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Curing Degree Evaluation of Reactive Adhesives Using Measurement Devices

Introduction

Reactive adhesives demonstrate their function upon transition from liquid to solid during the curing reaction.

Generally, adhesive strength measurement is used to judge curing of reactive adhesives. However, as applications expand beyond adhesion, the cured state and precise degree of curing required make it impossible to accurately judge curing on adhesive strength alone. Instead, we look at phenomena occurring during the adhesive curing process, investigating an evaluation method that uses measurement devices.

This article describes how curing degree evaluation of reactive adhesives using measurement devices is performed at ThreeBond.

We believe that understanding the state of the curing process and precise degree of curing for customers using adhesives in manufacturing processes will provide effective evaluation for effective information when setting up curing conditions.

Hereafter, reactive adhesive is shortened to adhesive.

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1. Background

1-1 Necessity of Checking the Degree of Curing

Various phenomena occur in the adhesive during the curing process, and these can be roughly divided into four categories.

- Changes in adhesive strength
- Changes in viscoelasticity
- Changes in functional group
- Changes in heating value

Generally, these changes in curing strength are used as the method by checking the degree of adhesive curing. This is then used to measure adhesive strength for the curing conditions. However, the following issues also arise.

- Fluctuations regularly occur within the breakage test itself
- Testing is readily influenced by adherend type and surface conditions

Because of these factors, this method is not suitable for judging the degree of curing for adhesive independently. This is why checking the degree of curing by using the analysis equipments is needed.

1-2 Using Measurement Devices to Judge the Degree of Curing

At ThreeBond, there are three ways with measurement devices are used to determine the degree of curing in the adhesive (Table 1). The analysis method (and measurement device) is chosen based on the phenomena occurring during the adhesive curing process.

In curing degree evaluation with a rheometer to observe changes in viscosity, changes in viscosity due to reactivity are continuously measured in order to check curing behavior. However, solids with a modulus of rigidity (shear modulus) of 10^7 Pa or more cannot be measured, making it difficult to measure the end point of the reaction in some adhesives. Therefore, this method is mainly used to evaluate the initial process during which a solid begins to form.

In curing degree evaluation using an FT-IR spectrophotometer to observe functional group changes, shifts in the amount of functional groups are checked under determined curing conditions. Curing behavior can also be checked through real-time FT-IR measurement which measures continuous changes in functional group amount. In either case, the required curing conditions are obtained by assuming that curing is completed when there is no further Change in the characteristic functional Groups.

In curing degree evaluation using DSC to observe heating value change, changes in the heating value are compared from before and after reaction under determined curing conditions. In either case, the required curing conditions are obtained by assuming that curing is completed when the heating value reaches zero. However, curing behavior cannot be checked through changes in heating value.

The three evaluation methods shown in Table 1 are explained in detail in the sections to follow.

Table 1 Curing Degree Evaluation Using Measurement Devices

Phenomena Occurring During the Curing Process	Measuring Device	Obtainable Information
Changes in viscoelasticity	Rheometer	1. Changes in viscoelasticity due to the reaction (viscosity change, curing behavior) 2. Gel point and crosslink initiation point due to the reaction
Changes in functional group	FT-IR (real-time FT-IR) spectrophotometer	1. Reduction in the functional group amount due to the reaction 2. Continuous change in the functional group amount (curing behavior)
Changes in heating value	DSC	1. Comparative heating value before and after reaction (reaction ratio).

2. Rheometers

2-1 Rheometer Curing Degree Evaluation

Rheometers are used to evaluate the degree of hardening through changes in viscosity during the curing process.

The adhesive changes from a liquid to a solid during the curing process. The phenomenon during curing where the adhesive solidifies indicates a change in viscosity, and therefore, a change in viscoelasticity. Rheometers quantify viscoelasticity with storage modulus (G'), loss modulus (G"), and tanδ (= G"/G'), and record its change in time. Here, storage rigidity (G') and loss rigidity (G") are indicated by solidity and liquidity, respectively.

Below we explain how to read the chart using the results of measuring changing in curing behavior of epoxy resin as an example (Fig. 1).

Section A: In the initial curing stage liquidity is high, and loss rigidity (G") expressing liquidity grows larger than storage rigidity (G') expressing solidity.

Section B: Increase as temperature increased, but at a certain point the curing reaction begins and the cured object forms part by part as it thickens and tanδ decreases.

Section C: As the reaction progressing and the crosslink reaction begins, a three-dimensional crosslinked structure forms and storage rigidity (G') increases sharply. When the ratio of solid to fluid is equal (G' = G"), tanδ = 1, called the gel point for the sake of convenience, the cured object begins to form as a single mass. From this point, a three-dimensional crosslinked structure forms rapidly, storage rigidity (G') increases and tanδ (G"/G') decreases further.

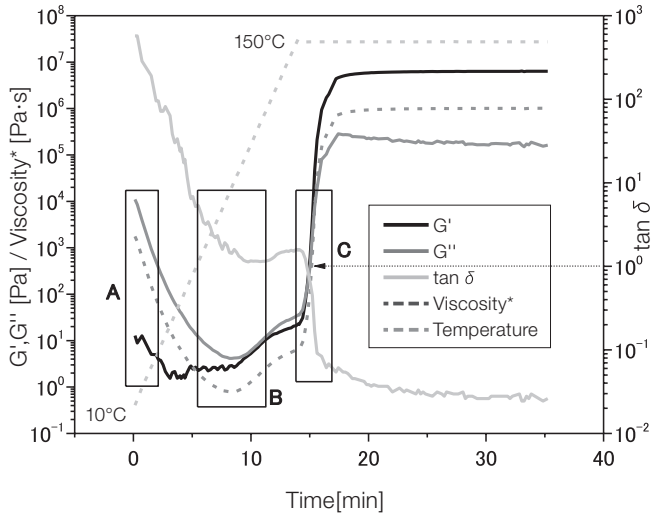


Fig. 1 Rheometer Epoxy Resin Measurement Results

We must be aware of measurement limitation when using a rheometer to perform Evaluation of the curing behaviour. Rheometers designed to evaluate liquids are limited to stiffness between 10^6 and 10^7 Pa. When measuring curing behavior, a stiffness balance of 10^6 to 10^7 Pa is maintained in hard materials (Fig. 2). In such cases, the graph may not show complete rigidity (reaction ratio 100%).

Rheometer measurement of the changes in viscoelasticity during the curing process such as those detailed above clarify partway cured adhesive viscosity changes and enable conditions where flow stops to be checked. This information can be used to set curing conditions in manufacturing processes using adhesives.

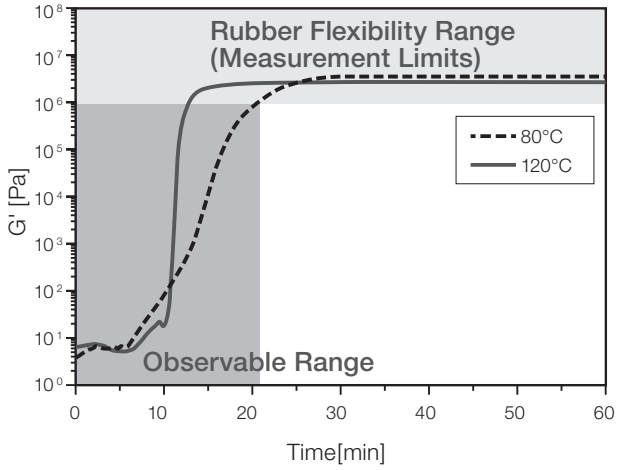


Fig. 2 Rheometer Measurement Limits

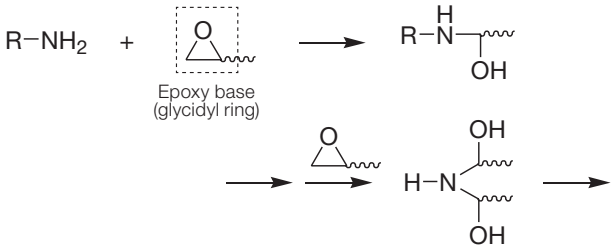
3. FT-IR (Fourier-Transform Infrared) Spectrophotometers

3-1 Overview

Adhesives contain functional groups tied to the reaction, such as epoxy or acrylic. This functional group change due to the polymerization reaction when heat or UV rays are applied, so when an FT-IR spectrophotometer is used to measure infrared absorption spectrum, reduction in the peak of the functional group involved in the reaction is observed.

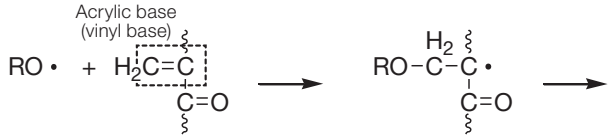
Functional Groups and Reaction Mechanisms

●Epoxy resin



* Peak change derived from epoxy base near 910 cm^{-1}

●Acrylic resin



* Peak change derived from acrylic base near 1635 cm^{-1} or 810 cm^{-1}

3-2 FT-IR Spectrophotometer Curing Degree Evaluation

Evaluating the degree of curing via changes in functional group is based on comparison of changes in the functional group before and after reaction. The spectrum of infrared absorption is measured for a "blank sample (before reaction)" and "survey sample (after reaction)", then the peak area and change in height of the functional group are used to calculate the degree of curing (reaction ratio). In these measurements, absorbance completely changes depending on the thickness of the measurement samples. As a result, when calculating the reaction ratio, benzene rings and others with no reaction-related change in peak area or height are used as a reference to compare the output intensity ratio[*1] to. If there are no components usable as a reference, calculation can be performed through changes in the functional group peak only.

*1:

$$\frac{\text{Absorption peak area and height involved in reaction (functional group peak)}}{\text{Absorption peak area and height not involved in reaction (reference peak)}}$$

Calculating the Reaction Ratio

$$\text{Reaction Rate (\%)} = \frac{A_0 - A_t}{A_0} \times 100$$

A_0 : Blank sample peak intensity ratio

A_t : Survey sample peak intensity ratio

$$A_0 = \frac{r_0}{r}$$ r_0 : Blank sample peak value

r_t : Survey sample peak value

$$A_t = \frac{r_t}{r}$$ r : Reference peak value

Using epoxy resin infrared absorption spectrum (Fig. 3) as an example, material is cured at 80°C × 60 min to calculate the reaction ratio below.

For A_0 : 0.3550 A_t : 0.0686

$$\text{Reaction Rate (\%)} = \frac{0.3550 - 0.0686}{0.3550} \times 100 = 81\%$$

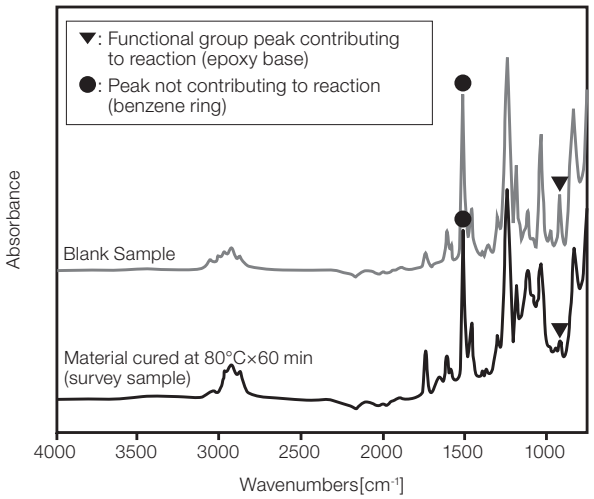


Fig. 3 Epoxy Resin Infrared Absorption Spectrum Measurement

However, measurement is difficult for resins with total amount of the functional group involved in the reaction that is very small, such as silicone resins.

3-3 Real-Time FT-IR Measurement Curing Behavior Evaluation

The FT-IR software enables continuous measurement of the infrared absorption spectrum using real-time FT-IR measurement. Using this method allows changes in functional groups to be monitored continuously (Fig. 4) so curing behavior is evaluated from reaction ratio changes calculated over time.

Additionally, an FT-IR spectrophotometer equipped with an ATR stage on the measuring part can measure the infrared absorption spectrum using attenuated total reflection, where only the area where the sample and the measuring part interface is observed. Using this, curability of deep areas can be evaluated by adjusting the film thickness of the UV curing resin on the ATR stage (Fig. 7).

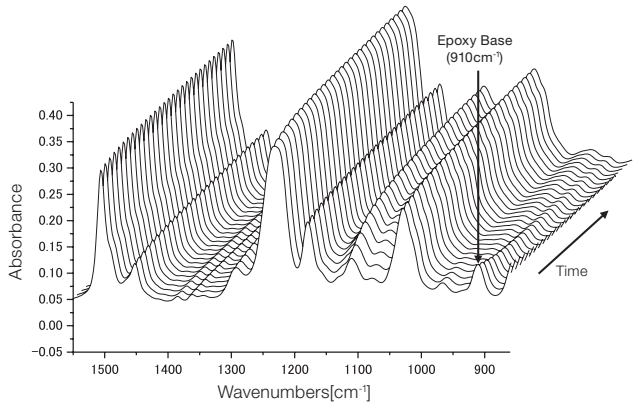


Fig. 4 Real-Time FT-IR Epoxy-Base Absorption Measurement Peak Change vs Time Elapsed

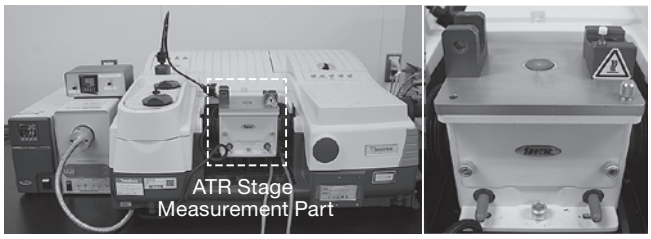


Fig. 5 ATR FT-IR Spectrophotometer

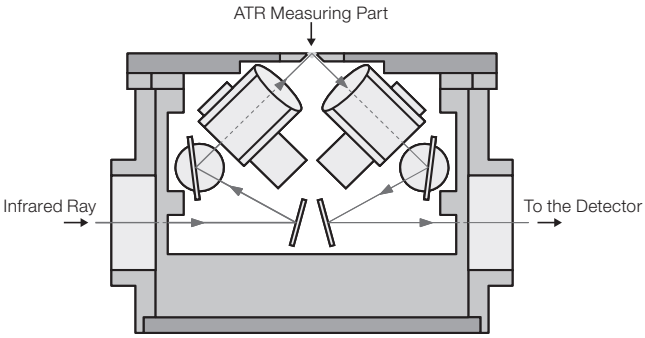


Fig. 6 ATR Technique Measurement Equipment Schematic (observing information in the area where the sample and measuring part interface)

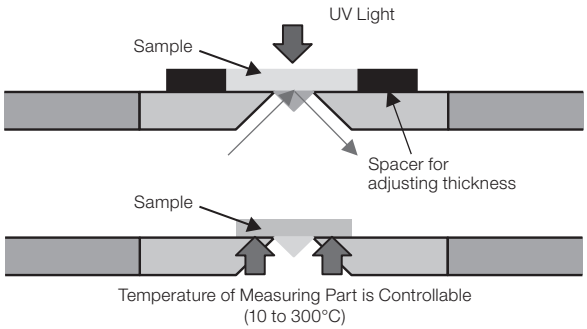


Fig. 7 ATR Stage Measuring Part Measurement Schematic (above: UV light measurement, below: heating measurement)

Using an ATR stage that heat can be applied to enables measurement of the infrared absorption spectrum and evaluation of curing behavior at any temperature applied to heat curing resin (Fig. 7).

3-4 Real-Time FT-IR Measurement

3-4-1 Deep Area UV Curing Resin Evaluation

Curing degree is different on the surface and in deep areas of UV curing resins. The curing reaction occurs later in deeper parts, this is because the surface absorbs the UV needed to cure, making it difficult for deeper areas to obtain a sufficient amount of light. The degree of curing must be checked (deep area curing) where it interfaces with the adherend when design change of the workpiece changes the film thickness of the UV curing resin, etc.

Because of this, real-time FT-IR spectrometry can be used for evaluation other than the physical process of change in film thickness.

The example of measurement in Fig. 8 shows real-time FT-IR measurement results for UV curing resin by thickness

This measurement method can be used to check the degree of curing for each thickness of film.

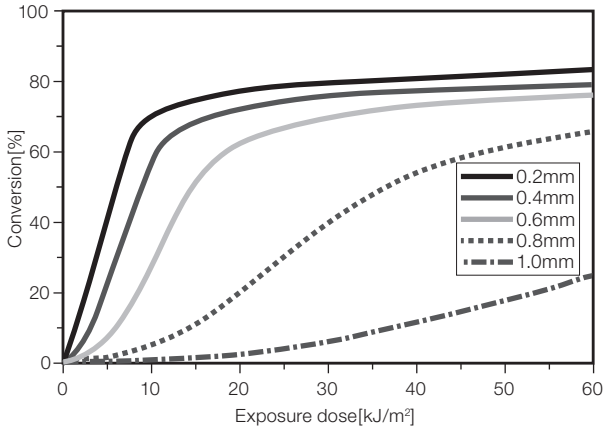


Fig. 8 Real-Time FT-IR by Resin Thickness Measurement Results

Lamp Type: High-Pressure Mercury Vapor Lamp
Illuminance: 100 mW/cm²
(UV Curing Resin)

3-4-2 Setting Curing Condition of Heat Curing Resin

When setting curing conditions for heat curing resins, the curing temperature and time must be set in order to ascertain the curability of the resin itself independent of the cured material. In these cases, curing behavior can be evaluated by curing temperature with real-time FT-IR measurement.

The example of measurement in Fig. 9 shows real-time FT-IR measurement results for epoxy resin by curing temperature Graphing the reaction ratio change for each

curing temperature makes it possible to easily check curing behavior over time.

Because FT-IR measurement is used to calculate the degree of curing based on change in the amount of the functional group, the reaction ratio may not be 100% depending on the type of resin as in Fig. 8, 9, etc. This is likely because as curing progresses, steric hindrances cause remnants of the functional group within the three-dimensional crosslinked structure, and these are observed.

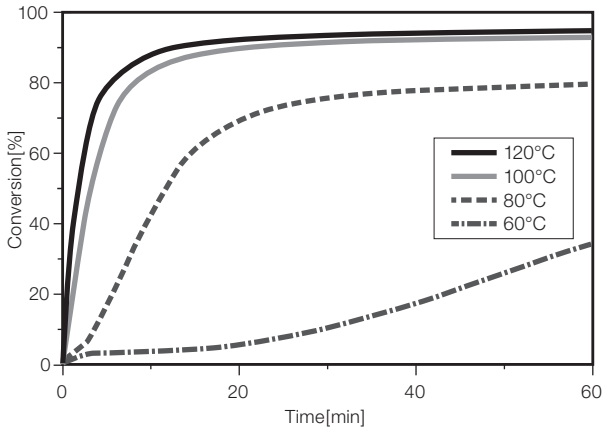


Fig. 9 Real-Time FT-IR by Curing Temperature Measurement Results (Epoxy Resin)

4. DSC (Differential Scanning Calorimetry)

4-1 DSC Curing Degree Evaluation

DSC analysis measures the balance of heat flow when heat is applied to a sample. There are two types of equipment, heat flux and input compensation, through which reaction start temperature, heating value, glass transition temperature, specific heat and other parameters can be measured. Among these, heating value can be used to evaluate the degree of curing (reaction ratio). Next, we will explain how the reaction rate is calculated using epoxy resin as an example. Heat is generated during the epoxy resin curing process. Therefore, total heating value (H_0) and residual heating value (H_t) are measured from the pre-cured sample and cured sample, respectively, using DSC (Fig. 10). The heating value varies depending on curing conditions. The reaction ratio is calculated by inputting obtained heating values into the following equation.

Calculating the Reaction Ratio

$$\text{Reaction Ratio (\%)} = \frac{H_0 - H_t}{H_0} \times 100$$

H_0 : Total Heating Value

H_t : Residual Heating Value

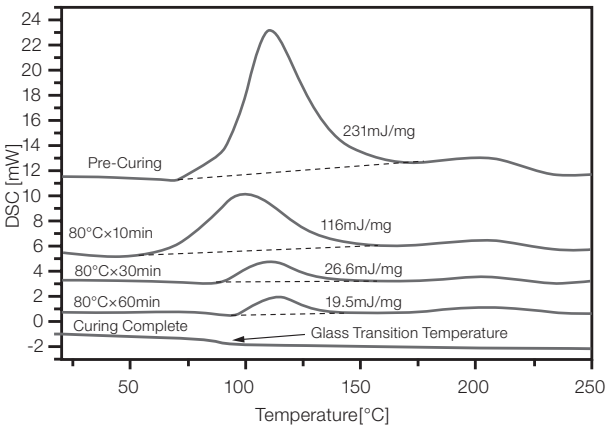


Fig. 10 Heating Value by Curing Condition Measurement Results (Epoxy Resin)

Take the following example for a reaction ratio for curing at 80°C × 60min.

$$\text{Reaction Ratio (\%)} = \frac{231 - 19.5}{231} \times 100 = 92$$

As an example of evaluation, the degree of curing can be checked for its corresponding part, and that result can be used to set the optimum curing conditions.

4-2 DSC Curing Conditions Estimation: Kinetic Analysis

Although curing behavior is not directly observable using DSC, it can be inferred through kinetic analysis.

Measurement is performed at at least three different temperature elevation speeds. Measurement is performed at each temperature elevation rate, the heating peaks obtained in those measurements are divided by each reaction fraction, and the temperature reached is recorded (Fig. 11).

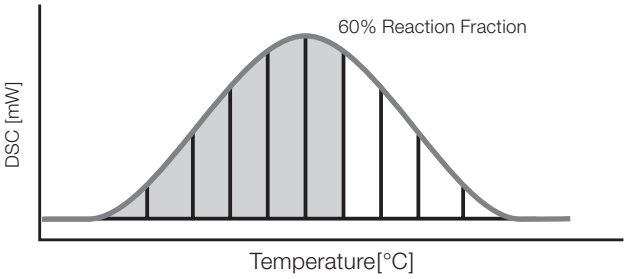


Fig. 11 Heating Peak Reaction Fraction Division

The temperature and heat elevation speed are converted to an Arrhenius plot, and data is obtained via value lines for each reaction fraction as below (Fig. 12).

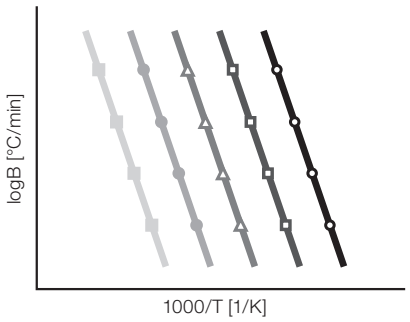


Fig. 12 Data for Each Reaction Fraction

The slope of the line is the activation energy. Activation energy is the minimum amount of energy required for the chemical reaction. The relationship between each temperature and the time required is calculated by inputting numerical values into the following state equation.

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E_a}{RT}\right) f(\alpha)$$

α : Reaction Value
t : Time
A : Frequency Factor
Ea : Activation Energy
R : Gas Constant
T : Absolute Temperature
f(α) : function of α

Using this formula, the relationship between temperature and time for each fraction is calculated to obtain the analysis results (Fig. 13).

A reaction ratio of 90% can be predicted at 140°C × 10 min for these materials.

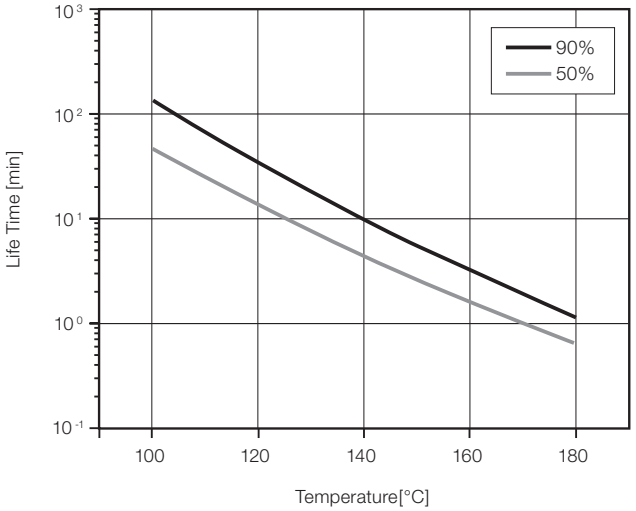


Fig. 13 Analysis Results (Reaction Fraction, Curing Temperature, Relation to Curing Temperature)

5. Curing Degree Evaluation Summary

Below is a summary of how we utilize phenomena occurring during the adhesive curing process and measurement devices that determines the degree of curing to perform evaluation (Table 2).

Table 2 Curing Degree Evaluation Summary

Measurement Device	Obtainable Information	Specific Points for Determining Curing Degree	Scope of Application
Rheometer	1. Changes in viscoelasticity due to the reaction (viscosity change, curing behavior) 2. Gel point and cross-linking reaction initiation point	Difficult to judge reaction end point due to device mechanics Enables initial process evaluation of solid formation	Initial process evaluation of curing speed evaluated due to device measurement limitations (G' = up to 10^7 Pa) * Curing behavior evaluation
FT-IR Real-time FT-IR	1. Reduction in the functional group amount due to the reaction 2. Continuous change in the functional group amount (curing behavior)	100% cured when the functional group related to the reaction is completely depleted (when change stops)	Curing reaction is observable from start to finish * Curing behavior evaluation, curing degree measurement
DSC	1. Comparative heating value before and after reaction.	100% cured when heat is no longer generated	Curing range when heating value can be observed * Curing degree evaluation

Closing

We introduced our evaluation methodology for checking the degree of curing in reactive adhesives by utilizing analyzers different from those usually employed in physical tests of adhesive strength measurement. In order to make accurate curing judgements, evaluation methods must be selected and combined according to usage objectives and applications.

For example, production processes optimization for parts using adhesives can be furthered by evaluating the degree of curing using a rheometer or real-time FT-IR spectrophotometer. Furthermore, these techniques can be used to clarify the cause of any issues that arise due to curing conditions.

At ThreeBond, we understand customer needs and select the optimal evaluation method to provide technical information useful when checking the degree of curing or setting curing conditions.

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