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COMPOSITES THEORY AND PRACTICE

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THE EFFECT OF MOLECULAR WEIGHTS OF POLY(PROPYLENE GLYCOL) ON RHEOLOGICAL PROPERTIES OF SHEAR THICKENING FLUIDS

Ceramic-polymer composites have great importance in many branches of industry. They are used, among the others in electronics, optoelectronics, plastics for the construction of nuclear reactors or spacecrafts. They also play an important role in the production of materials for the protection of the human body. These materials are formed of shear thickening fluids (STF), also referred to as dilatant fluids. They are non-Newtonian liquids, which are characterized by an increase in viscosity as a function of shear rate. Materials and devices based on shear thickening fluids dissipate an energy associated to shocks, impacts and vibrations very well. This paper presents the results of research on the effects of a molecular weight of dispersing agent on the rheological properties of shear thickening fluids. In the first step, liquids with poly(propylene glycol) of a molecular weight of 400, 425 or 725 g/mol (used as a dispersing agent) were prepared. As a ceramic powder, a nanosilica with an average particle size of 14 nm was used. Concentration of the powder was 12 vol.% or 15 vol.%. In the second step of this study, the rheological properties of the prepared fluids were analysed at 25°C. The effects of the type of used glycol and the content of solid phase on the rheological properties were examined. More favorable results were obtained for the systems of 15% by volume of the solid phase. The influence of the temperature on therheological properties was also checked. Parallel measurements for systems with a poly(propylene glycol) of a molecular weight of 400, 425, 725 g/mol and a powder 12 vol.% at 37°C were conducted. The effects of the viscosity leap were lower but were received at higher shear rates.

Keywords: **STF (shear thickening fluids), viscosity, nanosilica, poly(propylene glycol), ceramic-polymer composites**

WPŁYW MASY CZĄSTECZKOWEJ CIECZY DYSPERGUJĄCEJ NA WŁAŚCIWOŚCI REOLOGICZNE CIECZY ZAGĘSZCZANYCH ŚCINANIEM

Kompozyty ceramiczno-polimerowe mają bardzo duże znaczenie w wielu gałęziach przemysłu. Znajdują zastosowanie m.in. w elektronice, optoelektronice, tworzywach do konstrukcji reaktorów jądrowych czy statków kosmicznych. Istotną rolę odgrywają również przy produkcji materiałów służących ochronie ciała człowieka. Takie materiały powstają na bazie płynów zagęszczanych ścinaniem, nazywanych również dylatancyjnymi. Są to ciecze nienewtonowskie, które charakteryzuje wzrost wartości lepkości ze wzrostem szybkości ścinania. Materiały i urządzenia oparte na zawiesinach zagęszczanych ścinaniem bardzo dobrze rozpraszają energię towarzyszącą wstrząsom, uderzeniom oraz drganiom. W ramach pracy przedstawiono wyniki badań nad wpływem masy cząsteczkowej cieczy dyspergującej na właściwości reologiczne płynów zagęszczanych ścinaniem. W pierwszym etapie przygotowano zawiesiny, w których jako dyspergent zastosowano poli(glikole propylenowe) o masie cząsteczkowej 400, 425 lub 725 g/mol. Fazę stałą stanowiła nanokrzemionka o średniej wielkości ziarna 14 nm. Stężenie proszku wynosiło odpowiednio 12% obj. i 15% obj. W drugiej fazie prac zbadano właściwości reologiczne przygotowanych cieczy w temperaturze 25°C. Sprawdzono, jaki wpływ na właściwości reologiczne cieczy ma rodzaj glikolu i stężenie fazy stałej. Korzystniejsze wyniki uzyskano dla układów z 15% obj. nanokrzemionki. Spośród użytych despergentów najlepszym okazał się poli(glikol propylenowy) o masie cząsteczkowej 425 g/mol przy zawartości 15% obj. proszku. W celu sprawdzenia wpływu temperatury na właściwości reologiczne cieczy zagęszczanych ścinaniem przeprowadzono analogiczne badania w temperaturze 37°C. Zastosowanie podwyższonej temperatury spowodowało przesunięcie skoków dylatancji do wyższych szybkości ścinania, jednakże skoki te były niższe.

Słowa kluczowe: **ciecze zagęszczane ścinaniem, lepkość, nanokrzemionka, poli(glikol propylenowy), kompozyty ceramiczno-polimerowe**

INTRODUCTION

The development of a widely understood ceramic has been recently observed. Apart from the traditional applications in architecture, sanitary and decorative products it has also emerged in cutting-edge accomplishments. It has been used in the electronics, aerospace, nuclear and construction industry for several decades. Ceramic-polymer composites based on shear thickening fluids have a great potential in systems used for human body protection, guard houses against earthquakes and dampers [1-5]. The main characteristic of these suspensions, also referred to as dilatant fluids, is an increase in viscosity as a function of shear rate [6].

In industry, this property of liquids has a negative influence on the equipment and can cause the obstruction of pipelines and faster exploitation of mixers and rotors. However, as a result of the latest research, an increase in viscosity may be used as a very good value. Materials and devices based on shear thickening fluids dissipate an energy associated to shocks, impacts and vibrations very well.

The rheology and flow of colloidal suspensions has been a topic of vast numbers of works. There are many explanations of the mechanism of the dilatancy effect [7]. The theories of order - disorder transition (R.L. Hoffman) [8], hydrodynamic clustering (J. Bender, N.J. Wagner) [9] and particle flocculation (M. Kamibayashi, H. Ogura, Y. Otsubo) [10, 11] can be distinguished. Hoffman interpreted that below the critical shear rate, layers of particles form a two-dimensional network. The individual layers move to each other and the surface shear parallely. However, at high shear rates, corresponding to the critical value, chaotic motions of the particles are observed. The second explanation shows that the shear forces are able to overcome the repulsive Brownian forces. Particles form larger aggregates called clusters and the viscosity increases abruptly. According to the theory of particle flocculation, polymer chains adsorb onto the surface of powder particles (Fig. 1). A three-dimensional network formed by the connections between the dispergent molecules and the powder particles is created under the influence of a high shear rate. Bridges are made between the polymer and the powder and consequently viscosity is increased. This process is reversible. The individual particles of the powder and polymer molecule are received again after termination of the shear stress.

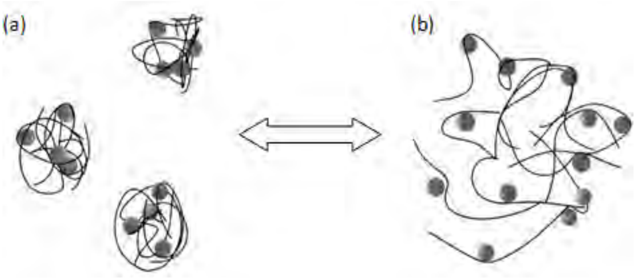


Fig. 1. Scheme of flocculation mechanism of solid particles in suspension: a) system in rest state; b) three-dimensional system

Rys. 1. Schemat mechanizmu flokulacji cząstek stałych w zawiesinie: a) układ w stanie spoczynku; b) układ trójwymiarowy

The aim of the study was to investigate the effect of the molecular weight of poly(propylene glycol) on the rheological properties of shear thickening fluids. The analysis of the rheological properties of ceramic slurries based on nanosilica in various organic liquids allowed the authors to determine the best composition for further research due to the fact that the viscosity jump depends on the concentration and the chain length of the added polymer as a dispersing agent [12, 13].

EXPERIMENTAL PROCEDURE

In the preparation of shear thickening fluids, fumed silica (*Sigma-Aldrich SF 14*) with an average particle size of 14 nm (SF 14) was used. The specific surface area measured by the BET method equaled 200 +/- 25 m^2/g. The density of the used powder was 1.53 g/cm^3. The SEM image in Figure 2 shows the microstructure of the silica particles. It can be observed that the spherical grains agglomerate and form a highly branched structure. The agglomerates reach the size of about 300÷400 nm.

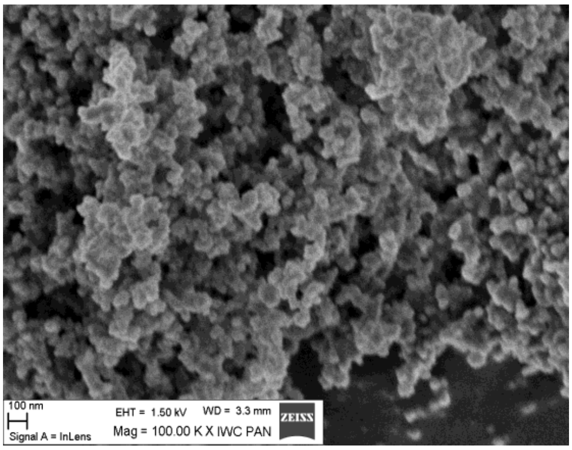


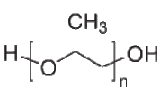
Fig. 2. Microstructure of nanosilica, magnification of 100 00 KX

Rys. 2. Mikrostruktura nanokrzemionki, powiększenie 100 00 KX

The liquid phase was poly(propylene glycol) (PPG) of a molecular weight of 400, 425 and 725 g/mol. Table 1 presents the physicochemical properties of the used dispersing agent.

TABLE 1. **Physicochemical properties of used dyspergents**

TABELA 1. **Właściwości fizykochemiczne stosowanych dyspergentów**

Dispersing agent	Density [g/cm^3]	Molecular weight [g/mol]	Molecular structure	Manufacturer
Poly(propylene glycol) (PPG)	1.130	400		*Sigma-Aldrich*
	1.004	425		
	1.007	725		

To obtain the suspension the materials were mixed. The composite consisted of 12 or 15 vol.% silica powder dispersed in PPG. The combination of components was homogenized with a mechanical stirrer in a thermostat for 3 hours. The water temperature was 55°C. A temperature rise decreased the viscosity and enabled movement of the mixer spindle. The agitator reached the rate of 100 rpm. Afterward, the homogeneous liquid had to return to room temperature. Rheological measurements were performed using a rotational rheometer Kinexus Pro (Malvern, UK) with a plate-plate measuring system. The sample was placed on an immovable plate. The gap between plates was 0.7 mm. The temperature of the examinations was 25 or 37°C. The shear rate increased from 1 to 500 s^{-1}. As a result, charts of viscosity as a function of shear rate (viscosity curves) were received.

RESULTS AND DISCUSSION

The aim of the study was to verify the effect of the molecular weight of poly(propylene glycol) on the rheological properties of prepared shear thickening fluids. At the beginning, neat glycols were exposed to shearing. As can be seen in Figure 3, neat PPGs had only insignificant dilatant behavior. The viscosity peaks were observed at a shear rate about 1.2 s^{-1}. After reaching the maximum, the viscosity gradually decreased (shear thinning) to a constant value at high shear rates. The viscosity curves for PPG 400 and PPG 425 were practically imposed (maximum viscosity was 0.12 Pa·s). The highest viscosity of 0.19 Pa·s was obtained by the poly(propylene glycol) of the molecular weight 725 g/mol. This is probably due to the difference in molecular weight. Glycol with a higher molecular weight contains longer polymer chains which easily become entangled. The final viscosity of the liquid is equal to 0.09 Pa·s for PPG 400 and 425 and 0.16 Pa·s for PPG 725. An increase in viscosity was observed only between the two initial measurement points and the resulting peaks were low. This may be due to the result of the numerical calculation of the viscosity of the plate-plate system.

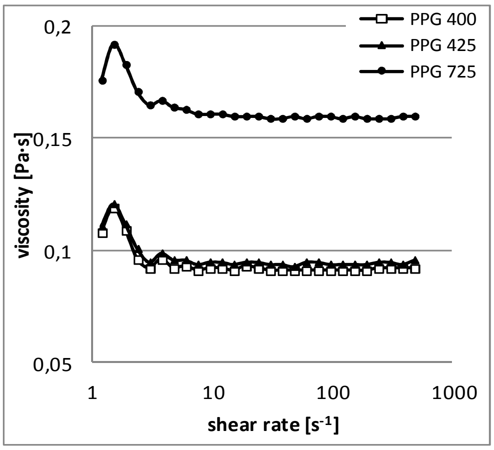


Fig. 3. Viscosity curves as function of shear rate for PPG 400, 425, 725 in 25°C

Rys. 3. Krzywe lepkości w funkcji szybkości ścinania dla PPG 400, 425, 725 w 25°C

In the second set of experiments, systems with SF 14 and poly(propylene glycol) with different molecular weight were examined. In Figure 4, the viscosity curves of suspensions with the 12 vol.% silica powder are presented. The fluids exhibited undoubted dilatant properties in all the cases but the viscosity maxima were different. The initial viscosity of the studied systems amounted to 17 Pa·s (with PPG 400), 2 Pa·s (with PPG 425) and 3 Pa·s (with PPG 725). The findings showed that the slurry with PPG 725 had the highest viscosity jump. It equaled 305 Pa·s at the shear rate of 12.3 s^{-1}. The lowest viscosity (141 Pa·s at shear rate 19.5 s^{-1}) was achieved by the fluid with PPG 425 but the dilatant leap was the widest. The liquid made of nanosilica and PPG 400 obtained intermediate viscosity following 223 Pa·s at the shear rate of 15.5 s^{-1}. The high viscosity is probably due to the formation of a three-dimensional network between the polymer chains adsorbed on the solid particles. After reaching the maximum viscosity a sudden drop was observed. This is probably because at a higher shear rate liquid separates from the upper plate. The results at high shear rates are not taken into account.

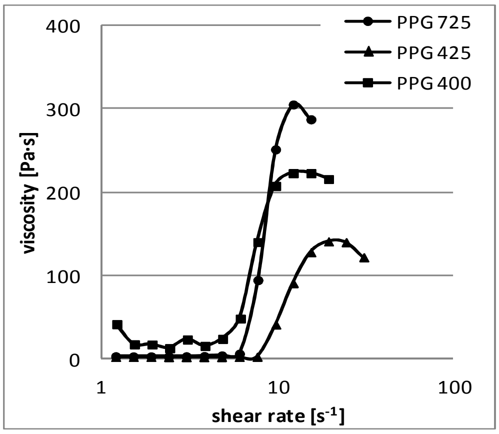


Fig. 4. Viscosity curves as function of shear rate for liquids based on SF 14 (12 vol.%) with PPG 400, 425, 725 in 25°C

Rys. 4. Krzywe lepkości w funkcji szybkości ścinania dla cieczy na bazie SF 14 (12% obj.) i PPG 400, 425, 725 w 25°C

Figure 5 illustrates the rheological behavior of slurries with a 15 vol.% solid phase. The initial viscosity of the studied systems numbered 4 Pa·s (with PPG 400), 10 Pa·s (with PPG 425) and 5 Pa·s (with PPG 725). The results showed that a higher content of powder positively affects the dilatant effect by increasing of the maximum of viscosity. The course of the charts of systems with PPG 425 and PPG 725 were similar but for the first one, the maximum of viscosity jump was higher. The suspension with the poly(propylene glycol) of a molecular weight of 425 g/mol reached the effect of viscosity leap 735 Pa·s at the shear rate of 9.8 s^{-1}. The effects for liquids made of PPG 725 and PPG 400 equaled 626 Pa·s (6.3 s^{-1}) and 333 Pa·s (15.5 s^{-1}), respectively.

In the next stage of the work, the temperature influence on the rheological properties was examined. The measurements for systems with nanosilica in the amount of 12 vol.% in 37°C were conducted. The effect of viscosity leap for suspensions with PPG 400, 425 and 725 in 37°C adequately equaled 79 Pa·s at 9.8 s^{-1}, 64 Pa·s at 49 s^{-1} and 187 Pa·s at 39 s^{-1}. On the basis of the results (Fig. 6), it was found that a higher temperature reduced the viscosity jumps of ceramic slurries.

With increasing temperature, the start of the dilatant peak had the tendency to shift towards a higher shear rate. The initial viscosity of these systems at both temperatures was comparable.

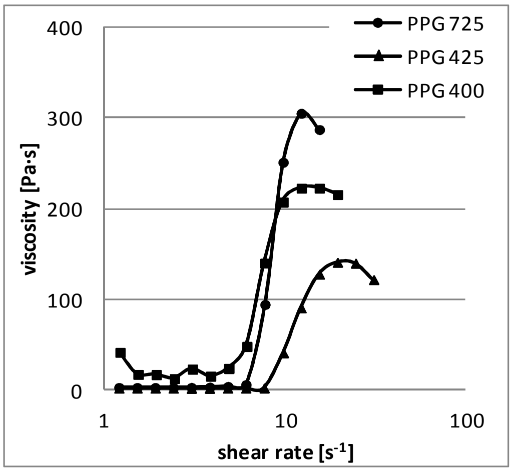


Fig. 5. Viscosity curves as function of shear rate for liquids based on SF 14 (15 vol.%) with PPG 400, 425, 725 in 25°C

Rys. 5. Krzywe lepkości w funkcji szybkości ścinania dla cieczy na bazie SF 14(15% obj.) i PPG 400, 425, 725 w 25°C

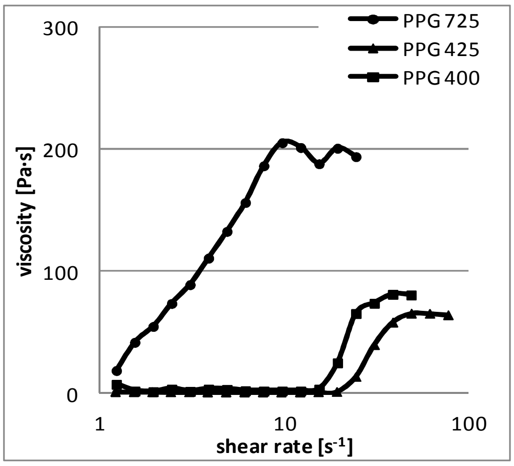


Fig. 6. Viscosity curves as function of shear rate for liquids based on SF 14 (12 vol.%) with PPG 400, 425, 725 in 37°C

Rys. 6. Krzywe lepkości w funkcji szybkości ścinania dla cieczy na bazie SF 14 (12% obj.) i PPG 400, 425, 725 w 37°C

CONCLUSIONS

Neat poly(propylene glycol) of a molecular weight of 400, 425 and 725 g/mol had only insignificant dilatant properties. It was supposed that the obtained results agree well with the theory of particle flocculation. The use of nanosilica and poly(propylene glycol) gave shear thickening fluids. The results indicated that both the silica concentration and molecular chain length of PPG play important roles in the shear thickening effect. The addition of nanosilica induced a rise in viscosity leaps. In all the cases, the viscosity increased from low values. Primarily, further studies should conducted to shift the viscosity towards higher values. The findings showed that a higher content of silica powder positively affects the dilatant behavior, i.e. a viscosity rise with increasing shear rate. The effects of viscosity leap in at a higher temperature were lower but occurred at higher shear rates.

Acknowledgements

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