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COMPOSITES THEORY AND PRACTICE

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SHEAR THICKENING CERAMIC-POLYMER COMPOSITE

Shear thickening fluids (STF), which are included in non-Newtonian fluids, are a good example of innovative ceramic--polymer composites. Their characteristic feature is that the viscosity increases with an increase in shear rate. The energy is dissipated during the impact due to the increasing resistance of STF. This is the reason why STF are so promising for applications protecting the human body. Body armours based on STF, because of their elasticity in comparison to conventional counterparts, proved to be more comfortable. This work is devoted to the development of a new composition of STF with the highest dilatant effect. Based on our research on STF, it was shown that the higher the dilatant effect is, the more energy is absorbed during the impact. In this case, four different systems were prepared in which the main component of the solid phase was submicron silica powders KE-P10 (particle size 100÷200 nm) or KE-P50 (particle size 500÷600 nm). In all the prepared systems, the carrier fluid was poly(propylene glycol) with a molecular weight of 2000 g/mol (PPG 2000). The rheological properties of the systems were determined. The influence of the solid phase concentration, size of the particles and the temperature on the dilatant effect properties were examined. Rheological stability in time was also presented in this paper for certain compositions. The most satisfying results were achieved by the systems with KE-P10 in the amount of 60 volume percent. The dilatant effect at the temperature of 25°C reached 11 243 Pa·s, while the beginning of shear thickening was observed at the shear rate of 0.88 s^{-1}. What is worth mentioning is that the obtained results are repeatable in different time intervals, meaning that the investigated fluid is rheologically stable in time. Despite the drop in the dilatant effect by 70% at higher temperatures, the dilatant effect remained on a high level of 3000 Pa·s. Regarding the obtained results, we can assume that body armour based on the ceramic-polymer composite would be suitable for protection even at higher temperatures.

Keywords: **STF (shear thickening fluids), silica, dilatant effect, poly(propylene glycol), protective materials**

MATERIAŁY KOMPOZYTOWE CERAMIKA-POLIMER ZAGĘSZCZANE ŚCINANIEM

Ciecze zagęszczane ścinaniem (STF), będące przykładem innowacyjnego kompozytu ceramika-polimer, zaliczane są do grupy płynów nienewtonowskich. Charakterystyczną dla STF cechą jest skokowy wzrost wartości lepkości wraz ze wzrostem wartości naprężeń lub sił ścinających. W przypadku uderzenia usztywniają się, dzięki czemu energia uderzenia jest częściowo rozpraszana. Nagły opór stawiany w momencie przyłożenia siły przez tego rodzaju zawiesiny stwarza możliwość ich szerokiego zastosowania przy produkcji systemów przeznaczonych do ochrony ciała człowieka. Pancerze bazujące na STF, ze względu na większą elastyczność (w porównaniu do swych konwencjonalnych odpowiedników), zapewniałyby wyższy komfort użytkowania oraz możliwość ochrony większej powierzchni ciała. W artykule przedstawiono wyniki badań mających na celu opracowanie nowego składu cieczy zagęszczanej ścinaniem, która charakteryzowałaby się możliwie najwyższymi skokami lepkości. Wstępne badania w zakresie otrzymywania cieczy zagęszczanych ścinaniem wskazują, iż układy wykazujące duży efekt dylatancji odznaczają się również wysokim stopniem absorpcji energii towarzyszącej uderzeniu. W oparciu o syntetyczne krzemionki o submikronowej wielkości cząstek: KE-P10 (wielkość ziarna 100÷200 nm) oraz KE-P50 (wielkość ziarna 500÷600 nm), stanowiące główny składnik fazy stałej, przygotowano cztery różne układy wykazujące efekt zagęszczania ścinaniem. We wszystkich omawianych przypadkach jako ciecz dyspergującą zastosowano poli(glikol propylenowy) o masie molowej wynoszącej 2 000 g/mol. Otrzymane ciecze poddano badaniom reologicznym. Zbadano wpływ stężenia fazy stałej, wielkości ziarna krzemionki oraz podwyższonej temperatury na właściwości dylatancyjne przygotowanych zawiesin. W artykule przedstawiono również wyniki badań stabilności parametrów reologicznych w czasie dla wybranych składów. Najlepsze rezultaty uzyskano dla cieczy, której fazę stałą stanowiła krzemionka KE-P10 w ilości 60% objętościowych. W tym przypadku wartość skoku lepkości (mierzona w temperaturze 25°C) wyniosła 11 243 Pa·s, a początek zagęszczania ścinaniem zaobserwowano przy szybkości ścinania równej 0,88 s^{-1}. Warto zaznaczyć, że wynik ten jest powtarzalny w różnych odstępach czasowych, co pozwala stwierdzić, iż opracowana ciecz jest reologicznie stabilna w czasie. W podwyższonej temperaturze - 36,6°C odnotowano spadek efektu zagęszczania ścinaniem o ponad 70%. Mimo to skok lepkości pozostał na bardzo wysokim poziomie - lepkość cieczy wzrosła niemal o 3 000 Pa·s. W związku z tak obiecującymi wynikami badań z dużym prawdopodobieństwem można stwierdzić, iż ochraniacze oparte na omawianym ceramiczno-polimerowym kompozycie należycie spełniałyby funkcje protekcyjne również w podwyższonej temperaturze.

Słowa kluczowe: **ciecze zagęszczane ścinaniem, krzemionka, skok lepkości, glikol polipropylenowy, materiały protekcyjne**

INTRODUCTION

Shear thickening fluid (STF) is a good example of an innovative ceramic-polymer composite which has the ability to suppress and dissipate impact energy. There are colloidal systems consisting of ceramic powder, often SiO_2, dispersed in an organic carrier fluid such as poly(ethylene glycol) or poly(propylene glycol). The typical feature of these liquids is an increase in viscosity with increasing shear stress [1-5]. The mechanism of shear thickening has been widely investigated and as a result of this research a few theories have been developed: Reynolds [2], order - disorder transition (ODT) [6], clustering [7] and particle flocculation [8]. A specific model is appropriate for precise interpretation of the shear thickening fluid depending on its parameters. Despite the differences among shear thickening mechanisms, there is mutual accurateness. Modifications of the internal fluid structure, which are caused by stress, block the possibility of flow, which can be seen as a rapid increase in viscosity. Generally, increases in fluid resistance as a result of an operative force cause problems with flow in technological installations. On the other hand, shear thickening fluids can be widely used in the production of systems for protection of the human body [9-11]. Protection systems based on STF are lighter and more flexible in comparison to their conventional equivalents. In order to ensure a sufficient degree of protection, the usage of a fluid which has an adequately high dilatant effect is needed. In this paper, we report the research on receiving innovative fluids composed of silica poly(propylene glycol), fulfilling such requirements. The influence of the solid phase concentration, silica particle size and temperature on the rheological properties was measured. Moreover, the stability of the rheological parameters in time was also examined.

EXPERIMENTAL PROCEDURE

Materials

Two submicron silica powders: KE-P10 and KE-P50 (*Nippon Shokubai Co.*) to prepare STF were used. The former particle size was 100÷200 nm, density of 1.96 g/cm^3 and surface area of 133.2 m^2/g, whereas the latter particle size was 500-600 nm, density of 1.89 g/cm^3 and surface area 227.4 m^2/g. The KE-P10 and KE-P50 microstructures are presented respectively in SEM images (*Zeiss ULTRA Plus*, Germany) in Figures 1 and 2.

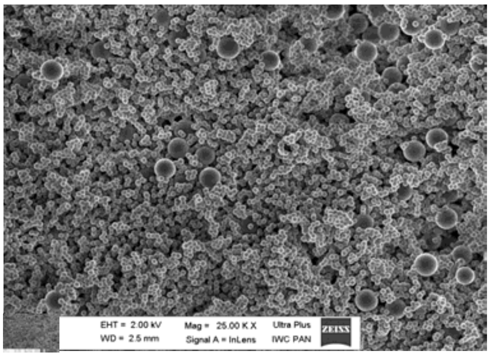

Fig. 1. SEM image of KE-P10 silica microstructure

Rys. 1. Zdjęcie mikrostruktury krzemionki KE-P10 wykonane za pomocą skaningowego mikroskopu elektronowego

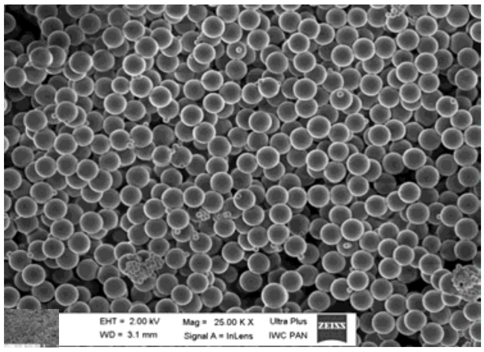

Fig. 2. SEM image of KE-P50 silica microstructure

Rys. 2. Zdjęcie mikrostruktury krzemionki KE-P50 wykonane za pomocą skaningowego mikroskopu elektronowego

Both images prove the spherical shape of the particles, as well as their lack of tendency to agglomeration. The solid phase apart from silica contains a small amount of organic phase. In all the prepared STF, the ratio of organic additive to ceramic powder was constant. The addition of organic dopant did not affect the silica properties or measured relationships, thus its influence was omitted. The carrier fluid was poly(propylene glycol) (*Sigma-Aldrich*) with a molecular weight of 2000 g/mol (PPG 2000).

Methods

The shear thickening fluids were obtained by homogenization of the solid phase and carrier fluid by a mechanical stirrer. The process of combining the substrates was carried out at a stirring rate of 300 rpm until a homogeneous system was created. Depending on the solid phase concentration, the stirring time was between 1.5÷2 hours. The compositions of the prepared fluids along with abbreviations used further in this paper are presented in Table 1.

TABLE 1. **Compositions of prepared shear thickening fluids**

TABELA 1. **Składy przygotowanych cieczy zagęszczanych ścinaniem**

Abbreviation used	Solid phase concentration [vol.%]	Ceramic powder	Carrier fluid
STF 1 (55%)	55	KE-P10	PPG 2000
STF 1 (60%)	60		
STF 2 (55%)	55	KE-P50	
STF 2 (60%)	60		

The rheological properties were measured on a rotational rheometer KinexusPro (Malvern, GB) equipped with two parallel plates, with a gap between them of 0.7 mm. The spin of the upper plate with an increasing speed from 0.1 to 3000 s^{-1} in 60 seconds caused the shear in the sample. Finally, dependency of dynamic viscosity on the shear rate (viscosity curve) was achieved. The measurements were carried out at the temperatures of 25 and 36.6°C.

RESULTS AND DISCUSSION

Figure 3 shows the flow curves of all the prepared systems. The measurements were performed at room temperature. An increase in STF 1 (55%) viscosity of 180 Pa·s can be observed when the shear rate is changed from 5.55 to 43.64 s^{-1}. The increase in solid loading of 5% makes the dilatant effect of STF 1 (60%) tremendously high and it reaches the value of 11243 Pa·s. In addition, the viscosity increase soars in STF 1 (60%), in contrast to STF 1 (55%). Moreover, the critical shear rate of STF 1 (60%) can be noted at a lower value of shear rate than in STF 1 (55%). Similar conclusions could be drawn in the case of STF 2. The system containing more solid particles exhibits a higher dilatant effect, which appears at the lower shear rate value. Furthermore, systems based on KE-P50 have lower dilatant effects than those, which contain KE-P10. S.R Raghavan et al. conducted similar research using 14 nm SiO_2 dispersed in poly(propylene glycol). Solid loading was in the range of 3÷10%$_{w/w}$. According to their results, at the low values of shear rate, an increase in volume fraction of the powders resulted in a more effective dilatant effect [13]. The data of W. Jiang et al., in which a polymethylmethacrylate dispersion in a mixture of glycerine and water (3:1) was investigated, gives a parallel conclusion [14].

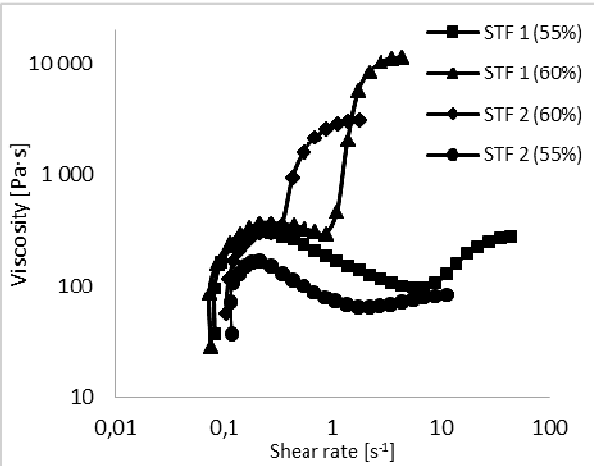

Fig. 3. Viscosity curves of prepared STF

Rys. 3. Krzywe lepkości przygotowanych cieczy zagęszczanych ścinaniem

The influence of temperature on the shear thickening properties was also investigated. In this case, the dilatant effect at 25.0 and 36.6°C was examined for all the prepared systems and is shown in Figure 4. It can be perceived that temperature causes a drop in the dilatant effect in both STF 1 and STF 2. According to the samples, the dilatant effect was reduced from 68 to 74%. It is worth mentioning that STF 1 (60%) is characterized by a high dilatant effect, despite the enhanced temperature. T. Tian et al. determined a comparable temperature effect on shear thickening properties [15].

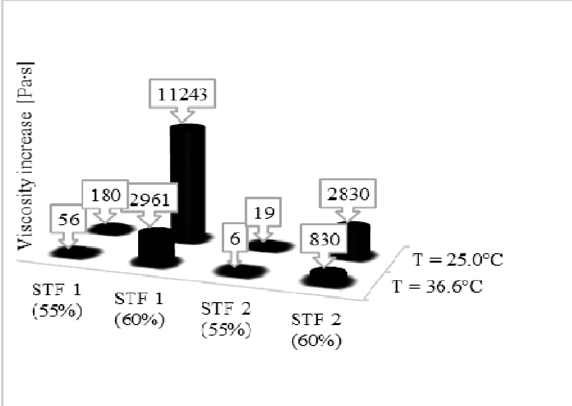

Fig. 4. Influence of temperature on dilatant effect

Rys. 4. Wpływ temperatury na wartość skoku lepkości

Stability of the rheological properties in time is crucial, considering the prospective commerialization aspect of STF usage for protection of the human body. Due to its importance, rheological measurements at the temperature of 36.6°C were carried out for STF 1 (60%) and STF 2 (60%) after different periods of time. The viscosity curves obtained in an experiment on STF 1 (60%) are shown in Figure 5. The dilatant effect in the reference measurement achieved the value of 2961 Pa·s, after 90 days 2769 Pa·s, after 120 days 2723 Pa·s and after 180 days 3226 Pa·s. Although there is a slight difference in the dilatant effect, it can be acknowledged that the sample is stable in time. The dilatant effect oscillates around 3000 Pa·s. What is more, a downward trend was not noticed. The differences in consecutive measurements are the consequence of the performed activities.

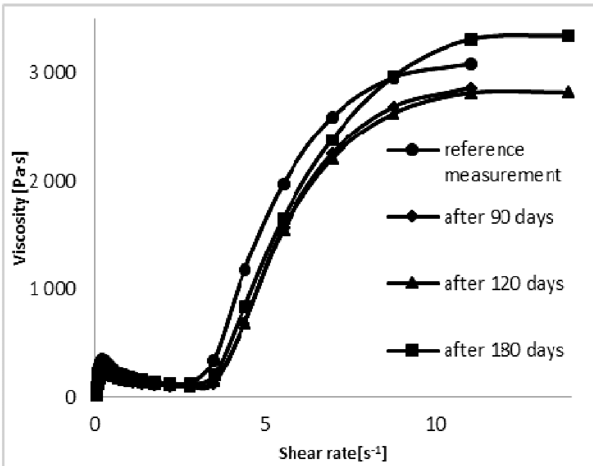

Fig. 5. Rheological stability in time for STF 1 (60%)

Rys. 5. Wpływ czasu na właściwości reologiczne cieczy STF 1 (60%)

The stability of STF 2 (60%) rheological properties in time is shown in Figure 6. The dilatant effect in the reference sample was 830 Pa·s, after 30 days the dilatant effect changed to 643 Pa·s and after 120 days it was 727 Pa·s. It can be supposed that the sample is stable in time despite the fact that there is a small difference in the values. The dilatant effect is around 700÷800 Pa·s. Although there were differences in consecutive measurements, a downward trend was not noticed. It might have been caused by the performed activities.

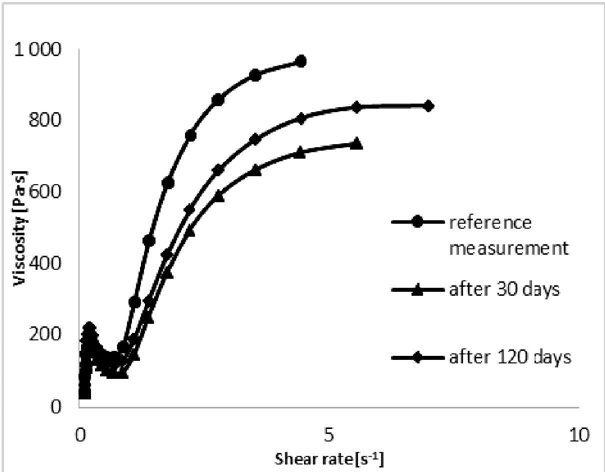

Fig. 6. Rheological stability in time for STF 2 (60%)

Rys. 6. Wpływ czasu na właściwości reologiczne cieczy STF 2 (60%)

CONCLUSIONS

Taking all the results of the studies provided into account, the influence of silica particle size, solid phase volume concentration, as well as higher temperature on the rheological properties of shear thickening liquids can be observed.

Systems containing silica KE-P10, in which the particle size was smaller than those with KE-P50, show a higher dilatant effect than the latter ones. This dependence was observed when the solid phase concentration was the same in both cases (systems). Moreover, in both cases it was proved that with the increase in solid phase, the dilatant effect increases. As was previously verified in other papers [12], increasing the temperature causes a drop in the dilatant effect. It was found that an increase in temperature from 25.0 to 36.0°C results in a decrease in the dilatant effect on an average level of 70%.

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