End-group analysis of perfluoropolyether used as hard disk lubricant using MALDI-TOF MS

ASMS Conference on Mass Spectrometry and Allied Topics 2021, FP 625

Toshiji Kudo[1], Aya Inoue[2], Tsuyoshi Shimizu[2] and Hiroshi Tani[3]
[1]Bruker Japan K.K., Japan
[2]MORESCO Corporation, Japan
[3]Kansai University, Japan

Introduction

MALDI-TOF MS has been often used for polymer analysis with its broad mass range and simplicity of spectra consisting mainly or only of singly charged signals. This allows impurity analysis or degradation analysis of polymer samples to be undertaken as this performance discriminates between different end-groups from mixture with high sensitivity. In this study, the end-group analysis of perfluoropolyether (PFPE) lubricant applied on hard disk medium surface at monolayer level thickness is presented. Due to low amount of the target analyte, extraction is not be applicable, and possible analytical methods are limited. However, high sensitivity analysis using MALDI-TOF MS could acquire results allowing the different end-groups of PFPE to be identified.

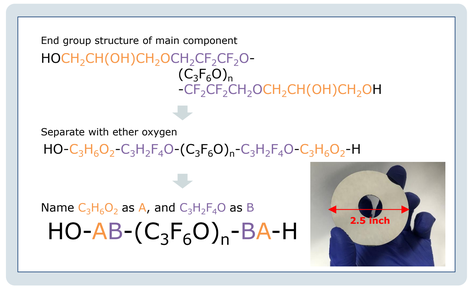

Fig. 1 Nomenclature of end-groups of PFPE in this study, and photograph of a disk sample.

Methods

The hard disk media samples (2.5” in diameter and 0.8 mm thick, Fig.1) were dipped into lubricant (MORESCO PHOSFAROL D-4OH, MORESCO Japan) solution to form lubricant monolayer which thickness is less than 1 nm on the surface. The molecular structure of D-4OH is shown in Fig.1. Then, UV light was irradiated to bind lubricant molecules covalently on the surface. Considering the preliminary work results, MALDI matrix was not used while sodium trifluoroacetate solution was sprayed using TM-Sprayer (HTX technology) as a cationization salt. And the sample was inserted into the mass spectrometer using the home-made adapter. For comparison, the original lubricant solution was analyzed also using normal target plate.

The autoflex maX MALDI-TOF mass spectrometer (Bruker) was used in positive reflector mode. The acquired data were analyzed with flexanalysis 3.4 (Bruker) and polytools 2.0 (Bruker).

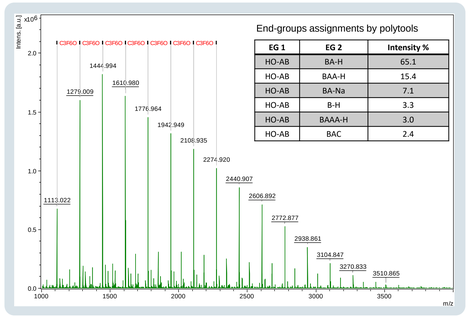

Fig. 2 Mass spectrum of solution sample with the end-groups assignments by polytools software.

Results

The data acquired from the solution sample (Fig.2) shows many signals with a regular repeating interval of 166 Da corresponding to the monomer unit (C_3F_6O) of the D-4OH, a PFPE. The observation of multiple signal series with same regular interval indicates that this sample is a mixture of different end-groups. The result of end-group analysis using Polytools 2.0 (the inset of Fig.2) indicates that components carrying more A-structure (that is hydroxy groups) than the main component present and are detected with good sensitivity.

The spectrum taken directly from hard disk medium before UV irradiation and its end-group analysis using Polytools 2.0 shows the detected signal series carry more hydroxy groups than the result of the solution sample (Fig.3). This indicates that components with more hydroxy group are easier to be adsorbed onto the surface of hard disk media during the production process when the ‘dipping method’ is used, and this is consistent with a past report[1]. Polytools 2.0 allows the averaged molecular weight information could be acquired from the spectrum, indicating that species which have more hydroxy groups have slightly larger average molecular weights and degrees of polymerization. This could be due to the synthesis condition of the perfluoropolyether. Fig.5 summarizes the relationship between end-groups and number averaged molecular weight as well as intensity and degree of polymerization. The spectrum from hard disk medium after UV irradiation (Fig.4) shows a result similar to that of before UV, but with less signal intensities (about a factor of 10) and a decreased number of signal series (9 to 5). It is considered that the UV irradiation results in covalent bonding between lubricant molecules and hard disk medium surface with a certain degree of efficiency, resulting in low signal intensities. But the major series is still the same as with the ones before UV irradiation (Fig.5). In addition, the average molecular weights of before and after UV irradiation are similar (Fig.5), implying that the chemical bond formation takes place uniformly and independent from end-groups structure and molecular weight of lubricant molecules.

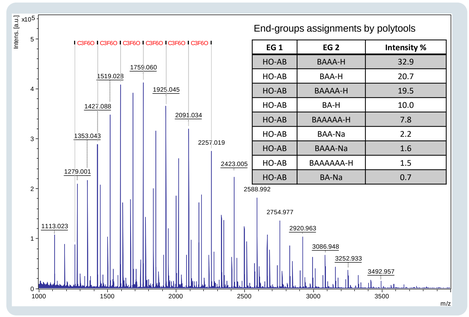

Fig. 3 Mass spectrum of disk sample before UV irradiation with the end-groups assignments.

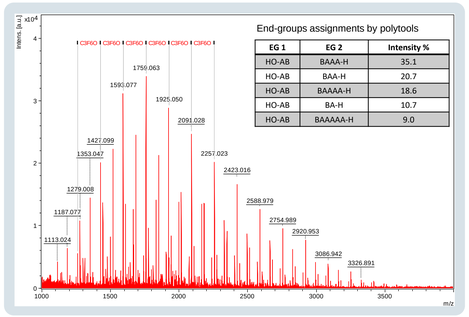

Fig. 4 Mass spectrum of disk sample after UV irradiation with the end-groups assignments.

reference: 1) Kudo et.al. Anal. Chem. 2011, 83, 5563–5569

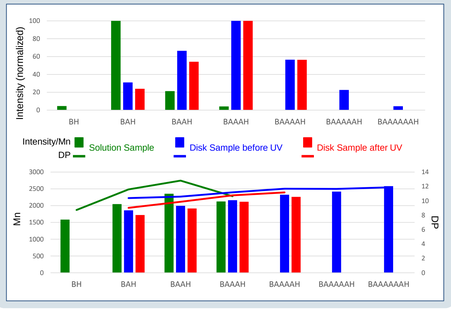

Fig. 5 Intensity, number averaged molecular weight (Mn) and degree of polymerization (DP) of each end-group species.

Conclusions

- End-groups analysis could be successfully done from monolayer level thin layer of PFPE on hard disk medium.
- Components with more hydroxy group are detected with higher intensity for disk samples, indicating higher affinity between disk surface and hydroxy group.
- Covalent bonding induced by UV irradiation takes place independent from end-groups structure and average molecular weight.

MALDI-TOF MS