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THERMAL OXIDATION CHARACTERISTIC OF ESTER OILS BASED ON RAMAN SPECTROSCOPY

TRACK OR CATEGORY

Lubrication Fundamentals II (Session 4G): Additives & Additive Degradation

AUTHORS AND INSTITUTIONS

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INTRODUCTION

Synthetic ester oils derived from renewable resources have been developed for applications in environmentally sensitive areas such as forests and agriculture areas due to their high biodegrade ability, and environmentally benign nature [1]. Their outstanding properties such as high thermal oxidative stability and biodegradability, good lubricating properties, low temperature flow characteristics and low volatility have resulted in a wide range of industrial applications(e.g. engine oils, two-stroke cycle oils, compressor oils, hydraulic fluids, greases and aviation oils) [2-3]. Thermal-oxidative degradation has been a persistent problem for lubricants, in particular for those synthetic esters mainly applied in industrial and engine oil, due to their high-temperature working conditions. Therefore, thermal-oxidation stability is one of the most important parameters responsible for extending the maximum service life of synthetic ester oil. Methods commonly used to analyze the thermal-oxidation stability and products of synthetic ester oils include thermal analysis, chemiluminescence, and chromatography-mass spectrometry. But all these methods cannot reveal the molecular structure changes of the oxidation process.

Raman spectroscopy is an efficiency tool to study molecular structures [4]. Raman spectroscopy combined with temperature control platform was used to test the change of lubricating oil under different temperatures [5-6]. In this work, how the Raman feature peaks of ester base oils influenced by online heating condition were studied based on continuous heating measure method by DXR laser microscopic Raman spectrometer. The change rules and characters of lubricant molecular structure during the thermal oxidation process were revealed by using this new method.

Experimental details

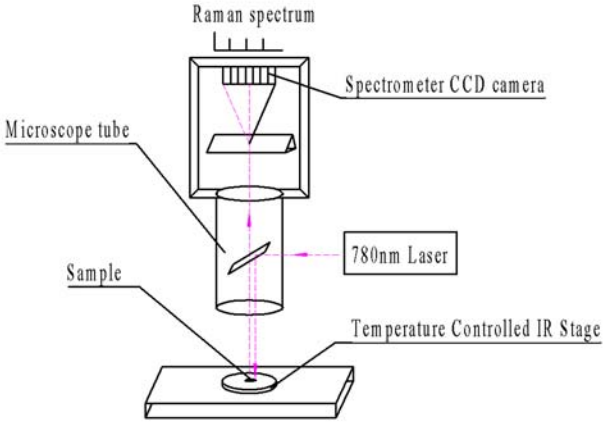

Fig.1. Scheme of the set-up with Raman spectroscopy coupled to temperature controlled stage

Raman spectra were recorded on a DXR Raman microscope (Thermo scientific, USA). The excitation wavelength was 780nm laser, and power on the sample about 20mW. A 10X magnification long working distance objective was used to focus the laser onto the sample and collect the scattered light in a backscattering geometry. The Linkam FTIR600 heating and freezing stage (Linkam Scientific Instruments, England) was installed under the objective lens of the DXR Raman microscope. Scheme of the set-up with Raman spectroscopy coupled to temperature controlled stage were shown in Fig.1.

Results and discussion

1. *The influence of temperature on Raman spectra of ester oils*

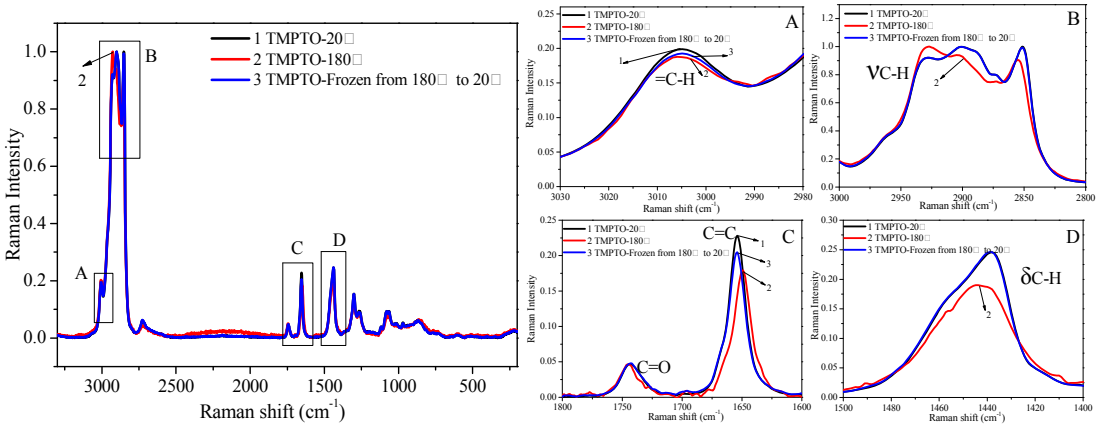

Fig.2. The Raman spectra of TMPTO under different temperature:(A) =C-H stretching vibration, (B) C-H stretching vibration peak of -CH_3 and -CH_2-, (C) C=O stretching vibration and C=C stretching vibration, (D) C-H shear vibration peak of -CH_2-

With the increase of temperature, the Raman spectra of ester base oils had different change. Fig. 2 shows the Raman spectra of TMPTO under different temperature. It can be seen that C-H stretching vibration peak of methyl and methylene and the shear vibration peak of methylene of ester oils are very sensitive to temperature. With the increase of temperature, the C-H stretching vibration peak intensity has different degrees of weakening and can basically recover after cooling. There is no obvious change on C=O stretching vibration peak with the temperature. The C=C stretching vibration peak position of TMPTO ester base oil shift to higher wave region and can recover after cooling. But the Raman intensity of =C-H and C=C of TMPTO ester oil cannot recover after cooling. The concentration of the =C-H and the C=C double bonds was decreased because of the chemical reaction. The Raman intensity dropped compared with the original status. The changes of the =C-H and C=C structures were irreversible.

2. *The influence of oxidation time on Raman spectra of ester oils*

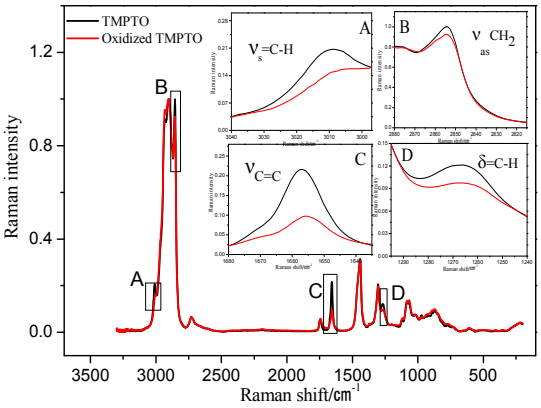

Fig.3 Raman spectra of TMPTO base oil before and after oxidation at 175℃: (A) =C-H stretching vibration(3006cm^{-1}), (B) -CH_2- symmetrical stretching vibration(2854cm^{-1}), (C) C=C stretching vibration(1655cm^{-1}) and (D) =C-H out of plane deformation vibration (1267cm^{-1})

The Raman spectra of TMPTO base oil before and after isothermal oxidation are shown in Fig.3. The results show that the Raman intensity of TDTM and DOA have no obvious changes under the isothermal condition, But the Raman intensity of =C-H, C=C and -CH_2- of TMPTO decreases with the increase of oxidation time.

The Raman spectra of TMPTO base oil with oxidation time were measured under isothermal oxidation condition (175℃) in Fig.4. During the thermal oxidation process, the Raman peaks associated with C=C and =C-H are decreased greatly. And the Raman intensity of the =C-H and C=C stretching vibrations dropped fast in the early oxidation stage with the violent reaction. The Raman intensity of -CH_2-symmetrical stretching vibration has a small degree of attenuation. Therefore, the main drawback restricts TMPTO wide application is its poor oxidative stability due to the presence of abundant unsaturated bonds (C=C) in the fatty acids moiety of TMPTO molecule, which are highly susceptible to radical attack and subsequently undergo oxidative degradation to form polar oxygen-containing compounds.

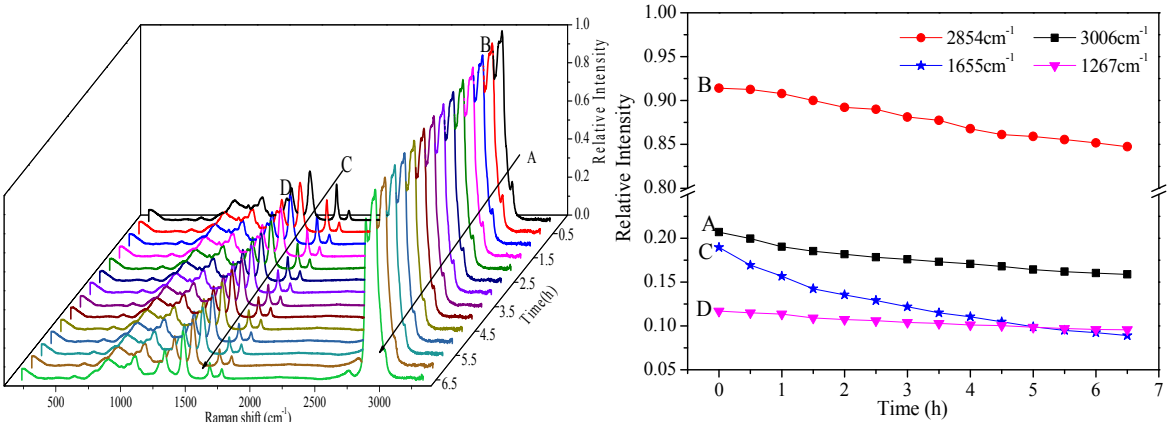

Fig.4 The Raman spectra of TMPTO base oil under different oxidation time at 175℃

Conclusions

In this paper, based on the continuous heating measure method by DXR laser microscopic Raman spectrometer, the change rules and characters of ester base oils(TDTM, DOA and TMPTO) molecular structure during the thermal oxidation process were revealed. The results can be concluded that:

(1) With the increase of temperature, the C-H stretching vibration peak intensity has different degrees of weakening and can basically recover after cooling. The Raman intensity of =C-H and C=C of TMPTO ester oil cannot recover after cooling.

(2) Under the isothermal condition, the Raman intensity of TDTM and DOA have no obvious changes, and the Raman intensity of =C-H, C=C and -CH_2- of TMPTO decreases with the increase of oxidation time.

ACKNOWLEDGMENTS

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KEYWORDS

Ester Oils; Thermal Oxidation; Raman Spectroscopy