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COMPOSITES THEORY AND PRACTICE

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APPLICATION OF HALLOYSITE IN FABRICATION OF COMPOSITE MATERIALS FOR ENERGY ABSORPTION

This work is devoted to the development of the composition as well as analysis of the rheological properties of shear thickening fluids (STF) based on pure halloysite (mineral from aluminosilicates group; H) and silica (SF14) doped halloysite dispersed in various organic liquids. The objective of this study was to form an intelligent composite using aluminosilicate tubes to dissipate energy and verify the applicability of the final suspensions to produce liquid armor. Halloysite is considered cheaper and more environmental friendly than pure SiO_2 for STF production. Herein, we present studies concerning the effects of the molecular weight of poly(propylene glycol) (PPG) and modified aluminosilicate by mixing in ethanol with a carrier fluid. We also report that the fabrication of STF with silica doped halloysite leads to novel organic/inorganic composite materials with unprecedented protection properties. By analyzing the results obtained from the study, it was concluded that the liquids with modified halloysite as a dopant of 1, 3, 5 and 10 vol.% solid phase had a higher viscosity than the reference liquid based only on nanosilica. The fluid with the most favorable rheological properties is the slurry based on nanosilica with 1 vol.% halloysite (previously mixed with EtOH and PPG 725) dispersed in a poly(propylene glycol) of 725 g/mol molecular weight. The maximum shear thickening value of this liquid equaled 557 Pa·s at a shear rate of 7.8 s^{-1}. In the final step of the research, a knife penetration resistance test was performed. It was observed that the protective properties of p-aramid fabrics interleaved with STF based on pure SF14 powder and doped with halloysite are comparable. Thus, synthetic nanosilica can be partially replaced.

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

ZASTOSOWANIE HALOIZYTU W OTRZYMYWANIU MATERIAŁÓW KOMPOZYTOWYCH DO ABSORPCJI ENERGII

W artykule przedstawiono wyniki badań nad opracowaniem składu cieczy zagęszczanych ścinaniem na bazie haloizytu (minerału z grupy glinokrzemianów; H) i krzemionki (SF14) domieszkowanej haloizytem zdyspergowanych w wybranych cieczach organicznych oraz ich charakterystykę reologiczną. Głównym celem badań było otrzymanie inteligentnego kompozytu, który wykorzystywałby częściowo rurkowy kształt cząstki haloizytu do rozpraszania energii, oraz sprawdzenie możliwości wdrożenia uzyskanych zawiesin do produkcji materiałów absorbujących energię, np. ciekłych pancerzy. Powszechnie jako fazę stałą stosuje się syntetyczną i drogą krzemionkę. Z uwagi na aspekt ekonomiczny i ekologiczny autorzy dokonali próby zastąpienia SiO_2 naturalnym glinokrzemianem, którego zasoby w Polsce oceniane są na około 10÷12 mln ton. W pracy przedstawiono wpływ masy molowej glikolu polipropylenowego (PPG) stosowanego jako dyspergent oraz modyfikacji powierzchni ziaren fazy stałej poprzez mieszanie z etanolem i PPG na właściwości reologiczne zawiesin. Artykuł zawiera również wyniki badań nad otrzymaniem cieczy zagęszczanych ścinaniem na bazie nanokrzemionki z udziałem haloizytu jako domieszki do opracowania materiału kompozytowego do ochrony ciała człowieka. Analizując otrzymane rezultaty, stwierdzono, iż ciecze z dodatkiem 1, 3, 5 i 10% obj. modyfikowanego haloizytu charakteryzowały się wyższymi lepkościami niż próbka referencyjna oparta tylko na SiO_2. Najlepsze właściwości reologiczne wykazuje zawiesina z dodatkiem 1%obj. glinokrzemianu (wcześniej poddanego procesowi modyfikacji powierzchni) zdyspergowanego w glikolu polipropylenowym o masie molowej 725 g/mol (PPG 725). Maksimum zagęszczania ścinaniem tej zawiesiny wynosiło 557 Pa·s przy szybkości ścinania 7,8 s^{-1}. W ostatniej fazie badań przeprowadzono testy odporności na uderzenia ostrzem. Zaobserwowano, iż materiały kompozytowe na bazie mat z włókien p-aramidowych przekładanych cieczami zagęszczanymi ścinaniem zarówno z SF14, jak i krzemionką z dodatkiem glinokrzemianu zapewniają porównywalne funkcje protekcyjne. Wykazano zatem, że syntetyczna nanokrzemionka może być częściowo zastąpiona haloizytem.

Słowa kluczowe: **ciecze zagęszczane ścinaniem, lepkość, haloizyt, nanokrzemionka, glikol polipropylenowy, absorpcja energii, kompozyty ceramiczno-polimerowe**

INTRODUCTION

Conventional body armors consist of approximately 20÷40 layers of neat Kevlar (para-aramid synthetic fiber developed by Stephanie Kwolek at DuPont in 1965) recurrently enhanced by rigid ceramic inserts for high threat situations [1-3]. This approach leads to high weight of the armor and reduces the mobility of the user. Moreover, it provides torso protection only.

Herein, we present a concept based on the innovation of capturing the benefits of non-Newtonian shear thickening fluid (STF) in a fabricated material. This idea is a superior shock-absorbing solution. The mechanism of shear thickening can be interpreted by many theories such as order-disorder transition (R.L. Hoffman) [4], hydrodynamic clustering (J. Bender, N.J. Wagner) [5] and particle flocculation (M. Kamibayashi, H. Ogura, Y. Otsubo) [6, 7]. Generally, with a growing shear rate, internal friction forces arise and consequently increasing viscosity are observed. Additionally, viscosity increases faster than linearly with shear rate. In the preparation of STF, a silica powder is commonly used as a solid phase. This material, when combined with polypropylene glycols as the dispersion medium, provides adequate rheological parameters. Assuming the theory of particle flocculation polymer chains adsorb onto the surface of SiO_2 particles. Polymeric bridges are made between the ceramic particles in which the stress suddenly jumps with an increasing shear rate and it appears to take on a solid-like behavior [8]. Regarding these mechanisms, the authors came up with a theory that halloysite and silica can coexist in the compounded system of shear thickening fluids. It is feasible to obtain STF based on halloysite due to its structure. Presumably, liquid flow resistance increases dramatically when the dispersant streams into the aluminosilicate tubes. Moreover, the clay is mined directly from the environment and it is a competitive material to an expensive and synthetic silica. However, because of its natural occurrence it is not uniform in shape. In this paper, we report research on the application of halloysite, pure and as a dopant, in the fabrication of composite materials for energy absorption. Here, the rheological properties of slurries and the stab resistance of STF-fiber composites are reported.

EXPERIMENTAL PROCEDURE

Materials

Silica fumed powder SF14 (*Sigma-Aldrich*) with an average particle size of 14 nm, density of 1.53 g/cm^3 and a specific surface area of 200 m^2/g was used. The halloysite doping powder H (*Intermark*) is characterized by an average particle size of 300 nm, density of 2.81 g/cm^3 and a specific BET-surface area of 69.18 m^2/g. The SEM images (*Zeiss ULTRA Plus*, Germany) in Figures 1 and 2 demonstrate the microstructure of the used solid materials. It can be observed that the spherical silica particles agglomerate and form a highly branched structure. The agglomerates reach a size of about 300÷400 nm. Table 1 gives the specific characteristics of SF 14. The second image is evidence that halloysite was not monodispersed. Apart from the tubes, angular plates were observed. Although the particles have different shapes, the focus of this study is to evaluate the ability of aluminosilicate clay particles in bulk to enhance the performance of shear thickening properties of undoped silica powder. All the carrier fluids were purchased from *Sigma-Aldrich*, including poly(propylene glycol) of molecular weights of 400, 425, 725 and 1000 g/mol denoted as PPG400, PPG425, PPG725 and PPG 1000, respectively. Table 2 presents the physicochemical properties of the carriers.

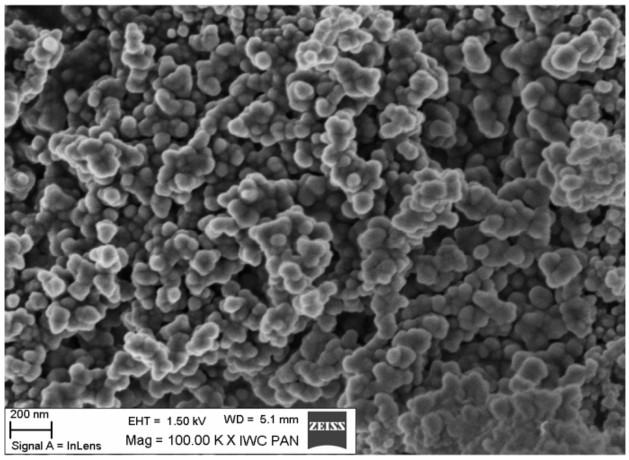


Fig. 1. Nanosilica microstructure

Rys. 1. Mikrostruktura nanokrzemionki

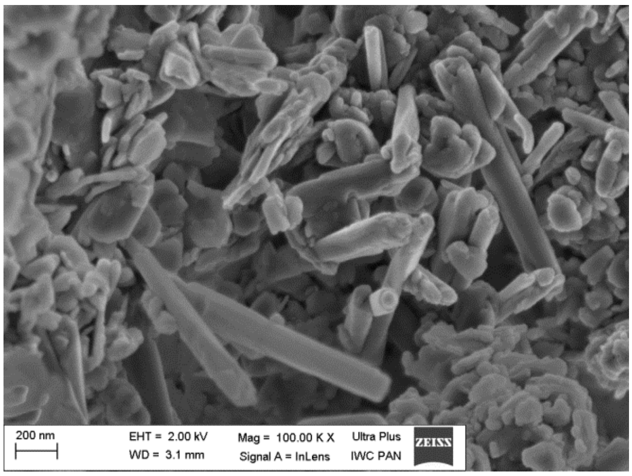


Fig. 2. Halloysite microstructure

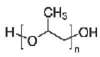
Rys. 2. Mikrostruktura haloizytu

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

TABELA 1. **Właściwości fizykochemiczne stosowanych proszków**

Powder	Average particle size [nm]	Specific surface area [m^2/g]	Density [g/cm^3]	Chemical formula	Producer
nanosilica	14	200 ±25	1.53	SiO_2	*Sigma-Aldrich*
halloysite	300	69.18	2.81	$Al_4[Si_4O_{10}](OH)_8 \cdot 10H_2O$	*Intermark*

TABLE 2. **Physicochemical properties of used carrier fluids**
TABELA 2. **Właściwości fizykochemiczne stosowanych dyspergentów**

Carrier liquids	Molecular weight	Density [g/cm^3]	Chemical formula	Producer
poly(propylene glycol) (PPG)	400	1.130		*Sigma-Aldrich*
	425	1.004		
	725	1.007		
	1000	1.003		

Methods

Our method is very simple in principle but greatly effective in achieving stable suspensions. The non-Newtonian fluids were synthesized by mixing the dry powders: silica and halloysite separately or together with an organic dispersant using a mechanical stirrer. The full fabrication conception is the subject of patent application No P-404327. After 3 hours, the resulting suspensions were subjected to viscosity measurements. The rheological properties were recorded on a rotational rheometer KinexusPro (Malvern, GB) equipped with two parallel plates, with a gap between them of 0.7 mm. The shear rate increased from 1 to 500 s^{-1}. Selected fluids were applied in the construction of liquid armor structures. The fabric used in the energy absorption tests was woven p-aramid. Squared target specimens of dimensions 100 x 100 mm were prepared. An individual test sample consisted of 30 neat layers of fiber mats. 55 g of STF enclosed in a polyethylene bag was inserted between the 28th and 29th layer of the textile. According to The Home Office Scientific Development Branch (HOSDB) standards, energy dissipation studies were performed on a knife penetration resistance test carried out with the blade shown in Figure 3. The total weight of the falling carriage was 1.9 kg, and the falling height was 126 cm with an impact energy of 24 J. All the samples were put on a form filled with ballistic plasticine which imitated the human body. All the measurements were taken at 25°C.

Fig. 3. Blade used in knife penetration resistance test

Rys. 3. Ostrze wykorzystywane w testach uderzeniowych

RESULTS AND DISCUSSION

The aim of the first step of the studies was to verify the rheological properties of the samples based on halloysite dispersed in each of the polypropylene glycols. The suspensions consisted of a 30 vol.% solid phase. The viscosity curves of the STF are depicted in Figure 4. It can be seen that systems with the PPG 400, PPG 425 and PPG 1000 showed the typical characteristic of shear thinning phenomena. Analysis of the data indicated that in the short-range shear rate, the viscosity of the sample with PPG 725 increased. Therefore, PPG 725 and halloysite as a dopant were selected for further studies.

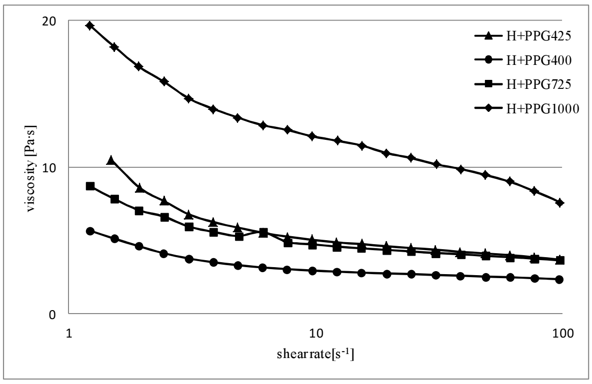


Fig. 4. Viscosity curves of STF based on halloysite and PPG

Rys. 4. Krzywe lepkości STF oparte na haloizycie i PPG

It is well known that the rheological properties of ceramic slurries based on silica allow one to fabricate the most favorable shear thickening fluids. Thus, we prepared suspensions with SF14 accompanied by halloysite. Firstly, a reference sample which consisted only of SiO_2 (12 vol.%) and PPG 725 was examined.

Figure 5 reveals the indisputable dilatant properties in this case. The onset viscosity value was 6 Pa·s observed at 6.1 s^{-1} and the highest viscosity value was 305 Pa·s obtained at 12.3 s^{-1}. After reaching the maximum viscosity, a slip between the plates of the measuring system occurs. The shear rate in this case is not a linear gradient, which is required for viscosity measurement. For this reason, the further course of the viscosity curve is always marked by a dashed line.

For the second set of the experiments silica fumed was mixed with pristine halloysite and PPG 725. The fluids consisted of 12 vol.% solid loading and the volume percent ratio of SF to the aluminosilicate clay was 99:1; 97:3; 95:5 and 90:10, respectively. The outcome of this work suggests that the change in volume fraction of halloysite effects the dilatant properties. As was shown in Figure 6, the most positive shear thickening properties were reached by the composition with the 3 and 1 vol.% halloysite addition. The maximum viscosity elevated to 17 and 5% in comparison to the reference sample but it was obtained at lower critical shear rate values. The higher concentration of halloysite decreased the viscosity.

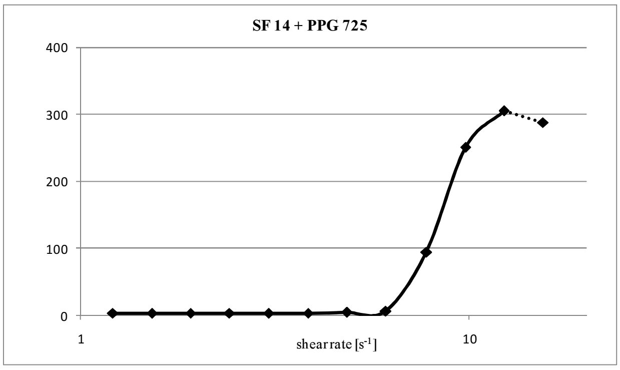


Fig. 5. Viscosity curve of reference sample based on SF14 and PPG 725

Rys. 5. Krzywa lepkości próbki referencyjnej opartej na SF14 i PPG 725

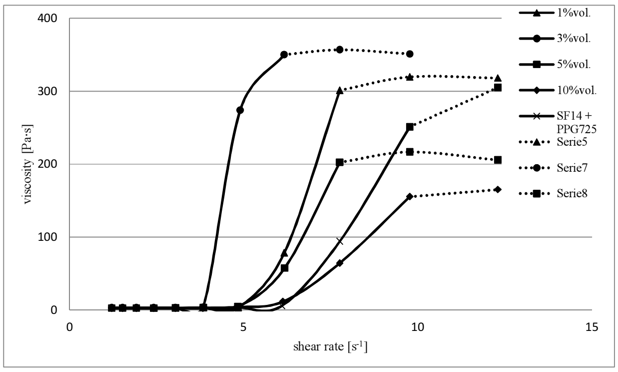


Fig. 6. Viscosity curves of STF based on SF14 doped halloysite dispersed in PPG 725

Rys. 6. Krzywe lepkości STF oparte na SF14 domieszkowanym haloizytem zdyspergowanym w PPG 725

The rheological properties of the fluids based on modified halloysite is of interest here. When the material is in contact with air and humidity, shear thickening tends to disappear as a consequence [9]. The powder was used after being mixed with ethanol and PPG 725 at the mass ratio of 3:4:2 in a ball mill PM100 (*Retsch*, Germany), dried and sieved. The operation was performed to eliminate water adsorbed on the surface of the particles. The mixtures were concentrated to 12 vol.% solids at the multiple volume ratio of silica to dopant again as 99:1; 97:3; 95:5 and 90:10. The results (Fig. 7) clearly indicate a positive amend in the shear thickening features. Here, all the curves showed higher viscosity values for the STF doped halloysite. Significant increases of 83, 44, 17, 13%, respectively were found. The fluid with 1 vol% aluminosilicate clay particles (557 Pa·s at a shear rate 7.8 s^{-1}) in bulk was selected for the knife penetration resistance test.

Three types of templates were examined: neat mat layers, layers inserted with STF based only on SF and on silica doped halloysite. The preparation of the tested samples was described in the *Experimental procedure* section. Table 3 reports the sample specifications and of deformation values averaged from three measurements. The sequence of photographs in Figure 8 present the deformations in ballistic plasticine. Reflecting upon the results, STF/p-aramid composite materials exhibit greater protection features during impact than the other samples. It was found that the STF/p-aramid systems noted a smaller deformation depth and greater deformation length through the shortest and longest path. Thus, a larger amount of energy is dissipated by the inserted textile. The structure with STF doped the halloysite reached a higher deformation length through the shortest path and a slightly shorter deformation length through the longest path. Hence, the addition of the powder does not reduce the protective properties of STF based on undoped silica.

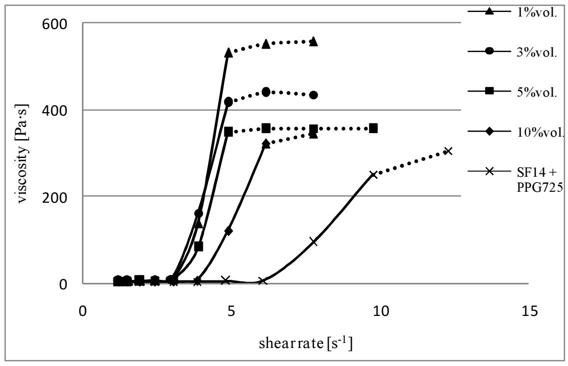


Fig. 7. Viscosity curves of STF based on SF14 doped by modified halloysite dispersed in PPG 725

Rys. 7. Krzywe lepkości STF oparte na SF14 domieszkowanym modyfikowanym haloizytem zdyspergowanym w PPG 725

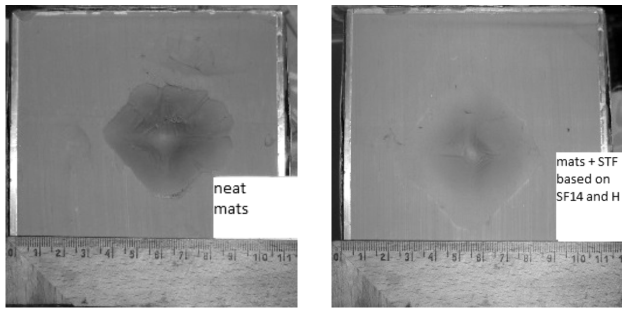


Fig. 8. Photographs of deformations in ballistic plasticine

Rys. 8. Zdjęcia przedstawiające deformacje plasteliny balistycznej

TABLE 3. **Sample specifications and deformation values**

TABELA 3. **Charakterystyka badanych próbek i wielkości deformacji**

Sample specification	Neat ballistic plasticine	30 SS mats	STF based on SF14 + 30mats	STF based on SF14 and H + 30mats
weight [g]	-	83	142	141
thickness [mm]	-	8.5	8.9	9.6
deformation depth [mm]	22	22	14	13
deformation length through shortest path [mm]	40	55	62	67
deformation length through longest path [mm]	40	45	51	49

CONCLUSIONS

We demonstrated an experimental proof-of-principle verification of our concept in the application of halloysite in the fabrication of composite materials for energy absorption. The results showed that PPG 400, 425, 725 failed to fulfill the shear thickening fluid properties in samples with 30 vol.% pristine halloysite. Only the viscosity of the sample dispersed in PPG 725 increased with the shear rate. The study discovered that the powder used after being milled with ethanol and PPG 725 improved the shear thickening properties. The fluid with 1 vol.% modified aluminosilicate clay particles in bulk acquired the highest viscosity in comparison to the STF without the dopant (increase of 83%). To fully prove the success of our method to substitute a portion of silica by halloysite in the fabrication of liquid armor, a penetration resistance test was performed. The results indicated that the addition of the powder does not reduce the protective properties.

Acknowledgements

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