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Effect of carbomer microgel pH and concentration on the Herschel–Bulkley parameters

Anna Story*, Grzegorz Story, Zdzisław Jaworski

West Pomeranian University of Technology, Szczecin,
Faculty of Chemical Technology and Engineering, Department of Chemical and Process Engineering
Piastów Ave. 42, 71-065 Szczecin, Poland

The article presents an experimental investigation of the rheological properties of carbomer microgels. All of the tested fluids were made up from commercial polyacrylic acid, Carbopol Ultrez 30. In total, eighteen microgels were prepared, differing in concentration; 0.2, 0.4 and 0.6 wt%, with six levels of neutralisation for pH from 4.0 to 9.0. Based on the experimental flow curves it was found that all tested microgels are yield stress shear-thinning fluids. Therefore, the Herschel–Bulkley model was used and its rheological parameters were determined. It was found that both the concentration and the pH value significantly affected the yield stress. As the Carbopol concentration increased, the yield point also increased. With the increasing value of pH, the yield stress first increased until a certain maximum level and then decreased. The maximum values of yield stress were obtained for pH = 6 to 7, depending on polymer concentration. It was also found that flow curves of the tested microgels could be described using one universal master curve, thus they have common rheological behaviour.

Keywords: microgel, Carbopol, Herschel–Bulkley model, yield stress fluid

1. INTRODUCTION

Real fluids that are widely used in various industrial sectors usually possess complex rheological behaviour. These fluids include, among others, food products, cosmetics, paints, slurries, pastes and polymers. Very often they are classified as viscoplastic yield stress fluids which show solid-like behaviour as long as the applied stress does not exceed a certain critical value (called the yield stress, τ_y), and a shear-thinning fluid behaviour above this threshold (Coussot, 2014).

The rheological characteristic of such fluids can be with a very good accordance to the Herschel–Bulkley model (Herschel and Bulkley, 1926) which combines the existence of yield stress with the Ostwald-de Waele model for the power law viscosity:

$$\tau = \tau_y + K\dot{\gamma}^n \tag{1}$$

where τ_y is the yield stress of the fluid, K is the consistency index and n is the flow behaviour index.

During processing of shear-thinning yield stress fluids, a specific flow pattern occurs inside the process equipment which leads to formation of unmixed regions. As an example of a process with such a negative

* Corresponding author, e-mail: Anna.Story@zut.edu.pl

phenomenon the mechanical mixing can be given, where near the rotating impeller an intensive mixing zone, called also cavern, is generated (Moore et al., 1995; Story and Jaworski, 2017; Wichterle and Wein, 1975; Wilkens et al., 2005). Outside the cavern the stirred fluid does not flow, therefore it is impossible to get a homogenous product. From the practical point of view, it constitutes a serious challenge for engineers and industry.

In order to better understand the behaviour of non-Newtonian fluid flow in process equipment, in addition to theoretical studies and different experimental techniques, numerical methods have been introduced, like Computational Fluid Dynamics (CFD). Nevertheless, to be able to run numerical simulations, it is necessary to know the exact rheological characteristics of the process medium obtained from the experiment. On the other hand, it is also very important and should be highlighted that every result received from numerical modelling has to be carefully checked and validated. Validation of predicted results can be done using several parameters, including: measurements of torque and forces (Bhole et al., 2009; Story and Jaworski, 2017), visual observations of flow field with using tracer dye (Story and Jaworski, 2017) or tracer particles (Bakker and Fasano, 1993) and evaluation of the dynamic response of the system on the saline solution (Saeed et al., 2008) or radioisotopes (Griffith et al., 2004) injection. Despite the fact these techniques are often regarded as sufficient to validate CFD results, in order to perform full validation the predicted flow fields should be also compared with experimental ones.

Measurements of fluid velocity can be done using various methods. Generally, they can be divided into non-invasive and invasive techniques, which consist in introducing a measuring probe into the volume of tested fluid. One of the disadvantages of the invasive techniques is that the measuring probe can deform the flow field, resulting in incorrect information about its velocity. The group of non-invasive techniques allows measurements of fluid velocity either at a single specific point, such as Laser Doppler Anemometry (LDA or LDV) or Acoustic Doppler Anemometry (ADV), or provide instant information on the distribution of fluid velocity throughout the entire measurement area, such as Planar Doppler Velocimetry (PDV or DGV), Particle Image Velocimetry (PIV) or Particle Tracking Velocimetry (PTV). All the mentioned techniques are optically based, thus they can be used only for optically transparent equipment and fluids. Unfortunately, most of the industrial liquids are inherently opaque which prevents the use of optical methods. Therefore, in research practice transparent model fluids are very often used (Gomez et al., 2010; Story and Jaworski, 2017; Story et al., 2018). The fluids can be prepared from different components like polyacrylic acid (PAA, e.g. Carbopol), polyvinyl alcohol (PVA), polyacrylamide (PAM), layered silicates (e.g. Laponite), xanthan gum, carboxymethyl cellulose (CMC). These materials differ in composition and molecular weight, which affect the rheological properties of the prepared model fluids. A characteristic feature of such model fluids is that depending on the type of the polymer, its concentration, pH value, used solvent and other parameters their rheological properties can be modified in a very wide range. Therefore they can easily mimic the non-Newtonian behaviour of the real processes medium.

The present study aims to provide a detailed experimental rheological characterisation of model fluids prepared of carbomer polymer. A carbomer, also known as polyacrylic acid (PAA), describes a series of synthetic, high-molecular polymers produced from monomers, mainly from acrylic acid, that are cross-linked by a small amount of polyethers (e.g. polyallyl sucrose). These polymers occur in the form of a white, fluffy powder with particles of colloidal size and a slightly acetic odour. As a powder, the polymer is highly coiled. Due to cross-linking, carbomers do not dissolve in water and do not form real solutions. In contact with water, carbomer particles start to uncoil and swell to form colloidal suspensions. They are weak acids (depending on powder concentration, pH is ranging from 2.5 to 3.5) and have low non-Newtonian properties. However, they are characterized by high sensitivity to pH changes, as reflected in large changes in liquid viscosity. Addition of a base (e.g. sodium hydroxide, NaOH) leads to ionization along the polymer backbone. The number of positive hydrogen ions H^+ decreases due to dissociation of the polyacrylic acid in a polar solvent. The uncompensated base ions (Na^+) increase the osmotic pressure and lead to an enormous expansion of polymer chains. Therefore, after neutralization, suspensions of carbomers very easily form

hydrogels. The level of microgel swelling can vary due to changes in the value of external factors, among which, apart from pH, ionic strength and temperature can be mentioned.

Depending on the method of synthesis, cross-linking agent, cross-link density or polymerization environment, different types of carbomer can be distinguished. One of the carbomer groups is known under the trade name of Carbopol, produced by Lubrizol Corporation (Wickliffe, Ohio, USA). In the whole Carbopol family there are many different types of carbomer which lead to obtaining microgels characterized by a broad range of rheological properties. Consequently, in industrial practice, Carbopol microgels are commonly used, among others, as viscosity modifiers or stabilizing and dispersing agents, especially in the pharmaceutical and cosmetics fields. Due to dozens of applications, some Carbopol types are well studied by many researchers, like Carbopol 934 (Abdullah et al., 2013; Craig et al., 1994; Gafiţanu et al., 2016; Shafiei et al., 2017; Singh et al., 2014), Carbopol 940 (Abdullah et al., 2013; Cui et al., 2017; Osmałek et al., 2017; Shafiei et al., 2018; Sipos et al., 2015; Story and Jaworski, 2017), Carbopol 980 (Kelessidis et al., 2011; Parente et al., 2015; Sipos et al., 2015; Varges et al., 2019; Wróblewska et al., 2019), Carbopol Ultrez 10 (Abdullah et al. 2013; Gutowski et al. 2012; Kelessidis and Hatzistamou, 2011; Sipos et al., 2014; Sipos et al., 2015). However, there is still a lack of detailed description for the Carbopol Ultrez 30 grade, therefore gels of this carbomer type were examined in this study.

The main purpose of the presented study was to provide a detailed and extensive rheological characterisation of model fluids prepared from Carbopol Ultrez 30 polymer. The tested microgels differ in concentration and value of pH index.

2. MATERIALS AND METHODS

2.1. Preparation of tested fluids

The undertaken research was carried out for one type of carbomer, namely Carbopol Ultrez 30 grade (CU30, Lubrizol). The preparation of tested fluids had a two-stage character. In the first stage aqueous suspensions of CU30 at concentrations of 0.2, 0.4 and 0.6 wt% were prepared using an electronic overhead stirrer (IKA, Eurostar power control-visc; IKA-Werke GmbH & Co. KG, Staufen, Germany) with a mechanical Prochem Maxflo T (PMT) impeller. The PMT impeller rotated at 300 rpm for a minimum of 3 hours to allow even dispersion of the polymer powder in distilled water. The prepared suspensions were characterized by values of the pH index approximately equal to pH $\approx$ 3.4, 3.2 and 3.0 for CU30 concentrations of 0.2, 0.4 and 0.6 wt%, respectively, and were characterized by low non-Newtonian properties.

In the next stage CU30 suspensions were gradually neutralized with small portions (0.1 ml) of 1 M sodium hydroxide (NaOH) to six different levels of pH index, pH = 4.0, 5.0, 6.0, 7.0, 8.0 and 9.0 which resulted in clear and high-viscosity gels characterized by different values of apparent viscosity. During the neutralization process, the prepared liquids were stirred for a minimum of 5 hours with impeller speed increasing up to 900 rpm. To ensure good mixing, the axial-radial impeller position was changed several times. Changes in pH were monitored using pH & Ion-Meter GLP 22+ (Crison) equipped with a 5021T sensor probe dedicated to viscous samples. The probe was constantly immersed in the prepared liquid, which allowed for continuous pH measurement. The pH value was considered stable when it did not change by 0.01 within 10 minutes. After reaching and stabilizing the pH value, the location of the pH probe was changed to verify constant pH throughout the volume. In the next step the CU30 microgels were placed in a low-pressure (about 60 mbar) chamber to remove air bubbles entrapped inside the fluid. Totally, eighteen liquids differing in polymer concentration and value of the pH index were prepared. Rheological measurements of the flow curves were taken about 24 hours after fluid preparation.

2.2. Rheological measurements

For all prepared liquids, differing in concentration and pH value, their flow curves, i.e. shear stress, τ, versus shear rate, $\dot{\gamma}$, were measured using the MCR 102 rheometer (Anton Paar). As the measuring system, a sandblasted cone-plate (CP50-1/S) was used with the roughness of 4 to 7 μm, to avoid wall slip, especially at low shear rates. The cone was characterized by a diameter of 50 mm and angle of 0.994°. Additionally, the rheometer was equipped with a Peltier temperature module with corrugated surface, which allowed for a quick set up of the temperature of microgel sample and keeping it at a constant level of T = 20.5°C. Before starting the regular measurements, the samples were pre-sheared for one minute and then left for five minutes to relaxation of the loading stress. The measurements were carried out for a logarithmically increasing wide range of shear rate, $\dot{\gamma} = 10^{-5} - 10^{3}$ s^{-1}, applying six measurement points per every decade. To prevent sample evaporation, the measuring system was surrounded by a humidifying chamber filled with warm water.

3. RESULTS AND DISCUSSION

The obtained flow characteristics of all tested Carbopol Ultrez 30 microgels are presented in Fig. 1 as the shear stress vs. shear rate, $\tau = f(\dot{\gamma})$. In the tested range of shear rate, the apparent viscosity of all tested microgels decreased with increasing value of $\dot{\gamma}$ and varied in the range from 1.6×10^{-1} to 7.9×10^{6} Pa·s. The gel concentration affected the value of the apparent viscosity of the tested fluids, although the greatest impact of concentration was observed for the extreme pH values of 4.0 and 9.0, with a smaller effect for the other pH values.

The results indicate complex, non-linear rheology of the studied hydrogels combined with the existence of the yield stress. Therefore, based on the experimental data, values of the rheological parameters of the Herschel–Bulkley (1) model were determined using SigmaPlot software and the curve fitting option for a three-parameter power model. They are collected in Table 1 together with the standard error, σ, and the determination coefficient, R^2. Theoretical flow curves of H–B model parameters are also shown in Fig. 1. Analysing the presented flow curves and values of σ and R^2 it can be concluded that the Herschel–Bulkley model adequately reproduces the experimental data of Carbopol Ultrez 30 microgels.

The data summarised in Table 1 show that in the tested range of pH, the yield stress strongly depends on the CU30 concentration. For each microgel pH value, an increase in Carbopol concentration always leads to an increase in the fluid yield stress. From among all tested microgels the maximum value of yield stress, $\tau_{y,\max} = 52.5$ Pa, was achieved for polymer concentration of 0.6 wt% and pH = 6.0, while the minimum value of yield stress, $\tau_{y,\min} = 10.3$ Pa, was achieved for $c_{\mathrm{CU30}} = 0.2$ wt% and pH = 4.0.

Based on the values of rheological parameters τ_y, K and n, the critical value of shear rate, $\dot{\gamma}_c$, was also calculated. Critical shear rate relates to the intersection of the lines $\tau = \tau_y$ and $\tau = K\,(\dot{\gamma})^n$ at the conventional point of balancing elastic and viscous forces. The critical values were estimated in the range of about 1.5 to 6.2 [s^{-1}].

Effects of the pH value and polymer concentration on the yield stress are presented in Fig. 2. For any constant polymer concentration and different pH values, the yield stress of the fluid first increased until reaching a certain maximum level, and then decreased. It was found that the maximum value of the yield stress was reached for pH equal to 6 in the case of polymer concentrations 0.2 and 0.6 wt%. The lack of clear extremum for 0.4 wt% microgel at pH = 6 may result from measurement uncertainty. The calculated values of confidence intervals for this microgel characterized by different pH were $\tau_y = 37.1 \pm 1.67$ and $\tau_y = 38.7 \pm 0.53$, for pH = 6 and pH = 7, respectively.

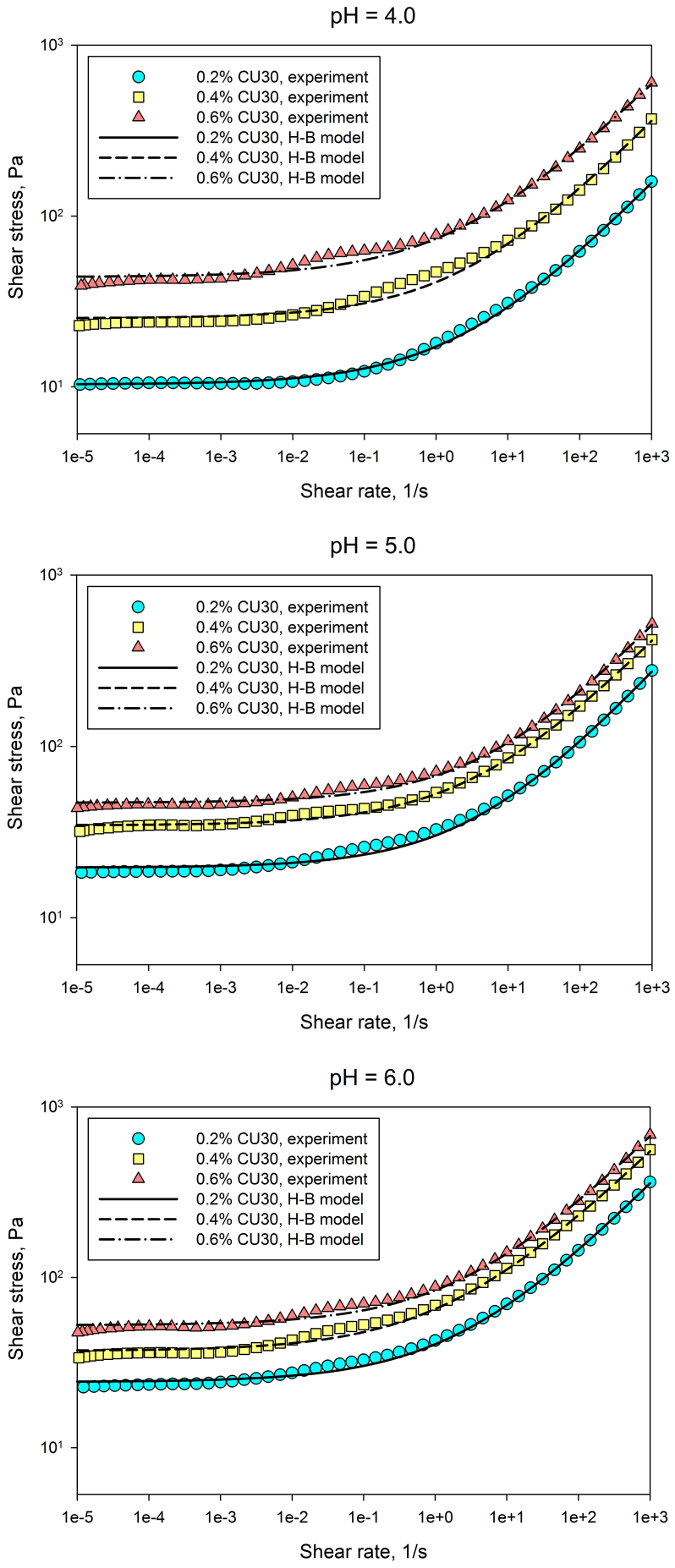
pH = 4.0
pH = 5.0
pH = 6.0
0.2% CU30, experiment
0.4% CU30, experiment
0.6% CU30, experiment
0.2% CU30, H-B model
0.4% CU30, H-B model
0.6% CU30, H-B model
Shear stress, Pa
Shear rate, 1/s
10^3
10^2
10^1
1e-5
1e-4
1e-3
1e-2
1e-1
1e+0
1e+1
1e+2
1e+3

Fig. 1

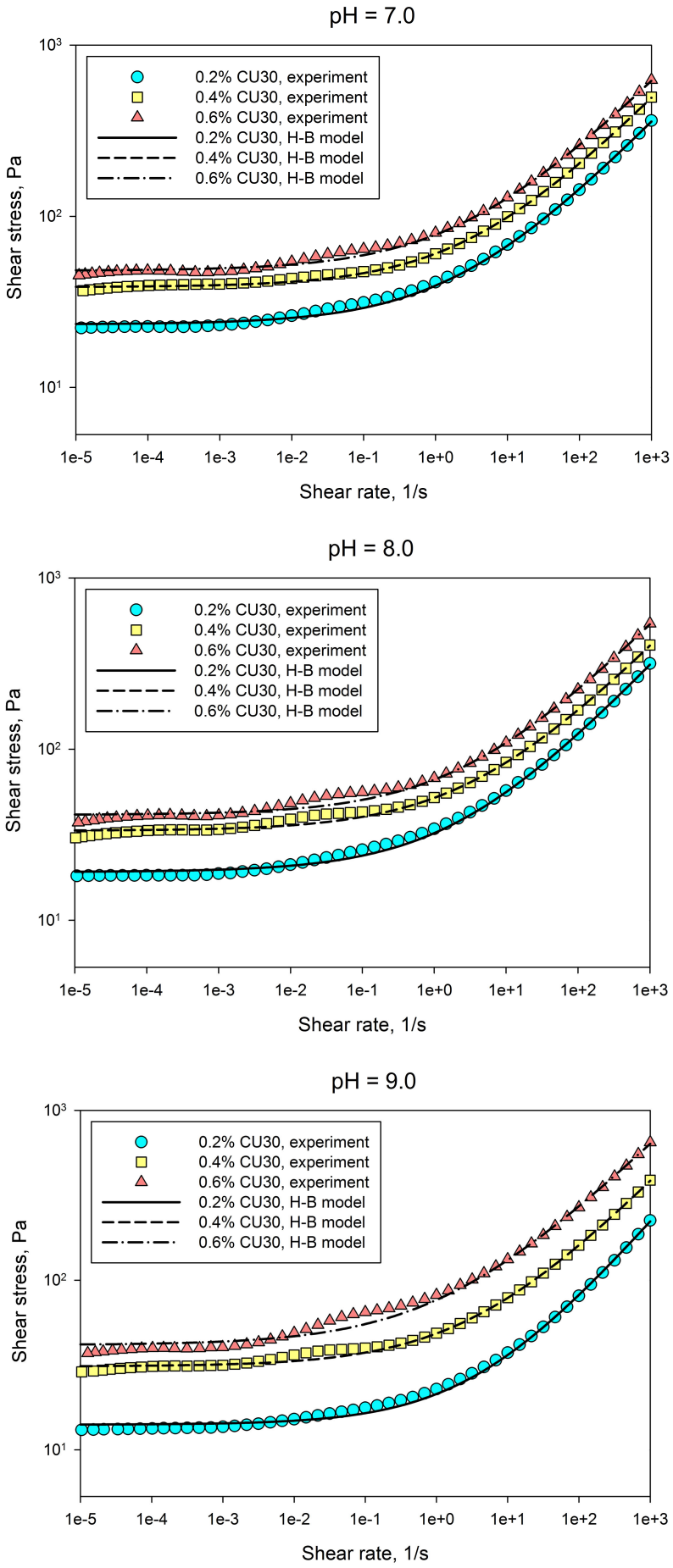

Fig. 1. Flow curves of tested CU30 microgels differing in concentration and pH value

Table 1. Herschel–Bulkley model parameters for tested CU30 suspensions

No.	pH	c_{CU30} [%]	τ_y [Pa]		K [Pa·s^n]		n [–]		R^2	$\dot{\gamma}_c$ [s^{-1}]
			value	σ	value	σ	value	σ		
1	4.0	0.2	10.3	0.1644	6.90	0.1545	0.442	0.0035	0.9992	2.4754
2		0.4	25.2	0.6493	15.9	0.6122	0.441	0.0060	0.9978	2.8413
3		0.6	44.0	0.8119	29.9	0.8146	0.421	0.0043	0.9988	2.5034
4	5.0	0.2	19.6	0.3127	10.7	0.2778	0.459	0.0041	0.9991	3.7386
5		0.4	34.7	0.3534	18.3	0.3352	0.439	0.0029	0.9995	4.2952
6		0.6	47.0	0.5679	20.7	0.5188	0.451	0.0039	0.9991	6.1608
7	6.0	0.2	24.3	0.3579	16.2	0.3416	0.437	0.0033	0.9993	2.5290
8		0.4	37.1	0.6466	28.3	0.6518	0.420	0.0036	0.9991	1.9053
9		0.6	52.5	0.7617	31.8	0.7423	0.461	0.0037	0.9991	2.9669
10	7.0	0.2	23.4	0.3061	16.0	0.2895	0.440	0.0028	0.9995	2.3726
11		0.4	38.7	0.2779	22.0	0.2644	0.438	0.0019	0.9998	3.6309
12		0.6	48.2	0.5253	30.0	0.5186	0.427	0.0027	0.9995	3.0357
13	8.0	0.2	19.2	0.2811	13.2	0.2583	0.449	0.0031	0.9994	2.3037
14		0.4	33.4	0.377	18.6	0.3655	0.432	0.0031	0.9994	3.8771
15		0.6	41.4	0.5708	25.1	0.5545	0.432	0.0035	0.9992	3.1847
16	9.0	0.2	14.1	0.201	7.26	0.1623	0.486	0.0035	0.9994	3.9190
17		0.4	31.1	0.3379	17.5	0.3242	0.436	0.0029	0.9995	3.7390
18		0.6	41.6	0.9528	35.1	0.9898	0.410	0.0044	0.9986	1.5134

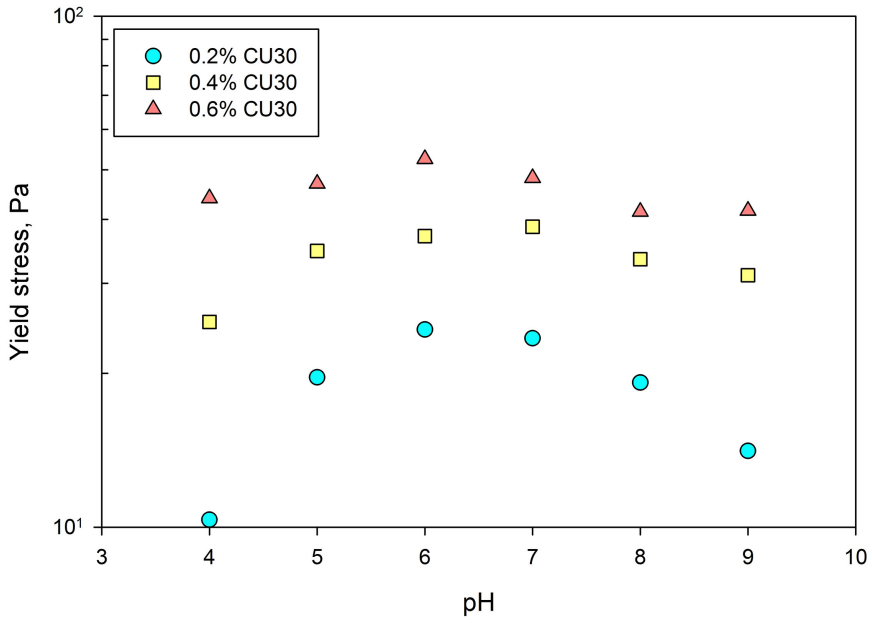

Fig. 2. Effect of the pH value and polymer concentration on the yield stress

In the next step, it was decided to carry out an assessment of the correctness of the universal master curve of the Herschel–Bulkley type defined by the equation (Bonnecaze and Cloitre, 2010):

$$\frac{\tau}{\tau_y} = 1 + K_0 \left(\frac{\eta_s \dot{\gamma}}{G_o} \right)^m \tag{2}$$

where the coefficient K_0 is slightly dependent on the material type, η_s is the solvent viscosity, G_o is the low-frequency shear modulus and the exponent m is approximately equal to 0.5. The results of fitting the universal model to the experimental data, for all of the tested CU30 gels with pH from 4 to 8, were presented in Fig. 3. The ordinate axis for the shear stress was standardised by the yield stress, and the abscissa axis for the shear rate was standardised by the characteristic time, η_s/G_0. It was found that all experimental results collapsed to nearly a common flow curve. The obtained value of K_0 coefficient was equal to 102.1 with its standard error of 1.81, while the value of m exponent was equal to 0.428 with its standard error of 0.003. The determination coefficient of the estimate was $R^2 = 0.9869$. Analysing the presented results it can be concluded that the rheological behaviour of all tested microgels of CU30 can be described using one master curve presented in the literature (Bonnecaze and Cloitre, 2010), thus they were characterized by a common flow mechanism.

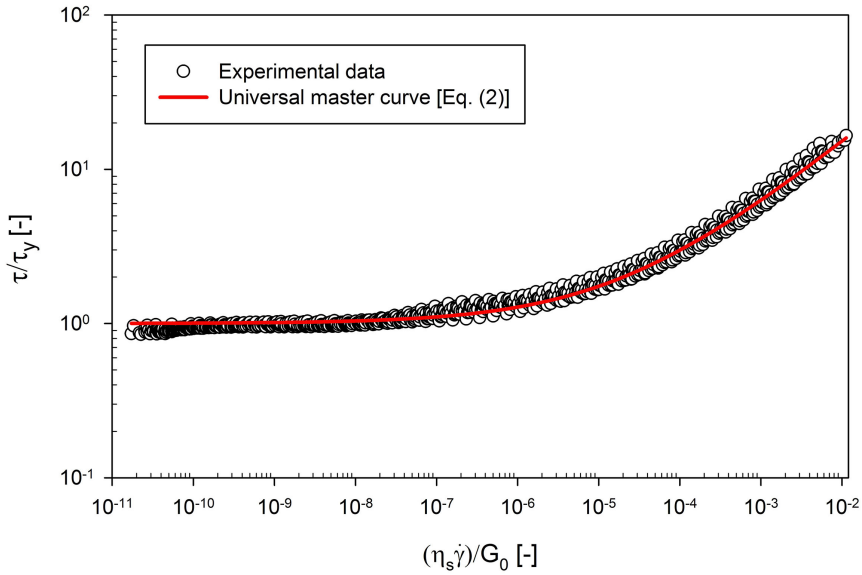

Fig. 3. The universal master curve of the Herschel–Bulkley type for tested CU30 microgels

4. CONCLUSIONS

Results of the rheological measurements were presented for Carbopol Ultrez 30 microgels of different concentration and pH value. It was found that both of these parameters significantly affected the apparent viscosity of the polymer microgels. Analysis of the flow characteristics showed that the prepared microgels were yield stress shear-thinning fluids. Hence, to describe their rheological behaviour the Herschel–Bulkley model was used, which fitted to experimental data with very good accuracy. Moreover, based on the master curve of the Herschel–Bulkley type from the literature, it was found that the shear rheology of tested microgels differing in concentration and pH value was universally characterized. The selection of an appropriate mathematical model describing the behaviour of carbomer suspensions under shear conditions is crucial for its application. Thus, the validated rheological model minimizes the risk of errors during numerical simulations or design calculations, and may enable the selection of optimal industrial technologies and operating parameters of individual apparatuses.

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SYMBOLS

G_o low-frequency shear modulus, Pa
K consistency coefficient, Pa·s^n
K_0 coefficient in Eq. (2), –
m exponent in Eq. (2), –
n flow index

Greek symbols

$\dot{\gamma}$ shear rate, s^{-1}
$\dot{\gamma}_c$ critical value of shear rate, s^{-1}
η_s solvent viscosity, Pa·s
τ shear stress, Pa
τ_y yield stress, Pa

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