

Applications note Polymer note

Solutions for Innovation

Polymernote

Chemical Analysis Instruments NMR / MS / GC-QMS / GC-TOFMS / DART-TOFMS / MALDI-TOFMS Surface Analysis & Morphological Observation Instruments XRF / XPS / SEM / TEM Applications: Analysis of Adhesives

JEOL solution



Polymernote

Characterization of Polymers by JEOL Solutions

Polymers are used in a wide range of fields such as food wrapping materials, medicine packing, and industrial materials and products. Properties and functionalities of polymer materials are dependent on various factors, including molecular weight, molecular weight distribution, molecular chemical structures (primary structures), morphology of molecular chains (secondary structures) depending on the spinning angles of chemical bonds, and crystalline or non-crystalline structures of inner-molecules and inter-molecules, as well as spherulite structure aggregates, phase separation structures and orientations (higher-order structures). It is of prime importance to analyze and evaluate the structures and properties of polymers as well as the correlation between these two factors, and to feed these analysis and evaluation results to the development and manufacturing sites for the enhancement of the performance and quality control of polymer materials and polymer products. On the other hand, industry in Japan is supported by functional molecules, which are becoming more advanced and more complicated. This makes it more difficult to characterize such polymers, thereby increasing the importance of multiple analyses that combine a variety of analytical methods. This Polymer note introduces a broad range of instruments used for polymer analysis and their applications.

Characterization of Polymers by JEOL Solutions	1			
Polymer Analysis Technologies	2			
Analysis of Various Polymer Materials	3			
1. Main Analytical Instruments				
Chemical Analysis Instruments				
1-1. Nuclear Magnetic Resonance System (NMR)	5			
1-2. Mass Spectrometer (MS)	7			
Gas Chromatograph Quadrupole Mass Spectrometer (GC-QMS)				
Gas Chromatograph Time-of-Flight Mass Spectrometer (GC-TOFMS)	7			
Direct Analysis in Real Time Time-of-Flight Mass Spectrometer (DART-TOFMS)	9			
Matrix Assisted Laser Desorption/Ionization Time-of-Flight Mass Spectrometer (MALDI-TOFMS)	11			
Surface Analysis & Morphological Observation Instruments				
1-3. X-ray Fluorescence Spectrometer (XRF)	13			
1-4. X-ray Photoelectron Spectrometer (XPS)	15			
1-5. Scanning Electron Microscope (SEM)				
1-6. Transmission Electron Microscope (TEM)				
2. Applications: Analysis of Adhesives				
2-1. Classification of Adhesives	27			
2-2. Analysis of Lacquer - Japan's oldest adhesive	28			
2-3. Analysis of Woodworking Adhesive	29			
2-4. Analysis of Instant Adhesive	33			
2-5. Analysis of Styrene-butadiene Rubber	34			
Depth Profile Analysis of Styrene-butadiene Rubber (SBR) irradiated with UV	37			

Polymer Analysis Technologies



a substance, as well as depth profile analysis

of thin film samples in combination with ion

sputtering.

ARF enables the average composition analysis of liquid, powder and solid specimens, standard-less quantitative analysis (simple quantification), and non-destructive qualitative/ quantificative analysis of additives and residual catalysts in synthetic polymers.

Analysis of Various Polymer Materials





Additives Other polymers

-regularity, bonding mode, etc.)



Material characterization

O Analysis of higher order structure (Crystal structure, orientation, Blend dispersed state)

O Surface, interface and local area analysis (Repellency, adhesion, foreign material analysis, chemical states, etc.)



0.5

Volume fraction of B



Image: Nuclear Magnetic Resonance System NMR

The Nuclear Magnetic Resonance (NMR) System is an instrument that is used for obtaining data that relates the local chemical environment of a nucleus by irradiating a sample with radio waves while it is placed in a static magnetic field. As each nucleus in a polymer can have a different chemical environment due to factors such as molecular structures and crystalline structures, observed peak positions (chemical shift values) will vary depending on the surrounding environment. NMR has a large number of applications for both solution and solid samples because it is capable of obtaining a wide range of chemical data including molecular structures, crystalline structures, quantification data and molecular mobility through non-destructive analysis methods.



Features Basic data obtained by NMR

- Signal positions (horizontal axis): chemical shift (environment surrounding nucleus data)
- Signal intensity (vertical axis): integrated values (component ratios)





Applications Mixture analysis

Solution NMR enables the analysis of not only single-component samples but also the individual components of composite samples with a mix of low and high weight molecules (without the need for fractionation).





Sample: detergent (neat) Top: 'H-NMR spectrum Bottom: Selective acquisition of polymer components Signals of water were excluded to analyze components of overlapping peaks.

Reference: JEOL Application Note: NM130004, NM130005

Sample: Styrofoam (heavy-toluene solution) Top: 1H-NMR spectrum Bottom: Selective acquisition of low-molecular components Polymer components were excluded and data of only low

molecular weight components are obtained.

Applications Quantitative analysis of polyethylene – solid-state NMR -



- 46% degree of crystallinity was obtained from the ratio between the CH_2 peak of the crystalline phase observed at 32.84 ppm (intensity ratio: 38.3%) and the non-crystalline phase CH_2 peak observed at 30.77 ppm (intensity ratio: 45.7%).

- An estimate of the branching ratio was made from the peak intensity ratio of other terminal components.



1 - 2 Mass Spectrometer: MS GC-QMS / TOFMS

The Gas Chromatograph - Mass Spectrometer (GC-MS) is an instrument for mass measurement of volatile compounds separated by gas chromatography. The Quadrupole Mass Spectrometer (QMS) is the most common mass spectrometer, which is used for various applications due to its compact size and versatility. Recently, the Time-of-Flight Mass Spectrometer (TOFMS) has also gained popularity for its higher resolution. Combined with various pretreatment units, GC-MS can analyze components in gas, liquid and solid samples.



Principle Gas Chromatograph-Mass Spectrometer (GC-MS)





Applications Qualitative analysis of adhesive - HS/GC/QMS methods



The Head Space (HS) analysis system is pretreatment unit that efficiently extracts volatile compounds from a sample by heating it enclosed in a vial. Adhesive TIC chromatogram

HS/GC/MS methods can quickly identify volatile compounds in adhesives.

Epoxy-based adhesive



Retention time (min)





Retention time (min)

Applications (

Applications Qualitative analysis of nylon 66 - pyrolysis/GC x GC/TOFMS methods





1st column (Non-polar) separation

Two-dimensional TIC chromatogram of nylon 66

Horizontal axis: 1st column separation (components in the order of boiling-points) Vertical axis: 2nd column separation (components in the order of polarity)

Two separation modes (boiling points and polarity) enable separation and detection of a large number of components.

For the Comprehensive Two-Dimensional Gas Chromatography (GC x GC) method, capillary columns of two different separation modes are used. With this method, a higher chromatographic resolution can be obtained in comparison with normal GC methods as a simultaneous analysis is conducted in the two separation modes.

Mass Spectrometer: MS DART-TOFMS

DART (Direct Analysis in Real Time) is a newly-developed ionization method called "ambient ionization" that ionizes samples under atmospheric pressure. Using this method, samples of various forms and states can be ionized for mass spectrometry by TOFMS simply by exposing the sample to DART[™] ion sources.



Principle DART ionization



Schematic of DART[™] ion source

M: Sample molecules

Helium gas introduced to the DART[™] ion source becomes excited helium atoms by means of a discharge from the needle electrode. Ionization progresses due to the interaction among excited helium atoms, atmospheric gas and sample molecules.



Below are the results of a DART-TOFMS analysis of two types of cyanoacrylate resin.

Main detected components

[Common components]

- Protonated molecules of ethyl cyanoacrylate (m/z126)
- $\rm C_4H_2\rm NO^+(\it m/z$ 80) and $\rm C_4H_4\rm NO_2^+(\it m/z$ 98) (fragment ions)

[Components observed in Sample 1 only]

- Polymer component containing allyl methacrylate and ethylene oxide (EO) subunits
- [Components observed in Sample 2 only]
- Tributyl citrate and tributyl acetylcitrate (plasticizer)



Applications Fast analysis of antioxidant "p-Phenylenediamines" in a rubber tire

Below are results of a DART-TOFMS analysis of a rubber tire section.

- N-Phenyl-p-phenylenediamine (PPPD)
- N-IsopropyI-N'-PhenyI-p-phenylenediamine (IPPD)
- N-(1.3-demethyl-butyl)-N'-Phenyl-p-phenylenediamine

(DMBPPD)

The existence of three antiozonants was confirmed.





Accurate mass measurement results

Component	lon species	Meas. <i>m/z</i>	Formula	Error (mDa)
IPPD	M+.	226.1472	C15H18N2	0.2
	[M + H] ⁺	227.1543	C15H19N2	-0.5
DMBPPD	M+.	268.1942	C18H24N2	0.3
	$[M + H]^+$	269.2014	C18H25N2	-0.4

Mass Spectrometer: MS MALDI Spiral-TOFMS

Matrix Assisted Laser Desorption/Ionization – Time-of-Flight Mass Spectrometer (MALDI-TOFMS) is a mass spectrometer capable of analyzing substances ranging from low molecular weight compounds such as amino acids to high molecular weight compounds such as synthetic polymers. JMS-S3000 "SpiralTOF^{TM"} is the highest-class resolution MALDI-TOFMS incorporating an integrated ion optical system that has a proprietary spiral orbit (SpiralTOF ion optical system).



Principle Matrix-assisted laser desorption/ionization method

When a sample mixed with the matrix is irradiated with a pulsed UV laser beam, the matrix will absorb the laser beam and vaporize. At the same time, the sample will also be emitted in a vapor form, which promotes the ionization process.



Applications Calculation of average molecular weight of polymer



Sample: Polymethylmethacrylate (PMMA) with average molecular weight of 4000

The average molecular weight of polymer is easily calculated using a MALDI-TOFMS analysis.

Calculation from MALDI mass spectrum



Applications Polymer structural analysis: TOF-TOF option

Product ion mass spectrum of Polypropylene glycol (PPG)



Estimated PPG product ion structure



PPG heptadecamer was selected as precursor ions for this TOF-TOF analysis. "m/z 23.0 [Na+]", which represents sodium adduct ions, and five product ion types reflecting the polymer structure were observed.

Principle Tandem mass spectrometry: TOF-TOF option

TOF-TOF option, which allows for tandem mass spectrometry, can be used to obtain structural data of organic compounds.

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- 1. Ion source: Ionizes the sample.
- 2. MS1: 1st-stage mass spectrometer. Selects specific ions (precursor ions).
- 3. Collision cell: Fragments precursor ions by making them collide with an inert gas (e.g. He).
- 4. MS2: 2nd-stage mass spectrometer. Analyzes ions generated by the collision (product ions).

1 - 3 X-ray Fluorescence Spectrometer

The X-ray Fluorescence Spectrometer (XRF) enables analysis of constituent elements and compositions by detecting fluorescent X-rays emitted from a specimen irradiated with X-rays. For polymer materials and products, XRF is capable of performing control analysis in connection with product safety by quick screening of the residual catalyst volume used for polymerization and RoHS-restricted heavy metal elements (Cd, Pb, Hg, Cr and Br) as well as by analysis of inorganic additive content used for functional improvement. Possible applications of the spectrometer also include analyzing inorganic surface treatment film deposits and thickness and identifying contamination mixed in during the manufacturing process. XRF is an element analysis instrument capable of easily analyzing elements that constitute a material in a non-destructive manner.



Principle Mechanism of fluorescent X-ray generation

When a specimen is irradiated with X-rays, electrons existing on an electron trajectory of atoms that constitute the sample are ejected, causing the transition of electrons form higher-order trajectories. Then, X-rays emitted from the sample are called fluorescent X-rays. Elements can be analyzed by measuring fluorescent X-ray energies characteristic of each element.



Principal component Analysis of additives contained in soft PVC

Soft PVC is produced by adding certain additives (e.g. plasticizer, filler, stabilizer, and pigment) into a base PVC. By considering plasticizer as the balance component, element components of other additives can be quantitatively determined.



Com	Result	
PVC	C ₂ H ₃ Cl	39.849
Filler	Ca	9.211
Stabilizer	Ва	0.054
	Pb	1.086
	Zn	0.012
Pigment	Cu	0.025
	Ti	0.018
Balance (plasticizer)	$C_{12}H_{19}CI_{2}$	49.743



Analysis of residual catalyst Sb in polyethylene terephthalate (PET)

Trace amounts of residual elements, used as catalysts for polymerization such as Sb and Ge, exist in the PET used for plastic bottles and food trays. XRF is capable of quickly analyzing such residual catalyst contents.



A high-precision analysis of any resin type can be made using the residual balance correction function in the FP method.





Measurement of thickness of aluminum evaporated layer on PVC surface Measurement of Si deposits coated on PET surface

Some products have materials evaporated or coated on their surface for the purpose of improved functionality of water/heat resistance and mechanical properties, and for surface protection. The thin-film FP method enables the measurement of the thickness and deposit quantity of such surface treatment layers.





RoHS

Screening of heavy metal elements in products

RoHS Solution is dedicated software that incorporates optimal measurement conditions and FP quantification conditions. The software provides high-precision standard-less measurement results. The right figure shows measurement results of the IRMM ERM-EC681 pellet (2 mmq).



1 - 4 X-ray Photoelectron Spectrometer

The X-ray Photoelectron Spectrometer (XPS) is an analysis instrument capable of quantitative, qualitative, and chemical-bonding state analyses of the top surface of a substance by analyzing photoelectrons that are generated when a specimen is irradiated with X-rays. Other applications of XPS include specimen surface cleaning by ion irradiation and internal structure analysis by repeated measurement and etching.





Basic information obtained with XPS

- Signal positions (horizontal axis): Element information (qualitative analysis)
- Signal intensity (vertical axis): Integrated values (quantitative analysis)
- Precise signal positions and shapes (split)
 Chemical shift (chemical-bonding state analysis)





A positive electrode of a lithium-ion battery was analyzed. From the electrode surface, electrolyte components such as Li, C, O, F, and P, and an active material, Co, were detected.



Sample: Li-ion battery positive electrode surface

Applications Analysis of polyethylene terephthalate (PET)

Analysis of polymer materials by XPS also provides information on functional groups of the materials; peaks of each functional group can be found by observing the relevant spectrum obtained by XPS. In this case, the benzene ring, carbonyl group and carboxyl group which are contained in PET were detected.



Chemical structure formula of PET

Intensity (arb.unit)

C1s spectrum of PET obtained by XPS

294 292 290 288 286 284 282 280 Binding energy (eV)



Applications Evaluation of surface-treated polymer material

Polymer materials are often used in combination with other substances as a composite material. Bonding strength plays an important role for such applications and it can be increased by various surface treatments that are applied to the bonding surface, e.g. discharge and addition of substances of various properties. Qualitative and quantitative analyses by XPS are useful for the evaluation of surface treatment agents applied to polymer materials.



Changes in surface conditions due to corona discharge treatment



PET film measurement data obtained by XPS before and after corona discharge show that the peak intensity of CO was increased after the treatment. It is thought that higher hydrophilicity was caused by the increased CO level because corona discharge treatment on PET is known to increase hydrophilicity.



XPS depth profile analysis by ion irradiation - XPS application using cluster ion beam -

XPS is capable of performing a depth profile analysis on polymer materials by alternating between ion-irradiated sample etching and XPS analysis. In recent years, cluster ion-beam irradiation units designed to hit an ion cluster onto a sample have expanded its applications. As etching causes only minor chemical damage to an organic sample when it is irradiated with a cluster ion beam, cluster ion-beam irradiation can be an effective technique for performing a depth profile analysis of polymer materials and cleaning of surface contamination.



Applications Depth profile analysis of a polymeric multi-layer film

A depth profile analysis was conducted using a combination of cluster ion beam and XPS. As a result, the layer structure of a polymeric multi-layer film was successfully analyzed at superior depth resolution of sub-10 nm.



Reference: JEOL Application Note: HS-004

1 - 5 Scanning Electron Microscope

The Scanning Electron Microscope (SEM) is an instrument for imaging the specimen surface by irradiating the surface with a focused electron beam and performing a two-dimensional scan. The SEM detects various signals including secondary electrons, backscattered electrons and characteristic X-rays generated by electron beam irradiation to obtain morphology of the specimen surface, crystalline information and chemical information (composition, etc.).

Owing to ease of operation for morphological observation and local area analysis of bulk specimens, the SEM is widely utilized in various applications ranging from basic research to industrial use.



V Principle

The SEM uses a condenser lens and an objective lens to focus the electron beam produced by an electron gun onto a specimen surface. The scanning coils then scan the electron beam in the X and Y directions and the detector acquires signals generated from the specimen. The monitor screen is synchronized with the electron beam scanning for observation.

SEM image magnification is determined by the electron beam scanning width "a" and the image display width "b".



Schematic of SEM configuration



Various signals are emitted from a specimen when it is hit by the electron beam, and such signals are converted into the required information by detectors. Different detectors are used to obtain the target information.



Applications Observation and analysis of reinforced plastic

Morphological observation

Morphology of a fractured specimen was observed by a secondary electron image.



The same region acquired as a secondary electron image was observed by a backscattered electron image. As a result, the different compositional contrast between fillers and substrate were obtained. It clearly reveals filler distribution and orientation.







50 µm

The following elemental analysis result by EDS shows the existence of Si and Ca in the filler. You can compare elemental information on any regions by point EDS analysis.





Applications Observation and analysis of polymer materials Observation

Observation of defects on a plastic lens

The cross section of a plastic lens was treated by Focused Ion Beam (FIB). These SEM images enable the thickness of each optical thin film to be measured. SEM observation revealed that a foreign substance (encircled in red) was deposited to the optical thin film at a site recognized as being abnormal.





Specimen: Plastic lens (blue-light cut glass)

0.5 µm

Elemental analysis

Cross sectional analysis for plastic card

EDS elemental maps of the cross section of the plastic card, to which a magnetic tape layer was adhered, were acquired. From the maps, it was found that a few layers with slightly different quantities of C and O exist beneath the magnetic tape layer in which large quantities of Fe and Ba are dispersed.



Specimen: Plastic card (with a magnetic tape layer)

50 μm

Observation at ultra-low accelerating voltage

Separator observation

Observation at extremely low voltage allows electron beam damage and charging on specimens to be reduced. The below image shows clearly surface morphology on a separator at extremely low voltage of 0.05 kV.



Toner particle analysis

Imaging in low vacuum is useful for observation of insulators because it is easy to reduce charging by this method. It is possible to observe and analyze non-conductive specimens without conductive coating.



500 µm

Specimen: Polypropylene separator in Li-ion battery Extremely low accelerating voltage of 0.05 kV.







Specimen : Toner accelerating voltage: 7 kV Vacuum: 70 Pa

500 nm



Observation of hydrated specimens - Cryo-SEM

The Cryo-SEM method enables the observation of hydrated specimens while preserving their morphologies by freezing them. With this method, a rapidly-frozen specimen is freeze-fractured or etched in a preparation chamber to expose the intended inner face of the specimen. The specimen is then introduced to the SEM stage for observation while it is cooled at liquid-nitrogen temperature.



Specimen: Acrylic polymer emulsion

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1 µm
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Schematic of Cryo-SEM



Liquid-state acrylic polymer emulsion was observed with the Cryo-SEM. While hydrated specimens are unavoidably deformed in normal-temperature SEM observation, the Cryo-SEM method allows such specimens to be observed in their native morphological structures by freezing them.

Transmission Electron Microscope

The transmission electron microscope (TEM) is an instrument for observing the internal structure of a specimen by passing an electron beam through a thin film specimen. The thickness of the specimen for TEM is less than 100 nm. Generally, since the polymer material is composed of light elements, it is necessary to perform staining with heavy metals. In addition to observing the fine structure, TEM can also perform electron diffraction to determine the crystal state of the specimen, elemental analysis, and three-dimensional reconstruction by the tomographic method.



Observation example



Specimen: ABS resin Specimen preparation: Ultrathin sectioning OsO₄staining





Specimen: Blended polymer (PE/PP) Specimen preparation: Ultrathin sectioning RuO₄staining





Specimen: Filler composed of styrene-butadiene

rubber (SBR) + carbon black Specimen preparation: Cryo ultrathin sectioning No staining





Specimen: Rubber plug

2 µm



Cryo-observation Cryo-observation of liposome in liquid solution

Liposome in liquid solution was rapidly frozen and observed by the TEM in a frozen state.

Specimen: Liposome Specimen preparation: Ice embedding method



Specimen: Liposome

200 nm

Ice embedding method

A thin film of ice is created in a hole on the porous carbon-support film and a specimen embedded in the ice is observed by the TEM.

Observation example Observation of a specimen in liquid solution: emulsion

Freeze fracturing - Replica method



Particulates dispersed in liquid solution condense when dried and it is difficult to grasp the original state of dispersion. However, rapid freezing physically fixes specimens dispersed in liquid solution, allowing for the observation of dispersion and aggregation states in water.





Specimen: Colloidal silica

The result shows how colloidal silica particulates are dispersed without being condensed.

Three-dimensional structure reconstruction

TEM tomography is a technique for reconstructing a three-dimensional structure from an acquired sequential tilt-series of projection images, similar to X-ray CT technology used in the medical field. Specimens subject to TEM observation are as thin as sub-100 nm. But compared with the spatial resolution (1 nm or less) of the TEM, this thickness is large. Computer processing of such tilt series of images acquired by TEM tomography allows for reconstruction of the three-dimensional structure inside a specimen at a nano-order resolution.



Observation example

Three-dimensional reconstruction by TEM (TEM tomography) Three-dimensional structure of block copolymer

Three-dimensional structures of two different types of block copolymer were reconstructed using TEM tomography. While the specimens are not distinguishable in two-dimensional images, the three-dimensional reconstruction images clearly show their differences.

Cylindrical structure (TEM image)



Three-dimensional reconstruction image (black-and-white-inverted)







Single row



Spherical structure (TEM image)

100 nm



(x, y, z) = (661, 661, 88 nm)



Specimen: Poly (styrene-block-isoprene) Specimen preparation: OsO_4 staining, ultrathin sectioning Tilt angle: -60° to +60° (1° steps) Data courtesy: Professor Hiroshi Jinnai, Tohoku University

YOKOGUSHI Applications Analysis of Adhesives

The performance of adhesives is significantly affected by the adhesive base compounds including natural polymers and synthetic polymers, as well as auxiliary compounds and additives used to add various functions. Therefore, it is important that the results of analyzing such adhesive components are fed back to the development and manufacturing processes.

This chapter provides example analysis cases for four types of adhesive: lacquer, a traditional Japanese organic adhesive; a vinyl acetate-based adhesive widely used for woodworking applications; a cyanoacrylate-based adhesive generally known as instant adhesive; and a highly versatile styrene-butadiene rubber (SBR).



2-2 Analysis of Lacquer - Japanese oldest adhesive -

Lacquer is a natural polymer material harvested from 3 kinds of lacquer trees native to Eastern Asia, and it has been used as a paint and adhesive material for at least 8,000 years. It has a unique trait of forming a brownish-red coating film without any organic solvent, the structures of which are not yet fully understood.

[Lacquer Trivia]

Raw lacquer: Lacquer tree sap. Raw lacquer is composed of "urushiol," which is the principal component, as well as a nitrogen-containing material and water balls containing plant gum and laccase enzyme dispersed across raw lacquer. Refined lacquer: Refined lacquer is treated using the traditional Nayashi and Kurome methods.

Analysis by Pyrolysis GC x GC-MS



Over 800 kinds of components were successfully separated and detected from a lacquer film sample through pyrolysis GC x GC measurement. Urushiol components were observed after about 45 minutes of retention time in Column I.

Urushiol

Material

Water balls

Nitrogen-containing

(Contains plant gum and laccase enzyme)



Pyrolysis temperature: 400 °C Column I: BPX5, 30 m x 0.25 mm, 0.25 µm Column II: BPX50, 2 m x 0.1 mm, 0.1 µm



Analysis by SEM

Raw lacquer cross-section



Refined black lacquer cross-section

Traces of oddly shaped and relatively large water balls and plant gum were observed on the crosssection of raw lacquer film due to the dispersion of different sized water balls in the raw lacquer liquid. Refined lacquer is a processed lacquer liquid that has small and consistently-sized water balls due to a stirring process called "nayashi" and that has water content below 5%. The dispersion of particles in refined black lacquer that are smaller than those in raw lacquer was confirmed using SEM.

Most black lacquer currently used in Japan is prepared by adding iron powder or an aqueous solution of iron hydroxide to lacquer, not by mixing it with black pigment. The black color is regarded to appear when urushiol and iron are chemically combined, but iron's chemical state in the blackening process is not fully understood.

An analysis using XPS detected a trace amount of iron in black lacquer, and comparison with a spectrum of a standard iron compound suggested that the iron detected in the lacquer specimen is FeO.

Corutesy: Dr. Yoshimi Kamiya, Tokyo Metropolitan Industrial Technology Research Institute

Analysis by XPS fe fe

2-3 Analysis of Woodworking Adhesive (Vinyl Acetate Emulsion Adhesive) Morphology of Vinyl Acetate Emulsion

Observation by Cryo-SEM

A woodworking adhesive (polyvinyl acetate emulsion) was observed using Cryo-SEM.

Observation of woodworking adhesive film formation process (surface structure)

A: After application 0 min.

B: After application 5 min.

C: After application 10 min.



5 µm

Cryo-SEM images of a specimen rapidly frozen by the metal contact method A: Immediately after application (0 min.), there is some space between the distributed individual particles.

B: 5 minutes after application, there is no space between the distributed individual particles.

C: 10 minutes after application, individual particles are bonded together, forming a film.

Internal structure observation of a woodworking adhesive resin particle (freeze-fractured surface)

D: Cryo-SEM image



0.5 µm

E: Freeze-fractured replica image (TEM)



200 nm

D: Cryo-SEM image of a freeze-fractured surface prepared by cutting a rapidly-frozen specimen with a Cryo knife using the metal contact method
 E: TEM image of the same specimen prepared using the freeze-fracture - replica method (at room temperature) (See p.25)
 Both techniques show fine structure present on the resin particle cross-section.

Analysis of Woodworking Adhesive (Vinyl Acetate Emulsion Adhesive) Analysis of Aromatic Additives in Woodworking Adhesive

Observation by NMR

Solid-state NMR sample tubes were filled with two neat adhesives from different manufacturers, Adhesive A and Adhesive B, which were put through ¹H and ¹³C-NMR measurements.

The blue brackets and arrows point out components observed only in Adhesive A.

These NMR spectra show that Adhesive A contains components not present in Adhesive B, which are highly-mobile low molecular components with aromatic rings and CH_2 .



Instruments: JNM-ECZ500R + 3.2 mm HXMAS probe Accumulation: 64 times (¹H-NMR), 10,000 times (¹³C-NMR) Repetition time: 5 seconds



Comparison of components in 2 types of woodworking adhesive using Pyrolysis GC-TOFMS

Qualitative analysis using the pyrolysis GC/EI method



Pyrolysis GC/El total ion current chromatograms of Adhesives A and B

- Hardened woodworking adhesives (A and B) were analyzed using the high-resolution GC-TOFMS equipped with a pyrolysis device, and pyrolyzed products from each adhesive were compared.
- Aromatic compounds generated by the cleavage from vinyl acetate resin side-chains, such as acetic acid, ethyl acetate, benzene, toluene, styrene, indene, 1,4-dihydronaphthalene, and naphthalene, were detected as common components in both adhesive samples.
- At least 4 different components were detected in Adhesive A and 2 of them were identified using a NIST library database search for the obtained mass spectra (EI: electron ionization) as diethylene glycol dibenzoate and 2,2'-(Ethane-1,2-diylbis(oxy)) bis(ethane-2,1-diyl) dibenzoate, respectively.





Many components derived from adhesives were quickly identified through the combined use of data obtained through pyrolysis and GC-TOFMS (EI: electron ionization) and a database search.

Estimation of unknown components derived from woodworking adhesive by means of pyrolysis GC-TOFMS using two different ionization methods

Component B

Component A



Mass spectra of Component A Top: El method, Bottom: Pl method

Mass spectra of Component B Top: El method, Bottom: Pl method

- Based on accurate mass measurement of ions observed by the El and Pl (photo ionization) methods, a composition analysis was conducted on two of the four components detected only in Adhesive A, which could not be identified in a library search (Component A and Component B).
- The molecular formula was estimated from the molecular ion composition formula from the mass spectra identified by the PI method.
- Fragment ions in the mass spectra identified by the EI method contain much structural information, enabling the estimation of the molecular structure by obtaining accurate composition formula for such fragment ions.



Accurate mass measurement of molecular ions acquired by the soft ionization method (PI method in this case) allows for the estimation of the elemental composition of the molecular ion components. The fragment ions observed by the EI method enable the estimation of the molecular structure.

Thus, data obtained using multiple ionization methods leads to more accurate qualitative analyses.

2-4 Analysis of Instant Adhesive (Cyanoacrylate-based Adhesive)

A sample of the Cyanoacrylate-based adhesive, generally known as instant adhesive, was dissolved with acetone and analyzed using the high-resolution MALDI-TOFMS.



Plotting software: msRepeatFinder Plotting reference unit: ethyl cyanoacrylate (C₆H₇NO₂)

The mass spectra show a group of peaks of multiple polymers in the instant additive. The Kendrick mass defect plot provides an overall picture of multilineage polymers existing in the adhesive, including components with observed weak peaks, and their molecular weight distribution.

Reference: JEOL Applications Note (MSTips No. 220). http://www.jeol.co.jp/applications/detail/1078.html

2-5 Analysis of Styrene-butadiene Rubber (SBR)

SBR is a widely used general purpose rubber and is synthesized by emulsion polymerization of styrene and butadiene. Among synthetic rubber, the production volume of SBR is largest while possessing excellent heat and abrasion resistance properties, thus being applied in a variety of fields.

Study of the dispersed state of the filler and elemental analysis were carried out from the cross section of the rubber. STEM BF images

STEM HAADF images

💻 200 nm

Accelerating voltage: 200 kV Specimen preparation: Cryo-ultramicrotomy

Analysis of Styrene-butadiene-based adhesive (SBR) by pyrolysis GC-TOFMS using FI (field ionization) method

Pyrolysis GC/EI total ion current chromatogram

Pyrolysis GC/FI total ion current chromatograms

El mass spectra of Olefin A and B

- An analysis result of pyrolysis GC-TOFMS of the SBR samples (with EI method) revealed that a large number of components were detected.
- Since the pyrolysates in the SBR were mostly hydrocarbon-based compounds, their mass spectra obtained by the El method were similar to each other. Thus, measurement by the FI (field ionization) method was also conducted since the method effectively detects molecular ions in hydrocarbon compounds.
- The presence of such hydrocarbon compounds was confirmed by creating an extracted ion current chromatogram of hydrocarbon compound molecular ions from the pyrolysis GC/FI data.

Molecular ions of the hydrocarbon compounds were clearly captured using the soft ionization method (FI method in this case).

Since SBR is insoluble in a solvent, measurement and analysis were conducted using a "solid-state NMR instrument" capable of measuring a solid sample without pretreatment.

The sample was cut into appropriate size pieces and put into a solid-state NMR sample tube for measurement.

¹³C-NMR spectrum ¹⁴C-NMR spectrum ¹⁴C-

Instruments: JNM-ECZ500R + 3.2 mm HXMAS probe Accumulation: 64 times (¹H-NMR), 10,000 times (¹³C-NMR) Repetition time: 5 seconds

 \rightarrow Derived from styrene \rightarrow Derived from butadiene \rightarrow Unknown

Peaks derived from SBR were observed in the ¹H-NMR and ¹³C-NMR spectra. The broader peak widths are thought to be caused by carbon black contained in the sample. Parameters such as the styrene-butadiene ratio can be analyzed from peak intensities.

Depth Profile Analysis of Styrene-butadiene Rubber (SBR) irradiated with UV

Specimen: SBR 1. Not UV-irradiated 2. UV-irradiated (2 months)

Analysis by SEM

The aggregation of zinc particles on the specimen surface caused by UV irradiation was confirmed by observation and analysis of the cross-section using SEM and EDS.

The XPS analysis of the specimen cross-section revealed that the chemical-bonding state of the zinc particles aggregated by means of UV irradiation on the specimen surface remained unchanged. A comparison with the standard spectra also shows that they are mostly zinc oxide.

In the THF extract of the non-UV-irradiated sample, 50-80 mer PEG was observed with a center of distribution around m/z 3000, which was thought to be a residual component of the emulsifier used for polymerization.

For the UV-irradiated sample, no PEG peak was observed down to a depth of 50 µm from the UV-irradiated surface. A group of PEG peaks and their decomposition products were observed near the depth of 100 µm.

These results suggest that the impact of UV irradiation reached down to near the depth of 100 $\mu m.$

SEM observation revealed changes in fine structure caused by UV irradiation, while the analysis results of EDS and XPS identified the composition of particles aggregated due to UV irradiation. Also, the depth profile analysis by means of MS elucidated chemical structure changes caused by UV irradiation, which could not be found with morphological observation.

*Appearance or specifications subject to change without notice.

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