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Influence of carrier fluid on the electrokinetic and rheological properties of shear thickening fluids

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ABSTRACT

This paper presents a study on the influence of hydroxyl groups and oxygen atoms together with chain length and branching of carrier fluid on the rheological and electrokinetic properties of shear thickening fluid (STF). An STF is non-Newtonian fluid behaviour in which the increase of viscosity increases with the applied shear rate. Ethylene glycol, triethylene glycol, 1,3-propanediol, glycerin, poly(propylene glycol) of different molecular weight and poly(propylene glycol) triol were used as the carrier fluids (dispersants). Silica powder with an average particle size of 100 nm was used as the solid phase. Zeta potential, particle size distribution (by DLS technique), steady-state and dynamic rheological measurements were conducted. Experimental results indicate that a different amount of hydroxyl groups and oxygen atoms together with chain length and branching of carrier fluids have a significant influence on the intermolecular interactions thereby and on the rheological properties of suspensions. Depending on the composition, it is possible to control rheological properties. The use of a suitable carrier fluid allows the required pattern flow to be obtained, from Newtonian through shear thinning to shear thickening, given specific shear conditions.

1. Introduction

Shear thickening fluids (STFs), also known as dilatant fluids, are defined as steady non-Newtonian fluids in which viscosity increases with shear strain or shear rate [1]. Despite the fact that shear thickening behaviour is less common in industry than shear thinning [2–4], interest in shear thickening materials is growing. This is due to their ability to dampen and dissipate vibrations [5–7]. Consequently, research into the application of these fluids in dampers, superior shock absorbing solutions and sports equipment such as knee and elbow pads, shin guards, helmets and skis have been recently conducted. The principal objective is to attempt to design lightweight and flexible vest armour with a high degree of energy absorption, thereby allowing protection of the whole body [8]. The main advantage resulting from the implementation of STF is a reversible change of rheological properties, which ensures flexibility and comfort of use of protective composite materials together with their remarkable protective parameters at the moment of impact.

Generally, in preparations of STFs, hard metal oxide particles such as SiO_2, Al_2O_3 or TiO_2 are used as a solid phase. Ethylene glycol [9], glycerin [10,11] poly(ethylene oxide) [12,13], poly(propylene glycol) [14,15] and water [16] act as a carrier fluid. It is known that silicone oil [17] and carbon tetrachloride [18] are also used.

Thanks to the use of high-tech rheometers, light scattering techniques [19,20], rheo-optical measurements [21,22] and Stokesian dynamics simulations [23,24], the shear thickening phenomenon is more clear now than it was ten years ago. Studies have shown that the dilatant effect is mainly due to the reorganisation of ceramic powder particles into a suspension and hydro-clusters formation, leading to an increase of internal friction and partially jamming the fluid flow, e.g. as in corn-starch solutions [25–34]. Scientists have paid less attention to the issue of the role of the dispersing medium on STF properties. Kamibayashi et al. is one of the few research groups to have addressed this subject. They have studied the SiO_2 nanoparticle dispersed in poly(ethylene oxide) with a wide range of molecular weights [35], and have postulated polymeric bridging theory. They assumed that, when high shear rates were applied to a suspension consisting of polymeric coils and nanoparticles, a three-dimensional structure was formed. The 3D network is a result of both polymer-polymer and particle-polymer connections (interchain associations). As a consequence, an increase in viscosity and elasticity was observed. Additionally, Osman et al. [36] and Shenoy et al. [37] have revealed that the polymeric coils could form different a conformation depending on the length and apparent functional groups of the polymer. How the polymeric chain adsorbs onto the surface of the solid particles significantly influences the mechanism of interaction, and thereby electrokinetic and rheological

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properties of the fluid [38–43]. Saito et al. has also studied a correlation between the particle size of nanosilica and associating polymer – hydrophobically modified ethoxylated urethane (HEUR) [44]. It was observed that at constant concentration but variable particle size of the solid phase the rheological nature of tested suspensions had changed from Newtonian by shear thinning to shear thickening. They have stated that the HEUR polymer causes an increase in the viscosity and dynamic modulus of samples, but their values decrease with decreasing particle size. Nevertheless, based on literature review, there is still no detailed information about the influence of hydroxyl groups, oxygen atoms and branching of carrier fluid on the electrokinetic and the rheological properties of STF. Previous research has focused above all only on the length of the polymeric chain used as a small addition to STFs [35–46]. Tang et al. as pioneers have numerically studied the flow behaviour of the power-law non-Newtonian model in the electroosmotic flow. The viscosity is defined as

$$\eta = \eta_0 \dot{\gamma}^{n-1}, \tag{1}$$

where for $n < 1$ the fluid is shear thinning, $n > 1$ the fluid is shear thickening and $n = 1$ the fluid is Newtonian ($\eta = \eta_0$). The exponent n plays an important role. It was found that the fluid rheological character is capable of changing the electroosmotic flow pattern significantly and the power-law. The research shows that shear thickening fluid is more difficult to grow into a plug-like flow than Newtonian fluid in a channel [47].

This work presents the studies concerning the effect of the type of carrier fluid on the rheological and electrokinetic properties of STF. For this purpose, liquids with a different amount of hydroxyl groups and oxygen atoms together with different chain length and branching were used as carrier fluids (dispersants). The main aim of the research was to examine how the nature of the carrier fluid affects intermolecular interactions and the dilatant effect of studied suspensions.

2. Materials and methods

2.1. Materials

An amorphous silica powder (*Nippon Shokubai*) made by the Stöber process with an average particle size in the range of 100–200 nm, density of 1.96 g/cm^3 and a specific surface area of 132.2 m2/g was used as the solid phase. Specific surface area, density and microscopic studies were carried out to characterize the physicochemical properties of solid materials. Identification of the specific surface area was evaluated by a Brunauer-Emmett-Teller adsorption isotherm on ASAP 2020 (Micromeritics, USA). Density was determined using helium pycnometer AccuPyc 1330 Pycnometer (Micromeritics, USA). The morphology and the microstructure were investigated by Scanning Electron Microscopy, SEM (DSM 950, Zeiss, Germany). The SEM image (Fig. 1) showed the spherical shape of silica powder, where particle size was in the range from 0.1 to 0.2 µm. It was observed that the particles exhibited a slight tendency to agglomerate.

Ethylene glycol, triethylene glycol, 1,3-propanediol, glycerin, poly(-propylene glycol) of different molecular weight and poly(propylene glycol) triol were used as the carrier fluids (Fig. 2). All were supplied by Sigma-Aldrich. Table 1 presents their physicochemical properties.

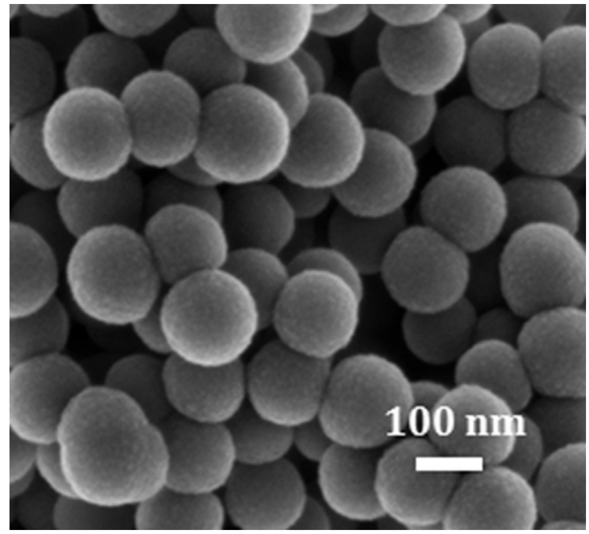

Fig. 1. SEM image of silica.

2.2. Characterization of the electrokinetic properties of SiO_2 suspensions

The characterization of the electrokinetic properties of SiO_2 suspensions were examined in order to investigate the influence of the microstructure of the carrier fluid on the stability of the suspension, which can significantly affect its rheological behaviour. It is known that by increasing the stability of the suspensions and, as a consequence, decreasing the particles' interactions, the shear-thickening effect can be reduced if not suppressed [48]. The numerical calculation shows this effect can be particularly seen for long and brush polymer structures [49]. The characterization of the electrokinetic properties of SiO_2 suspensions was examined by zeta potential and particle size distribution measurements.

The zeta potential and particle size distribution measurements of suspensions based on 0.01 wt% SiO_2 in aqueous (measurements were conduct in deionized water of pH 7.3) and non-aqueous dispersions were conducted on a ZetasizerNanoZS(Malvern Instruments, UK). The apparatus determines the size by measuring the Brownian motion of the particles in a suspension using Dynamic Light Scattering. The zeta potential was measured using Laser Doppler Micro-electrophoresis depending on the carrier fluid. Before measurements were taken, the samples were ultrasonicated to remove air bubbles and breakup agglomerates at a frequency of approximately 40 kHz for 5 min. After that, samples were poured into a *DipCell* cuvette for zeta potential measurements and *DT S0012* for particle size measurements. The dielectric constants of the carriers used in zeta potential measurements were determined based on literature and experimental data [50]. The backscattering angle of laser radiation used in particle size distribution measurements was 173°. All studies were taken at 25 °C and replicated three times.

2.3. Preparation of shear thickening fluids

The suspensions were obtained by mixing dry silica powder with an organic dispersant or water using the R50D mechanical stirrer (Ingenieurbüro CAT, Germany) with a stainless steel propeller mixing for 1–3 h. The mixing time depended on the composition and lasted until the sample was completely homogeneous. The mixing speed was from 100 to 300 rpm, and the solid loading was 50 vol%. Application of 50 vol% of the powder allowed authors to obtain a stable suspension over time. Application of a lower concentration of powder resulted in the sedimentation of suspension where a short organic chain of carrier fluid was applied, e.g. EG, 1,3-PD. On the other hand, application of more than 50 vol% of ceramic powder, in the case of a long polymer chain such as PPGtriol, was impossible to obtain.

2.4. Characterization of the rheological properties of SiO_2 suspensions

To determine viscosity as a function of shear rate and viscoelastic properties of the samples a KinexusPro rotational rheometer (Malvern