ThreeBond
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Three Bond's Evaluation Technologies

Introduction

Given the importance of accurately assessing the performance of various products, evaluation technologies play an essential role in manufacturing. Three Bond strives to establish measurement methods and to build the facilities required for various products, drawing on its own unique concepts. This issue provides a summary of our evaluation technologies.

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1. Observation

Observation constitutes the basis for all analysis. Various observations involve not just visually inspecting the subject being observed, but magnifying it. Observations with an optical microscope provide more information than simple visual observations. However, optical microscopes often suffer from shallow depth of field. In such cases, we use scanning electron microscopes (SEM). We may also need to measure minute contact surface areas; if so, we draw on surface roughness and three-dimensional profile measurement techniques.

1-1. Optical microscope observation

Subjects measuring from several cm to100 μm are generally observed using digital microscopes. Digital microscopic observations allow observations in relatively natural conditions, making it possible to reduce both brightness and reflected light and to perform integrated imaging of natural light over relatively longer integration times. Other optical microscope observation methods include the following:

- Profile magnification in 3-D mode
- Confirmation of dispersion characteristics using phase-contrast microscope

1-2. Scanning electron microscope (SEM) observation

Although scanning electron microscopes do not provide color information, they do provide three-dimensional imaging information. The test specimens used in SEM observations range from several cm to 0.1 μm in size. At Three Bond, we use a compact low-vacuum SEM unit, which permits observations of a sample as-is under a vacuum without the vapor deposition process. Observations can easily be made to magnifications ranging up to 3,000x. For cases requiring higher-resolution imaging, magnification of 50,000x can be achieved after spattering with osmium oxide. For samples measuring approximately 30 mm square, several images can be superimposed to obtain a single panoramic image. In addition, the characteristics of the electron beam can be applied to perform elemental analysis.

1-3. Surface roughness measurement

This instrument measures various parameters representing the surface roughness of processed surfaces, expressing the unevenness of the surface in accordance with Japanese Industrial Standards (JIS).

1-4. Dimension measurement (non-contact three-dimensional measurement device)

This instrument measures surface morphology at vertical resolutions of 0.01 μm. This device is normally used to measure specific points, but can also be used to map and draw the contours of the measured surface.

2. Physical Measurement

2-1. Strength measurement using the universal testing machine

The universal testing machine measures the stress generated in a test specimen by applying displacement at constant rates. The jigs can be switched to change the direction of the stress placed on the sample to measure tensile, compressional, bending, and peeling stress. The machine can also be used to measure resin adhesive force, resin strength, elongation percentage, Young's modulus, and other parameters. If the measured values are to be used as standards, care is required to select the appropriate specimen shape (dimensions).

2-2. Torque measurement

A torque wrench is used to manually measure the tightening, breaking, and residual torque of bolt sealants such as anaerobic sealants and sealants for MEC (precoated) bolts.

2-3. Pressure resistance tests

This test measures the pressure resistance of liquid gaskets and pipe sealants. The procedure involves assembling the jigs and applying pressure, then visually inspecting for leaks while monitoring the pressure gauge. Pressure-proof flanges for testing are used to evaluate the pressure resistance of liquid gaskets. Pipe sealant pressure resistance is evaluated using assembled pipe components.

3. Characteristics

3-1. Workability investigation

3-1-1. Flow property analysis with rheometer

One parameter assessed to evaluate the flow properties of liquid samples is viscosity. Since most adhesives and sealants are non-Newtonian fluids, we must evaluate the flow behavior of samples based on flow curves obtained by changing the shear velocity (or shear stress) applied to the sample. Stress controlled rheometers can control stress through torque control and can be used to evaluate highly viscous samples—for example, in paste form. Additionally, we can evaluate sagging and leveling

behavior for specific intended applications based on viscoelastic properties.

3-1-2. Sedimentation velocity analysis

We can evaluate the stability of particles contained in a liquid sample by observing light transmitted through or scattered by a liquid sample placed in a transparent vessel in the near-infrared range. When particles settle, the intensity of transmitted light in the upper part of the vessel increases, while light scattering increases in the lower portion. The effects of inter-particle interactions (e.g., coagulation) can be evaluated based on the charts obtained.

3-2. Curing behavior

3-2-1. Analysis of the curing process for sealants and adhesives

Identifying the curing state for sealants and adhesives is a common requirement. However, results can differ, depending on whether the curing process is observed as a chemical reaction or a mechanical process. Three Bond approaches the problem from both perspectives, drawing on both chemical and physical measurement techniques. Recent years have seen advances in techniques for making continuous measurements of the reaction process. However, the curing process is extremely difficult to define precisely. For this reason, evaluations are currently based on assessments of the state of the sealant/adhesive at various points in the curing process.

- Measurement of time course of reaction using real-time FT-IR (fourier transform infrared spectrometer)
- Observation of exothermic reaction using DSC (differential scanning calorimeter)
- Observation of change in viscosity with rheometer

3-2-2. Curing rate measurement

This method for evaluating the status of curing materials includes observations of the heat value of the unreacted material and of the rate of change of functional groups based on infrared absorption spectrum measurement.

- DSC
- Photo-DSC
- FT-IR

3-2-3. Reaction rate analysis

Activation energy is analyzed using DSC. Kinetic analysis is performed with software based on an equation of state; theoretical reaction rates can be visualized in graphs. (Figure 1)

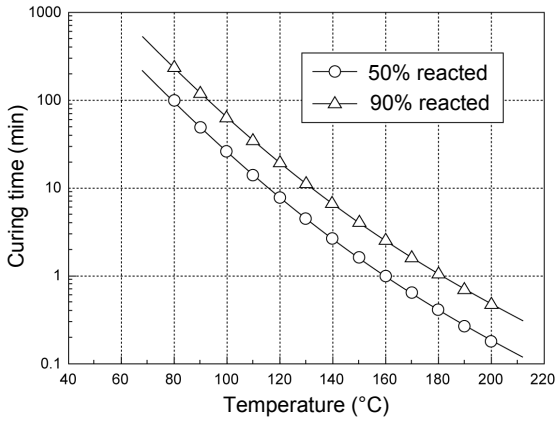

Figure 1. Curing rate of liquid epoxy resins

3-3. Modulus measurement

Modulus measurement is one method for expressing the viscoelastic properties of solid high-polymer materials. Modulus is either static or dynamic. Static modulus is measured using the universal testing machine, while dynamic modulus is measured using the dynamic mechanical analysis (DMA) unit. The measured parameters are generally temperature and change in the modulus of elasticity. The changes in adhesive strength and electrical characteristics with temperature are known to correlate with temperature dispersion of viscoelastic properties. By determining the thermal dispersion of modulus of elasticity, we can estimate the applicable temperature range of the sealant/adhesive in question.

Modulus measurements entail applying stress to a test specimen to create displacement and observing the amount of displacement and the phase lag. Thus, the shape (dimensions) of the test specimen is an important element.

Additionally, a change in elasticity (recovery) can be evaluated by creep & recovery observations to determine changes in the curing material over time.

3-4. Physical property study

3-4-1. Thermal analysis

3-4-1-1. Dynamic mechanical analysis (dynamic thermomechanical measurement)

In dynamic mechanical analysis (DMA), temperature is changed continuously while applying stress to the test specimen. The generated displacement and phase lag are measured to evaluate mechanical characteristics. This approach is used primarily to study changes in modulus of elasticity with temperature. As stated previously, the

temperature dispersion of hot strength correlates with the temperature dispersion of the modulus of elasticity measured by DMA.

3-4-1-2. Differential scanning calorimeter (DSC)

The DSC controls and changes the temperature inside the sample chamber to measure differences in heat flux between the test specimen and reference specimen as a function of temperature, permitting measurements of the heat of reaction, specific heat, reaction initiation temperature, and various transition points (e.g., melting point) of the resin.

3-4-1-3. Thermal gravimetric analyzer (TGA)

The TGA measures changes in the weight of the sample with changing temperature and over time. The TGA can be used to identify the decomposition temperature, melting point, and boiling point of liquids and solids, as well as changes in weight upon heating (e.g., loss on heat, total outgassing).

3-4-1-4. Thermal mechanical analyzer (TMA)

The TMA lets us measure the coefficient of linear expansion of a test specimen. It is important to know the difference in the coefficients of linear expansion of the adhesive and the adherend, since such differences, where present, can generate strain, resulting in undesirable effects, such as the destruction or exfoliation of the adherend or adhesive.

3-4-2. Measurement of the glass transition temperature (Tg) by various measuring instruments

While high-polymer materials such as sealants and adhesives may seem solid, their molecular structure is in motion at the atomic level. While most parts are stationary and hard as glass at low temperatures, they begin to move above a certain temperature, displaying rubber elasticity. This temperature is known as the glass transition temperature (Tg). In addition to hardness, changes in the kinetic state of the molecular structure also cause changes in the coefficient of thermal expansion, specific heat, electrical characteristics, adhesive strength, resin strength, and chemical resistance.

If we define the criteria for thermal resistance of a test specimen as the retention of physical properties at the same level as specimens measured at room temperature, we can estimate thermal resistance simply by measuring Tg. No other evaluation method would be needed. However, since high-polymer materials have a range of molecular weight distributions, Tg will be a range of temperatures, not a specific point. For high-polymer materials, it would be more appropriate to refer to Tg as the glass transition range, not the glass transition temperature.

Several techniques exist for measuring Tg. Three Bond measures Tg via DSC, TMA, or DMA (DMS). Note that differences in measuring instrument, technique, and curing conditions, even for the same adhesive/sealant, will result in differences in measured Tg. This means comparisons using Tg values provided in catalogs and technical references are meaningless without specific information on the techniques/conditions under which the values were obtained.

(1) DSC: With DSC, Tg is determined by measuring the change in specific heat associated with the phase transition in the molecular structure occurring near the temperature. In general, the temperature at which the phase change begins is regarded as Tg. Thermodynamically, Tg measured by DSC is considered most reliable.

(2) TMA: The Tg measured by TMA corresponds to the point of discontinuity (point of inflection) in the curve of the coefficient of linear expansion. The intersection of the extrapolated lines below and above the point of inflection is defined as Tg. In curing materials for which reaction remains incomplete, initial measurements will indicate shrinkage on curing. Reactions must be given time to complete before measurement is performed to determine Tg.

(3) DMA (DMS): E” (loss elastic modulus) represents the component of the applied stress absorbed by the sample and lost. Since the freedom of molecular motion is large in the Tg range, E” will also be large. The Tg (glass transition temperature) measured by DMA corresponds to the peak of E”. Since the peak value of tan δ is larger than that of E”, the former is sometimes used as Tg. However, strictly speaking, this has been judged academically inappropriate, and is now used less often. However, the peak tan δ values tends to give values that coincide with those found in actual applications and are sometimes used as apparent glass transition temperatures. Since Tg measurements can be made by DMA by observing changes in the state of the curing material, the curing reaction need not be complete. This method is often used to measure Tg under a range of curing conditions.

3-4-3. Thermal conductivity measurements

Two types of thermal conductivity measurements are used: the hot wire method and the steady-state method. In general, test specimens with a thickness of 2 cm or more are used for measurements. The hot-wire method is used for thin films. Other techniques include those entailing visualization schemes.

- Measurement either by the hot-wire or steady-state method
- Observations of heat transfer by thermography

3-4-4. Wettability

Measuring the contact angle of a liquid on a solid surface using the contact angle meter lets us measure the wettability between a resin and a particular adherend, an important factor in adhesion. Measuring the contact angle of a liquid whose interfacial tension component for a given solid surface is known also makes it possible to determine the surface free energy of the solid surface (surface tension of the solid).

3-4-5. Electrical insulation property measurements

3-4-5-1. Volume and surface resistivities

Volume resistivity and surface resistivity refer, respectively, to electrical resistance per unit volume and per unit surface area. High-resistivity measuring units are used to measure these values. However, accurate measurement of volume and surface resistivities requires resin and electrode to be in contact. The measurement methods provided in ASTM and JIS recommend forming the resin into thin plates and pressing these plates onto the electrode. However, this does not guarantee contact with the electrode, which can impair measurement accuracy. Additionally, mercury, the material recommended for the electrode to avoid the above problem, is increasingly falling out of favor due to environmental considerations. For these reasons, Three Bond has developed an electrode pattern using a copper-lined glass epoxy plate. The test specimen is sandwiched between this plate and a copper plate, with any air bubbles carefully removed, and cured for measurements. Test specimens prepared in this way are characterized by solid contact between the resin and electrode.

3-4-5-2. Dielectric properties

Materials displaying small values in both the dielectric constant and dielectric dissipation factor are regarded to have good electrical insulation properties. As with electrical resistivity measurements, test specimens for measurement are prepared by sandwiching the resin between a substrate having an electrode pattern and a substrate that acts as a common electrode, then curing the assembly. This eliminates error factors such as air layers from the test specimen. While the applicable frequency range of the measuring device is 20 Hz to 1 MHz, the range for the test specimen assembly used at Three Bond is 100 Hz to 1 MHz. In general, the term *dielectric constant* corresponds to *relative dielectric constant*.

* Dielectric constant (ε): Degree of polarization generated within a test specimen in an alternating field
* Relative dielectric constant ($\varepsilon\gamma$): Ratio of the material's dielectric constant to that of a vacuum
* Dielectric dissipation factor: Degree of electric power loss; losses via the electrical insulation material can generate heat or oscillations.

3-4-5-3. Insulation degradation test

Resin is coated onto a comb-teeth electrode and cured, after which resin degradation is evaluated by applying a direct voltage under specific conditions. Using materials that experience migration such as silver for the comb-teeth electrode allows migration performance testing.

3-4-5-4. Dielectric pressure resistance test

When an electrically insulating material is sandwiched between electrodes and subjected to a voltage, a minute leakage current is produced at low voltages. When a certain voltage is exceeded, the current rapidly increases, resulting in electric discharge, and the insulating property between the electrodes is lost. This phenomenon is known as dielectric breakdown. Although conventionally expressed in units of (kV/mm), where measured voltage is divided by sample thickness (mm), the dielectric breakdown voltage in practice is not proportional to sample thickness, corresponding instead to the power approximation of sample thickness. Three Bond has created test substrates with different gap widths to make it possible to obtain results for four or more points, which can then be plotted on a graph for approximations to determine dielectric breakdown voltage.

4. Qualitative and Quantitative Analysis

4-1. Compositional qualification

Compositional qualification refers to the rough classification of the primary ingredient of the test specimen—for example, whether it belongs to an epoxy or a silicone system. The sample can be

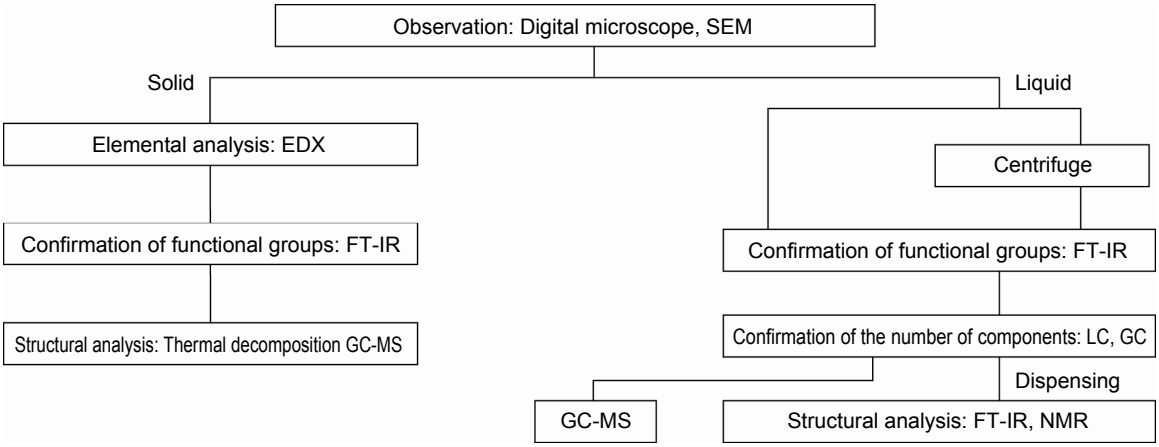

Figure 2. Analysis method for major components of unknown materials

analyzed as-is or chemically separated to the specified extent before analysis. (Figure 2)

4-2. Analysis of the generated gas

The gas generated when using adhesives may pose problems in certain cases. To investigate this problem, Three Bond used a total outgas volume measurement system and the GC-MS (gas chromatography mass spectrometry) system for compositional analysis.

- Total outgas volume measurement with TGA
- Compositional analysis using GC-MS

4-3. Pretreatment for quantitative compositional analysis of specific components

4-3-1. Measurement of impurity ion concentrations

Impurity ions refer to the free ions present on the surface of or within the solid adhesive/sealant. Impurity ions contained within the resin trigger corrosion in the presence of water. In general, fewer impurity ions are believed to enhance adhesive/sealant performance. The method for evaluating impurity ions depends on which ions are to be captured. For example, rinsing with pure water will capture ions adhering to the surface of the solid adhesive, while extraction at high temperatures and pressures will permit the capture of ions present at relatively deeper portions of the adhesive. The extraction method affects measured ion concentrations.

To perform a quantitative analysis of ion concentrations, we can measure the electrical conductivity of the extraction solution obtained to evaluate total ion concentrations, or separately quantify ion species via ion chromatography (IC) analysis.

4-3-2. Quantification of low molecular weight siloxane

Low molecular weight siloxane is relatively volatile and a known causative factor leading to contact faults. Low molecular weight siloxane can be extracted using solvents such as n-hexane or acetone and quantitatively measured by GC (gas chromatography).

4-3-3. Water vapor permeability measurement

Water vapor permeability can be measured by measuring the water vapor permeability directly or the water vapor transmission rate. The former is a value characteristic of the resin itself, while the latter represents the performance of the sample formed into a film. At Three Bond, water vapor permeability is measured using a differential-pressure gas permeability meter, while the water vapor transmission rate is measured by the cup method. Since results with the cup method depend on film thickness, the water vapor transmission rate is generally used for products having specific dimensions, such as plastic wrapping materials for food.

4-3-4. Molecular weight distribution measurement

The molecular weight distribution of high polymers that dissolve in a solvent is often measured. SEC (size-exclusion chromatography, GPC), a liquid chromatography technique, is used to measure molecular weight distributions. This separation technique separates substances solely by molecule size, unlike normal HPLC (high-performance liquid chromatography), which relies on interactions such as adsorption. In the

actual analysis of adhesives and sealants, the separation columns used are selected based on the target molecular weight, while THF, an effective solvent when used with materials found in adhesives and sealants, is often used as the solvent. The measurement results are converted values based on the standard polystyrene sample.

4-3-5. Elemental analysis

This technique quantifies the composition ratio of various elements. The samples are first decomposed by thermolysis in high-purity acids, and the solution is used as samples for ICP-MS (inductively coupled plasma mass spectrometry) analysis or for atomic absorption spectrometry analysis for qualitative and quantitative analysis of the elements contained in the sample. Both analysis methods are capable of measuring concentrations on the order of ppm to ppb.

- Other methods
  - EDS (energy dispersive X-ray spectrometer)
    Concentration analyzed on percent orders
  - ESCA (electron spectroscopy for chemical analysis)
    Concentrations analyzed as percent values
  - XRF (X-ray fluorescence analysis)
    Concentration analyzed on the order of ppm for certain elements

4-3-6. Trace water content measurement

The Karl Fischer titration method is one method for measuring the trace water content of a sample. With the Karl Fischer method, selective reactions between iodine and water are used to measure the absolute volume of water in a given sample. The instrument is equipped with a water vaporization unit that makes it possible to handle solid samples and samples that do not readily dissolve in the Karl Fischer reagent. Trace water concentrations can be measured as percent values or on the order of ppm.

4-3-7. Measurement of solid content and ash content

(1) Thermal decomposition by TGA

TGA is used to heat samples to 550°C in nitrogen (900°C for silicone). The organic components are thermally decomposed to measure the ratio of organic to inorganic components in the resin.

(2) Solid content measuring device

Heated-air dried weight measurement lets us measure moisture content, solid content, and volatile content of resins.

4-3-8. Trace component analysis

Trace components in the analyzed sample are isolated based on differences in polarity and other characteristics in HPLC and GC analysis, then qualitatively and quantitatively measured by comparing retention times and detected amounts against a reference standard. Samples that do not decompose and gasify upon heating are measured by GC. Samples displaying unstable behavior when heated, samples that do not gasify, or samples separated by components into different fractions for measurement by other instruments are measured by HPLC.

4-3-9. Total halogen analysis

The total halogen content (F, Cl, Br, I) of the sample can be measured quantitatively by the flask-combustion method. Note that the results based on this method are susceptible to errors involving technician skill or contamination from the laboratory environment. At Three Bond, to prevent errors attributable to laboratory and analytical environments, we perform high-sensitivity halogen quantification with an instrument that integrates a pretreatment unit for combustion and absorption and an analyzer unit (the ion chromatography instrument).

Conclusion

Analysis and evaluation technologies for R&D at Three Bond are based on the client's perspective. This is why we have more facilities dedicated to investigating the characteristics and physical properties of our products than structural analysis. In developing our measurement techniques, we go beyond the information required by JIS to obtain a range of other critical information.

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