheological equations were selected and adjusted to the results of emulsion properties tests. The following models were analysed: Bingham, Casson, and Herschel-Bulkley. The models parameters were established based the experimental data, and then the parameters of different models, for each emulsion, were compared. As a result of the rheological properties tests, it was shown that of the emulsions produced are the yielding and viscous fluids that are diluted by shear and can be described with a high accuracy by the Herschel-Bulkley model.

Słowa kluczowe: właściwości reologiczne, emulsje parafinowe, krzywe płynięcia, modelowanie.

Streszczenie W artykule przedstawiono wyniki badań reologicznych emulsji parafinowych. Analizowane emulsje zostały opracowane w celu zastosowania ich na opakowania przeznaczone do żywności. Przedstawiono problem modelowania właściwości reologicznych tych emulsji. Analizie poddano wpływ sposobu wytwarzania emulsji na zmienność ich charakterystyk reologicznych. Wykazano, że zastosowanie procesu dwukrotnej homogenizacji znacząco poprawia właściwości istotne ze względu na planowane zastosowanie do nanoszenia na opakowania papierowe. Przeprowadzono modelowanie tego rodzaju emulsji w celu opisu krzywych ich płynięcia. W procesie modelowania dopasowano wybrane stosowane powszechnie równania reologiczne do wyników badań emulsji. Uwzględniono modele: Binghama, Cassona oraz Herschela-Bulkleya. Wyznaczono i porównano parametry reologiczne modeli. W wyniku przeprowadzonych badań wykazano, że właściwości reologiczne wytworzonych emulsji wykazują cechy płynów plastyczno-lepkich rozrzedzanych ścinaniem oraz z wysoką dokładnością opisywane są przez model Herschela-Bulkleya.

INTRODUCTION

One of the basic objectives of experimental research in technical sciences is the development of prognostic models, which can provide information about the behaviour of the examined objects obtained under the influence of changes in the input quantities (independent variables).

In the case of object design, it is important to examine and analyse the impact of the process variables on the developed object's properties. For this purpose, experiments are planned, and the results are an important source of information in explaining and forecasting the impact of the process variables on product properties. This knowledge ensures appropriate planning of production process parameter values in order to obtain the required features of the manufactured object.

Properly planned and reliably realized experimental research provides a specific set of data, which can be used to solve a given problem, and it requires the assessment of their credibility and conversion into the form of an appropriate mathematical model.

In technical sciences, the quality of regression models is assessed on the basis of the statistical significance of the model and of the R2 coefficient of determination, assessing to what extent the developed model maps the results of experimental research.

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However, the most important for practical applications is the quality measure of prognostic models which is relative error, calculated as the quotient of the difference between the value determined on the basis of the model and the value determined experimentally to the measured value **[L. 1]**.

In the case of designing the rheological properties of the object, which in the presented studies were paraffinic ecological emulsions, their composition, as well as the method of production play an important role. Paraffin impregnates used for surface coating food packaging require the determination of their functional characteristics and precise identification of the area of application **[L. 2]**.

In the literature on the area, numerous publications deal with the problems of the impact of different parameters on rheological properties in various application areas **[L. 3–5]**. Researchers attempt to generalize the obtained results by applying mathematical models to their descriptions, often by determining the values of parameters of existing models with the use of their own results to obtain the model of analysed object **[L. 6–9]**.

The rheological properties of emulsions depend on many factors. Emulsions rarely show only viscous or elastic properties, and the complexity of their physicochemical state describes well the analysis of viscose-elastic features. Rheological research is particularly useful for quality control of raw materials and ready emulsions; assessment of the impact of technological processes on the quality of the final product; assessment of the influence of other factors, such as composition, temperature and storage time, on the quality of the product, determining the impact of the qualitative and quantitative composition of emulsifiers and dispersing phases on the characteristics of the obtained emulsions.

Due to the planned application of the developed emulsions for coating the surface of paper packaging, rheological properties are an important determinant of the proper course of the application process. The rheological properties of emulsions are of direct importance in the processes of its application to various types of paper packaging and must be within the limits appropriate to the parameters of this process. Therefore, in the scope of the modelling process, we analysed the possibility of using standard rheological models to describe experimental data from the emulsion tests and to determine rheological parameters based on these models. The article presents the results regarding the modelling of rheological properties of adequately composed water-paraffin emulsions. Information on the method of preparation and the characteristics of the emulsion was presented earlier in the article **[L. 10]**.

MATERIALS AND METHODS

The investigations covered the properties of emulsions developed as part of a project aimed at designing impregnates for paper packaging used in the food industry.

The materials for the tests were the selected emulsions produced at the Institute of Heavy Organic Synthesis "Blachownia." The paraffin Emulsions 1 and 2 were tested, each of which was analyzed, taking into account different production methods according to the following determinations: M- without homogenization, H1- using the homogenization process, and H2 – using a twofold homogenization. Emulsions 1 and 2 were prepared using commercial emulsifiers.

Due to the planned use of emulsions in the food packaging industry, it was necessary to develop an emulsion containing only ingredients authorized for use in this area. After analyse of the research results on the impact of the manufacturing process on the quality of the emulsion, twofold homogenization was selected as proper for the aim achievement. Then modelling studies, the rheology of 1H2, 2H2, 3H2, 4H2 emulsions prepared using twofold homogenization, were prepared. The emulsions differed in composition, in particular, the emulsifier used and the dry weight content.

To determine the rheological properties of paraffin emulsions, a rotary rheometer MCR-101 with an air bearing, produced by Anton Paar, was used. The tests were performed using a CP50-1 cone-plate measurement system with a measuring gap of 104 μm. The results of the measurements of shear stresses and apparent viscosity carried out at a shear rate change in the range up to 100 s-1 were analysed. Each measurement was repeated three times.

In the modelling process, the results of rheological research of the developed emulsions were used. The test results were analysed for the possibility of describing the course of the flow curves with standard rheological models. Regression analysis was used to determine the parameters of rheological models.

RESULTS AND DISCUSSION

The results of measurements of shear stresses from three repetitions for exemplary emulsions: 1M, 1H1, and1H2, of the same composition but made using different processes (without homogenization, with one-fold homogenization and with twofold homogenization) are shown in **Figures 1–3**. On each of the drawings, data from each of the three repetitions of measurements are marked.

Similar differences in the course of the emulsion flow curve depending on the method of its preparation were observed for Emulsion 2.

Table 1 shows the average variability of results obtained in subsequent measurements of shear stress at different shear rate values for Emulsions 1 and 2 made using different processes. The variability was calculated as the quotient of the standard deviation to the mean value (of three measurements). The coefficient of variation is presented as a percentage.

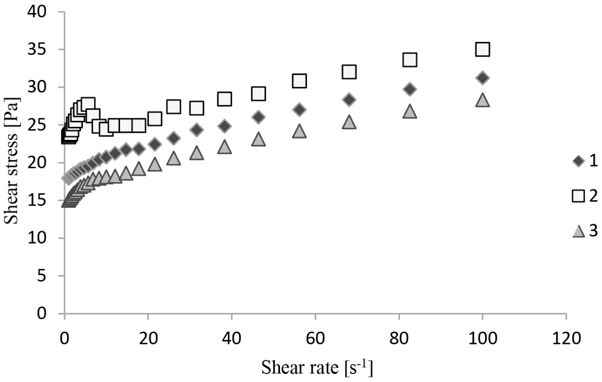

Fig. 1. Results from three replications of shear stress measurements depending on the shear rate of Emulsion 1M (without homogenization)

Rys. 1. Wyniki z trzech powtórzeń pomiarów naprężeń stycznych w zależności od szybkości ścinania emulsji 1M (bez homogenizacji)

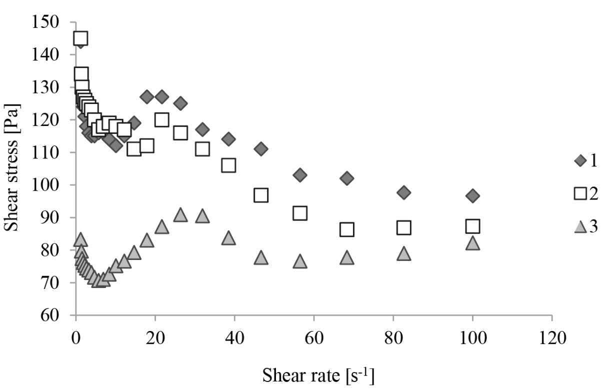

Fig. 2. Results from three replications of shear stress measurements depending on the shear rate of Emulsion 1M (one-fold homogenization)

Rys. 2. Wyniki z trzech powtórzeń pomiarów naprężeń stycznych w zależności od szybkości ścinania emulsji 1H1 (jednokrotna homogenizacja)

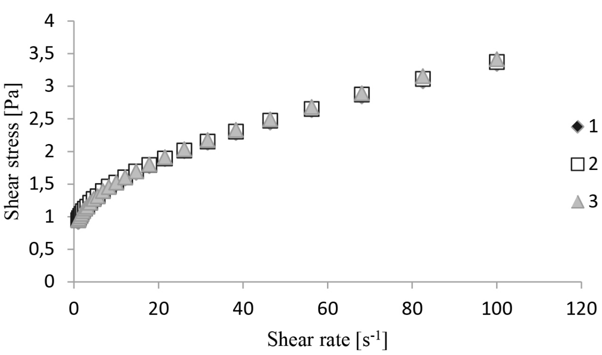

Fig. 3. Results from three replications of shear stress measurements depending on the shear rate of Emulsion 1M (twofold homogenization)

Rys. 3. Wyniki z trzech powtórzeń pomiarów naprężeń stycznych w zależności od szybkości ścinania emulsji 1H2 (dwukrotna homogenizacja)

Table 1. Average values of the variable's coefficient of the measurements of shear stress during emulsion shearing

Tabela 1. Średnia wartość współczynnika zmienności wyników z pomiarów naprężeń stycznych przy ścinaniu emulsji

Emulsion	1M	1H1	1H2	2M	2H1	2H2
	%					
Average variability of shear stress	17.8	21.2	1	12.1	26.3	0.9
Average variable of apparent viscosity	17.8	20.5	0.9	12	25.9	1

Changes in shear stress depending on the shear rate testify to the non-Newtonian nature of the flow of the emulsions studied.

The analysis of the results **(Figs. 1–3)** and the coefficients of variation of shear stress **(Tab. 1)** indicate the importance of the production method of the emulsion for its rheological properties and the repeatability of emulsion flow depending on the shear rate. Emulsions prepared using twofold homogenization are characterized by the best repeatability of rheological properties, namely, shear stress and viscosity. Emulsions 1H2 and 2H2 show significantly better features, compared to those obtained without the homogenization, due to planned use, including lower values of apparent viscosity in the range of the tested shear rates and lower values of the yield point. Therefore, in subsequent analyses, different emulsions were taken into account due to composition but produced using the twofold homogenization method.

RHEOLOGICAL MODELS OF EMULSIONS FLOW

In the modelling process, the results of investigations of the developed emulsions (1H2, 2H2, 3H2, and 4H2) were used.

The influences of the shear rate on shear stresses and the yield stress of the developed emulsions were analysed. The courses of changes in shear stresses, depending on the shear rate, are non-linear, which indicates a non-Newtonian character of flow. Because the analysis of the measurement results showed that the tested emulsions have the characteristics of viscous-like fluids to describe the course of the flow curves, the following standard rheological models for this type of fluids were used **[L. 11]**:

- Bingham model

$$\tau = \tau_o + \eta\dot{\gamma} ,$$

- Herschel-Bulkley model

$$\tau = \tau_o + k\dot{\gamma}^n ,$$

- Casson model

$$\tau^{\frac{1}{2}} = \tau_o^{1/2} + \left(\eta_C \dot{\gamma}\right)^{1/2}$$

τ_o – field stress, Pa
η – viscosity of fluid, Pa·s
$\dot{\gamma}$ – shear rate s^{-1}
k – correlation ratio, $Pa \cdot s^n$
η_C – viscosity of Casson, Pa·s

Models parameters were obtained using regression analysis.

Figs. 4–7 show the flow curves.

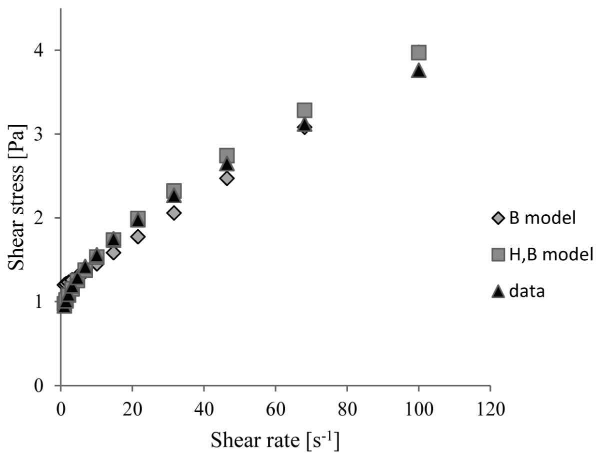

Fig. 4. Emulsion 1H2 flow curves, data, and model calculations

Rys. 4. Krzywe płynięcia emulsji 1H2, dane i wyliczenia modeli

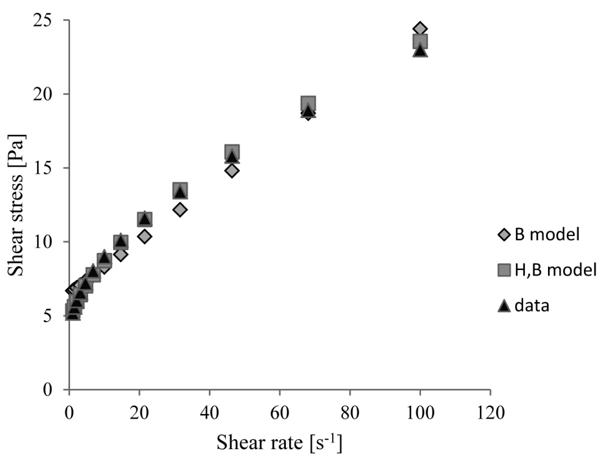

Fig. 5. Emulsion 2H2 flow curves, data, and model calculations

Rys. 5. Krzywe płynięcia emulsji 2H2, dane i wyliczenia modeli

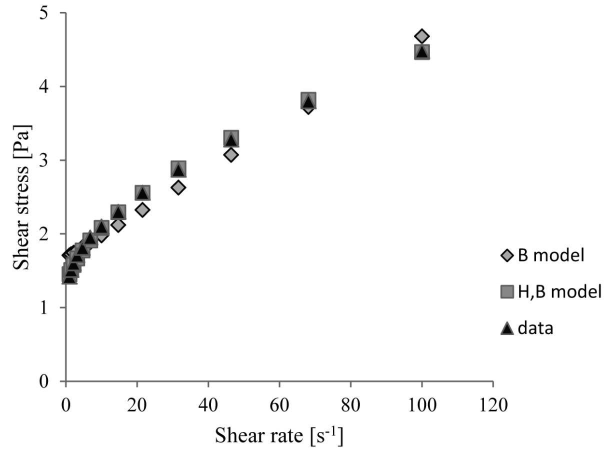

Fig. 6. Emulsion 3H2 flow curves, data, and model calculations

Rys. 6. Krzywe płynięcia emulsji 3H2, dane i wyliczenia modeli

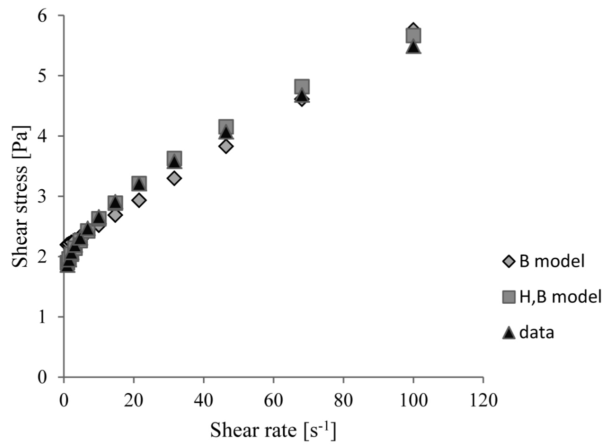

Fig. 7. Emulsion 4H2 flow curves, data, and model calculations

Rys. 7. Krzywe płynięcia emulsji 4H2, dane i wyliczenia modeli

All applied rheological models were able to reproduce the measurement data well. The correlation coefficients of experimental data and calculations of the Bingham model for all emulsions were 0.98, for the data and calculations of the Casson model – 0.999, and for the Herschel, Bulkley model – 1.00 **(Tab. 2)**. The Herschel, Bulkley model and the Casson model better reflect the real relationships between shear rate and shear stress, especially in the case of lower shear rates. The differences between calculations of these models and data from measurements were much smaller than for calculations of the Bingham model. For example, **Fig. 8** shows the differences between calculations of models and data for Emulsion 3H2. **Table 2** presents the rheological parameters characterizing individual emulsions according to models' calculations, and the correlation coefficients with data.

Table 2. The rheological parameters of models and correlation coefficients with data.
Tabela 2. Parametry reologiczne modeli i współczynniki korelacji z danymi

Emulsion	Bingham model			Herschel-Bulkley model				Cassona model		
	$\tau = \tau_0 + \eta * \gamma'$			$\tau = \tau_0 + k * \dot{\gamma}^n$				$\tau^{1/2}=\tau_0^{1/2}+(\eta_c * \dot{\gamma})^{1/2}$		
	τ_0 [Pa]	η [Pa s]	R	τ_0 [Pa]	k [Pa s]	n	R	τ_0 [Pa]	η_c [Pa s]	R
1H2	1.174	0.028	0.981	0.81	0.166	0.635	0.999	0.86	0.011	0.999
2H2	6.51	0.179	0.983	4.32	1.01	0.641	1.000	4.29	0.077	0.999
3H2	1.683	0.03	0.981	1.23	0.224	0.582	1.000	1.25	0.01	0.999
4H2	2.164	0.036	0.981	1.67	0.23	0.617	1.000	1.64	0.011	0.999

The yield stress for individual emulsions determined on the basis of the Casson and Herschel-Bulkley models differ slightly when compare to the calculations based the Bingham model, but the differences are significant. All models have high determination rates. The Bingham model explains 96% variation in shear stresses, while both the Casson and Herschel-Bulkley models explain 99%, which means that they better describe the properties of the emulsions studied.

According to all models, the smallest values of yield stress and the lowest values of viscosity indexes were determined for Emulsion 1H2 that containing emulsifiers that are not approved for use in contact with food. Emulsion 3H2 and Emulsion 4H2 are characterized by equally good rheological indexes, and they also meet the requirements for the intended use.

Differences in shear stress calculations of models and data from measurements showed a downward trend for all analysed emulsions with an increase in the shear rate above $10 s^{-1}$. **Fig. 8** shows the differences between calculations of models and data for 3H2 emulsions.

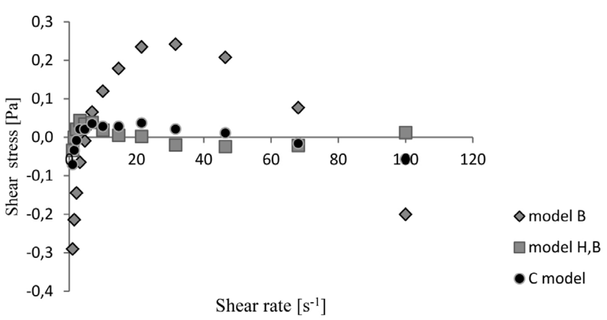

Fig. 8. Differences in shear stresses calculated from individual models and measurement data
Rys. 8. Różnice naprężeń stycznych wyliczonych z poszczególnych modeli i danych z pomiarów

The Herschel-Bulkley model and the Casson model imitate the actual relationship between shear rate and shear stress better than the Bingham model. Especially in the case of lower shear rates, the difference between the calculations of these models and the data from the measurements is much smaller than for the calculations of the Bingham model. Because the Herschel-Bulkley model is considered as the simplest model describing non-linear rheological properties of viscous liquids, in the case of the analysed emulsions, this equation should be used to describe the flow of the investigated emulsions **[L. 11]**.

The curves of changes in viscosity as a function of shear stresses were similar for all emulsions. However, values of apparent viscosity differed significantly in the range of small shear stresses. The curves established based the measurement data of viscosity as a function of tangential stresses are shown in **Fig. 9**. The values of viscosity of Emulsion 2H2 were many times higher than the viscosity of the other emulsions analysed.

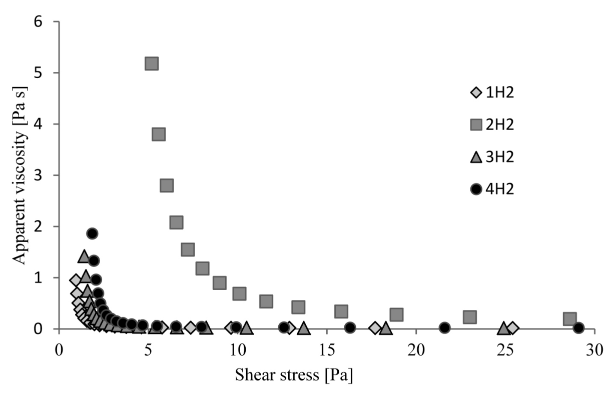

Fig. 9. Apparent viscosity of investigated emulsion
Rys. 9. Lepkość pozorna badanych emulsji

All analysed emulsions produced using twofold homogenization are viscous liquids that are shear thinning.

CONCLUSIONS

1. The use of twofold homogenization in the process of emulsion production is an effective method of obtaining a product with low variability of rheological behaviour and characterized by a significantly lower yield stress.

2. The developed emulsions are visco-elastic liquids that have yield stress and a non-linear flow curve. They have the character of liquid diluted with shear.
3. The rheological behaviours of the developed emulsions are well described by both equations of the Casson and Herschel-Bulkley models.
4. As a result of the tests, it was shown that Emulsions 3H2 and 4H2 are emulsions possessing rheological properties required in the application processes for paper packaging.

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REFERENCES

1. Trzos M.: Variability of results in issues of repeatability and reproducibility of tribological characteristics determination. Tribologia 6, 2011, 227–239 (in Polish).
2. Iłowska J. et.al.: Paraffin based emulsions as impregnates for food packaging, 2nd Innovations in Food Packaging, Monachium, 03–06.10.2017.
3. Zhang K., Ni O.: Rheological properties and stability of highly concentrated water-in-oil emulsions with different emulsifiers, J. Dispers. Sci. Technol. (2014).
4. García-Zapateiro L.A. et al: Formulation of lubricating greases from renewable base stocks and thickener agents: A rheological approach. Industrial Crops and Products 54 (2014) 115–121.
5. Dimitri C. et al.: Influence of particle-size distribution and temperature on the rheological properties of highly concentrated Inconel feedstock alloy 718. Powder Technology 322 (2017) 273–289.
6. Pajouhandeh A. et al.: Experimental measurement and modeling of nanoparticle-stabilized emulsion rheological behavior. Colloids and Surfaces A: Physicochem. Eng. Aspects 520 (2017) 597–611.
7. Tripathi S. et al.: Rheological behavior of high internal phase water-in-oil emulsions: Effects of droplet size, phase mass fractions, salt concentration and aging. Chemical Engineering Science 174 (2017) 290–301.
8. Chan R.W., Rodriguez M.L.: A simple-shear rheometer for linear viscoelastic characterization of vocal fold tissues at phonatory frequencies J. Acoust. Soc. Am., 124 (2008), pp. 1207–1219.
9. Lenk R., Krivoshchepov A.P.: Effect of surface-active substances on the rheological properties of silicon carbide suspensions in paraffin. J. Am. Ceram. Soc. 83 (2000) 273–276.
10. Drabik J. et al.: Paraffin waxes for paper and cardboard food packaging . Impregnaty parafinowe do papierowych i tekturowych opakowań do żywności. Przemysł Chemiczny 96/12(2017) (in Polish).
11. Zhu H. et al. Non-Newtonian fluids with a yield stress/ J. Non-Newtonian Fluid Mech. 129 (2005) 177–181.