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THE EFFECT OF NANO-SiO$_2$ PARTICLE SIZE DISTRIBUTION ON RHEOLOGICAL BEHAVIOUR OF SHEAR THICKENING FLUIDS

WPŁYW ROZKŁADU WIELKOŚCI ZIARNA CZĄSTEK NANO-SiO$_2$ NA WŁAŚCIWOŚCI REOLOGICZNE CIECZY ZAGĘSZCZANYCH ŚCINANIEM

In present work the influence of particle size distribution on the dilatant effect of shear thickening fluid was investigated. As a ceramic powder a mixture of silicas 200 and 7 nm in ratio 95:5, 90:10, 85:15, 80:20, 75:25, 50:50 was used. A dispersing agent was poly (propylene glycol) of a molecular weight of 425 g/mol. The as prepared slurries were examined on a rotational rheometer Kinexus Pro with a plate-plate measuring system at room temperature, where the viscosity as a function of shear rate was investigated. The measurement showed that by partially replacing greater particle size by smaller one, it is possible to shift the onset of shear thickening to the higher value of shear rate, however, the decreases of dilatant effect is observed. The influence of particle size distribution on a maximum volume fraction also was investigated. The maximum volume fraction which was passible to obtain was 35 vol%.

Keywords: shear thickening fluids, nanosilica, particle size distribution, dilatant effect, poly (propylene glycol)

W niniejszej pracy przedstawiono wyniki badań dotyczące wpływu rozkładu wielkości ziarna na właściwości zagęszczania ścinaniem. Fazę stałą stanowiła mieszanina nanokrzemionki o średnich wielkościach ziarna 7 i 200 nm, gdzie stosunek nanokrzemionki 200 nm do nanokrzemionki 7 nm wynosił odpowiednio 95:5, 90:10, 85:15, 80:20, 75:25 i 50:50. Jako ciecz dyspergującą zastosowano glikol polipropylenowy o masie molowej 425 g/mol. Badania reologiczne lepkości w funkcji wzrastającej szybkości ścinania wykonano za pomocą reometru rotacyjnego Kinexus Pro w układzie płytka-płytka. Szybkość ścinania zmieniała się od 1 do 1000 s^{-1}. Wyniki przeprowadzonych badań pokazały, że poprzez częściowe zastąpienie nanokrzemionki 200 nm nanokrzemionką 7 nm możliwe jest przesunięcie początku zagęszczania ścinaniem w stronę wyższych szybkości ścinania, jednakże skok dylatancyjny obniża się. W ramach pracy zbadano również wpływ rozkładu wielkości ziarna na maksymalne stężenie fazy stałej. Maksymalne stężenie fazy stałej wyniosło 35%obj.

1. Introduction

Possibility of application of shear thickening fluid to so called liquid armours has paid the attention of many researchers in the last decade [1-6]. The great advantage of shear thickening fluid is that it generally consists of nanosilica and polyglycols. Silica is inexpesive, widespread available ceramic powder, which may be natural orgin. Moreover, exhibit wide range of morphology and properties, but the most important point is that is lightweight and tough, which is very important in liquid armour designing. This unique properties of nanosilica cause that liquid armour which consist of Kevlar® soaked by/with shear thickening fluid is flexible, because consist of only from 2 to 6 layers of Kevlar. Furthermore, can protect the whole body, which in the case of traditional vest is impossible. The traditional vest protects only the trunk, because it is too rigid due to the fact that to good protection from 20 to 40 layers of Kevlar® must be used.

The main shear thickening behaviour which is used in liquid armour designing is reversible increase in viscosity with increases shear rate. In the literature several factors influencing shear thickening such as particle shape [7] and size [8,9], particle volume fraction [9,10], particle size distribution [7], particle-particle interaction [11], continuous phase viscosity, as well as the type, rate, and time of deformation can be found [12]. It was noticed that all of these parameters affect the interparticles forces [13], which result in shifting the position or modification of the size of the jump. Despite the fact that some basic knowledge has been already achieved, further investigations of influence of these parameters are required, due to the fact that the used compounds, preparation of the slurry and the investigation method also affect the shear thickening behaviour.

In this work, the influence of particle size distribution on the dilatant effect of shear thickening fluids was examined. In order to prepare the slurry the mixture of two nanosilica powders 7 and 200 nm in appropriate ratio dispersed in poly propylene glycol was used. Concentration of nanosilica 7 nm was changing from 5 to 50%. The influence of particle size distribution on the dilatant effect of shear thickening fluids

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was examined by rotational rheometer Kinexus Pro with a plate-plate system at room temperature, where the viscosity as a function of shear rate was investigated.

2. Experimental

To the preparation of shear thickening fluids two colloidal silica powders of different particle size were used. Table 1 shows the characteristic of these powders.

TABLE 1

Characteristic of the ceramic powders

ceramic powder	Silica Fumed (SF)	
average particle size specified by the manufacturer (nm)	7	200
average particle size from BET (nm)	12	20
specific surface area (m^2/g)	333.6	196.4
density (g/cm^3)	1.53	
producer	Sigma-Aldrich	

The average particle size of the ceramic powders was determined in two ways: by data from producer and based on BET data (assuming that the particles are spherical) using the equation:

$$\Phi = \frac{6}{S \cdot \rho}$$

where Φ [m] is the average diameter of a spherical particle, S [m^2/g] is the specific surface area of powder and ρ [g/m^3] is the density value of silica powder. The specific surface area was determined by a Brunauer-Emmett-Teller adsorption isotherm ASAP 2020 (Micromeritics, USA). The density of powder was measured by an AccuPyc II 1340 Pycnometer (Micromeritics, USA). As a dispersing agent, a poly(propylene glycol) of a molecular weight of 425 g/mol (PPG425) was used. The poly (propylene glycol) was purchased from Sigma-Aldrich (USA). The density of the dispersing agent was 1.13g/cm³.

In order to investigate the influence of particle size distribution on the dilatant effect of shear thickening fluid in the first step a particle size distribution of each powder was evaluated. In this case, nanosilica powder was dispersed in poly (propylene glycol) of a molecular weight of 425 g/mol and ultrasonicated for 5 min to better disperse particles in the solution before the measurements. Then, the particle size distributions were examined by using dynamic light scattering on a Malvern Zetasizer Nano-ZS (Malvern Instruments).

In the next step the shear thickening fluids were prepared by mixing two silica powders in an appropriate ratio with poly (propylene glycol) of a molecular weight of 425 g/mol. The SF200:SF7 ratio was changing from 95:5, 90:10, 85:15, 80:20, 75:25 to 50:50 and the total solid loading was varied from 20 to 35 vol%. All slurries were mixed by mechanical stirrer for 3 h at 55°C. The higher temperature of mixing allowed the authors to decrease the dilatant effect enough and stir the slurry easily. After homogenization, when the temperature of the slurry decreased to the room temperature (24 h),

the rheological behaviour of slurries depends on particle size distribution was evaluated. In this case, the viscosity as a function of shear rate was investigated. The rheological measurements were carried out on a rotational rheometer Kinexus Pro (Malvern, England) with a plate-plate system at room temperature. The gap between the two plates was 0.7 mm. The shear rate was measured from 1 to 1000 s⁻¹.

3. Results and discussion

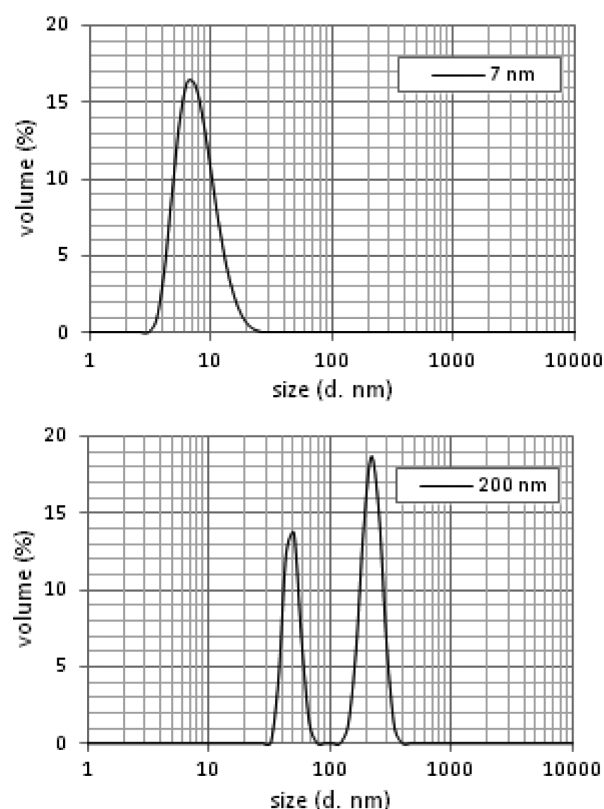Fig. 1. shows the particle size distribution of two nanosilica powders 7 and 200 nm.

Fig. 1. Particle size distribution of investigated SiO_2 powder

It was shown that the average particle size of nanosilica specified by the manufacturer to be 7 nm was similar to the results obtained by using dynamic light scattering. The particle size distribution in that powder was quite narrow and varied from 4 to 24 nm. The particle size distribution of the second powder was bimodal. The first peak was observed at 50 nm, where the particle size varied from 38 to 68 nm. The average particle size of the second peak was determined to be 220 nm. The particle size distribution in that peak varied from 140 to 295 nm. The bimodal nature of second powder can indicate the formation of hard aggregates with average particle size 220 nm, which were difficult to disperse in the slurry.

In the next step the influence of particle size of nanosilica on the rheological properties of shear thickening fluid was investigated. As it was shown in previous works [8, 9, 12] the particle size played the important role in a hydroclusters formation. The measurements showed that the application of silica of bigger particle size resulted in increased dilatant effect, however, the onset of shear thickening at lower values

of shear rate was observed (Fig. 2.). In the suspension containing nanosilica 7 nm the onset of shear thickening at shear rate equaled 25 s^{-1} was observed. The critical viscosity was noticed at shear rate equaled 50 s^{-1} and dilatant effect was around 187 Pa·s. At the second slurry based on nanosilica 200 nm the onset of shear thickening was determinate to be 5 s^{-1}. The critical viscosity was observed at shear rate equaled 15 s^{-1} and dilatant effect was around 880 Pa·s.
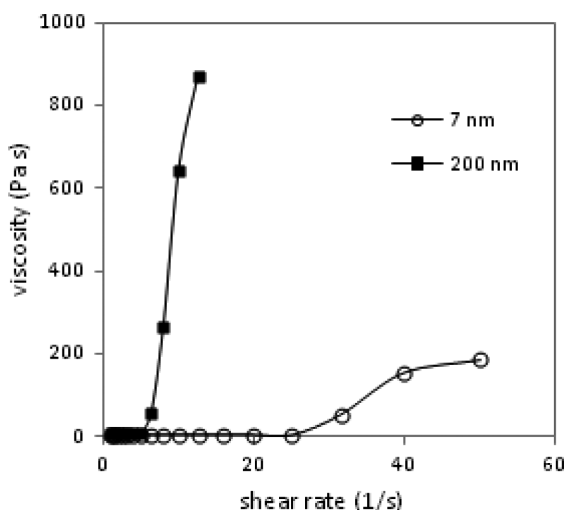

Fig. 2. Effect of particle diameter on shear thickening behaviour of 20 vol% nano-SiO$_2$ suspensions

Due to the fact that in many shear thickening fluid applications for example protecting clothes based on shear thickening fluid the unbounded move is required, the onset of shear thickening should be higher than 10 s^{-1}. As it was shown in Fig. 2. in spite of the high dilatant effect of suspension based on silica 200 nm, the onset of shear thickening was too low to apply this kind of material in protecting clothes such as liquid armour. In this case, better results were received for slurry containing silica of 7 nm where the value of onset of shear thickening was considerably higher.

In further work the authors focused on the shifting the onset of shear thickening to the higher values of shear rates. According to the assumption that the radius of the particles can be seen to have an inverse quadratic dependence on the shear rate (considering the particles are spherical in nature) [12] and the receiving data, in the next step two kind of investigated powders were mixed together and as prepared slurries were examined in order to determined the influence of particle size distribution on dilatant effect of shear thickening fluid (Fig. 3.).

As it was expected with increasing concentration of the silica 7 nm in a total volume fraction, the shifting of the onset of shear thickening to the higher values of shear rates was observed. It indicates that by replacing the greater particle size of nanosilica by smaller nanosilica particles the shifting of the onset of shear thickening to the higher values of shear rates is possible. By replaced 5 vol% of silica 200 nm by silica 7 nm only the small shifting equaled 1 s^{-1} was observed. With next 5, 10 and 15 vol% the onset of the shear thickening was shifted to the shear rate equaled 10 s^{-1}. The best results were received with 25 and 50 vol% of exchanging where the onset of shear thickening were 16 and 20 s^{-1}. The particle size distribution

also affected the critical viscosity of the suspension. With an increasing concentration of the silica 7 nm, a decreasing of the critical viscosity was observed. The most important changes were observed between slurry based on only silica 7 nm and slurry with 50 vol% of this powder, where increased in critical viscosity for about 40 Pa·s without changing the critical shear rate was noticed. In the slurries containing from 10 to 25 vol% of this powder critical viscosity was around 530 Pa·s and occurred at shear rate around 25 s^{-1}. The interesting data were also received for slurry containing only 5 vol% of silica 7 nm where the critical viscosity was a little higher than for suspension based only on silica 200 nm (900 Pa·s). Also the critical shear rate was a little higher and equaled 20 s^{-1}.
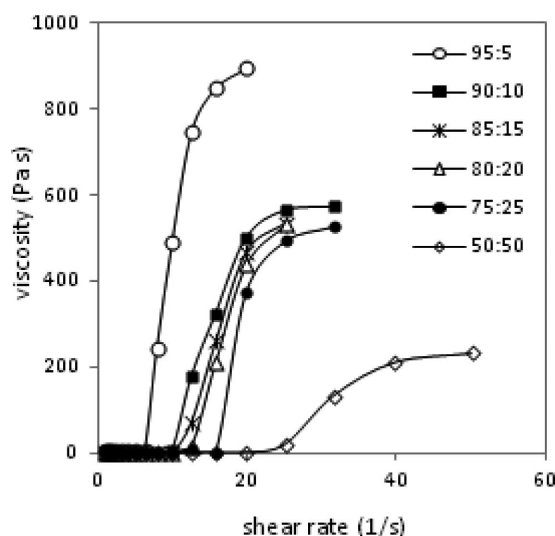

Fig. 3. Effect of particle size distribution on dilatant effect of nano-SiO$_2$ suspensions
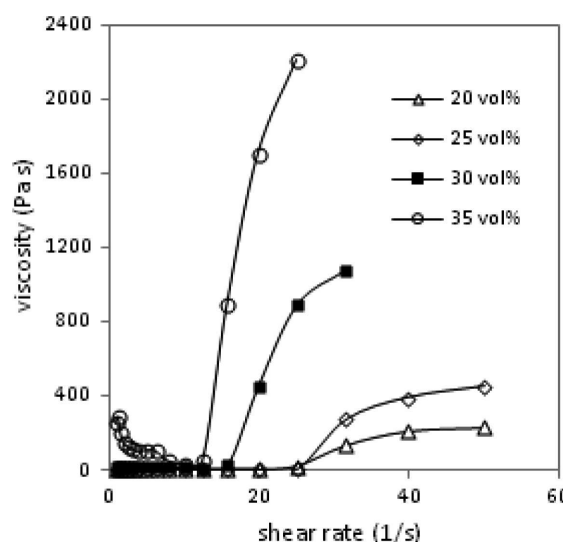

Fig. 4. Effect of particle concentration on dilatant effect of nano-SiO$_2$ suspensions

Fig. 4 shows the effect of particle volume fraction on dilatant effect of suspensions based on nanosilica 7 and 200 nm at ratio 50:50. It was noticed that the addition of the particles to a liquid (poly (propylene glycol)) resulted in an increased in the dilatant effect of the suspensions, however, the critical viscosities at the lower values of shear rate were observed.

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Also the onset of shear thickening decreased with the increasing particles concentration. The onsets of shear thickening respectively for 20, 25, 30 and 35 vol% of powder at 25, 25, 13 and 10 s^{-1} were observed. The critical viscosities increased significantly from 233 Pa·s for suspension containing 20 vol% of ceramic powder to 2210 Pa·s for suspension containing 35 vol% of ceramic powder. The critical shear rates of those suspensions at 50 and 25 s^{-1} were observed. Application of 25 vol% of powder did not change the onset of shear thickening and the critical shear rate in respect to the suspension containing 20 vol% of ceramic powder, however, the higher critical viscosity around 450 Pa·s was observed. Suspension containing 30 vol% of powder exhibited shear thickening behaviour at shear rate around 13 s^{-1}, where the critical shear rate and critical viscosity were determined to be 40 s^{-1} and 1122 Pa·s.

Replacing the 50 vol% silica 200 nm by silica 7 nm did not change the maximum volume fraction. These results are not with agreement with previous works, which suggests that difference in the diameter of particle allows increasing particles concentration in the slurry, due to the fact that gaps between larger particles can be filled by the particles of lower diameters. It indicates that the diameter of the greater particle was lower than the manufacturer and the data received from dynamic light scattering were suggested. Therefore, the particle size received from BET was closer to the true.

4. Conclusion

In this work the influence of particle size distribution on dilatant effect of shear thickening fluid was investigated. The measurements showed that by replacing the part of greater silica particle by silica of lower particle size it is possible to shifts the onset shear thickening to the lower value of shear rates. The particle size distribution also affects the dilatant effect by reducing a critical viscosity and shifts it to the higher values of shear rates.

In this work the influence of particle size distribution on maximum volume fraction also was examined. The measurements showed that the partially replacement the greater particle size by smaller one did not change the maximum volume fraction. It can indicates that the diameter of the greater particle was lower than the manufacturer and the data received from dynamic light scattering were suggested or the gaps between bigger particles were lower than the diameter of the smaller particles.

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