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COMPOSITES THEORY AND PRACTICE

Paulina Nakonieczna[1]*, Łukasz Wierzbicki[1], Beata Śladowska[1], Marcin Leonowicz[1], Janusz Lisiecki[2] Dominik Nowakowski[2]

[1]Faculty of Materials Science and Engineering, Warsaw University of Technology, ul. Wołoska 141, 02-507, Warsaw, Poland
[2]Air Force Institute of Technology, ul. ks. Bolesława 6, 01-494 Warsaw, Poland
**Corresponding author. E-mail: Paulina.Nakonieczna@wimpw.edu.pl*

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COMPOSITES WITH IMPACT ABSORPTION ABILITY BASED ON SHEAR THICKENING FLUIDS AND AUXETIC FOAMS

The issue of energy absorption during impact is present in various aspects of life. The possibility of dissipating unwanted energy gives huge opportunities for a variety applications such as helmets, car bumpers, smart body armours and protective pads. Nevertheless, there are numerous technical problems with achieving a compromise between good energy absorption efficiency and other important properties such as flexibility, weight and thickness. The article describes a study of composite structures based on shear thickening fluids (STF) and auxetic foams. The composites are developed as a potential component of products with high energy absorbing efficiency. The study reports on the rheological behavior of STF and force absorbing properties of the manufactured composites. In the experiment, two types of STF and eleven types of auxetic foams were used. Force absorbing tests for the produced samples were performed by dropping an impactor with the energy of 5 J. It was proved that the addition of STF to the auxetic foams increases the force absorbing efficiency.

Keywords: **shear thickening fluid, auxetic foams, force absorbing systems, rheological properties**

KOMPOZYTY NA BAZIE POLIMEROWYCH PIAN AUKSETYCZNYCH ORAZ CIECZY ZAGĘSZCZANYCH ŚCINANIEM JAKO MATERIAŁY ABSORBUJĄCE SIŁĘ UDERZENIA

W dzisiejszych czasach odporność na gwałtowne uderzenie bądź atak jest zagadnieniem często badanym przez wiele instytucji naukowych. Już nie tylko w przypadku wypadków samochodowych czy podczas uprawiania sportów ekstremalnych, ale również jako zabezpieczanie przez gwałtownym atakiem, zdolność do rozpraszania energii jest niezwykle ważna. Połączenie wygody oraz zapewnienie bezpieczeństwa jest bardzo ważnym kierunkiem badań. W artykule opisano kompozyty powstałe na bazie cieczy zagęszczanych ścinaniem oraz auksetycznych pian polimerowych, wytworzonych w celu uzyskania wysokiej zdolności pochłaniania siły uderzenia. Do produkcji cieczy zagęszczanych ścinaniem zastosowano dwa rodzaje krzemionek - nanometryczną oraz mikrometryczną, natomiast jako materiały auksetyczne zastosowano różne rodzaje pian polieterowych o różnej gęstości i różnej wartości współczynnika Poissona. Połączenie tych materiałów pozwoliło uzyskać dobre właściwości energochłonne, co stwarza potencjalną możliwość do zastosowań w przemyśle.

Słowa kluczowe: **ciecze zagęszczane ścinaniem, piany auksetyczne, układy absorbcji siły uderzenia, reologia**

INTRODUCTION

Nowadays, the issue of energy absorption during impacts gives many opportunities to develop new solutions. Recently, researchers have designed new materials which are proposed as high energy absorption materials, e.g. lightweight hybrid structures with Kevlar [1], metal foams [2] and polymeric structural foams [3]. They can be used as a good energy absorbing materials, but on the other hand, in order to utilize them for sports, body armour or workplace health and safety applications, they have to fulfill a variety of prerequisites before they can be used in the industry. Achieving a balance between high flexibility, good energy absorption and very fast reaction to impact are the most important requirements.

Auxetic materials

Auxetics are structures or materials which exhibit a negative Poisson's Ratio [4]. They are a specific kind of materials which become thicker when stretched and thinner when compressed [5]. These materials have been known for over 100 years and can be found in nature but they are very rare [6]. Currently, a variety of auxetic materials have been fabricated based on polymeric and metallic foams, microporous polymers and carbon fiber laminates. The most popular materials which usually are used to produce auxetic materials are synthetic polymers like: polytetrafluorethylene, polyether and polyester. The great interest of this kind of materials is due to their negative values of Poisson's Ratio and their unique behavior under deformation. Auxetic materials produced with polymeric foams have a huge potential in a broad range of applications. For example apparel [7], car seats [8], crash barriers [9], or anti-vibration gloves [10]. These materials have excellent properties for impact applications - they exhibit high energy and force absorption under impact [11].

Shear thickening fluids (STFs)

Shear thickening fluid - often called a dilatant fluid - is a non-Newtonian fluid with particular properties related to response to violent impact [12]. The unique properties of STFs are due to their increasing viscosity with a growing shear rate. At lower shear rates the STF has a low viscosity and when the shear rate exceeds the critical value, the viscosity increases abruptly [12]. In addition, STF has an excellent energy absorption capacity [13]. STF has been characterized as a material with very good protecting properties. What is more, during typical applications STFs are characterized by high flexibility, perfectly matching the protected surface, but in the case of a sudden impact, the viscosity of STF increases - up to solid-like properties - significantly increasing the protection level [14]. The unique properties of STFs make them smart materials that combine the functions of a sensor, processor and actuator. STFs could create a great energy absorption system which can be used in smart armours or sport protectors. The design of composites based on STF and polymeric foams for energy absorption applications seems to be an effective solution in light of their specific properties [15].

EXPERIMENTAL PROCEDURE

Materials

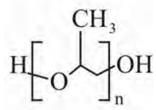
Two types of amorphous silica were used: nanometric FS200-300 from Sigma-Aldrich, USA and micrometric KE-S250 from Nippon Shokubai. The properties of the silicas used in this experiment are shown in Table 1.

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

Symbol	Average particle size [μm]	Bulk density [g/cm^3]	Material form
FS200-300	0.2÷0.3	1.53	Powder
KE250	2.00÷2.40	1.94	Powder

In order to obtain STF, amorphous silica was dispersed in poly(propylene) glycols with different molar masses of 400 and 2000 g/mol. The parameters of the dispersing media used in these studies are presented in Table 2.

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

Organic liquid	Density [g/cm^3]	Molar mass [g/mol]	Structure
PPG400	1.001	400	
PPG2000	1.005	2000	

Furthermore, for tailoring the rheological properties of STFs, microspheres from AkzoNobel were used. The average particle size of the d30 microspheres is approximately 55÷85 μm with a density of 0.03 ±0.003 g/cm^3.

To produce composites with STF auxetic polyether foams were used. Selected auxetic foams are presented in Table 3. The foams were kindly provided by the Air Force Institute of Technology, Warsaw.

TABLE 3. **Selected auxetic polyether foams**
TABELA 3. **Wykaz polieterowych pian auksetycznych**

Sample number	Density [kg/m^3]	Poisson's Ratio
138	42.3	–0.138
142	71.9	–0.100
143	48.6	–0.034
181	60.1	–0.140
186	41.2	–0.080
201	60.1	–0.064
204	54.7	–0.088
240	61.4	–0.101
241	57.9	–0.114
533	83.9	–0.027
744	83.2	–0.066

Method

Amorphous silica was mixed in appropriate proportions with the dispersing media. Rheological studies were performed using an ARES rheometer, equipped with two parallel plates (ϕ25 mm) with a gap between them of 0.3 mm. All the viscosity measurements were taken at the temperature of 25°C.

In order to study the effect of the synergetic combination of shear thickening fluid with auxetic foam on force absorbing efficiency, three types of samples were prepared: auxetic foams sealed in a silicone mould, shear thickening fluid sealed in a silicone mould and auxetic foams impregnated with shear thickening fluid sealed in silicone moulds. Testing of the force absorbing efficiency was performed based on British standard BS 7971-4:2002 "*Protective clothing and equipment for use in violent situations and in training. Limb protectors. Requirements and test methods*". Impact tests were carried out using a free fall impact tower. The force absorbing tests for the produced samples was performed by dropping an impactor with an energy of 5 J. The dependence between the force and time was registered by a force sensor.

The impact force absorption capability was calculated using the formula:

$$F_A = (1 - F_p/F_r)\cdot 100\%$$

where: F_p - value of force registered after falling on sample, F_r - value of basic force (falling on an anvil without the sample).

RESULTS AND DISCUSSION

Rheology

The dependence of the viscosity on the shear rate for the suspensions composed with different volume fractions of fumed silica dispersed in poly(propylene) glycol PPG400 is presented in Figure 1.

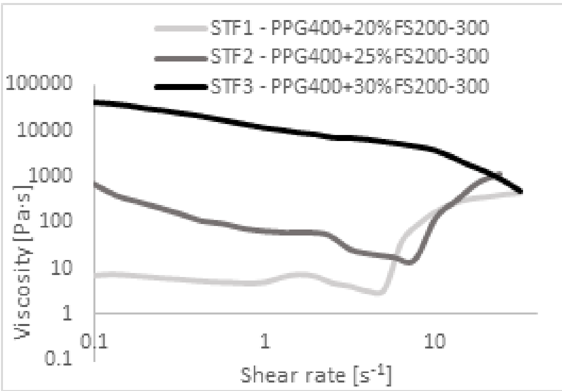


Fig. 1 Viscosity versus shear rate for 20, 25, 30% of volume fraction of fumed silica FS200-300 dispersed in poly(propylene)glycol PPG400

Rys. 1 Krzywe lepkości dla cieczy na bazie glikolu PPG400 oraz krzemionki FS200-300 w ilości 20, 25, 30% objętościowych

One can see that a higher concentration of solid phase causes higher initial viscosity of the fluid. What is more, two samples STF1 and STF2 show the dilatancy effect - the viscosity increases with a growing shear rate, whereas STF3 shows a shear thinning property. This, however, can be an artifact. It must be mentioned that because of the very high initial viscosity of STF3, the fluid was pushed out of the gap between the two parallel plates of the rheometer during measurement. Thus, with the passing time less fluid and more air was at the measuring point. Therefore, the rheometer records a decrease in the viscosity over time, but it was not associated with shear thinning behavior. Nevertheless, the initial viscosity of STF3 was too high to impregnate the auxetic foams.

In Figure 2, we can see that all the fluids exhibit shear thickening properties. An increasing volume fraction of the solid phase results in higher initial and maximum viscosity values obtained during the rheological studies. This is caused by the fact that with a growing shear rate, more particles are one in closer proximity to each other, which results in increasing internal friction in the system. Moreover, since we increase the volume fraction of the solid phase, the mean free path of the particles decreases, which also leads to a decrease in the critical shear rate. The best shear thickening properties were achieved by STF7, however, the initial viscosities for STF7 and STF6 were again too high for auxetic foam impregnation. Hence, STF2 and STF5 were chosen for the further studies.

TABLE 4. **Shear thickening fluids based on PPG2000, FS200--300, KE250 and d30 microspheres**

TABELA 4. **Ciecze zagęszczane ścinaniem na bazie PPG2000, FS200-300, KE250 oraz mikrosfer d30**

Sample	FS200-300 [% of vol. fraction]	KE250 [% of vol. fraction] d30 microspheres [% of vol. fraction]	Initial viscosity [Pa·s]	Maximum viscosity [Pa·s]	
STF4	6.7	40	20	6.58	66.33
STF5	12.5	40	20	16.09	341.16
STF6	14.7	40	20	17.08	761.30
STF7	18.2	40	20	24.48	1308.19

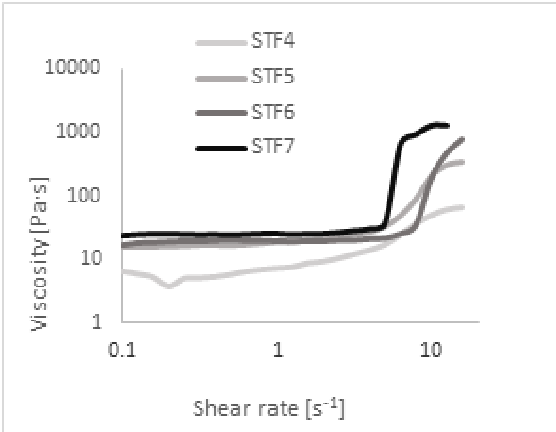


Fig. 2. Viscosity versus shear rate for different amounts of fumed silica volume FS200-300, 40% KE250 and 20% d30 microspheres, dispersed in poly(propylene)glycol PPG2000

Rys. 2. Krzywe lepkości dla cieczy na bazie glikolu PPG2000, krzemionek KE250 40%, FS200-300, w różnych ilościach wraz z dodatkiem mikrosfer w ilości 20%

Force absorbing efficiency

Figure 3 shows the average values of absorbed force by auxetic foams sealed in silicone moulds. All the values obtained by these specimens are presented in Table 5. The highest average value of absorbed force was obtained by auxetic foam 744.

The average value of absorbed force per 1 g of sample was also the highest for specimen 744. Foam 744 has quite a high absolute value of Poisson's Ratio (|-0.066|) compared to the rest of the foams with a similar density. In Tables 3 and 5, we can see that force absorbing efficiency is related to the density of the foams and also to Poisson's ratio. The absolute value of Poisson's ratio is crucial for force absorbing efficiency in the case of a similar value of density of the foams. None of the samples were destroyed.

TABLE 5. **Results of force absorbing test for polyether auxetic foams in silicone moulds**

TABELA 5. **Wyniki absorpcji siły uderzenia pian auksetycznych polieterowych w formach silikonowych**

Sample number	Average value of absorbed force [%]	Mass [g]	Average value of absorbed force per 1g [%]	Poisson's Ratio
138	39.28	50.32	0.78	–0.138
142	43.55	49.81	0.87	–0.100
143	41.05	50.55	0.81	–0.034
181	39.76	49.15	0.81	–0.140
186	37.51	52.12	0.72	–0.080
201	45.95	56.03	0.82	–0.064
204	42.44	55.19	0.77	–0.088
240	45.05	55.25	0.82	–0.101
241	40.83	54.40	0.75	–0.114
533	48.38	53.39	0.91	–0.027
744	52.28	56.50	0.93	–0.066

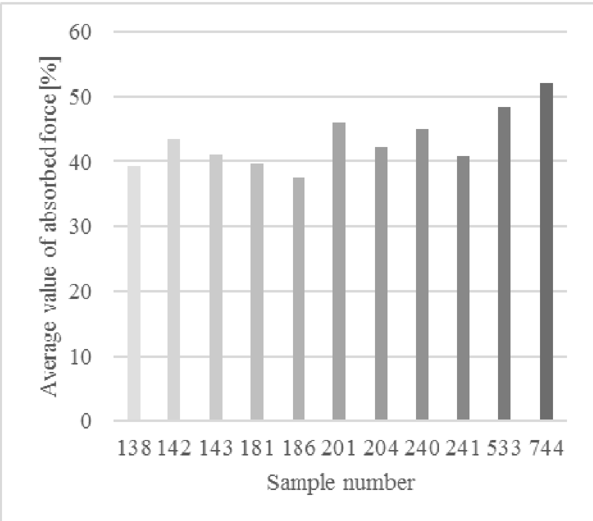


Fig. 3. Average value of absorbed force in silicone for auxetic foams moulds after three strikes at same point

Rys. 3. Średnia wartość absorpcji siły uderzenia pian auksetycznych zamkniętych w formach silikonowych po 3 uderzeniach w ten sam punkt

TABLE 6. **Results for composites based on foam 744 and two types of dilatant fluid (STF2 and STF5)**

TABELA 6. **Wyniki dla kompozytu na bazie piany 744 i dwóch rodzajów cieczy dylatacyjnych (STF2 i STF5)**

Types of fluid	Average value of absorbed force [%]	Mass [g]	Average value of absorbed force per 1 g [%]
STF2	72.29	75.85	0.95
STF5	59.94	58.13	1.03

As was mentioned before, the best STFs based on two different dispersing media (PPG400, PPG2000) whose initial viscosity allowed impregnation of the auxetic foams were STF2 and STF5. Auxetic foam 744 was chosen to create the composites. The results of the force absorption efficiency of the composite specimens are presented in Figure 4.

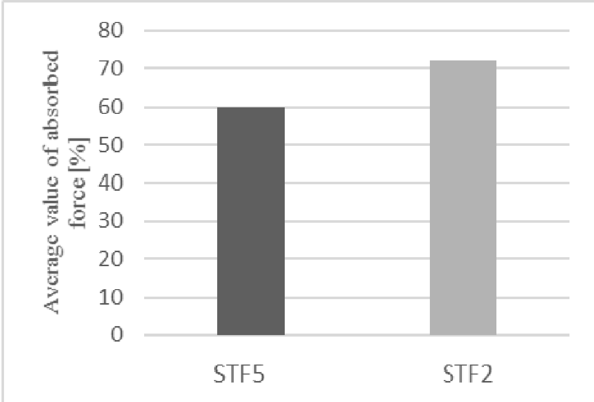


Fig. 4. Average total value of absorbed force for composites based on foam 744 and two types of dilatant fluids

Rys. 4. Średnia absorpcja siły uderzenia dla kompozytu na bazie piany 744 i dwóch rodzajów cieczy dylatacyjnych

One can clearly see that the sample based on STF2 has a greater ability to absorb impact force than the one based on STF5. To be more specific, the STF2 sample was able to absorb an average value of 72.28% of the impact force, which is over 20% more than the force absorption efficiency of pure auxetic foam 744 sealed in a silicone mould according to Table 5. On the other hand, the specimen based on STF5 has a better average value of absorbed force per 1 g. This is related to the higher density of STF2, which is caused due to the presence of the low density of the microspheres in STF5. What is more, impregnation of the 744 auxetic foam was much more time consuming for STF5, as a result shear thickening fluid based on PPG400 with 25 vol.% FS200-300 (STF2) was chosen for the subsequent studies.

In Figure 5 we can see that pure STF2, sealed in a silicone mould is able to absorb an average value of impact force of 58.56% for 10 g, and 73.32% for 25 g respectively. Moreover, a higher amount of STF2 is able to absorb more impact force per 1 g of sample (Table 7).

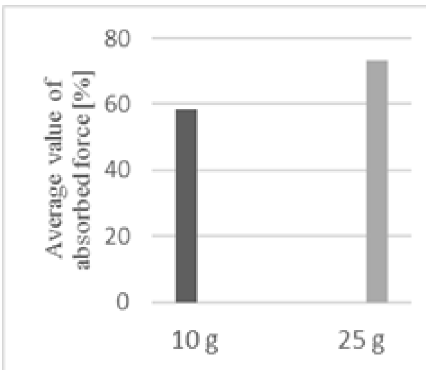


Fig. 5. Average value of absorbed force for 10 and 25 g of STF2

Rys. 5. Średnia zdolność do absorpcji siły uderzenia 10 i 25 g cieczy STF2

TABLE 7. **Results of force absorbing efficiency for samples based on 10 and 25 g of STF2 sealed in silicone mould**
TABELA 7. **Wyniki absorpcji siły uderzenia dla 10 i 25 g cieczy STF2 zamkniętej w formie silikonowej**

Amount of STF2 in sample [g]	Average value of absorbed force [%]	Mass [g]	Average value of absorbed force per 1 g [%]
10	58.56	63.21	0.93
25	73.32	73.24	1.00

In Table 8 and Figure 6 the results of the force absorbing efficiency for the eleven types of auxetic foams impregnated with 10g of STF2 are presented. It was found that the composite structure based on foam 744 and STF2 has the best absorption properties compared to the samples based on other foams. Nevertheless, the sample based on foam 533 had a higher value of absorbed force per 1 g of specimen. It is assumed to be a consequence of the highest density of this two foams.

TABLE 8. **Results of total absorbed force for composites based on STF2 and eleven types of auxetic polyether foams**
TABELA 8. **Wyniki zdolności do absorpcji siły uderzenia dla kompozytu na bazie STF2 oraz pian auksetycznych**

Number of used foam	Average value of absorbed force [%]	Mass [g]	Average value of absorbed force per 1 g [%]
138	61.31	57.68	1.06
142	62.40	61.94	1.01
143	61.16	59.51	1.03
181	60.94	61.64	0.99
186	58.54	55.62	1.05
201	58.92	63.80	0.92
204	55.31	55.72	1.00
240	60.53	63.68	0.95
241	59.33	57.63	1.03
533	68.01	62.35	1.09
744	69.67	66.33	1.05

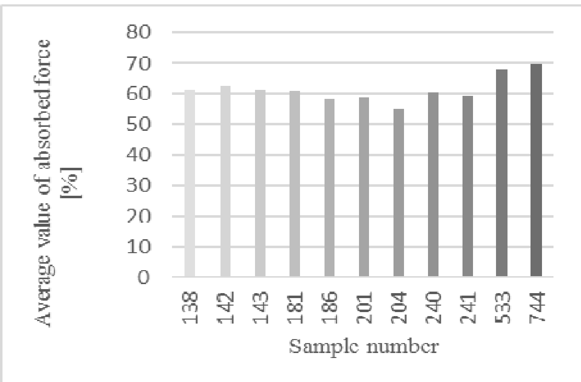


Fig. 6. Average value of impact force absorbed by produced composites
Rys. 6. Średnia absorpcja siły uderzenia dla wytworzonych kompozytów

None of the tested samples were destroyed and there was no leakage of fluid from the samples after the test. The samples were deformed and then they returned to their initial shape.

CONCLUSIONS

Composites based on two types of poly(propylene) glycols, two amorphous silicas, microspheres and auxetic polyether foams were produced. The most effective shear thickening properties were obtained by STF2 based on PPG400 and 25% volume fraction of solid phase FS200-300. It was found that the force absorption ability depends on the amount of STF2 sealed in a silicon mould - the absorbed force increases from 58.56% (sample with 10 g STF2) to 73.32% (sample with 25 g STF2).

The best absorbing composites were achieved by using the foams with the highest density. In the case of similar values of foam density (83.9 kg/m^3 for foam 533 and 83.2 kg/m^3 for foam 744), better absorbing results were achieved when the absolute value of Poisson's Ratio was higher (|–0.066| for 744 and |–0.027| for 533). The composites based on STF2 and auxetic foam 744 have about 1.5 times greater force absorption properties than foam 744 itself sealed in a silicon mould, and about 1.2 times better force absorption efficiency than the same amount of pure STF2 sealed in a silicon mould. Impregnation of the auxetic foam 744 with STF2 increases the force absorbing efficiency up to 1.05% per 1 g of sample when compared to either pure foam (0.93% per 1 g of sample) or pure STF2 (0.93% - 1% per 1 g of sample) sealed in silicon moulds. To recap, it has been proved that impregnation of auxetic polyether foams with STF2 increases the force absorbing efficiency due to the synergetic action of shear thickening fluid and auxetic foam.

Acknowledgement

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