Wall slip of vaseline in steady shear rheometry

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Abstract

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. Using both a strain-controlled ARES rheometer and a stress-controlled AR1000 rheometer, the steady shear flow behavior was investigated with various experimental conditions ; the surface roughness, sample preparation, plate diameter, gap size, shearing time, and loading methods were varied. A stress-controlled rheometer was suitable for investigating the flow behavior of semisolid ointment bases which show severe wall slip effects. In the conditions of parallel plates attached with sand paper, treated sample, smaller diameter fixture, larger gap size, shorter shearing time, and normal force control loading method, the wall slip effects could be minimized. A critical shear stress for the onset of slip was extended to above 10,000 $dyne/cm^2$. 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 selecting proper fixture properties and experimental conditions.

Keywords : vaseline, wall slip, steady shear flow behavior, strain-controlled rheometer, stress-controlled rheometer

1. Introduction

Vaseline (soft paraffin, petrolatum, petroleum jelly) and related materials are widely employed in the pharmaceutical, cosmetic, food, textile, paper and other industries. Especially, it is used as a major ingredient in a wide variety of topical ointment formulations. Therefore, the quality of the ointment is strongly affected by the properties of vaseline. Through characterizing and understanding the rheological properties of vaseline, better decisions can be made as to the choice of a specific grade of vaseline for a particular product and the subsequent manufacture of the product (Barry, 1974; Barry and Grace, 1970; 1971; Fu and Lidgate, 1985; Pena et al., 1994).

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 (Barnes, 1995; Ma and Barbosa-

Canovas, 1995). It is called "wall slip" when the no-slip condition is invalid.

Wall slip for polymer melts has been studied in detail and appears to involve "true slip", that is, a discontinuity in velocity at the wall. It is generally associated with the flow instabilities (sharkskin and melt fracture) occurring during extrusion (Kalika and Denn, 1987; Person and Denn, 1997). However, for the other systems, such as polymer solutions, gels, concentrated suspensions, emulsions, semisolid materials and foams, true slip does not occur. In these systems, wall slip is considered to occur through an "apparent slip" caused by large velocity gradients in a thin region adjacent to the wall, where the viscosity is low because of a reduced concentration of the suspended phase (Aral and Kalyon, 1994; Jana et al., 1995). This created thin region can be treated as a slipping layer.

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 question of slip was first addressed by Mooney (1931), who used capillaries with different radii to deter-

mine the flow curve. He found that the flow curves depended on the radius of the capillary, once the stress exceeded a critical value.

Since this result was reported, theoretical and experimental studies have been conducted to determine the magnitude of slip, i.e., the slip velocity, which is in some cases highly considerable (Hill, 1998; Black and Graham, 1999; Hay et al., 2000). In earlier experimental studies, the slip velocity was analyzed by a basic concept of the Mooney method rather than through direct velocity measurements (Yoshimura and Prudhomme, 1988; Hatzikiriakos and Dealy, 1992). This limitation was recently overcome through the adaptation of the well-known visualization or laser Doppler anemometry technique (Kalyon et al., 1993; Münstedt et al., 2000).

Gevgilili and Kalyon (2001) corrected the wall slip effect in nonlinear stress relaxation behavior of polyethylene melt using flow visualization technique. They reported that the presence of wall slip reduces significantly the range of strains for which the strain-dependent relaxation modulus can be determined.

It was accepted that the microscopic nature of the wall can promote or inhibit macroscopic slip (Kraynik and Schowalter, 1981). Ramamurthy (1986) showed that the onset of surface distortions could be delayed to significantly higher values of melt throughput by a change in the materials of construction of the die.

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 (Meyvis et al., 2001; Citerne et al., 2001). Another method is to change the nature of the wall material. For example, Ghanta et al. (1999) suggested that the brass is more effective to eliminate instability than the strainless-steel capillary die. In some cases, the physicochemical nature of the wall can be altered to reduce repulsion effects by the absorption of certain chemical species (Hatzikiriakos and Dealy, 1991).

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.

2. Experiments

2.1. Materials

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 (Longworth and French, 1969).

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 paper. Untreated and treated samples were used to obtain the information of the effect of sample preparation on wall slip.

2.2. Apparatus and experimental conditions

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.

As vaseline is a semisolid material, it is difficult to obtain a stress-free initial state even for fresh and unsheared sample, since sample loading involves squeezing and trimming of the material. Moreover, the normal stress resulting from material compression during the sample loading relaxed very slowly. In this study, the materials were squeezed to a thickness that was slightly smaller than the desired value and then increasing the gap. Using this method, relaxation time of the normal stress could be reduced to an hour.

3. Results and discussion

3.1. Detection of wall slip

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. Similar phenomenon was reported in previous researches for the other materials such as lubricating greases and commercial mayonnaises (Mas and Magnin, 1994; Plucinski et al., 1998). Mas and Magnin (1994) suggested that it was caused by a failure of the material structure. However, Plucinski et al. (1998) reported that the onset of slippage resulted in a significant reduction in shear stress, thus exhibiting the local minimum stress at low shear rates.

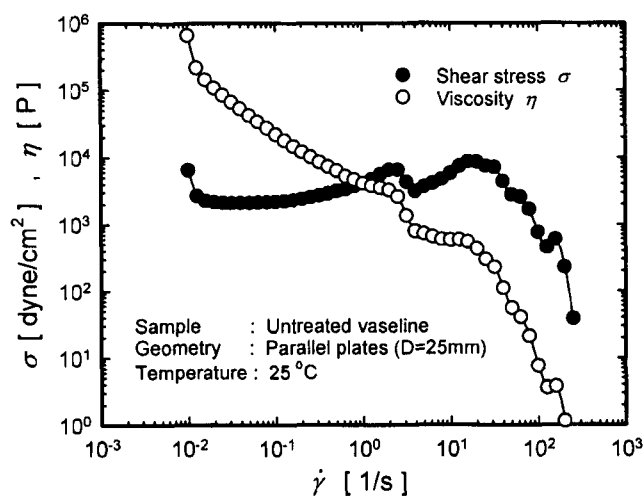In order to investigate this phenomenon more evidently,

Fig. 1. Flow curves for untreated vaseline at 25°C obtained by a strain-controlled ARES rheometer using the parallel plates with smooth surface.

Fig. 2. Comparison of flow curves for untreated vaseline at 37°C obtained by a strain-controlled ARES rheometer using the parallel plates with smooth surface, serrated plates and parallel plates attached with sandpaper.

the direct visualization technique was introduced in this work. In the direct visualization technique, a straight line marker is drawn from plate to plate, passing through the free surface of the sample. If the no-slip condition is valid, the marks between the tools and sample become continuous. Slip is characterized by discontinuous marks at the fluid-wall interface.

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 reported by Plucinski et al. (1998).

During the sample loading, as explained in the experiments section, the upper plate is moved down and then up slowly to reduce the relaxation time. Therefore it was expected that the structure of vaseline was broken down more easily near the wall of the upper plate. This partial destruction of structure caused a slippage in the upper plate firstly. Also the difference of nature of wall material is another reason. In parallel plates with smooth surface, the upper is titanium plate and the lower plate is hardcoated aluminum plate.

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. Therefore, it can be suggested that a non-monotonic nature of the shear stress vs. shear rate curve was severely affected by the wall slip.

To determine the optimum experimental conditions which exclude the wall slip, the influences of the principal variables which were likely to govern the wall slip were systematically examined step by step.
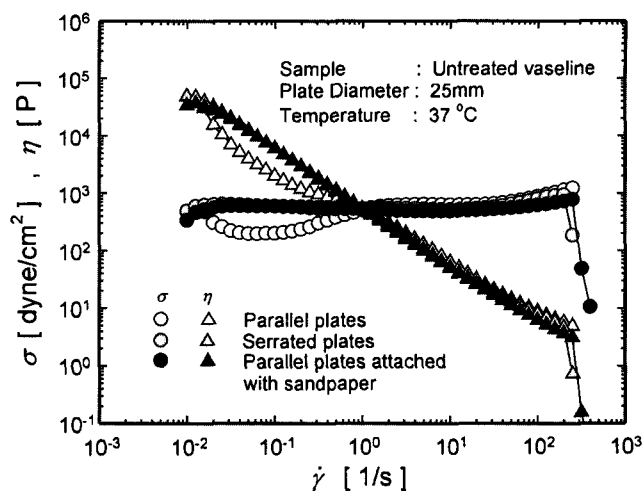
3.2. Effect of surface roughness

Fig. 2 shows the steady shear flow behavior of untreated vaseline at 37°C. This result was also obtained by a strain-controlled ARES rheometer. 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.

The irregular behavior generated by the wall slip in the initial shear rate region became to be obscure when the serrated plates were used. Thus, it can be said that the serrated plates are more effective to reduce the slip occurred in the initial shear rate region. This result was also observed when a marker line technique was adopted. In high shear rate region, the double slip did not occur in contrast to the parallel plates. However, severe fracture phenomenon was observed above a shear rate of about 3 1/s. It could be known by observing the sample during the test. In this work a video camera was used. Fracture may be a second major problem encountered in rheometrical studies for structured semisolid materials, though it has been less frequently discussed in the literature than slip.

In the case of the parallel plates attached with sand paper, an initial slip phenomenon was more reduced and a shear rate where the fracture occurred was delayed to a higher value of about 10 1/s. Thus, the parallel pates attached with sand paper were the most effective fixtures to reduce the wall slip.

One major practical way to eliminate slip is to use rough surfaces. However, excessive roughness may promote fracture caused by the occurrence of secondary flows in the sample. The serrated plates used in this study had a groove in both upper and lower surfaces. It is thought that the groove was too deep so a severe fracture occurred in high

shear rate region. The 60 cW sandpaper was used to roughen the smooth surface of the parallel plates. Here cW means the grain number per unit area, and hence the smaller cW number represents the more rougher surface. In our preliminary experiments, the double slippage occurred at high shear rate region when using the larger number of sandpaper than 60 cW, while a critical shear rate was shifted to a lower value when using the smaller number of sandpaper than 60 cW.

It was found from the visualization technique that once slip, whether single or double sided, was initiated the slope of the marker line remained unchanged with time. This indicates that the sample rotated as a rigid body. The measured torque was, however, increased continuously with shear rate. Therefore, it can be known that the slip layer thickness underwent changes as the shear rate was increased.

3.3. Effect of sample preparation

Fig. 3 illustrates the steady shear flow behavior of

untreated and treated vaseline using the parallel plates attached with sand paper. Fig. 3(a) is the flow curve at 25 °C obtained by a strain-controlled ARES rheometer. The flow behavior of untreated vaseline is similar to that of treated one. It is difficult to distinguish the effect of sample preparation on wall slip from Fig. 3(a). For both untreated and treated vaseline, the onset of slippage occurred in the start of shear rate. At high shear rate region, fracture was also detected.

The different slip behavior between the untreated and treated vaseline is, however, distinctly detected from Fig. 3(b) which demonstrates the shear viscosity vs. shear stress relationship at 30°C. This flow curve was obtained by a stress-controlled AR1000 rheometer. 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 (1995), 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.

An interesting result is observed when the flow curves of Fig. 3(b) were represented as the shear stress vs. shear rate relationship as shown in Fig. 4. A critical shear rate where the onset of slip occurred is about 0.01 1/s. It was the starting point of shear rate in a strain-controlled ARES rheometer. When considering the wall slip, it is found to be difficult to examine the flow curve of vaseline with a strain-controlled rheometer, because generally the measurable minimum range of shear rate is about 0.01 1/s. Therefore, a stress-controlled rheometer is more useful to investigate the steady shear rheological properties of semi-solid materials which have lower values of critical shear rate or shear stress.

Furthermore, comparing with Fig. 3(b) and Fig. 4, it is clear that the wall slip phenomena appear more signifi-
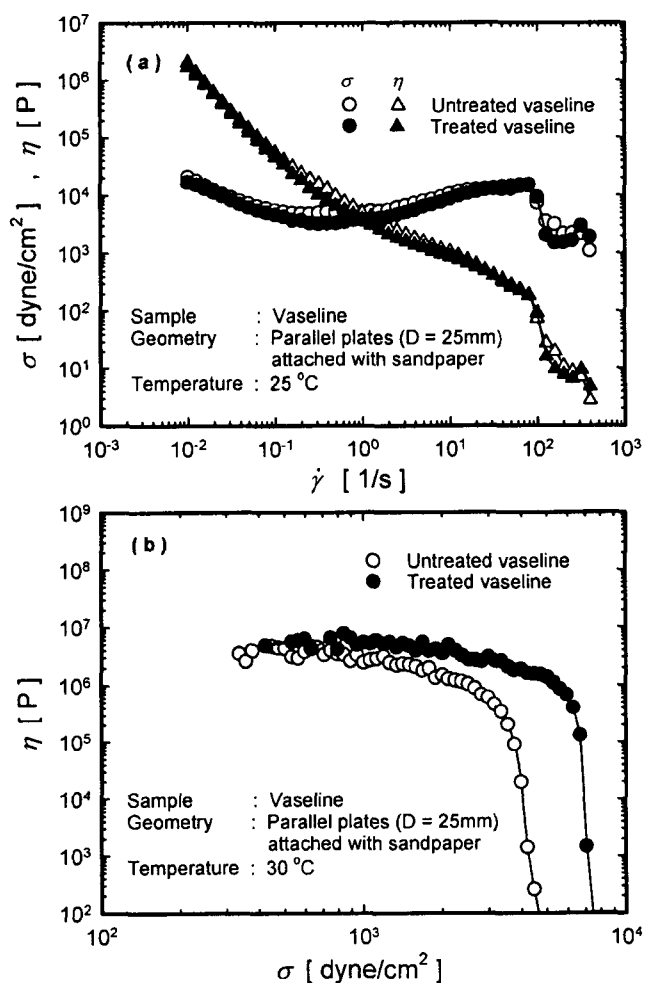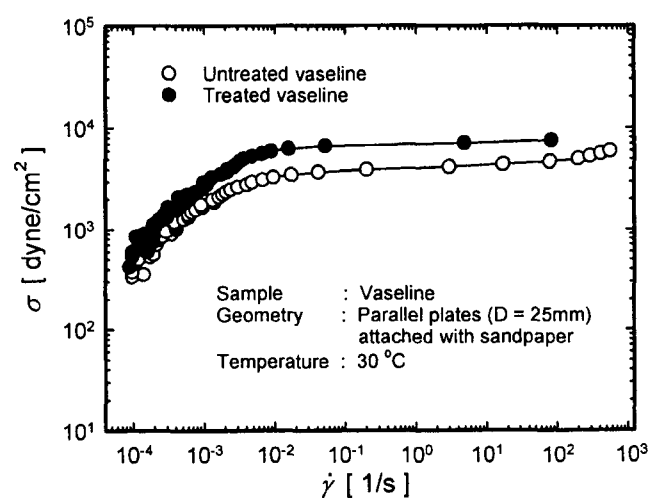

Fig. 3. Effect of sample preparation on the flow curves obtained by (a) a strain-controlled ARES rheometer and (b) a stress-controlled AR1000 rheometer.

Fig. 4. Shear stress vs. shear rate flow curves at 30°C measured with a stress-controlled AR1000 rheometer.

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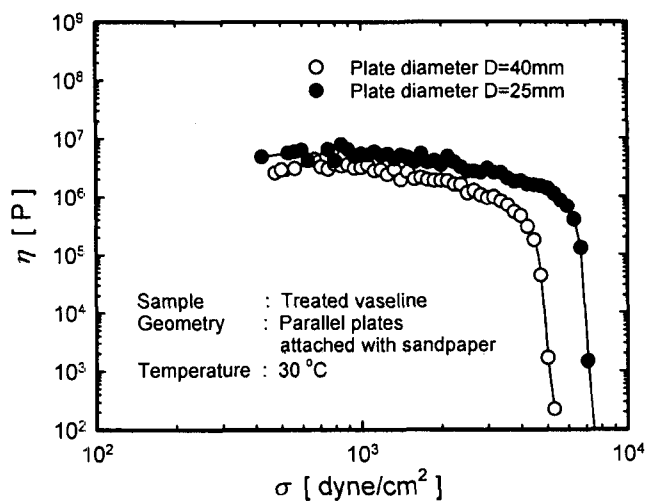

Fig. 6. Effect of gap size on the flow curves for treated vaseline at 30°C.

cantly when shear viscosity is plotted against shear stress (Franco et al., 1998). Hence, the results obtained by a stress-controlled rheometer will only be discussed from the next section.

3.4. Effect of plate diameter

The effect of plate diameter on the wall slip is shown in Fig. 5 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. From a sudden decrease in shear viscosity with increasing shear stress, it is observed that the onset of wall slip occurred at high shear stress region. 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.

It could be explained by the contact area between wall and sample. As the plate diameter is increased the contact area is also increased. In this case the probability of occurrence of the wall slip and the structural destruction of sample during the sample loading will be increased.

3.5. Effect of gap size

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. 6 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.

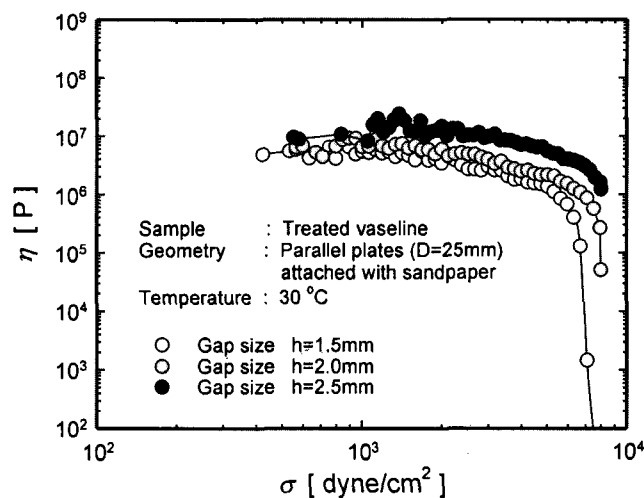During the gap setting, the upper plate slowly came down

to a desired position with compression of a sample contained within the fixtures. In this process, the structure of vaseline was broken down in some degree since a semisolid material such as vaseline has a weak three-dimensional network structure easily destroyed by the external force. Increasing the gap size could, therefore, reduce the degree of structural destruction which caused an occurrence of slip layer adjacent to the wall. The influence of gap size on the wall slip could be explained by this reason.

3.6. Effect of shearing time

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. For instance, in the case of shearing time 3s, the shearing was done for 3 s at each shear stress, and the average shear rate during the period was used for viscosity calculation. The results are shown in Fig. 7. A critical shear stress was 7,000 dyn/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.

The obtained results represent transient data since the steady state could not be reached during these time scales. In general, sufficient shearing time to reach the steady state is required at least above 10 min for semisolid materials. As shown in Fig. 7, however, the wall slip would become a serious problem in long shearing time. Moreover, the experimental data were dependent on the shearing time because the sample showed a time-dependent flow behavior. Thus, the shorter shearing time was chosen to reduce a slip, although the experimental data were not truly equilibrium-state shear stresses.

3.7. Effect of loading methods

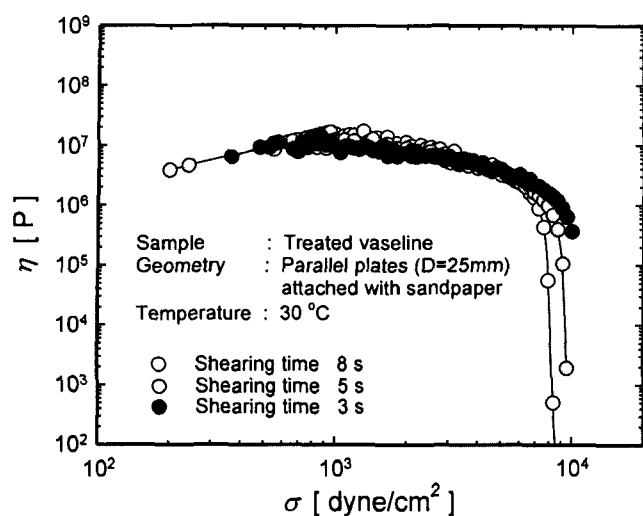When working with structured samples, there is a danger

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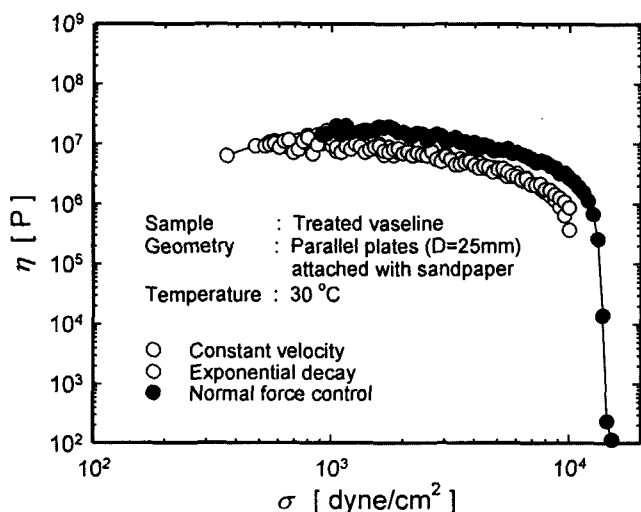

Fig. 8. Effect of loading methods on the flow curves for treated vaseline at 30°C.

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. For constant velocity, the rate and force of closing is constant but generates appreciable force on the sample. For exponential decay, the rate of closure is decreased exponentially and hence even more structure is retained. For use of normal force control, in contrast, the rheometer automates compensation for normal force generated during gap closure by monitoring this force and slowing the closure to allow relaxation of the sample and decay of the force. Therefore, it is inevitable that any standard closing method destroys a significant proportion of the viscoelastic structure of semisolid materials.

Fig. 8 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/cm².

4. Conclusions

In this work, using both a strain-controlled ARES rheometer and a stress-controlled AR1000 rheometer, the steady shear flow behavior of vaseline was investigated with various experimental conditions to eliminate the wall slip occurring at the fluid-wall interface.

It was found from the visualization technique that once slip, whether single or double sided, was initiated the slope of the marker line remained unchanged with time. This indicates that the sample rotated as a rigid body. The measured torque was, however, increased continuously with shear rate. Therefore, it can be known that the slip layer thickness underwent changes as the shear rate was increased.

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/cm².

Acknowledgments

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