The kinematic viscosities in the undiluted solutions of propylene glycol and the polypropylene glycols were proportional to their molecular weights, but the friction coefficients and compressibilities in polypropylene glycols hardly depended on their molecular weights except for those in propylene glycol. In the friction coefficient measurement, the sliding metal surface was oxidized by strong mechanical shearing force and heat. The boundary lubricant film formation between the polypropylene glycols and the metal oxide layer on the sliding surface was investigated by the contact angle and infrared absorption measurements. The contact angle of the polypropylene glycol at 40°C decreased with an increase in the heat-treated temperature of the metal plate. The infrared absorbance of the polypropylene glycol at 3496 cm⁻¹ was proportional to the lubricant film thickness, but the absorbance intercept in the plot of the absorbance vs. the film thickness was negative at zero film thickness. The negative intercept indicates that the hydroxyl group of the polypropylene glycol disappeared owing to the adsorption of the lubricant molecules to the metal oxide surface. The molecular weight dependence of the friction coefficient was explained by the boundary lubricant film formation of the polypropylene glycol on the metal oxide surface.

Keywords: polypropylene glycol, friction coefficient, compressibility, contact angle, infrared absorbance, boundary lubrication, metal oxide surface

1. Introduction

The viscosity of water-glycol hydraulic fluid was usually controlled by the amount of the thickener molecules, but these molecules were cleaved by the mechanical shearing force on the sliding surface [1,2]. The decrease in the lubricant viscosity had been evaluated by the ASTM ultrasonic shear stability test by using the continuous ultrasonic irradiation method with the sonic oscillator operated at 10 kHz [1,3,4]. Since the preparation of a large amount of the cleaved lubricant sample for the friction coefficient measurement was inefficient by using the above ultrasonic homogenizer, the undiluted ethylene glycol and polyethylene glycols with molecular weights of 200, 400, and 600 were used as the test lubricant samples which could be regarded as the completely cleaved samples with the particular molecular weights [5]. The kinematic viscosities in the undiluted solutions of ethylene glycol and the polyethylene glycols were proportional to their molecular weights, but the friction coefficients in polyethylene glycols hardly depended on their molecular weights except for those in ethylene glycol [5]. In the friction coefficient measurements with the tribometer, a strong mechanical shearing force [1,2] and heat were applied to the sliding metal surface, and the metal surface was changed into the metal oxide surface. The metal oxide surface was chemically reactive and various substances were adsorbed on the metal oxide surface [6,7]. Oiliness agents such as carboxylic acids were adsorbed on the metal oxide surface [8]. Polyethylene glycol is diol compound which has two hydroxyl groups per a lubricant molecule, and seems to form the boundary lubricant film on the metal oxide layer on the sliding surface. The purpose of this paper is to clarify the mechanism for the molecular weight dependence of the friction coefficient by using the diol compounds of propylene glycol and polypropylene glycols which are similar to ethylene glycol and polyethylene glycols, and to directly observe the boundary lubricant film formation between the polypropylene glycol molecules and the surface hydroxyl groups on the metal oxide surface by using the contact angle measurement and the infrared adsorption measurement.
2. Experimental Methods

Propylene glycol and polypropylene glycols with the average molecular weights of 400, 1000, 2000 and 3000 (Wako Pure Chemical Industries, Ltd.) were used without further purifications as glycol antifreeze and thickeners in water-glycol hydraulic fluids. They are abbreviated as PG, PPG400, PPG1000, PPG2000 and PEG3000, respectively. The friction coefficient in the lubricant was measured by using a ball-on-disk arrangement on a CSM High Temperature Tribometer. A bearing steel ball (JIS SUJ2) of 6 mm diameter was installed at the bottom of the ball holder, and a 50 mm diameter stainless steel petri dish (JIS SUS304, AS ONE Corporation) 15 mm high and 0.6 mm thick was placed in the sample holder with a blocking ring and clamps. 2 g of the lubricant was added in the petri dish in the sample holder, and the liquid temperature was controlled at 40°C by the heater in the tribometer. The running-in was done in the stainless petri dish containing the lubricant for 30 min at 40°C, a sliding speed of 0.005 m/s and a constant load of 1 N (i.e., 0.44 GPa). The friction coefficient was measured for 30 min at sliding speeds from 0.001 to 0.15 m/s, and the same temperature and load as those of the running-in.

The ultrasonic velocity in the lubricant at 40°C was measured by using the pulse-echo technique described by McClements and Povey [9,10]. Two ultrasonic transducers with 3 MHz frequency (PIEZOTITE 7D-10-3000B, Murata Manufacturing Co., Ltd.) were attached with adhesive to both sides of a glass cuvette (GS-40, AS ONE Corporation) 45 mm high, 40 mm wide and 1.2 mm thick with a 10 mm path length. One transducer generated the signal which traveled through the lubricant, and the other received the signal which was observed with a digital storage oscilloscope connected with the computer for the data analysis, respectively. When the pulse reached an interface connected with the computer, a series of echoes was received. The ultrasonic velocity \( u \) in the lubricant was calculated within the accuracy of 0.1% from the following relationship by using the path length \( d \) and the time \( t \) between the first and second echoes [9]:

\[
u = \frac{2d}{t}
\]  

The adiabatic compressibility \( \beta \) in the lubricant with density \( \rho \) was obtained by using the formula as [11]

\[
\beta = \frac{1}{\rho u^2}
\]

A metal plate tested for the FTIR or contact angle measurement was a commercial product of a rolled stainless steel plate (JIS SUS304, 74% Fe, 18% Cr, and 8% Ni), which was 50 mm in length and width, and 1 mm in thickness. The metal plate was polished with alumina of average diameter of 10-20 µm, and was washed with detergent. After the metal plate was washed with distilled water, it was dried in hot air [12]. The arithmetic average roughness, \( R_a \), and the maximum height roughness, \( R_{\text{max}} \), were 0.14 and 1.21 µm, respectively.

Prior to measure the contact angle, the metal plate was unheated or was heat-treated for 10 min at 130-230°C. The drop shape method was applied to measure the contact angles of undiluted PPG400 on the stainless steel plate on the hot plate at 40°C [13,14]. Because the receding angle became zero by the adsorption of PPG molecules on the metal oxide surface, the contact angle of PPG400 on the metal oxide surface was represented only by the advancing angle.

In order to measure the infrared absorbance of PPG on the metal plate, 1 µl of 5% ethanol solution of PPG3000 was spread on the unheated stainless steel plate on a hot plate (AS ONE Corporation DP-2S) at 60°C where the oxidation of PPG hardly occurred, since the unheated stainless steel plate surface repelled PEG400 because of the strong surface tension. The lubricant film of PPG3000 on the unheated stainless steel plate was unstable for a long time of the experiment. Then, the metal plate was heat-treated for 10 min on the hot plate at 130-210°C in the similar manner to the contact angle measurement, in order to spread PPG3000 stably on the metal surface for the FTIR measurement. Afterwards the lubricant spread on the metal plate was left for 5 min on the hot plate at 60°C. In case that the lubricant film thickness formed on the metal plate was not uniform after the lubricant was spread on the heat-treated metal plate, the film thickness was adjusted mechanically to become uniform by using a disposable plastic tip of a micropipette. The area of the lubricant film on a metal plate was measured by a computer analysis of a picture which was taken with a digital camera. The lubricant film thickness was calculated from the ratio of the lubricant volume to film area. On the other hand, the weight of lubricant on the metal plate was measured to a precision of 10⁻³ g with a Sartorius balance BP211D, which was grounded enough to remove the static electricity from the metal plate. The lubricant film thickness was also calculated from the ratio of the lubricant weight to film area and the density [12]. The change in the infrared absorbance of the hydroxyl groups of PPG3000 at 3496 cm⁻¹, caused by the change in the lubricant film thickness, was measured with a reflection type of JASCO spectrophotometer FT/IR-400 that was connected with the infrared reflectance attachment RF-81S.

3. Results and Discussion

Propylene glycol and polypropylene glycols with the average molecular weights 400-3000 contained in the water-glycol hydraulic fluids are a homologous series of liquid organic compounds at 40°C. The molecular weight dependence on the kinematic viscosities in the undiluted solutions of PG and PPG400-3000 was measured as shown in Fig. 1. The kinematic viscosities were proportional to the molecular weights of the...
In order to obtain the relation between the friction coefficient and the molecular weight, the friction coefficients of the undiluted solutions of PG and PPG400-3000 were measured at a constant load of 1 N and sliding speeds from 0.001 to 0.15 m/s as shown in Fig. 1. The friction coefficient of the undiluted PPG decreased with an increase in the molecular weight at a sliding speed of 0.001 m/s. Because the molecular weight dependence of the friction coefficient of PPG was similar to the chain length dependence of the friction coefficient of the long straight-chain fatty acid which was adsorbed on the steel pin and balls under boundary lubrication [16], the friction coefficients in PPG at a sliding speed of 0.001 m/s seemed to be governed by the boundary lubricant film formation between the PPG molecules and the metal sliding surface. On the other hand, the friction coefficients in PPG400 to PPG3000 were almost constant at 0.005-0.15 m/s, but the friction coefficient of PG was 1.3 times as large as those in PPG400 to PPG3000. Since the friction force applied on the bottom point of the ball in the ball holder was measured by means of a transducer attached to the measuring arm in the tribometer, it would be related to the information of the lubricant film which was located at the height above the stainless petri dish surface. The friction coefficients measured at the slow speed of 0.001 m/s and at the high speed of 0.15 m/s correspond to the structure of the lubricating oil film formed on the petri dish surface and that in the bulk phase above the petri dish surface, respectively. As seen from Fig. 1, the friction coefficients of PPG1000-3000 were almost constant at the sliding speed 0.001 to 0.15 m/s, and the structure of the lubricant film formed on the petri dish surface might be maintained in the bulk phase above the petri dish surface. The molecular weight dependences of the friction coefficients and the kinematic viscosities of PG and PPGs in Fig. 1 were similar to those of ethylene glycol (EG) and polyethylene glycols (PEG) [5].

Under the same experimental conditions as the friction coefficient measurement in Fig. 1, the compressibilities of PG and PPG400-3000 were obtained by using the ultrasonic velocities and densities measured at 40°C in Eq. (2), and were shown in Fig. 2. The compressibilities of the homologous series of PPGs seemed to be hardly dependent on their molecular weights except for that of PG. The compressibilities of the homologous series of PEGs were also hardly dependent on their molecular weights except for that of EG [5]. Both PG and EG were the monomers of PPG and PEG, and had the similar chemical structures to those of PPG and PEG, but did not have ether linkage -C-O-C-. The difference between the friction coefficients and the compressibilities of PPGs and those of PG in Figs. 1 and 2 might be caused by the ether linkage.

A strong mechanical shearing force and heat were applied to the sliding metal surface in the friction coefficient measurement, and the metal surface was changed into the metal oxide surface which was chemically reactive, because the metal oxide surface had amphoteric surface hydroxyl groups and various substances from ions to macromolecules were adsorbed on the metal oxide surface [6,7,17]. In order to investigate the interaction between the PPG molecules and the metal oxide surface, the contact angle of undiluted PPG400 was measured on the stainless steel plate on the hot plate at 40°C, because PPG400 was completely vaporized at the high temperature above 150°C. Figure 3 shows a drop of PPG400 on the unheat-treated stainless steel plate and the contact angle was measured from the angle between the tangent and the liquid-solid interface line between the PPG400 and the metal plate. The contact angle of PPG400 decreased with increasing heat-treated time of the stainless steel plate at 190°C and became almost constant after 10 min, as shown in Fig. 4. This indicates that the formation of the metal oxide film was saturated in 10 min. As a result, the heat-treated time was determined to be 10 min in order to compare the contact angles on the stainless steel plate at various temperatures. Figure 5 shows the
plot of contact angle of PPG400 at 40°C against the heat-treated temperature of the stainless steel plate. The contact angle of PPG400 decreased with increasing heat-treated temperature of the metal plate for 10 min. Since the amount of the metal oxide film increased with increasing heat-treated temperature [18], the decrease in the contact angle in Fig. 5 indicated the interaction between the PPG400 molecules and the metal oxide surface.

In order to investigate the interaction between the PPG molecules and the metal oxide surface by the infrared absorbance method, PPG400 was spread on the unheat-treated stainless steel plate and the heat-treated plates at 130-150°C, respectively. Since both the unheated and heat-treated stainless steel plate surfaces repelled PPG400 because of the strong surface tension of PPG400 as shown in Fig. 5, the lubricant film with a unique film thickness could not be obtained for the infrared absorbance measurement. Figure 6 shows the PPG3000 lubricant films on an unheat-treated stainless steel plate and on a heat-treated stainless steel plate at 190°C for 10 min, respectively. As seen from Fig. 6a, the lubricant film of PPG3000 on the unheated stainless steel plate was unstable for a long time of the experiment. However, since the interaction between the two hydroxyl groups at the both ends of the PPG3000 molecule was weaker than that of the PPG400 molecule from the view point of the difference in the molecular chain length, PPG3000 in Fig. 6b was spread more stably than PPG400 on the metal surface heat-treated for 10 min on the hot plate at 130-230°C in the similar temperature range to that of the contact angle measurement. The difference between the lubricant film morphologies in Fig. 6a and 6b on the metal plates illustrates directly the interaction between PPG3000 and the metal oxide surface. Figure 7 shows the infrared absorption spectra of PPG3000 on a heat-treated stainless steel plate at 190°C for 10 min. The infrared spectra of PPG3000 exhibited the peak of the O-H stretching vibration at 3496 cm⁻¹ and the strength of the peak increased with increasing volume of PPG3000 spread on the metal plate. The infrared absorbance calculated from the transmittance at 3496 cm⁻¹ in Fig. 7.
was plotted against the lubricant film thickness which was spread on the heat-treated stainless steel plate as shown in Fig. 8a and 8b. In the ordinary calibration curve measurement of the organic compound, the sample is dissolved in the suitable organic solvent (e.g. nujol) which does not have absorption peaks at the particular wave numbers. However, PPG3000 could not be dissolved into the organic solvent, because PPG3000 and the organic solvent were separated with each other. Then, the change in the number of the PPG3000 molecules above the metal surface was performed by the change in the lubricant film thickness of undiluted PPG3000 on the metal plate. The absorbance of PPG3000 was proportional to the lubricant film thickness, but the absorbance intercept in the plot of the absorbance vs. the film thickness was negative at zero film thickness. A linear relationship with a negative intercept was observed for the PPG3000 lubricant film on the stainless steel plate heat-treated at 130-230°C, respectively. The negative intercept indicates that the hydroxyl groups disappeared owing to the adsorption of PPG3000 to the metal oxide surface. If the hydrogen bond between the hydroxyl groups of PPG3000 and those of the metal oxide film was observed by the infrared absorbance measurement, a straight line in Fig. 8 had the intercept through the origin. Since 1,3-butanediol in the lubricated sliding of aluminum-on-steel system has been reported to form a stable complex with surface aluminum atom [19,20], the negative intercept in the linear relationship also means that the attractive interaction between the hydroxyl groups of PPG3000 and those on metal oxide surface was caused by a chemical interaction other than hydrogen bond, in addition to the hydrogen bond between the -OH groups of PPG3000 and those of the metal oxide film.

Figure 8 indicates that the PPG3000 molecules were adsorbed on the metal oxide surface. In the ordinary method, the lubricant weight was measured to a precision of 10^{-5} g with a Sartorius weighing balance BP211D, which was grounded enough to remove the static electricity from the metal plate [12]. Since the static electricity was not removed easily in a short time even by the ground, the measurement of the lubricant weight was repeated until the three or five stable weight data of the lubricant were obtained continuously after more than 30 min. Figure 9 shows the plots of PPG3000 weights against lubricant volumes spread on stainless steel plates unheat-treated and heat-treated at 190°C for 10 min. The weight of PPG3000 on the unheat-treated plate was proportional to the spread lubricant volume through the origin, because the PPG3000 molecules were not adsorbed on the metal surface without the oxide film and were located disorderly on the metal surface. However, the weight of PPG3000 on the unheat-treated plate deviated from a linear relationship in Fig. 9. The deviation from the linear relationship indicates that the dipole moment of the lubricant molecules was strongly oriented in a constant direction on the metal oxide surface. As a result, the static electricity did not disappear by the ground after 30 min as shown in Fig. 9 and was also kept for more than a day. The adsorbed layer of PPG molecules strongly oriented on the stainless steel plate might indicate the possibility of the adsorbed layer of the thin film.
lubrication of the polymers which formed the adsorbed layers up to 10 nm thick on solid surfaces and had a much higher viscosity on the surface than that in the bulk solution [21-23].

The minimum film thicknesses of PPG400 for point contact in elastohydrodynamic lubrication were calculated to be 3.5 and 16.6 nm at a sliding speed of 0.01 and 0.1 m/s, a constant load of 1 N and 40°C by using the model by Hamrock and Dowson, respectively [24]. The friction coefficients under the different lubricant film thicknesses at the sliding speeds of 0.01 and 0.1 m/s were expected to be different, but they were almost constant as shown in Fig. 1. Furthermore, the friction coefficients did not depend on the molecular weights of PPG, although the kinematic viscosity increased with increasing molecular weight (Fig. 1). Therefore, PPG400 in the water-glycol hydraulic fluid was not merely a solvent, but controlled the friction coefficient owing to the boundary lubricant film formation between the PPG400 molecules and the metal oxide film on the sliding surface as shown in the contact angle and infrared measurements in Figs. 5, 6 and 8. In this research, the metal oxide film played an important role in controlling the friction on the sliding surface. However, we do not have the instruments to measure the amount of the oxide film. The relationship between the friction coefficient, the contact angle, the infrared absorbance and the amount of the metal oxide film must be clarified in the near future.

4. Conclusion

The friction coefficients in undiluted polypropylene glycols did not depend on their molecular weights at the sliding speed 0.005-0.15 m/s, although the kinematic viscosities were proportional to their molecular weights. The contact angle of PPG at 40°C decreased with an increase in the heat-treated temperature of the metal plate. The infrared absorbance of PPG at 3496 cm⁻¹ was proportional to the lubricant film thickness, but the absorbance intercept in the plot of the absorbance vs. the film thickness was negative at zero film thickness. The negative intercept indicated that PPG formed the boundary lubricant film on the metal oxide layer on the sliding surface. Therefore, PPG in the water-glycol hydraulic fluid was not merely a solvent, but controlled the friction coefficient owing to the boundary lubricant film formation between the PPG molecules and the metal oxide film on the sliding surface.

References


