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Effects of Temperature and Pressure on ZDDP

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Abstract A recent theoretical study proposed that the anti-wear property of zinc dialkyl dithio phosphate (ZDDP) is due to the formation of chemically connected networks as a result of pressure-induced cross-linkage of phosphate groups of thermally decomposed ZDDP. To investigate the initial decomposition processes and the possibility of linking of phosphate groups in the decomposed product, in-situ high-pressure and high-temperature infrared (IR) spectroscopy using synchrotron radiation were performed on the original ZDDP. At room temperature no substantial structural change was observed up to 21.2 GPa, a pressure far exceeding the predicted onset of a structural transformation for the model zinc phosphate at 7 GPa. The observed Pressure induced broadening of the IR peaks is most likely associated with structural disorder or amorphization of ZDDP which is completely reversible upon decompression. When ZDDP is heated under pressure, an irreversible transformation was observed around 225 °C and 18.4 GPa. The experimental results show that ZDDP undergoes substantial decomposition at high pressures and high temperatures but no hint of cross-linkage of phosphate groups was found.

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Introduction

Zinc dialkyl dithio phosphate (ZDDP) is the most successful anti-wear additive used in the lubricant for automobile engines. Since the introduction of this product to the industry more than 5 decades ago, intensive effort utilizing a variety of experimental techniques has been devoted to the characterization of this material under different environmental conditions [1]. It is now recognized that ZDDP decompose in oil to form zinc phosphate chains that accumulate on surface forming a thin film [2]. Despite the longevity of ZDDP as an effective and dependable anti-wear protection, recently there is growing environmental concern on the residues and the undesirable side-effect that the phosphorus in ZDDP deactivates the catalyst by forming a coating on the surface [3]. There is some urgency in the industry to search for alternative wear inhibitors. A key element towards this goal is the detailed understanding on the mechanism for the novel anti-wear functionality of ZDDP, which is still lacking.

The chemistry of ZDDP upon thermal treatment has been well documented [4, 5]. It was reported that ZDDP oil preheated at 150 °C shows a decrease in the length of the polyphosphate chains [5]. However, extensive thermal decomposition was observed when ZDDP samples were heated to 200 °C. Moreover, the films formed are much thinner and showed catastrophic wear [5]. In contrast to the extensive studies on temperature effect, information on the effect of pressure to the anti-wear property of ZDDP is comparatively scarce. It is already known that ZDDP does not inhibit wear directly. It decomposes at high temperature and possibly with rubbing, forms a protective zinc phosphate film. Insight into possible molecular mechanisms for the functionality of ZDDP additives in lubricant under pressure has appeared in a recent theoretical study on a model system [6]. The computer simulations using first principles molecular dynamics methods were performed on molecular zinc phosphate. Cross linkage of phosphate groups was found to occur at a relatively low pressure of 7 GPa (1 GPa = 10 kbar ca. 10,000 atmosphere) and completed at 17 GPa under ambient temperature. It was then suggested that the network structure is the precursor of the thin film and that the increased connectivity between zinc phosphates increases the hardness of the film and forms a mechanically protective barrier. This study provides new insight into the conventional interpretation of anti-wear mechanism where the formation of protective films is associated with long chains of polyphosphates. However, it is surprising that a network structure can occur at such relatively mild conditions. In reality, the pressure required to induce the polymerization may be acquired via rubbing of the interfaces. In passing, it is noteworthy that so far there is no direct experimental evidence to confirm or dispute the formation of zinc phosphate glass in ZDDP films.

The main goal of the present study is to investigate the effects of extreme pressures and temperatures on the structures of ZDDP. The technique employed is infrared (IR) absorption spectroscopy. Infrared spectrum of a well defined material can be used as a finger-print to monitor structural changes. The IR spectra of pure ZDDP and several lubricant additives have been well characterized [7] and the thermal effect studied up to 250 °C [8]. In recent years, owing to the advances in synchrotron radiation technologies, IR spectroscopy has been extended to high pressure and high temperature using diamond anvil cells (DAC) [9]. In the present study, structural changes associated with high pressure and high temperature on a commercial ZDDP sample is monitored with IR spectroscopy under in-situ conditions. To the best of our knowledge, this is the first systematic investigation on the effect of pressure directly on ZDDP itself.

Experimental

Progress in understanding of properties of materials at high pressure in many respects is connected to the DAC technique [9]. The two opposing anvils are brilliant-cut diamonds with small flat surfaces ground on their tips. High pressures are then generated in the DAC by taking a small force applied to a large area and transferring that same force to a small area. Depending on the size of the diamonds and the cell configuration, pressures from a few kbars to mega-bars can be generated. For IR measurements, low fluorescence type IIa diamonds were used as anvils.

To mimic conditions at high pressure and high temperature, a hydrothermal diamond anvil cell (HDAC) was used [10]. A typical HDAC consists of local electric resistive heaters made of molybdenum or nickel–chromium wire around the tungsten carbide seats that support the diamond anvils. Ceramic supports under the seats minimize the heat loss so that approximately 150 W is sufficient to produce a temperature of 1,000 °C. The temperature can be measured using chromel-alumel (K-type) thermocouples.

A rhenium gasket is used to contain the ZDDP sample between two opposing diamond anvils having faces 1.0 mm in diameter. The gasket is usually 0.125–0.250 mm thick with a hole 0.500 mm in diameter. A ruby chip was placed on the sample as the pressure calibrant. The pressure was determined using the standard ruby fluorescence method corrected for temperature effect [11–13]. ZDDP was loaded into the HDAC with KBr as both pressure transmitting media and dilutor to facilitate the IR measurements in absorption mode. Infrared radiation from the U2A beamline at the National Synchrotron Light Source, Brookhaven National Laboratory was focused on a 100 µm × 100 µm spot on the sample through the diamonds. An IR microscope is coupled to a Bruker IFS 66v/S vacuum FTIR spectrometer using a resolution of 4 cm^{-1}. IR spectra were measured on the practical temperature range from ambient to 200 °C and pressure up to 21 GPa.

Results and Discussion

Cold Compression

The first set of experiments was designed to test the theoretical hypothesis of pressure-induced cross-linkage at low temperature. To this end, a ZDDP sample was placed in the DAC and the pressure was increased gradually while keeping the entire assembly at room temperature (i.e., cold compression). IR spectra measured with increasing pressure from 0 to 21.2 GPa (up-stroke) and then on decompression (down-stroke) over the frequency range 600–1,800 cm^{-1} and 2,600–3,120 cm^{-1} are shown in Fig. 1.

The IR spectrum obtained at 0 GPa is very similar to that in previous studies [7]. The absorption features from 2,920 to 3,000 cm^{-1} are assigned to the C–H stretching vibrations of the alkyl groups. For example, IR bands observed at 2,982, 2,934 and 2,873 cm^{-1} are associated with asymmetric CH_3 stretching, CH stretching and symmetric CH_3 stretching respectively. The peaks observed from 1,300 to 1,400 cm^{-1} are associated with the H–C–H asymmetric (1,466 and 1,452 cm^{-1}) and symmetric (1,385,

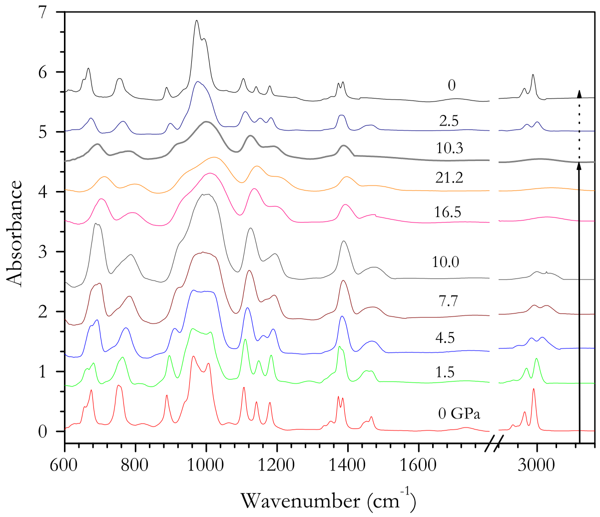

Fig. 1 Room temperature Infrared spectra for ZDDP as a function of static pressure. Pressures in GPa are labeled above each spectrum. The absorbance has been normalized with respect to beam current of the synchrotron light source. The spectra under different pressures have been offset vertically for clarity. Solid arrow indicates compression (up-stroke). Dotted arrow indicates decompression (down-stroke)

1,373 and 1,347 cm^{-1}) bending modes. The spectral region most relevant to the present study is from 920 to 1,200 cm^{-1}. The triplet at 1,180, 1,140 and 1,102 cm^{-1} is attributed to C–O–(P) vibrations while the strong bands at 1,006 cm^{-1} and 964 cm^{-1} are associated with P–O–(C) vibrations. The lower energy absorption at 888 cm^{-1} is due to the C–C stretching in the alkyl groups while those at 753 cm^{-1} and 675 cm^{-1} are associated with P–S stretching vibrations.

On increasing pressure, the IR spectra exhibit the normal trend that the absorption intensities weakened slightly but the widths of the peaks broadened substantially and the vibrations shifted to higher frequencies. In the spectral regions relevant to the vibrations of the P and O atoms, apart from theses changes, there is no obvious sign that might suggest substantial structural modification. In the P–S stretching region at 600–700 cm^{-1}, the shoulder at 660 cm^{-1} in the ambient IR spectrum broadened and merged into the main feature. Similarly, in the 920–1,200 cm^{-1} region, the main spectral features remain largely unaltered even up to 21.2 GPa, the highest pressure attempted in this study. This pressure already far exceeds the practical limit of the pressure that can be achieved by rubbing the surfaces.

Upon decompression, the IR spectra gradually recover the distinct features observed in the initial zero pressure spectrum. More importantly, positions (frequencies) of the all absorption peaks are the almost identical to the starting material except for the region of 920–1,000 cm^{-1} where the band positions (993 and 972 cm^{-1}) for the recovered material are a little different than the original band positions (1,006 and 964 cm^{-1}). Slight variations observed in the same spectral region can be attributed to a difference in the texture and thinning of the sample after compression.

The lack of distinct change on compression and the full recovery of the spectral features upon decompression are strong evidences that there are no physical or chemical change of the starting material. These results demonstrate unequivocally that, at room temperature, there is no permanent pressure-induced structural change in ZDDP, even up to a pressure of 21 GPa. The observation that ZDDP does not transform on cold compression is consistent with the conventional picture that ZDDP must decompose to other intermediate species to form anti-wear films. It is noteworthy that the theoretical calculations employed a simple model system, the zinc phosphate. Experimental high pressure study [14] of this model system at room temperature indeed found evidences of pressure-induced cross-linking at the predicted pressure range. Therefore, the theoretical prediction was successful for the model system but did not fully account for the complexity of ZDDP.

High-Pressure High-Temperature Effect

Under normal operating conditions, the effects of both temperature and pressure on the formation of anti-wear film have to be considered. To examine these effects, a commercial sample of ZDDP was loaded in a HDAC [10]. The sample was first compressed to 15.1 GPa at room temperature. The pressure and the temperature were then increased slowly. The measured IR spectra under high pressure and high temperature are shown in Fig. 2. Once again, the IR spectral features broadened on compression. However, when the temperature is raised to 55 °C (328 K) at 16.5 GPa from 15.1 GPa and ambient temperature, no change in the IR spectrum was observed. The spectrum remains largely unchanged upon further compression to 17.5 GPa at a temperature of 200 °C (473 K). This result is highly significant as it shows that ZDDP is stable under relatively high static pressure at moderate temperature.

The profile of the IR spectrum changed abruptly upon further heating to 225 °C (498 K), although remnants of the prominent absorption bands are still visible. For example, in the characteristic vibrational bands involving P and O atoms from 940 to 1,160 cm^{-1}, the double peak feature clearly identifiable at 17.5 GPa and 200 °C becomes very broad and now extend from 840 to over 1,200 cm^{-1}. The same trend is also observed for the alkyl C-H stretching and bending vibrations at ca. 3,000 and 1,400 cm^{-1}, respectively (*vide supra*). There is no distinct absorption feature in the IR active C-H stretch region at ca. 3,000 cm^{-1} when the pressure is higher than 17.5 GPa at 100 °C (373 K). Moreover, the IR band at ca. 800 cm^{-1} assigned to C–C stretches has disappeared at 225 °C and

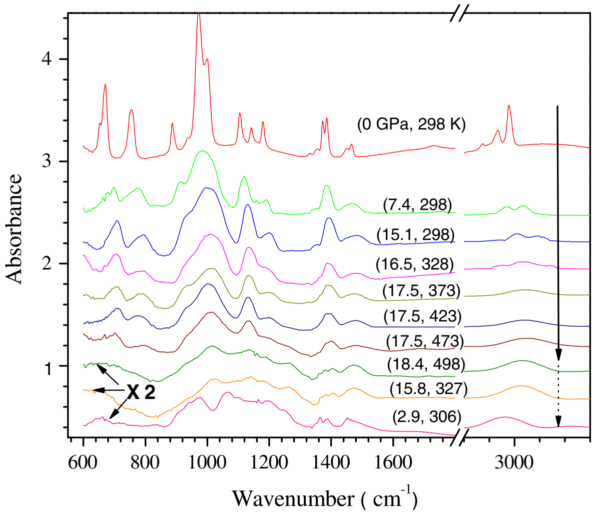

Fig. 2 High pressure–high temperature Infrared spectra for ZDDP. Pressures and temperatures under which the spectrum was collected are labeled above each spectrum in (GPa, K). The absorbance has been normalized with respect to beam current of the synchrotron light source. The spectra under different pressures/temperatures have been offset vertically for clarity. Solid arrow indicates compression (up-stroke). Dotted arrow indicates decompression (down-stroke). The bottom three spectra have been scaled by a factor of 2 for clarity purposes

18.4 GPa. The changes in the IR spectrum are permanent. Upon cooling and the release of pressure, the spectral features sharpened somewhat but there was no recovery to the starting material. Taken in all, the study of the changes in the IR spectra suggests an irreversible thermal degradation of the ZDDP starting at 220 °C. The thermal degradation is likely due to breaking of the C–C bonds of the alkyl chains. This observation may be compared with the thermal degradation temperature of >300 °C for short chain hydrocarbons under ambient pressure [5].

The present IR study even at highest pressure (18.4 GPa) and temperature (498 K) yielded no new features in the spectral region from 700 to 1,000 cm^{-1}, where characteristic vibrational modes of polyphosphate chains would have been observed. It has been reported that the P–O–P bridge vibrational frequencies in the shortest polyphosphate, pyrophosphate ($P_2O_7^{4-}$) occurs at 960–900 cm^{-1} and 800–700 cm^{-1} corresponding to antisymmetric and symmetric stretchings [15]. The lack of these characteristic IR modes indicates even under extreme pressure and temperature conditions there is no cross-linkage of phosphate groups in ZDDP. Although the spectrum of decompressed and temperature quenched sample (2.9 GPa and 306 K) exhibits residual features at 977, 1,067, 1,376 and 1,453 cm^{-1}, these frequencies are close to those observed in the original uncompressed sample rather than a possible polyphosphate.

Cross-linking of phosphate groups, if to occur at high temperatures, is in competition with the decomposition of ZDDP. Present results clearly show that decomposition is dominant at high pressure. However, the simple zinc phosphate may cross link at high pressures as suggested in a recent experiment [14]. The thermal decomposition of ZDDP upon heating under pressure is in agreement with the results obtained from thermal treatment of ZDDP at ambient pressure. When ZDDP oil solutions were pre-heated at 150 °C, the anti-wear films were found to be thicker and showed a decrease in polyphosphate chains [5]. Extensive decomposition has been reported when ZDDP oil solutions were heated at 200 °C [5]. Moreover, the thermal decomposition temperature at ambient pressure of 200 °C is very close to the 225 °C obtained in the present experiment at 17.5 GPa. In the latter, the slightly higher-decomposition temperature can be attributed to the pressure effect.

The proposed molecular mechanism [6] on the formation of a network structure although very pleasing, studies have found that in mild rubbing conditions the surface film present is mainly a thick phosphate film. In severe, heavily loaded/high-sliding speed conditions, a much thinner film with high sulphur content is formed. The latter observation suggests the decomposition of ZDDP will involve complex chemical reactions [1, 16, 17]. In addition, there are indications that the nature and formation mechanism of the film may be linked to hydrolysis and/or chemical intermediates at the surface during film formation [17, 18]. Thus a simple tribo-pressure mechanical explanation may not be sufficient. Moreover, it is recognized that the anti-wear properties of ZDDP is also dependent on the alkyl group structure. Therefore, zinc phosphate may be an over-simplistic model for the thermal decomposed product of ZDDP.

Conclusions

We reported the first in-situ IR study on the stability of a commercial ZDDP under extreme pressure and temperature conditions. On cold compression, the results show that ZDDP is remarkably stable under static pressure. At very high temperature and pressure, ZDDP was found to degrade. Under the current experimental P-T conditions, there is no substantial spectroscopic evidence to confirm the formation of a network glass structure as the result of cross-linkage via the phosphate groups. The results reported here show that the cross-linkage of phosphate groups in decomposed ZDDP may not be induced by pressure alone as suggested from the computer simulation [6], even though it was indeed observed in the model zinc phosphate system [14]. Therefore, the proposed molecular mechanism for the functionality of anti-wear property may not be extrapolated straightforwardly to the realistic and more complex ZDDP system.

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