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References

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● Direct analysis of hard disk media lubricants using MALDI-TOF MS

The high sensitivity of the Bruker MALDI-TOF MS autoflex maX allows for direct measurement and end group analysis of the fluorinated synthetic polymers used as lubricants at the monolayer level from industrial components.

Abstract

In this application note, we will present a case study of the analysis of a lubricant (fluorinated synthetic polymer) thinly applied to hard disk media at the near monolayer level. Since the subject of analysis is at the monolayer level and of a minute quantity, analysis is complicated by the difficulty of extraction and the limited analysis methods available for lubricants that have been applied. However, good results have been obtained thanks to the high sensitivity of the MALDI-TOF MS.

Introduction

The MALDI-TOF MS is a mass spectrometer suitable for a wide range of applications, from biological substances such as proteins, oligonucleotides, and lipids to general synthetic compounds. It is often used to analyze synthetic polymers because it can handle a relatively broad range of molecular weights, and its spectrum is usually simple as it tends not to generate multivalent ions. MALDI-TOF MS is also used for impurity analysis and degradation analysis as it is

capable of highly sensitive measurements and can clearly identify the components of mixtures — even in mixtures with different end groups — as long as the mass (molecular weight) is different. We took advantage of these features to analyze the end groups of a fluorinated synthetic polymer thinly applied to hard disk media at the near monolayer level.

Keywords:
autoflex maX,
polytools, polymer,
perfluoropolyether

Sample Preparation

The lubricant (D-4OH, MORESCO) was applied to a hard disk media to create a film with a thickness of about 1 nm by immersing the media in the lubricant solution. As per the examination of conditions ahead of time, the MALDI matrix was not used, and the cationizing agent (sodium trifluoroacetate) was added by spraying using the TM-Sprayer and the disk media sample was introduced into the MALDI-TOF MS device using a specially designed adapter. In general, when conducting measurements with the MALDI-TOF, a sample solution is prepared and mixed with a matrix solution and a cationizing agent solution if necessary. Then the mixture applied on a target plate may be dried to a solid state before being introduced into the device. This has meant that the sample does not necessarily need to be a solution as long as it is planar as MALDI imaging in recent years. For comparative purposes, we also measured the solution sample before it was applied to the hard disk media. Only cationizing agents were used for this sample, too.

MALDI-TOF MS Measurement Conditions

The device used was the autoflex maX. This model is capable of highspeed measurement with a 2000 Hz laser and has an improved dynamic range due to its 10-bit digitizer. Measurement was performed in Positive Reflector mode. Peaks were picked using flexanalysis software, after which polymer spectrum analysis software polytools 2.0 was used to analyze the measured data.

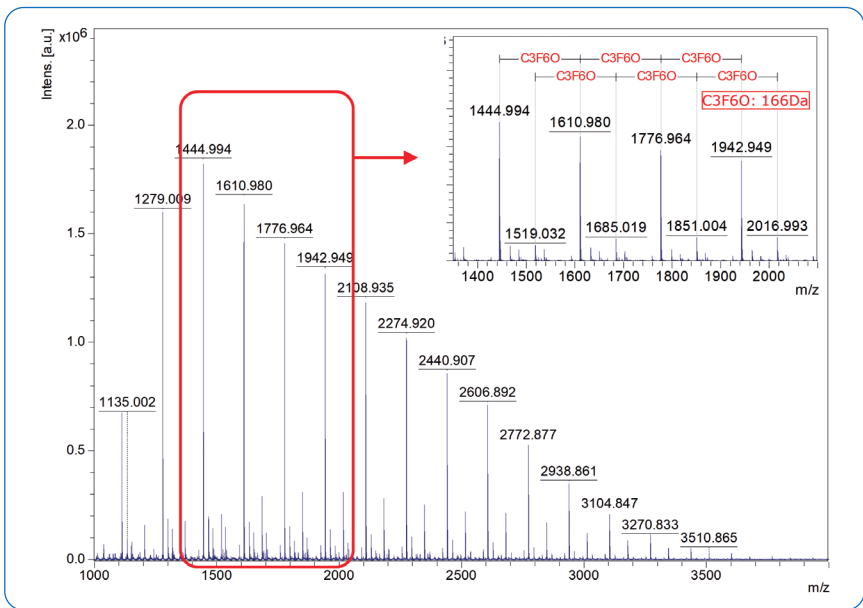


Figure 1: Spectrum of the Solution Sample

Analysis Results

Figure 1 shows the spectrum of the solution sample. A series with a different degree of polymerization was observed at C_3F_6O monomer unit (166 Da) intervals. Multiple series were also observed at the same 166 Da interval but with mass shift, indicating a mixture with different end groups.

Figure 2 shows the results of end group analysis with polytools 2.0.

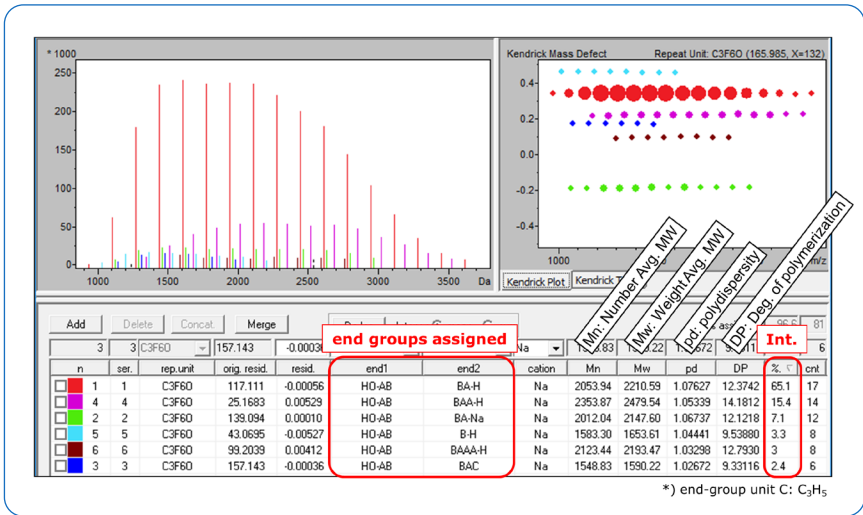


Figure 2: End Group Analysis of the Solution Sample with polytools 2.0.

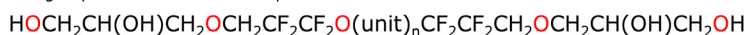
Please refer to Fig. 3 for the end group structure of the main component of this sample and the nomenclature used in this application note. Based on the polytools results, we see that — in addition to the end groups corresponding to the main components — end groups with different numbers of structure A, especially those containing greater quantities of structure A, were detected in large numbers.

Figure 4 shows the spectrum measured directly from the hard disk media and Figure 5 shows the polytools analysis results. It is clear that there are greater quantities of structure A in the end groups than in the solution sample. This indicates that a component with a large number of structure A, that is, hydroxyl groups, is more likely to be preferentially adsorbed to the surface of the hard disk media during immersion, which is a trend consistent with past findings¹⁾. Another feature of the MALDI-TOF MS is that (average) molecular weight information can be obtained in addition to end group information due to its ability to ionize and detect molecules without destroying them. Due to this feature, we can also see that components with greater quantities of structure A tend to have a larger average molecular weight.

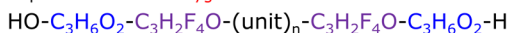
Conclusions

Using the MALDI-TOF MS, we analyzed lubricant at the monolayer level when applied to the surface of the hard disk media and obtained data on the end groups and average molecular weight. This analysis was an example to demonstrate the high sensitivity of the MALDI-TOF MS and its ability to directly take measurements from industrial components without dissolving them. The use of the MALDI-TOF MS has expanded in the chemical industry in recent years, and further developments are expected in the future.

End group structure of main component



Separate with ether oxygen



Name $\text{C}_3\text{H}_6\text{O}_2$ as A, and $\text{C}_3\text{H}_2\text{F}_4\text{O}$ as B



Figure 3: End Group Notation Method used in this Application Note

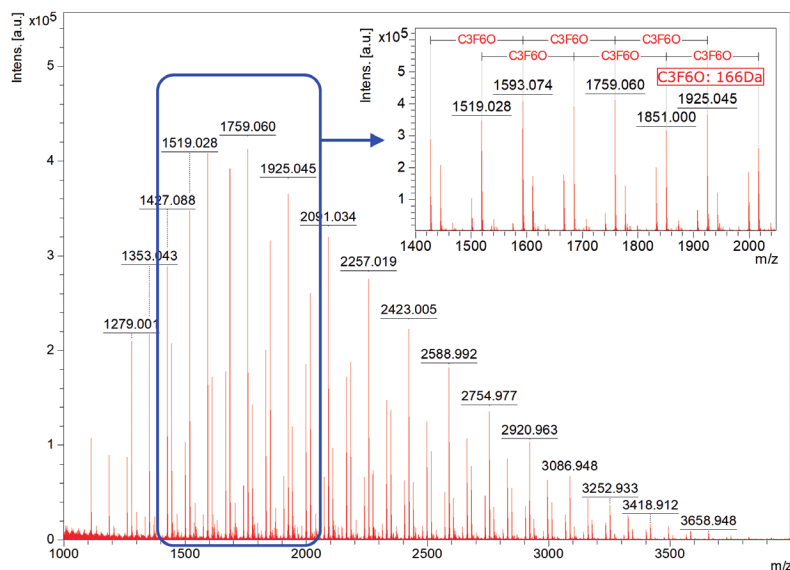


Figure 4: Spectrum measured directly from Hard Disk Media

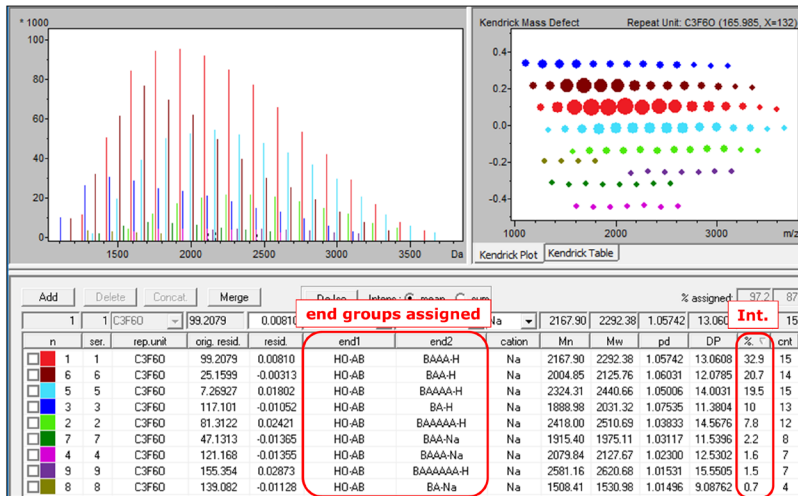


Figure 5: End Group Analysis of Disk Samples with polytools 2.0.