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Rheological Fluids as a Potential Component of Textile Products

Abstract
Rheological fluids belong to the group of smart materials which can also form a component of some textile products. In this study shear thickening fluids (STF) and magnetorheological fluids (MRF) were synthesised. STF is a colloidal suspension of silica nanoparticles in an organic liquid carrier. The viscosity of STFs depends on the shear rate, which means that for a sufficiently high shear rate their properties change from the characteristic of a liquid to that typical for a solid body. This process is rapid and fully reversible. MRF is a non-colloid suspension of micrometric iron particles in a carrier liquid, usually oil. Under the action of an external magnetic field the particles form a chain-like structure and the MRFs change the viscosity, with their properties becoming characteristic of an elastic solid. In this study flexible body armours which are able to protect limbs were elaborated. Such systems can also be used for other flexible shields such as mates, blankets etc., as well as to find civilian applications, for example sport protective clothing.

Key words: *shear thickening fluid, magneto-rheological fluids, liquid body armour.*

Introduction

Smart materials find application in almost all branches of industry. They also comprise a component of a number of textile products. Rheological, non-Newtonian fluids represent an interesting group of such materials. Most materials behave in such a way that they have a combination of viscous and elastic response under stress or deformation. Among real liquids Newtonian and non-Newtonian fluids can be distinguished. Viscosity is one of the rheological parameters which can characterise liquids. By measurement of the viscosity versus share rate one can classify the liquid into a particular group. If the viscosity decreases vs. the shear rate the liquid has shear thinning properties, and when the viscosity rapidly increases, the shear thickening or dilatancy effect is observed. Rheological classification of liquids is presented in ***Figure 1*** [1]. The shear thickening effect appears in suspensions of various concentration and morphology of the solid phase. The shear thickening of fluids can be explained by a few theories, the most popular being the clustering theory. According to its main assumption, the particles at low shear rates are prevented from aggregation by repulsive and Brownian forces. With an increase in the shear rate, hydrodynamic forces also increase and particles form chains, blocking the flow of the fluid. The next potential explanation of the dilatancy phenomenon is the Order – Disorder Transition (ODT) theory, which claims that the spherically shaped particles exist in ordered arrangement before the shear thickening effect takes place and transfer to a disordered state under the action of mechanical shear [2]. Moreover the shear thickening properties could be caused by bridging flocculation of the polymer chains on ceramic grains. The polymer chains can bound more than one particle [3 - 5].

Magnetorheological fluids (MRF) represent an important group of smart materials which change their properties in a controlled manner, under the influence of a magnetic field [6]. The phenomenon of a substantial change in the rheological properties in an external magnetic field is called the magnetorheological effect. Magnetorheological fluids are made in the form of a suspension of ferromagnetic particles, having a size in the range of 1 - 10 µm, in a nonmagnetic carrier liquid. The magnetic particles used in MRFs are mostly powders of ferromagnetic metals and alloys having high magnetic saturation magnetisation, such as iron, cobalt, nickel and their alloys. As non-magnetic carrier liquids, synthetic or natural oils, water, kerosene or ethylene glycol are used. The liquid carrier plays the role of a dispersant medium for the metallic particles and assures their homogeneous distribution [7]. Additionally a stabiliser, which prevents sedimentation and agglomeration of the particles, must be used. As a stabiliser, mostly colloidal silica or oleic acid are used. An external magnetic field magnetises the ferromagnetic particles, which form stiff chains aligned along the magnetic field direction. This phenomenon leads to a substantial change in the microstructure and rheological properties of the MRF [8, 9].

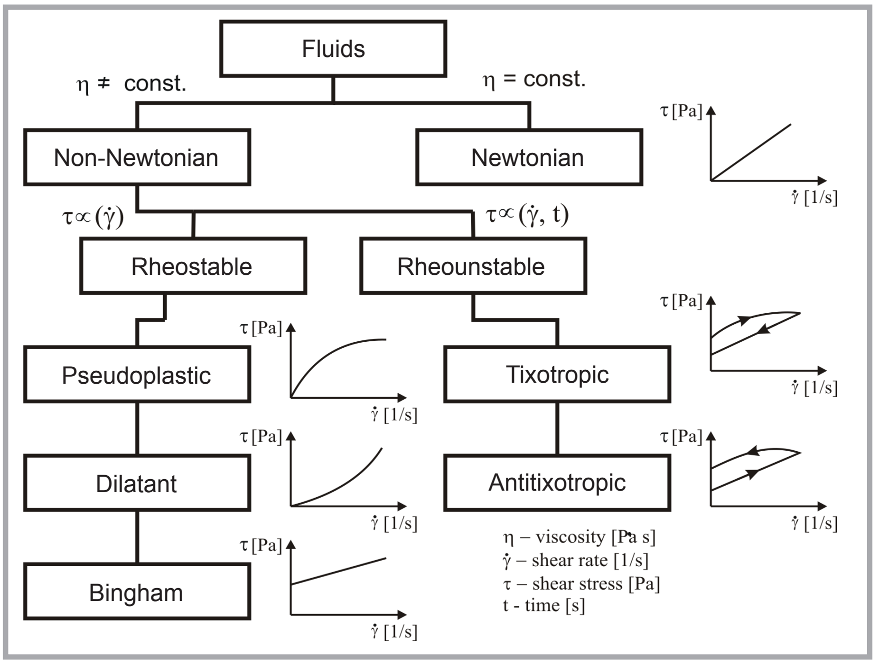


Figure 1. *Rheological classification of liquids.*

First of all the action of the magnetic field leads to an increase in viscosity, by an order of 10^6 Pas, as well as an increase in mechanical strength [10, 11].

One of the possibilities of improving the ballistic performance of current soft armours is the application of non-Newtonian fluids, among which are the widely studied shear thickening fluids, which are supposed, in some cases, to improve fabric ballistic performance [12 - 14]. However, although such research has been carried out since 2003, the effectiveness and mechanisms of energy dissipation for STF/Kevlar composites is an open question [15].

Recently magnetorheological fluids have also been considered as non-Newtonian fluid reinforcement for soft armours. MRFs are widely used in dampers, clutches and brakes [15 - 17]. However, information on their application in armours is limited [18, 19]. Both materials provide an opportunity to enhance energy dissipation in composite systems containing paraaramide fabrics and a liquid component. One has to bear in mind that the application of a magnetic field in body armour may cause some problems, however, as the contemporary soldier is equipped with sources of energy for numerous electronic devices he uses. Of course, the MRF may also be applied in protective elements of military vehicles, blankets and other flexible shelters.

In this study various shear thickening and magnetorheological fluids were synthesised. Their rheological parameters were studied in light of their application in smart body armour.

Experimental

Shear thickening fluids

The shear thickening fluids synthesised in this experiment were made of 7 nm Silica Fumed, of specific surface 390 m^2g^{-1}, dispersed in polypropylene glycol, and various molecular weight: 400, 425, 725 g/mol (PPG400, PPG425, PPG725), respectively.

The rheological properties were measured using an Ares TA Instruments Rheometer, working in the plate-plate mode, gap 0.3 mm, at a temperature of 25 °C.

Magnetorheological fluids

Two grades of iron particles, supplied by BASF, Germany, of 5 μm (OM-grade) and 1.8 μm size (HQ-grade) were used. Additionally three synthetic oils with a kinematic viscosity of 15, 100 and 320 mm^2s^{-1} were applied.

Characterisation of the fluids was carried out using an Ares TA Instruments Rheometer, equipped with a magnetic coil. A plate-plate head of 20 mm diameter with a 1 mm gap was used. The rheological properties were measured in static and dynamic (oscillate) modes. In the static mode the viscosity and shear stress versus the shear rate were measured without a magnetic field and in a magnetic field strength of 159 kAm^{-1} (200 mT). The range of the shear rate was 0.1 - 650 s^{-1} in the logarithmic scale. The dynamic mode enabled the measurement of rheological parameters such as the complex shear modulus $G*$, storage modulus G' and loss modulus G'', versus a magnetic field with 99 Hz oscillation and deformation amplitude of 0.5%. Dynamic measurements were made in a magnetic field intensity within the range of 0 - 230 kAm^{-1}.

Composites structures with STF, MRF

The structures for ballistic tests were made with the use of Twaron® CT709 para-aramide fabrics and ultra-high molecular weight polyethylene (UDSB71). STF and MRF were placed between the layers in plastic bags. Ballistic performance tests were conducted on a specially designed and built workstation with a vertical structure, equipped with a magnetic coil. The dimensions of the samples was 100 × 100 mm, and the distance between the sample and gun was about 0.5 m, with shots being fired in the vertical direction. 9 mm Parabellum FMJ with a lead core and 7.62 × 25 mm FMJS bullets were applied. A magnetic field of 159 kA/m was applied under ballistic testing for the samples with magnetorheological fluids. Lines of the magnetic field were perpendicular to the direction of the projectile motion axes and parallel to the target surface.

The backface signature in ballistic clay and the total number of fabric layers of the target samples damaged were measured after impact. Each test was conducted three times for a given target structure and average results recorded.

Flexibility tests of STF composite samples

Two-dimensional drape tests were performed to measure the flexibility of the targets, as shown in ***Table 1***. In all cases a 35 g weight was used, and encapsulated ballistic targets used as the test specimens were attached at a quarter of its length to the surface. The bending angle is reported as a measure of target flexibility, with larger angles indicating greater flexibility. The thickness of the specimens was also measured with a micrometer at the center of the targets.

Results

Shear thickening fluids

Initially suspensions containing various silica (Fumed Silica 7 nm) concentrations were dispersed in polypropylene glycol of 400 $gmol^{-1}$ molecular mass. One can notice (***Figure 2***) that the increase in the concentration of the solid component is followed by an improvement in the dilatancy effect, providing higher dynamic viscosity at a smaller shear rate.

The effect of the molecular mass of polypropylene glycol on the change in dynamic viscosity versus the shear rate is shown in ***Figure 3***. The silica concentration was constant – 15 vol.%. One can see that the increase in molecular mass is accompanied by the growth of viscosity.

On the basis of the results presented in ***Figures 2*** and ***3*** one can conclude that the viscosity of STFs can be controlled, to some extent, by a proper combination of the solid component content and molecular mass of the carrier liquid. This information is particularly crucial for application of STF in personal body armour and protective pads, since such a behavior enables the elasticity of the armour during exploitation as well as abrupt "solidification" under the action of a knife or bullet.

The best properties, i.e. the highest increase in dynamic viscosity, are shown by the STF, presented in ***Figure 2***. This fluid contains 25 vol.% of silica 7 nm, dispersed in polypropylene glycol (Mn = 400 g/mol). The critical shear rate, at which the viscosity starts to abruptly increase, is about 4 s^{-1}. The highest viscosity, 1200 Pas, was achieved at a share rate of 25 s^{-1}.

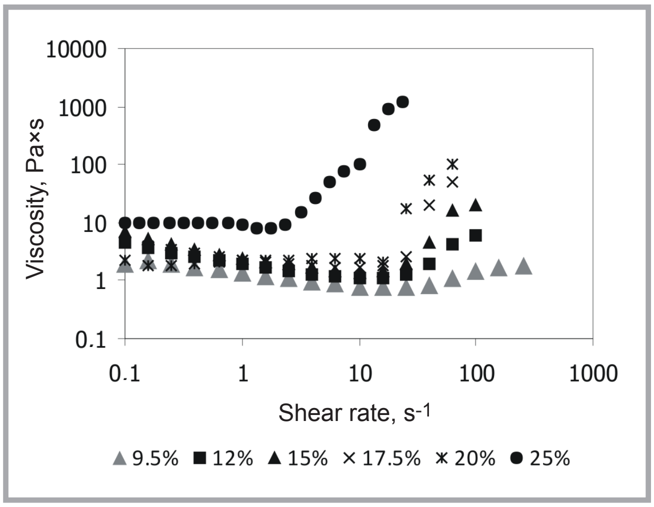


Figure 2. Dynamic viscosity versus shear rate for various concentrations of silica 9.5, 12, 15, 17.5, 20 and 25 vol.%; carrier liquid - polypropylene glycol (Mn = 400 g/mol).

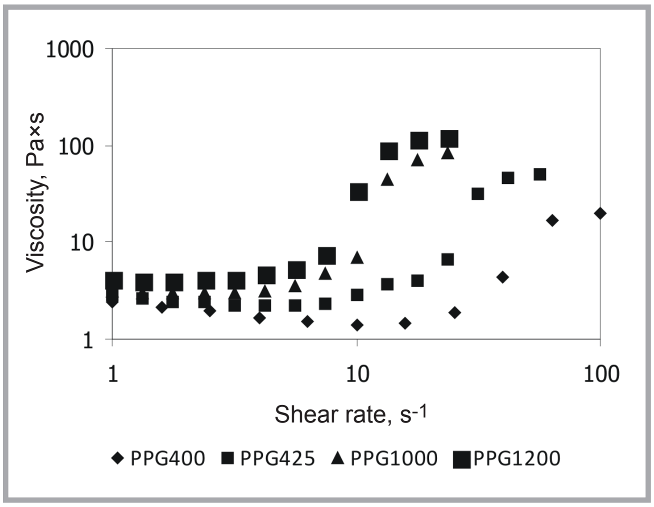
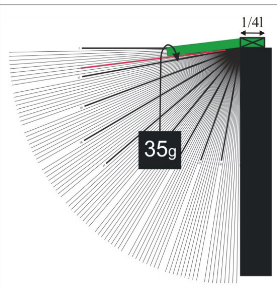
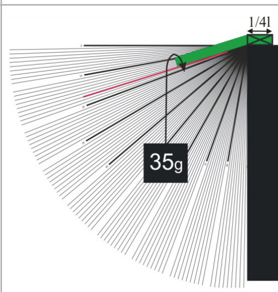


Figure 3. Dynamic viscosity versus shear rate for various polypropylene glycols (molecular mass: 400, 425, 1000 and 1200 gmol-1). Silica concentration – 15 vol.%.

This particular STF was used for ballistic tests, the results of which are shown in ***Table 1***. Two different structures of armour were prepared. Armour based on ultra-high molecular weight polyethylene (UDSB71) was shot using a 7.62 × 25 mm FMJS gun. Perforation did not occur, although the substrate was deformed by 16.5 mm. Deflection in the elastic test was 7°, and thickness of the sample 16mm. The average number of layers damaged was 11. A similar aerial mass occurred for the armour prepared with ultra-high molecular weight polyethylene (UDSB71) with colloidal insert. The sample also appeared to be bulletproof, but the deformation decreased to 14.5 mm. The sample also had lower thickness (11 mm) and was more flexible, which can be easily noticed in the elastic test (deflection 17°). The average number of damaged layers was 8.

Table 1. Results of ballistic and elasticity test for structures with STF.

Armour based on ultra-high molegular weight polyethylene(UDSB71)	without colloedal insert	with colloedal insert
Bullet	7.62 × 25 mm FMJS	
Areal density, gm^{-2}	12 150	12 330
Deflection, °	 7	 17
Thickness, mm	16	11
Average backface signature (after 3 shots), mm	16.5	14.5
Standard deviation, mm	1.22	0.40

Magnetorheological fluids (MRF)

The effect of iron powder particle size and oil viscosity on the rheological properties of the MRFs was evaluated. For study of the effect of particle size on the properties of the MRF, carbonyl iron particles of 5 µm (OM) and 1.8 µm (HQ) size, dispersed in OKS 3760 oil (kinematic viscosity 100 mm^2s^{-1}), were synthesised. The iron concentration was 75 wt.%. As a stabiliser Aerosil A200 was used (***Figure 4***).

As can be seen in ***Figure 4***, the MRF with particles of 5 µm shows, for a shear rate of 0.1 s^{-1}, changes in viscosity and shear stress from starting values (without magnetic field) of 135 Pas and 13.5 Pa, respectively, up to final values (at a magnetic field strength 159 kA/m) of about 10^5 Pas and 10^4 Pa, respectively. A two orders of magnitude increase in the viscosity and shear stress in a magnetic field is observed for particle size 1.8 µm. Analysing the effect of powder particles on the starting parameters (without magnetic field), one can notice that properties of about an order of magnitude can be obtained for fluid processed on the basis of HQ iron, with particles of 1.8 µm, because smaller particles at the same weight fraction fill the liquid to a greater degree, resulting in an increasing viscosity, which is consistent with the results presented by other authors [12]. These differences disappear in a magnetic field strength of 159 kA/m, where the leading role is played the mass of particles.

Changes in the shear module are presented in ***Figure 5***. As one can see, both the MRFs studied exhibit similar values of the complex shear modulus *G**, storage modulus *G'* and loss modulus *G"* versus the magnetic field strength, varying in the range of 0 - 150 kA/m. In the case of MRF with smaller particles of 1.8 µm, a slightly more intensive increase in the module is shown for lower values of the magnetic field, whereas for higher fields the module stabilise, which is not observed for the MRF with larger particles of 5 µm. The plateau effect for the dynamic module observed for higher magnetic fields is related to the magnetic saturation of particles. A further increase in the field does not affect the module.

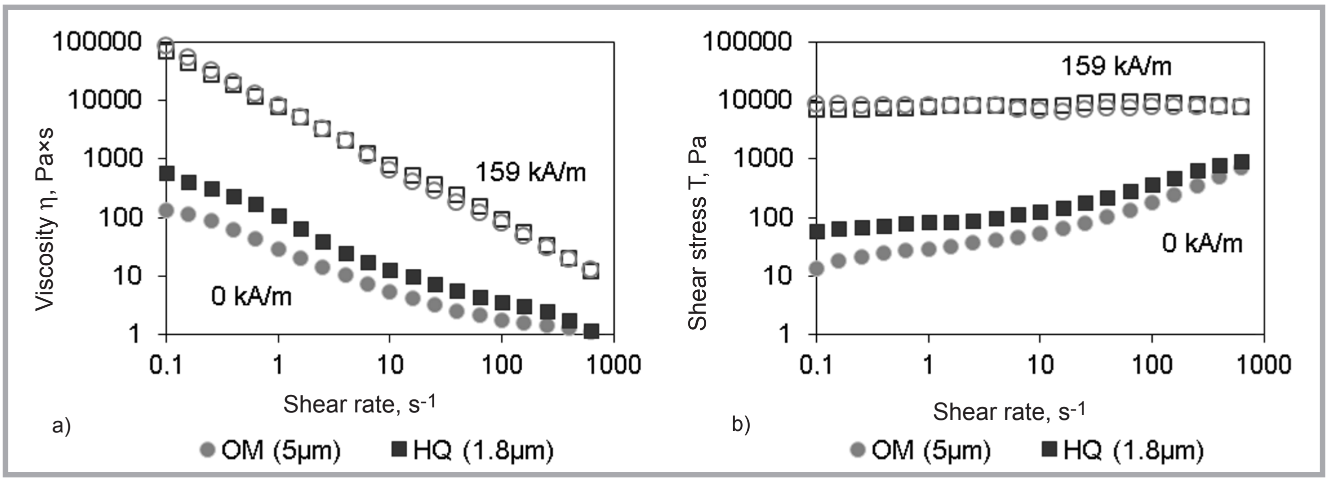


Figure 4. *Viscosity (a) and shear stress (b) versus shear rate for magnetorheological fluids with iron particles of 5 µm (OM) and 1.8 µm (HQ) size, without an external magnetic field and in an magnetic field strength of 159 kA/m, static regime; shear rate 0.1 - 650* s^{-1}.

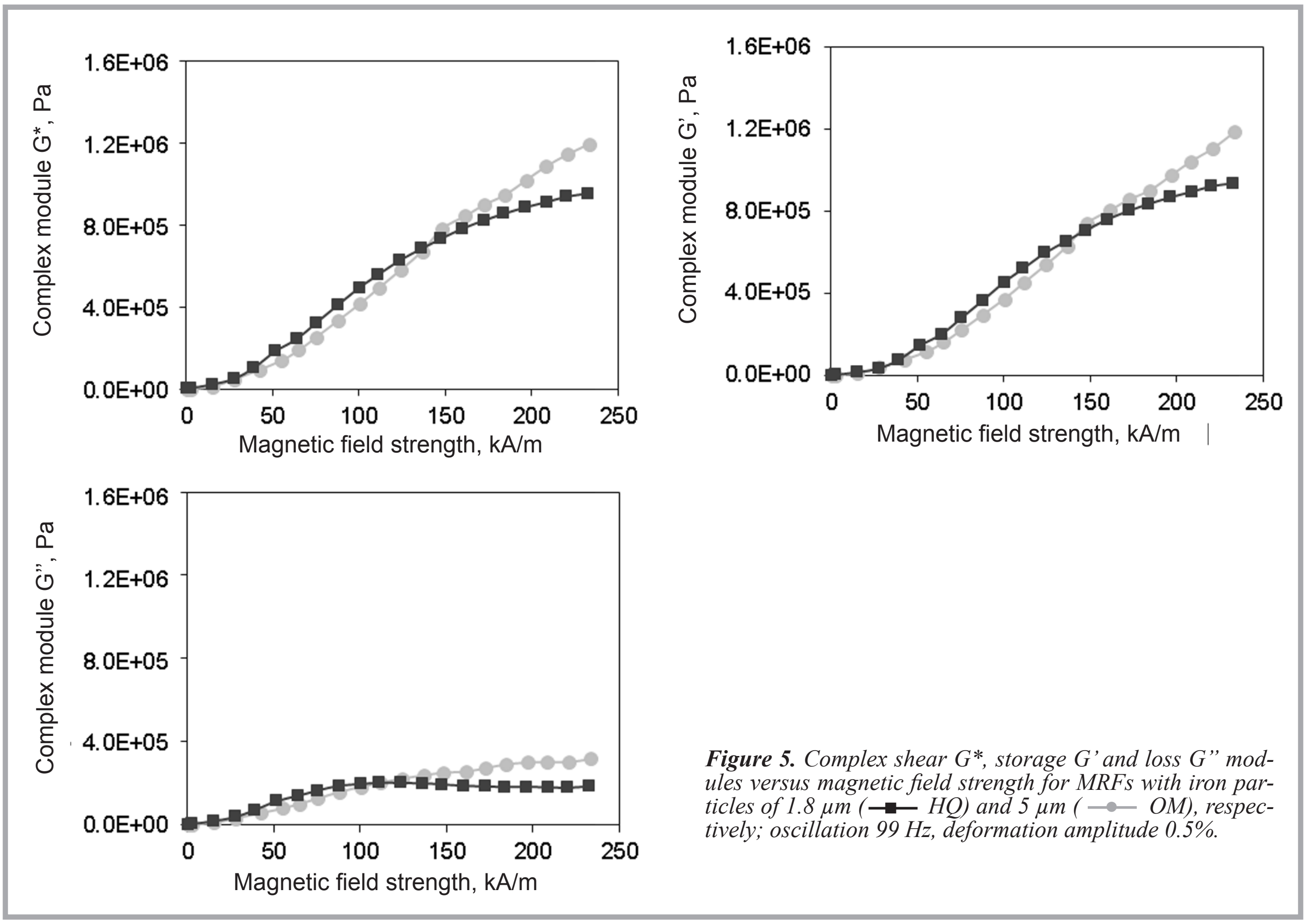


Figure 5. *Complex shear G*, storage G' and loss G" modules versus magnetic field strength for MRFs with iron particles of 1.8 µm (—■— HQ) and 5 µm (—●— OM), respectively; oscillation 99 Hz, deformation amplitude 0.5%.*

For MRF with larger particles of 5 µm a magnetic field strength of 230 kA/m does not saturate the magnetisation and a plateau is not observed.

In order to assess the effect of the viscosity of the carrier oil on rheological properties of MRFs, three fluids, each containing 75 wt.% of HQ iron (5 µm particles) and oils of various kinematic viscosity: 15, 100 and 320 mm^2/s, were synthesized. All these MRFs contained stabiliser silica Aerosil A200. Results of measurements of the dynamic viscosity and shear stress versus the shear rate, performed in a static regime without a magnetic field and in a magnetic field strength of 159 kA/m, for MRFs with various oils, are shown in ***Figure 6.***

Changes in the dynamic viscosity and shear strength versus the shear rate demonstrate a non-Newtonian character for all oils tested. An increase in the shear rate results in the decreasing viscosity of the MRF in both states: without a magnetic field and in a magnetic field strength of 159 kA/m. On the other hand the shear stress grows versus the shear rate without a field, but in a magnetic field strength of 159 kA/m it is almost constant at a level close to the value of the dynamic yield stress. The low-

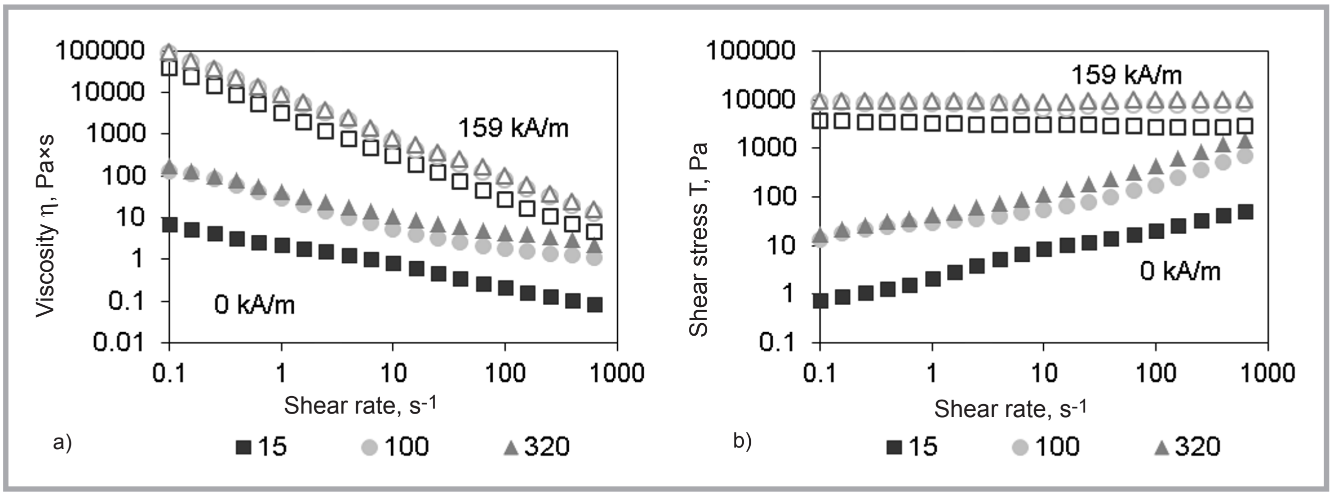


Figure 6. *Dynamic viscosity (a) and shear stress (b) versus shear rate for MRFs synthesised on the basis of oils with kinematic viscosity: 15, 100 and 320 mm²/s without a magnetic field and in a magnetic field strength of 159 kA/m. Static regime.*

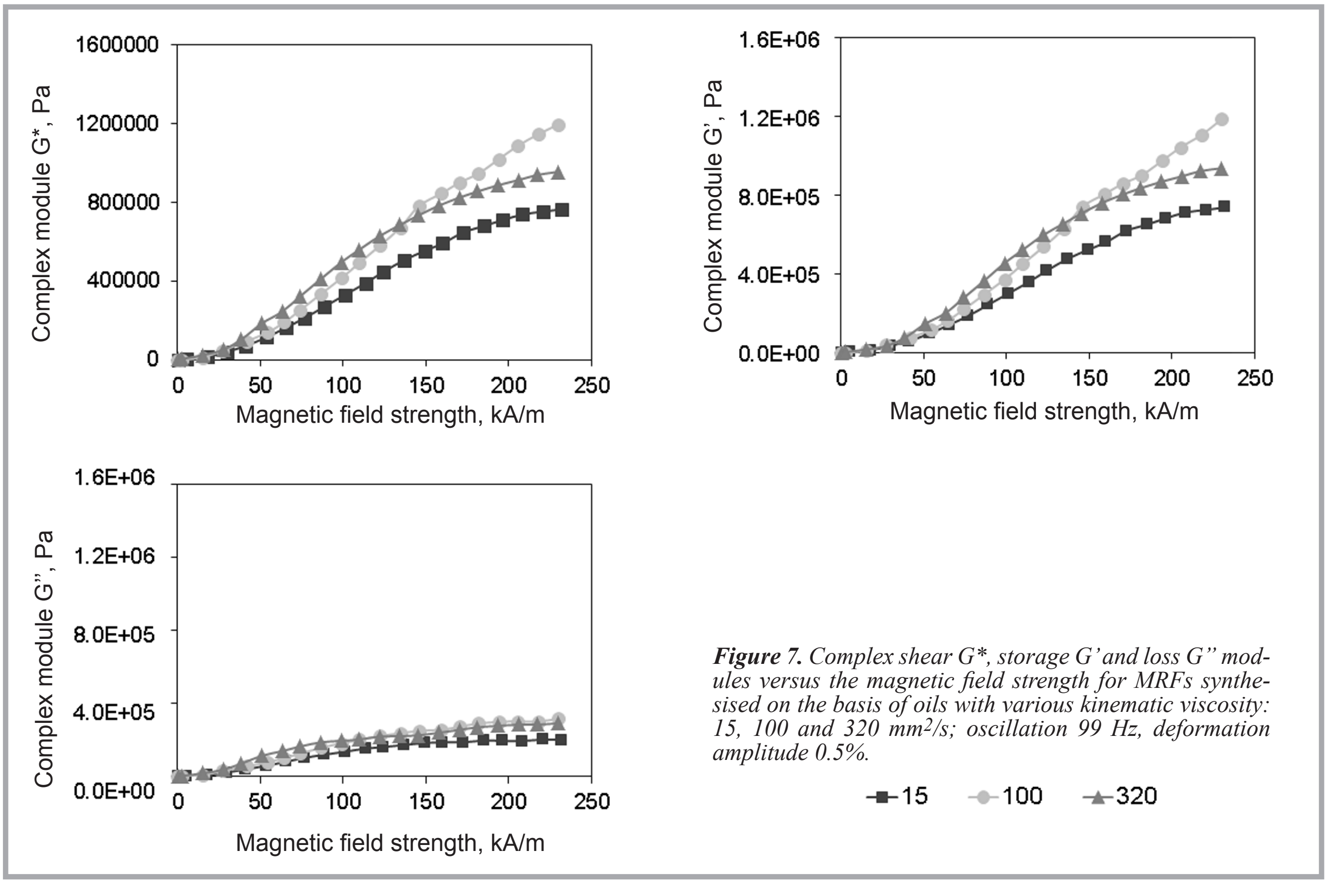


Figure 7. *Complex shear G*, storage G' and loss G'' modules versus the magnetic field strength for MRFs synthesised on the basis of oils with various kinematic viscosity: 15, 100 and 320 mm²/s; oscillation 99 Hz, deformation amplitude 0.5%.*

est values of viscosity and shear stress were obtained for the MRF prepared on the basis of oil with kinematic viscosity class 15 mm^2s^{-1} (***Figure 6***). However, in the magnetic field the dynamic viscosity of this MRF grows by four orders of magnitude. MRFs with oils of 100 and 320 mm^2/s kinematic viscosity show a three orders of magnitude change in these parameters in the field. On the basis of these results one can conclude that the application of oil with low kinematic viscosity enables to achieve a greater difference in the magneto-rheological effect without a magnetic field and in a field. However, the higher kinematic viscosity of the carrier oil enabled to achieve slightly higher values of dynamic viscosity in the field.

Values of the dynamic module versus the magnetic field with oils of various kinematic viscosity are shown in ***Figure 7***. For all the MRFs prepared on the basis of oils with various classes of kinematic viscosity the character of changes in the module versus the magnetic field was identical. An increase in the magnetic field causes an increase in the module. For a particular, critical magnetic field strength the values of the module stabilise, which is related to the magnetic saturation of the chains of iron particles.

As one can notice in ***Figure 7***, the plateau of the dynamic module, evidencing the magnetic saturation of the iron particles, exhibits MRFs with oils of the lowest (15 mm^2/s) and highest (320 mm^2/s)

Table 2. Results of tests of shooting with 9 mm bullets at structures made from layers of Twaron® CT709 and containing plastic bags with the MRF.

	Structure	
	18 layers	18 layers and bag with MRF
Total number of layers	18	18
Magnetic field strength, kA/m	0	159
Areal density of target, g/m^2	3 990	8 990
Perforation	No	
Number of damaged layers	6	4
Average backface signature, mm	48.33	45.00
Standard deviation, mm	0.47	0.82

kinematic viscosity. For the MRF with oil of 100 mm^2/s viscosity the shear G^* and storage module G' increase, even above the maximum magnetic field strength applied of 230 kA/m. For this MRE the highest values of the module were achieved (G^* = 1.2, G' = 1.2, G'' = 0.3 MPa). Comparing changes in the storage modulus G' and loss modulus G'' in a magnetic field, one can notice that the MRF with oil of 15 mm^2/s viscosity shows, within the entire range of the field tested, domination of elastic properties over viscous ones ($G' > G''$). The MRFs prepared on the basis of oils with higher viscosity initially exhibit domination of viscous properties, which subsequently change to an elastic character. For the MRF with oil of 100 mm^2/s viscosity this transformation occurs in a field of 14 kA/m.

For ballistic tests MRF on the basis of oil with viscosity 100 mm^2/s, containing 75 wt.% of 5 µm iron particles was prepared. As a stabiliser Aerosil 200 was applied. Results of tests of shooting with 9 mm bullets at structures made from Twaron® CT709 and containing plastic bags with the MRF are shown in ***Table 2***.

The results presented in ***Table 2*** show that neither of the two structures tested was fully perforated. For the specimen made of 18 layers of Twaron® CT709, each was perforated, with the depth of deformation being 48 mm. The second specimen also contained 18 layers of Twaron® CT709 and additionally a plastic bag with the MRF was applied. In a magnetic field strength of 160 kAm^{-1}, 4 layers of the fabrics were perforated and the deformation depth decreased by 3 mm. The mass of the structure, however, increased more than twice.

Concluding remarks

A series of shear thickening fluids and magneto-rheological fluids were synthesised.

It was found that colloidal nanosilica dispersed in polypropylene glycol exhibits a shear thickening (dilatancy) effect. The best properties are shown by the composition made of 7 nm Silica Fumed and polypropylene glycol with a molecular mass of 400. Variation of the silica content and molecular mass of the glycol enables tailoring of the properties of the shear thickening fluids.

The tests performed showed that both shear thickening and magneto-rheological fluids improve the protective property of armours prepared on the basis of paraaramide fabrics. The ballistic tests proved that the application of shear thickening fluid improves the resistivity to penetration of 7.62 × 25 mm FMJS bullets by 12% and causes a decrease in the number of punctured layers of the fabrics. Magneto-rheological fluid also decreases the number of punctured layers of the fabrics and the deformation depth, but increases the mass of the structure.

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