The influence of carbon nanotube addition on the properties of shear thickening fluid

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Abstract. The properties of shear thickening fluid (STF), based on polypropylene glycol and amorphous silica, modified by the addition of multiwalled carbon nanotubes (MWCNTs), were studied. The STF's viscosity increases abruptly during impact tests. The addition of a small amount of carbon nanotubes (CNTs) to the STF, leads to an increase of the maximal viscosity from 2128 to 12,213 Pa·s. To show the differences between various compositions, the microstructures of fluids were observed by scanning electron microscopy. A pronounced influence of the CNTs on the ability of impact force absorption was noticed. The protective structure containing 55 and 0.25 vol% of fumed silica and CNTs, respectively, is able to absorb up to 74% of impact force.

Keywords. Shear thickening fluids; rheology; carbon nanotubes; fumed silica; force absorbing systems.

1. Introduction

Shear thickening fluids (STFs) can be used as a component of structures with high energy absorbing efficiency [1–3]. This possibility results from the fact that the viscosity of the STF increases abruptly with an increase of shear stress. In the case of sudden strike, STFs change properties from being viscous to elastic, providing a rigid, protective layer. This change is fully reversible—after the strike, the STF comes back to the liquid state. STFs are promising for various applications, such as liquid body armour [4,5], sport protectors, such as smart knee pads [6] and others. The STFs consist of suspensions of solid phases in a carrier liquid. Polyethylene or polypropylene glycols and nanoparticles of fumed silica are mostly used for the fabrication of STFs [7,8]. STFs can also contain some additional modifications. The reported values of the maximum viscosity of modified STFs are 600 Pa·s for STFs with SiC nanowires [9], 265 Pa·s for STFs modified with calcinated colloidal silica microspheres [10] and 168 Pa·s for STFs with graphene oxide [11]. The properties of STFs could also be modified by the addition of graphene nanoplatelets [12].

In this paper, the basic composition of the STF was modified by the minor addition of multiwalled carbon nanotubes (MWCNTs). The rheological properties and impact absorption abilities were measured and discussed.

2. Methods and materials

STFs were fabricated by mixing amorphous silica KE-S50, with an average particle size of 500 nm, from Nippon

Shokubai, with polypropylene glycol having a molar mass of 2000 g mol^{-1} . The contents of silica were 50, 53 and 55 vol%, respectively. The compositions of STFs were modified by the addition of MWCNTs (Nanocyl NC7000, with a diameter of 9.5 nm and a length of $1.5 \mu\text{m}$), with the amounts of 0.05, 0.15 and 0.25 vol%. The relationship between the viscosity and shear rate was determined using an ARES rheometer, equipped with two parallel plates ($\Phi 25 \text{ mm}$), with the gap being 0.3 mm. All the viscosity measurements were performed at room temperature. The solid components, fumed silica and carbon nanotubes (CNTs) were observed using HITACHI SU 8000 and S 5500 scanning electron microscopes (SEM).

The impact protective structures were fabricated by impregnation of polyester three-dimensional woven fabric M8180 from Baltex Ltd. (thickness of 7 mm and aerial mass of $500\text{--}550 \text{ g m}^{-2}$) with the STF and sealing it in silicone forms ($130 \times 30 \times 15 \text{ mm}$). The impact tests were carried out using a home-made impact tower, by dropping an impactor, with an energy of 5 J, onto the sample. The procedure is 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'. The rig for testing of the force absorption consists of a steel anvil and steel impactor that can be dropped on the anvil with required energy. The force sensor, for the registration of the force vs. time, is located under the anvil. Initially, the reference test, by dropping the impactor directly on the anvil (without the sample), was carried out. Subsequently the samples, $130 \times 30 \times 15 \text{ mm}$, were mounted on the anvil using tapes with four 2 kg weights. The impactor was elevated to the position

Figure 1. Viscosity vs. shear rate for the STFs with different contents of CNTs.

Table 1. Viscosity and shear rate for the STFs with different contents of CNTs*.

KE-S50 (vol%)	MWCNT (vol%)	Zero-shear-viscosity (Pa·s)	Highest viscosity (Pa·s)	Critical shear rate (s ⁻¹)
50	0	13	42	5.0
	0.05	17	66	6.3
	0.15	25	81	4.0
	0.25	58	94	3.2
53	0	15	375	2.5
	0.05	16	192	3.9
	0.15	19	740	2.0
	0.25	32	750	1.9
55	0	24	2128	0.6
	0.05	34	2996	0.8
	0.15	69	10,995	0.3
	0.25	36	12,213	0.6

*The experimental error in the viscosity and critical shear rate measurements can be in the range of 1–10% [13].

providing the impact energy of 5 J and dropped. The ability of force absorbing was calculated from relationship (1):

$$E = 1 - \frac{F_1}{F_2} * 100\% \quad (1)$$

where F_1 is the force recorded directly for the empty anvil (reference force) and F_2 is the force recorded for the sample.

3. Results and discussion

The values of the zero-shear-viscosity (z-s-v), the highest viscosity and the critical shear rate (shear rate at which viscosity increases abruptly) are presented in figure 1 and table 1.

The highest viscosity and the critical shear rate at which a drastic increase of the viscosity begins depend on both the concentration of fumed silica and CNTs. The highest viscosities were recorded for the fluids containing 55 vol% of silica.

Increasing the volume fraction of CNTs results in an increase in the value of the highest viscosity. The STF with 55 vol% of silica and 0.25 vol% of CNTs shows the highest value of the highest viscosity (12,213.3 Pa·s). This value is almost six times higher than the result for the CNT-free fluid. The critical strain rate initially slightly increases, for 0.05% CNT, and subsequently, for higher CNT concentrations, it noticeably decreases. The modified fluids also generally have higher zero-shear-viscosity, which means that they can be more efficiently immobilized in fabric spacer. Concentrations of CNTs higher than 0.25 vol% lead to a drastic increase of the

Figure 2. SEM images of (a) the starting mixture of KE-S50 silica and agglomerates of CNTs, (b) image of the KE-S50 silica, (c and d) the arrangement of solid components in the STF.

Figure 3. The mean values of absorbed force for STFs sealed in silicone forms after one, two and three strikes.

zero-shear-viscosity. The STF becomes friable and turns into a paste, making impregnation of the fabric impossible.

The solid substrates of the STFs were subjected to SEM observations (figure 2a and b). It can be seen that the silica used for testing has a slight tendency to agglomerate and the particles have a spherical shape (figure 2a and b). In addition, it has a fairly uniform size distribution with low surface

development. The CNTs, in contrast, have a huge tendency to agglomerate, forming bundles (figure 2a).

The silica powder and CNTs were mixed before STF fabrication (figure 2a). One can see that CNT agglomerates are covered by small particles of silica. In figure 2c and d the distribution of silica and CNTs in the STF is shown. The agglomerates disappeared and only silica particles are visible. We assume that mixing of fumed silica with CNTs in a carrier liquid leads to breaking of the agglomerates of the nanotubes and their even dispersion in the voids between the silica particles, leading to a higher friction in the course of shearing. This is evidenced by the lack of the agglomerates in figure 2c and d. This fact results in an increase in both the zero-shear-viscosity and the highest viscosity for the STFs containing CNTs, and show better force absorbing ability.

The synthesized STFs were used for impregnation of 3D fabric, which was subsequently sealed in thin silicon forms (130 × 30 × 15 mm) for impact tests. In figure 3, the average values of the absorbed impact force, after one, two and three strikes in the same place, are shown. One can see that a higher amount of fumed silica provides an increase in the absorbed force. The addition of CNTs causes an additional increase

in the force absorbing properties. The sample based on STF containing 55 vol% KE-S50 and 0.25 vol% CNTs shows the best absorbing properties (74% on the 1st strike).

The lowest value of absorbed force, for the first strike, was obtained for STF with 53% KE-S50 (66%). However, it is also shown that impregnation of the fabric spacer with the STF having 53 vol% of fumed silica and 0.25 vol% of CNT results in the force absorbing efficiency of 1.24% per 1 g of the sample when compared to pure silica, exhibiting 1.17% per 1 g of sample. The mean value of the stability changes is 4.6%. The best stability, which corresponds to a change of only 3.1%, is observed in the sample with 55 vol% of fumed silica and 0.25 vol% of CNTs in the fabric spacer. A slight decrease in absorbed force, after the 3rd strike, is caused by the change in the structure of silicon forms. The STF's structure does not undergo destruction because its properties change by the reversible rearrangement of silica particles in the carrier liquid. One can clearly see that the STFs modified by CNTs have a greater ability to absorb impact force than the ones based on fumed silica only.

4. Conclusions

Increasing the volume fraction of the CNTs in the silica-based STFs results in higher z-s-v and the highest viscosity values obtained in the rheological tests. This is caused by the fact that in modified fluids more particles are in a closer proximity to each other, which results in an increasing internal friction in the samples. Dispersed nanotubes have better opportunities to penetrate the voids within the silica clusters and block the deformation of the suspension.

The improved rheological properties have a positive influence on the impact force absorbing efficiency. The protective

structure containing 55 and 0.25 vol% of fumed silica and CNTs, respectively, is able to absorb up to 74% of impact force.

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