APPLICATION NOTE

No. V254

Curing of an acrylate – Rheology with simultaneous FTIR spectroscopy

Introduction

Anybody who has ever worked with glues knows that timing is one of the crucial issues. Subsequently technical leaflets for glues sometimes look like timetables. Terms like pot life, open time, time for minor adjustments, curing time or time to reach maximum bonding strength, are used to describe the properties of glues and to give guidance for their successful application.

For the development of new glues such times have to fit the application to create a product that the target market will accept. For example, depending on the method to apply the glue, the open time needs to be adjusted to avoid curing before the parts have been joined.

A rheometer is an essential tool to characterize not only the uncured glue but especially the curing process itself. Regardless of whether a drying glue, a 2-component system, a thermally curing glue or a UV curing glue is investigated, the Thermo Scientific™ HAAKE™ MARS™ Rheometer and its wide range of accessories are the perfect tools to characterize curing behaviors.

Still, the classical limitation of rheological methods remains: a rheometer can only tell us what happens during the curing but it does not tell us why. The “why“ becomes especially important when we want to understand why a batch of glue shows properties other than those expected or when we want to develop glue for a new application. To overcome this limitation, the rheological data needs to be combined with data from another analytical method able to detect what happens on the molecular scale. The molecular data provides the complementary “why” information to the rheological measurements. A perfect match is FTIR spectroscopy, a technique that can identify and quantify different chemical groups in a substance or in a mixture of substances.

Rheometers and spectrometers are two different types of analysis, each often with its own instrument. The disadvantage of running tests on two separate instruments is the extra effort it takes to prepare two different samples

Figure 1: Setup with the HAAKE MARS Rheometer, Rheonaut module* and Thermo Scientific Nicolet iS20 FTIR spectrometer

following different procedures for each method. Plus, as a consequence, this approach makes it virtually impossible to collect both sets of data on two identical samples under exactly the same conditions.

To combine rheological tests with FTIR spectroscopy without the aforementioned disadvantages, the Rheonaut module has been developed. This module is a unique combination of a temperature control module and an attenuated total reflection (ATR) cell with its own IR detector. With the Rheonaut module, the HAAKE MARS Rheometer can be combined with an FTIR spectrometer a single OR for complete analytical setup (Figure 1). Only with this unique combination is it possible to record the mechanical changes of the curing glue while simultaneously and, even more importantly, collecting IR spectra on the same sample to track the chemical changes inside the sample.

Experimental

A consumer-grade, 2-component acrylate glue was prepared by mixing both components outside the rheometer according to its technical leaflet. Part of this mixture was transferred into the rheometer.

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When designing the test method, two important facts about curing materials have to be kept in mind:

1. The curing reaction starts already outside the rheometer. To be able to compare different datasets, the test method contains an element to reset the internal time at the the moment the 2 components start to be mixed (Figure 2, steps 3 and 4). Otherwise, any deviation in the loading procedure would lead to an undefined offset on the time axis.

2. The biggest changes happen during the first moments of the curing process. The test method has been optimized to start the test as quickly as possible after the sample is put onto the lower plate. The upper geometry is lowered to 10 mm before loading the sample to shorten the time to reach the measuring gap (Figure 2, step 6). The test itself starts immediately after the measuring gap has been reached without any time for thermal or mechanical equilibration.

The rheological part of the test method is an oscillation time curve (Figure 2, step 10) where the oscillation parameters are kept constant to detect only changes in the sample due to the curing. Since drastic changes of the moduli are expected during the test, the rheometer's controlled deformation (CD)-mode is used to ensure optimum signal quality throughout the whole test. A small amplitude within the sample's linear viscoelastic range (LVR) is selected, which still yields data with a good signal-to-noise ratio from the uncured glue. The evaluation can be based on the storage modulus G' representing the elastic part of the viscoelastic properties and the loss modulus G" representing the viscous part (Figure 3).

Figure 2: Test method for 2-component glues shown in Thermo Scientific™ HAAKE™ RheoWin™ Measuring and Evaluation Software. In steps 3 and 4 the time is reset when the 2 components mix outside the rheometer. In step 5 the upper geometry moves to a 10 mm gap to minimize lift travel after the sample is put onto the lower plate. Step 8 moves the upper geometry to the measuring gap, and step 10 starts the test without waiting for temperature equilibration.

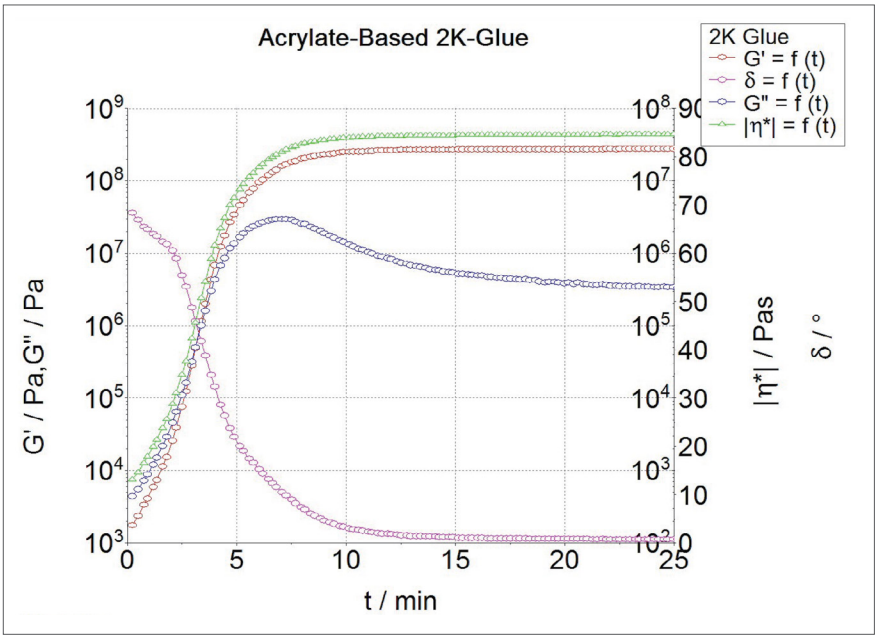

Figure 3: Curing of an acrylate glue; development of the moduli G' and G", the complex viscosity |h*| and the phase angle Δ over time

The freshly prepared glue is mainly viscous; G“ dominates over G’ with phase angle (δ) values around 70° (purely viscous: δ = 90°, purely elastic: δ = 0°). The curing reaction proceeds quickly; after 3.2 min the crossover point where G“ = G’ or δ = 45° is reached. From this so-called gel time on, the glue behaves as mainly elastic because a wide meshed network has developed throughout the sample. Joining and fixing the two parts to be glued together has to be done well before the gel time is reached. Otherwise any movement in the glue line is either no longer possible or would reduce the final bonding strength. After 10 min δ drops to 3° and G’ reaches an almost constant value when the glue reaches its final strength. Although, strictly speaking, acrylate glues continue to cure at a slow rate, reaching their final strength after 12 – 24 h.

Simultaneously with the rheological data, FTIR spectra have been collected about every 13 s yielding 115 IR spectra during the 25 min of the rheological test. The spectra show several characteristic signals, which can be correlated with the progress of the chemical reaction (Figure 4). The signal at 1637 cm^{-1} for example is characteristic for the C=C-bond of the acrylate monomer. Its decrease over time illustrates the consummation of the monomer during the curing reaction.

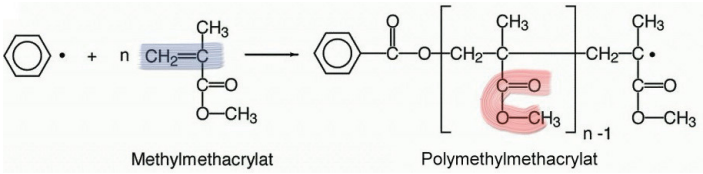

Figure 4: Radical polymerization of methylmethacrylate (MMA) to polymethylmethacrylate (PMMA). Marked in blue: C=C-bond of the monomer. Marked in red: ester bond in the polymer.

The signal at 1241 cm^{-1} on the other hand is, amongst others, characteristic for the O=C-O-C ester bond in the polymeric acrylate formed during the curing of the glue (Figure 5).

Thermo Scientific™ OMNIC™ Spectroscopy Software with its optional OMNIC Series add-on allows the spectra to be lined up in chronological order in a 3D-graph and characteristic spectral changes to be evaluated during the time of the test (Figure 6).

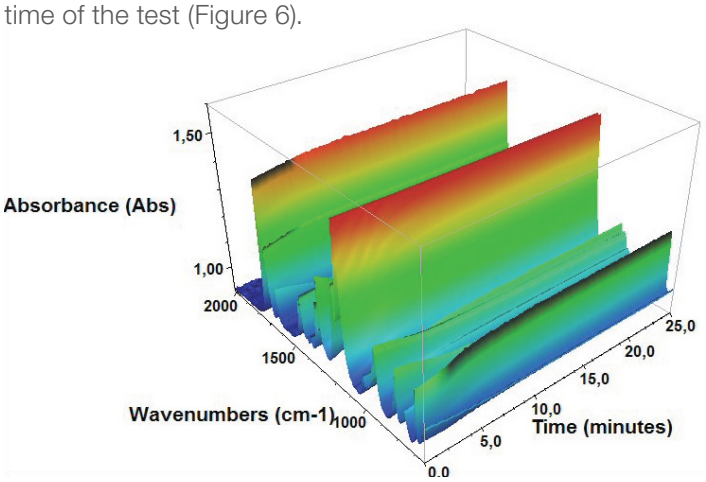

Figure 6: 3D profile illustrating the time-dependent change of the IR spectra collected during the curing of the sample in the rheometer, created with the OMNIC Series software

Cutting through the data set along the characteristic wave numbers results in absorbance profiles, which show the changing amounts of the corresponding chemical groups in the sample.

Combining the rheological data with the spectroscopic profiles shows that the initial increase of the moduli corresponds with the decreasing amount of monomer (Figure 7).

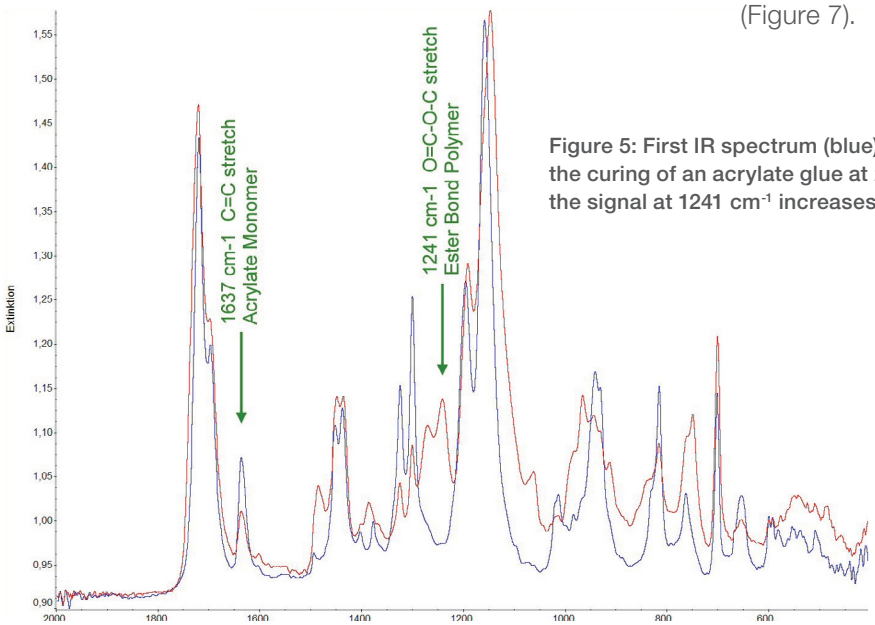

Figure 5: First IR spectrum (blue) and last IR spectrum after 25 min (red) collected during the curing of an acrylate glue at 23 °C. The signal at 1637 cm^{-1} decreases over time while the signal at 1241 cm^{-1} increases.

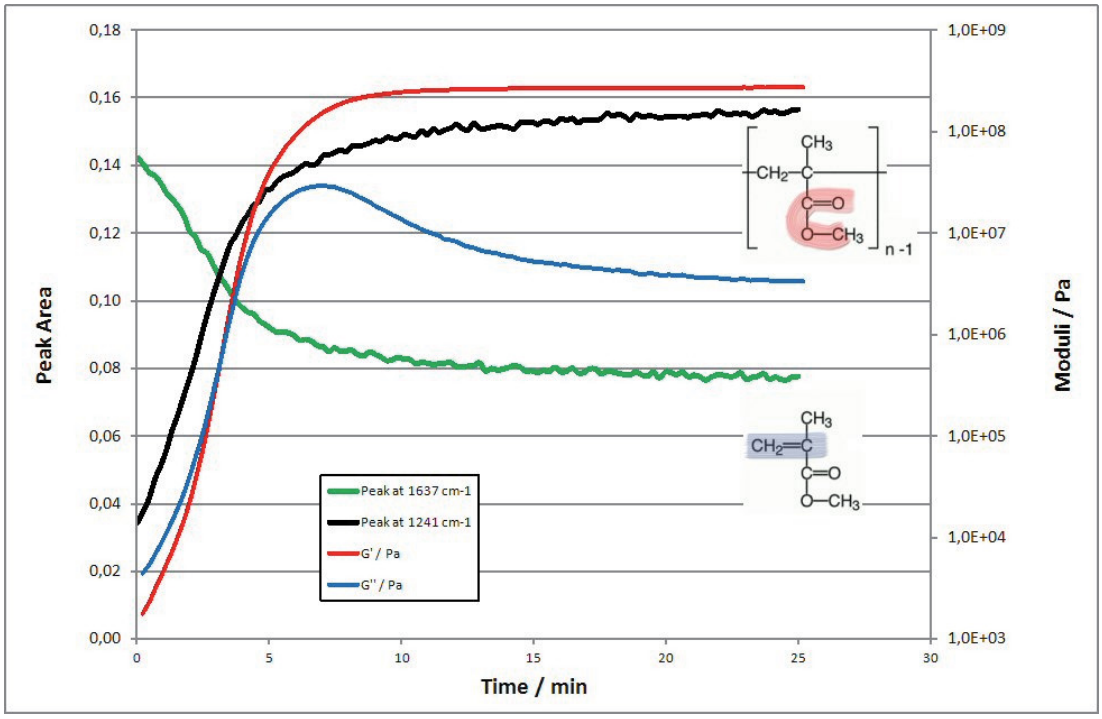

Figure 7: Curing of the acrylate glue monitored with rheology and simultaneous FTIR. The increase of the sample's moduli (red and blue) corresponds with the decreasing signal of the monomer (green) and the increasing signal of the polymer's ester bond (black).

When G' reaches its plateau value after 10 min the decrease of the monomer slows down significantly due to the reduced mobility of the monomer in the solidifying glue. The increase of the ester bond in the polymer is also reduced but still continues with twice the speed of the monomer's decrease. This indicates that intramolecular processes are more important for the final curing stage compared to reactions of the free monomer, which dominated the initial part of the curing.

With this information it is possible to understand why the curing process runs the way it does. Subsequently a targeted approach to optimize a glue or to design a completely new formulation is now possible. For example, it's known whether it would be better to add more monomer or to increase the temperature to increase the mobility of the existing monomer.

Summary

An oscillation time sweep is a well-established method to characterize the curing of glues and similar curing materials. It shows the transition from the liquid to the solid state based on the mechanical properties of the glue. The rheological results can answer questions about the dosing and application properties of the liquid glue as well as the toughness of glue bond. The evaluation of the changing rheological properties gives the characteristic time spans like the pot life, the curing speed and the time to reach maximum strength of the bond.

Using the Rheonaut module, the HAAKE MARS Rheometer can be combined with an FTIR spectrometer to simultaneously record on the same sample what happens during the curing process and why it happens on a molecular level. This significantly reduces the time for sample preparation and analyses and excludes any uncertainties due to different sample composition or sample treatment when running both analyses separately.

The unique combination of rheological and spectroscopic methods not only increases the quality of the data collected but also increases the time efficiency and cost efficiency of an analysis like the one described in this report.

* Resultec developed the Rheonaut module for exclusive resale by Thermo Fisher Scientific • FTIR data collected on a previous generation spectrometer

Find out more at **thermofisher.com/rheometers**

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