회전형 레오메터를 사용한 바셀린의 항복응력 측정

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Yield Stress Measurements of Vaseline (Petrolatum) Using Rotational Rheometers

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Introduction

Vaseline (petrolatum, white soft paraffin) consists of both solid and liquid hydrocarbons in the form of a gel structure; the gel structure is composed of a three-dimensional crystalline network which encloses and immobilizes the liquid hydrocarbons. Because of this gel structure, vaseline shows the viscoplastic flow behavior a yield stress[1]. The yield stress is a very important property for semisolid dosage forms such as vaseline, since their flow behavior exhibits a dramatic change near a yield stress.

The yield stress measurement methods can be classified as direct and indirect methods[2-4]. Direct methods generally rely on some independent assessments of a yield stress as the critical shear stress at which a material yields or starts to flow. For example, stress relaxation, creep/recovery experiment, stress growth experiment, vane method and dynamic mechanical tests belong to these direct methods. Indirect measurements simply involve the extrapolation of the shear rate vs. shear stress data to zero shear rate with or without the help of flow models.

Though the yield stress measurement methods have long been investigated by many workers, it is still difficult to determine the accurate yield stress values of semisolid materials up to this time.

The aim of this study is to investigate some yield stress measurement methods and determine the accurate yield stress value of vaseline. For this purpose, the rheological properties of vaseline at 25～50 ℃ have been measured using both a strain-controlled rheometer (Advanced Rheometric Expansion System : ARES-200FRTN1) and a stress-controlled rheometer (Rheolyst : AR 1000). From these experimental data, the yield stress of vaseline was determined from the extrapolation of the flow curves (indirect method), the stress sweep data (direct method), and the creep/recovery experiment (direct method).

Experimental

Materials

In this study the commercial white vaseline (Sung-Kwang Co.) was used as a main ingredient (base) of semisolid dosage forms. According to the previous studies, the melting temperature of vaseline has been reported to be about 42~47 ℃. Vaseline was melted at 70 ℃ in the water bath, and then cooled in an ambient environment to room temperature for a day. From this procedure, a homogeneous sample was obtained.

Measurement Systems and Experimental Conditions

Using a strain-controlled rheometer (ARES-200FRTN1), the shear rate dependence of steady flow properties was investigated over a wide range of shear rate ($\dot{\gamma}$=0.025~2000 1/s). From these data, the yield stress was calculated by applying some viscoplastic flow models[5-10].

In addition, the stress dependence of steady flow properties was measured using a stress-controlled rheometer (AR 1000). It has been known that a stress-controlled rheometer is more effective to detect the yield stress of a material than a strain-controlled rheometer. The range of imposed shear stresses was σ=0.5~20000 dyne/cm^2 in a stress sweep test. Finally, several initial stresses were applied to estimate the creep and creep recovery behaviors of vaseline.

The sandpaper (60 cW) attached parallel plates with a diameter of 25 mm was chosen as a measuring device and the gap size between the two plates was kept constant at 2.5 mm. The temperature range employed was 25~50 ℃ in all experiments.

Viscoplastic Flow Models

A yield stress cannot be determined directly from the measured flow curves in the case of using a strain-controlled rheometer. Thus, how to represent a yield stress from the experimental data has been a main problem for a long time. To solve the matter, the model fitting (extrapolation) of the flow curve was adopted in this study. The flow models used are listed in Table 1.

Table 1. Flow models used in this study.

Flow model	Equation
Bingham [5]	$\sigma = \sigma_y + k\dot{\gamma}$
Casson [6]	$\sigma^{1/2} = \sigma_y^{1/2} + k\,\dot{\gamma}^{1/2}$
Herschel-Bulkley [7]	$\sigma = \sigma_y + k\,\dot{\gamma}^n$
Mizrahi-Berk [8]	$\sigma^{1/2} = \sigma^{1/2} + k\,\dot{\gamma}^n$
Volcadlo [9]	$\sigma = (\sigma_y^{1/2} + k\,\dot{\gamma})^n$
Heinz-Casson [10]	$\sigma^n = \sigma_y^n + k\,\dot{\gamma}^n$

Results and Discussion

Yield stress is the stress needed to initiate flow and the starting point of the flow on the shear stress. Since a material with a yield stress has been known to have a network structure that can be disrupted by shear, vaseline after being sheared could be expected to have a yield stress. At each applied temperature and stress, the yield stresses could be anticipated to have different values.

From the results of Fig. 1 and Fig. 2, the yield stress values determined using a strain-controlled rheometer is shown to be higher than those measured using a stress-controlled rheometer. In addition, it is also observed that the yield stress of vaseline disappears above 45 ℃.

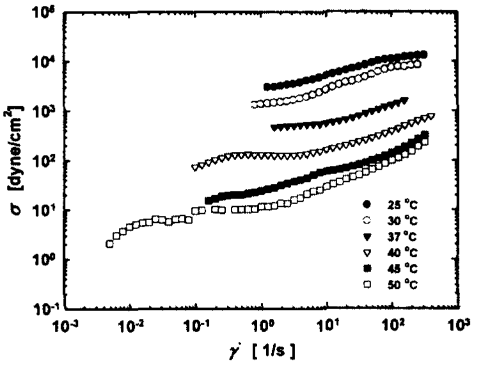

Fig. 1. Flow curves for vaseline at different temperatures obtained using a strain-controlled rheometer (ARES-200FRTN1).

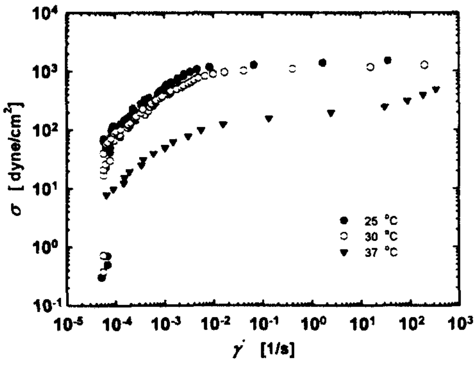

Fig. 2. Flow curves for vaseline at different temperatures obtained using a stress-controlled rheometer (AR 1000).

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