

Structure Analysis of Base Oils under High Pressure Using X-Ray Diffraction

Tomoko HIRAYAMA^{*1}, Kazuaki NEMOTO¹, Susumu HAYASE¹, Takashi MATSUOKA¹
¹Doshisha Univ., Kyotanabe, Kyoto 610-0394, Japan

Introduction

The microscopic structure of lubricants has received much attention recently because of its great influence on the tribological properties of the sliding surface under lubrication conditions, especially under elastohydrodynamic ones. As is well known, the structure of a conventional lubricating oil transforms into a quasi-solid structure under high pressure, as occurs in continuously variable transmission mechanics, for example^[1-3]. Past studies have focused mainly on the macro-characteristics of lubricants under high pressure, such as their viscosity and bulk modulus^[4-11]. Nevertheless, some studies have revealed that the tribological properties largely depend on the molecular structure of the oil^[12-14]. Several simulation studies using molecular dynamics techniques have investigated the molecular structure of lubricating oil under high pressure^[15-18]. Such studies indicate the obvious growing attention being paid to the microscopic behavior of lubricating oils.

X-ray diffraction (XRD) is traditionally used for obtaining information about the microscopic structure of materials, even amorphous and liquid ones^[19,20]. The structure is estimated by analyzing the intensity profiles of the scattered X-rays. The macroscopic tribological properties may be closely linked to the molecular structure of the lubricants; however, there have been no reports of directly investigating the microscopic structure of lubricating oils using XRD in the tribology field.

We have now used XRD to analyze the structure of lubricating oils, focusing especially on their microscopic behavior under static high pressure. Considering that conventional lubricating oils consist of several base oils, we selected two simple base oils as samples: n-hexadecane and dicyclohexyl. The former is a chain hydrocarbon, while the latter is a dual-cyclic hydrocarbon that has been used as the base oil for traction fluids^[21]. The simple and contrasting structures of these two oils make them well suited for an initial trial study. We used synchrotron radiation X-rays to analyze their structure because they have high brightness and a wide energy range. In addition, using them enabled us to quickly obtain accurate intensity profiles compared to using X-rays in common laboratories. In particular, we investigated the microscopic structure of the base oils at atmospheric pressure and their microscopic behavior under high pressure, as a first trial. Two X-ray diffractometers with a cubic multi-anvil press were used for the analysis: the 'Max80' at the KEK synchrotron facilities and the 'SMAP2' at the SPring-8 synchrotron facilities, as shown in Figure 1.

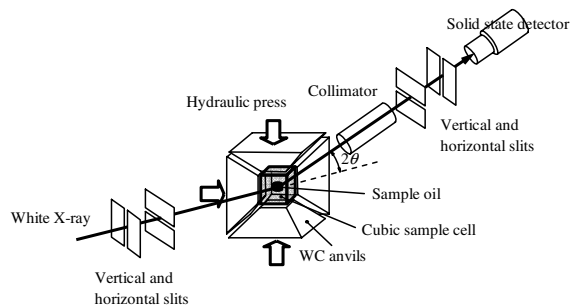


Fig. 1 Optical alignment of diffractometers with cubic multi-anvil press

Results and Discussion

We compressed a sample cell to 180 MPa by loading the multi-anvils and then decreasing the pressure stepwise, measuring the intensity profiles at each step. The scattering intensity profiles obtained for dicyclohexyl are shown in Figure 1. The figure clearly shows that the scattering intensity at atmospheric pressure was smooth and continuous without any sharp peaks except one broad peak at around 29 keV from the liquid, as mentioned above. The profiles became narrower and sharper as the pressure was increased, resulting in several strong peaks. This indicates that the structure of the sample oil changed from liquid to solid with increasing pressure. Some intensity peaks were independent of pressure in the figure. When the sample was a single crystal, not all the diffracted intensity was caught by the one-dimensional detector in the apparatuses we used. If the samples had been a polycrystal, a ring diffraction pattern would have been appeared, and all the peaks would have been captured even by the one-dimensional detector. Now, some peaks, such as those at around $E = 25$ and 36 keV, appeared in some cases but not in others. It means that the solid is not a polycrystal or amorphous but a single crystal (or polycrystal growing into a single crystal). The diffraction pattern for the n-hexadecane showed the same tendency as that for the dicyclohexyl.

In the anvil press process, the sharp intensity peaks that diffracted from the crystal were not observed until the pressure exceeded 160 MPa. A pressure-viscosity report by the ASME^[1] says that the 2-cyclohexylethyl transforms into solid phase at about 200 MPa and 20 °C, as measured using Bridgman falling weight equipment^[29]. This confirms the reliability of the pressure calibration of our experiments. The two strong diffraction peaks at 25 and 36 keV for 2θ of 6 deg. correspond to crystal lattice spacing (d) of 4.7 and 3.2 Å, respectively. We attribute these two peaks to

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the arrangement of the C-C bonds because the two spacings are almost integral multiples of C-C bond spacing, $d = 1.54 \text{ \AA}$. That is, the sample oil transformed into a single crystal while keeping the C-C bond structure of the liquid phase as the base structure.

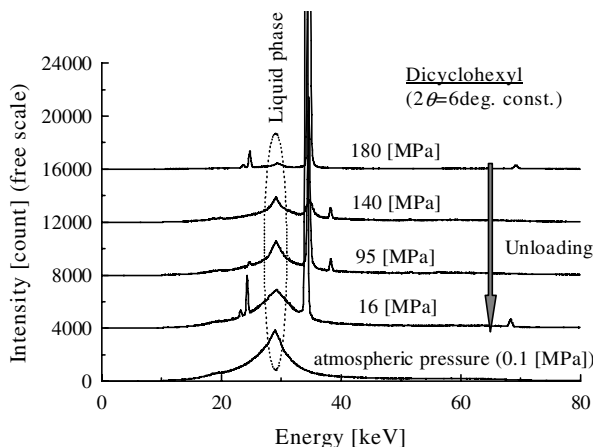


Fig. 2 Scattering intensity profiles of dicyclohexyl in the unloading process from high pressure

Conclusion

We analyzed the microscopic structure of two simple base oils (n-hexadecane and dicyclohexyl) under high pressure using synchrotron radiation X-ray diffraction. The obtained results are summarized as follows:

- Oil solidification was observed through the change in intensity profiles under high pressure. The solids were not amorphous but single crystal. The pressure inducing the dicyclohexyl to transform into crystal was about 160 MPa, which roughly agrees with the ASME pressure-viscosity report. The history of the phase transition had a large hysteresis; that is, once phase transition began, crystals left even at almost atmosphere pressure in the unloading process.
- To investigate the degree of crystallization of dicyclohexyl over time, we measured the intensity profiles at 5-min. intervals at a constant pressure. The oil crystallized over time, and the time span for the crystallization was on the order of about an hour.

The conditions using in this study were quite different from actual tribological conditions; they featured rapid dynamic compression under a shearing force. The insights obtained about the microscopic behavior of oils should facilitate the design of lubricant molecules to achieve better tribological performance. The structure of oil crystals under high pressure needs to be clarified to enable analysis using multi-axis diffractometers for molecular design. This work is simply the first step in structural analysis using synchrotron radiation.

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* thirayam@mail.doshisha.ac.jp