



Rheological behavior of hydrophobic fumed silica suspensions in different alkanes



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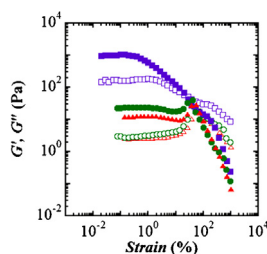
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HIGHLIGHTS

- Hydrophobic fumed silica modified by hexadecyl chain were well dispersed in three alkanes.
- Rheological behavior of suspensions depended on chain length of dispersion mediums.
- Suspensions in hexadecane were harder and more easily broken up than those in octane and dodecane.
- Suspensions in octane and dodecane showed unprecedented behavior in nonlinear regions.

GRAPHICAL ABSTRACT

Storage (G' : filled symbols) and loss (G'' : opened symbols) moduli of hexadecyltrimethoxysilane-treated fumed silica, VP-NKC 130 dispersed in octane (red triangles), dodecane (green circles) and hexadecane (purple squares) as a function of strain at the silica concentration of $\phi=0.07$ and at a fixed angular frequency 0.01 rad/s.



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ABSTRACT

Rheological behavior of hydrophobic fumed silica with hexadecyl chains dispersed in three alkanes: octane, dodecane, and hexadecane, were investigated as a function of the silica concentration, in order to understand the mutual interactions between the hexadecyl chains and the different alkanes. From a results of transient shear stress and steady-state shear viscosity tests, we can report that aggregated structures of the suspensions in hexadecane were harder and more easily broken up under shear than those in octane and dodecane. Small amplitude oscillatory shear (SAOS) tests showed that all suspensions behaved as a gel-like matter. According to the fractal gel model, the suspension in hexadecane was classified as a transient gel, whereas the suspensions in octane and dodecane corresponded to a strong-link gel. However, the fractal dimensions of all suspensions were almost independent of the dispersion medium. Large amplitude oscillatory shear (LAOS) tests showed that the reduced storage and loss moduli of the suspensions in hexadecane were superimposed on the respective curves, irrespective of the silica concentration, whereas those in octane and dodecane strongly depended on the silica concentration. Such differences indicated that the former dispersion medium was better incorporated with the hexadecyl chains than the latter dispersion media.

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1. Introduction

Hydrophobic fumed silica powders are often prepared by the modification of surface silanol groups with alkyl groups through chemical reactions. These powders provide a volume-filling network structure (gel) in polar liquids owing to the strong mutual

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interactions between the alkyl groups. Thus, the corresponding fumed silica suspensions show some interesting rheological responses, which have previously been observed by Lee and Rupprecht [1], Khan and co-workers [2] and Kawaguchi's groups [3–7]. Lee and Rupprecht, as well as Khan et al. have mainly focused on steady-state shear viscosities and linear dynamic viscoelastic moduli, together with the storage modulus at a fixed strain as a function time. Kawaguchi et al. have investigated not only steady-state shear viscosities and linear dynamic viscoelastic moduli [3–5,7], but also the transient shear stress [6].

On the other hand, a systematic study of the rheological behavior of hydrophobic fumed silica suspensions in non-polar liquids such as alkanes has not been previously performed. Ando and Kawaguchi [6] have reported the preliminary results of steady-state shear stress experiments for a hexadecyltrimethoxysilane-treated fumed silica suspension, at fixed silica content, in hexadecane. Such a hydrophobic suspension was in the sol state and it showed shear thinning behavior, which is usually observed for suspensions with weakly aggregated structures in the particles whose structures are being gradually deformed under shear flow.

Mucic et al. [8,9] have performed an in-depth investigation of the adsorption of different alkane oils into alkyltrimethylammonium bromide layers, which were spread at water and alkane oil interfaces. The authors pointed out that for short chain surfactants, the oil molecules were embedded into the surfactant layer, whereas for long chain surfactants, the short alkane oils were squeezed out from the surfactant layer.

Thus, it can be expected that when the hexadecyltrimethoxysilane-treated fumed silica powders are suspended in a series of alkanes with different chain lengths, the mutual interactions between hexadecyl chains on the corresponding fumed silica should vary systematically, and should provide new and sophisticated rheological responses of the hydrophobic silica suspensions. In this study, we investigated the rheological responses of the hydrophobic fumed silica powders with hexadecyl chains, dispersed in three different alkanes, namely octane, dodecane, and hexadecane, as a function of silica concentration. The rheological measurements were carried out using the following tests: the transient shear stress test, the steady-state shear viscosity test, the small amplitude oscillatory shear (SAOS) test, and the large amplitude oscillatory shear (LAOS) test. The effects of alkyl chain length in the dispersion medium on the rheological behavior of hydrophobic silica suspensions will be discussed. This will be done in terms of the incorporation or mutual interaction of different alkanes with the hexadecyl chains attached on the silica surface.

2. Materials and methods

2.1. Materials

Hydrophobic fumed silica powders, VP-NKC130 (Nippon Aerosil Co. Ltd, Yokkaichi, Japan) were obtained by silane coupling reactions between hexadecyltrimethoxysilane and silanol groups of Aerosil 130 silica powders. According to the manufacturer of the VP-NKC130, the primary silica has an average diameter of 16 nm, a surface area of 130 m²/g, and a silanol density of 0.1 nm⁻², but the silica powders tend to form aggregates in air due to the interactions between the hexadecyl chains attached on the silica surfaces. Additionally, a carbon content in the corresponding silica is 8.8% (w/w) and then, the volume of the hexadecyl chain may be negligible to determine volume fraction due to a small carbon content of the silica particle.

Special grade octane, dodecane, and hexadecane purchased from Wako Pure Chemical Industries, Ltd. were distilled under reduced pressure and they were used for dispersion media. The

viscosities of octane, dodecane and hexadecane at 25 °C are 0.570, 1.383, and 3.039 mPa s, respectively [10,11].

2.2. Preparation of silica suspensions

To prepare hydrophobic silica suspensions, a specific weighed amount of the VP-NKC130 silica powder was added to 5 mL of dispersion medium in a 30 mL glass bottle. The silica concentrations, expressed by the volume fraction (ϕ) of silica in the suspensions, ranged from 0.05 to 0.09. The resulting suspensions were agitated for 1 min and then deformed for 2 min using a hybrid mixer (Keyence HM-500). Hereafter, the suspensions were dispersed at 1500 rpm and 25 °C for 1 day, by a mixer (Tokyo Rikakikai EYELA CM1000) in an incubator (Sanyo MIR-153). They were then subjected to the rheological measurements after having been shaken for 1 min, followed by 2 min of deforming, using the same hybrid mixer.

2.3. Rheological measurements

The suspensions were preconditioned by shearing at a fixed shear rate of 1000 s⁻¹ for 10 min, followed by a 2 min rest period. They were then subjected to shear flow at given shear rates ranging from 0.01 to 1000 s⁻¹, in order to confirm the achievement of a steady state as a function of time. This was usually carried out during a 60 min period at 25 °C, using a rheometer (Paar Physica MCR-300) with a cone-plate fixture, with a cone angle of 1° and a diameter of 50 mm (CP50-1).

For every measurement of the small amplitude oscillatory shear (SAOS) tests and large amplitude oscillatory shear (LAOS) tests, the suspensions were preconditioned by shearing at a shear rate of 1000 s⁻¹ for 10 min. Subsequently they were carried out the suspensions were subjected to dynamic measurements of storage (G') and loss (G'') moduli at a fixed strain of 0.01% and a constant angular frequency of 1 rad/s using the same rheometer as the shear flow measurements. After the steady state values of G' and G'' were obtained, the samples were allowed to rest for 5 min, after which their dynamic strain sweep measurements were performed by the strain sweep mode and the angular frequency mode using the same rheometer. The former mode was carried out ranging from 0.01 to 1000% at a fixed angular frequency of 1 rad/s, whereas the latter mode was carried out ranging from 1 to 100 rad/s at a fixed shear strain less than 1%. In order to confirm whether the slippages of the samples occur or not, smooth and serrated plates were used for the measurements. Moreover, respective measurements were repeated at least twice and their experimental errors were within 10%.

3. Results and discussion

Any differences in the rheological responses between the smooth and serrated plates were not observed. Thus, it can be concluded that the slippages of the samples do not occur in this study.

3.1. Transient shear stress

For rheological complex suspensions, it is important to understand the transient behavior before examining the steady-state responses. Fig. 1a–c shows typical shear stress developments of the suspensions with $\phi = 0.07$ in octane, dodecane, and hexadecane at the shear rates of 0.1, 1, 10, 100, and 1000 s⁻¹ together with an inset for the shorter time than 30 s, respectively.

For the suspensions in octane and dodecane, the shear stress at the lowest shear rate of 0.1 s⁻¹ gradually increases with an increase in time. The shear stresses below a shear rate of 100 s⁻¹ increase

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