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THE ROLE OF GLYCEROL DERIVATIVE IN A PREPARATION OF SHEAR THICKENING FLUIDS FOR LIQUID ARMOUR APPLICATIONS

In this paper, the influence of a glycerol derivative (glycerol monoacrylate) synthesized by the authors on the dilatant effect of shear thickening fluid was investigated. It was assumed that the monomer synthesized from acrylic acid and glycidol, owing to the presence of two hydroxyl groups, allows one to enhance the dilatant effect of the investigated slurries by creating a three-dimensional network between the powder particle and dispersing agent. The dilatant effect was examined with respect to the solid loading and molecular weight of the dispersing agent. As the ceramic powder, a nanosilica with an average particle size of 14 nm was used. Poly (propylene glycol) of a molecular weight of 400 and 725 g/mol played the role of dispersant. The solid loading was changed from 12 to 15 vol.%. The measurements showed that by applying even a small amount of glycerol monoacrylate (0.5 wt.%), it was possible to enhance the dilatant effect of the investigated slurries. It was also observed that by increasing the solid loading and/or using a poly (propylene glycol) of a higher molecular weight, it was possible to increase the critical viscosity even threefold. Furthermore, the rheological properties of the slurry return to the initial state when the external force ceases. The influence of temperature and quantity of impacts also were investigated. The measurements showed that by increasing the temperature of the shear thickening fluid from room temperature to human body temperature, resulted in a decreased dilatant effect of the slurry. However, the onset of shear thickening and critical shear rate shifted to higher values of shear rate. Moreover, widening of the dilatant jump was observed. Similar results were obtained as a result of the using the fluid several times. The studies have shown that with each successive impact, the dilatant effect decreases.

Keywords: shear thickening fluids, nanosilica, glycerol monoacrylate, dilatant effect, poly (propylene glycol)

ROLA POCHODNEJ GLICEROLU W OTRZYMYWANIU CIECZY ZAGĘSZCZANYCH ŚCINANIEM DO ZASTOSOWAŃ SPECJALNYCH

W niniejszej pracy przedstawiono wyniki badań dotyczących wpływu pochodnej glicerolu (monoakrylanu glicerolu) na właściwości zagęszczania ścinaniem cieczy opartych na nanokrzemionce S fumed silica o średniej wielkości ziarna 14 nm. Monoakrylan glicerolu został zsyntezowany przez autorów w jednoetapowej reakcji kwasu akrylowego z glicydołem. Jako produkty reakcji otrzymano dwa izomery: akrylan 2,3-dihydroksypropylu oraz akrylan 1,3-dihydroksypropylu w stosunku wagowym 70:30. Założono, że obecność dwóch grup hydroksylowych w cząsteczce monoakrylanu glicerolu, jak również możliwość tworzenia wiązań wodorowych pomiędzy grupami -OH polimeru może pozytywnie wpływać na skok dylatancyjny badanych zawiesin. Efekt dylatacji badano zarówno pod względem masy molowej cieczy dyspergującej, jak i stężenia fazy stałej. Jako ciecz dyspergującą zastosowano glikol polipropylenowy o masie molowej 400 i 725 g/mol. Stężenie fazy stałej zmieniało się w zakresie 12-15% obj. Wyniki badań pokazały, że dodatek nawet niewielkiej ilości monoakrylanu glicerolu (0,5% wag.) pozytywnie wpływa na wzrost efektu zagęszczania ścinaniem. Zaobserwowano również, iż wzrost stężenia fazy stałej i/lub zastosowanie glikolu polipropylenowego o wyższej masie molowej skutkuje nawet trzykrotnym wzrostem maksimum zagęszczania ścinaniem. Co więcej, proces ten jest odwracalny. Oznacza to, że badany monomer nie tworzy trwałych wiązań z proszkiem ceramicznym i cieczą dyspergującą. W pracy zbadano również wpływ temperatury i ilości pomiarów na efekt zagęszczania ścinaniem. Badania pokazały, że wzrost temperatury negatywnie wpływa na wysokość skoku dylatancyjnego. Podwyższenie temperatury zawiesiny (25,0°C) do temperatury ciała człowieka (36,6°C) znacznie obniżyło maksimum zagęszczania ścinaniem, jednakże skok był przesunięty w stronę wyższych szybkości ścinania. Zaobserwowano również znaczne wydłużenie skoku dylatancyjnego. Podobne rezultaty uzyskano w wyniku kilkukrotnego użycia cieczy. Badania pokazały, że wraz ze wzrostem ilości penetracji maleje efekt zagęszczania ścinaniem.

Słowa kluczowe: ciecz zagęszczana ścinaniem, nanokrzemionka, monoakrylan glicerolu, efekt dylatacji, glikol polipropylenowy

INTRODUCTION

Shear thickening fluids belong to the group of intelligent materials whose rheological properties change in a predictable and reversible way when an external force

is applied. It was shown that under the influence of impact, the rheological behaviour of the dilatant material changes from that of a liquid to behaviour charac-

teristic for solids. The unique properties of shear thickening fluid make the dilatant effect potentially attractive for those branches of industry where during normal operation flexibility is required, but in emergency cases e.g. injury risk, sudden “hardening” occurs. Therefore, shear thickening fluid finds an application in protective clothing, which can be used in the military or sport industry, as well as in dampers or devices protecting buildings from seismic shocks [1, 2].

In the literature, a few theories can be found which try to explain shear thickening behaviour e.g. the theory of order-disorder transition [3, 4], hydrocluster formation [5, 6] or the theory of flocculation [7, 8]. The first of them, discovered in 1972 by Hoffman, assumes that at lower shear rates, layers of powder particles form a two-dimensional hexagonal network, where the individual layers move in a strictly orderly manner. When the shear rate exceeds its critical value, disintegration of the hexagonal network occurs and unpredictable movement of the ceramic particles can be observed. The random location of the particles leads ceramic particle interactions and partial retention of the flow ability, which result in an increase in viscosity [9]. In 1989, a simulation proposed by Brady et al. using the method of Stokesian dynamics showed that shear thickening can be due to changes in the interactions between particles when the critical shear rate occurs. The measurement showed that at higher shear rates, the hydrodynamic force overcomes the repulsive interparticle forces which result in hydrocluster formation. The particles collide and the material becomes macroscopically rigid [10]. The last, but also the newest theory discovered by Kamibayashi et al. in 2009 is based on the adsorption of polymer chains on particle surfaces. Kamibayashi assumes that above the critical shear rate between the ceramic particles and the dispersant, a three-dimensional network is created. The polymeric binders formed between the polymers inhibit the flow of the particles, which result in increase in viscosity [7].

With reference to the theory of flocculation, in the present study the influence of glycerol monoacrylate (monomer synthesized by the authors) on the dilatant effect of shear thickening fluid was investigated. It was assumed that glycerol monoacrylate, due to the presence of two hydroxyl groups in the structure, will be able to create a three-dimensional network between the ceramic surface and polymer chain at higher shear rate. It should result in a significant increase in the viscosity of the ceramic suspension. Furthermore, the slurry should return to its initial state when the external force ceases. The effect of glycerol monoacrylate was tested regarding

the solid loading, molecular weight of the dispersing agent, temperature and number of times of penetration.

EXPERIMENTAL PROCEDURE

Materials

In this work, fumed silica (FS) of an average particle size of 14 nm was used as the ceramic powder. The fumed silica was provided by Sigma-Aldrich (USA). The density measured by an AccuPyc II 1340 Pycnometer (Micromeritics, USA) was determined to be 1.53 g/cm³. The specific surface area was 200 m²/g. The specific surface area was evaluated by a Brunauer-Emmett-Teller adsorption isotherm, ASAP 2020 (Micromeritics, USA). Figure 1 shows a SEM image of the investigated powder.

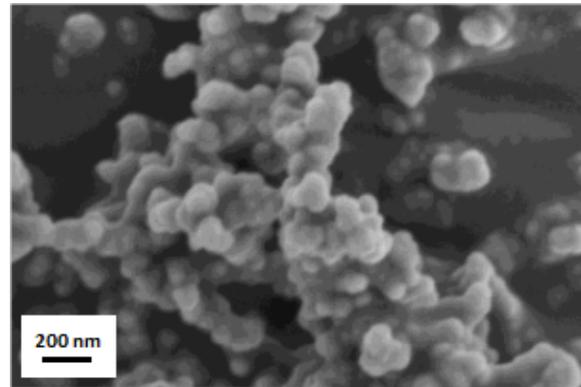


Fig. 1. SEM image of fumed silica

Rys. 1. Zdjęcie mikrostruktury proszku ceramicznego fumed silica wykonane za pomocą skaningowego mikroskopu elektronowego

It was observed that the ceramic particles are spherical, moreover, they are strongly agglomerated. The average agglomerate size was around 300–400 nm. As the dispersant, a poly (propylene glycol) of a molecular weight of 400 and 725 g/mol was used. The poly (propylene glycol) was purchased from Sigma-Aldrich (USA). The density of the dispersing agents was respectively 1.130 and 1.007 g/cm³.

As the glycerol derivatives, a glycerol monoacrylate was used. The monomer was synthesized at the Faculty of Chemistry, Warsaw University of Technology in a one-step reaction from glycidol and acrylic acid where two isomers, 2,3-dihydroxypropyl acrylate and 1,3-dihydroxypropyl acrylate, were received as the product. Figure 2 shows the chemical structures of the synthesized monomers and their synthesis reaction.

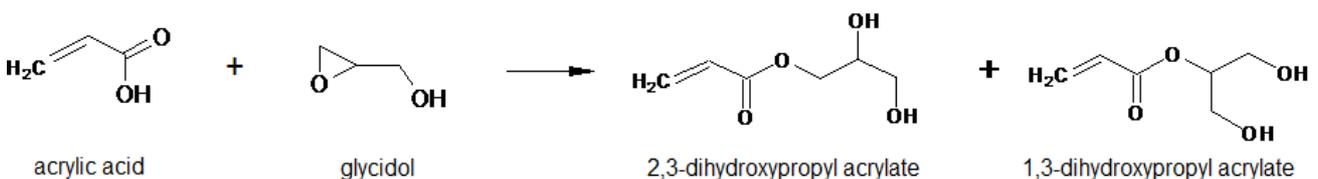


Fig. 2. Chemical structures of glycerol monoacrylate and its synthesis reaction

Rys. 2. Wzór strukturalny oraz reakcja otrzymania monoakrylanu glicerolu

Method

Figure 3 shows the scheme of the shear thickening fluid preparation.

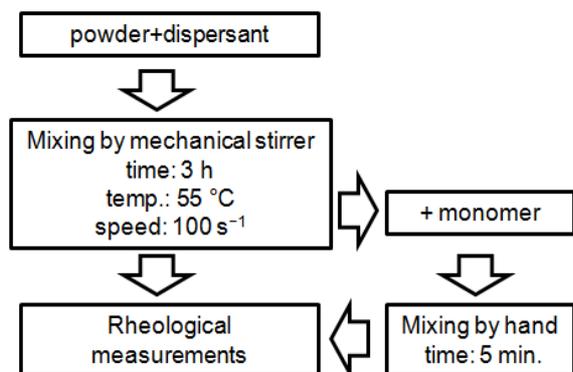


Fig. 3. Scheme of shear thickening fluid preparation

Rys. 3. Schemat sposobu przygotowania cieczy zagęszczanych ścinaniem

In the first step, the ceramic powder and dispersant were mixed together in an appropriate ratio by a mechanical stirrer with a speed of 100 rpm during 3 hours. For better homogenization, all the slurries were mixed at 55°C. It allowed us to decrease the dilatant effect significantly and mix the slurry easily. In the next step, when the temperature of the suspension decreased to room temperature, the monomer was added in the appropriate ratio. The glycerol monoacrylate content was changed from 0.5 to 1.0 wt.% with respect to the weight of the ceramic slurry. The as-prepared suspension was left for 24 hours to homogenize and then investigated by a rotational rheometer, Kinexus Pro (Malvern, England) with a plate-plate system. All the slurries were investigated at two temperatures, 25.0 and 36.6°C. The gap between the two plates was 0.7 mm. The shear rate was measured from 1 to 1000 s⁻¹.

RESULTS AND DISCUSSION

In the first step, the influence of the amount of glycerol monoacrylate on the shear thickening behaviour and its change, depending on the solid loading and kind of dispersing agent, was measured. Figure 4a) shows the dilatant effect of slurries containing 12 vol.% ceramic powder depending on the glycerol monoacrylate content. The measurements showed that the addition of even a small amount of glycerol monoacrylate resulted in an increase in the dilatant effect of the slurries. With an increasing monomer content, the dilatant effect increased, however, it occurred at a lower value of shear rate. The critical viscosity of the suspension containing only fumed silica and poly (propylene glycol) occurred at the shear rate of 25 s⁻¹ and equaled 137 Pa·s. The addition of 0.5 wt.% glycerol monoacrylate increased the critical viscosity to 216 Pa·s, however, it shifted to a lower shear rate, 16 s⁻¹. The highest critical viscosity, 272 Pa·s, was reached by the addition

of 1.0 wt.% glycerol monoacrylate. In this case, the maximum dilatant effect occurred at 10 s⁻¹. The onsets of shear thickening of slurries containing respectively only fumed silica and poly (propylene glycol), the addition of 0.5 wt.% glycerol monoacrylate and 1.0 wt.% monomer at shear rates 2.5, 2.0 and 3.0 s⁻¹ were observed. Figure 3b) presents the influence of glycerol monoacrylate on the dilatant effect containing 15 vol.% ceramic powder. It was observed that an increase in solid loading allowed us to reach a higher value of critical viscosity. The critical viscosity of the slurry without the additive was at shear rate 16 s⁻¹ and equaled 337 Pa·s. By adding 0.5 wt.% monomer, it was possible to reach a critical viscosity around 562 Pa·s, which was almost three times higher than for the slurry containing only 12 vol.% ceramic powder. This suspension with 1 wt.% glycerol monoacrylate exhibited a critical viscosity around 763 Pa·s. The critical shear rates of slurries containing 0.5 and 1.0 wt.% monomer at shear rates 10 and 6 were observed. In this case, shifting the onset of shear thickening to lower values of shear rate with an increasing monomer content was observed. The onsets of shear thickening of slurries containing respectively only fumed silica and poly (propylene glycol), an addition of 0.5 wt.% glycerol monoacrylate and 1.0 wt.% monomer at shear rates 1.9, 1.2 and 1.2 s⁻¹ were observed.

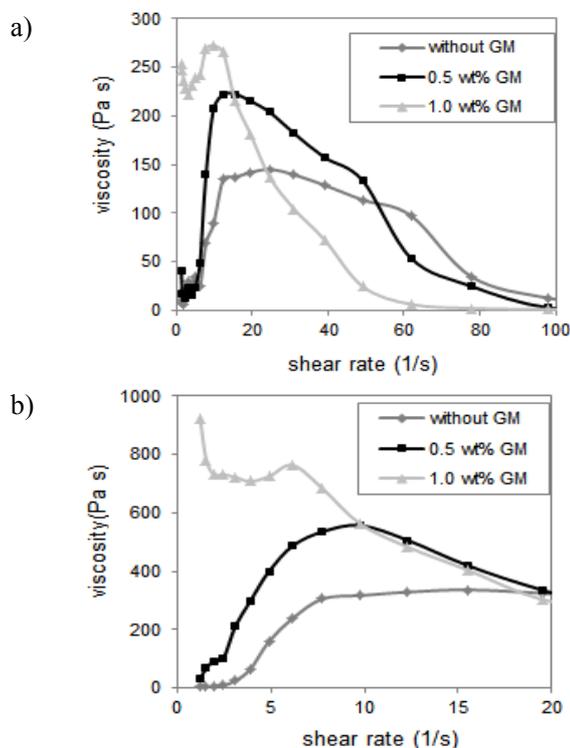


Fig. 4. Influence of glycerol monoacrylate (GM) content on dilatant effect of shear thickening fluid dispersed in poly (propylene glycol) of molecular weight of 400 g/mol containing: a) 12 vol.%, b) 15 vol.% ceramic powder

Rys. 4. Wpływ zawartości procentowej monoakrylanu glicerolu (GM) na właściwości zagęszczania ścinaniem cieczy zdyspergowanych w glikolu polipropylenowym o masie molowej 400 g/mol zawierającej: a) 12% obj., b) 15% obj. fazy stałej

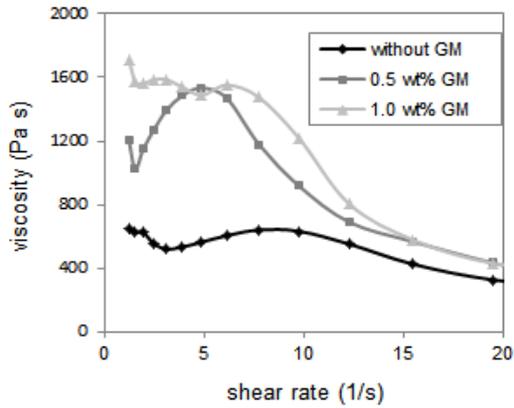


Fig. 5. Influence of glycerol monoacrylate (GM) content on dilatant effect of shear thickening fluid dispersed in poly (propylene glycol) of molecular weight of 725 g/mol containing 15 vol.% ceramic powder

Rys. 5. Wpływ zawartości procentowej monoakrylanu glicerolu (GM) na właściwości zagęszczania ścinaniem cieczy zdyspergowanych w glikolu polipropylenowym o masie molowej 725 g/mol zawierającej 15% obj. fazy stałej

Figure 5 shows the influence of glycerol monoacrylate on the dilatant effect of shear thickening fluid based on fumed silica and poly (propylene glycol) of a molecular weight of 725 g/mol. It was noticed that applying a dispersing agent of a higher molecular weight also had an affect on the relationship between the monomer content and dilatant effect of the suspensions. The critical viscosity of the suspension without glycerol monoacrylate was at shear rate 8 s^{-1} and equaled $642 \text{ Pa}\cdot\text{s}$. The addition of 0.5 wt.% monomer resulted in an increase in critical viscosity to $1490 \text{ Pa}\cdot\text{s}$, however, the dilatant effect at a lower shear rate, equaling 5 s^{-1} , was observed. The highest value of critical viscosity was shown by the slurry containing 1 wt.% glycerol monoacrylate. The critical viscosity of this slurry was at 2 s^{-1} and equaled $1600 \text{ Pa}\cdot\text{s}$. In this case, glycerol monoacrylate also had an affect on the onset of shear thickening by shifting it to lower values of shear rate. The onset of shear thickening for the slurry without glycerol monoacrylate was noticed at 3 s^{-1} . The addition of monomer shifted the onset of shear thickening to 1.5 s^{-1} both for the slurry containing 0.5 and 1.0 wt.% glycerol monoacrylate. The positive effect of glycerol monoacrylate on the critical viscosity of the shear thickening fluids is probably associated with the theory of flocculation. It can be assumed that at a higher shear rate, a three-dimensional network formed by the connection between the fumed silica particles, glycerol monoacrylate and poly (propylene glycol) is created, wherein glycerol monoacrylate plays the role of cross-linking agent which enhances the interaction between the ceramic particles and dispersing agent. This results in an increase in the dilatant effect of the suspension. The phenomenon of change of dispersant conformation or/and nanosilica agglomeration degree which lead to the depletion flocculation phenomenon [11, 12], also should be considered at this point. The solid loading and length of the polymer chain also have an influence

on the connection between the ceramic powder and polymer, which was confirmed by the presented results.

In the next step, the authors focused on the application point of view by investigating the influence of temperature and the quality of the samples after using them a few times. Figure 6 shows the effect of temperature on the dilatant effect of the slurry based on 14 nm fumed silica dispersed in poly (propylene glycol) of a molecular weight of 400 g/mol, containing 0.5 wt.% glycerol monoacrylate. Research at two temperatures was performed: room temperature and the temperature of the human body. The measurements showed that the higher temperature resulted in a significant decrease in the dilatant effect of the investigated slurries. It indicates that temperature is an important factor which should be taken into account if protective clothes based on a shear thickening fluid are to be produced. The critical viscosity of the slurry measured at 25°C was observed at 10 s^{-1} and equaled $562 \text{ Pa}\cdot\text{s}$. Increasing the temperature to 36.6°C resulted in a shift of the maximum viscosity to 25 s^{-1} where the viscosity was $222 \text{ Pa}\cdot\text{s}$.

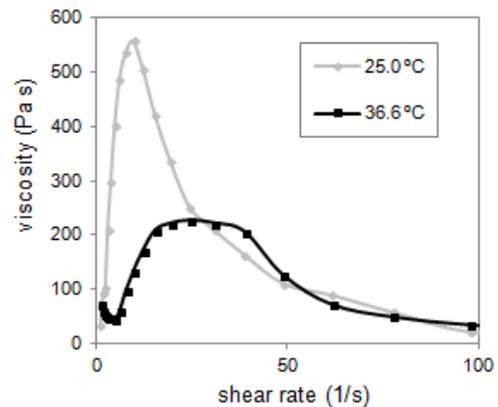


Fig. 6. Effect of temperature on dilatant effect of slurry based on 14 nm fumed silica dispersed in poly (propylene glycol) of molecular weight of 400 g/mol, containing 0.5 wt.% glycerol monoacrylate

Rys. 6. Wpływ temperatury na właściwości zagęszczania ścinaniem cieczy opartej na silica fumed 14 nm zdyspergowanej w glikolu polipropylenowym o masie molowej 400 g/mol z dodatkiem 0.5% wag. monoakrylanu glicerolu

Figure 7 shows the effect of the number of times of use on the dilatant effect of the slurry based on 14 nm fumed silica dispersed in poly (propylene glycol) of a molecular weight of 400 g/mol which contained 0.5 wt.% glycerol monoacrylate. The measurements showed that with increasing times of use, the dilatant effect decreased, however, the onset of shear thickening and critical shear rate to a higher value of shear rate shifted. The critical viscosity of the slurry before use was around $562 \text{ Pa}\cdot\text{s}$ and was observed at 10 s^{-1} . After one time of use, the critical viscosity decreased diametrically to $231 \text{ Pa}\cdot\text{s}$, however, at shear rate 32 s^{-1} . After the second use, the maximum viscosity did not change significantly. Critical viscosity at shear rate 25 s^{-1} was observed and equaled $200 \text{ Pa}\cdot\text{s}$. Widening of the dilatant jump was also noticed. The observed changes in

the dilatant effect can be explained by the shear thickening phenomenon where when an external force is working, there is resistance by the shear thickening fluid. The release of energy that accompanied this phenomenon increased the temperature inside the slurry, which reduces the dilatant effect of the shear thickening fluid.

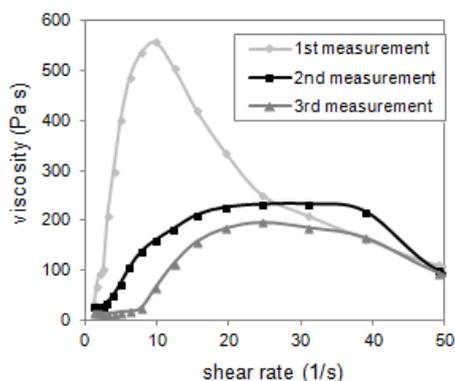


Fig. 6. Influence of times of use on dilatant effect of slurry based on 14 nm fumed silica dispersed in poly (propylene glycol) of molecular weight of 400 g/mol, containing 0.5 wt.% glycerol monoacrylate

Rys. 6. Wpływ ilości pomiarów na właściwości zagęszczania ścinaniem cieczy opartej na fumed silica 14 nm zdyspergowanej w glikolu polipropylenowym o masie molowej 400 g/mol z dodatkiem 0.5% wag. monoakrylanu glicerolu

CONCLUSIONS

In this work, the influence of glycerol monoacrylate content on the shear thickening behaviour and change depending on the solid loading and the kind of dispersing agent was measured. The measurements showed that by adding glycerol monoacrylate to the shear thickening fluid, it is possible to more than double the critical viscosity of the suspension. The concentration of powder and molecular weight of the monomer also play an important role in this process. It was observed that by increasing the solid loading and/or application of a dispersing agent of a higher molecular weight, it was possible to increase the dilatant effect significantly.

In this work the influence of temperature and the quality of the samples after a few times of use also were investigated. It was shown that both temperature and the number of times of use are important factors which should be taken into account when advanced body

armours are to be produced. The measurements showed that an increase in temperature resulted in a diametrical decrease in the dilatant effect of the investigated slurries. A similar conclusion could be provided in the case of times of use where the measurement showed a reduction in the dilatant effect with an increasing quantity of impacts.

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