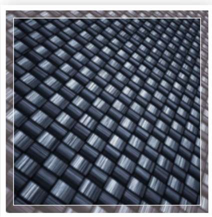
C10G-E037

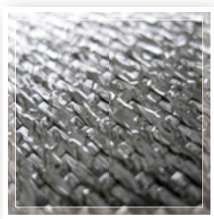
Excellence in Science

Contributing to Improved CFRP Performance and Reliability

CFRP Analysis, Testing and Inspection Evaluation Instruments







Analysis, Testing, and Inspection Evaluation Instruments That Contribute to Improved Performance and Reliability in Carbon Fiber Reinforced Plastics (CFRPs)

Testing & Inspection Instruments for CFRP Industry

Carbon fiber reinforced plastics (CFRP) have been widely adopted as a material in the latest aircraft and automotive frames. Among all composite materials, CFRPs are particularly lightweight, possess high specific strength, and are even highly corrosion-resistant. Accordingly, their use is expected to grow in a variety of fields.

Particularly in the transportation field, lightweight materials lead to lower fuel consumption, which has a direct connection to reducing environmental load. In addition, this feature can be appreciated firsthand, as CFRPs are already utilized as raw materials in sporting goods and other everyday products.

In Japan, which leads the world in the development and production of carbon fiber and plastic raw materials, research has accelerated in the search for even higher performance materials and processing methods. Shimadzu provides a range of instruments and systems for analysis, testing, and inspection evaluations (from analysis and testing pre-treatment to data analysis), thereby contributing to resolving a variety of problems at each phase, from the development of CFRP raw materials to product durability evaluations.

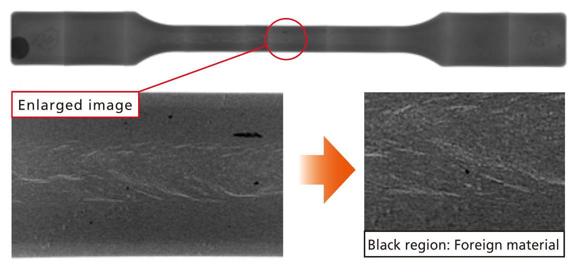
Analysis/Measurement/ Inspection Evaluation Items		Analysis/Testing/ Inspection Evaluation Instruments
Static tests	Tensile, bending, compression, peeling (adhesive strength/surface treatment evaluation), interlaminar shear	Autograph AG-X plus/AGS-X Precision Universal Tester MCT Micro Compression Tester
Fatigue tests	Fatigue life, durability	EHF Series Servopulsers
Impact tests	High-speed tensile, puncture	Hydroshot HITS-T10 High-Speed Tensile Testing Machine Hydroshot HITS-P10 High-Speed Puncture Impact Testing Machine
State observations	Cross section, surface, resin-fiber interface	SPM-9700 Scanning Probe Microscope
Internal observations	Voids, cracks, fiber orientation, fiber density	inspeXio SMX-225CT/100CT Microfocus X-Ray CT System SMX-1000/1000L Plus Microfocus X-Ray Fluoroscopy System
Fracture observations	Matrix failures, fiber failures, peeling	HyperVision HPV-2A/HPV-X High-Speed Video Camera
Thermal analysis	Glass transition, melting point, coefficient of thermal expansion, setting reaction	DSC-60 Plus Differential Scanning Calorimeter TGA-50/51 Thermogravimetric Analyzer DTG-60 TG/DTA Simultaneous Measuring Instrument TMA-60 Thermomechanical Analyzer
Composition analysis	Matrix resin, additives, elemental analysis, carbon fiber level	Combustion Ion Chromatograph Applied GC/GC-MS System, Thermal Decomposition Analysis System ICPE-9000 ICP Emission Spectrometer IRAffinity-1/IRTracer-100 Fourier Transform Infrared Spectrophotometer TGA-50/51 Thermogravimetric Analyzer DTG-60 TG/DTA Simultaneous Measuring Instrument
Viscosity measurements	Thermosetting resin reactivity evaluations, thermoplastic resin injection molding evaluations	CFT-500D Flowtester
Degradation evaluations	Weather resistance, heat resistance	IRAffinity-1/IRTracer-100 Fourier Transform Infrared Spectrophotometer TGA-50/51 Thermogravimetric Analyzer DTG-60 TG/DTA Simultaneous Measuring Instrument
Solvent analysis	Organic solvent component analysis	GC-MS/DART-MS Mass Spectrometers

Nondestructive Inspections and Measurements of Physical Properties of CFRPs

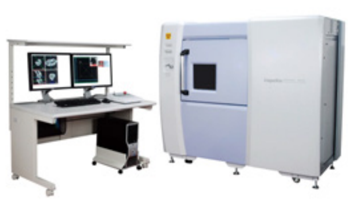
It is known that the material characteristics of carbon fiber reinforced thermoplastics (CFRTPs) are easily affected by the orientation of the fibers and voids occurring inside products. Accordingly, internal structural observations using nondestructive inspection systems are required for the development of new, more effective raw materials, and for quality management of existing products. To clarify factors related to the degradation of material characteristics, it is essential to perform evaluative tests using precision universal testing machines and extensometers capable of implementing high-speed sampling and high-precision elongation measurements. In addition, CFRTPs are known to undergo failure via a complicated process. Thus, observation of the point of origin of the failure and the propagation of cracks using a high-speed video camera is another important material analysis method.
The following introduces an example of the multifaceted evaluation of the characteristics of a CFRTP sample with internal voids, using a microfocus X-ray fluoroscopy system, X-ray CT system, precision universal tester, high-speed tensile testing machine, non-contact extensometer, and high-speed video camera.

X-Ray Fluoroscopic Observations – Confirmation of Foreign Material –

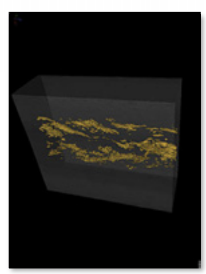
Microfocus X-Ray Fluoroscopy System
SMX-1000 Plus



X-Ray CT Observations – Void Extraction –



Microfocus X-Ray CT System
inspeXio SMX-100CT

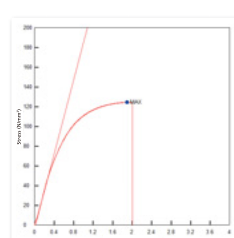


Voids are extracted using the 3D image analysis software's void extraction function.
Further color processing of extracted regions enables clear confirmation of the void regions.

Static Tensile Tests and High-Speed Tensile Tests – Strength Tests and Fracture Observations –

Autograph Precision Universal Tester
AG-X plus

Non-Contact Extensometer
TRViewX

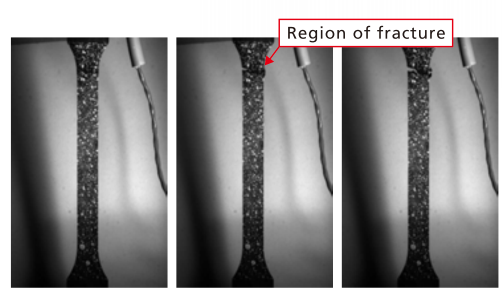


Modulus of Elasticity	Tensile Strength	Fracture Elongation
(MPa)	(MPa)	(%)
18861	124	1.890

- Static Strength Characteristic Evaluations -

High-Speed Tensile Testing Machine
HITS-T10

High-Speed Video Camera
HyperVision HPV-X



- High-Speed Fracture Observations -

Sample provided by: Gifu University

Internal Structural Observations of CFRTPs Using a High-Sensitivity X-Ray CT System

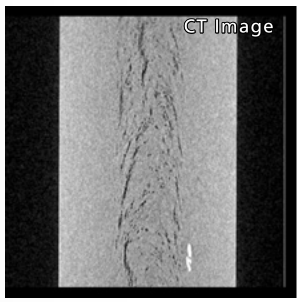
When products are manufactured using injection molding, the orientation of the internal fibers, which is related to the physical characteristics of the product, warping, and other molding defects, is affected by the flow of the resin.
Accordingly, observing the orientation of the internal fibers is very important. The conventional approach to observing fiber orientation is to section (cut) a sample, and then observe and photograph a cross section. However, this method requires labor-intensive evaluations, and it is difficult to accurately assess the three-dimensional structure.
This section introduces non-destructive observations using an X-ray CT system as a way of solving these problems. Using an X-ray CT system enables the non-destructive observation of the orientation of fibers and voids within the sample. This makes it possible to observe the internal state before performing the test and, therefore, acquire data in which the test results are firmly correlated with the internal structure.

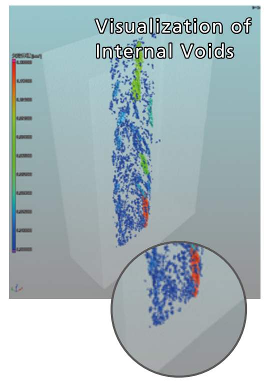
Analysis Example

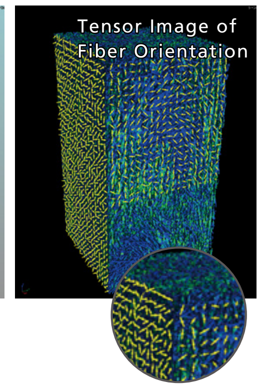
Fluoroscopic Image

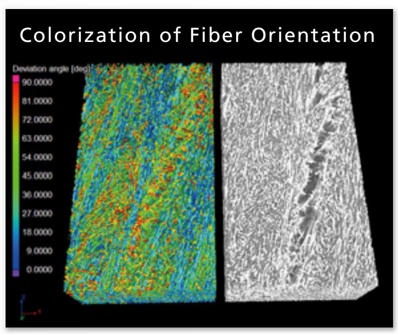
Fluoroscopic Image (Enlarged)

Sample provided by: Gifu University









- CT Image

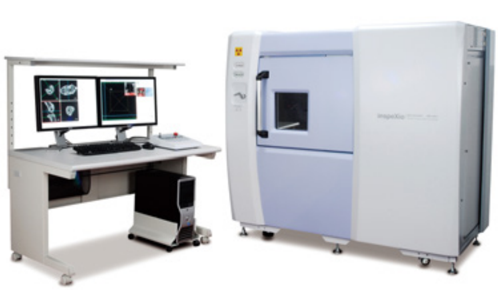
  A cross section of the interior of the sample can be visualized. The black region represents internal voids. The white region represents foreign material.
- Visualization of Internal Voids

  The colored region represents the colorized voids. 3D observations are possible.
- Tensor Image of Fiber Orientation

  The imaging area is partitioned into a matrix of hundreds of regions. The average of the fiber orientations in the respective regions is then displayed as a tensor.
- Colorization of Fiber Orientation

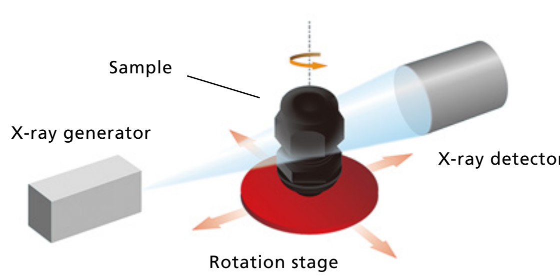
  The vertical direction in the image is taken as 0° (blue), and the angle of the fiber orientation is then displayed in color. Red represents a 90° orientation.

Instrument Used



Microfocus X-Ray CT System
inspeXio SMX-100CT

System Configuration and Basic Principles



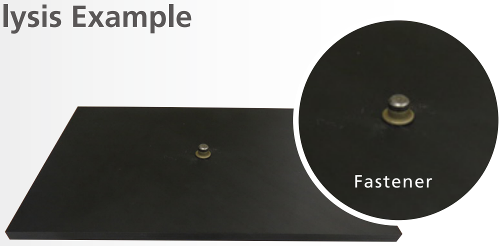
The measurement target (sample) is placed between the X-ray generator and the X-ray detector. X-ray fluoroscopic data is collected from every angle by rotating the sample 360°, and computed tomographic images (CT images) are calculated.

Observing Defects in CFRPs Around Inserted Metal Parts Using High-Output X-Ray CT Systems

Metal fasteners are often used to join CFRPs with non-CFRP components. In structures combining CFRPs with metal parts, the demand for shape observations has always been strong since the respective material characteristics are different. However, because of the large density difference between the materials, artifacts (noise) produced by the metal parts have made it quite difficult to observe in detail the shape of the CFRP in the vicinity of the metal parts.

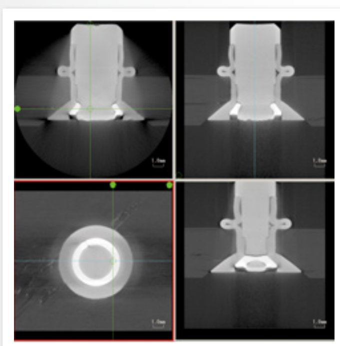
Here, as a means of solving this problem, we introduce the inspeXio SMX-225CT FPD microfocus X-ray CT system. The inspeXio SMX-225CT FPD enables the interior structure to be visualized more clearly than with conventional systems, even when the observational field consists of materials with a large density difference. Thus, more detailed observations are now possible for internal defects and delaminations in CFRPs in the vicinity of metal parts.

Analysis Example

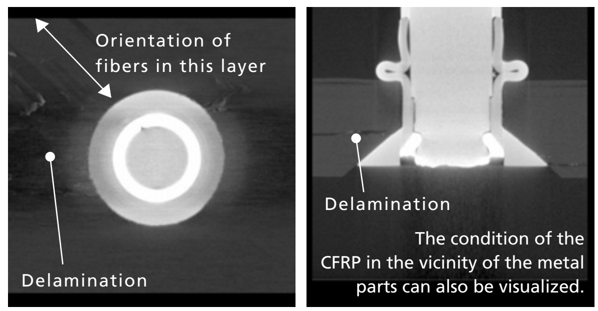


CFRP sample

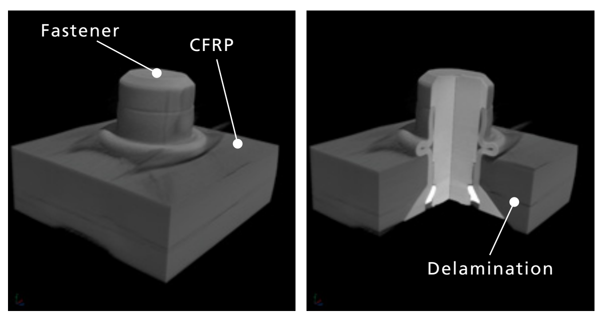
Test Sample for Evaluating Lightning Damage in a CFRP Laminate with a Fastener



Tomographic Images in the Vicinity of the Fastener



Creating tomographic images enables the observation of interlaminar peeling within the sample.



Creating 3D images based on the tomographic images enables the 3D spread of the peeling to be observed.

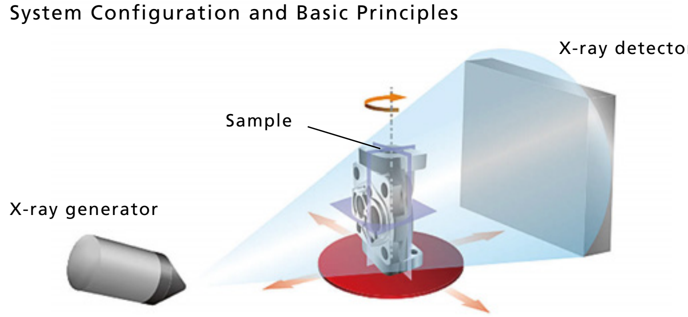
Sample provided by: Advanced Composite Research Center, Institute of Aeronautical Technology, Japan Aerospace Exploration Agency (JAXA)

Reference: Y. Hirano, et al., "Damage Behavior of CFRP Laminate with a Fastener Subjected to Simulated Lightning Current", ECCM-15, Tu.4.5.1, Venice, Italy, 24-28 June 2012

Instrument Used

FPD Microfocus X-Ray CT System
inspeXio SMX-225CT FPD

System Configuration and Basic Principles

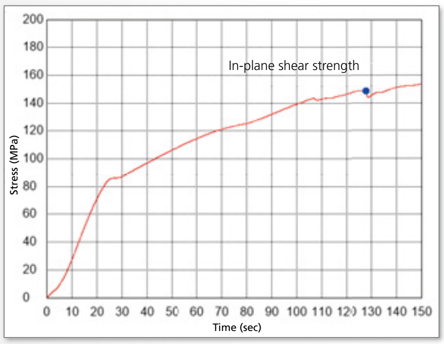


The measurement target (sample) is placed between the X-ray generator and the X-ray detector. X-ray fluoroscopic data is collected from every angle by rotating the sample 360°, and computed tomographic images (CT images) are calculated.

In-Plane Shea Testing - Double V-Notched Shear Method

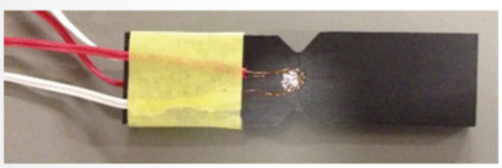
CFRP strength evaluation methods are specified by various ASTM standards. This section presents test examples conforming to the "In-Plane Shea Testing - Double V-Notched Shear Method" (ASTM D5379), as well as jigs conforming to various standards.
CFRP in-plane shear strength, in-plane shear failure strain, and in-plane shear modulus of elasticity are obtained via in-plane shear testing using a double-V-notched sample. The tests are applicable to unidirectional (UD) reinforced materials, and laminated plates (such as orthogonal laminates and quasi-isotropic laminates) consisting of unidirectional reinforced layers or fiber reinforced layers.

Testing Example



The in-plane shear strength for a V-notched sample is obtained using a jig compliant to ASTM D5379.

The stress drop in the chart is detected, and the in-plane shear strength is calculated as 148 MPa.



A shear strain measurement can also be performed by affixing a strain gage in the ±45° direction.

Instrument Used

Autograph Precision Universal Tester
AG-X plus

ASTM D5379 Compliant Jig

ASTM D6484 / D6484M

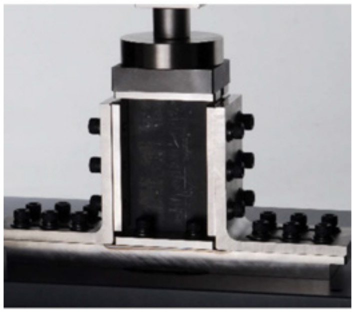
Testing Open-Hole Compressive Strength of Polymer-Matrix Composite Laminates

ASTM D6484 is a typical method for obtaining the compressive strength of porous samples of CFRPs. In this method (shear load method), the compressive strength of the porous region is determined by applying a force in the longitudinal direction of the sample on both sides. In contrast, with methods specified by JIS K7093, compressive strength is determined by applying a direct compressive force to the edge of the sample (edge loading method). It is known that comparable results are obtained using a smaller sample and smaller jig in comparison with the ASTM D6484 approach.

ASTM D7137 / D7137M

Testing Compressive Residual Strength Properties of Damaged Polymer-Matrix Composite Plates

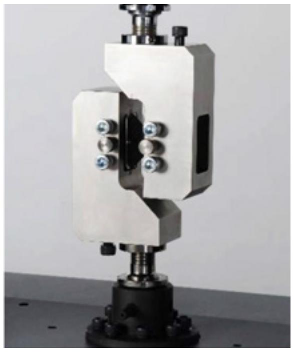
In this compression test based on ASTM D7137/D7137M, a sample damaged by an impact test is used. The impact test is covered by ASTM D7136. This jig was developed by Boeing. A rectangular sample of a composite material to which an impact force has already been applied is positioned in the jig, and applied with a compressive load. The residual strength for the sample can be determined by comparing the load at which the sample fails with the compressive strength without the impact. Assessing the resistance to damage of layered composite plates is useful both for product development and materials selection.



ASTM D7078 / D7078M

Evaluation Testing of Shear Properties of Composite Materials by the V-Notched Rail Shear Method

In this test, a sample prepared with 90-degree V notches on both the top and bottom edges is held at both ends, and subjected to shearing. With ASTM D5379, a load is applied at the top and bottom edges. With D7078, however, gripping the surface enables a higher shear load to be applied. Also, a larger sample can be tested in comparison to D5379.



ASTM D6671 / D6671M

Evaluating the Compression Characteristics of Polymer-Matrix Composite Laminated Plates Using a Combined Loading Compression (CLC) Test Jig

The combined loading compression (CLC) test method combines a shear load with an end face load. A strip-shaped sample with no tabs is used; this offers, which has the advantage of enabling a simultaneous strength evaluation and measurement of the modulus of elasticity.
The strip-shaped sample is fastened by upper and lower blocks aligned with the orientation of the short sides, and the sample end face is directly compressed.

Tensile Tests of Carbon Fibers

Carbon fibers are an indispensable component of carbon fiber reinforced plastics (CFRPs). An important industrial raw materials, they have 1/4 the specific gravity and 10 times the specific strength of general ferrous materials. When designing carbon fiber composite materials, the physical properties of the composite material are significantly affected by the physical properties of the carbon fibers themselves, the filling ratio of the carbon fibers in the resin, and the orientation of the carbon fibers.
This section introduces sample measurements of tensile strength and modulus of elasticity as a method for evaluating carbon fiber strength.

Testing Example

In this test, as shown in Fig. 1, the sample is fastened to a sample mount consisting of a paper, metal, or plastic sheet. This is attached to grips, and then subjected to a tensile test. In the applicable standards, detailed explanations are provided with respect to the shape of the mount, the type of adhesive used when positioning the carbon fibers on the mount, and the carbon fiber positioning method. (For details, refer to ISO11566:1996(JIS R7606:2000).) For this test, clip type grips were used, with a gripping strength that can be adjusted to suit the sample strength.

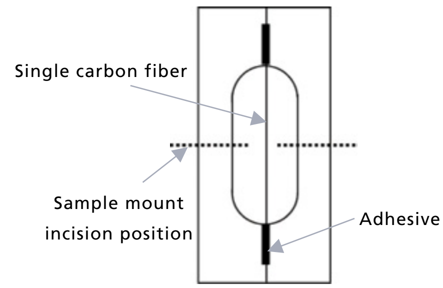
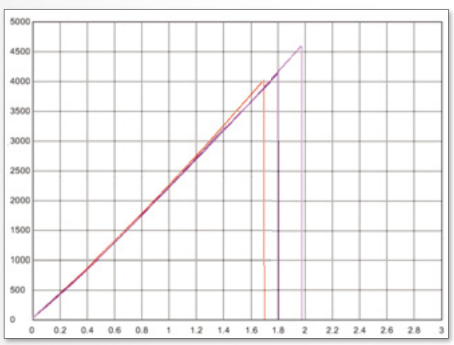
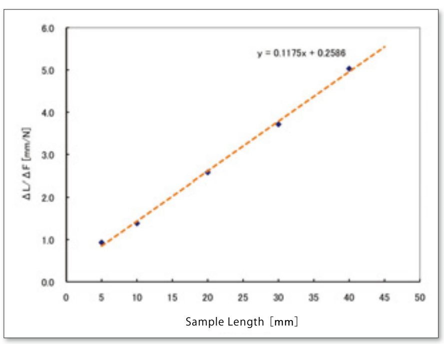


Fig. 1 Sample and Mount (Frame)

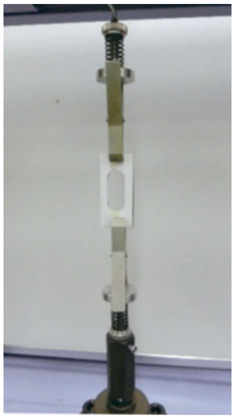


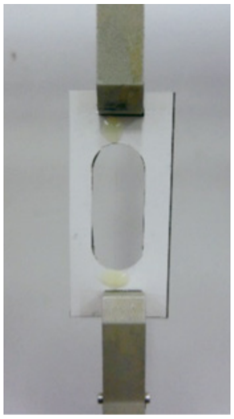


Sample Name	Diameter	Tensile Strength	Modulus of Elasticity	Elongation at Time of Fracture
Carbon fiber	6.8 µm	4250 MPa	231.6 GPa	1.82%

Instrument Used

Autograph Precision Universal Tester
AG-X plus





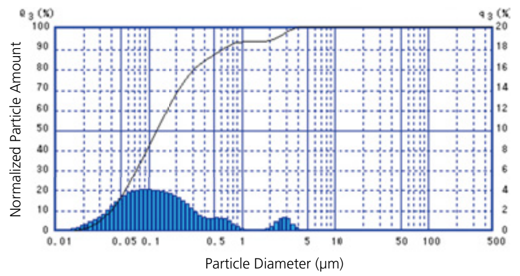
Clip Type Grips

Evaluation of CNT Solvent Dispersion Characteristics

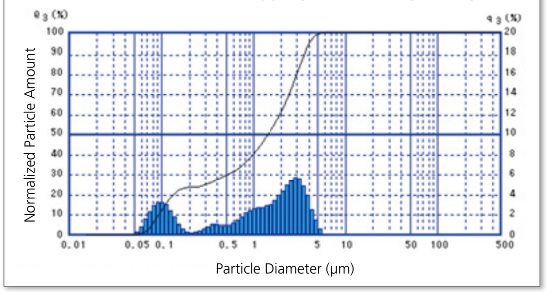
A laser diffraction particle size analyzer can determine the size and proportion of carbon nanotubes (CNT) in a sample. Furthermore, the aggregation of the CNT and the change in aggregation can be assessed using real-time measurement functions. The laser diffraction and scattering method is a means of determining a particle distribution from the distribution of the intensity of light scattered by the particles. A short-wavelength light source is required to investigate smaller particles. The SALD-7500nano used here utilizes a 405 nm laser, which has a shorter wavelength than conventional 680 nm lasers, enabling measurements as small as 7 nm.

Testing Examples

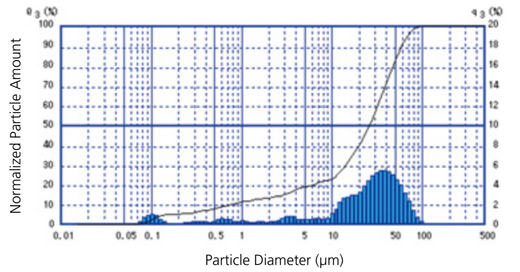
[1] Directly After the Sample Is Introduced



[2] 10 Seconds Later CNT Aggregation Is Progressing



[3] 60 Seconds Later CNT Aggregation Is Progressing Further



These measurements show the change over time in the CNT dispersed in the solvent.
It is evident that CNT aggregation progresses gradually, and the particle size increases.

Instrument Used

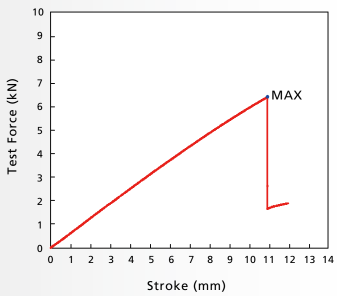
Particle Size Analyzer
SALD-7500nano

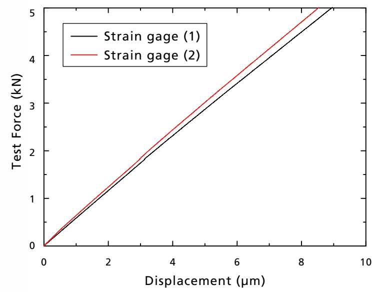
- Evaluation of the dispersion and aggregation characteristics of particles is realized with a wide measurement range and in real time, which plays the most important role in utilization of nanoparticles
- It was developed to meet the pressing need for accurate and high-sensitivity particle size measurement of low concentration or high-light absorption nanoparticles. This system achieves approx. ten times conventional sensitivity levels in the nano region, and can even measure low concentration samples at less than 1 ppm. This enables heretofore impossible measurements of low-concentration nanoparticles.

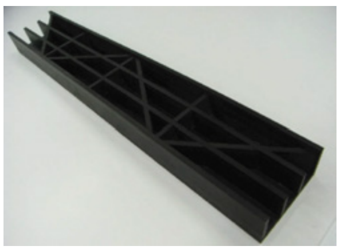
Bending Tests of Ribbed GFRP Structures

Fiber reinforced composite materials, which have a higher specific strength than conventional materials, are increasingly applied in a variety of industrial products. This is in anticipation of savings in transportation costs for general industrial products, and large-scale improvements in fuel consumption for automobiles, motorcycles, and other transportation equipment. Glass fiber reinforced plastic (GFPR), is an important raw material utilized as a main compound in screws, electronic boards and other small parts, as well as automotive spoilers and other large-scale parts.
Large parts are sometimes designed with a ribbed or honeycombed internal structure to heighten the rigidity of the part. This section introduces an example of an actual 3-point bending test of a ribbed GFRP structure.

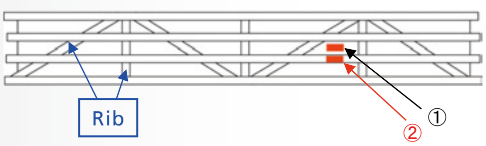
Testing Example



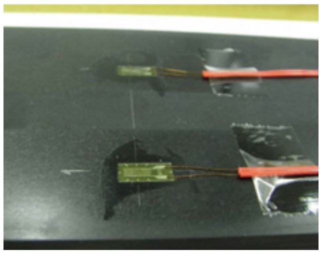




Sample



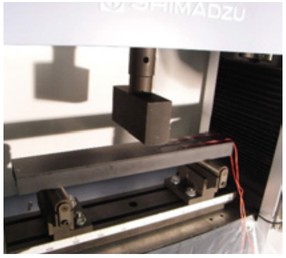
Strain gage



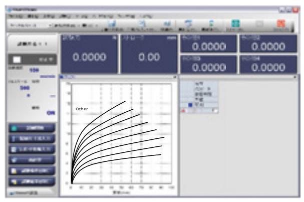
For strength designing of large structures, it is important to actually measure the local strength characteristics of the components. Strain gages were attached to a part without reinforcement with ribs ① and a part reinforced with ribs ②, and the respective amounts of deformation were compared. A tendency for higher rigidity in the part reinforced by ribs was suggested by the amount of deformation measured by the strain gages. In terms of the data from the strain gages, up to 8 channels of output can be imported to a computer in synchrony with data from the tester on test force, stroke, and elongation. The use of this function for accurate, multi-point measurements of the strain-stress characteristics of samples can serve a role in the construction of strength design models for complicated structures.

Instrument Used

Autograph Precision Universal Tester
AG-X plus



Bending Test Jig

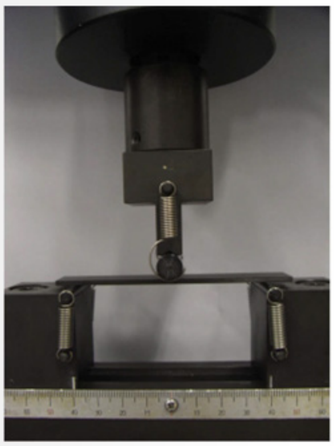


Material Testing Software
TRAPEZIUMX (8 Channel-Compatible Version)

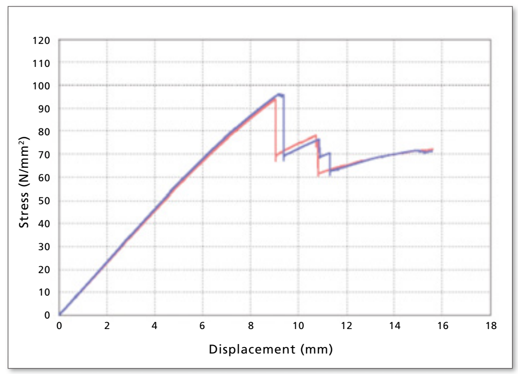
Static 3-Point Bending Tests of CFRPs

Carbon fiber reinforced plastics (CFRPs) provide excellent specific strength, even in comparison to other composite materials. Such plastics were quickly adopted in the aviation and aerospace fields, where they have contributed significantly to reducing fuselage weight. Initially, CFRPs were only used as a partial replacement of metal materials. In recent aircraft, however, composite materials primarily composed of CFRPs represent 50 % of fuselage weight. Subsequent technological developments are expected to bring improved productivity and lower costs, and CFRP usage is anticipated to extend to automobile chassis and other primary components. Here, a CFRP cloth material was subjected to 3-point bending tests using a precision universal tester, and the strength of the material was evaluated.

Testing Example



3-Point Bending Test



Stress - Displacement Curve

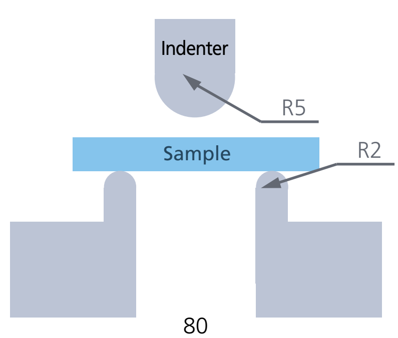
Instrument Used

In 3-point bending tests as per JIS K7074, the indenter radius is specified as 5 mm, the support radius is specified as 2 mm, and the standard dimensions of the sample are specified as follows.

Length (*l*) = 100 ± 1 mm
Width (*b*) = 15 ± 0.2 mm
Thickness (*h*) = 2 ± 0.4 mm

When tests are performed using a sample with the standard dimensions, the distance between supports (L) will be 80 ±0.2 mm. In addition, when TRAPEZIUMX software is used, the bending stress can be calculated and plotted automatically from the test force and the sample dimensions. At the same time, the bending fracture strength and other characteristic values can be obtained with a few simple operations.

Autograph Precision Universal Tester
AG-X plus

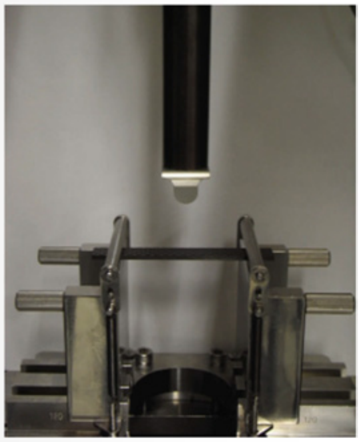


3-Point Bending Schematic Diagram

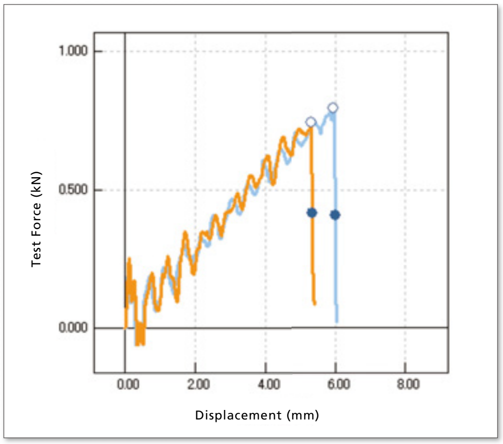
CFRP 3-Point Bending Impact Test

To date, CFRPs utilizing thermosetting resins, which are not ideal in terms of cost, productivity, or potential for recycling, have been mainstream. As a result, they have been rarely used in transport vehicles except for aircraft. However, in the last few years, technology related to CFRPs utilizing thermoplastic resins has improved remarkably, so progress is being made in alleviating the above-mentioned disadvantages. In future, it is likely that CFRPs will be used in mass-produced vehicles, there by requiring evaluations of the material.
JIS K 7084 provides standards for testing machines in which a weight free-falls. This experiment high lights the use of a high-speed puncture impact testing machine, in which the speed is reduced only slightly on contact.

Testing Example



Evaluation System for High-Speed
3-Point Bending Impact Tests



Test Force – Displacement Curve

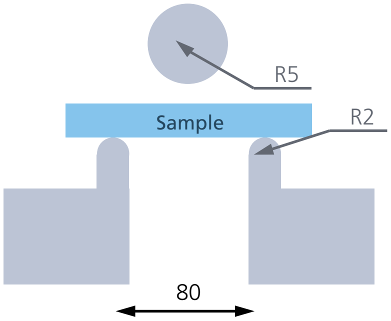
Instrument Used

In JIS K 7084, the indenter radius is specified as 5 mm, and the radius of each sample support is specified as 2 mm. The test speed is 3.8 m/s.
The standard dimensions of the sample are prescribed as follows.

Length (*l*) = 80 ± 1 mm
Width (*b*) = 10 ± 0.2 mm
Thickness (*h*) = 2 ± 0.2 mm

When tests are performed using a sample with the standard dimensions, the distance between supports (L) will be 60 ±0.2 mm. In JIS K 7084, the test force sensor precision is specified as ±5 % of the test force value, and the sampling time is specified as 10 μs max. In this system, the test force sensor precision is satisfied for tests of 100 N or more. In addition, sampling times of up to 1 μs are possible.

High-Speed Tensile Testing Machine
HITS-T10

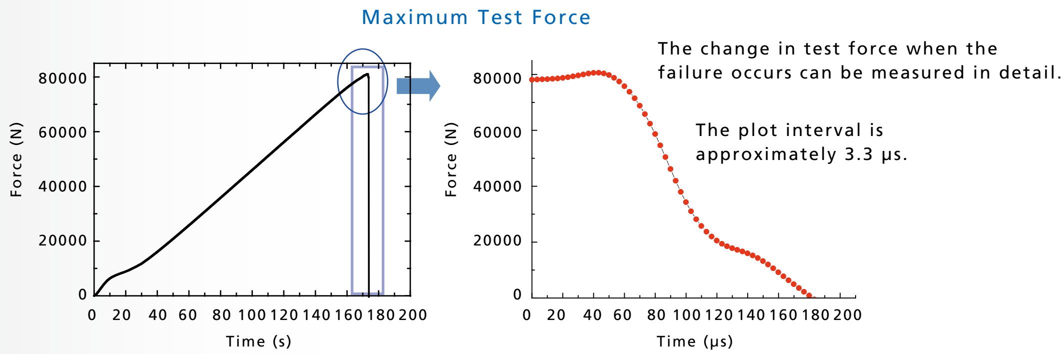


3-Point Bending Schematic Diagram

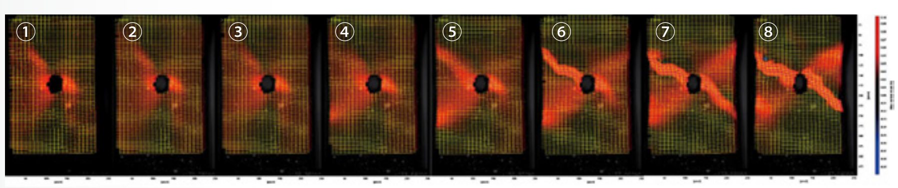
Static Failure Observations of CFRPs
- Ultra High-Speed Strain Distribution Visualization System Using DIC Analysis -

Tensile test evaluations of CFRPs require more detailed analysis of strength characteristics. In addition to obtaining S-S curves, techniques are needed for observing and visualizing the failure behavior, and in-plane strain distribution.
At Shimadzu, 300 kHz test force data storage and failure detection are performed with a loading amplifier. A trigger signal is then transmitted to a high-speed video camera (capable of recording 256 consecutive frames at up to 10 million frames/sec), enabling observation of the CFRP failure process from the perspective of high time resolution measurement. Furthermore, the use of the digital image correlation (DIC) method enables displacement measurements and 2D mapping of strain based on recorded data from the high-speed video camera.
In addition, a rigid, specially shaped lower grip has been developed to accurately carry the sudden decrease in test force to the load cell, enabling reliable observations of the behavior at the moment of failure.

Static Tensile Test (High-speed 300 kHz sampling at test speeds of 5 mm/min)

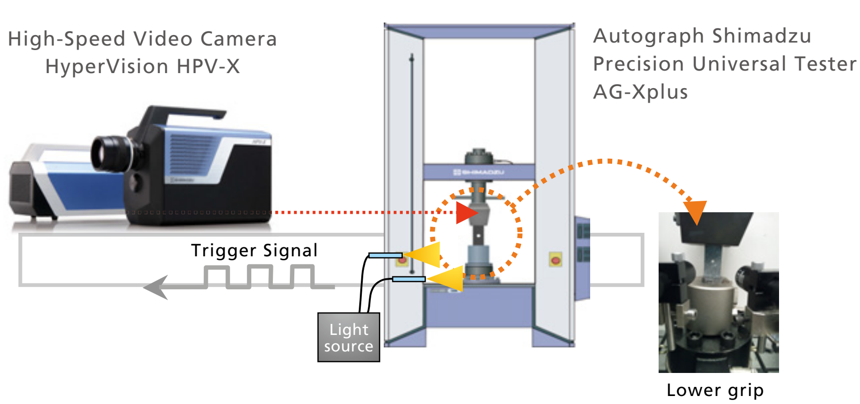


Visualization of In-Plane Strain by DIC Analysis



It is evident that the strain is concentrated not only in the 45° direction, but also in the -45° direction.

Schematic of the System



Sample Information

[Stracking sequence]
Quasi-isotropic lamination
[45/0/-45/90]2S

[Shape]
L150 mm × W36 mm × t2.9 mm;
Hole diameter 6 mm
Random marks are applied to the sample observation surface.

Reference: Murakami et al., Failure Observations and Internal Observations of CFRP, 37th Composite Materials Symposium Lecture Summary, pages 123–124.

This tensile strength testing machine, compatible with observations of the sample failure behavior, was developed through application of cooperative research with the Advanced Composite Research Center, Institute of Aeronautical Technology, Japan Aerospace Exploration Agency (JAXA)

Impact Tension Observations of CFRPs Using a High-Speed Video Camera

For the purpose of practical applications of CFRPs, evaluations and tests of composite materials are implemented from a variety of perspectives, and in a variety of situations. In particular, observing the processes that lead to CFRP failure is important in terms of improving the strength of components, and in performing quality management. The CFRP failure process consists of an extremely fast brittle fracture, so with conventional high-speed video cameras, it was not possible to observe in detail the point of origin and propagation of cracks. In this section, we introduce an example of CFRP impact failure observations using the Hydroshot HITS-T10 high-speed tensile testing machine, and the HPV-X, the latest high-speed video camera, which is capable of 256-frame video imaging at a maximum resolution of 400×250 pixels and at a maximum imaging speed of 10 million frames per second.

Samples and Instruments Used

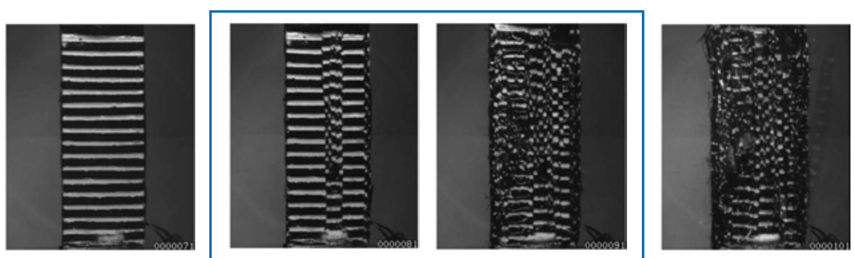
- Sample : CFRP unidirectional laminate (with glass epoxy tab attached; the sample evaluation region is marked with white lines 0.5 mm in width, at 1 mm intervals)
  T800SC prepreg unidirectional laminate, 8 mm wide × 74 mm long × 0.6 mm thick; 20 mm sample evaluation region

- Instruments Used : HPV-X high speed-video camera (imaging speed of 10 million frames per second)
  HPV-2A high-speed video camera (Imaging speed of 1 million frames per second)
  A stroboscopic light source is used.
  Hydroshot HITS-T10 High-Speed Tensile Testing Machine (grips for composite materials used; test speed: 10 m/s)

Testing Example

Data Collected by the HPV-2A

I Failure status analysis Image data at 10 μs Intervals



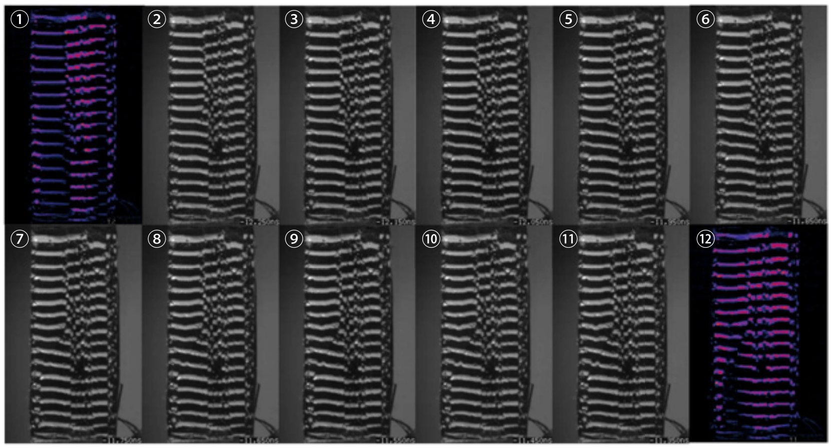
Attention!

Sudden failure progression

II Analysis of the point of origin of a crack
Sequential image data at 1 μs Intervals
(imaging speed: 1 million frames per second)

Imaging data must be acquired at even higher speeds to clarify the details of the crack propagation.

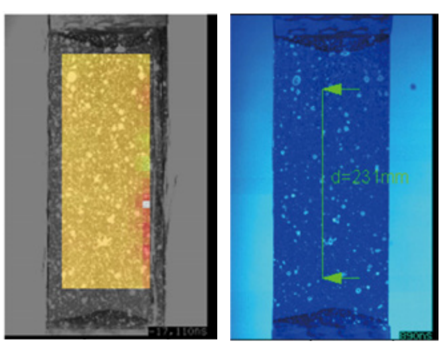
III Detailed analysis of crack propagation Sequential imaging data at 0.1 μs intervals (imaging speed: 10 million frames per second)

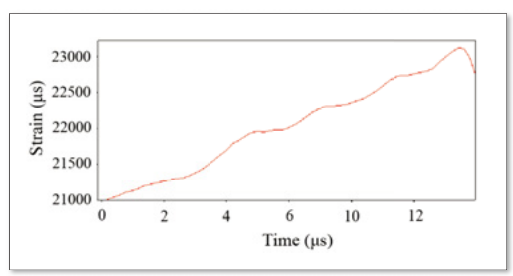


The sequence of 12 frames above shows that cracks originating in the central region develop toward cracks in the longitudinal direction originating on the left edge of the sample, and they are finally connected. The red line indicates the approximate length of the crack originating in the central region, and the blue length shows the approximate length of the crack originated at the left edge of the sample. The rapid progression of the cracks is evident in frames ⑥ to ⑩.
Images ① and ⑫ only illustrate the results of differential image analysis (Note 1).

Note 1: This is the implementation of difference calculation between images, with the first frame after imaging starts as the base image.
If there are imaging differences between the compared frames, the brightness of those areas will increase, so it is easy to identify the failure regions in the sample.

Supplement: Digital Image Correlation (DIC) Analysis (imaging speed: 10 million frames per second)

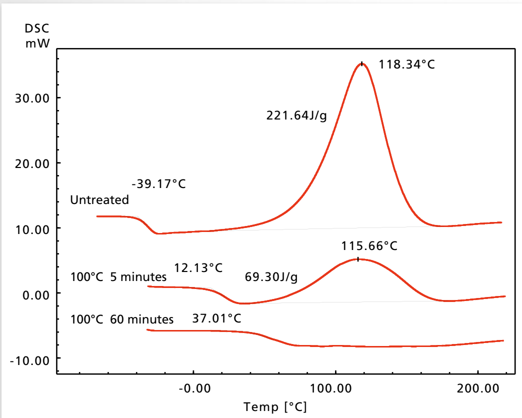




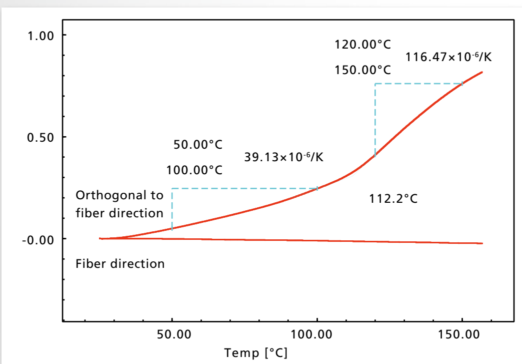
Marking the sample surface with a random pattern and then performing DIC analysis makes it possible to visualize the strain distribution occurring on the sample, and to measure the amount of change in strain between two arbitrarily selected points.

Evaluation of CFRP Thermal Characteristics

With thermal analysis instruments, a variety of physical and chemical changes, including fusion, transition, crystallization, expansion, contraction, decomposition, and combustion, are measured while the sample is heated or cooled. Typical methods include DSC, TGA, and TMA, which are effective in evaluating the thermal properties of thermoplastic resins, thermosetting resins, and composite materials.



The hardening reaction of an epoxy resin used as a matrix was evaluated using DSC. The glass transition of an untreated sample was observed at -39.1 °C, after which significant heat generation due to the hardening was measured, with a peak of 118 °C. Little heat was generated by a sample treated for 5 minutes at 100 °C, since hardening had already progressed. Furthermore, heat generation was not observed in a sample treated for 60 minutes, since hardening was essentially complete. In this way, DSC enables the investigation of the relationship between heat treatment and hardening progression. In addition, it is evident that as hardening progresses, the glass transition shifts to higher temperatures.



Changes in the size of a CFRP sample in the carbon fiber direction and orthogonal direction were measured during heating. In the orthogonal direction, thermal expansion increased in accordance with heating, but in the fiber direction, virtually no change was evident. Also, in the measurements in the orthogonal direction, a glass transition was detected in the vicinity of 110 °C. It is evident that the coefficient of thermal expansion changes before and after the glass transition. With TMA, it is possible to track changes in dimensions with respect to temperature in detail.

Differential Scanning Calorimeter
DSC-60 Plus

Differences in thermal flow to a standard substance and sample during heating (temperature differences) are measured to evaluate the temperatures at which fusion, transition, crystallization, and chemical reactions occur as well as changes in heat quantity.

- Stable baseline over a wide temperature range
- High-sensitivity, high-resolution sensor
- Equipped with a liquid nitrogen cooling tank

Thermomechanical Analyzer
TMA-60

This system is capable of measuring changes in dimensions with respect to sample temperature (thermomechanical characteristics) using a variety of measurement methods (expansion, tension, and penetration). With an automatic sample length measurement function and safety mechanisms, this system offers a high-level fusion of performance, functionality, and operability.

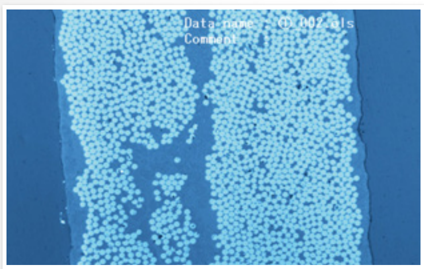
- Supports measurements of samples with a variety of shapes using various measurement methods
- High-accuracy, low-drift displacement sensor adopted
- Accurate automatic length measurements

Evaluation of CFRP Thermal Characteristics

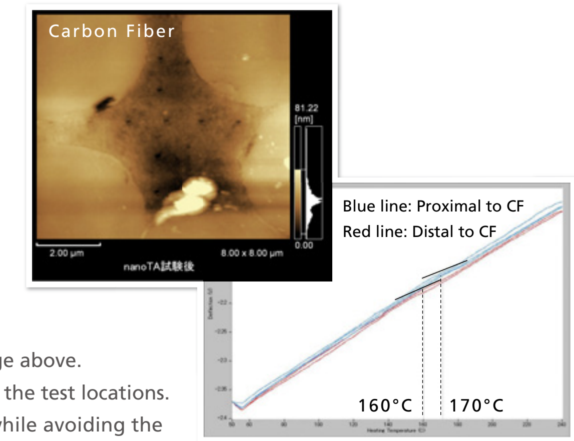
The submicron region thermal characteristics analysis system provides a new approach utilizing scanning probe microscopy.
In addition to the analysis of glass transition temperatures and fusion temperatures in the submicron region, this system can be used for the analysis of heat conduction. (This analysis system was developed combining the Shimadzu SPM-9700 scanning probe microscope and the Japan Thermal Consulting nano-TA2 nanothermal analysis system.)

Example of Microscopic CFRP Analysis

Conventional thermal analysis test methods could not be applied to obtain the thermophysical properties of only the fiber or resin components of CFRPs (optical photograph below) or other composite materials, due to issues with probe diameter and test position setting accuracy. This system makes such measurements possible. (Sample: UD laminate $[0]_2$)



CFRP Cross Sectional View (optical image)



Thermomechanical Characteristic Curve for Microscopic Part

Testing was implemented on the central resin part in the optical image above.
The marks arranged in a cross shape in the AFM image (top right) are the test locations.
In addition to showing that it is possible to test only the resin part while avoiding the carbon fiber (CF), the test results (graph at right) reveal that the glass transition temperature differs with the distance from the resin.

Conducted through collaborative research with the Advanced Composite Research Center, Institute of Aeronautical Technology, Japan Aerospace Exploration Agency (JAXA)

*This photograph shows one example of the combined system.

Submicron Region Thermal Characteristics Analysis System

System Features

- Capable of analyzing heat characteristics in the submicron region

  Use of a probe with a tip diameter of 50 nm or less allows tests in a submicron region. Tests can also be performed just in proximity to surface layers.

- Test positions can be specified using AFM images.

  Positioning using a piezoelectric element ensures high accuracy.

- Maximum heating speed of 600,000 °C /min

  Heating is dramatically faster in comparison to conventional thermal analysis test methods.

- Applicable fields

  These include glass transition temperature analyses for thermoplastic resins, and analyses of the characteristics of each part of multilayer films.

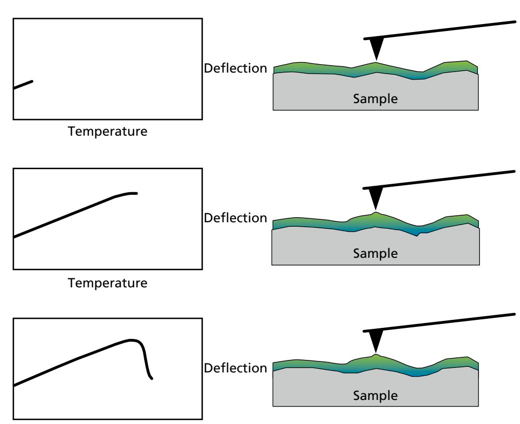


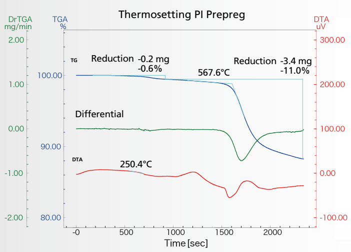
Illustration of the Basic Principles Behind the Submicron Region Thermomechanical Characteristics Test Method

When the probe tip is heated, the sample surface typically expands, and the probe begins to be deflected at the same time.
This deflection eases when the temperature reaches the point of fusion or other form of softening. By acquiring such information, it is possible to analyze thermal characteristics in a submicron region.

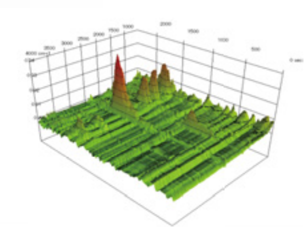
Analysis of CFRP Evolved Gas Using TG-FTIR and Py-GC/MS

Epoxy resin is generally used in CFRPs, but its resistance to heat is limited. As a result, CFRPs utilizing polyimide resin, which is highly heat resistant, are being developed. This section introduces the results from an analysis of a prepreg intermediate raw material, a sheet-shaped composite material with thermosetting polyimide as the matrix, impregnated with carbon fibers. The analysis is performed using TG-FTIR and Py-GC/MS.

TG-FTIR Data

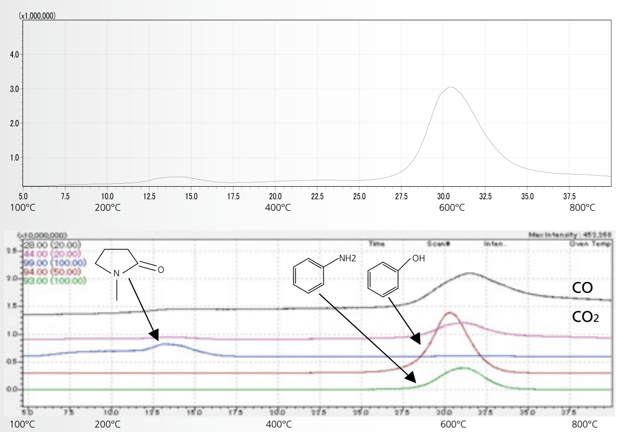


TG-DTA Curve for Thermosetting Polyimide Prepreg



Thermosetting Polyimide Prepreg 3D IR Spectral Image

Py-GC/MS Data



Thermogram for Thermosetting Polyimide Prepreg: TIC (total ion chromatogram, top figure) and MC (mass chromatogram, bottom figure)

The figure at top left is a chart of the TG-DTA measurements, and the figure at right is a 3D IR spectral image, measured in real time. From the DTA curve, a glass transition in the vicinity of 250 °C is evident. In addition, from the TG curve, a slight weight reduction at about 200 °C to 400 °C is evident. From the results of an IR spectral search, it is predicted that the gas generated is N-methylpyrrolidone (NMP). This is consistent with the fact that NMP is the solvent used to dissolve the polyimide. If there is any residual NMP, not only will voids form during molding, but the glass transition temperature will be inadvertently lowered. TG-FTIR is thus an effective means of checking for residual NMP. Furthermore, in the TG curve, decomposition accompanied by significant weight reduction starts in the vicinity of 550 °C. It is evident that primarily CO_2, CO, and phenol are generated in the vicinity of this temperature.

For more detailed analysis of the decomposition gases, measurements were performed with Py-GC/MS in EGA (evolved gas analysis) mode. The upper figure at the bottom shows the total ion chromatogram (TIC) for the gases generated with respect to temperature. Gas generation peaks in the vicinity of 270 °C and 600 °C are evident. The lower figure at the bottom is the characteristic ion mass chromatogram (MC) for the generated gas. The generation of NMP, aniline, phenol, CO, and CO_2 is shown as a time series. These are anticipated as aromatic polyimide decomposition products. The more detailed gas generation mechanism can be confirmed using Py-GC/MS.

TG-FTIR

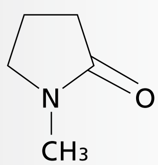
Py-GC/MS

TG-FTIR, in the figure at left, combines a simultaneous differential thermal and thermogravimetric measurement system (DTG-60) and a Fourier transform infrared spectrophotometer (FTIR). With TG-FTIR, the measurement sample is heated, and evaporation, volatilization, desorption, decomposition and other reactions involving a change of mass are measured quantitatively by the TG unit. In addition, the infrared spectra of the gases generated are measured using FTIR. In this way, it is possible to perform a qualitative analysis simultaneously, thereby obtaining information related to the molecular structure of the sample, and identifying the gases generated. With Py-GC/MS, in the figure at right, the measurement sample is heated, and measurements are taken of the mass spectrum of any volatile components (from volatilization, desorption, or decomposition) generated. Compounds can be qualified by performing a mass spectral library search. Quantitation of trace components can also be performed. In addition, the use of EGA (evolved gas analysis) enables measurements of the temperature correlation (thermogram) between the heating temperature and the generated gases.

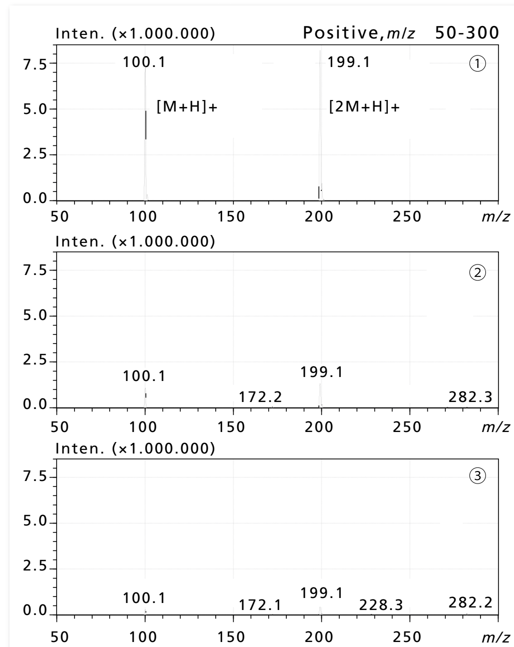
Analysis of CFRP Residual Organic Solvents Using DART-MS

Direct Analysis in Real Time (DART) is an LCMS ionization source that ionizes the surface of a sample under atmospheric pressure conditions. In combination with the LCMS-2020/8030, which feature high-speed scanning and high-speed polarity switching, qualitative analysis of target compounds can be performed very easily.
This method is used for analyzing various samples, including organic synthetic compounds, spots developed in TLC, inks on paper, pills, additives in resins, pigments, lipids, metal complexes, and surfactants.
This section presents an analysis of CFRP residual organic solvents using the DART-MS method.

① Thermosetting polyimide prepreg (untreated), ② thermosetting polyimide prepreg (dried), and ③ thermoplastic polyimide prepreg were analyzed with DART-MS.
The spectra at right are the positive mass spectra (*m/z* 50 to 300) for each sample.
An organic solvent (N-methylpyrrolidone) was used in the molding of the thermosetting polyimide used in this measurement.
Accordingly, the N-methylpyrrolidone related ions, $[M+H]^+$ (*m/z* 100) and $[2M+H]^+$ (*m/z* 199), are detected with very high intensities in spectrum ①. The intensity of the peaks in ② is relatively weak in comparison to ①, but in comparison to ③, the peaks are detected with significant intensities.



N-methylpyrrolidone
C_5H_9NO
Mw 99



Sample provided by: Advanced Composite Research Center, Institute of Aeronautical Technology, Japan Aerospace Exploration Agency (JAXA)

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