C10G-E105

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Recycled Plastic Analysis Solutions

Recycled Plastic

Various plastic recycling measures are being implemented in response to growing awareness about needing to establish a carbon-free and recycling-oriented society. The typical process involves collecting, sorting, shredding, washing, drying, and otherwise processing plastic waste before it can be recycled and used again in new products.

Plastic recycling primarily involves one of these two processes: “material recycling,” which uses waste plastic directly in the form of plastic as a raw material for reuse in new products, and “chemical recycling,” which chemically decomposes waste plastic for reuse as a raw material in new products.

The following describes applications used in plastic recycling processes.

Evaluation Criteria Flow	Structural Analysis	Mechanical Properties	Impurities Analysis	Multifaceted Evaluation
Sorting / Collection	Polymer identification P. 4 Blend ratio confirmation P. 5 P. 6 Discoloration confirmation P. 12		RoHS/ELV screening analysis P. 17	UV ray degradation P. 21
Wash	Moisture content confirmation P. 7		Cleaning level confirmation (odor) P. 19 Cleaning level confirmation (organic matter) P. 20	
Repolymerization	Molecular weight distribution confirmation P. 8 Polymer structural analysis P. 9			
Mold	Crystallinity confirmation P. 10 Discoloration confirmation P. 11	High-speed tensile testing P. 13 Hardness testing P. 14 Void check P. 15 Rheological evaluation P. 16	Hazardous element analysis P. 18	Differences due to formulation ratios P. 22 Differences due to heat treatment P. 23

Other Analytical/Evaluation Technologies

- Manufacturing Processes
- After Molding
- Failure Analysis

Material Recycling Process Flow

Collect → Primary sorting → Shred → Wash → Secondary sorting → Melt Knead → Mold

Chemical Recycling Process Flow

Collect → Primary sorting → Shred → Wash → Thermally Decompose → Repolymer-ization → Melt Knead → Mold

Application of Recycled Plastic

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Differentiation of Resins in Carbon Fiber Reinforced Plastics (CFRP) by FTIR

Application

Analysis with a Fourier transform infrared (FTIR) spectrophotometer can confirm the resin components contained in CFRP materials before recycling.

benefits

- By using FTIR, plastics with a dark or black color can also be measured.
- A plastics spectral library can be used to differentiate between components in CFRP base materials.

■ Measurement Results (Extract)

Here, an epoxy resin (EP) CFRP was measured as a thermosetting CFRP, and polyether imide (PEI), polyamide 6 (PA6), and polyether ether ketone (PEEK) were measured as thermoplastic CFRPs. Fig. 1 shows the appearance of the CFRPs. Fig. 2 shows the infrared (IR) spectra and the spectrum search results for the CFRPs. In all cases, the search results were in agreement with the resins used.

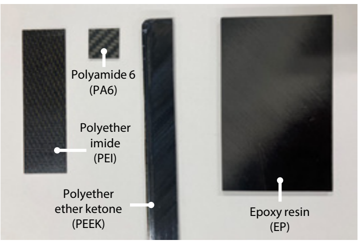


Fig. 1 Appearance of CFRP Samples

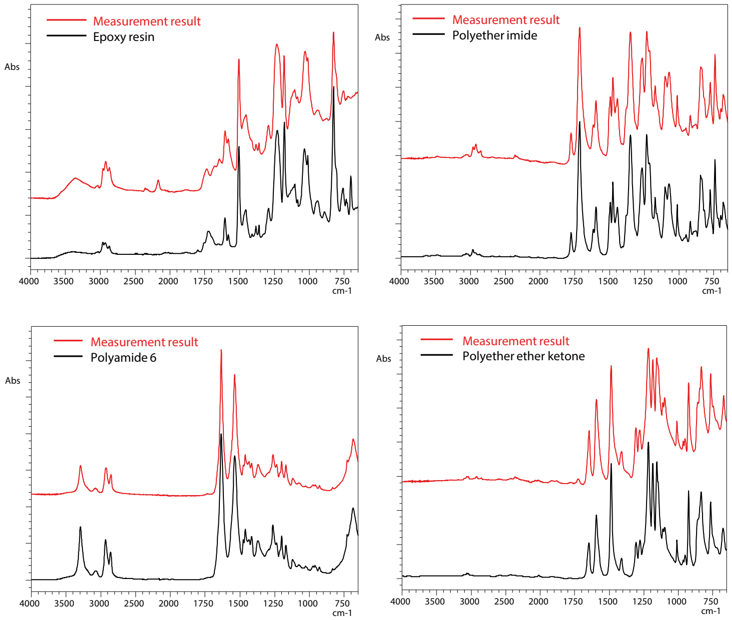


Fig. 2 IR Spectrum of CFRP (red) and measurement result (black)

Fourier Transform Infrared Spectrophotometer

This system measures the infrared spectra of organic matter, such as plastics, to qualitatively and quantitatively analyze components they contain based on their unique peak wavenumber and peak intensity characteristics.

- Samples can be measured quickly, within a few seconds to several minutes.
- By comparing results to a variety of library data, many organic substances can be qualitatively analyzed.
- Quantitative analysis is also possible by creating calibration curves using standard samples.

Product

Quantitative Analysis of Recycled Plastics Using FTIR – Individual Calculation Method –

Application

Analysis with a Fourier transform infrared (FTIR) spectrophotometer can be used to quickly measure the plastic mixture ratios that affect purchase prices or recycling methods.

benefits

FTIR allows quick calculations of component compositions because no pretreatment is necessary.

■ Measurement Results (Extract)

The following describes a study of using FTIR for analyzing the quantities of polyethylene (PE), polypropylene (PP), polystyrene (PS), and polyethylene terephthalate (PET) in recycled plastic. The recycled plastics in sheet form shown in Fig. 3 were measured this time. Table 1 shows the composition of the five samples that were used to create the calibration curves. Samples 1 to 5, with known concentrations, were measured four times each by changing the point for measurement each time. The calculated average infrared spectra are shown in Fig. 4. The calibration curves created for PE, PP, PS and PET are shown in Fig. 5. Next, two samples with unknown concentrations were measured and quantitated using the calibration curves shown in Fig. 5. Table 2 shows the quantitative analysis results. The results suggest that for samples in sheet form, the individual calculation method described in this article may be able to obtain quantitation values that indicate a correlation with NMR values.

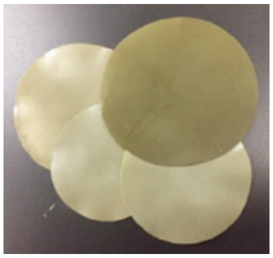


Fig. 3 Samples for Analysis

Table 1 Composition of Samples Used to Create Calibration Curves

	Composition (wt%)				
	PE	PP	PS	PET	other
Sample 1	89	9	1	<1	1
Sample 2	74	14	3	2	7
Sample 3	21	65	4	4	6
Sample 4	20	68	10	1	1
Sample 5	14	79	4	1	2

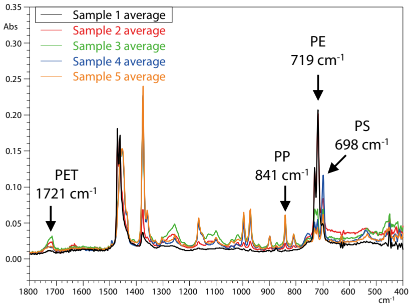


Fig. 4 Infrared Spectra of Samples 1, 2, 3, 4 and 5 (Average of four measurements)

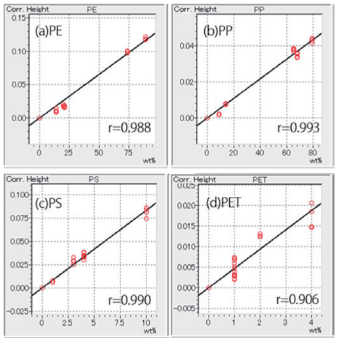


Fig. 5 Calibration Curves (a) PE, (b) PP, (c) PS, (d) PET

Table 2 Results of Quantitative Analysis Using FTIR and Reference Values Using NMR (Unit: wt%)

Unknown 1	Measurement 1	Measurement 2	Measurement 3	Measurement 4	Measurement 5	Average	NMR Value
PE	59.0	59.0	59.0	56.9	55.5	57.9	56
PP	28.7	25.8	29.0	28.9	31.3	28.7	23
PS	8.3	8.9	8.5	8.5	8.1	8.5	10
PET	2.7	3.3	3.0	3.0	2.7	3.0	3

Unknown 2	Measurement 1	Measurement 2	Measurement 3	Measurement 4	Measurement 5	Average	NMR Value
PE	89.1	89.9	87.9	90.7	91.1	89.8	89
PP	4.0	4.1	3.8	4.3	3.7	4.0	9
PS	0.8	1.1	1.2	1.1	1.1	1.1	1
PET	0.2	0.3	0.5	0.5	0.5	0.4	<1

Measurement of Polyethylene (PE)-Polypropylene (PP) Blend Samples

Application

Analysis using a differential scanning calorimeter (DSC) allows measuring the ratios of components in a plastic mixture.

benefits

- DSC analysis does not require chemical pretreatment, making it an easy way to measure component ratios in mixtures.
- Some crystalline polymers can be qualified based on their peak temperature.

■ Measurement Results (Extract)

The composition ratio of a mixture of low-density polyethylene (LDPE) and polypropylene (PP) was determined. The blue line in Fig. 6 is the DSC curve of the mixture, The peak 114.9°C corresponds to LDPE and 176.0 °C corresponds to PP melting. The content is calculated by dividing the amount of heat melted by the amount of heat melted by LDPE and PP separately measured. A measurement result of 79.1:20.9 was obtained for a sample mixed with LDPE:PP = 80:20 by weight.

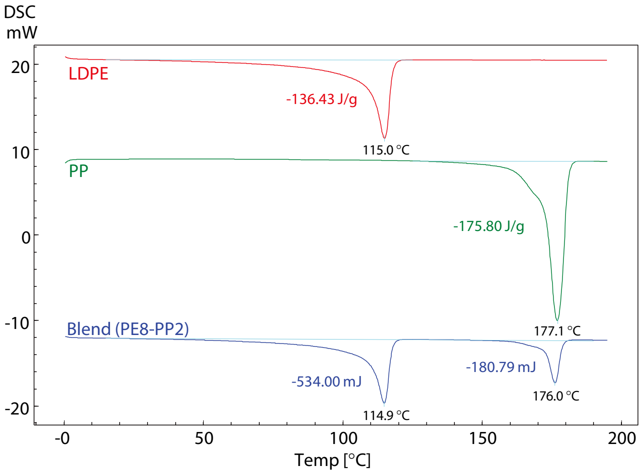


Fig. 6 DSC Curves of LDPE, PP and Blend Sample

Amount of LDPE = 534 mJ ÷ 136.43 mJ/mg = 3.91 mg
Amount of PP = 180.79 mJ ÷ 175.80 mJ/mg = 1.03 mg

Calculated ratio 3.91:1.03 = 79.1:20.9

Differential Scanning Calorimeter

DSC units determine the change in temperature and heat content of samples due to melting, glass transition, crystallization, or other transitions or reactions by measuring temperature differences between the sample and a reference substance.

- Measurements only require sample quantities of about 10 mg.
- Each measurement requires only about 30 minutes (depending on the heating rate and temperature range measured).

Product

Measurement of Plastic Moisture Content

A moisture analyzer can measure the moisture content in plastics, which can determine the physical properties and quality of products.

benefits

- Enables quick, easy, and accurate moisture content measurements.
- Samples can be measured in less time than the loss-on-drying method using a thermostatic chamber.

■ Measurement Results (Extract)

Using the Loss-on-Drying Method to Measure the Moisture Content in Plastic Pellets

JIS and other standards specify the loss-on-drying method as the official method for determining the moisture content in plastics. The following describes measurements using a thermostatic chamber and analysis conditions commonly used for the loss-on-drying method.

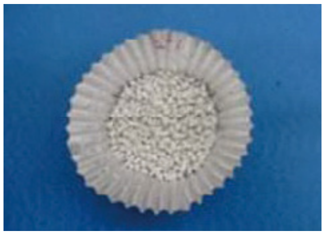


Fig. 7 Status of Plastic Pellets before being Placed in Thermostatic Chamber

【Drying Conditions】
Drying temperature: 105 °C
Drying ending condition: 5 hrs
Sample quantity: 5 g
【Results】
Moisture content: 0.27 %
Drying time: 5 hrs

The loss-on-drying method specifies 5 hours of drying in a thermostatic chamber, which means a long time will elapse before moisture content results are obtained.

Using the moisture analyzer at the same 105 °C drying temperature as the loss-on-drying method (TIME mode) resulted in values 0.02 % lower than the loss-on-drying method. If even a measurement time of 1 hour using the TIME mode is considered too long, then the drying temperature can be increased. Drying at 150 °C resulted in the same moisture content values as the loss-on-drying method. However, drying at 150 °C caused some of the pellets to melt.

Using the Moisture Analyzer to Measure the Moisture Content in Plastic Pellets

A moisture analyzer allows the drying conditions to be variously changed, such as varying the sample state or shortening the drying time. For the MOC63u moisture analyzer, the drying temperature can be specified in 1 °C steps between 50 and 200 °C and four modes are available for stopping drying. In this example, the TIME mode was used to stop drying when a specified time elapsed after drying started and drying temperatures were set to 105 °C and 150 °C.

Fig. 8 Plastic Pellets on the Moisture Analyzer after Drying

【Drying Conditions】
Drying temperature: 105 °C
Drying ending condition: 1 hrs
Sample quantity: 20 g
【Results】
Moisture content: 0.25 %
Drying time: 1 hrs
【Drying Conditions】
Drying temperature: 150 °C
Drying ending condition: 15 min
Sample quantity: 20 g
【Results】
Moisture content: 0.27 %
Drying time: 15 min

Table 3 Moisture Content and Measurement Time for Each Measurement Method

Measurement Method	Moisture Content	Measurement Time
Loss-on-Drying Method	0.27 %	5 hrs
TIME Mode(105 °C)	0.25 %	1 hrs
TIME Mode(150 °C)	0.27 %	15 min

Unibloc Moisture Analyzer

In many fields, a moisture analyzer is a necessary tool for quality control requirements. With the MOC63u, you can easily obtain accurate data. Simply place material on the pan and shut the cover. The MOC63u will start to measure. The MOC63u adapts to various materials and increases your work efficiency.

- Moisture content can be measured in plastics of various shapes.
- Temperatures on the pan can be set to between 50 and 200 °C.

Product

GPC Analysis of Synthetic Resin Containers Composed Mainly of Polylactic Acid

Application

GPC (gel permeation chromatography) can be used to determine the molecular weight distribution of repolymerized plastics.

benefits

- It is possible to measure the molecular weight distribution related to the properties of resin.
- Using a mixed gel column can reduce analysis time and solvent consumption by 50 %.

■ Measurement Results (Extract)

Polylactic acid (PLA) is a biodegradable plastic made from starch and sugar derived from plants. Using a Nexera GPC system and a Shodex GPC KF-805L column with a linear calibration curve, containers (cups made of PLA) containing PLA were analyzed.
Fig. 9 shows the chromatogram of a PLA cup (0.2%, prepared with eluent).

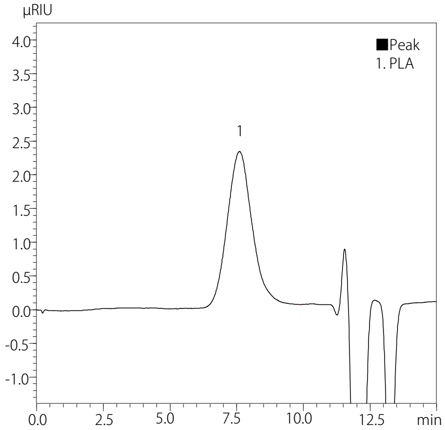


Fig. 9 GPC Chromatogram of Polylactic Acid Cup

Calibration curves were constructed using standard markers for polystyrene (PS) in the molecular weight range of 580 to 3.73 million. Fig. 10 shows the calibration curve. The calibration curve was used to calculate the molecular weight distribution of PLA cups. Table 4 shows the number average molecular weight (Mn), weight average molecular weight (Mw), and molecular weight distribution (polydispersity: Mw/Mn). These calculations are equivalent to the molecular weight of polystyrene.

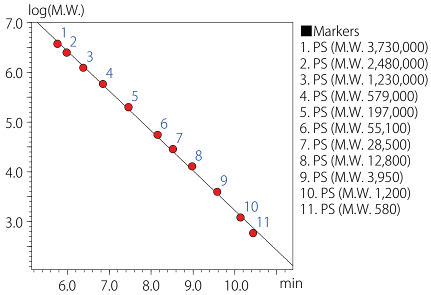


Fig. 10 Calibration Curve with Standard Polystyrene

Table 4 GPC Calculation Results

Mn	Mw	Mw/Mn
81,900	179,600	2.19

When analyzing samples with a wide range of molecular weights, from small molecules to macromolecules, two columns, one for small molecule analysis and the other for macromolecule analysis, are generally used in conjunction. This lengthens the analysis time and increases solvent consumption. Using a mixed gel column that covers a wide range of molecular weights can greatly reduce analysis time and solvent consumption.

High Performance Liquid Chromatograph GPC System

GPC is a type of size exclusion chromatography that can be used to determine the molecular weight distribution of high molecular weight substances. It is widely used for quality control in order to understand the differences in the physical properties of polymers.

- Most common method for understanding molecular weight distribution
- Mixed gel column reduces analysis time and solvent consumption

Product

Analysis of Synthetic Polymer Using a Benchtop MALDI-TOF Mass Spectrometer

Application

Benchtop MALDI-TOF MS enables the analysis of end groups that influence the properties and quality of polymers.

benefits

- The molecular weight distribution of polymers with an average molecular weight of several thousand can be measured.
- Analysis of the end groups allows evaluation of the purity and functionality of the polymer.

■ Measurement Results (Extract)

We compared polycarbonate (PC) sold as a reagent with PC for compact disks. Each was dissolved in an organic solvent and mixed with the polymer matrix Dithranol. As can be seen in the enlarged view in Fig. 11, each signal is detected as a monoisotopic peak, clearly showing the 254 repeating units that are monomer units of the PC. Also, the mass spectrum in Fig. 11 shows that there are several repeating components of the PC monomer unit 254. Since it is known that an end-capping group is applied to PC, we assumed the three chemical structures shown in Fig. 12 and analyzed them, and found that the oligomeric components belong to both-end capped type, single-end capped type and cyclic type, respectively. In addition, commercial reagents have a slightly higher number of single-end capped type, cyclic type oligomers.

In this way, MALDI-TOF MS enables the comparative evaluation of samples with different grades of the same polymer.

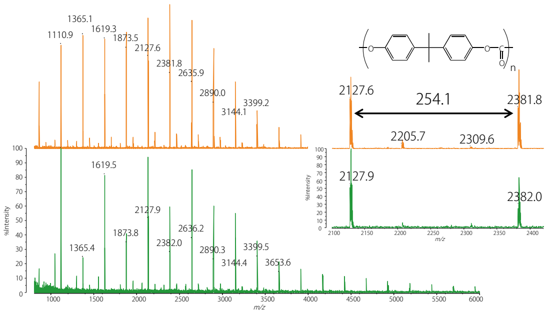


Fig. 11 Mass Spectrum of PC Oligomer
Top: Standard, Bottom: Compact Disc

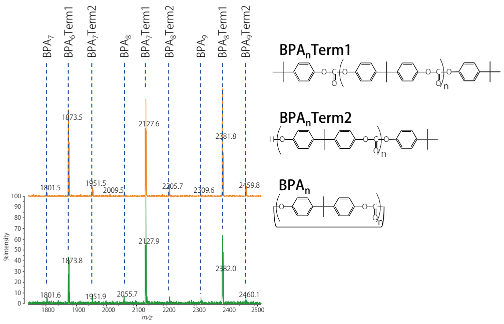


Fig. 12 End-terminal Group Analysis of PC Oligomers
Top: Standard, Bottom: Compact Disc

Benchtop Linear MALDI-TOF Mass Spectrometer

Compact benchtop linear mode MALDI-TOF mass spectrometer delivers excellent performance.

- Best-in-class MS resolution for linear mode
- Rapid measurement with a 200 Hz solid-state laser
- Newly designed load lock chamber allows smooth sample exchange
- Ion source cleaning function using UV laser for multi-analyte measurement

Product

Characterization of Polyethylene by Thermal Analysis

Application

Thermal analysis can measure the crystallinity and thermal decomposition properties of plastics.

benefits

- The level of crystallization can be measured using a differential scanning calorimeter (DSC).
- The simultaneous thermogravimetric and differential thermal analyzer (TG-DTA) enables the measurement of thermal decomposition processes (heat resistance).

■ Measurement Results (Extract)

DSC Measurement

The hardness, impact resistance, transparency, and other physical properties of polymer materials change depending on the degree of crystallinity. The degree of crystallinity can be calculated by the following equation using the melting peak area (heat of fusion) measured by DSC.

Crystallinity (%) = (Measured heat of fusion / Heat of fusion for perfect crystal) × 100

Fig. 13 shows an example in which three types of polyethylene (LDPE, HDPE, UHMW-PE) were measured and their crystallinities were obtained. Here, 290 J/g was used as the heat of fusion for a perfect crystal. From this data, it can be understood that crystallinity increases and the melting peak temperature shifts to higher temperatures as the density of the polyethylene becomes greater.

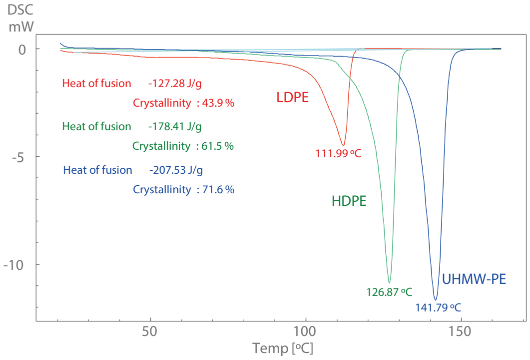


Fig. 13 DSC Measurement Data

TG-DTA Measurement

It is possible to evaluate the heat resistance of materials by measuring the process of thermal decomposition.

Fig. 14 shows the results of a measurement of the thermal decomposition characteristics of LDPE and HDPE with a TG-DTA in a nitrogen atmosphere. The data show that decomposition begins at a lower temperature in LDPE than in HDPE, indicating that LDPE has lower heat resistance.

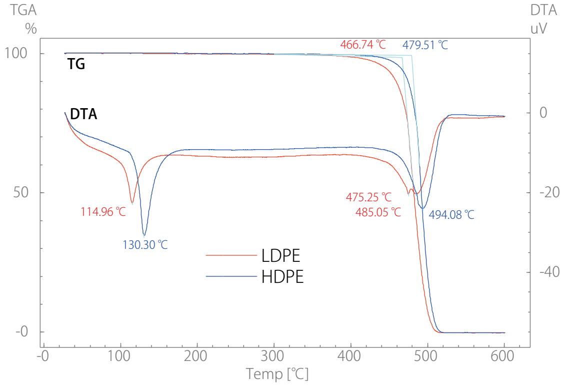


Fig. 14 TG-DTA Measurement Data

TG-DTA Simultaneous Measuring Instrument

By measuring weight changes and differential thermal values at the same time, TG-DTA units can measure decomposition and other changes in detail.

- Measurements only require sample quantities of about 10 mg.
- The measurement atmosphere can be changed to nitrogen, air, etc.

Product

Using UV for Polymer Transmittance Testing

Application

UV-VIS spectrophotometers can be used to determine the transmittance and color of recycled plastics.

benefits

They are useful for measuring plastic transmittance and efficiently deciding whether a plastic passes/fails to satisfy specified criteria.

■ Measurement Results (Extract)

The red film was regarded as the acceptable product and evaluation was performed using "Cutoff - Over" in the spectral evaluation function to differentiate the red film from the yellow film. When "Cutoff - Over" is selected, judgment is made based on the wavelength at the point when the measured transmittance has exceeded the threshold in the set wavelength range. In this example, we set the criterion of a pass judgment to the condition that the wavelength at which transmittance exceeds 50 % is 550 nm or higher.

Fig. 16 shows the obtained transmittance spectrum of each sample and Fig. 17 shows the spectral evaluation results. "PASS" is indicated for the red film since the evaluation value is 579 nm. However, the yellow film received a "FAIL" and is highlighted in the table due to having a cutoff wavelength below 550 nm. The column color in the evaluation result table changes when a result deviates from the set evaluation criteria, allowing users to determine at a glance whether a test has passed or failed.

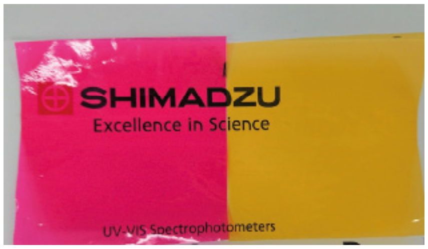


Fig. 15 Picture of Samples

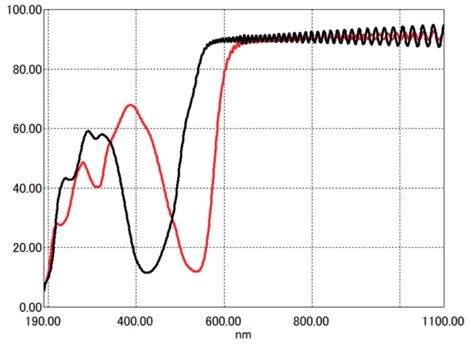
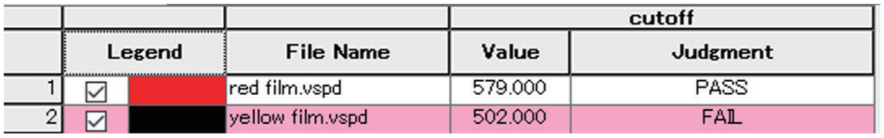


Fig. 16 Measurement Results



			cutoff	
	Legend	File Name	Value	Judgment
1	☑ 🟥	red film.vspd	579.000	PASS
2	☑ ⬛	yellow film.vspd	502.000	FAIL

Fig. 17 Spectral Evaluation Results

UV-VIS Spectrophotometer

UV-VIS spectrophotometers are used to measure transmittance or reflectance in the UV-to-visible light range. In addition to measuring liquids, they can also measure solid samples and films. Discrimination between colors is also possible by measuring transmittance or reflectance.

- Enables measuring the transmittance of plastics.
- In combination with the spectral evaluation function, they can be used to decide whether samples pass or fail transmittance criteria.

Product

Analysis of Discoloration and Coloration Using FTIR and EDX

Application

Fourier transform infrared (FTIR) spectrophotometers and energy dispersive X-ray fluorescence (EDX) spectrometers can be used to determine discoloration or colorant components.

benefits

- The causes of plastic discoloration can be analyzed by integrating the data from an EDX unit, which is adept at analyzing inorganic elements, with data from an FTIR unit, which is adept at identifying and characterizing organic substances.
- FTIR and EDX systems can help increase quality control efficiency by measuring samples more quickly.

Measurement Results (Extract)

FTIR and EDX were used to take measurements from white resin and green resin (Fig. 18) and identify the coloring compounds in each resin. Fig. 19 shows infrared spectra for white resin and green resin and a spectrum search result. The results showed that polyethylene is the resin component present in both the white resin and green resin. It is presumed that no coloring component was detected because only a very small quantity is present in each sample.

Fig. 18 White Resin (left) and Green Resin (right)

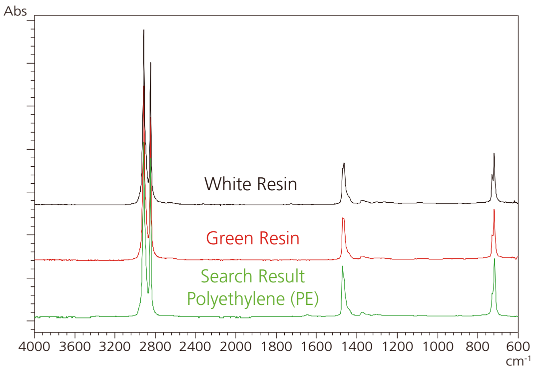


Fig. 19 Infrared Spectra and Search Result

Table 5 shows the quantitative results and Fig. 20 shows the qualitative profiles. 13Al, 14Si, 15P, and 16S were detected in both the white resin and green resin, and 17Cl and 29Cu were only detected in the green resin. FTIR analysis showed the resins are polyethylene, which is normally transparent, so detected elements are expected to contribute to resin coloration.

Table 5 Quantitative Results

Units: % -: Undetected

	Cl	Si	P	Al	S	Cu	C_2H_4
White	-	0.010	0.007	0.007	0.003	-	99.97
Green	0.030	0.012	0.007	0.006	0.003	0.002	99.94

Note: Polyethylene (C2H4) was set as the balance.[1]

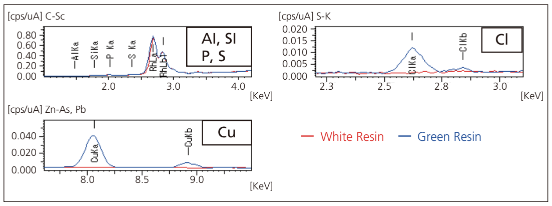


Fig. 20 Qualitative Profiles

Energy Dispersive X-ray Fluorescence Spectrometer

Energy dispersive X-ray fluorescence spectrometers are used to investigate the types and concentrations of elements contained in samples by irradiating the sample with X-rays and then analyzing the energy level (wavelength) or intensity of fluorescent X-rays emitted from the sample in response.

- EDX can measure elements ranging from $_6$C to $_{92}$U.
- EDX enables colorant and discoloration component analysis without pretreatment.

Product

High-Speed Tensile Test of CNF-Reinforced Plastic

Application

High-speed tensile testing measurements can provide data that is essential for determining the impact characteristics of parts.

benefits

- Plastic properties with respect to impacts, collisions, and dropping can be evaluated.
- The data obtained can be used to simulate impacts and dropping.

■ Measurement Results (Extract)

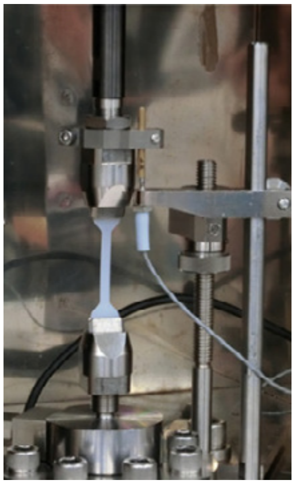


Fig. 21 Condition of Tests

Two specimens were prepared, one using high density polyethylene (HDPE) and the other being HDPE reinforced with 10 % CNF (CNF10 %/HDPE). Fig. 22 shows examples of the stress-displacement curves of the HDPE and CNF10 %/HDPE at various strain rates. Both materials exhibited lower tensile strength as the test speed decreased and higher tensile strength at higher test speeds. Moreover, the slopes of the stress-displacement curves also became larger as the test speed increased.

Fig. 23 shows the relationship between the strain rate and tensile strength. From the results in Fig. 23, CNF10 %/HDPE displayed larger tensile strength under all strain rate conditions. The tensile strength also increased at higher test speeds.

Thus, the deformation behavior of plastic materials changes depending on how fast loads are applied. That means material property information is required during the design stage in order to predict product impact and dropping performance.

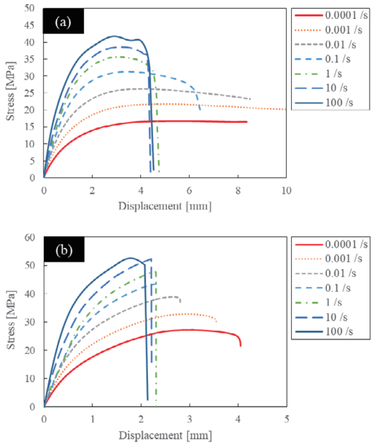


Fig. 22 Stress-Displacement Curves

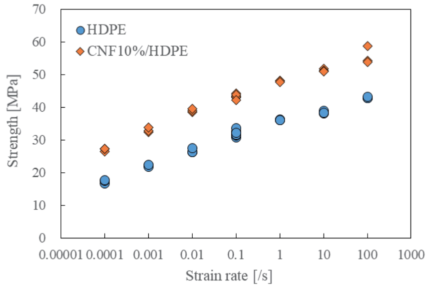


Fig. 23 Relationship Between Strain Rate and Tensile Strength

High-Speed Impact Testing Machine

This enables tensile testing at speeds up to 20 m/s in order to obtain fundamental data about the high-speed deformation behavior of materials.

- Enables ISO 22183-compliant testing for increasing the reliability of high-speed testing.
- Both temperature dependence and strain rate dependence can be evaluated simultaneously by varying both the temperature environment and testing speed at the same time.
- Used in combination with an HPV-X2 high-speed video camera, it enables high-speed strain measurements.

Product

Hardness Test of Plastic Materials (ISO/TS 19278:2019)

Application

Dynamic ultra micro hardness tester measurements can be used for hardness testing related to the consistency of quality.

benefits

- Dynamic ultra micro hardness testers can measure ultra-small or thin specimens that cannot be compared by conventional Rockwell hardness testing.
- Hardness can be compared/evaluated using the same testing parameters regardless of the material.

■ Measurement Results (Extract)

Table 6 shows the hardness test results (average values), Fig. 24 shows the hardness test results (average values) and error ranges, and Fig. 25 shows the force-depth curves.

With these sample materials, indentation ranged from 11.2 μm to 23.5 μm at a load of approximately 500 mN, and results showing hardness values of 45.7 to 227.8 were obtained. According to hardness, the results showed that the softest material was HDPE and the hardest was PS, as shown below.

PS > ABS/PMMA > PP > HDPE

Table 6 Hardness Test Results (Average Values)

Sample	Force [mN]	Depth [μm]	Indentation hardnessH_{IT} [N/mm^2]	Standard deviation
PP	502.3	16.4	103.1	1.59
HDPE	502.2	23.5	045.7	0.87
ABS/PMMA	502.1	12.1	193.8	8.74
PS	502.2	11.2	227.8	6.15

*Polystyrene (PS), Acrylonitrile Butadiene Styrene (ABS), Polymethyl Methacrylate (PMMA), Polypropylene (PP), High Density Polyethylene (HDPE)

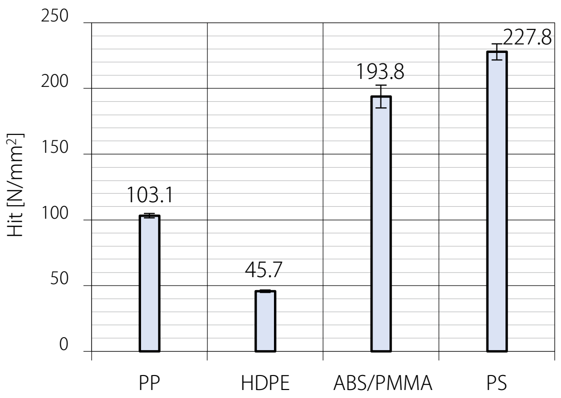


Fig. 24 Hardness Test Results (Average Values) and Error Ranges

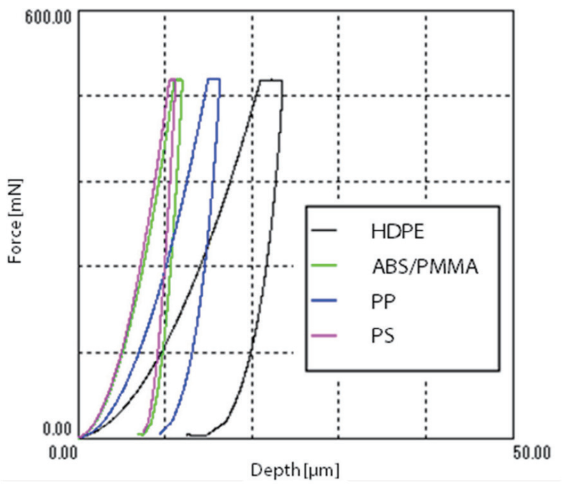
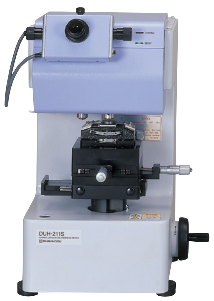


Fig. 25 Force-Depth Curves

Dynamic Ultra Micro Hardness Tester

Surface properties are evaluated based on the relationship between the force used to press an indenter into a specimen and the resulting indentation depth.

- Specimens can be secured in a vise without using an adhesive.
- Tests can be performed easily by simply selecting the testing mode in the software.
- The ability to measure penetration depths up to 100 μm means a wide hardness range can be measured.



Product

Using X-Ray CT to Analyze Internal Voids in Molded Plastic

Application

X-ray CT systems enable nondestructive observation of internal voids in molded plastic parts for void analysis/evaluation using software designed specifically for that purpose.

benefits

- Enables nondestructive observation of internal voids.
- The volume of voids and a histogram of their abundance can be determined using dedicated data analysis software.

■ Measurement Results (Extract)

The following shows an example of using X-ray CT to measure a molded plastic cable clamp. Voids inside molded plastic parts can be observed nondestructively, as shown in the MRP images (Fig. 26 left). Any vertical, horizontal, or angled cross-section can be freely observed from a single X-ray CT measurement. Using optional defect and inclusion analysis software, voids within molded plastic parts can be shown color-coded based on void volume (Fig. 27 left) or graphed by volume as a histogram (Fig. 27 right).

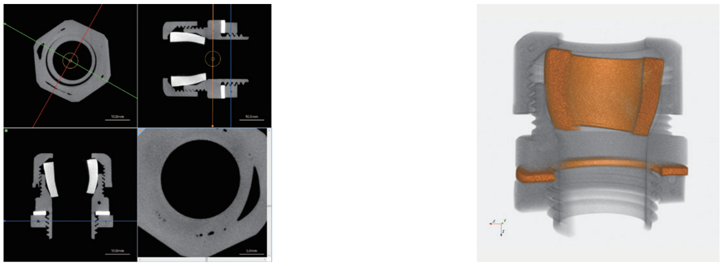


Fig. 26 MPR Images (left) and 3D Image (right) of Molded Plastic Part (Cable Clamp)

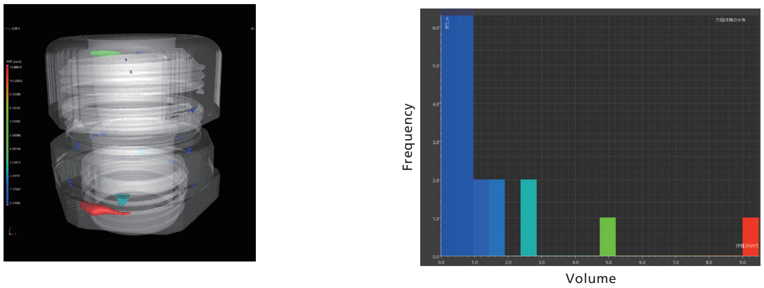


Fig. 27 Internal Void Analysis Results (left) and Histogram (right)

Benchtop X-Ray CT System

The item (workpiece) being inspected is placed between the X-ray generator and X-ray detector and then the item is rotated 360 degrees to collect X-ray transmission data from various angles for calculating cross-sectional images. That enables nondestructive three-dimensional observation inside molded plastic parts.

- Despite its benchtop design, it is equipped with a high-power X-ray generator, enabling observation of thick molded plastic parts.
- Just a 3-step process enables starting observations. Scanning takes as little as 12 seconds.

Product

Evaluation of the Flow Characteristics of General Purpose Plastics

Application

Rheometer measurements can be used to evaluate rheological properties that are important for manufacturing high-quality molded items.

benefits

Rheological properties, which affect the quality of molded parts, can be evaluated easily and with good reproducibility.

■ Measurement Results (Extract)

The rheological properties of thermoplastics when they soften at high temperatures vary depending on the material. Constant heating rate testing provides a simple and effective way to measure the rheological properties of plastics at respective temperatures. The temperature rise test is a method of testing while increasing the temperature at a constant rate over the course of the test time. In this test, it is possible to continuously measure the process of the sample from the solid region to the transition region and the rubbery elastic region to the flow region. The softening temperature (Ts) when the sample moves from the solid region to the transition region and the flow beginning temperature (Tfb) at which the sample flows out can be measured. The behavior of flow curves during constant heating is shown in Fig. 28. Typical property valve behaviors during constant heating rate testing are described in Table 7.

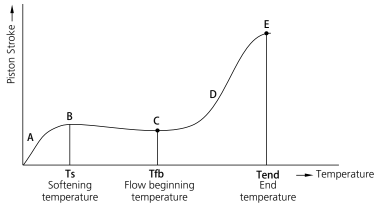


Fig. 28 Stroke-Temperature Graph

Four types of materials were measured—polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), and polycarbonate (PC). The stroke vs temperature graph for respective polymers is shown in Fig. 29. When looking at PE, shown in blue, and PP, shown in red, the temperature at the last point of the graph (the end of the flow of the sample) is about 230 °C for both, but the temperature at which the outflow starts is about 30 °C lower for PE than for PP. In other words, PE has a smaller slope of the curve after the start of the outflow, indicating a slow decrease in viscosity with increasing temperature. In this way, the difference in the shape of the graph shows the difference in the characteristics of each sample. Test results for respective materials are shown in Table 8. It can be seen that both temperature and viscosity vary greatly from sample to sample.

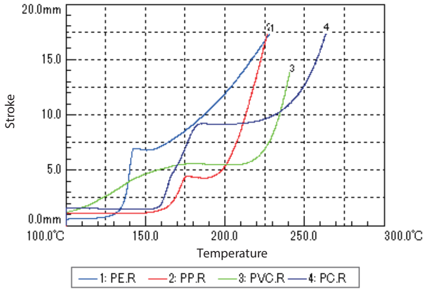


Fig. 29 Stroke-Temperature Graph

Table 7 Name and Definition of Each Value

Symbol	Name	Definition
AB	Softening zone (Softening curve)	Stage in which the sample is deformed by the compressive load and its internal porosity is gradually reduced.
TS	Softening temperature	Temperature at which the internal porosity is eliminated, and the sample becomes a transparent substance or phase that is apparently homogeneous and has a homogeneous stress distribution.
BC	Stop zone (Stop curve)	Zone in which the piston position does not clearly change within a limited period of time and sample outflow from the die orifice is not clearly seen.
Tfb	Flow beginning temperature	Temperature at which the piston slightly goes up due to thermal expansion of the sample and then it clearly starts going down again.
CDE	Outflow zone (Outflow curve)	Zone in which the sample clearly flows out from the die orifice.

Table 8 Test results

Sample Name	Softening Temperature (°C)	Flow Beginning Temperature (°C)	½ Method Temperature (°C)	½ Method Viscosity (Pa•s)
Polyethylene	142.4	153.6	203.6	16,370
Polypropylene	175.6	187.2	215.6	5,716
Polyvinyl chloride	175.3	208.2	234.4	6,138
Polycarbonate	183.1	205.1	253.9	10,590

Capillary Rheometer Flowtester

Flowmeters are used to evaluate the viscosity properties of plastics and other flowable materials, based on the relationship between temperature, pressure, and flow speed.

- Rheometers can be used for either constant-temperature testing at a fixed temperature or for constant-heating rate testing with the temperature increased at fixed increments.
- Highly reproducible data can even be obtained from evaluating the rheological properties of thermoset plastics that quickly harden when heated.

Product

RoHS Screening Analysis by EDX

Application

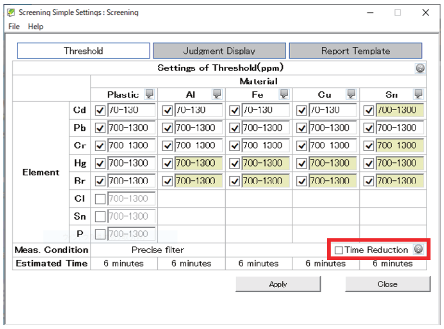
Energy dispersive X-ray fluorescence (EDX) spectrometer measurements can be used to easily screen for RoHS substances in plastics.

benefits

- Performance improvements contribute to shorter analysis times.
- The software can automatically select the optimal calibration curve for the given sample.

Measurement Results (Extract)

Due to increased sensitivity and improved analytical algorithms, EDX systems now offer significantly shorter measurement times.
EDX-7200 includes PCEDX-Navi software that makes RoHS screening analysis easy, even for users without analytical experience. As soon as the system determines that the concentration of the element being controlled is clearly higher or lower than the corresponding threshold values, or is within a gray zone, this function automatically skips to the next measurement condition, which helps improve analysis throughput. The window for setting threshold values and enabling the automatic time-reduction function is shown in Fig. 30. Analysis results are shown in Table 9 and Fig. 31. It shows that the automatic time-reduction function shortened the measurement time from 400 seconds to 51 seconds.



Settings of Threshold(ppm)

Element	Plastic	Al	Fe	Cu	Sn
Cd	☑ 70-130	☑ 70-130	☑ 70-130	☑ 70-130	☑ 700-1300
Pb	☑ 700-1300	☑ 700-1300	☑ 700-1300	☑ 700-1300	☑ 700-1300
Cr	☑ 700 1300	☑ 700 1300	☑ 700 1300	☑ 700 1300	☑ 700 1300
Hg	☑ 700-1300	☑ 700-1300	☑ 700-1300	☑ 700-1300	☑ 700-1300
Br	☑ 700-1300	☑ 700-1300	☑ 700-1300	☑ 700-1300	☑ 700-1300
Cl	☐ 700-1300				
Sn	☐ 700-1300				
P	☐ 700-1300				
Meas. Condition	Precise filter				☐ Time Reduction
Estimated Time	6 minutes	6 minutes	6 minutes	6 minutes	6 minutes

Fig. 30 Window for Setting Threshold Values and Enabling the Automatic Time-Reduction Function

Fig. 31 Plastic Material

Table 9 Plastic Material Analysis Results

Automatic Time-Reduction	ON				OFF			
Element	Quantitation Value [ppm]	3σ [ppm]	Pass/Fail Result	Analysis Time [sec]	Quantitation Value [ppm]	3σ [ppm]	Pass/Fail Result	Analysis Time [sec]
$_{46}$Cd	283.9	14.4	NG	14	283.3	6.6	NG	100
$_{51}$Sb	34.5	14.7	OK		26.6	5.4	OK	
$_{82}$Pb	9.1	2.8	OK	11	10.2	1.0	OK	100
$_{80}$Hg	N.D.*	1.2	OK		N.D.*	0.4	OK	
$_{35}$Br	1.8	1.0	OK		1.3	0.3	OK	
$_{24}$Cr	13.5	5.6	OK	11	10.5	1.9	OK	100
$_{17}$Cl	94.2	56.8	OK	15	98.2	22.1	OK	100
	Total			51	Total			400

* N.D.: Not Detected

Energy Dispersive X-ray Fluorescence Spectrometer

The composition of inorganic elements can be analyzed without pretreatment.

- EDX can measure elements ranging from $_{11}$Na to $_{92}$U.
- The outstanding energy resolution improves the reliability of analytical results by minimizing the effects of peaks from different elements overlapping.

Product

Precision Analysis of Toxic Elements in Plastic

Application

ICP atomic emission spectrometers (ICP-AES) can measure hazardous elements that are restricted by a variety of environmental regulations.

benefits

ICP-AES systems can accurately measure hazardous elements (such as Cd, Pb, Cr, Hg, and As) in plastics.

■ Measurement Results (Extract)

We conducted analysis of a polyethylene standard material using the Shimadzu ICPE-9800 series multitype ICP atomic emission spectrometer, and three different digestion methods: the dry ashing method, the wet decomposition method, and the microwave sample digestion method. Table 10 shows the analytical results. Fig. 32 shows the spectral profiles. The detection limits were lower than the maximum permissible RoHS values, demonstrating that analysis can be conducted with high sensitivity.

Comparison of pretreatment methods: Good results that were consistent with the certified values were obtained for Cd and Pb using the dry ashing method, for Cd, Cr, Hg, and As by the wet digestion method (Kjeldahl method), and for all of the elements by the microwave sample digestion method. Low values are thought to have occurred due to the evaporation of Hg and As at high temperatures using the dry ashing method, and due to the precipitation of lead sulfate that occurs as a result of the reaction of Pb with the sulfuric acid used for digestion in the wet digestion method.

Table 10 Analytical Results of Polyethylene Resin (unit: mg/kg)

		Sample name	BCR680				BCR681			
Element	RoHS Maximum Permissive Value	Detection Limit (3σ)	Preparation			Certified Value	Preparation			Certified Value
			Dry Ashing	Wet Decomposition	Microwave Decomposition		Dry Ashing	Wet Decomposition	Microwave Decomposition	
Cd	100	0.02	140	140	141	140.8	21.1	21.3	21.6	21.7
Pb	1000	0.2	106	<	107	107.6	13.2	<	13.7	13.8
Cr	1000 *	0.03	106	112	115	114.6	16.1	17.3	17.9	17.7
Hg	1000	0.2	<	24.2	25.3	25.3	<	4.3	4.4	4.5
As	-	0.5	27	30	31	30.9	3	4	4	3.93

Detection limit: Detection limit when conducting pretreatment with sample dilution 0.2 g/20 mL
<: Below the detection limit
*: Cr^{6+} Maximum permissible value

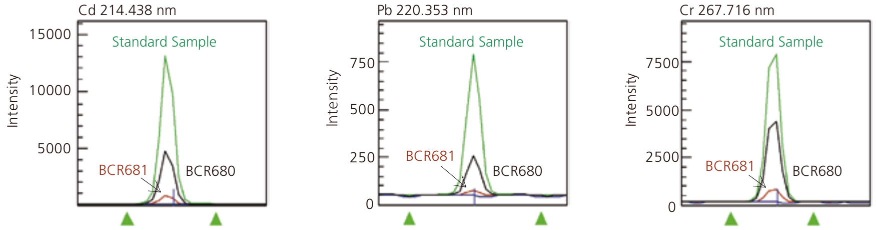


Fig. 32 Spectral Profiles of Polyethylene

Simultaneous ICP Atomic Emission Spectrometer

ICP-AES systems can analyze elements in samples dissolved in solutions. They enable rapid simultaneous analysis of many elements, regardless of the element concentration.

- All elements can be measured simultaneously.
- It achieves a broad dynamic range from ppb to percent-level concentrations.

Product

Analysis of Acetaldehyde and Limonene in Recycled PET Using an HS-GC/MS System

Application

Gas chromatograph mass spectrometer (GC-MS) systems can analyze residual components in rinse solutions.

benefits

Using a headspace sampler (HS) unit, common residual components (acetaldehyde and limonene) in polyethylene terephthalate (PET) containers can be analyzed without having to dissolve the PET container in solvent.

■ Measurement Results (Extract)

Six types of samples with different pretreatment states were prepared. Sample types included pellets and freeze-ground pellet powder obtained from a recycler, two types of PET bottles that contained commercially marketed bottled water, and one PET bottle type each that contained lemon tea and orange juice. Each type of sample was sealed inside an HS vial. The state and quantity of each sample are indicated in Table 11. Fig. 33 shows a TIC chromatogram of the powder sample as a typical sample.

Table 11 Information about Each Pretreated Sample

Sample	State	Qty
Pellets[*1]	Pellets	5 g
Powder[*1]	Powder	0.5 g
Water 1[*2]	Cut into pieces with scissors	1 g
Water 2[*2]	Cut into pieces with scissors	1 g
Lemon Tea[*2]	Cut into pieces with scissors	1 g
Orange Juice[*2]	Cut into pieces with scissors	1 g

*1 PET sample provided by a recycling company (identical samples in pellet and powder state)
*2 PET bottles for commercial beverages (lightly washed with water and cut with scissors)

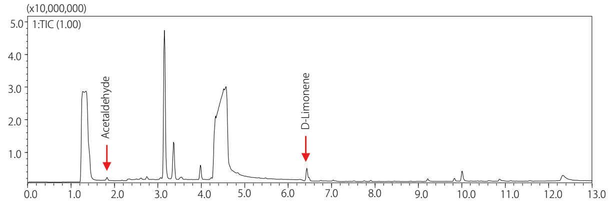


Fig. 33 TIC Chromatogram of Powder Sample

Calibration curves were prepared by successively diluting samples with acetone solution to seal 2, 20, 100, and 200 μg quantities of acetaldehyde and 20, 100, and 200 ng quantities of limonene in headspace sample vials. Calibration curves for acetaldehyde and limonene are shown in Figs. 34 and 35 respectively. Table 12 lists the quantities of acetaldehyde and limonene per gram of sample that resulted from analyzing the sample quantities sealed in the respective vials.

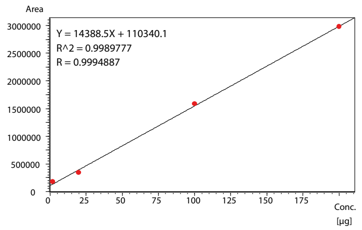


Fig. 34 Acetaldehyde Calibration Curve

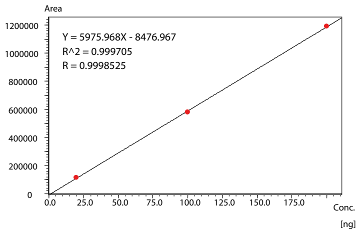


Fig. 35 Limonene Calibration Curve

Table 12 Quantitative Analysis Results for Each Sample

Sample	Calculated Quantity of Acetaldehyde (μg/g)	Calculated Quantity of Limonene (ng/g)
Pellets	2.3	96
Powder	25	140
Water 1	63	N.D.
Water 2	8.7	N.D.[*1]
Lemon Tea	23	N.D.[*1]
Orange Juice	15	N.D.[*1]

*1 Though limonene was not detected, terpinene, a substance similar to limonene, was detected at an adjacent retention time.

Gas Chromatograph Mass Spectrometer

The GC unit separates the components in organic compounds in samples and then the mass spectrometer analyzes the component masses. The components are qualitatively and quantitatively analyzed based on the signal intensity level in mass spectra.

- By using a headspace sampler (HS) unit, the quantities of acetaldehyde and limonene contained in the sample can be analyzed without dissolving them in a solvent.
- Target components that are otherwise difficult to identify due to high contaminant levels can be analyzed by qualitative-quantitative analysis.

Product

TOC – Determination According to USP 661.2 Testing of Plastic Packaging Systems and Their Materials of Construction

Application

Total organic carbon (TOC) analyzers can measure the TOC levels in purified water and TOC leached from plastic packaging materials.

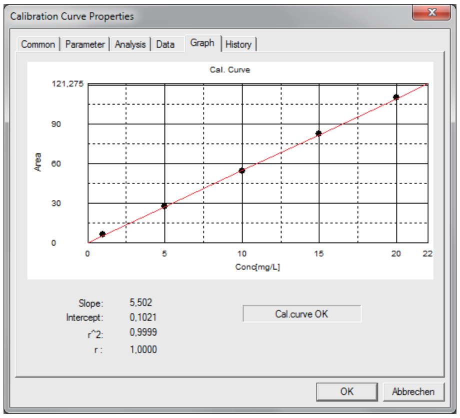
benefits

Shimadzu TOC analyzers enable compliance with plastic drug packaging TOC testing requirements mandated by USP661 "Plastic Packaging Systems and Their Materials of Construction."

■ Measurement Results (Extract)

The TOC determination is performed according to the USP. This regulation describes the TOC determination for pure water, purified water and water for injection. It does not prescribe any particular oxidation technique for TOC determination. The TOC systems, however, must be able to differentiate between inorganic and organic carbon. This can be carried out either via removal of the inorganic carbon (NPOC method) or via a separate determination (difference method). The limit of detection for TOC should be at least 0.05 mg /L. The applicability of the method must be determined via a system suitability test. However, material extracts may have TOC values that are higher than those of purified water because of extracted organic substances. Thus, the TOC analyses performed should have a limit of detection of 0.2 mg/L and should have a demonstrated linear dynamic range from 0.2 to 20 mg/L.

To prove the required dynamic range, a calibration using the TOC-L_{CPH} (with high-sensitivity catalyst) was carried out in a range of 1.0 to 20 mg/L (Fig. 36). These results show that the TOC-L_{CPH} with high-sensitivity catalyst covers the required linear dynamic range from 0.2 to 20 mg/L. This means both applications, purified water and this extraction solution, can be measured with a single TOC-L_{CPH} instrument.



Slope: 5,502
Intercept: 0,1021
r^2: 0,9999
r : 1,0000

Fig. 36 Calibration Curve 20 mg/L, Results

Total Organic Carbon Analyzer

The combustive catalytic oxidation type TOC analyzer measures the total organic carbon (carbon content) by acidifying the organic matter in water with carbon dioxide at a high temperature and then detecting the carbon in the infrared gas analyzer. TOC analyzers are used in a wide variety of fields, such as for quality control of public drinking water or other water.

- The combustive catalytic oxidation method has a 4 µg/L detection limit, which is the highest detection sensitivity available.
- It can efficiently oxidize not only small organic molecules that break down easily but also insoluble or large organic matter molecules that are resistant to decomposition.
- Ultra-wide range from 4 µg/L to 30,000 mg/L

Product

Evaluation of UV-Degraded Plastics by FTIR and Dynamic Ultra Micro Hardness Tester

Application

A Fourier transform infrared (FTIR) spectrophotometer and a dynamic ultra micro hardness tester can be used to analyze plastic degradation.

benefits

- Plastic degradation due to exposure to ultraviolet light can be evaluated based on analysis using multiple models.
- Changes in the chemical structure of plastics by degradation can be confirmed using FTIR.
- Changes in the hardness of plastics by degradation can be evaluated with a dynamic ultra micro hardness tester.

■ Measurement Results (Extract)

We evaluated the ultraviolet (UV) degradation of plastics that are frequently used in automotive parts. Changes in the chemical structure of the plastic surface under UV irradiation were evaluated by using a Fourier transform infrared (FTIR) spectrophotometer (Fig. 37 left), and changes in hardness were evaluated with a dynamic ultra micro hardness tester (Fig. 37 right). As a result, it was found that structural changes due to oxidation occurred at the surface of the plastics under UV irradiation, and hardness tended to increase. These evaluation data are useful when selecting additives to be added to plastics and for the improvement of functionality.

Fig. 37 Fourier Transform Infrared Spectrophotometer (Left)
Dynamic Ultra Micro Hardness Tester (Right)

Fig. 38 and Fig. 39 show the infrared spectra of PP and PC, respectively, after UV irradiation for 0 h,1 h and 100 h using a super accelerated weathering chamber. Focusing on the C=O stretching vibration at around 1750 cm^{-1} (yellow boxes in the figures), when the samples were exposed to UV irradiation for 100 h, an increase in peak intensity was observed in the PP, and a change in the peak shape could be confirmed in the PC. These results clarified the fact that the surface of both plastics undergoes oxidative degradation under exposure to UV irradiation, and after 100 h, the structural changes associated with degradation have progressed to the point where changes in the peaks can be clearly detected.

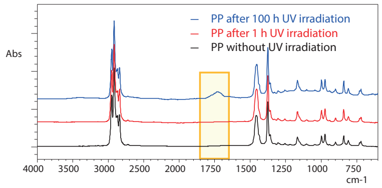


Fig. 38 Infrared Spectrum of Polypropylene (PP)

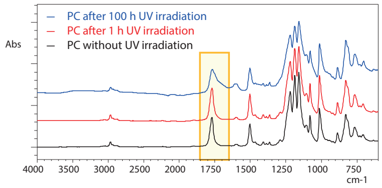


Fig. 39 Infrared Spectrum of Polycarbonate (PC)

The following describes evaluating hardness changes in PP and PC plastics after UV irradiation for 0 h, 1 h and 100 h. The measurement results are shown in Fig. 40 and Fig. 41. It can be understood that the surfaces of both the PP and PC samples became harder as a result of UV irradiation. In the FTIR measurements, the structural changes in the samples became remarkable after 100 h, but in the hardness test, a clear difference in the hardness of the samples could be observed after only 1 h. These results suggest that the intrinsic flexibility of resins decreases due to oxidative degradation of the sample surface by UV radiation, and as a result, cracking may occur more easily.

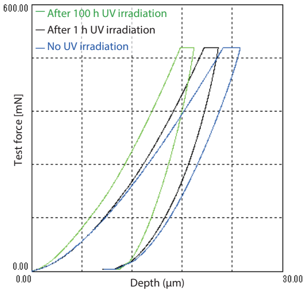


Fig. 40 Measurement Results of Hardness Test of Polypropylene (PP)

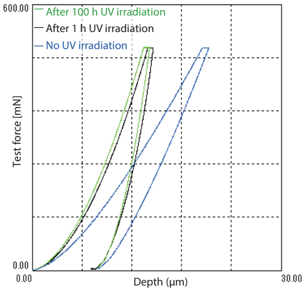


Fig. 41 Measurement Results of Hardness Test of Polycarbonate (PC)

Multifaceted Evaluation of Plastics: Differences Due to PC/ABS Resin Compounding Ratio

Application

Analysis with a UV-VIS spectrophotometer (UV), universal testing machine, differential scanning calorimeter (DSC), and Fourier transform infrared (FTIR) spectrophotometer can be used to check the elemental composition after molding and determine performance in terms of strength.

benefits

- If an evaluation method is used that provides linear increases with respect to material input ratios, then the mixture ratios of unknown materials can be predicted.
- Multifaceted evaluations are less likely to result in an incorrect decision than evaluations based on a single control criterion.

■ Measurement Results (Extract)

The relationship between the compounding ratio and various properties was evaluated using five types of Polycarbonate (PC)/acrylonitrile-butadiene-styrene (ABS) test specimens molded with different compounding ratios of PC and ABS (PC:ABS=0:100, 25:75, 50:50, 75:25, 100:0) (Fig. 42). The agreement of the compounding ratios and the composition ratios after molding were also evaluated.

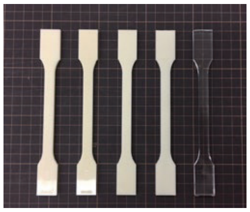
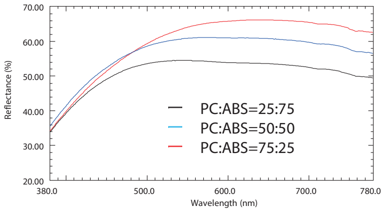


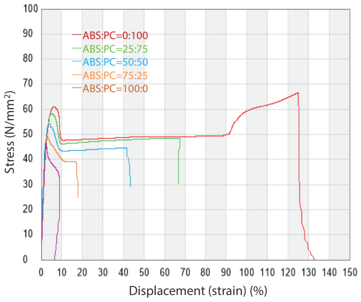
Fig. 42 Appearance of 5 Specimens

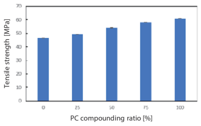


PC:ABS	Yellowness
25:75	20.52
50:50	12.99
75:25	8.48

The greater the ratio of ABS, the higher the yellowness.

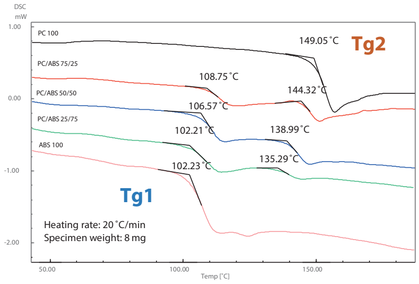
Fig. 43 UV data

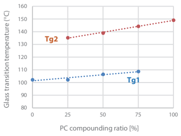




A linear relationship was obtained between the elastic modulus and blending ratio.

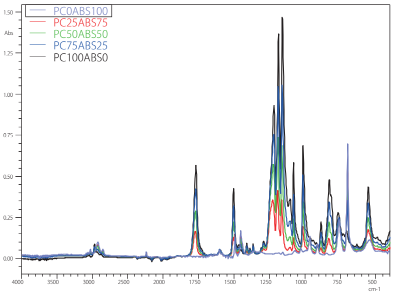
Fig. 44 Testing Machine Data

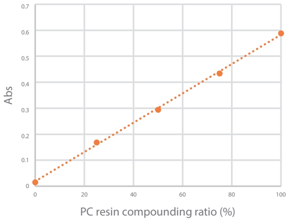




A linear relationship with the blending ratio was obtained for ABS-derived glass transition temperature Tg1 and PC-derived glass transition temperature Tg2.

Fig. 45 DSC Data





A proportional relationship was obtained between the blending ratio and the PC-derived C = O bond peak strength, confirming the consistency between the blending ratio and the post-molding component ratio.

Fig. 46 FTIR Data

Multifaceted Evaluation of Plastics: Difference of Heat Treatment Conditions

Application

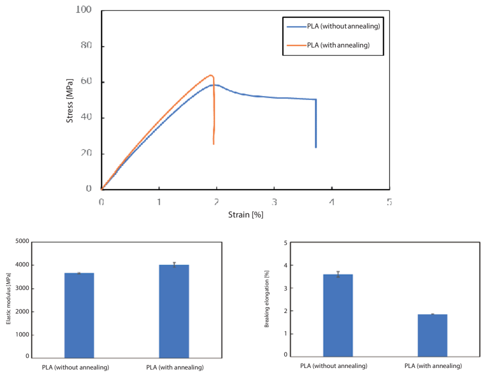
Analysis based on a universal testing machine, dynamic ultra micro hardness tester, differential scanning calorimeter (DSC), and Fourier transform infrared (FTIR) spectrophotometer can be used to evaluate changes in the properties of recycled materials due to heating circumstances when kneading or molding molten polymers.

benefits

- Using DSC, FTIR, and other instruments for a multifaceted evaluation is more effective for analyzing the causes of property changes.
- Property value changes due to heat treatment can be evaluated using a universal testing machine or hardness tester.

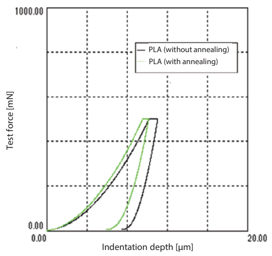
Measurement Results (Extract)

The difference in properties of polylactic acid resin (PLA) due to annealing treatment was evaluated by tensile testing and hardness testing, and the state of crystallization in the respective specimens was then evaluated by DSC and FTIR. Annealing was carried out at 100 °C for 30 minutes.



In the annealed sample, the elastic modulus increased and the elongation at break decreased.

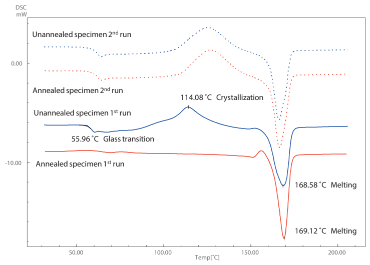
Fig. 47 Tensile Testing Data



Specimen	H_{IT} [MPa]
PLA (without annealing)	221.5
PLA (with annealing)	277.6

In the annealed sample, HIT (indentation hardness) was higher for the sample with annealing.

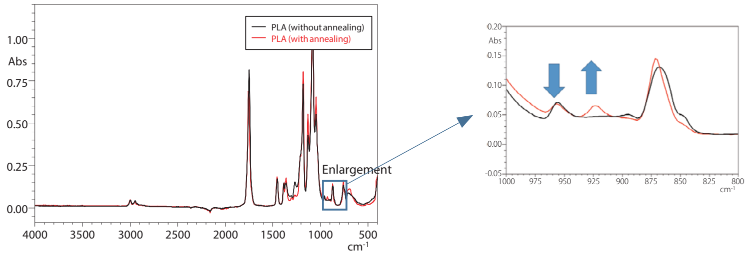
Fig. 48 Hardness Testing Data with Dynamic Ultra Micro Hardness Tester



Specimen	Tg [°C]	Crystallization [°C]	Melting [°C]
PLA (without annealing)	55.96	114.08	168.58
PLA (with annealing)	-	-	169.12

Comparing the 1st run measurement results, in the measurement of the unannealed PLA, a glass transition point of 55.96 °C and a peak of crystallization at 114.08 °C were detected. In the measurement of the annealed PLA, these features did not appear in the DSC curve, and it was found that crystallization proceeded with annealing treatment.

Fig. 49 DSC Data



Crystallization proceeded with annealing treatment, and the amorphous peak at around 955 cm^{-1} decreased. Conversely, the peak originating from C-C skeletal stretching vibration in the α crystal increased at around 921 cm^{-1}. Thus, the FTIR analysis results revealed that the amorphous property decreases and crystallization proceeds with annealing, and the crystal form changes to the crystal.

Fig. 50 FTIR Data

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