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COMPOSITES THEORY AND PRACTICE

Łukasz Wierzbicki[1]*, Anna Danelska[2], Karolina Olszewska[3], Mariusz Tryznowski[2], Dorota Zielińska[3]
Iwona Kucińska[3], Mikołaj Szafran[2], Marcin Leonowicz[1]

[1] Warsaw University of Technology, Faculty of Materials Science and Engineering, ul. Wołoska 141, 02-507 Warsaw, Poland
[2] Warsaw University of Technology, Faculty of Chemistry, ul. Noakowskiego 3, 00-664 Warsaw, Poland
[3] Institute of Security Technologies MORATEX, ul. M. Skłodowskiej-Curie 3, 90-965 Łódź, Poland
**Corresponding author. E-mail: lwierzbicki@inmat.pw.edu.pl*

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SHEAR THICKENING FLUIDS BASED ON NANOSIZED SILICA SUSPENSIONS FOR ADVANCED BODY ARMOUR

Composite structures built of para-aramid fabric and shear thickening fluid (STF) are developed in the light of their potential application in smart body armour. The study reports on the rheological behaviour of nanosized silica suspensions. Depending on the oligomer chemical structure and molecular weight, we observe different behaviour under shear stress. The STF composed of PPG400 and containing various volume fraction of FS showed good time stability. The compositions containing 6.5 and 11.7 vol. % of silica maintain their rheological properties, although the composition with the highest concentration of solid phase lost about 20% of its maximum viscosity value after 40 days in a closed vial. The addition of colloidal shear thickening fluids to para-aramid woven fabric (Twaron® CT709) showed enhanced ballistic penetration resistance of the elaborated system for Parabellum 9mm bullet.

Keywords: shear, thickening, fluid, armour, rheology, para-aramid composites

CIECZ ZAGĘSZCZANA ŚCINANIEM NA BAZIE NANOKRZEMIONKI W ZASTOSOWANIU NA INTELIGENTNE PANCERZE PASYWNE

Struktury kompozytowe na bazie tkanin paraaramidowych oraz cieczy zagęszczanych ścinaniem są opracowywane z myślą o zastosowaniu ich przy budowie inteligentnych pancerzy pasywnych. Przedstawione badania pokazują, jak zmieniają się właściwości reologiczne zawiesin koloidalnych na bazie nanokrzemionki w zależności od chemicznej struktury oligomeru, jego masy cząsteczkowej oraz stężenia fazy stałej. Dla cieczy zagęszczanych ścinaniem o różnych stężeniach nanokrzemionki przedstawiono wyniki testu stabilności właściwości reologicznych po 40 dniach od wytworzenia. Kompozycje o stężeniu 6,5 i 11,7% objętościowych fazy stałej wykazują stałe właściwości reologiczne w badanym czasie. Krzywa lepkości dla cieczy dylatancyjnej zawierającej 17,7% objętościowych fazy stałej posiada ten sam charakter w dniu wytworzenia oraz po 40 dniach, jednak maksymalna wartość lepkości uzyskana dla cieczy po 40 dniach jest mniejsza o około 20%. Kompozyty wytworzone na bazie cieczy koloidalnej o właściwościach dylatancyjnych oraz tkanin paraaramidowych (Twaron® CT709) wykazują zwiększoną wytrzymałość balistyczną w stosunku do czystej tkaniny paraaramidowej dla pocisku Parabellum 9 mm.

Słowa kluczowe: ciecz zagęszczana ścinaniem, ciecz dylatancyjna, pancerz, reologia, kompozyty paraaramidowe

INTRODUCTION

Over the centuries, safety has been one of the most desirable human feelings. People have always tried to cover their bodies with a uniform to protect themselves against various types of injuries during unsafe situations [1, 2]. Nowadays, these kinds of uniforms are called body armours, and usually they are made of high-strength ballistic fabrics. Recently, one of the most-widely discussed ways of enhancing the ballistic resistance of textile armours is their impregnation with a shear thickening fluid (STF) [3]. STF is a rheologically stable non-Newtonian fluid, the viscosity of which increases with a growing shear rate [4]. The shear thickening phenomenon can be explained by a few theories such as clustering theory [5], Order - Disorder Transition (ODT) [6] and flocculation theory [7]. The shear thickening behaviour of fluids has drawn substantial scientific attention due to its potential applications in liquid armour [8, 9]. Statistics state thaton a battle field, 16% of fatal and 70% of minor wounds result from injuries in the neck and extremities. The application of STF enables the fabrication of flexible body armour, including sleeves and collars. STF turns into a solid body under the impact of a knife, spike or bullet, protecting in this way those parts of the body.

In this study, various shear thickening fluids were synthesized. The dependence of their viscosity on the shear rate and time stability were measured and discussed. Ballistic penetration tests of paraaramid woven fabric impregnated with STF were performed.

EXPERIMENTAL PROCEDURE

Materials

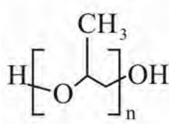
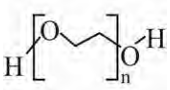
14 nm fumed silica (FS) was utilized for the investigations. The characteristic properties of the silica used in this experiment are shown in Table 1.

TABLE 1. **Characteristic properties of fumed silica used in this study**
TABELA 1. **Właściwości krzemionki użytej w trakcie badań**

Manufacturer	Average grain size [nm]	Specific surface BET [m^2g^{-1}]	Material form
Sigma Aldrich®	14	200 ±25	Powder

The powder was dispersed in different concentrations in various organic media such as poly(propylene) glycol with different average molecular weights 400, 425, 725 (PPG400, PPG425, PPG725) and poly(ethylene)oxide with a molecular weight of 300 (PEO 300). The formulas and features of the inorganic media used in these studies are collected in Table 2.

TABLE 2. **Characteristics of dispersing media**
TABELA 2. **Właściwości fazy ciągłej użytej w trakcie badań**

Organic liquid	Manufacturer	Density [gcm^{-3}]	Structure
Poly(propylene) glycol Mn~400	Sigma Aldrich®	1.001	
Poly(propylene) glycol Mn~425	Sigma Aldrich®	1.004	
Poly(propylene) glycol Mn~725	Sigma Aldrich®	1.007	
Poly(ethylene) oxide Mn~300	Merck®	1.13	

For fabrication of the impregnates with the rheological fluid, the woven fabric Twaron® CT 709 (surface mass of 200 ± 5 gm^{-2}, Teijin) was used.

Method

Fumed silica was mixed in appropriate concentrations with the dispersing media. Rheological studies were performed using an ARES rheometer, equipped with two parallel plates, with a gap between them of 0.3 mm. All the viscosity measurements were taken at 25°C.

The impregnation method of the fabric with the STF consisted of the following stages:

- the textile was cut into square pieces of 100 x 100 mm single layers of the fabric were either covered with the STF using a coater or single layers were immersed in the STF and its excess was removed,
- the samples were sealed in pouches made of a polyethylene foil.

The composite structures with the STF for ballistic tests were in two forms:

1. A various number of fabric layers impregnated with the STF were closed inside a pouch made of a polyethylene foil.
2. Layers of the fabric were separated by pouches filled with 50 g of rheological fluid.

The ballistic tests were performed according to procedure No. PBB-01:1996 ”Ballistic Test”. The fabrication method of the composite ballistic structures is the subject of a patent application.

RESULTS AND DISCUSSION

The dependence of the viscosity on the shear rate for the suspensions composed with different concentrations of fumed silica dispersed in poly(propylene)glycol, with an average molecular weight of 400 are shown in Figure 1. One can clearly see that the increasing volume fraction of the solid phase results in a greater dilatancy effect. We can obtain higher viscosity values at lower shear rates.

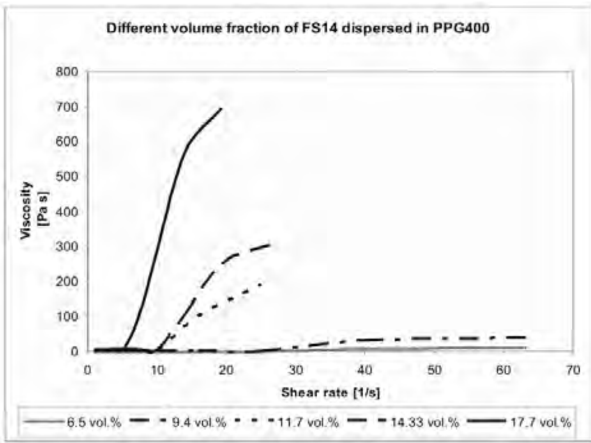


Fig. 1. Viscosity vs. shear rate for various volume fractions of fumed silica 14 nm, dispersed in poly(propylene) glycol (Mn = 400)

Rys. 1. Wykres przedstawiający zależność lepkości od szybkości ścinania dla cieczy o różnych stężeniach krzemionki o średniej wielkości cząstek 14 nm, zdyspergowanych w glikolu polipropylenowym 400

The rheological behaviour of fumed silica dispersed in the poly(propylene) glycol differing in average molecular weight is shown in Figure 2. The higher molecular weight of the oligomer provides higher viscosity values, but obtained at lower shear rates.

The dependencies shown in Figures 1 and 2 indicate that the change of volume fraction of the FS and molecular weight of the oligomer enables tailoring of the STF properties. This information is especially significant for application of the STF in smart body armour, because such behaviour enables flexibility of the armour during movement and provides appropriate stiffness in the case of projectile impact or blade attack. The most appropriate would be the combination of very high values of viscosity with high values of shear rates.

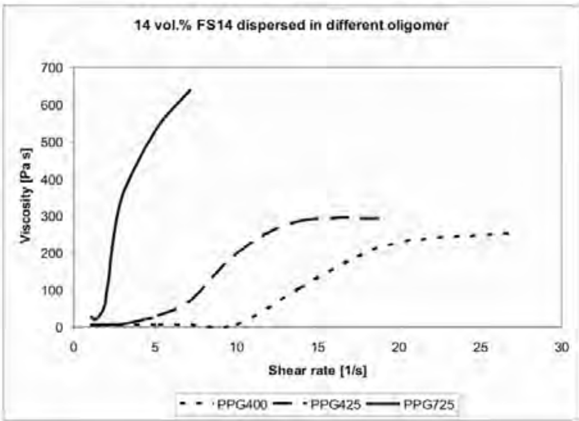


Fig. 2. Viscosity versus shear rate for 14% vol. fumed silica 14 nm, dispersed in poly(propylene)glycol having different molecular weight

Rys. 2. Wykres przedstawiający zależność lepkości od szybkości ścinania dla cieczy o 14% obj. stężeniu krzemionki o średniej wielkość cząstek 14 nm, zdyspergowanej w glikolach propylenowych o różnych masach cząsteczkowych

Another important issue is the time stability of the STF. Advanced liquid armour must maintain its protective properties for a long time, which depends on the durability of all the used components.

Therefore time stability tests were performed. All the fluids studied were kept for 40 days in a closed vial at room temperature. After this time the STFs were still homogeneous and exhibited shear thickening properties, however, the composition containing the highest concentration of solid phase lost about 20% of its viscosity value. Investigations of stability for a longer time are in progress.

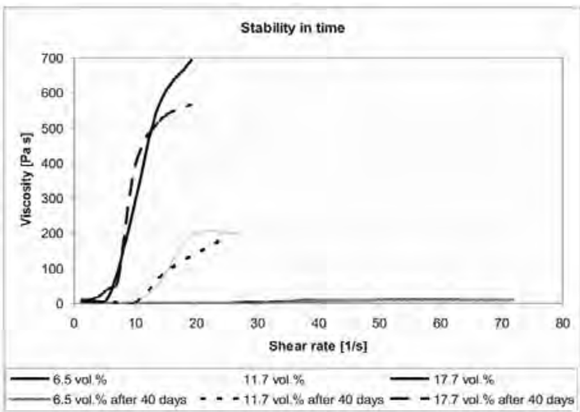


Fig. 3. Viscosity versus shear rate for different volume fraction of fumed silica 14 nm, dispersed in poly(propylene) glycol (Mn = 400) after 40 days

Rys. 3. Wykres przedstawiający zależność lepkości od szybkości ścinania dla cieczy składających się z różnych stężeń krzemionki o średniej wielkości cząstek 14 nm, zdyspergowanych w glikolu polipropylenowym 400, sporządzony w dniu wytworzenia cieczy oraz po 40 dniach

The best shear thickening properties are shown by the composition presented in Figure 4. The fluid which was made of a 24.5% volume fraction of fumed silica 14 nm, dispersed in poly(ethylene) oxide 300, has a critical shear rate value of about 30 s^{-1}. The highest viscosity value is 900 Pa s obtained at a 70 s^{-1} shear rate. This fluid was used in the ballistic penetration test. The results of this test are shown in Table 3.

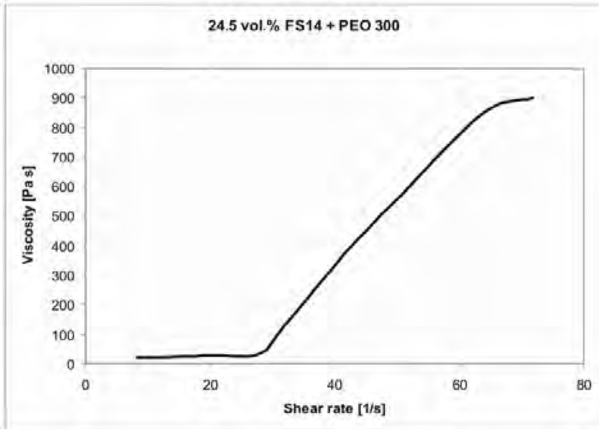


Fig. 4. Viscosity versus shear rate for shear thickening fluid made of 24.5 vol.% fumed silica, 14 nm, dispersed in poli(ethylene)oxide (Mn = 300)

Rys. 4. Wykres przedstawiający zależność lepkości od szybkości ścinania dla cieczy składającej się z 24.5% obj. krzemionki o średniej wielkości cząstek 14 nm, zdyspergowanej w glikolu polietylenowym 300

TABLE 3. **Results of ballistic penetration test**
TABELA 3. **Wyniki testów balistycznych**

Construction Twaron®CT709+STF 100 mm x 100 mm	**Mass [gm^{-2}]**	**Mass of used liquid [g]**	**Deformation depth [mm]**	**Penetration Yes/No**
16 clean layers	2810	-	22	No
16 layers impregnated with STF	3900	10	24	No
10 clean layers STF in PE bag 6 clean layers	7800	50	16	No
4 layers impregnated with STF	7800	71	28	Yes

Various types of ballistic structures were made. Initially, 16 clean layers of the para-aramid woven fabrics Twaron® CT 709, were shoot with a 9 mm gun. There was no penetration of the layers, although the deformation depth was 22 mm.

The same structure, impregnated with 10 g of the STF, appeared to be bullet-proof as well, but the deformation depth was 24 mm. However, using 50 g of the STF closed in a polyethylene bag slightly enhanced the ballistic penetration resistance. The deformation depth was about 30% lower for the same number of Twaron® layers used.

The 4 layers of para-aramid woven fabrics impregnated with 71 g of the STF were penetrated by the gun projectile. It is possible, that the shear thickening properties are weakened when the Twaron® layers are impregnated with the fluid, instead of applying it in polyethylene bags. When the fluid is placed in the PE bags, the fumed silica, dispersed in the oligomer is able to form chains which are responsible for increasing the viscosity. The impregnated fabrics could hinder the shear thickening properties of the fluid used for impregnation.

The best performance was shown by the structure composed of 16 layers of the fabric separated by a polyethylene bag filled with 50 g of the STF. The specimen was not penetrated and the deformation depth was reduced to 16 mm.

CONCLUSIONS

The studies revealed that the fumed silica, dispersed in polypropylene glycol, or polyethylene oxide, demonstrates shear thickening properties. The material composed of the FS and PEO300 possessed the best combination of properties (high viscosity obtained at high shear rate). The change of volume fraction of the FS and variation of the molecular weight of the oligomer enables tailoring of the STF properties.

The STF composed of PPG400 and FS showed good time stability.

The preliminary variants of flexible body armor systems containing STF were designed. The results of the ballistic tests show that application of the STF closed in a polyethylene bag and placed among a series of fabric layers, results in a reduction of the deformation depth by about 30%.

Acknowledgement

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