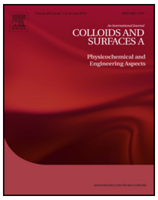
Colloids and Surfaces A: Physicochem. Eng. Aspects 458 (2014) 142–146

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa



Effects of heating and shearing on the rheological properties of poly(tetra fluoro-ethylene) suspensions in silicone oil

Toshiaki Yamaguchi[a], Keisuke Kayano[b], Kazutaka Noro[b], Masami Kawaguchi[a,*]

[a] *Division of Chemistry for Materials, Graduate School of Engineering, Mie University 1577 Kurimamachiya, Tsu 514-8507, Mie, Japan*
[b] *Sumico Lubricant Co., Ltd. Kamikasada, Inabe, Inabe 511-0207, Mie, Japan*

HIGHLIGHTS

- Effects of heating and shearing on the rheological responses of PTFE suspensions in silicone oil were measured.
- Shearing treatment for the rheological properties was more effective than heating treatment.
- Comparison of the steady state flow curves to the Herschel–Bulkley equation was fine, regardless of the treatments.

ARTICLE INFO

Article history:
Received 13 July 2013
Received in revised form 27 January 2014
Accepted 4 February 2014
Available online 12 February 2014

Keywords:
Suspension
Silicone oil
PTFE particles
Heating
Shearing
Rheology

ABSTRACT

The effects of heating and shearing on the rheological properties of poly(tetra fluoro-ethylene) (PTFE, 0.2 μm particles) suspensions in silicone oil 1000 cSt were investigated. The suspensions were heated at 140 °C for 1 day and then sheared at a rate of 1000 s^{-1} for 30 min. Four suspensions were prepared: the unheated and unsheared suspension, the heated and unsheared suspension, the unheated and sheared suspension, and the heated and sheared suspension. Hysteresis loops, stress–strain (*S*–*S*) sweep curves, oscillatory dynamic moduli, and steady state shear flow curves of the suspensions were measured at 25 °C. No hysteresis was observed in the hysteresis loops for any of the suspensions. Two yield stresses were observed in the *S*–*S* sweep curves of the unsheared suspensions. Shearing caused the lower yield stress to fade but retained the higher yield stress. The *S*–*S* sweep curves of the sheared suspensions were nearly superimposable regardless of heating. The movement of the position of a target in the sheared suspensions occurred at a larger strain than that in the unsheared suspensions. Shearing caused changes in the oscillatory dynamic moduli of storage (G') and loss (G'') as a function of strain: the unsheared suspensions behaved as solid-like viscoelastic matter, whereas the sheared suspensions gave similar magnitudes of the G' and G'' values in the linear regions. Beyond the linear region, the G'' value showed strain overshoot regardless of the treatment. The steady state shear flow curves of the suspensions were compared with the Herschel–Bulkley equation; their fits were comparable and the calculated parameters in the equation were well correlated to the historical treatments of the suspensions.

1. Introduction

Silicone oils are widely applied in industrial products due to their unique properties of high lubricity, non-toxicity, extensive spreading, and stable film formation [1]. Owing to such inert characteristics, they are usually employed as suspensions consisting essentially of a liquid (continuous phase) and solid particles (dispersed phase) [2–9]. The solids are generally organic or inorganic particles with a variety of shapes, such as rods, disks, and prolate or oblate spheroids. Silicone oils are often employed as a continuous phase in electrorheological fluids due to their low relative polarizabilities [2].

The individual particles in the continuous phase of a suspension remain separate due to repulsive interparticle forces, or aggregate when attractive interparticle forces dominate. Thus, the type of dominant interparticle interaction, such as electrostatic repulsion, van der Waals forces, and steric repulsion, should determine the microstructure of the solid particle phase. These interparticle interactions also control their characteristic rheological responses, such as yield stress, shear-thinning, shear-thickening, and thixotropy.

---

[*] Corresponding author. Tel.: +81 59 231 9432; fax: +81 59 231 9433.
E-mail address: kawaguti@chem.mie-u.ac.jp (M. Kawaguchi).

http://dx.doi.org/10.1016/j.colsurfa.2014.02.011
0927-7757/© 2014 Elsevier B.V. All rights reserved.

Therefore, understanding of the corresponding rheological properties would allow us to obtain useful information about the formation of stable suspensions [2,10,11].

If non-polar and inert particles are dispersed into silicone oils to prepare suspensions, van der Waals forces should play an important role in the microstructural arrangement of the particles. Even for inert suspensions, particle microstructures should be formed at higher particle concentrations, and such microstructures should be characterized by non-Newtonian rheological responses. Thus, examination of the rheological behavior should lead to a clear understanding of interparticle attractive forces at work in the suspensions.

In this paper, we report our studies of the hysteresis loops, yield stresses, dynamic moduli, and steady state stresses of suspensions, comprising a silicone oil continuous phase (85% of the mass of the suspension) and a dispersed phase of inert poly (tetra fluoro-ethylene) (PTFE) particles. Such PTFE suspensions in silicone oil can be classified as inert suspensions, in which van der Waals forces dictate the particle microstructures. We explored the effects of shearing and heating on the rheological properties of the suspensions. Finally, we focused on the steady state shear flow curves and compared them with the Herschel–Bulkley equation [12].

2. Materials and methods

2.1. Samples

Silicone oil with a dynamic viscosity of 1000 cSt ($M_w = 17 \times 10^3$) was supplied from Dow Corning Toray Co., Ltd. PTFE particles with diameters of 0.2 µm (TLP-10F-1) supplied from Du Pont-Mitsui Fluorochemicals Co., Ltd were sphere in the shape and polydisperse.

To prepare the suspension, PTFE particles (30 g) were added to the silicone oil (170 g) in a 500 mL polypropylene bottle. After agitation at 3600 rpm for 1 day in a mixer (T.K. Mycolloider Model L, Tokushu Kika Kogyo Co. Ltd.), the mixture was treated in a three roller mill (Model S-2 × 6, Inoue Mfg. Inc.) at ambient temperature for 5 min. Half of the resulting suspension, designated as the unsheared suspension was set aside. The remaining portion was heated at 140 °C in an oven (Model DX400, Yamato Scientific Co. Ltd.) for 1 day (the heated suspension). After heat treatment, the two suspensions were stored in the oven at 25 °C.

To investigate the effects of shearing on the rheological properties, the suspensions were sheared for 30 min at 25 °C at a shear rate of 1000 s^{-1} using a rheometer (HAAKE RheoScope 1, Thermo Scientific) with a cone-plate fixture (cone angle = 1°, diameter = 35 mm (C35/1-Ti) and a frosted glass plate, which is designed by the concept of rheo-optics consisting of rheological and microscopic technique. The microscope is embedded under the plate. The image of the sample can be observed with a 20 times magnification objective, and it can be captured at 15 flames per second. Each image size is 190 × 140 $\mu\mathrm{m}^2$ with a resolution of 1 µm. The frosted glass plate prevented wall slip in the suspension samples. Therefore, four suspensions were prepared: the unheated and unsheared suspension (suspension A), the heated and unsheared suspension (suspension B), the unheated and sheared suspension (suspension C), and the heated and sheared suspension (suspension D).

2.2. Rheological measurements

For the rheological studies, the suspensions C and D were allowed to stand for 60 min after shearing, and then were subjected to hysteresis loop measurements from 0.01 to 1000 s^{-1} over 1000 s. Shear stress steps were examined from 0.1 to 1500 Pa, and dynamic viscoelastic moduli were measured under strain oscillatory ranges from 0.01% to 1000% at a fixed angular frequency of 1 rad s^{-1}. Transient steady state stresses were evaluated at fixed shear rates ranging from 0.1 to 1000 s^{-1} and at 25 °C using the same rheometer with the same configuration described above. An identical set of rheological responses were measured for the unsheared suspensions A and B. The rheological measurements were repeated at least twice and their experimental errors in the rheological data were within 5%.

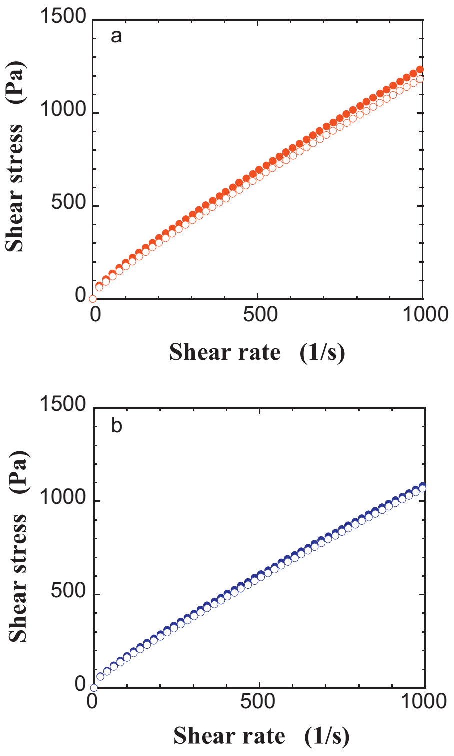


Fig. 1. Hysteresis loops of (a) the suspensions A (filled symbol) and C (open symbol) and (b) the suspensions B (filled symbol) and D (open symbol).

3. Results and discussion

3.1. Hysteresis loops

Hysteresis loop measurements examine the thixotropic behavior of colloidal dispersions owing to changes in microstructures, such as network-like structures, under shear flow. Thixotropic behavior is displayed when the shear stress measured by progressively increasing the shear rate is larger than that measured when it is progressively decreased.

Fig. 1a and b shows hysteresis loops of the unheated and heated suspensions, respectively, to explore the effects of heating and shearing. Hysteresis was not observed in any of the suspensions and the repeating loops could be superimposed on a single curve for all the suspensions (not shown). The suspensions subjected to shearing produced smaller shear stresses than those without shearing at a fixed shear rate. Therefore, shearing caused a partial break down of the microstructures in the suspension regardless of the heat treatment, leading to lower shear stresses. Moreover, heating caused a similar break down of the microstructures that resulted in lower shear stress compared to the unheated suspension.

Fig. 2a and b shows the stress–strain (*S*–*S*) sweep curves of the unheated and heated suspensions, respectively. In these curves, differences were observed between the sheared and the unsheared suspensions regardless of heating treatment. The first yield stresses of the unheated and heated suspensions at strains of 6% and 10% in the *S*–*S* sweep curves, decreased, and the second yield stresses, at a