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COMPOSITES THEORY AND PRACTICE

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# THE INFLUENCE OF NANO-$SiO_2$ PARTICLE SIZE ON DILATANT EFFECT OF SHEAR THICKENING FLUIDS

**Recently, the shear thickening phenomenon has drawn the attention of many researchers. The ability of shear thickening fluid to resist operative force creates a possibility of applying this kind of material wherever there is a necessity to dampen and disperse energy. Therefore, dilatant slurries have found their application in dampers, devices that protect buildings against seismic shocks or military applications in so called "liquid armor". A great deal of research has focused on investigation of the mechanism and influence of parameters such as volume fraction, polydispersity and medium viscosity of the dilatant effect, however, some fields are still unexplored. In this work, the influence of nanosilica particle size on the dilatant effect of shear thickening fluids was investigated. For the tests, nanosilica with diameters of 7 and 200 nm was chosen. The suspension was prepared by dispersing the nanosilica into poly (propylene glycol) of a molecular weight of 400 g/mol. The concentration of the ceramic powder varied from 12 to 30 vol.%. The influence of the particle size on the dilatant effect was observed by a rotational rheometer Kinexus Pro with a plate-plate system. In this case, viscosity as a function of shear rate was measured. The shear rate increased from 1 to 1000 $s^{-1}$. The measurement showed that the diameter of silica particles has a significant influence on the rheological properties of the investigated suspensions. With an increase in particle size the dilatant effect increases. However, its position is shifted to a lower shear rate. The maximum volume fraction and relative viscosity of the suspension also was examined. The measurements showed that with increasing particle size, the relative viscosity of the suspension decreases, which result in an increase in the maximum volume fraction of nano-$SiO_2$.**

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

## WPŁYW WIELKOŚCI CZĄSTEK NANO-$SiO_2$ NA WŁAŚCIWOŚCI REOLOGICZNE CIECZY ZAGĘSZCZANYCH ŚCINANIEM

**Ciecze zagęszczane ścinaniem (dylatancyjne) należą do grupy płynów nienewtonowskich, charakteryzujących się wzrostem lepkości wraz ze wzrostem szybkości ścinania lub przyłożonego naprężenia ścinającego. Właściwość tych cieczy stanowi problem w wielu procesach technologicznych. Efekt zagęszczania ścinaniem utrudnia bowiem procesy mieszania i przepływu, powodując przeciążenia aparatury. W ostatnich latach wiele badań poświęcono wyjaśnieniu zarówno mechanizmu, jak i wpływu różnych parametrów na zjawisko dylatancji. Możliwość lepszego zrozumienia efektu zagęszczania ścinaniem dała nowe spojrzenie na możliwości aplikacyjne danych zawiesin. Obecnie ciecze dylatancyjne znajdują zastosowanie wszędzie tam, gdzie potrzebne jest stawianie oporu działającej sile. Przykładem może być tu odzież ochronna składająca się z tkanin balistycznych nasączonych płynem zagęszczanym ścinaniem, tłumiki czy też urządzenia chroniące budynki przed wstrząsami sejsmicznymi. Duże zainteresowanie skupia się także wokół tzw. ciekłych pancerzy. Pomimo wielu badań koncentrujących się wokół poznania czy też lepszego zrozumienia efektu dylatancji dalsza eksploracja tego zjawiska jest potrzebna. Wiele parametrów, takich jak wpływ stężenia fazy stałej, środka dyspergującego czy oddziaływań międzycząsteczkowych zostało zbadanych, jednakże wciąż istnieje znaczna ilość obszarów wymagająca dalszych testów. W niniejszej pracy przedstawiono wyniki badań dotyczące wpływu wielkości ziarna na zjawisko dylatancji zawiesin ceramicznych opartych na nanokrzemionce. Średnia wielkość ziarna wynosiła odpowiednio 7 i 200 nm. Jako środek dyspergujący we wszystkich badań zastosowano glikol (polipropylenowy) o masie cząsteczkowej 400 g/mol. W celu zbadania wpływu wielkości ziarna na efekt dylatancji przygotowano zawiesiny o różnym stężeniu fazy stałej (12, 15, 20, 25 i 30% obj.). Wszystkie ciecze były poddawane badaniom właściwości reologicznych (lepkości w funkcji ścinania). W tym celu wykorzystano reometr rotacyjny Kinexus Pro z układem płytka-płytka. Wyniki przeprowadzonych badań pokazały, że wielkość ziarna ma znaczący wpływ na początek i wartość skoku dylatancji. Ze wzrostem wielkości ziarna zaobserwowano znaczny wzrost skoku dylatancji badanej zawiesiny. Warto jednak zauważyć, że wartość szybkości ścinania, przy której skok ten występuje proporcjonalnie, maleje. W ramach pracy zbadano również wpływ wielkości ziarna na ilość proszku, jaką można załadować jednorazowo, zachowując przy tym odpowiednie właściwości badanych zawiesin. W tym przypadku najlepsze wyniki otrzymano, stosując nanokrzemionkę o średniej wielkości ziarna 200 nm.**

**Słowa kluczowe:** ciecze zagęszczane ścinaniem, nanokrzemionka, wielkość ziarna, efekt dylatancji, glikol polipropylenowy

## INTRODUCTION

Shear thickening is a non-Newtonian flow behavior whose viscosity increases with an increase in shear rate or applied stress. This effect is undesirable in technology as it hinders the processes of mixing and flow, causing equipment overload. However, the dilatant effect is potentially interesting in certain industries. Shear thickening fluids due to their unique behavior to dampen energy, nowadays, find an application in dampers, liquid couplings, ski boot cushioning, rotary speed limiters, shock absorber fillings and body armours [1, 2].

Much of the attention has been focused on the mechanism of shear thickening, including neutron scattering [3-6], rheo-optical experiments [7, 8] and others. One of the earliest experiments performed by Hoffman in 1972 suggested that shear thickening is a consequence of the transition of a powder particle from an ordered state to a disordered state (order-disorder transition) [9, 10]. However, further investigation showed that the order-disorder transition is not the sole mechanism which can explain the dilatancy effect. Simulation predictions by Brady et al. using the method of Stokesian dynamics (1989) provide computational evidence that the dilatant effect occurs due to the formation of jamming clusters resulting from hydrodynamic lubrication forces between the particles, often denoted by the term "hydroclusters" [11-14]. This method was next used by Boersma et al. and Melrose et al. who confirm the correctness of the Brady theory [15-17].

As well as the mechanism, the influence of some parameters has also been studied exhaustively. In literature, many papers presenting the result of the influence of particle shape, particle volume fraction, particle-particle interaction, continuous phase viscosity, as well as the type, rate, and time of deformation can be found [1]. It was shown that all of these parameters have a significant influence on the dilatant effect of shear thickening fluid by shifting the position or changing the size of the jump. Another important factor which determines the dilatancy effect is particle size [1]. Changes in the particle size, shape, surface chemistry, and ionic strength and in the properties of suspending medium, affect the interparticle forces which dominate the viscosity at low shear stress [18]. In literature, many papers presenting the preparation and investigation of shear thickening fluid can be found, however, there are only limited measurements of the influence of particle size on shear thickening behaviour. Study of the difference is critical to formulating a suspension that behaves as needed for specific processes or applications.

In this work, the influence of nanosilica particle size on the dilatant effect of shear thickening fluids was investigated. The nanosilica particle size varied from 7 to 200 nm. The performed rheological measurements allowed further understanding of the influence of the particle size on the dilatant effect and maximum the volume fraction of shear thickening fluids.

## EXPERIMENTAL PROCEDURES

To investigate the influence of powder particle size on the rheological properties of shear thickening fluids, silica fumed with an average particle size of 7 and 200 nm was used. Both ceramic powders were purchased from Sigma-Aldrich (USA). The specific surface area of each powder measured by a Brunauer--Emmett-Teller adsorption isotherm ASAP 2020 (Micromeritics, USA) was determined to be 333.6 and 196.4 $m^2/g$, respectively for the 7 and 200 nm. The density of the powder was evaluated by an AccuPyc II 1340 Pycnometer (Micromeritics, USA) and equals 1.53 $g/cm^3$. As a dispersing agent, a poly(propylene glycol) of a molecular weight of 400 g/mol was used. The poly(propylene glycol) also was provided by Sigma-Aldrich (USA). The density of the dispersing agent was 1.13 $g/cm^3$.

In order to prepare the ceramic slurry for further investigation, in the first step, the powder and dispersing agent were put in an appropriate ratio into a plastic beaker and mixed with a mechanical stirrer at 100 rotations per minute 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. The concentration of the ceramic powder varied from 12 to 30 vol.%. After homogenization, the suspension was left for one day to lower the mixing temperature to room temperature and then the rheological properties were 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 $s^{-1}$.

## RESULTS AND DISCUSSION

Figure 1 presents the effect of the particle diameter on the shear thickening properties of nano-$SiO_2$ suspensions with different volume fractions - 12, 15 and 20 vol.%. The measurement showed that all the slurries exhibit shear thickening behavior. It was noticed that the onset of shear thickening and critical shear rate strongly depend on the diameter of the silica particles. It can indicate that the particle-particle interactions and cluster formation are strongly influenced by the particle diameter in the nanometer range. With an increase in particle size, shifting of the onset of shear thickening and critical shear rate to lower values of shear rate was observed. This is in agreement with 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) [1]

$$\dot{\gamma} \propto \frac{1}{d^2}$$

The particle size also affects the critical viscosity of the suspension. With an increasing particle diameter, an increase in the critical viscosity was observed.

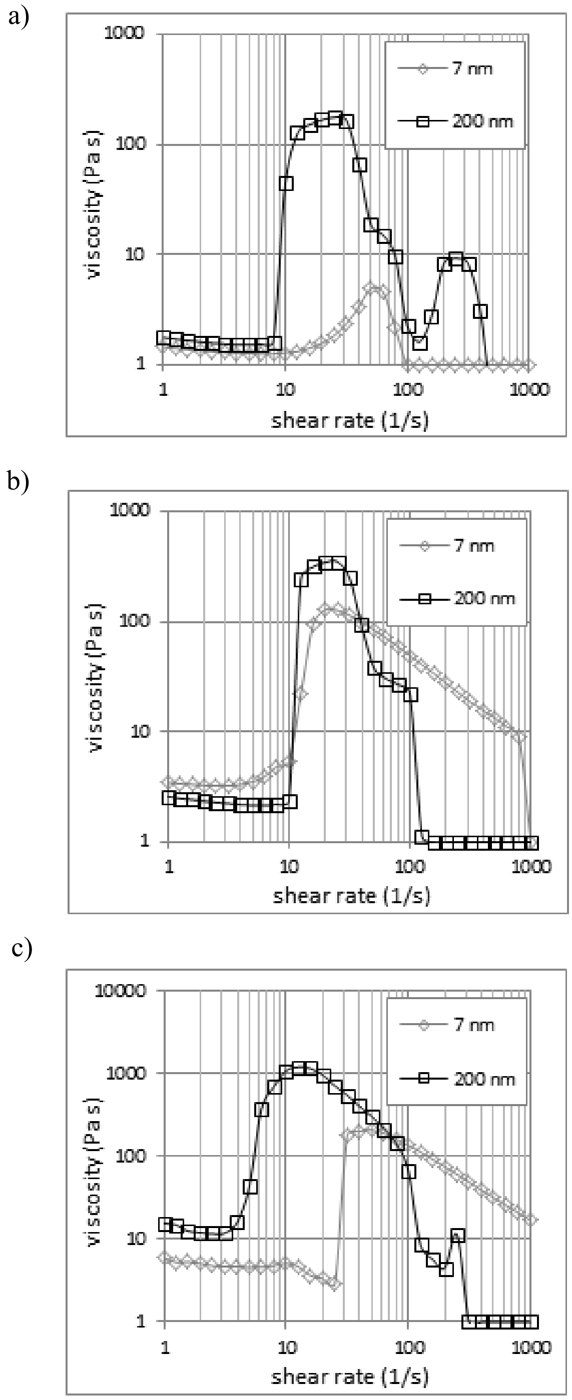


Fig. 1. Effect of particle diameter on shear thickening behavior of a) 12 vol.%, b) 15 vol.%, c) 20 vol.% nano-$SiO_2$ suspensions

Rys. 1. Wpływ wielkości cząstek na właściwości zagęszczania ścinaniem zawiesin nanokrzemionkowych zawierających: a) 12% obj., b) 15% obj., c) 20% obj. fazy stałej

As can be seen in Figure 1a, the dilatant effect of the suspension containing 12 vol.% silica with an average particle size of 7 nm is insignificant. The onset of shear thickening and critical shear rate of this suspension occurred at shear rates of 6 and 50 $s^{-1}$, respectively. The critical viscosity was 5 Pa·s. On the other hand, the onset of shear thickening of the suspension containing 12 vol.% of 200 nm silica occurred at lower shear rates, 5 $s^{-1}$. However, in this suspension two jumps were detected. The first was at shear rate 25 $s^{-1}$ where the critical viscosity was 177 Pa·s and the second at shear rate 251 $s^{-1}$ where the critical viscosity was much lower, 9 Pa·s. The tendency of the viscosity curves presented in Figures 1b and 1c are similar to the curves from Fig.1a, however, the onset of non-Newtonian behaviour occurred at a lower shear rate. Moreover, the critical viscosity both for suspensions containing 15 and 20 vol.% nanosilica was higher. It indicates that the dilatant effect also depends on the volume fraction of the particle. This phenomenon would possible to be explained by the assumption that an increase in weight fraction shortens the distance between the silica nanoparticles, therefore it is easier to form clusters and exhibit shear-thickening behavior [19]. In this case, the critical viscosities of the suspension containing 15 vol.% 7 nm silica and the suspension containing 15 vol.% 200 nm silica occurred at shear rates 20 and 25 $s^{-1}$, and equal 129 and 353 Pa·s. The onsets of shear thickening were established at 3 and 5 $s^{-1}$, respectively. The critical viscosity of the suspension containing 20 vol.% 7 nm silica and the suspension containing 20 vol.% 200 nm silica occurred at shear rates 50 and 13 $s^{-1}$, and equal 210 and 1200 Pa·s. The onsets of shear thickening occurred at 25 and 3 $s^{-1}$.

Figure 2 presents the effect of particle concentration on the relative viscosity of the nano-$SiO_2$ suspensions depending on the nanosilica particle size. It can be seen that the relative viscosity of each suspension strongly depends on the concentration of the ceramic powder. The addition of particles to a liquid (poly (propylene glycol)) results in an increase in the liquid viscosity which is in agreement with previous works [20]. However, the relationship between the relative viscosity and particle size cannot be easily determined.

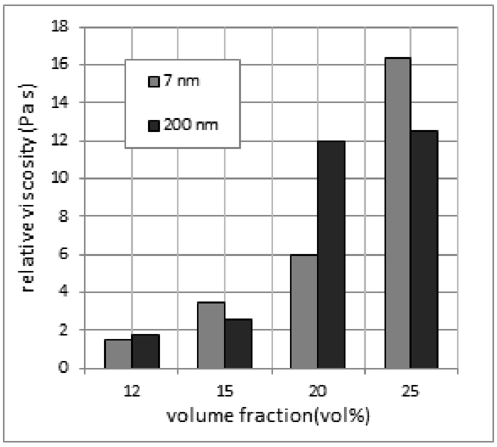


Fig. 2. Effect of particle concentration on relative viscosity of nano-$SiO_2$ suspensions depending on nanosilica particle size

Rys. 2. Wpływ stężenia fazy stałej na lepkość dynamiczną zawiesin opartych na nano-$SiO_2$ o średniej wielkości ziarna 7 i 200 nm

The relative viscosity of the suspensions containing 12 and 15 vol.% powder with the average particle size of 7 and 200 nm was 2 ± 1 Pa·s. Significant changes in the relative viscosity of the fluid based on $SiO_2$ of 7 and

 

200 nm were observed for a suspension containing 20 vol.%. The difference in the viscosity of these suspensions was around 6 Pa·s. The relative viscosities were determined to be 6 and 12 Pa·s for the $SiO_2$ of 7 and 200 nm, respectively. Increasing the solid loading to 25 vol.% results in changing the relationship between the viscosity values. A higher relative viscosity occurred for the fluid containing silica with the average particle size of 7 nm. The relative viscosity of the second suspension based on silica with the average particle size of 200 nm was around 16 Pa·s. The received data can not significantly indicate the influence of particle size on the relative viscosity of the investigated fluid. In this case, further investigations are needed.

TABLE 1. **Effect of particle diameter on maximum volume fraction of nano-$SiO_2$ suspensions**
TABELA 1. **Wpływ wielkości ziarna na maksymalne stężenie fazy stałej zawiesin nanokrzemionkowych**

| Powder | SF7 | SF200 |
|---|---|---|
| Maximum volume fraction [vol.%] | 25 | 30 |
| Relative viscosity [Pa·s] | 16 | 100 |
| Onset of shear thickening [1/s] | 12 | 2 |
| Critical shear rate [1/s] | 25 | 6 |
| Critical viscosity [Pa·s] | 638 | 2865 |

The data presented in Table 1 show the influence of the particle size on the maximum volume fraction and accompanying them, the rheological properties of the ceramic slurry. As can be observed, it was possible to obtain a higher volume fraction using the silica with the average particle size of 200 nm (30 vol%). Although, the suspension with such solid loading still behaved like a liquid and showed a meaningful dilatant effect (2865 Pa·s), it was characterized by a high relative viscosity around 100 Pa·s. Moreover, the onset of shear thickening and critical shear rate occurred quite fast (2 and 6 $s^{-1}$). The maximum volume fraction in the suspension with silica of 7 nm was 25 vol.%. Despite the fact that the relative viscosity, onset of shear thickening and critical shear rate occurred at a higher shear rate (16, 12, 25 $s^{-1}$), the critical viscosity was much lower, 638 Pa·s.

## CONCLUSION

In this study, the influence of nanosilica particle size on the dilatant effect of shear thickening fluids was investigated. The measurements showed that the shear thickening properties can be controlled by several different parameters. The application of silica with a greater particle size results in an increased critical viscosity and maximum volume fraction. The particle size also affects the onset of shear thickening by shifting the jump to a lower shear rate when the suspension has larger silica particles. It indicates that the particle-particle interactions and the cluster formation are strongly influenced by the particle diameter in the nanometer range.

The same conclusion can be provided in regards to the influence of volume fraction. With an increasing solid content, the critical viscosity increases, however, the onset of shear thickening and critical shear rate occur at a lower shear rate. It indicates that the dilatant effect also depends on the volume fraction of the particle. This phenomenon could possibly be explained by the assumption that the increase in weight fraction shortens the distance between the silica nanoparticles, therefore it is easier to form clusters and exhibit shear-thickening behavior.

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