Surface and Micro-Analysis of Organic Materials

Review

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Abstract

This paper is a review of the technical approaches taken at Toyota Central R&D Labs. (TCRDL) toward the surface and micro-analysis of organic materials. For organic microanalysis techniques, which are suitable for analysis of the degradation of organic materials, a depth analysis technique using micro-IR and a distribution analysis technique using derivatization-XMA have been developed. The former technique provides a great deal of information about organic chemical structure and the latter has higher sensitivity and higher lateral resolution than micro-IR. For organic surface analysis techniques, which are suitable for the analysis of adhesion and lubrication, a new method for time-of-flight mass spectrometry (TOF-SIMS) and a new type of surface analysis using a combination of SEIRA and ATR have been developed. Looking ahead to future trends, it is anticipated that "organic surface and micro-analysis" will evolve into "organic nanoanalysis", which will permit nanometer-order lateral and depth resolution, via the application of two approaches for extending the applicability of conventional organic analysis techniques to smaller scales, and for extending the applicability of nanometer scale analysis techniques to organic chemical analysis.

Keywords: Micro-IR, Derivatization-XMA, TOF-SIMS, Ag-deposition/TOF-SIMS, SEIRA-ATR, Surface analysis, Microanalysis

1. Introduction

Along with the advances made in industrial products in recent years has come a rise in the importance of chemical information concerning micro-areas, top-surfaces, and lateral and depth distribution of products. A wide variety of surface and micro-analysis techniques have been used to meet this demand, such as X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), secondary ion mass spectrometry (SIMS), electron probe x-ray microanalysis (XMA), transmission electron microscopy (TEM) and scanning electron microscopy (SEM). However, the main function of these techniques is elemental analysis, and their abilities are insufficient for analysis of the degradation of organic materials, identification of deposits composed of organic materials, and the analysis of adsorbed organic lubricants. Therefore, we have attempted to develop surface and micro-analysis techniques for organic materials as a new technical field via three approaches, i.e., improvement of conventional organic analysis techniques such as IR, improvement of conventional elemental microanalysis techniques such as XMA, and development of a new method of time-of-flight secondary ion mass spectrometry (TOF-SIMS). This report describes the background, provides an overview of these approaches, and discusses future challenges for this technical field.

2. Need for surface and micro-analysis in the automobile industry

2. 1 Troubleshooting

With precision functional parts and coatings, the presence of a small deposit can cause create problems. To prevent these problems from occurring, it has been necessary to identify the composition and origin of these small deposits. For electric devices, XMA, which has micron-order lateral resolution, and AES, which has sub-micron-order lateral resolution, have mainly been used to obtain information on the elemental composition of such deposits. In the case of coatings, on the other hand, most deposits are composed of organic materials, and micro-IR has been widely used to identify the composition of deposits larger than several dozen microns in size. However, there has been strong demand for a microanalysis technique with higher lateral resolution than micro-IR for use on the smaller deposits often present on devices .

2. 2 Degradation

Degradation of coatings and other organic construction materials has been extremely important issue for many years. In the case of coatings used in outdoor applications, degradation occurs on the surface which is exposed to the weather. With interior parts, which are not directly exposed to the weather, degradation will often occur at the sites where the parts interface with other materials. Therefore, the distribution of chemical structure must be evaluated at either surface or interface regions, and line analysis of cross sections in depth direction using micro-IR has been widely used for this purpose. Recently, however, to facilitate more rapid evaluation of material life, analytical methods with greater sensitivity that makes it possible to evaluate a small change in chemical structure in the early stages of the degradation have been required. Thus, there is strong demand for a new type of microanalysis technique, with greater sensitivity than micro-IR.

2. 3 Adhesion

Adhesive defects, which occur at metal/metal, metal/resin, and resin/resin interfaces, often cause severe problems in the design and/or structural strength of automobiles. There are two major factors that affect adhesion: functional groups present on the surface in contact with the other material and the presence of contaminants deposited on the surface that inhibit adhesion. XPS and derivatization-XPS have been widely used and are the most suitable techniques for the analysis of functional groups at the surface, while TOF-SIMS is thought to be the most suitable technique for analysis of adhesion inhibitors. Silicone oil is commonly detected by TOF-SIMS on defective parts. Although TOF-SIMS provides highly sensitive detection of silicone oil, it cannot determine properties such as molecular weight or end groups, which provide valuable information about the origin of the adhesion defect. Thus, a new TOF-SIMS measurement method with the ability to detect molecular ions is required.

2. 4 Lubrication

Lubrication is important issue in engines and transmissions, as it has the potential to affect the driving characteristics of an automobile. Lubricant additives, which are added to oils, function by forming an organic and/or inorganic thin film on the friction surface. Information concerning the structure of the thin film is extremely important for analysis of the lubrication mechanism. TOF-SIMS is not only suitable for the analysis of thin films, but also can be expected to provide information about organic chemical structures. In order to apply TOF-SIMS to the analysis of actual lubrication systems, however, some fundamental data must first be acquired through the use of model compounds, owing to the present lack of a database for TOF-SIMS analysis of adsorbed materials.

3. Technical approaches at TCRDL

Given the background described above, TCRDL (Toyota Central R&D Labs.) has attempted to develop both an organic microanalysis technique that would make it possible to evaluate the depth or the lateral distribution of an organic chemical composition at micron-order resolution, as well as an organic surface analysis technique that would make it possible to evaluate the top-surface chemical composition of organic materials. For organic microanalysis, we have developed a "micro-IR depth analysis technique," which provides a great deal of information about organic chemical composition, and "derivatization-XMA," which has high sensitivity for functional groups of interest and has higher lateral resolution than micro-IR.[1, 2] For organic surface analysis, we have developed a number of new TOF-SIMS analytical techniques, including "Ag-deposition/TOF-SIMS", and a new micro-IR technique that utilizes "surface-enhancement infrared absorption (SEIRA-ATR)".

3. 1 Depth analysis using micro-IR

Although the limit of lateral resolution for micro-IR is about 10 microns, the combination of the micro-IR and the use of a microtome with an oblique cutting technique has enabled the depth measurement of the distribution of chemical structures at micron-order resolution. The principle is shown in **Fig. 1**. When the cutting angle is 1 degree, the length of the cutting surface is 100 times the corresponding depth. Therefore, using micro-IR in 100-micron steps to perform line analysis in depth direction, we can evaluate the depth distribution of chemical structures with 1-micron depth resolution. This technique has been applied to evaluation of the difference between accelerated degradation tests for coatings, investigation of the migration behavior of a plasticizer in poly(vinyl chloride) (PVC), and analysis of rubber degradation by ozone.[1, 3] Recently, a new cutting technique has been developed at TCRDL, with which it is possible to obtain a cutting surface much easier and more rapidly than with the use of a microtome. A report of this technique will soon be published. Through the utilization of this technique and the hexagonal mapping-ATR prism developed at TCRDL,[4] the range of applications will expand at a rapid pace.

3. 2 Derivatization-XMA

In order to fulfill the need for the rapid evaluation of degradation, we have developed a new method for the analysis of polymer degradation, referred to as "derivatization-XMA", which is designed to increase the sensitivity and the resolution of evalution through the use of derivatization and XMA, respectively.[2] The functional groups of interest are C=C, which is generated by the dehydrochlorination of PVC, C=O, which is generated by the oxidation of polyolefins, and COOH and OH, which are generated by the oxidation of polyolefins and the

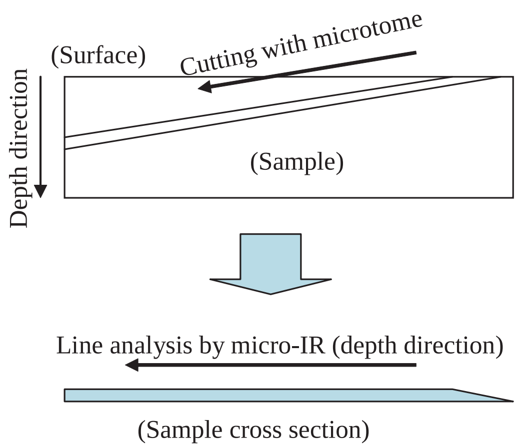

Fig. 1 Schematic illustration for the principle of depth analysis with the combination of infrared spectroscopy and microtoming.

hydrolysis of polycondensations.[5-7] Investigation into derivatization of epoxy groups has confirmed that this technique is applicable not only to the analysis of polymer degradation but also to the analysis of the hardening process of thermoset polymers.[8] The details of this technique are described in the first report in this special issue.

3. 3 TOF-SIMS

TOF-SIMS was proposed as a new type of surface analysis instrument by Benninghoven et al. in 1985.[9] The principle is shown in **Fig. 2**. A sample is sputtered with a primary ion, causing the emission of secondary ions from the sample surface, which are then analyzed by a time-of-flight mass analyzer. In cases in which the number of primary ions is significantly smaller than the number of atoms constituting the surface, the secondary ions are emitted with little destruction of organic molecules, and the secondary ion mass spectrum includes a great deal of information about the organic chemical structure of the material. However, as mentioned earlier, in order to apply TOF-SIMS to actual industrial materials, some fundamental data must first be accumulated for each material, owing to the lack of a published database. We have applied TOF-SIMS to the analysis of organic electroluminescent devices and to the analysis of adsorbed lubricant additives, by performing our investigations using fundamental data in each case.[10, 11] Details of the technique's application to lubrication are described in the second report in this special issue.

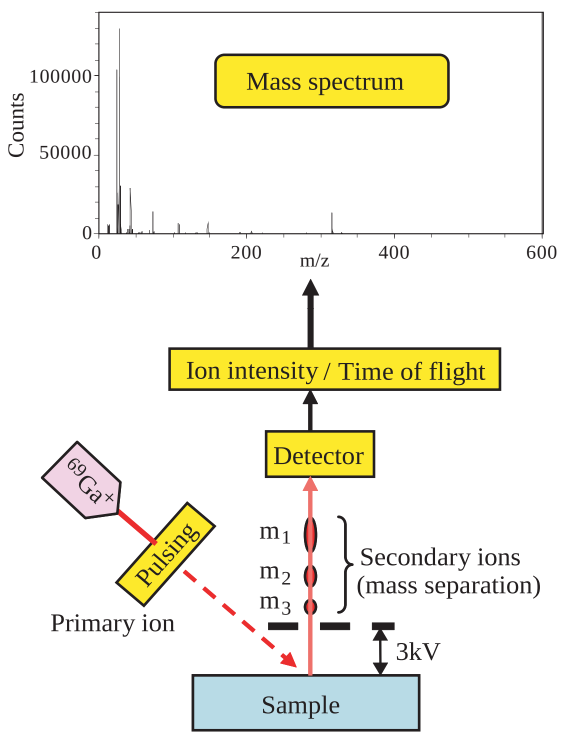

Fig. 2 Schematic illustration for the principle of TOF-SIMS.

TOF-SIMS is best suited to the analysis of a small amount of a surface contaminant such as silicone oil, which often causes severe problems related to adhesion in automobile parts. Although TOF-SIMS is extremely sensitive for silicone oil, we have been unable to identify individual types of silicone oil using conventional TOF-SIMS measurement techniques. In response, we developed a new TOF-SIMS measurement method referred to as "Ag-deposition/TOF-SIMS" for the detection of molecular ions of silicone oil with a molecular weight greater than 1000 on solid surfaces.[12] This method has been confirmed as applicable not only to the analysis of silicone oil but also to the analysis of other organic materials such as fluorine oil, lubricant additives, and polymer additives. The detail of this Ag-deposition/TOF-SIMS are described in the third report in this special issue.

3. 4 SEIRA

As described in **sections 3. 1** and **3. 2**, micro-IR is not suitable for the analysis of trace components or nanometer-order ultra-thin films. However, the SEIRA effect, by which infrared absorption intensity is enhanced to a high degree on a thin film of silver or gold, was found by Herstein et al. in 1980[13]; we attempted to develop a new type of highly sensitive surface analysis technique by applying this effect to micro-ATR and succeeded in the analysis of nanometer-order ultra-thin films on a solid surface. By using this technique together with TOF-SIMS for surface analysis, we will be able to analyze the organic chemical structure of a solid surface based on its mass spectrum as well as its IR spectrum. Details of SEIRA will be described in a report in a later issue.

4. Challenges for the future

As described above, we are presently working on the development of a surface and micro-analysis technique with micron-order lateral resolution. In the future, however, we will push toward the development of a technique for "organic nano-analysis", which will permit nanometer-order lateral and depth resolution. This technique will likely have applications in the analysis of nanodevices, nanotribology, nanostructures of polyelectrolytes, structures of interfaces between thin films, and structures of adhesion interfaces. We are proposing two approaches to take for the achievement of this goal. The first is "top-down," which is an approach for extending the applicability of conventional organic analysis techniques to smaller scales, and the second is "bottom-up," which is an approach for extending the applicability of nanometer-scale analysis techniques such as scanning probe microanalysis (SPM) to organic chemical analysis. Specific examples of these two approaches are described in the following sections.

4. 1 Top-down

Infrared near-field micro-spectroscopy (SNOM-IR) has been developed to enable IR analysis at a lateral resolution higher than the diffraction limit of infrared light.[14)] Although the limit of lateral resolution of conventional micro-IR is about 10 microns, as described earlier, it has been verified that the use of near-field techniques makes it possible to exceed this limitation. To date, lateral resolution of about 1 micron has been achieved. In the future, sub-micron-order resolution will likely be achieved through improvements in the light path and development of more highly sensitive detectors.

4. 2 Bottom-up

Since the development of the scanning tunneling microscope (STM) by Binnig et al. in 1982, many variations have come along, including the atomic force microscope (AFM), scanning viscoelasticity microscope (SVM), and friction force microscopy (FFM). These techniques are referred to in a general sense as SPM. Recently, Lieber et al. proposed a new SPM technique called chemical force microscopy (CFM) that enables evaluation of the distribution of organic functional groups at nanometer-level lateral resolution via chemical modification of an AFM probe.[15)] Before successful application of CFM to the evaluation of actual industrial materials, however, there remain many challenges to overcome, such as modifications methods and morphological effects.

5. Conclusion

TCRDL has attempted to develop an organic microanalysis technique that makes it possible to evaluate the depth or lateral distribution of an organic chemical composition with micron-ordered resolution, and an organic surface analysis technique that makes it possible to evaluate chemical composition at the top-surface of organic materials. These efforts resulted in the development of the "micro-IR depth analysis technique" and "derivatization-XMA" for use in organic micro-analysis and new techniques for TOF-SIMS, including "Ag-deposition/TOF-SIMS," and a new technique for micro-IR utilizing "surface-enhancement infrared absorption" for organic surface analysis. In the future, it is expected that "organic surface and micro-analysis" will evolve into "organic nanoanalysis" via the top-down and bottom-up approaches.

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