ThreeBond
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ThreeBond's Evaluation Techniques Vol. 2

Introduction

Over 15 years have passed since ThreeBond's evaluation techniques were summarized in Technical News No. 71. In the intervening years, market needs and product requirements have diversified, leading to changes in the necessary evaluation techniques. In Technical News No. 71, the authors provided a broad introduction into evaluation techniques utilizing ThreeBond's equipment. The authors of this article present Vol. 2, with information regarding adhesive strength evaluation, component analysis methods, and rheological evaluation, which is one of the most significant evaluation methods in adhesives.

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1. Rheological Evaluation

Understanding rheology (an adhesive's fluidity, drip, and spreadability) is crucial when handling adhesives. The results of rheological evaluation of adhesives is often difficult to judge without applying adhesives with actual equipment. Quantifying the tactile sense from manual application is challenging. ThreeBond tackles this issue by performing evaluation using various measurement methods. In this article, the authors provide an introduction to ThreeBond's equipment and measurement items related to rheological evaluation.

1-1 Viscosity

Viscosity is the most widely used measurement item in rheological evaluation. It can be determined from the resistance generated when a steady flow is continuously applied to an adhesive under constant conditions for a certain period of time. Adhesives with high resistance have higher viscosity, while those with low resistance have low viscosity. Consequently, viscosity is measured as a reference to ascertain the spreadability and fluidity of adhesives. On the other hand, since the results vary depending on the measurement conditions, it is necessary to understand these conditions accurately and to perform measurements under uniform conditions when evaluating adhesives. Data in ThreeBond's technical documentation always specifies the measurement conditions when presenting the viscosity measurement results.

1-2 B-type viscometers

B-type viscometers are rotational viscometers that measure the resistance of a liquid to determine its viscosity. This is achieved by immersing a rotor in the liquid and continuously rotating it in a constant direction. These devices provide a simple measuring method and results that are easy to understand. ThreeBond utilizes B-type viscometers for examining adhesives such as cyanoacrylate and epoxy resin. However, these devices cannot offer stable measurement of thixotropic adhesives or those with extremely high viscosity because the rotor is unable to follow the adhesive, resulting in gaps between the adhesive and the rotor. Additionally, because a sample of 300-500g is required for measurement, these devices cannot measure small samples and take time to adjust the sample's temperature.

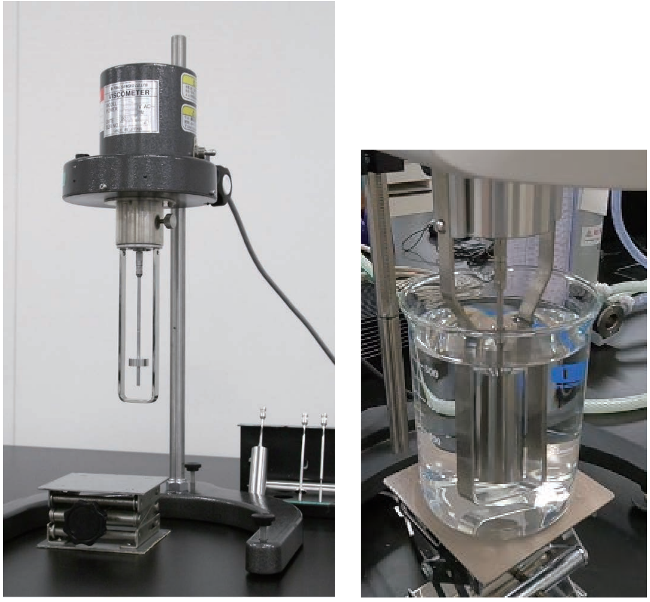

Fig. 1 B-type Viscometer (manufactured by Toki Sangyo Co., Ltd)

1-3 E-type viscometers

E-type viscometers measure viscosity by sandwiching the sample between an angled rotor and a measurement cup. They can measure thixotropic liquids, which are difficult for B-type viscometers to measure. They can also provide simple adjustment of the sample's temperature and measure small samples. Furthermore, since the shear rate applied to the resin is constant, it can accurately measure viscosity. This type of viscometer is the most widely used at ThreeBond, evaluating a wide range of resins, including epoxy resin, acrylic resin, and modified silicone.

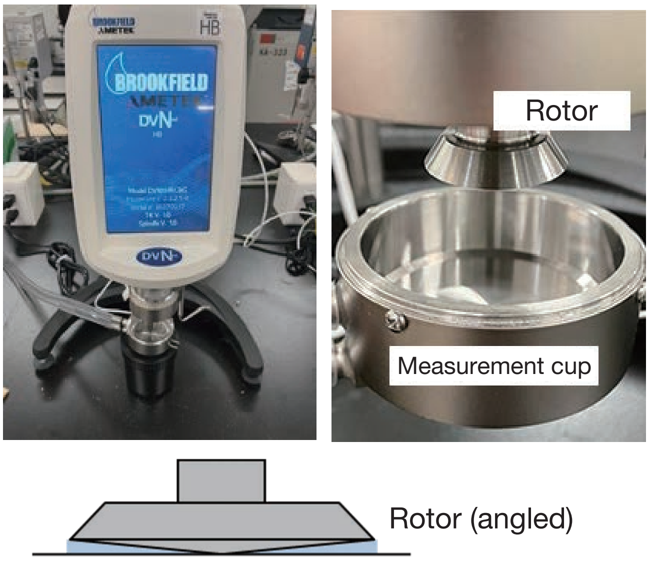

Fig. 2 E-type Viscometer (supplied by AMETEK Brookfield)

1-4 Rheometers

Although rheometers have the same basic measurement mechanism as E-type viscometers, they also offer high torque resolution and the ability to measure while continuously controlling various parameters. In steady flow measurements, flow curves and temperature-viscosity curves can be precisely controlled and measured. Furthermore, oscillation measurements (dynamic viscoelasticity measurements) can be performed, enabling analysis of both the liquid-like and solid-like properties of adhesives. Based on the measurement results, it is possible to quantitatively assess the sensation that users feel during manual application and the curing behavior of the adhesive.

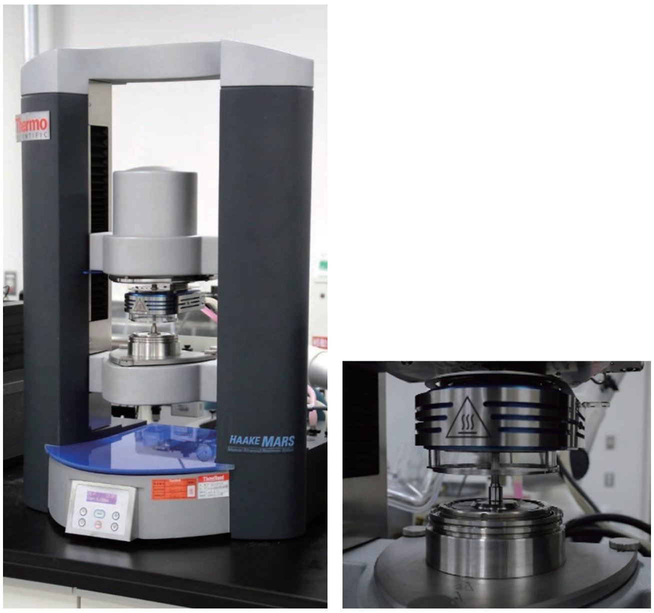

Fig. 3 HAAKE MARS60 Rheometer (manufactured by Thermo Fisher Scientific Inc.)

1-5 Flow curves

Adhesives are composed of various raw materials, including liquids and solids, which results in many of them exhibiting changes in viscosity depending on the shear rate. Consequently, measuring viscosity under a single condition is not sufficient to accurately understand the properties of an adhesive. Therefore, it is necessary to evaluate viscosity at different shear rates to obtain a continuous profile of an adhesive's viscosity.

Flow curves are curved lines that represent the shear stress and viscosity values corresponding to each shear rate. Typically, the curve is plotted with viscosity and shear stress on the vertical axes and shear rate on the horizontal axis. Fig. 4 shows the behavior of a thixotropic adhesive, where viscosity decreases as the shear rate increases.

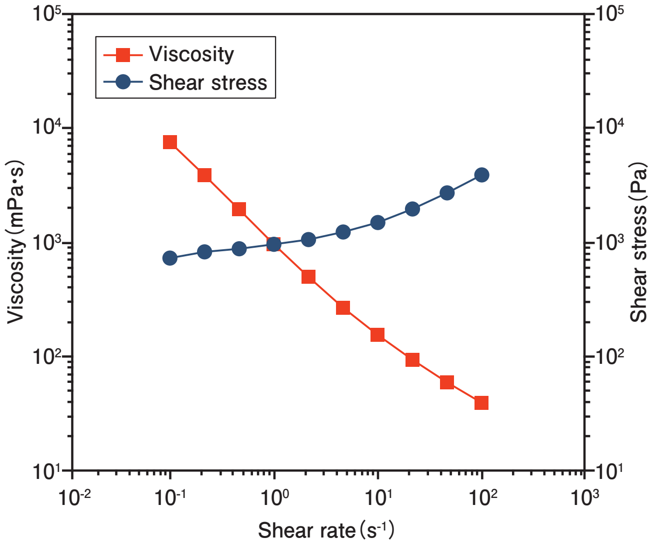

Fig. 4 Example of a Flow Curve

1-6 Temperature-viscosity curves

The viscosity of liquid adhesives changes depending on the temperature. When evaluating the properties of an adhesive during bonding or under actual usage temperatures, as with the aforementioned flow curves, it is necessary to understand how the viscosity changes with continuous temperature variations. Temperature-viscosity curves are curved lines that represent how viscosity depends on the temperature at a particular shear rate or shear stress. During measurement, the results are plotted with viscosity on the vertical axis and temperature on the horizontal axis. By combining this data with the flow curves presented earlier, it is possible to measure how viscosity depends on temperature under various conditions. This method aids in understanding the various properties of adhesives, such as their spreadability in actual usage environments. Fig. 5 shows the behavior of an adhesive thinning as the temperature increases.

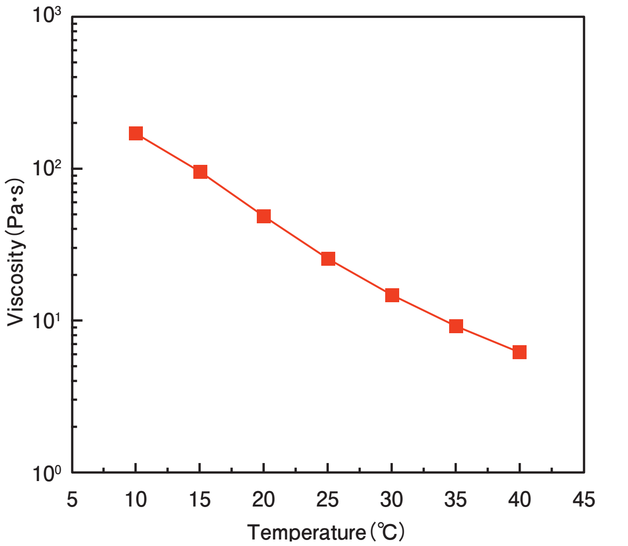

Fig. 5 Example of a Temperature-viscosity Curve

1-7 Dynamic viscoelasticity measurement

Viscoelasticity refers to properties that express both viscosity (liquid) and elasticity (solid). Materials that possess this combined property are called viscoelastic materials. In other words, viscoelasticity is the coexistence of both "flowing" and "non-flowing" characteristics. Many adhesives and sealants possess viscoelasticity. Evaluation of dynamic viscoelasticity is primarily conducted using oscillation measurements with a rheometer.

1-8 Stress-dependency measurement

This method evaluates the stress (or strain) dependency of viscoelasticity by varying shear stress or strain under a constant frequency (angular velocity). In this measurement, the inflection point of the storage modulus (G') is defined as yield stress. The region before this point, where G' is independent of shear stress or strain, is referred to as the linear region. The region beyond, where G' changes, is considered the nonlinear or failure region. As the applied stress is gradually increased, the adhesive transitions from solid-like to liquid-like behavior. By observing the material's response around the transition point, it is possible to assess the shear rate and shear stress involved when the adhesive is discharged from a nozzle. Fig. 6 shows how the storage modulus (G') decreases as shear stress or strain increases.

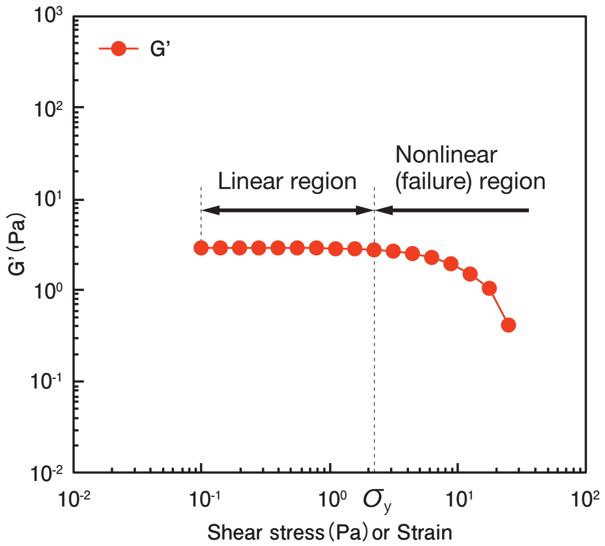

Fig. 6 Relationship Between the Storage Modulus (G') and Shear Stress/Strain

1-9 Time-dependency measurement

This method measures changes to viscoelasticity over time while maintaining constant shear stress or strain and frequency. It is mostly used to check the curing behavior of adhesives. By confirming the results of a low elastic modulus status that gradually increases, it is possible to confirm under what conditions and how much time is necessary for adhesives to cure. It is possible to equip a rheometer with either heat equipment or UV light equipment, allowing the curing behavior of various adhesives to be measured.

Fig. 7 shows the curing behavior of ThreeBond's Two-component Room-temperature-curing Resin at a temperature of 25°C after mixing the main agent with the curing agent. The measurement uses G' obtained from oscillation measurements.

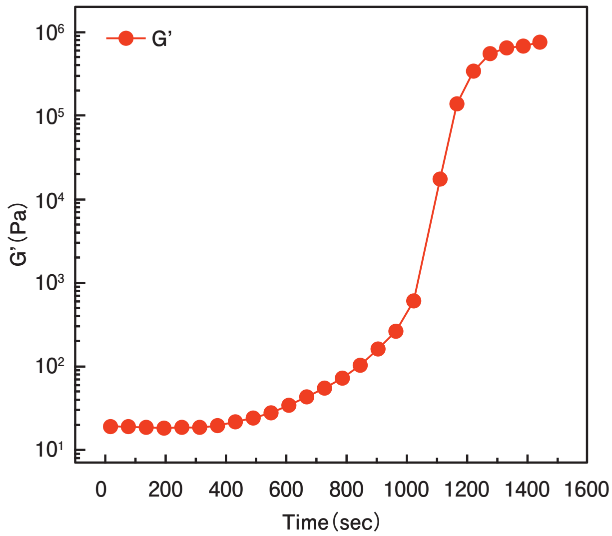

Fig. 7 Behavior of Adhesive during Curing

2. Adhesive Strength Evaluation

The measurement of adhesive strength between adherends is an extremely important item. Testing methods for adhesive strength vary widely depending on the level of stress applied. For example, if an adhesive is hard, the tensile shear adhesive strength increases but the peel strength decreases. In such cases, the results vary depending on the measurement method, making it essential to select the most appropriate method after assessing the usage environment. In this section, the authors provide an introduction to ThreeBond's equipment and items that can be measured.

2-1 Universal testers

Universal testers can apply displacement to a sample at a constant speed and measure the stress generated during this process. The shear rate can be freely set between 0.1 mm/min and 1,000 mm/min, and the temperature can be controlled within the range of -40°C to 150°C using an electric furnace. As a result, it is possible to quantify the adhesive strength of materials under actual usage environments.

Fig. 8 Universal Tester and Measurement during Heating (tester manufactured by Shimadzu Corporation)

2-2 Tensile shear bond strength

Tensile shear bond strength testing is the most commonly used testing method for evaluation of adhesive strength. It is measured using strip-like test pieces.

Test pieces made of materials such as metal or plastic are bonded together with the adhesive, and the load at the point of failure is measured by displacing the test pieces in opposite directions. By defining the bonded area, it becomes possible to determine the adhesive strength per unit area. At ThreeBond, the length and width of the adhesive area are specified to ensure stable and consistent values during measurements.

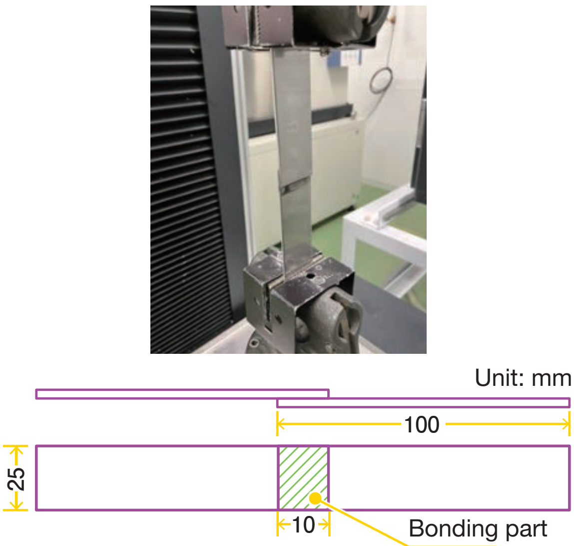

Fig. 9 Photograph taken During Measurement and Illustration of Test Pieces (Tensile Shear Bond Strength Testing)

2-3 Peel strength

Peel strength is measured by applying force to a thin T-shaped test piece or in a 90° or 180° angle to a test piece, which is bonded with cured adhesive to a film-like test piece, and reading the stress at the point of failure.

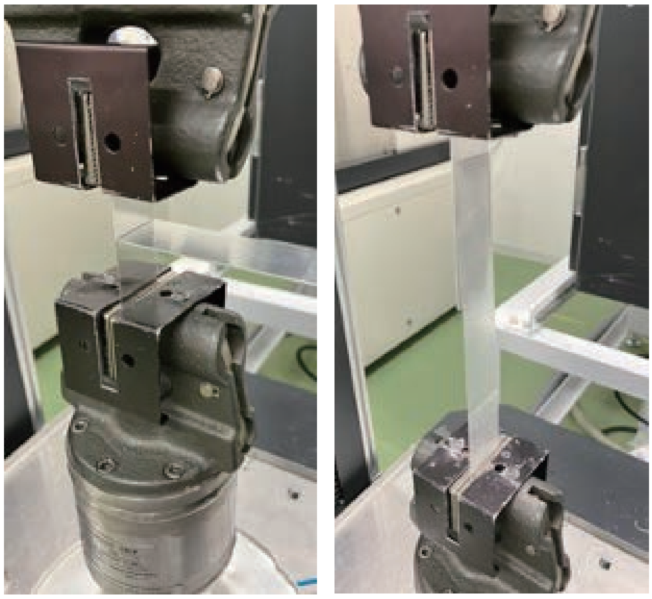

Fig. 10 Measurement Photos of T-shaped (left) and Film-like (right) Test Pieces (Peel Strength Testing)

Tensile shear bond strength tends to be higher in hard resins. However, the same trend does not necessarily apply to peel strength.

Areas subject to strong impacts or vibrations may experience forces not only in the shear direction but also in the peel direction.

In general, flexible resins tend to have higher peel strength.

2-4 Adhesive and adherend failure types

Aside from checking the adhesive strength, another method of verifying the performance of an adhesive is to examine the failure type after failure occurs.

● Cohesive failure

The adhesive remains on both sides of the adherend. This is an ideal failure type, showing that adhesive strength between the adherend and adhesive is maintained.

● Interfacial failure

The adhesive peels off the interface of the adherend. This failure type demonstrates that the strength of the adhesion to the adherend is not sufficient.

● Material failure

A phenomenon that occurs when the adhesive strength is stronger than that of the material. As with cohesive failure, this is an ideal result, demonstrating that the performance of the adhesive is sufficient.

In practice, cases of complete cohesive failure are rare, with the majority of cases involving a combination of interfacial failure and cohesive failure. Therefore, assessment is based on two factors: the cohesive ratio relative to the total area of the cohesive portion and the adhesive strength.

2-5 Tensile strength and elongation

The strength and elongation of the adhesive alone are also important evaluation items when checking physical properties. ThreeBond produces dumbbell-shaped test pieces of a predetermined size and applies a load in the tensile direction using a universal tester. By calculating the stress from the cross-sectional area and load at the time of failure, the elongation rate is then determined as the percentage ratio of the actual elongation to the original length, based on the deformation of the adhesive at the time of failure.

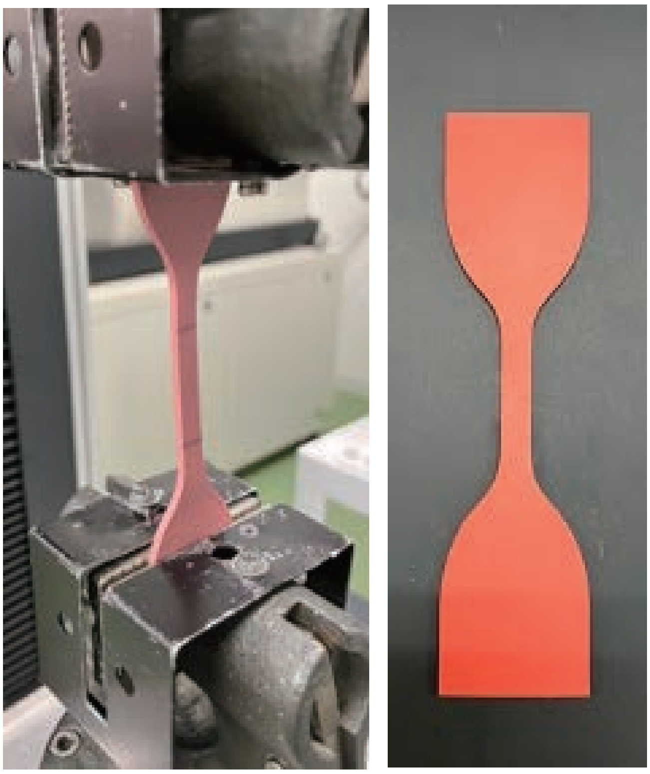

Fig. 11 Photos of the Measurement Process and the Dumbbell Test Piece

2-6 Poisson's ratio and Young's modulus

The items discussed so far pertain to actual strength. However, in recent years, strength verification is often conducted with stress calculations using simulations, making it necessary to measure the Poisson's ratio and Young's modulus of the adhesive.

● Poisson's ratio

The ratio of transversal strain to longitudinal strain (strain ratio in the orthogonal direction)

$$\mu=\varepsilon\_d/\varepsilon\_L$$

Longitudinal strain: $\varepsilon\_L=(\varDelta L)/L$

Transversal strain: $\varepsilon\_d=(\varDelta d)/d$

● Young's modulus

The stress per unit cross-sectional area that occurs when a test piece is subjected to a certain displacement

$$E=(\triangle\delta)/(\triangle\varepsilon)$$

E: Young's modulus Pa {kgf/cm2}

$\triangle\delta$: Stress per unit cross-sectional area

$\triangle\varepsilon$: Strain

The Poisson's ratio and Young's modulus can be measured accurately through minute speed control using a universal tester and monitoring displacement using a high precision camera.

3. Adhesive component analysis methods

In addition to analysis of adhesives' physical properties, the need for analysis to ensure compliance with regulatory requirements for component management has also grown in recent years. Examples of analysis subjects include outgas components under different adhesive curing conditions and the contained quantity of substances such as phthalate esters and low molecular weight siloxane, which are subject to regulatory limits.

At ThreeBond, evaluation of the equivalency of adhesive raw materials is also important. The following section introduces the most frequently used equipment from the company's range of analytical devices.

3-1 Outline of GC-MS

A GC-MS is a device that combines a gas chromatograph (GC), which heats volatile components in a mixed sample to separate them by converting them into gas, and a mass spectrometer (MS), which detects the separated samples. Next, the authors outline ThreeBond's main measurement methods: liquid injection, thermal desorption and pyrolysis, and headspace sampling.

3-2 Liquid injection

Liquid injection is a measurement method that involves diluting a sample with a solvent such as acetone or hexane to a 1% concentration. It is a common technique used in GC-MS analysis. ThreeBond has an autosampler, which allows for efficient measurement.

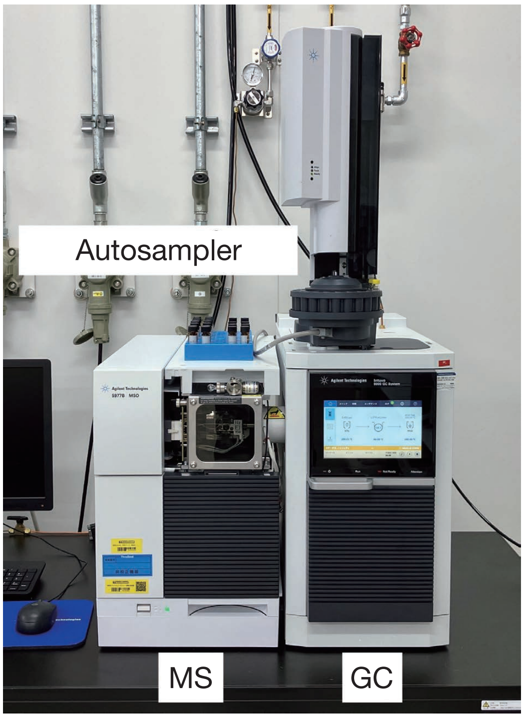

Fig. 12 GC-MS (Liquid Injection) (manufactured by Agilent Technologies, Inc.)

3-3 Thermal desorption and pyrolysis

● Thermal desorption

Under this measurement method, a volatile component is introduced directly into the MS section of the device, and heats the sample at approximately 350°C.

● Pyrolysis

Under this measurement method, a volatile component is introduced into the MS section of the device after separating it in the GC section and the sample is heated at approximately 570 to 690°C.

Thermal desorption is used for measurement when analyzing the components of general adhesives. Pyrolysis is used for measurement when analyzing components expected to have a high decomposition temperature, such as components with high heat resistance. This method is also used for measuring the content of phthalate esters, analyzing low molecular weight siloxane, and other types of analysis.

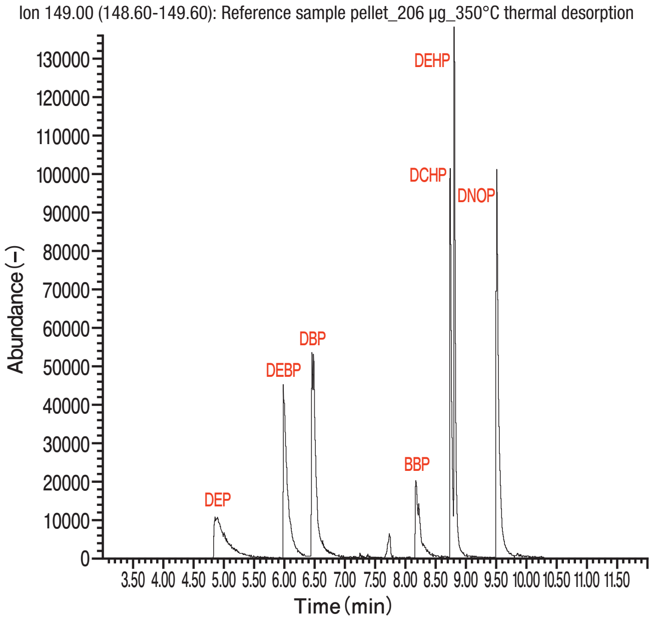

Fig. 13 Analysis of Phthalate Esters (example)

3-4 Headspace sampling

Headspace sampling is a method that allows analysis of volatile organic compounds in liquids and solids. A sample, either a liquid or a solid form, is placed in a vial (airtight container) and left to stand at a constant temperature, resulting in volatile components in the sample diffusing into the gas phase and reaching equilibrium. The gas phase within the container is referred to as the headspace. In samples with simple compositions, the composition of the gas phase reflects that of the original sample. By taking a portion of the gas phase once equilibrium is reached and introducing it into a GC for analysis, qualitative and quantitative analysis of the components present in the original sample can be performed. The temperature of heating the vial and the time varies depending on the target components. At ThreeBond, this method is used in the analysis of outgas components produced during adhesive curing, among other applications.

Closing

The evaluation and analysis techniques using equipment introduced in this article are measurement methods that have been newly introduced and developed in response to the diversification of the adhesive market and customer requirements. To continue responding flexibly to future needs, ThreeBond strives to further enhance evaluation and analysis techniques, along with those already developed, and provide useful technical information.

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