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## Relation between Dielectric Relaxation and Rheological Properties of Lubricating Greases

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The dielectric spectroscopy method was applied to the investigation of the dynamics of base oil and thickener of lubricating grease. In order to observe the dielectric relaxations both of base oil and thickener, the lubricating grease formed from polyol ester base oil and lithium 12-hydroxy stearate thickener was prepared. Apparent viscosity, dynamic viscoelasticity and creep properties were measured, and the temperature characteristics of these rheological properties were compared to that of dielectric relaxation time. Prepared lubricating grease showed two dielectric relaxation processes. The dielectric relaxation observed in low-frequency and high-frequency regions were attributed to thickener and polyol ester base oil, respectively. The dielectric relaxation time of the high-frequency relaxation exhibited non-Arrhenius-type temperature dependence. This temperature characteristic is similar to that of viscoelastic relaxation time, shift factor obtained from superposition of creep compliance data, and viscosity of polyol ester base oil. On the other hand, the dielectric relaxation time of the low-frequency relaxation showed Arrhenius-type temperature dependence. However, no clear relation was observed between the dielectric relaxation in low-frequency region and the rheological properties measured in this study.

**Keywords:** lubricating grease, dielectric relaxation, rheology, base oil, thickener, molecular motion, polyol ester, lithium 12-hydroxy stearate

### 1. Introduction

Lubricating greases are widely used as lubricants in various machine bearings, gears and sliding parts. Grease lubrication has several advantages over oil lubrication. In general, grease lubrication does not require the supplying system, and lubricating grease stays in place, prevents lubricant from leaking, and prevents entry of harmful contaminants such as dust, moisture, corrosive gas, and so on [1,2]. These characteristics are brought by the unique rheological behavior of the lubricating grease.

Lubricating grease is defined as a solid or semisolid lubricant consisting of a thickening agent (soap or other additives) in a fluid lubricant (usually petroleum lubricating oil) [3]. Thickener forms network structure and base oil is held in the structure [4]. Because of this network structure, lubricating greases show complex rheological behavior such as yield stress and thixotropy

[5,6]. These complicated rheological properties of lubricating greases are caused by deformation, destruction and reconstruction of the network structure, and also related to the interaction between thickener and base oil. Therefore, rheological properties of lubricating greases have a strong tie to the molecular motions of thickener and base oil.

In the present work, dielectric spectroscopy method was applied to the investigation of the dynamics of lubricating greases. Dielectric spectroscopy is a powerful tool to the investigation of the structures and molecular dynamics of materials. It is well known that dielectric  $\alpha$ -relaxation time and viscosity of liquid substance show very similar temperature dependences. In previous studies [7-10], we confirmed that the high-pressure viscosity of polar lubricating oils can be estimated from dielectric relaxation data. In this study, dielectric relaxation and rheological properties of the lubricating grease, which was formed from polyol ester

base oil and lithium 12-hydroxy stearate thickener, had been measured. The relation between dielectric relaxation characteristics and several rheological properties of lubricating greases was investigated.

## 2. Experimental Methods

### 2.1. Materials

In order to detect the dielectric relaxation of both base oil and thickener, the sample grease that was formed from polar base oil and lithium 12-hydroxy stearate thickener was prepared. Since lithium 12-hydroxy stearate have highly polar hydroxyl group, dielectric relaxation of the thickener can be observed by using this substance as a thickener of lubricating grease. As for the base oil, we tested several ester oil-based greases experimentally, and finally neopentyl glycol bis(3,5,5-trimethyl hexanoate) was selected in terms of the balance of dielectric relaxation strength between base oil and thickener. This polyol ester base oil is named NPGC9. NPGC9 and lithium 12-hydroxy stearate were used as the base oil and the thickener of sample lubricating grease. This lubricating grease is named POE-G. Further, in order to investigate the influence of base oil on dielectric relaxation behavior of thickener, the grease formed from poly- $\alpha$ -olefin (non-polar base oil) and lithium 12-hydroxy stearate was also tested. This lubricating grease is named PAO-G. The main properties of the sample lubricating greases were listed in Table 1.

Table 1 The properties of sample lubricating greases

	POE-G	PAO-G
Base oil	NPGC9 ester	Poly- $\alpha$ -olefin
Viscosity, mm <sup>2</sup> s <sup>-1</sup>	13.1(at 40°C) 3.12(at 100°C)	46.7(at 40°C) 7.76(at 100°C)
Viscosity index	98	135
Density at 15 °C, gcm <sup>-3</sup>	0.832	0.913
Thickener	Lithium 12-hydroxy stearate	
Content, mass%	10	
Grease properties <sup>*1</sup>		
Worked penetration	305	272
Unworked penetration	355	271
Dropping point, °C	191	204
Oil separation, mass% (100 °C, 24 h)	4.0	1.9

\*1 JIS K 2220, 2003

### 2.2. Dielectric measurements

The equivalent parallel capacitance  $C_p$  and the equivalent parallel conductance  $G$  of the sample-filled capacitor were measured at frequency from 20 Hz to 2 MHz with a LCR meter (Agilent E4980A) under the applied voltage of 1 V. The relative dielectric constant  $\epsilon_r'$  and the relative dielectric loss factor  $\epsilon_r''$  were calculated from  $C_p$ ,  $G$  and the frequency  $f$  by the following equations:

$$\epsilon_r' = C_p / C_0 \quad (1)$$

$$\epsilon_r'' = G / 2\pi f C_0 \quad (2)$$

where  $C_0$  is the vacuum capacitance of the capacitor used. The dielectric measurements were performed as a function of temperature from -80 to +80°C.

The apparatus used for the dielectric measurements is shown schematically in Fig. 1. The multi-plate air-spaced type rotary variable capacitor shown in Fig. 2 was used for the measurements. The maximum air capacitance of the capacitor was 78.2 pF. The sample lubricating grease was filled between the electrodes of the capacitor, and rotor electrode was set to the position where the rotor and the stator electrodes were fully meshed together, i.e. the maximum capacitance position. The grease-filled capacitor was put into a glass tube. The glass tube was immersed into a heat transfer fluid. Temperature of the sample lubricating greases was detected with a platinum resistance sensor placed in the vicinity of the sample-filled capacitor. In the temperature rang from -80 to 25°C, ethanol was used for the heat transfer fluid. Liquid nitrogen was poured into a Dewar vessel and cooled the heat transfer fluid below -80°C. Temperature of heat transfer fluid was not regulated in this work. Temperature was raised spontaneously, and dielectric measurements were made when the target temperature was reached. At temperatures above -30°C, the heat transfer fluid was heated with electric immersion heater. At temperature above 25°C, water was used for the heat transfer fluid instead of ethanol.

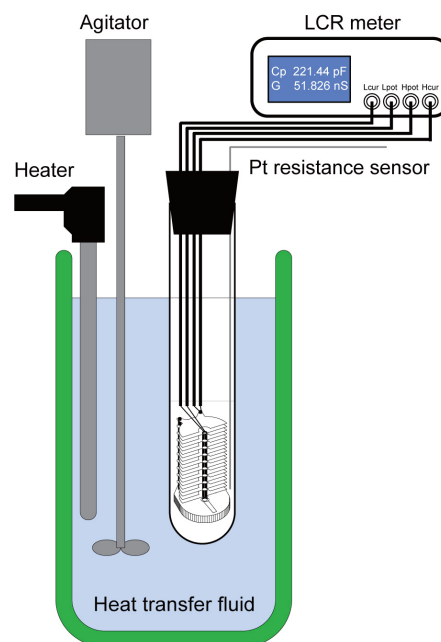


Fig. 1 Schematic drawings of the measuring apparatus for dielectric properties of lubricating greases

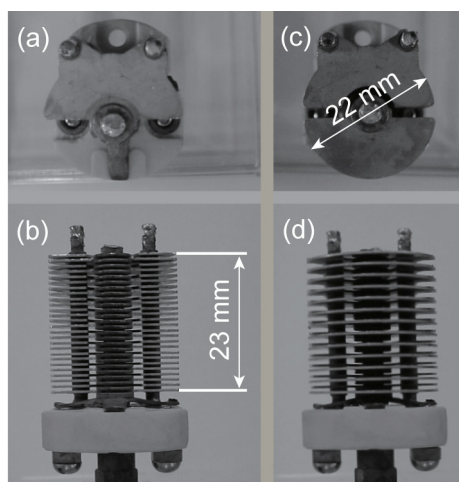


Fig. 2 Capacitor for dielectric measurements: (a) top view at the maximum capacitance position, (b) front view at the maximum capacitance position, (c) top view at the minimum capacitance position, and (d) front view at the minimum capacitance position

### 2.3. Rheological measurements

Rheological properties were measured with stress-controlled rheometer (Anton Paar MCR100). In this study, apparent viscosity, dynamic viscoelasticity, and creep and creep recovery properties were measured. Rheological measurements were conducted only for POE-G.

#### 2.3.1. Apparent viscosity

A plate-plate configuration with rotor diameter of 25 mm and gap distance of 1 mm was used. Abrasive papers of 400 grit size were pasted both on the rotor and on the stationary disk to avoid a wall slip. The constant shear rate of  $1 \text{ s}^{-1}$  was applied to the sample, and the resulting stress was measured for 300 s. Apparent viscosities were calculated from the ratio of stress to shear rate. Measurements were performed in the temperature range from -60 to  $80^\circ\text{C}$ .

#### 2.3.2. Dynamic viscoelasticity

A plate-plate configuration was used for dynamic viscoelastic measurements. Since the generating torque changed according to the temperature, rotor diameter was changed from 8 to 25 mm. Gap distance was set at 1 mm. Oscillation at constant strain of 0.1% was applied to the sample lubricating grease in the frequency range from 0.05 to 100 Hz, and storage modulus  $G'$  and loss modulus  $G''$  were recorded. We confirmed in advance that selected strain was within the linear viscoelastic region. Measurements were performed in the temperature range from -89 to  $25^\circ\text{C}$ . No abrasive paper was used in these measurements. This is because strain is so small that the wall slip does not occur.

#### 2.3.3. Creep

A plate-plate configuration with rotor diameter of 25 mm and gap distance of 1 mm was used. The constant torque (stress) was applied instantaneously, and the strain of the sample was measured for 50 s. Measurements were performed in the temperature range from -80 to  $80^\circ\text{C}$ . Applied torque was changed from 0.01 to 15 mNm in accordance with the magnitude of displacement of the sample. No abrasive paper was used in these measurements.

## 3. Results

### 3.1. Dielectric properties

Figure 3 shows dielectric relaxation curves of POE-G. Upper graph is dielectric constant and lower graph is dielectric loss as a function of frequency. The value of dielectric constant decreased with increasing in frequency, and clear dielectric loss peaks have been observed. From the detailed observation of the dielectric relaxation curves, we can confirm the existence of different two dielectric relaxation processes. In order to show these two dielectric relaxation processes clearly, dielectric loss curve of POE-G at temperature of  $-53^\circ\text{C}$  is picked out and shown in Fig. 4. In this figure dielectric loss curves of PAO-G and NPGC9 base oil at the same temperature are shown together. Two clear dielectric relaxation peaks are found in the dielectric loss curve of POE-G. The loss peak frequency of low-frequency relaxation (LF relaxation) in POE-G approximately coincides with the loss peak frequency of PAO-G. PAO-G is the lubricating grease that is the combination of non-polar base oil and lithium 12-hydroxy stearate. Since a non-polar material does not show dielectric relaxation, the relaxation of PAO-G is attributed to the hydroxyl group in lithium 12-hydroxy stearate.

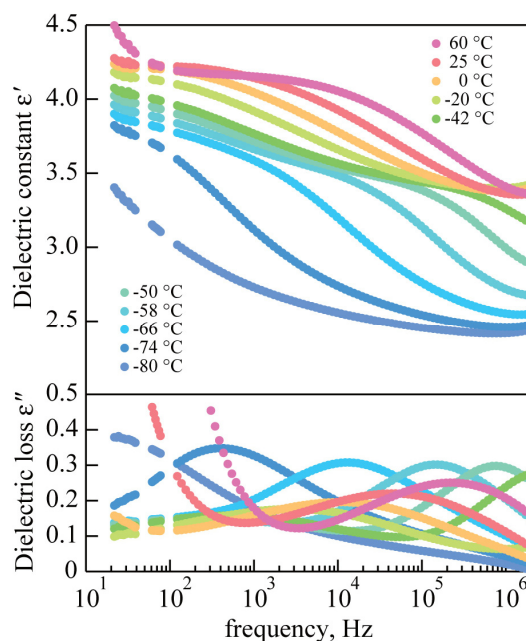


Fig. 3 Dielectric relaxation curves of POE-G



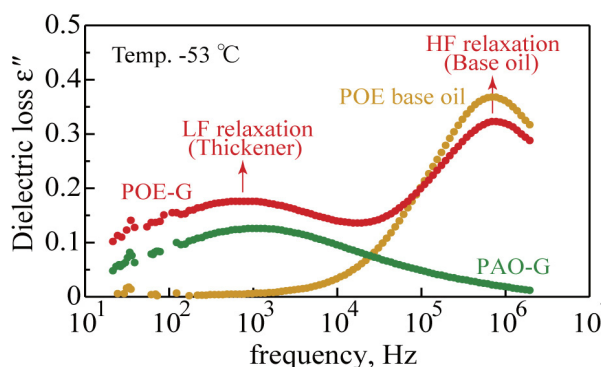


Fig. 4 Dielectric loss curves of POE-G, PAO-G, and NPGC9 at -53°C

Therefore, the thickener causes LF relaxation of POE-G. The loss peak frequency of high-frequency relaxation (HF-relaxation) in POE-G coincides with the loss peak frequency of NPGC9 base oil. Therefore, NPGC9 causes HF relaxation of POE-G. The dielectric loss curve of LF relaxation was very broad compared to that of HF relaxation. When the orientational motion of permanent electric dipoles of various scales takes place, distribution of dielectric relaxation time broadens, and as a result, a broad dielectric loss curve is observed. Since hydroxyl group exists in lithium 12-hydroxy stearate, thickener forms a hydrogen bond network between thickener molecules. It is considered that the hydrogen bond network of POE-G involves various scales of structure and broad dielectric loss curves are observed.

## 3.2. Rheological properties

### 3.2.1. Apparent viscosity

Figure 5 shows a time dependence of the apparent viscosity of POE-G obtained at various temperatures. The apparent viscosity of POE-G decreased with time because of thixotropy of lubricating grease. In the

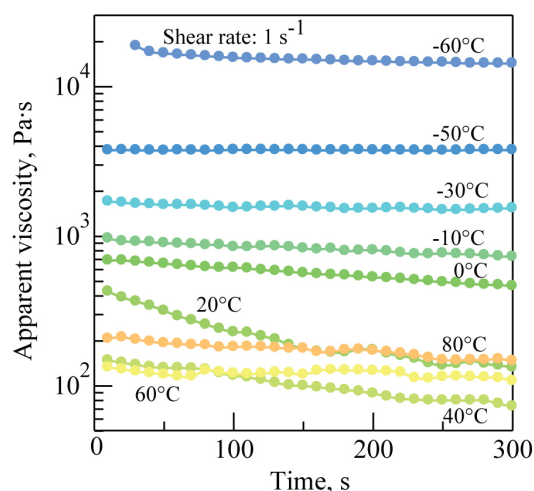


Fig. 5 Time dependence of the apparent viscosity of POE-G

temperature range below room temperature, the lower the temperature, the more the apparent viscosity of POE-G increased. However, this relation was reversed above room temperature. Although apparent viscosity measurements of POE-G were performed several times, this phenomenon was observed every time. In general, apparent viscosity of lubricating greases decreases with increasing temperature. The reason why the apparent viscosity of POE-G showed such temperature dependence cannot be elucidated at present.

### 3.2.2. Dynamic viscoelasticity

Figure 6 shows  $G'$  and  $G''$  of POE-G as a function of frequency at various temperatures. Filled circles and open circles indicate  $G'$  and  $G''$ , respectively. On the whole,  $G'$  increased monotonically with increasing frequency at constant temperature. The value of  $G'$  increased with decreasing temperature at fixed frequency.  $G'$  showed almost constant value of about 0.6 GPa at -89°C. The peak of  $G''$  was observed from -76 to -83°C in this frequency window.

For thermorheologically simple materials, it is possible to obtain rheological property curves at different temperature levels which can be shifted along the time or frequency axis to generate a single curve known as a master curve [11]. The distance of the shift is referred to as shift factor  $a_T$ . This method is known as the time-temperature superposition principle. This method was applied to the dynamic viscoelastic data of POE-G. Figure 7 shows the master curves of  $G'$  and  $G''$  of POE-G. A temperature of -79°C was selected as the reference temperature of the superposition. The dynamic viscoelastic data at each temperature produced fine composite curves of storage modulus and loss modulus.

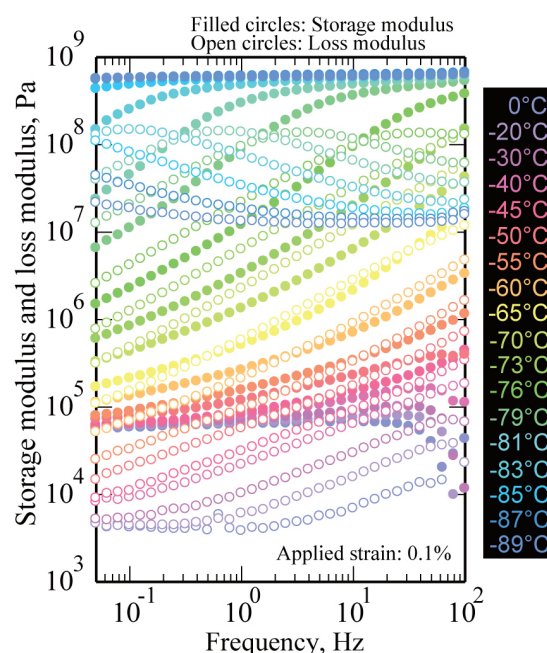


Fig. 6 Storage modulus and loss modulus of POE-G

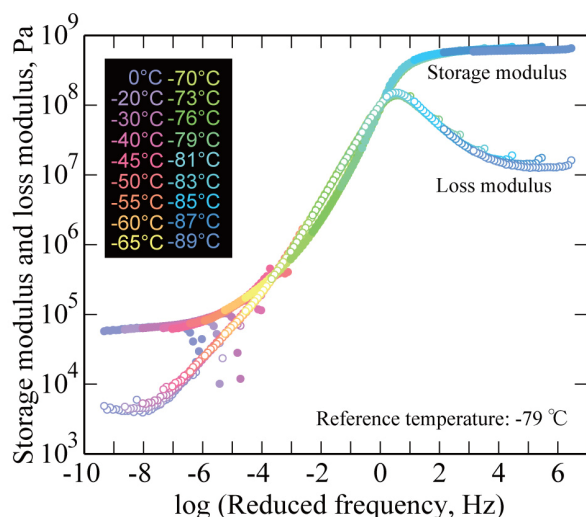


Fig. 7 Master curves of storage modulus and loss modulus of POE-G

The viscoelastic relaxation time,  $\tau_M$ , can be obtained from a peak frequency of loss modulus,  $f_{M\_max}$ , by following equation:

$$\tau_M = 1/2\pi f_{M\_max} \quad (3)$$

where  $\tau_M$  is the viscoelastic relaxation time and  $f_{M\_max}$  is the loss modulus peak frequency. The viscoelastic relaxation time characterizes the mobility of molecules. The viscoelastic relaxation time of POE-G at -79°C is 45.5 ms.

### 3.2.3. Creep

Figure 8 shows the creep curves of POE-G at temperatures from -80 to 0°C. The vertical axis indicates the creep compliance. The creep compliance increased with time. The higher the temperature, the higher the value of creep compliance. Like the case of dynamic viscoelasticity, time-temperature superposition was performed to the results of creep measurements. Figure 9 shows the master curve of creep data. Reference temperature of superposition was -65°C. Very smooth composite curve was obtained.

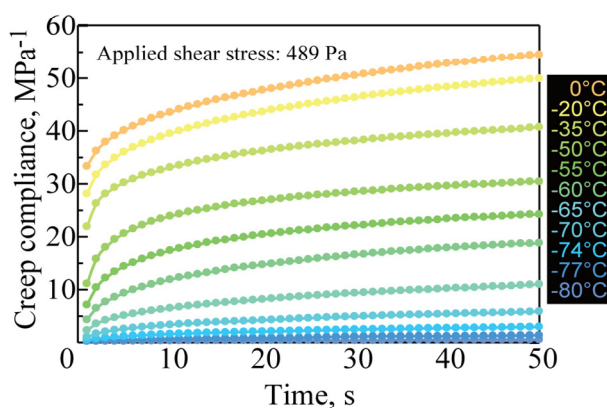


Fig. 8 Creep compliance curves of POE-G

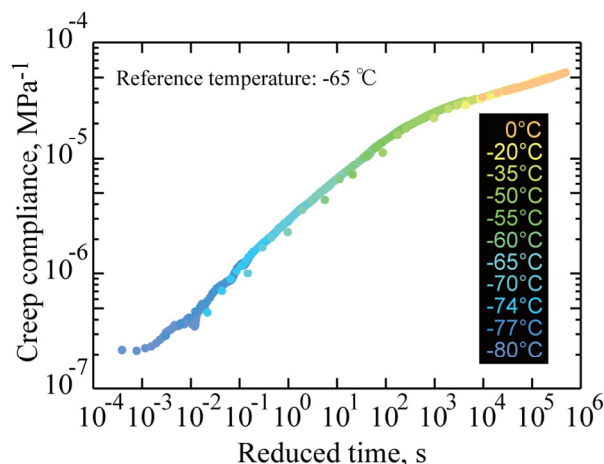


Fig. 9 Master curve of creep compliance of POE-G

## 4. Discussion

Two dielectric relaxation processes, HF relaxation and LF relaxation, were observed in POE-G. The LF and the HF relaxation processes are attributed to the thickener and the NPGC9 base oil, respectively. From the peak frequency of dielectric loss, dielectric relaxation time can be calculated from the following equation:

$$\tau_D = 1/2\pi f_{D\_max} \quad (4)$$

where  $\tau_D$  is the dielectric relaxation time and  $f_{D\_max}$  is the dielectric loss peak frequency. The dielectric relaxation time becomes the criterion of the speed of polarization formation, and related to the mobility of electric dipoles.

Temperature dependence of dielectric relaxation time, apparent viscosity, viscoelastic relaxation time, shift factor obtained from creep compliance data, and viscosity of NPGC9 base oil are described by the Arrhenius plots in Fig. 10. As for the apparent viscosity, the data after 300 s were shown. Since the frequency window of the rheological measurement is not so wide, the viscoelastic relaxation time data obtained from the dynamic viscoelastic measurement is limited in narrow temperature range. Therefore, the viscoelastic relaxation time was calculated using the shift factor obtained from the time-temperature superposition of the dynamic viscoelastic data. The viscoelastic relaxation time at temperature  $T$  can be obtained from the viscoelastic relaxation time at reference temperature,  $\tau_M(T_0)$ , and the shift factor  $a_T(T)$  by the following equation:

$$\tau_M(T) = a_T(T) \times \tau_M(T_0) \quad (5)$$

The dielectric relaxation time of the POE-G LF relaxation showed Arrhenius-type temperature dependence. On the other hand, the dielectric relaxation time of the HF relaxation exhibited non-Arrhenius-type temperature dependence.

Temperature dependence of the viscoelastic relaxation time, and the shift factor obtained from the superposition of creep compliance data of POE-G showed very similar to that of the dielectric relaxation

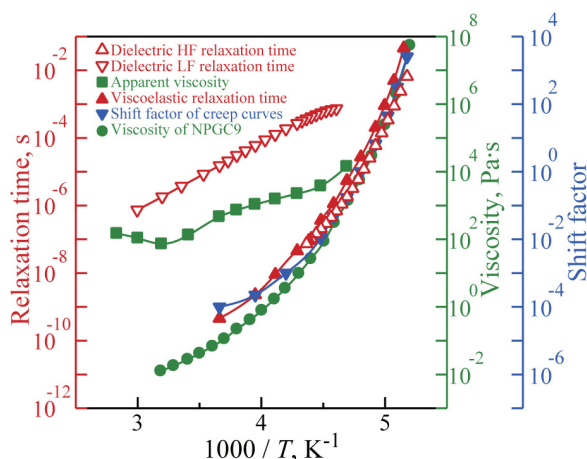


Fig. 10 Temperature dependence of dielectric relaxation time and various rheological properties of POE-G

time of the HF relaxation. These temperature dependences are also similar to the viscosity change with temperature of NPGC9, which is the base oil of POE-G. Therefore, HF dielectric relaxation, dynamic viscoelastic property and creep behavior of POE-G depend on the mobility of the base oil in the grease.

The temperature dependence of LF dielectric relaxation time is different from that of any rheological properties of POE-G. LF dielectric relaxation is due to the presence of hydroxyl group in the thickener molecules. However, this is not related to any rheological properties. This dielectric LF relaxation is probably caused by the local motion of hydroxyl groups in the thickener fibers.

## 5. Conclusions

Dielectric spectroscopy method was applied to investigate the dynamics of the base oil and the thickener in the lubricating grease POE-G. Apparent viscosity, dynamic viscoelasticity, and creep compliance of POE-G were measured and compared these temperature characteristics to that of the dielectric relaxation time. The conclusions obtained in this study are as follows:

- (1) Two dielectric relaxation processes were observed in POE-G.
- (2) The dielectric relaxation observed in low-frequency and high-frequency regions are attributed to thickener and polyol ester base oil, respectively.
- (3) Time-temperature superposition principle was applicable for the dynamic viscoelastic data and the creep compliance data of POE-G.
- (4) Temperature dependence of the dielectric relaxation time of HF relaxation is similar to that of viscoelastic relaxation time and shift factor of creep compliance of POE-G, and also similar to that of viscosity of polyol ester base oil.

- (5) No clear relation was observed between temperature characteristics of the dielectric relaxation in low-frequency region and the rheological properties measured in this study.

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