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EFFECT OF SiO₂ PARTICLE SIZE AND LENGTH OF POLY(PROPYLENE GLYCOL) CHAIN ON RHEOLOGICAL PROPERTIES OF SHEAR THICKENING FLUIDS

The rheological properties of shear thickening fluids based on silica powder of particles size in range $0.10 - 2.80 \mu m$ and poly(propylene glycol) of 425, 1000, 2000 g/mol molar mass were investigated. The effect of particle size and the length of the polymeric chain was considered. The objective of this study was to understand basic trends of physicochemical properties of used materials on the onset and the maximum of shear thickening and dilatant effect. Outcome of the research suggested that an increase in the particle size caused a decrease in dilatant effect and shift towards higher shear rate values. Application of carrier fluid of higher molar mass allowed to increase dilatant effect but it resulted in the increase of the initial viscosity of the fluid.

Keywords: shear thickening fluids, dilatant effect, onset of shear thickening, silica, poly(propylene glycol)

1. Introduction

Shear thickening fluids (STF) are non-Newtonian fluids characterized by increasing viscosity with applied shear rate: with growing shear rate an internal friction forces arise which, in the macroscale, is manifested by rapid increase of viscosity. In preparation of STF, silica powder [1,2] as solid phase and poly(ethylene glycol) [3] and poly(propylene glycol) [4] as carrier fluids are adopted. The flow of STF is derived from internal connections between used materials and is primarily influenced by molar mass of carrier fluid [5], particle size [6], particle size distribution [7,8], solid loading [9] and dopants [10]. These factors are commonly known in the literature but the relationship between all of them has not been yet precisely studied. The detailed characterization of materials is necessary for optimization of suitable composition of STF depending on the applications. Based on literature review, a few mechanisms of shear thickening are known. This phenomenon can be interpreted by order – disorder transition [11], hydrodynamic clustering [12] and particle flocculation theories [5]. None of these explanations is universal - a dependence on the examined system can be noticed. Therefore, this phenomenon still requires research in various fields to achieve comprehensive knowledge of this process. STF are very important composite materials in production at shock absorbing devices such as liquid armours [13] or sport protectors. In order to design a suitable material it is necessary to investigate the rheological properties of STF such as the onset and maximum of shear thickening and dilatant effect which depend on materials used (Fig.1).



Fig.1. Rheological parameters of shear thickening fluids

2. Materials and experimental procedure

The STF were based on spherical silica of particles size $0.10 \sim 0.20 \mu m$ (SS-10), $0.50 \sim 0.60 \mu m$ (SS-50), $0.90 \sim 1.30 \mu m$ (SS-100), $1.30 \sim 1.60 \mu m$ (SS-150) and $2.20 \sim 2.80 \mu m$ (SS-250). SEM images (Zeiss ULTRA Plus, Germany) compiled in Fig.2 reveal the morphology and the particles size of the solid phase. Micrographs data showing that the silica particles slightly agglomerate, although mainly single grains were observed. The carrier fluid was poly(propylene glycol) (PPG) with an average molar mass of 425g/mol, 1000g/mol and 2000g/mol. Table 1 represents physicochemical properties of materials used. Density measurements were carried out

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Fig. 2. SEM images of spherical silica powders: a) SS-10, b) SS-50, c) SS-100, d) SS-150, e) SS-250

TABLE 1

Physicochemical characterization of materials used

CERAMIC POWDER					
abbreviation	particle size[µm]	ze[µm] specific surface area [m ² /g] density [g/cm ³]		producer	
SS-10	0.10~0.20	132.2	1.96	Nippon Shokubai Co.	
SS-50	0.50~0.60	227.4	1.89		
SS-100	0.90~1.30	37.2	1.94		
SS-150	1.30~1.60	150.2	1.93		
SS-250	2.20~2.80	1.3	1.94		
CARRIER FLUID					
abbreviation	density [g/cm ³]	molar mass [g/mol]	chemical structure	producer	
PPG 425	1.004	425			
PPG 1000	1.010	1000	(H[OCH(CH ₃)CH ₂] _n OH	Sigma-Aldrich	
PPG 2000	1.005	2000			

using helium pycnometer AccuPyc II 1340 Pycnometer (Micromeritics, USA) and specific surface area was tested using ASAP 2020 (Micromeritics, USA). All fluids consisted of 50vol% of solid phase.

The fluids were obtained by mixing dry silica powder with organic dispersant using mechanical stirrer for 1 hour. Subsequently the viscosity measurements were done tor the resulting STF. For examination of rheological properties a rotational rheometer KinexusPro (Malvern, GB) equipped with two parallel plates was used. The gap was set to 0.7mm. The viscosity measurements were taken at room temperature (25°C) in the range of shear rates from 0.1 to 3000 s⁻¹.

3. Results and discussion

All prepared fluids showed shear thickening behaviour. The conducted studies showed the influence of particle size of the ceramic powder on the value of the onset of shear thickening (Table 2). It can be concluded that an increase in the SiO_2 particle size caused a shift of the onset of shear thickening towards lower values of shear rate.

According to the Barnes' theory (Eq. 1) [14] spherical particles enables the determination of the onset of shear thickening as

$$\dot{\gamma} = \frac{1}{d^2} \left[1/s \right] \tag{1}$$

where $\dot{\gamma}$ is the onset of shear thickening [1/s] and *d* is the particle size of ceramic powder [m]. Barnes research related to suspensions characterized by viscosity in the range of 0.1-10 mPa·s.

TABLE 2 Onset of shear thickening for non-Newtonian systems based on different particle size of ceramic powders and solid loading 50vol%, dispersed in poly(propylene glycol) of different molar mass

avanaganartiala	onset of shear thickening [1/s]				
averageparticle size	e according to the barnes formula	experimental data			
[10-6 m]		PPG 425	PPG 1000	PPG 2000	
0.1	100	3.33	2.77	0.08	
0.5	4	8.14	1.60	0.08	
1.0	1	2.02	0.10	0.04	
1.5	0.44	1.25	0.10	0.11	
2.5	0.16	0.48	0.10	0.09	

Table 2 shows the calculated values of the onset of shear thickening by the Barnes' theory and a comparison of them with the data obtained during the investigations. It was observed that the theoretical values do not agree with the received data obtained during the study. Probably the difference in viscosities of investigated suspensions is caused by an aberrance of the formula and calculations. All examined samples tested in the study had viscosity above 0.1Pa·s. The higher viscosity indicate a reduction in the distance between the individual components of the suspension, thus interactions between them were different. Consequently, it changed dependence between the onset of shear thickening

and particle size. The rheological model should be more complicated relating to other interactions (attractive van der Waals forces, repulsive electrostatic forces, Brownian motion, force-distance relation of particles connected by a carrier fluid in quazi-solid situation under shear rate). In general, an increase in the particle size causes an increase in onset of shear rate.

The obtained outcome of the onset of shear thickening resulted in a relation between the particle size and the shear rate at maximum of shear thickening (Fig.3.).



Fig. 3. Shear rate at maximum of shear thickening depending on particle size of ceramic powder

The performed experiments have shown that an increase in the particle size caused a decrease in the maximum value of the shear rate. An exception was silica powder of 100nm particle size. In this case, the maximum shear rate was lower than observed in the fluid based on silica 500nm.

Based on the data analysis, an increase in particle diameter caused decrease in the dilatant effect (Fig. 4.).



Fig. 4. Dilatant effect depending on particle size of ceramic powder

It testified theory that the larger particles of the solid phase the larger the distance between them and the weaker internal interactions. Thus, it has directly caused reduction of viscosity and dilatants effect. The distance h between the particles of the ceramic powder depending on the particle diameter is shown in Table 3. The calculations were run based on the Eq. 2 [15]. 1514

$$h = D[(\frac{1}{3\pi\varphi} + \frac{5}{6})^{\frac{1}{2}} - 1]$$
(2)

where *h* is the distance between the particles, *D* is the particle diameter [m] and ϕ is the solid loading.

TABLE 3 depending on

Distance between the particles of the ceramic powder depending on the particle diameter according to the Eq. 2

particle diameter [nm]	solid loading [vol%]	distance between the particles of the ceramic powder [nm]
100		2.26
500		11.28
1000	50	22.57
1500		33.85
2500		56.42

The rheological properties strongly depend also on the type of the poly(propylene glycol). This is considered as the length of the polymeric chain of PPG. This may be attributed to changes in initial viscosity of the samples, depending on the carrier fluid. In the case of the fluids based on PPG425 the onset of shear thickening in almost all cases decreased linearly with increasing particle diameter. Understanding of this phenomenon parallel provides an easy estimation of the beginning of the shear thickening depending on the particle size. Other observations were noticed for the samples containing PPG1000. The onset of shear thickening was initially rapidly declining in the particle size range 0,1-1 μ m and in the range 1 – 2.5 μ m it essentially did not change. For fluids consisting of PPG2000 in the whole particle size range the value of the onset of shear thickening was low and remained at almost steady level due to the high viscosity of the prepared samples. Additionally, an increase in the polymeric chain length caused an increase in the dilatant effect in the whole range of particle size.

4. Conclusions

In this study, the influence of SiO_2 particle size and length of poly(propylene glycol) chains on rheological properties of shear thickening fluids was investigated. The measurements showed that both of these parameters have the significant influence on the rheological properties of suspensions. It was demonstrated that by the selection of proper composition of the fluid it is possible to control onset and maximum of shear thickening as well as the high of the dilatant effect. It allows to predict and adjust the rheological properties of fluids at the stage of their design.

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REFERENCES:

- S.R. Raghavan, S.A. Khan, J. Colloid Interf. Sci. 185, 57–67 (1997)
- [2] K. Yu, H. Cao, K. Qian, X. Sha, Y. Chen, J. Nanopart. Res. 14, 747 (2012)
- [3] Q. Wu, J. Ruan, B. Huang, Z. Zhou, J. Zou, J. Cent. South Univ. T., 13, 1-5 (2006)
- [4] F.J. Galindo-Rosales, F.J. Rubio-Hernandez, J.F. Velazquez-Navarro, Rheol. Acta. 48, 699–708 (2009)
- [5] M. Kamibayashi, H. Ogura, Y Otsubo, J. Colloid Interf. Sci. 321, 294–30 (2008)
- [6] B.J. Maranzano, N.J. Wanger, J. Chem. Phys. 114, 10514– 10527 (2001)
- [7] S. Ookawara, S. Ogawa, K. Ogawa, Kagaku Kogaku Ronbun. 28, 779-784 (2002)
- [8] A. Idźkowska, M. Szafran, Arch. Metall. Mater., 58, 1323– 1326 (2013)
- [9] M. Chellamuthu, E.M. Arndt, J.P. Rothstein, Soft Matter. 5, 2117–2124 (2009)
- [10] M.D. Chadwick, J.W. Goodwin, B. Vincent, E.J. Lawson, P.D.A. Mills, Colloid Surface 196, 235–245 (2002)
- [11] R. L. Hoffman, T. Soc. Rheol. 16, 155-173 (1972)
- [12] J. Bender, N. J. Wagner, J. Rheol. 40, 899–916 (1996)
- [13] Patent No., US, 7, 226, 878, B2
- [14] H.A. Barnes, J. Rheol. 32, 329–366 (1989)
- [15] T. Isobe, Y. Hotta, K. Watari, Mater. Sci. Eng.: B, 148, 192– 195 (2008)