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Research Article

DETERMINATION OF SUITABLE RHEOLOGICAL MODEL FOR POLYETHYLENE GLYCOLS AND SILICA PARTICLE MIXTURES

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Abstract: *Shear thickening fluids are smart materials that show a sudden increase in viscosity when exceeding critical shear rates. Different theories have been proposed to explain these properties of shear thickening. The most used of these theories are Order-Disorder Transition and Hydro-Cluster Theory. Due to their reversible properties, shear thickening fluids have been used in many areas. High molecular weight polyethylene glycols showed faster shear thickening fluids behavior. The molecular weight of polyethylene glycol affects many parameters. These parameters are physical bonds, aggregations of molecular, solid particle interactions, and functional groups in the chain. Due to their effect, rheological behaviors of low and high molecular weight polyethylene glycols differ. The mixtures of polyethylene glycols and fumed silica particles show a colloidal distribution. The distribution of fumed silica particle molecules in polyethylene glycol, interaction with each other restriction, and movement of the bulks have affected rheological properties. Physical interactions are manifested in the structure. The mixture showed non-Newtonian behavior in the first and second regions as well. Rheological behaviors of mixtures were compared with experimental data using non-Newtonian models. Power Law, Bingham, Casson, Herschel-Bulkley, and Sisko model equations were used. Silica particle-PEGs mixtures show pseudo plastic in the first region and dilatant fluid behavior in the second region. In the first region, the Power Law model was determined as the most suitable model for experimental data. In the second region, the Herschel-Bulkley model was found to be the most suitable model that was determined by statistical analysis.*

Keywords: *Fumed silica, polyethylene glycol, shear thickening fluid, non-Newtonian models.*

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1. Introduction

Shear thickening fluid (STF) is a type of non-Newtonian fluid. In the shear thickening phenomenon, after the shear rate reaches a critical point, the viscosity of a fluid significantly increases. Different theories were proposed to explain these properties of shear thickening fluids. Order-Disorder Transition and Hydro-Cluster Theory are the most used of these theories [1–3].

In the early researches, the viscosity mechanisms of STFs were examined and parameters that affect these mechanisms were tried to determine. The effects of particle shapes [4], particle hardness [5], polyethylene glycol [6], and temperature [7] on shear thickening behavior have been investigated in various studies. In the literature, PEG [8,9] and EG [10,11], were used as a liquid medium, spherical [12] and fumed silica [13,14] as solid particles in STFs produced using a wide variety of suspensions.

In a study in the literature, the shear behavior of low molecular weight polyethylene glycol and silica suspensions were investigated. In rheological measurements, it was observed that fumed silica particles formed immobile aggregates in polyethylene glycol. Fumed silica, an amorphous silicon dioxide, consists of nano-sized, non-porous spherical particles branched aggregates. This system showed a complex steady shear behavior; shear-thickening between two shear-thinning regions. Shear-thinning behavior was observed in suspension that consists of polyethylene glycol of low molecular weight [15].

In an emulsion application in literature, the development and characterization processes of a continuous phase with fumed silica and surfactant were carried out. Ecological continuous phases were developed with the help of a green surfactant and fumed silica. A significant increase in viscoelastic flow was detected for the fumed silica-water system. This rheological change is related to the interaction of silica chains, as seen in the SEM images. As a result of the microstructure and the proposed properties, an increase in the physical stability of more concentrated systems was observed. It was determined that the viscoelastic properties related to the interaction between silica chains increase [16].

In another study with silica particles, size characterization was made by Sedimentation Field Flow when used as a food additive. There are four types of silica particles found as additives in food and personal care products. Dimensional characterization was made using analyzes such as SEM and TEM. Nanoparticle sizes of some samples organized into clusters or aggregates were determined by different analytical techniques. Along with the SEM observations, the added silicon oxide particles were identified and the particle size distribution was verified [17].

In the literature, the rheology of shear thickening of fumed silica and polyethylene glycol was investigated with nano-clay additive. The shear thickening properties of the mixture prepared in different concentrations, a modified clay, and fumed silica-polyethylene glycol were determined. The change in rheological properties of the mixture was studied when fumed silica or nano-clay was used in equal weight in polyethylene glycol. In the case of nano-clay addition at a temperature of 298 K, the increase in critical viscosity is less than that observed for the same amount of fumed silica. According to the rheological results, the elasticity and thermal stability of the mixture increased significantly with the addition of nano additives [18].

Shear thickening fluids are used in many fields due to their unique properties mentioned above. Personal body armor [19–21], protective clothing [8,22,23], and their use as vibration dampers [24,25] are the most common uses of these fluids. Yarn pull-out, surface friction, impact, and ballistic test of STF impregnated high-performance fabrics will be our future studies. Commercial use of these fabrics has become widespread in the defense industry. Increasing the energy absorption efficiency of the mentioned fabrics is commercially important.

Many studies were done to explain the effectiveness of these smart fluids in energy absorption. In this study, the comparison of rheological measurements of different molecular weight polyethylene glycols and fumed silica mixtures were made. By examining the non-Newtonian models, it was tried to decide the model suitable for the rheological results of the suspension produced. It is thought that determining the non-Newtonian model of the produced mixtures will be effective in explaining the role of these fluids in energy absorption.

2. Materials and Methods

This study is to determine the most appropriate rheological model for shear thickening fluids produced using polyethylene glycols with different molecular weights. The rheological behavior of the STFs obtained by keeping constant the production method, the solid particles, and the concentration of suspension was examined. Fumed silica (Aerosil 200) which has a particle size of 12 nm and a specific surface area of 200 m^2/g was used as the solid particle in the production of STFs. Three different polyethylene glycols (PEGs) with different molar mass were used as the solvent. The average molar mass of PEGs used in this study was selected as 200, 300, and 400 g/mol. The physical and chemical properties of the polyethylene glycols and silica nanoparticles used as shown in Table 1 and Table 2.

Table 1. Properties of PEGs

Properties	PEG 200	PEG 300	PEG 400
Molecular weight (g/mol)	200	300	400
Density (kg/m^3)	1.1238	1.1250	1.1300
Flash temperature (℃)	150	220	305

Table 2. Properties of silica nanoparticle

Properties	Aerosil 200
Surface area (m^2/g)	200
Particle diameter (nm)	12
Tamped density (kg/m^3)	50
SiO_2 content (%)	99.8

Polyethylene glycols and silica particles were mixed with a high-speed mechanical mixer at 6000 rpm during the production of STFs. Silica particles were gradually added to prevent agglomeration and mixed until the suspension became homogeneous. The amount of fumed silica particles in the suspension was 25%(w/w).

Rheological properties of STFs were determined using Anton Paar MCR 102 tension controlled rheometer. Tests were carried out using a 25 mm diameter parallel plate apparatus. The gap between the plates was kept constant at 0.3 mm and all tests were performed at 25 ℃. Rheological measurements were made of 0-1000 s^{-1} shear rates. In the mixture, while shear-thinning behavior was observed at low shear rates, shear thickening was observed at high shear rates. In general, these mixtures exhibited the behavior of shear thinning between 0-200 s^{-1} and shear thickening between 200-1000 s^{-1} shear rates. The experimental parameters followed in the research are shown in Table 3.

Table 3. Experimental parameters

Sample	Temperature (K)	Time (hours)	Mixing Speed (rpm)	Aerosil	PEGs
1	298	-	-	-	200
2	298	1	6000	200	200
3	298	1	6000	200	300
4	298	1	6000	200	400

Table 4. Rheological model equations

No	**Models**	**Equations**
1	Power law	$\tau = \kappa.(\dot{\gamma})^n$
2	Bingham	$\tau = \tau_0 + \kappa.\dot{\gamma}$
3	Casson	$\tau^{0.5} = \tau_0 + \kappa.\dot{\gamma}^{0.5}$
4	Herschel-Bulkley	$\tau = \tau_0 + \kappa.\dot{\gamma}^n$
5	Sisko	$\tau = \kappa_\infty.\dot{\gamma} + \kappa.\dot{\gamma}^n$

The Non-Newtonian model equations used in the study given in Table 4. Correlation coefficients of theoretical equations in Table 5 and statistical error functions in Table 6 were analyzed and the most appropriate model equations were determined.

Table 5. Correlation coefficients for fumed silica-PEG mixtures in the first and second region at 298 K

Exp	**Model**	**First Region**				**Second Region**			
		n	**κ**	**τ_0**	**κ_∞**	**n**	**κ**	**τ_0**	**κ_∞**
1	1	0.99603	0.55967			0.99381	0.05621		
	2		0.05497	-0.0164			0.05371	0.17591	
	3		0.23450	-0.0035			0.23121	0.02931	
	4	0.98263	0.06033	-0.0569		1.04198	0.03936	1.39054	
	5	-0.0604	-0.0185		0.05495	0.89655	0.00625		0.05080
2	1	0.71471	6.68161			1.10787	18.5767		
	2		1.40504	25.9932			45.0013	-4814.7	
	3		1.00378	3.13339			7.05974	-24.101	
	4	0.75561	5.28216	6.66720		0.00001	3.14□10^9	-3.1□10^9	
	5	0.54776	8.59815		0.70092	-29.025	6.55876		37.8124
3	1	0.67095	12.3609			1.10693	27.8202		
	2		2.05292	43.4444			64.9175	-5784.3	
	3		1.18513	4.28628			8.48633	-26.051	
	4	0.67320	12.2001	0.61131		0.00006	5.70□10^8	-5.7□10^8	
	5	0.77710	11.5665		-1.4006	-43.856	10.4237		56.2807
	1	0.51375	32.6211			0.75771	325.867		
	2		2.98760	73.4298			54.1392	8191.11	
	3		1.27240	6.27467			6.42013	45.4158	
	4	0.50149	34.8680	-4.1584		0.35619	9118.50	-46340	
	5	0.47222	34.6863		0.44050	-52.208	12.1758		66.3696

Root mean square error (RMSE), Chi-square (□^{2}), residual sum of squares (SSR), error sum of squares (SSE), sum of squares (SST) and R-squared are statistical parameters. In order to investigate the reliability of the results, the most appropriate model was determined by applying statistical tests such as RMSE and Chi-square in the equations. In Table 6, the most suitable model equations were determined by statistical analysis.

Table 6. Statistical analysis for fumed silica-PEG mixtures in the first and second region

Exp	**Model**	**First Region**				**Second Region**			
		R^2	**RMSE**	**SSE**	**□^{2}**	**R^2**	**RMSE**	**SSE**	**□^{2}**
	1	0.99875	0.13729	0.13193	0.04398	0.99967	0.24562	0.42230	0.14077
	2	0.99877	0.13709	0.13155	0.04385	0.99967	0.24629	0.42460	0.14153
	3	0.99876	0.13750	0.13234	0.04411	0.99967	0.24598	0.42353	0.14118

1	4	0.99881	0.13481	0.12722	0.04241	0.99958	0.27639	0.53473	0.17824
	5	0.99877	0.13708	0.13153	0.04384	0.99967	0.24561	0.42227	0.14076
2	1	0.99791	4.58217	146.974	48.9914	0.86263	4456.45	1.39□10^{8}	4.63□10^{7}
	2	0.98922	10.4050	757.853	252.618	0.88312	4110.84	1.18□10^{8}	3.94□10^{7}
	3	0.99719	5.31310	197.603	65.8677	0.87038	4329.07	1.31□10^{8}	4.37□10^{7}
	4	0.99852	3.85050	103.784	34.5947	0.97611	1954.75	2.68□10^{7}	8.92□10^{6}
	5	0.99823	4.21485	124.355	41.4516	0.85599	4562.98	1.46□10^{8}	4.86□10^{7}
3	1	0.99891	4.85223	164.809	54.9364	0.93150	4389.34	1.35□10^{8}	1.50□10^{7}
	2	0.97982	20.8963	3056.60	1018.87	0.94462	3946.71	1.09□10^{8}	3.64□10^{7}
	3	0.99377	11.6118	943.830	314.610	0.93691	4212.50	1.24□10^{8}	4.14□10^{7}
	4	0.99891	4.84813	164.531	54.8435	0.99764	814.909	4.65□10^{6}	1.55□10^{6}
	5	0.99909	4.44115	138.067	46.0222	0.92450	4608.38	1.49□10^{8}	4.96□10^{7}
4	1	0.98645	11.9746	1003.73	334.578	0.95106	3116.68	6.80□10^{7}	2.27□10^{7}
	2	0.93399	26.4341	4891.34	1630.45	0.93098	3701.28	9.59□10^{7}	3.20□10^{7}
	3	0.97189	17.2508	2083.14	694.380	0.94131	3413.05	8.15□10^{7}	2.72□10^{7}
	4	0.98652	11.9459	998.937	332.979	0.97994	1995.69	2.79□10^{7}	9.29□10^{6}
	5	0.98669	11.8707	986.393	328.798	0.87380	5005.06	1.75□10^{8}	5.85□10^{7}

3. Results and Discussion

It is seen in Figure 1 PEG 200 showed Newtonian behavior. In the first region, all Fumed silica-PEG suspensions to the critical shear rate showed shear-thinning behavior, and then in the second region shear thickening behavior was seen. In all suspensions increase of molecular mass of polyethylene glycol used as a liquid medium cause higher viscosity of the mixture. Critical shear rate is an important parameter for solidation. This value defines the line between solid and liquid medium. Increasing PEG's molecular mass causes decreasing in critical shear rate.

In Figure 2, the relation between the shear rate and the shear stress of the fumed silica-PEGs mixtures was investigated. While non-Newtonian properties are observed in the mixtures, Newtonian properties are also observed in polyethylene glycol 200.

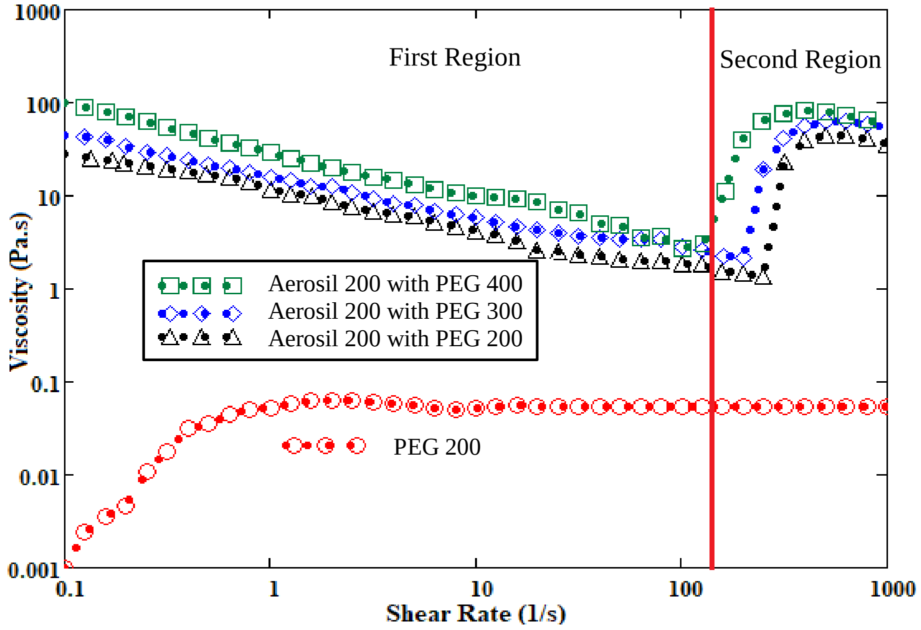

Figure 1. Change of viscosity with different shear rate for fumed silica-PEG mixtures

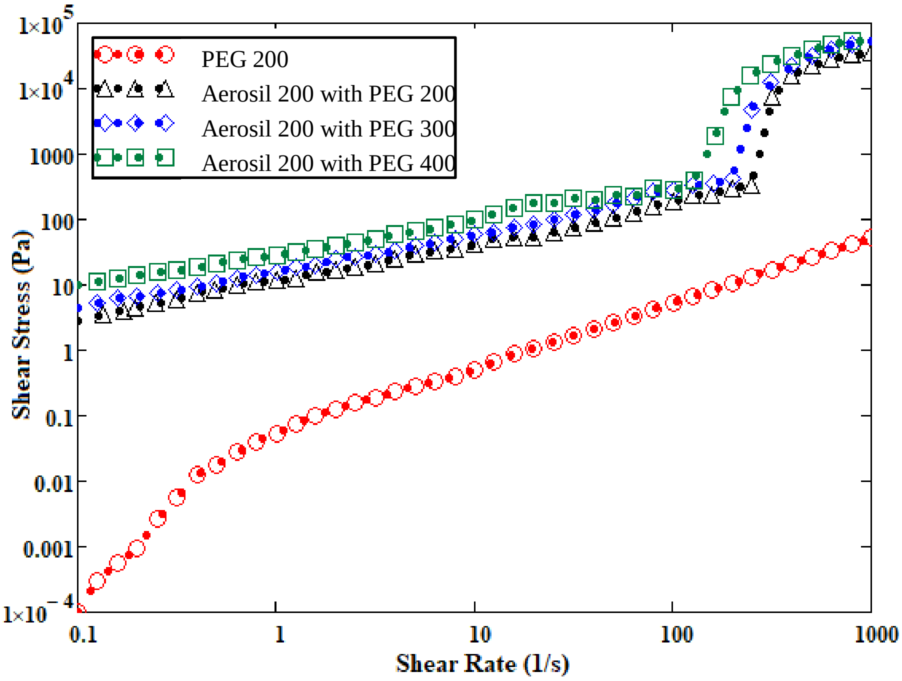

Figure 2. Change of shear stress with the different shear rate for fumed silica-PEG mixtures

In the FTIR spectrum in Fig. 4; 3450 cm^{-1} O-H stretching vibrations, 2950 cm^{-1} C-H stretching vibrations, and 1550 cm^{-1} C=O stretching vibrations. It also shows 1150 cm^{-1} C-O stretching vibrations, 1050 cm^{-1} Si-O-Si stretching vibrations, and 850 cm^{-1} Si-O stretching vibrations. FTIR spectrum of the samples was made with Shimadzu S11025C device.

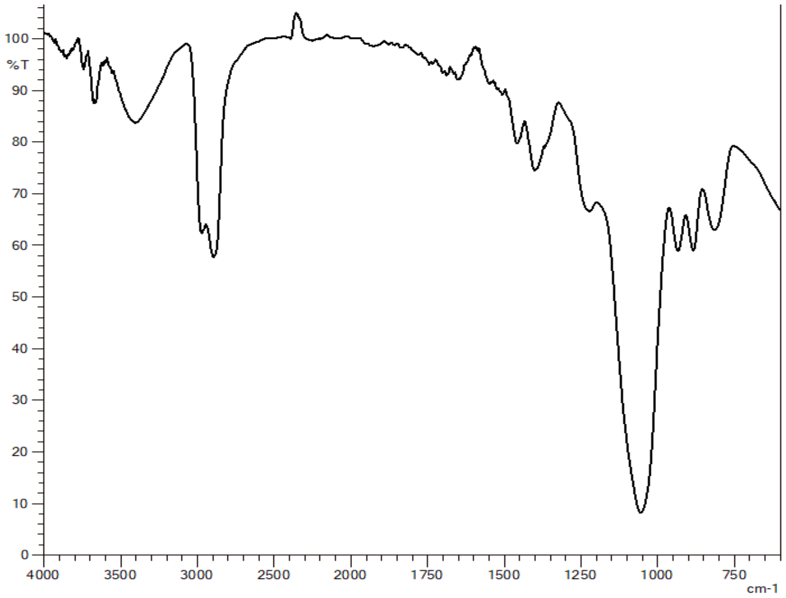

Figure 3. FTIR Spectrum for the mixture of Aerosil 200 and polyethylene glycol 200

4. Conclusions

In this study, fumed silica was dispersed in polyethylene glycol in colloidal structure. Physical attraction forces formed between them enabled the formation of shear thickening fluid by providing interaction between molecules. Three different PEGs were used to determine the effect of different PEGs in suspensions. The rheological behaviors of the suspensions produced were determined. It was observed that as the molecular weight increases, the critical shear rate decreases, and the viscosity increases. The experimental data and theoretical models were compared by statistical analysis. The most appropriate model was selected by determining the error functions and correlation coefficients. For fumed silica-PEG mixtures that have different rheological behavior in the first and second regions, the model equations are calculated separately. In order to investigate the reliability of the results obtained from the models, the values in which root mean square error (RMSE), Chi-square (X^2), residual sum of squares (SSR), error sum of squares (SSE), and the total sum of squares (SST) errors are minimum if R-squared (SST) errors are examined in these models. These statistical models were compared to have more accurate results. Fumed silica-PEG mixtures showed pseudo-plastic behavior in the first region and dilatant liquid behavior in the second region. In the first region, the Sisko model was determined as the most appropriate model for experimental data. In the second region, the Herschel-Bulkley model was found to be the most appropriate model.

The compliance to the Research and Publication Ethics: This study was carried out in accordance with the rules of research and publication ethics.

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References

[1] Hoffman R. L.,"Discontinuous and dilatant viscosity behavior in concentrated suspensions. II. Theory and experimental tests", *J. Colloid Interface Sci.*, 46(3), 491-506, 1974.

[2] Bossis G. and Brady J. F., "The rheology of Brownian suspensions," *J. Chem. Phys.*, 91(3), 1866-1874, 1989.

[3] Boersma W. H., Laven J., and Stein H. N., "Viscoelastic properties of concentrated shear-thickening dispersions," *J. Colloid Interface Sci.*, 149(1), 10-22, 1992.

[4] Lee B. W., Kim I. J., and Kim C. G., "The influence of the particle size of silica on the ballistic performance of fabrics impregnated with silica colloidal suspension," *J. Compos. Mater.*, 43(23), 2679-2698, 2009.

[5] Kalman D. P., Merrill R. L., Wagner N. J., and Wetzel E. D., "Effect of particle hardness on the penetration behavior of fabrics intercalated with dry particles and concentrated particle-fluid suspensions," *ACS Appl. Mater. Interfaces*, 1(11), 2602-2012, 2009.

[6] Baharvandi H. R., Alebooyeh M., Alizadeh M., Heydari M. S., Kordani N. and Khaksari P., "The influences of particle–particle interaction and viscosity of carrier fluid on characteristics of silica and calcium carbonate suspensions-coated Twaron® composite," *J. Exp. Nanosci.*, 11(7), 550–563, 2016.

[7] Hasanzadeh M., V. Mottaghitalab, and M. Rezaei, "Rheological and viscoelastic behavior of concentrated colloidal suspensions of silica nanoparticles: A response surface methodology approach," *Adv. Powder Technol.*, 26(6), 1570–1577, 2015.

[8] Gürgen S., “An investigation on composite laminates including shear thickening fluid under stab condition,” *J. Compos. Mater.,* 53(8), 1111–1122, 2019.

[9] Xu Y., “Stabbing Resistance of Soft Ballistic Body Armour Impregnated with Shear Thickening Fluid,” Ph. D. thesis, University of Manchester, Manchester, UK, 2016.

[10]Chen Q., Liu M., Xuan S., Jiang W., Cao S., and Gong X., “Shear dependent electrical property of conductive shear thickening fluid,” *Mater. Des.*, 121, 92–100, 2017.

[11]Sun L. L., Xiong D. S., and Xu C. Y., “Application of shear thickening fluid in ultra high molecular weight polyethylene fabric,” *J. Appl. Polym. Sci.,* 129(4), 1922–1928, 2013.

[12]Ge J., Tan Z., Li W. and Zhang H., “The rheological properties of shear thickening fluid reinforced with SiC nanowires,” *Results Phys.*, 7, 3369–3372, 2017.

[13]Hasanzadeh M. and Mottaghitalab V., “Tuning of the rheological properties of concentrated silica suspensions using carbon nanotubes,” *Rheol. Acta,* 55(9), 759–766, 2016.

[14]Zabet M., Trinh K., Toghiani H., Lacy T. E., Pittman C. U., and Kundu S., “Anisotropic Nanoparticles Contributing to Shear-Thickening Behavior of Fumed Silica Suspensions,” *ACS Omega*, 2(12), 8877–8887, 2017.

[15]Rubio-Hernández F. J., Gómez-Merino A. I., Páez-Flor N. M., and Velázquez-Navarro J. F., “On the steady shear behavior of hydrophobic fumed silica suspensions in PPG and PEG of low molecular weight,” *Soft Materials*, 15(1), 55-63, 2017.

[16]Santos J., Calero N., Trujillo-Cayado L. A. and Muñoz J., “Development and characterisation of a continuous phase based on a fumed silica and a green surfactant with emulsion applications,” *Colloids Surfaces A Physicochem. Engineering Aspects*, 555(20), 351-357, 2018.

[17]Contado C., Ravani L. and Passarella M., “Size characterization by Sedimentation Field Flow Fractionation of silica particles used as food additives,” *Anal. Chim. Acta*, 788, 183-192, 2013.

[18]Singh M., Verma S. K., Biswas I. and Mehta R., “Rheology of fumed silica and polyethylene glycol shear thickening suspension with nano-clay as an additive,” *Def. Sci. J.*, 69(4), 402-408, 2019.

[19]Mawkhlieng U. and Majumdar A., “Designing of hybrid soft body armour using high-performance unidirectional and woven fabrics impregnated with shear thickening fluid,” *Compos. Struct.*, 253, 2020.

[20]Majumdar A.,. Laha A, Bhattacharjee D., Biswas I. and Verma S., “Soft body armour development by silica particle based shear thickening fluid coated p-aramid fabrics,” *J. Text. Inst.*, 110(10), 1515–1518, 2019.

[21] Arora S., Majumdar A. and Butola B. S., “Soft armour design by angular stacking of shear thickening fluid impregnated high-performance fabrics for quasi-isotropic ballistic response,” *Compos. Struct.*, 233, 2020.

[22]Li T. T., Cen X., Peng H., Ren H., Han L., Lou C.W. and Lin J.H., “Rheological response and quasi-static stab resistance of STF/MWCNTs-impregnated aramid fabrics with different textures,” *J. Ind. Text.*, 50(3), 380–397, 2020.

[23]Zarei M. and Aalaie J., "Application of shear thickening fluids in material development," *J. Mater. Res. Technol.*, 9(5), 10411–10433, 2020.

[24]Lin K., Zhou A., Liu H., Liu Y. and Huang C., "Shear thickening fluid damper and its application to vibration mitigation of stay cable," *Structures*, 26, 214–223, 2020.

[25]Gürgen S. and Sofuoğlu M. A., "Vibration attenuation of sandwich structures filled with shear thickening fluids," *Compos. Part B Eng.*, 186, 2020.