Wall Slip of Vaseline (Petrolatum) in Steady Shear Rheometry : Its Observation and Elimination (or Minimization)

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INTRODUCTION

The no-slip condition between a fluid and a solid boundary in contact with the fluid is one of the most classical assumptions in continuum fluid mechanics. For Newtonian fluids, the assumption of no-slip at a fluid-wall interface leads to good agreement with experimental observations. However, rheologically complex fluids are known to violate the no-slip boundary condition when certain critical conditions are exceeded[1]. It is called wall slip when the no-slip condition is invalid.

The apparent rheological properties of semisolid materials, such as vaseline studied in this work, contain the wall slip effect as well as the material properties caused by a structural destruction. Moreover, the slip effect is expected to be more dramatic than any other materials. Thus, the neglect of the possible wall slip effect can result in a misinterpretation of primary viscometric data.

The common method to eliminate the wall slip at the fluid-wall interface is to alter the surface roughness of the wall. This is done physically by sand blasting, sticking profiled material or bonding a rough surface such as sandpaper to parallel plates[2]. Another method is to change the nature of the wall material. For example, Ghanta et al.[3] suggested that the brass is more effective to eliminate instability than the strainless-steel capillary die. In some cases, the physico-chemical nature of the wall can be altered to reduce repulsion effects by the absorption of certain chemical species[4].

In the present work, the steady shear flow properties of vaseline generally used as a base of the pharmaceutical dosage forms were studied in the consideration of wall slip phenomenon. The purpose of this study was to show that how slip may affect the experimental steady-state flow curves of semisolid ointment bases and to discuss the ways to eliminate (or minimize) wall slip effect in a rotational rheometer.

EXPERIMENTAL

The commercial white vaseline (Sung-Kwang Co., Korea) used as a main base of semisolid dosage forms was selected in this study. It is known that vaseline consists of both solid and liquid hydrocarbons (normal, iso, and ring paraffins) in the form of a gel structure. This gel structure is composed of a three-dimensional crystalline network which encloses and immobilizes the liquid hydrocarbons[5].

Vaseline was melted at 70 °C in the water bath and then cooled in an ambient environment to room temperature during a day to obtain the desired homogeneity. This is called a treated sample in this study. Untreated and treated samples were used to obtain the information of the effect of sample preparation on wall slip.

Among standard rotational instruments, both a strain-controlled Advanced Rheometric Expansion System (model : ARES) [Rheometric Scientific Inc., USA] and a stress-controlled Rheolyst Rheomter (model : AR1000) [TA Instruments Ltd., UK] were used to study the steady shear flow properties of vaseline.

Parallel plates with smooth surface, serrated plates specially designed in Rheometric Scientific Inc., and parallel plates attached with sandpaper fixtures were used to investigate the effect of surface roughness. The plate diameter was chosen as 25 and 50 mm for ARES, and 25 and 40 mm for AR1000, respectively. The experiments were carried out employing various gap sizes in the range from 1.5 to 2.5 mm at temperatures of 25, 30, and 37 °C.

RESULTS AND DISCUSSION

Fig. 1 shows the steady shear flow behavior of untreated vaseline at 25 °C. This result was obtained by a strain-controlled ARES rheometer using the parallel plates with smooth surface. In low shear rate region, it is observed that the shear stress has a minimum value. In order to investigate this phenomenon more evidently, the direct visualization technique was introduced in this work. From our experiments, it was found that the marker line separated from the upper plate at low shear rate region. It indicates that the initial minimum shear stress was due to the slippage near the wall.

As the shear rate was increased, an additional slip was generated in the lower plate at a shear rate of about 1 1/s, indicating that the double slip occurred in high shear rate region. Above this critical shear rate, sample was migrated from the center to the edge of the plate. The maximum stress in high shear rate region could be explained by this reason.

Fig. 2 shows the steady shear flow behavior of untreated vaseline at 37 °C. To examine the effect of surface roughness of the wall, the serrated plates and parallel plates attached with sand paper were used as well as the parallel plates with smooth surface. In the case of the parallel plates attached with sand paper, an initial slip phenomenon was more reduced and a critical shear rate was delayed to a higher value of about 10 1/s. Thus, the parallel plates attached with sand paper were the most effective fixtures to reduce the wall slip.

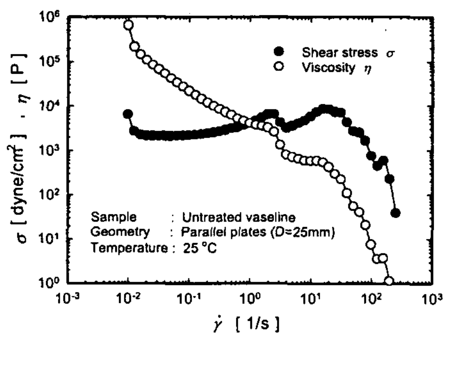

Fig. 1. Flow curves for untreated vaseline at 25 °C using the parallel plates with smooth surface.

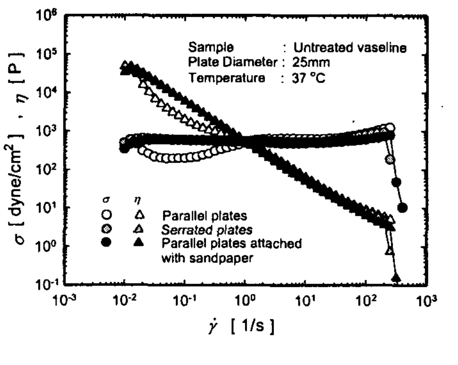

Fig. 2. Effect of surface roughness on the flow curves for untreated vaseline at 37 °C.

Fig. 3 illustrates the steady shear flow behavior of untreated and treated vaseline at 30 °C using the parallel plates attached with sand paper. The treated vaseline delayed the onset of a sudden decrease in shear viscosity to higher shear stress region. According to a comprehensive review article by Barnes[1], a sudden decrease in shear viscosity is due to the slip at the wall during steady shear flow. Therefore, it might be suggested that treated vaseline is more effective to reduce the wall slip.

The effect of plate diameter on the wall slip is shown in Fig. 4 which represents the flow curves of treated vaseline at 30 °C. A stress-controlled AR1000 rheometer was used and the diameter of the parallel plates was 25 and 40 mm in each case. A critical shear stress was about 4,000 dyne/cm^2 in plate diameter of 40 mm, and 6,000 dyne/cm^2 in that of 25 mm, respectively. As a consequence, it can be suggested that the smaller plate diameter could delay the critical shear stress to a higher value.

To determine the proper gap size that can minimize the wall slip, the height between the upper and lower plates was varied with 1.5, 2.0 and 2.5 mm. Fig. 5 illustrates the flow curves of treated vaseline at 30 °C with various gap sizes. It is found that the point of onset of wall slip, taken as a critical shear stress where the shear viscosity decreases suddenly, was delayed to higher values as the gap size was increased. That is, the larger gap size is more effective to eliminate the wall slip in a rotational rheometer.

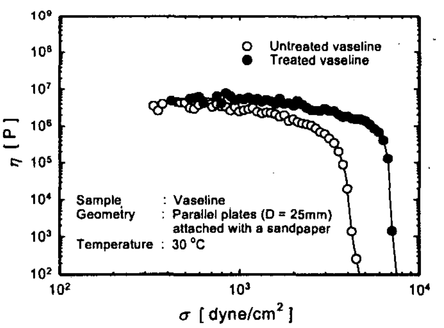

Fig. 3. Effect of sample preparation on the flow curves for vaseline at 30 °C.

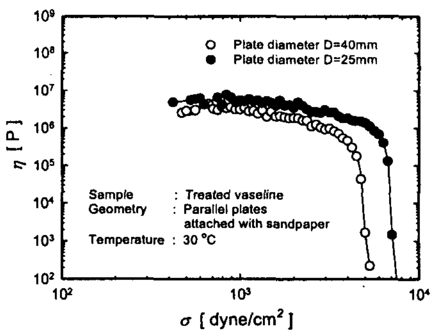

Fig. 4. Effect of plate diameter on the flow curves for treated vaseline at 30 °C.

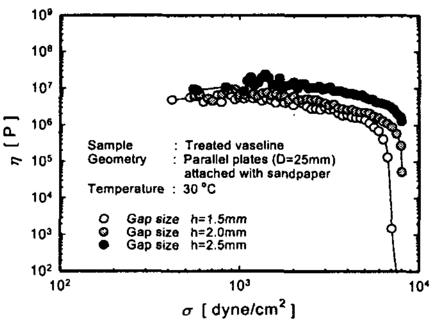

Fig. 5. Effect of gap size on the flow curves for treated vaseline at 30 °C.

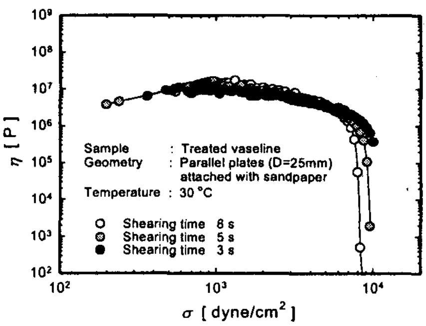

Fig. 6. Effect of shearing time on the flow curves for treated vaseline at 30 °C.

In order to understand the effect of shearing time on the wall slip phenomenon, the steady shear flow behavior was examined with altering the shearing time from 3 to 8 s. The results are shown in Fig. 6. A critical shear stress was 7,000 dyne/cm^2 in shearing time 8 s. As the shearing time was decreased from 8 to 3 s, a critical shear stress was shifted to higher values.

When working with structured samples, there is a danger that the action of closure will destroy the structure to some extent. With a stress-controlled AR1000 rheometer, there are up to three ways in which the gap can be closed; constant velocity, exponential decay, and closure under normal force control. Fig. 7 represents the effect of loading methods for treated vaseline at 30 °C. It can be seen that the normal force control was the most effective method to eliminate the wall slip. Using this method, a critical shear stress was extended to above 10,000 dyne/cm^2.

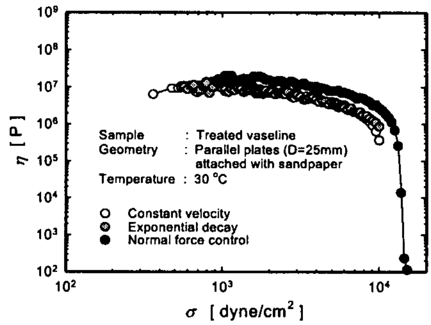

Fig. 7. Effect of loading methods on the flow curves for treated vaseline at 30 °C.

CONCLUSIONS

From this study, the data obtained by a strain-controlled rheometer were found to be less meaningful. A stress-controlled rheometer was much more suitable for investigating the flow behavior of semisolid materials which show severe wall slip phenomenon.

The wall slip effects could not be perfectly eliminated by any experimental conditions. However, the slip was delayed to higher value of shear stress by selection of proper fixture properties and experimental conditions. From our study, the optimum conditions to minimize the wall slip were determined as follows; parallel plates attached with sand paper (properly rough surface), treated sample, smaller diameter fixture, larger gap size, shorter shearing time, and normal force control loading method. In these conditions, a critical shear stress for the onset of slip could be extended from 4,000 to above 10,000 dyne/cm^2.

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