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Dilatant effect enhancers for silica dispersions in poly(propylene glycols)

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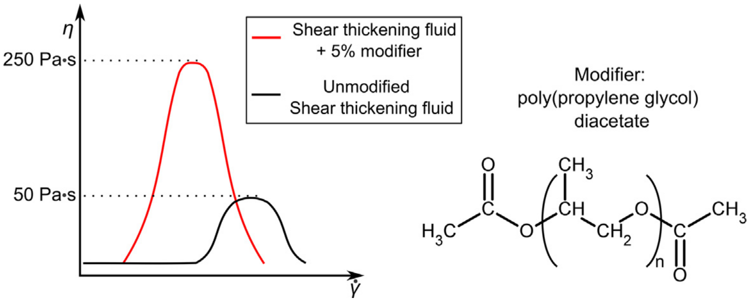
GRAPHICAL ABSTRACT



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ABSTRACT

Shear thickening fluids have found many applications in energy damping materials such as sports guards and liquid body armors. Therefore, an additive which could tailor the dilatant properties of such fluids without significantly affecting other properties, especially zero shear viscosity, could significantly increase the versatility of protective materials based on shear thickening fluids. In this paper, poly(propylene glycols) (PPGs) diacetates are investigated as dilatant effect enhancers for nano-silica dispersions in poly(propylene glycols). The influence of the modifiers on rheological properties of the dispersion is studied and discussed. Additionally, FTIR and rheological properties measurements are conducted in order to determine relative interactions strength between hydroxyl groups of PPGs and silica and carbonyl groups of PPG diacetates. Our findings suggest that the relative attractive interaction strength in studied systems can be arranged in the following order: C=O—C=O < C=O—OH < OH—OH. Therefore, the addition of PPG diacetate hinders the attractive interactions between liquid and solid. We report that the addition of diacetates can lead both to enhancement and deterioration of dilatant effect depending on the concentration of the modifier and its chain length. Based on conducted measurements and literature data, mechanism explaining that phenomenon is suggested. As a result, we propose an easy to make and cheap dilatant effect enhancer for widely used shear thickening fluids which, when used in small amounts (1–2.5%), raises the viscosity jump drastically. Additionally, the presence of the modifier does not significantly affect the zero shear viscosity of the shear thickening fluid.

1. Introduction

Incorporation of shear thickening fluids (STF) into liquid body armors, sports protectors and vibration damping materials raises the need for better control over shear thickening phenomena [1–5]. Silica dispersions in organic media are one of the most promising systems for such applications [1–5]. The rheological character of these shear thickening dispersions is explained by hydrocluster model (Fig. 1) [6–8].

At low shear rates, the solid particles are randomly suspended in the dispersion (equilibrium state). The formation of layered

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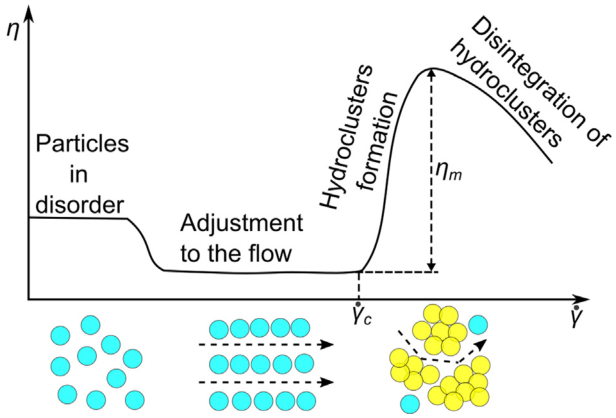

Fig. 1. Visualization of rheological behavior of shear thickening silica dispersions in accordance with the hydrocluster model. η_m is the viscosity jump and $\dot{\gamma}_c$ is the critical shear rate. Blue circles represent silica particles, yellow ones represent silica particles in hydroclusters. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

structures of solid particles occurs as the share rate increases and thus shear thinning behavior is observed. Layered structures disorder when the shear rate exceeds critical value ($\dot{\gamma}_c$). Groups of particles, known as hydroclusters, are being formed which results in a high increase in viscosity [6–8]. This increase in viscosity is also called the dilatant effect [9]. Further increase in shear rate leads to the disintegration of hydroclusters and shear thinning behavior is observed once more [6]. As the viscosity jump increases, the energy scattering ability of STF increases as well and thus its performance in guards and armors [1,2,6].

There are various factors which influence the properties of silica STF: solid phase concentration; solid particle size; solid particle size distribution; properties of the liquid phase. The dependence of dispersion rheological properties on silica concentration and its particle size has been already well established [4,10]. Moreover, recent studies have been focused on the modification of silica surface and its impact on rheological properties of STFs [11,12]. Various liquid phases have been also studied, e.g. ethylene glycol (EG), propylene glycol (PG), poly(ethylene glycol) (PEG), poly(propylene glycol) (PPG) and poly(ethylene imine) (PEI) [4,5,9,10,13–17]. According to the current knowledge, the simplest way to enhance the viscosity jump (η_m) of STF is to increase the silica concentration or to use silica of smaller particle size [13]. Both methods lead to increase in zero shear viscosity (η_0), which is usually unfavorable for industrial applications. Furthermore, the second method can be expensive due to the high cost of silica with a small diameter and narrow size distribution [10,18]. The influence of interactions present in silica dispersions (e.g. H-bonds and electrostatic interactions) on rheological properties and stability of silica dispersions has recently been investigated in several publications [16,19–25], however, to the best of authors' knowledge, there is only a little attempt to enhance the dumping properties of STFs by chemical modification of commonly applied liquid phases – PEGs and PPGs [20].

The first silica dispersions which captured researchers' attention were water-based and have been the most extensively studied silica colloids [23–25]. These aqueous sols are remarkably resistant to flocculation caused by electrolytes, even when pH is close to point of zero charge. Both colloidal silica and fumed silica aqueous sols exhibit that stability [26,27]. The behavior of organic dispersions strongly depends on the type of the continuous phase. In nonpolar liquids (ex. hydrocarbons) interactions between continuous and solid phases are limited, therefore silica particles tend to form interparticle linkages (H-bonds between Si—OH groups) which leads to gel formation [22,23,28]. On the other hand, there are numerous reports on stable silica dispersions in polar organic solvents, such as low molecular weight alcohols, acetone and dioxane [29–31] and also in oligomers including PEI [17], PEG and PPG [10,20,21]. Researchers associate sols stability with the presence of short-range repulsion forces between solid state particles that can be measured with atomic force microscopy. This phenomenon is observed in aqueous sols [32,33] and in silica dispersions in polar organic liquids such as ethylene glycol and PEI [17,34]. Researchers correlate these repulsion forces with the presence of thin solvation layer formed on the surface of silica particles which are suspended in liquid matrix. The nature of this layer is still disputed among scientists [32,33,35]. According to one of the theories, the solvation layer is formed due to the formation of hydrogen bonds (H-bonds) between suspending matrix molecules and Si—OH groups of the suspended phase. Solid phase particles are surrounded by the molecules of the continuous phase and have limited ability to form interparticle interaction, thus the sols exhibit high stability [33,35]. On the other hand, Vigil et al. proposes that a thin layer of silica-gel is formed on the surface of silica particles as a result of interaction with liquid phase molecules (in this case water) [32]. That layer consists of silanol and silicic acid groups and sterically impedes the interactions between solid particles in the dispersion. Swarna et al. investigated the interactions between suspending matrix and cornstarch in aqueous suspensions with the addition of polyols such as glycerol, EG and PEG [19]. Cornstarch, like hydrophilic silica, is able to form interparticle H-bonds with other solid particles and the molecules of suspending matrix. Addition of molecules with polar groups results in an increased number of polar interactions between molecules of the liquid phase. According to authors, new H-bond linkages impose certain arrangement of molecules of the liquid phase, which affects the rheological properties of the whole dispersion. As a result, an increase in η_m and η_0 values of the starch aqueous dispersion is observed. In another research, Raghavan et al. also points out the influence of H-bond formation on properties and stability of STFs [20]. Authors studied rheological properties of fumed silica dispersions in EG, PG, PEGs and PPGs and conclude that H-bonds have a greater impact on the behavior of silica dispersions than electrostatic interactions or Van der Waals forces. There seems to be an agreement among researchers that the existence of attractive forces between dispersed nanoparticles is crucial for the dispersion to exhibit shear thickening behavior, which is yet again summarized by a recent study of Yang et al. [24]. When the dispersion is at rest or under shear stress lower than the critical value, the attractive forces between molecules of the liquid phase and SiO_2 particles (in this case H-bonds) overcome the silica tendency to agglomerate. As the shear stress rises over the critical value, the H-bonds break and the solid particles connect with each other forming hydroclusters which disrupt the flow leading to an increase in the viscosity of the dispersion.

In this study, interactions between silica nanoparticles and liquid suspending medium (PPG) are tailored by addition of PPG diacetates. Rheological properties of prepared mixtures are measured to determine the viscosity jumps (η_m) and critical shear rates ($\dot{\gamma}_c$). In order to understand how interactions between all components of the dispersion are altered, IR spectra of mixtures with and without silica nanoparticles containing different amounts of modifier are collected. This approach is derived from earlier publications on the matter [19,36–39]. As a result, this work presents an easy to conduct chemical modification of the continuous phase of STF which significantly changes its rheological properties and provides insight into modification mechanism, which could lead to better understanding of shear thickening phenomenon [40,41].