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

Tomoko HIRAYAMA[1)], Kazuaki NEMOTO[1)], Takanori HATTORI[2)]

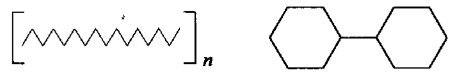
[1)]Doshisha University, [2)]JAEA

The microscopic structures of two base oils under high pressure were analysed using a synchrotron radiation X-ray diffraction method. By applying the synchrotron radiation X-ray to the sample oil, radial distribution functions of the samples were clearly obtained under normal pressure, and scattering intensity profiles of the sample were observed under several high pressure conditions. These results show that the oil transitioned from liquid to crystal with increasing pressure. In addition, under constant high pressure, oil crystallized with time, making the transition in about an hour.

Keywords: Base oils, High pressure, Crystallization, X-ray diffraction

1. Introduction

Microscopic structure of a lubricant has been focused on a lot recently because it affects macroscopic properties, especially under tribological conditions[1-6]. The purpose of this study is to analyze microscopic structure of base oils under high pressure using synchrotron radiation X-ray diffraction and to determine exactly the pressure at which the oil transitions from liquid to solid. Two base oils, n-hexadecane $(CH_3(CH_2)_{14}CH_3)_n$ and dicyclohexyl $C_6H_{11}C_6H_{11}$, were prepared as sample oils. The former is a normal alkane, and the latter a dual-cyclic alkane. The molecular geometries of these oils are shown in Figure 1.



(a) n-hexadecane (b) dicycrohexyl

Fig. 1 Molecular geometries of sample oils

2. Methods

We used two beam lines with a cubic multi-anvil type apparatus to analyze microscopic structure under high pressure; One is installed in BL14B1 at SPring-8; the other is 'Max80 in AR-NE5C at the High Energy Accelerator Research Organization, KEK. The former beam line belongs to JAEA.

3. Results and Discussions

At first, Figure 2 shows the structure factors of the sample oils analyzed with the obtained intensity profiles. As can be seen in the figure, both sample oils have several peaks at almost the same Q values. This is due to the similarities of the structures of these samples. Both n-hexadecane and dicyclohexyl consist of carbon and hydrogen, and the ratio of carbon to hydrogen is 0.32 and 0.35, respectively. As a result, their structure factors are very similar.

Second, we discuss the results at normal pressure. In Figure 3 and 4, it can be seen that there are several peaks of the PDF and the RDF. The peaks around r=1.1 Å and 1.54 Å correspond to the C-H and C-C bonds of sample oils, respectively. As a whole, we were able to confirm the success of the structure analysis by comparing it with the common bond distance at normal pressure.

Third, we discuss the phase transition under high pressure. Figure 5 shows some scattering intensity profiles of dicyclohexyl at several pressures. These profiles were obtained under the constant setting 2θ=6 degree. As the pressure increased, the intensity profiles became sharper, coming to several strong peaks. As a whole, the higher the pressure became, the narrower and sharper the intensity peaks became. This indicates that the sample oil was changing its structure from liquid to crystal with the increased pressure. This result shows that oil transitions from liquid to crystal at about 16 MPa.

Finally, we discuss the progress of crystallization with time. To investigate the degree of crystallization of the dicyclohexyl with time, intensity profiles were obtained at intervals of 300 seconds at a constant pressure of 820 MPa. The obtained results are shown in Figure 6. From the figure, we can see that the plot of intensity became sharper with time. This indicates that the crystallization of oil proceeds with time.

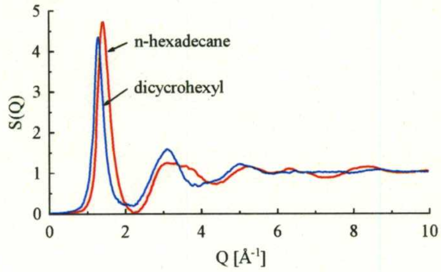


Fig. 2 Structure factor of sample oils

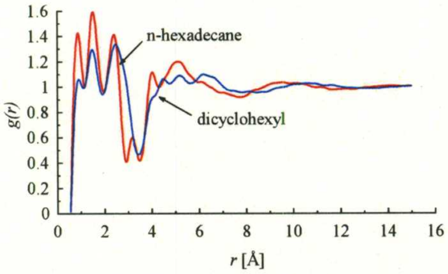


Fig. 3 Pair distribution functions of sample oils

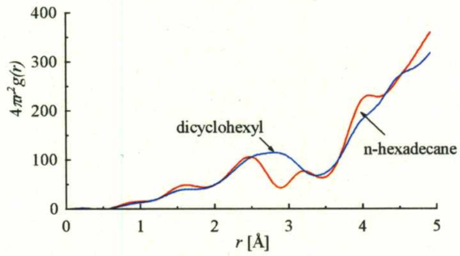
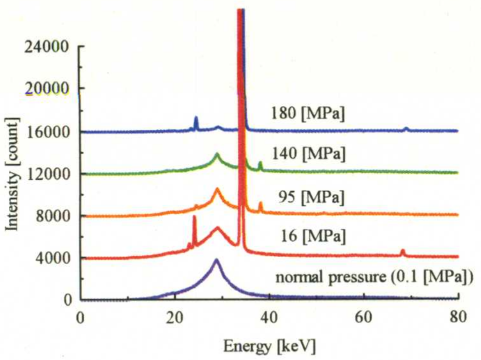


Fig. 4 Radial distribution functions of sample oils



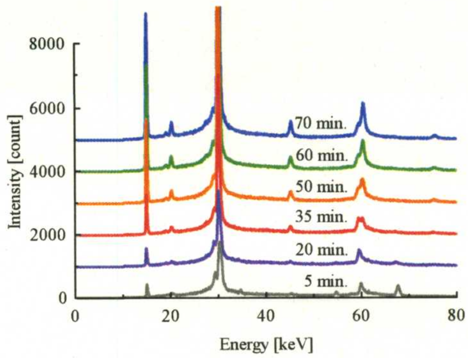


Fig. 5 Scattering intensity profiles of dicyclohexyl increasing pressure value (left)
Fig. 6 Scattering intensity profiles of dicyclohexyl at 820 MPa (right)

4. Conclusions

Conclusions of this study are summarized as follows:

1. The PDF and RDF of the n-hexadecane and dicyclohexyl were clearly obtained by X-ray diffraction method without any degeneration of the oils. It was confirmed that they correspond to their microscopic structures at normal pressure.
2. Crystallization of the oil under high pressure was observed through the change of intensity profiles. The pressure inducing the dicyclohexyl to transit to crystal is about 16 MPa.
3. To investigate the degree of crystallization of dicyclohexyl with time, intensity profiles were obtained at 300 second intervals at a constant pressure. The crystallization of the oil with time was observed in a time span on the order of an hour.

5. Acknowledgement

We wish to express sincere gratitude to Prof. K. Tsuji (Keio University), and Dr. T. Kikegawa (KEK), Dr. T. Hattori and Dr. Y. Katayama (Japan Atomic Energy Agency) for their sincere cooperation. This work was sponsored by the Ministry of Education, Science and Culture of Japan (No. 18760114).

6. References

[1] Ohno, N., *Mechanical properties of traction oil*, J. Japanese society of Tribologists, 46, 5 (2000) 349-354 (in Japanese).

[2] Fujishiro, I., *Raman scattering measurements of lubricant over glass transition pressure*, Proceedings of International Seminar on Microstructures and Mechanical Properties of New Engineering Materials (IMMM'93), 13, 1 (1993) 275-264.

[3] Nakamura, Y, *Measurement of physical properties of lubricants under high pressure by Brillouin scattering in a diamond anvil cell*, Journal of Tribology, Transactions of the ASME, 117, 3 (1995) 519-523.

[4] Nakamura, Y., *High Pressure Viscosity and Traction Characteristics*, J. Japanese society of Tribologists, 46, 5 (2000) 368-373 (in Japanese).

[5] Tamura, H. et al., *Molecular Dynamics Simulation for Lubricants*, J. Japanese society of Tribologists, 45, 9 (2000) 655-660 (in Japanese).

[6] Tamai, Y., *Rheological properties of lubricating oil and its relation to molecular structure*, J. Japan Petrol. Institute, 25, 3 (1982) 127-135.