Comparison of different methods of physisorption films with a combination of PPG and ta-C coating. (Impedance method, Cryo-TEM/EDX, AFM scratch method)

Kodai Urano*, Taichi Kaneko*, Yutaka Mabuchi*, Genki Kamei**, Riki Takano***, Noritsugu Umehara***,
Takayuki Tokoroyama***, Junichi Shimanuki****, Shusaku Ogiu****
*Utsunomiya University, **Shell Lubricants Japan, *** Nagoya University, ****NISSAN ARC

1. Background and Objectives

Recently, against the backdrop of global warming, the automotive industry is seeking to improve the fuel efficiency of automobile engines to reduce carbon dioxide emissions.

In addition, with the spread of series hybrid vehicles, the equivalent average oil temperature of engines is expected to decrease. Therefore, effective technology to reduce engine friction in the low and medium temperature range is required to further improve fuel economy.

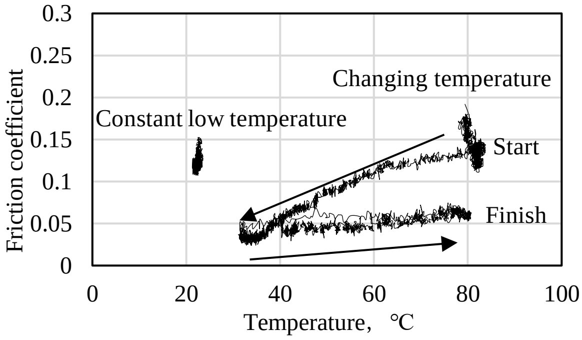


Fig.1 Friction coefficient for low temperature constant test and temperature change test with PPG250.

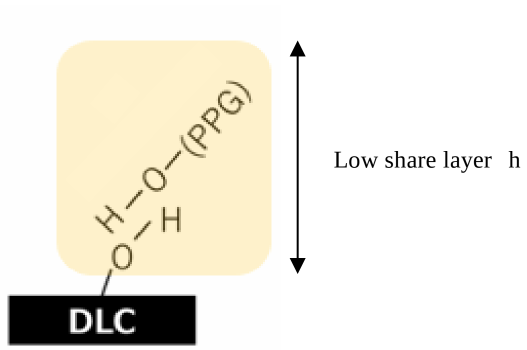


Fig.2 Model of low shear layer with combination of PPG and DLC

In a previous study [1], it was found that the combination of polypropylene glycol (PPG) and hydrogen-free DLC film (ta-C, tetra-hederal amorphous carbon), which is expected to be a next-generation base oil, showed a high coefficient of friction in a test at a constant low temperature. The coefficient of friction is lowered when the heater is turned off and the temperature is gradually lowered after sliding at a high temperature, and then the coefficient of friction remains low even when the temperature is further increased (Fig.1). This is thought to be due to the covalent bonding of PPG-derived OH groups to the surface of the ta-C film during high-temperature sliding and the hydrogen bonding of PPG OH groups to these OH groups at low temperatures, forming an adsorption film that becomes a low-shear layer, resulting in low friction[2] (Fig.2).

In addition, the molecular weight of PPG can be varied, which may lead to a thicker low-shear layer and further low friction. In a previous study [3], friction test results with PPG of different molecular weights showed that the coefficient of friction decreased after sliding at 80°C for all molecular weights of PPG, and the coefficient of friction decreased the most for PPG4000, although there was some variation in the amount by which the coefficient of friction decreased. However, physisorption films formed at low temperatures are difficult to analyze because their adsorption strength is weak, and they are easily detached by washing. Therefore, the objective of this study is to analyze the thickness of the low-shear layer due to differences in the molecular weight of PPG by using three analytical methods that have the potential to visualize physisorption films: the impedance method [4], Cryo-TEM/EDX, and AFM, and to verify the validity of the measurement method by verifying these results.

2. Experimental procedure

2.1 Samples

A disk of SUJ2 steel, hardness HRC64, accuracy No.29, diameter 31.1mm, thickness 2.4mm, and surface roughness 0.0091 µm was used as the base material for the ta-C film, and a 0.5µm ITF-made ta-C film (MFA) with a surface roughness of 0.004µm was deposited. The mating material was SUJ2 steel, hardness HRC64, precision No.29, and 3/8-inch diameter bearing balls. Polyalphaolefin 4 (PAO4) with 10mass% PPG was used as the test oil. PPG with different molecular weights was used to investigate the friction characteristics of different molecular weights. In addition, PPG250 and chromium (Cr) complex as a coloring agent was used to identify the surface layer by Cryo-TEM/EDX. The density and kinematic viscosity of each are shown in Table 1.

Table 1 Density and viscosity characteristics of each PPG.

	PPG250	PPG250+Cr	PPG4000	PAO4
molecular weight	250	250	4000	-
Density at 15℃, g/cm³	1.016	1.016	1.007	0.856
kinematic viscosity at 40℃, mm²/s	23.78	23.78	433.50	18.00
kinematic viscosity at 100℃, mm²/s	3.21	3.21	67.43	4.00

2.2 Experimental conditions

A ball-on-disk test was conducted under lubrication using a light-load friction testing machine. The load was 120g (maximum Hertzian contact surface pressure: 500MPa) and the sliding speed was 100rpm (peripheral speed: 0.08m/s). To analyze the frictional properties of PPG with different molecular weights, two types of tests were conducted: a temperature change test in which sliding was performed for one hour at 80°C, followed by sliding for one hour while the heater was turned off and the temperature was lowered to 20°C. A constant temperature test in which sliding was performed for two hours at a constant 20°C. PPG250 and PPG4000 were analyzed as representative points.

3. Results

Fig.3 shows a summary of the adsorption film thickness analyzed in this study. By impedance method, adsorption films of 20nm for PPG250 and 50 to 110nm for PPG4000 were confirmed; by Cryo-TEM/EDX, adsorption films of 6 to 20nm for PPG250 were confirmed; and by AFM, adsorption films of 6nm for PPG250 and 120nm for PPG4000 were confirmed.

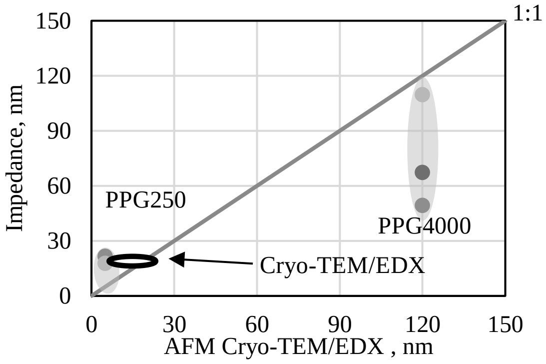
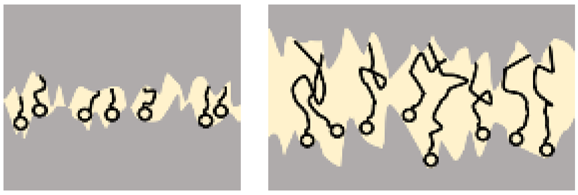


Fig.3 Adsorption film thickness for each method

4. Consideration

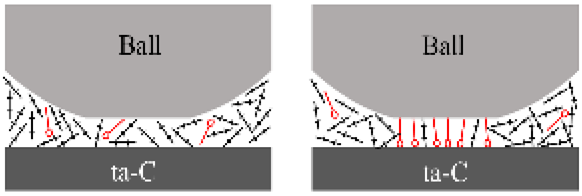
Comparison of the results of the three analyses showed an approximate correlation. Both impedance and AFM results showed that the adsorption film thickness of PPG4000 was thicker than that of PPG250. The reason for the lower coefficient of friction with higher molecular weight may be due to the formation of a thicker low-shear layer and less surface-to-surface contact, as shown in Fig.4.

The adsorption film thickness of PPG4000 by the impedance method was thinner than that by AFM. The reason for this may be that the impedance method calculations use the dielectric constant of PAO4 with 10mass% PPG4000, as shown in the a) of Fig.5, but in the actual interface, PPG4000 is concentrated as shown in the b) of Fig.5, and the dielectric constant used is different. Therefore, we calculated the concentration of PPG4000 with a dielectric constant that would make the oil film thickness by the impedance method and the oil film thickness by AFM equal to 1:1, which was 65-90mass%, suggesting that PPG4000 is becoming increasingly concentrated as an adsorbed layer.



a) Small molecular weight b) Large molecular weight

Fig.4 Adsorption model for different molecular weights of PPG



a) Initial model (PPG:10mass%) b) Modified model (PPG:65~90mass%)

Fig.5 Adsorption membrane model by impedance method

5. Conclusion

(1) The impedance method, Cryo-TEM/EDX, and AFM showed approximate correlation, and the adsorption film became thicker the larger the molecular weight of PPG.

(2) The reason for the better lubrication and lower friction with higher molecular weight PPG is thought to be the formation of a thicker low-shear layer, which suppresses surface contact.

(3) The concentration of PPG4000 with a dielectric constant that would make the oil film thickness by the impedance method and the oil film thickness by AFM equal 1:1 was calculated backward, resulting in a high concentration of 65-90mass%.

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