

Detailed analysis of curing reactions of polyurethane resins using the Rheonaut technology for simultaneous rheometry and FTIR

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Introduction

For a comprehensive understanding of a material, usually more than just one analytical technique is required. Techniques complementing rheological measurements are e.g. GPC, thermal analysis, microscopy, and FTIR spectroscopy. By combining two analytical techniques in one instrument the amount of information gathered from one single sample is maximized. The present study introduces dynamic rheometry and FTIR spectroscopy being employed simultaneously to monitor structure development during the reactive processing of a polyurethane resin system. It is certainly intuitive that rheological properties of polymers depend on molecular mobility, which is influenced by molecular structure. And although both, rheometry and FTIR spectroscopy can record dynamic progressions, they cannot detect interactions when used in parallel. This requires their combination in one instrument to analyze one sample at the same time under exactly the same conditions. Since infrared spectroscopy is a tool capable of identifying the nature of molecular structures and transformations, the addition of an FTIR spectrometer to a rotational rheometer gives the researcher another level of detail pertaining to the comprehension of rheological applications.

Experimental

Instrumentation

Why FTIR spectroscopy in combination with rheology? With a rheometer the steady state and time dependent viscoelastic properties of a material can be studied as a function of stress and/or strain. However the viscoelastic properties of a material depend on the structure and especially the structural changes of the material on the molecular level. Infrared spectroscopy is an excellent tool for determining the identity and quantities of molecules in a sample. Using the RHEONAUT both physical and chemical information can be obtained on a sample at the same time using one instrument. The result enables a comparison of chemical information with rheological properties. The RHEONAUT operates in the mid-infrared spectral range since all fundamental absorption bands of a sample are typically found between $400 - 4000 \text{ cm}^{-1}$ ($2.5 - 25 \mu\text{m}$). This covers the so-called fingerprint region which is generally accepted as unique for each molecule.

With the patented¹ RHEONAUT module a standard FTIR spectrometer with side port and the Thermo Scientific HAAKE MARS rheometer are coupled to form one measuring unit. Suitable spectrometer model is e.g. Thermo Scientific Nicolet iS10 as used in this showcase. The station-

ary plate of the rheometer features a monolithic diamond element that serves as the ATR (attenuated total reflection) sensor, offering a single internal reflection. It has an excellent inertness to chemical properties of materials and abrasion.

Compared to standard infrared transmission spectroscopy or specular reflection spectroscopy techniques, the sample thickness can thus be adjusted to the rheological needs and is independent from the infrared spectroscopy requirements. Accordingly, any plate or cone geometry up to a diameter of 60 mm can be used for all testing methods offered by a rotational rheometer. The diamond is integrated in the center of the lower plate and thanks to a motordriven horizontal movement of the lower plate the ATR sensor can be positioned at different distances between the center and a maximum of 45 mm.

The RHEONAUT module can be equipped with two different temperature control units, either with a Peltier temperature control unit ($0-100 \text{ }^\circ\text{C}$) or an electrical unit for temperatures from ambient up to $400 \text{ }^\circ\text{C}$. Several wire grid polarizers are optionally available in manual and automated versions to set the infrared radiation polarization direction both parallel and perpendicular to a fixed reference direction of the sample.

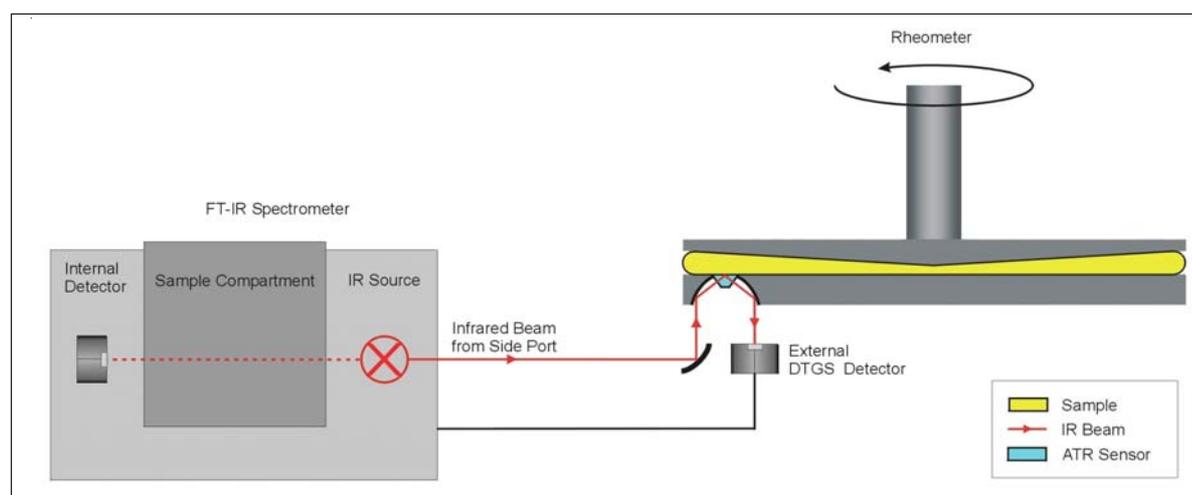


Fig. 1: Schematic diagram of coupling an FTIR spectrometer to the Thermo Scientific HAAKE MARS rheometer



Fig. 2: Thermo Scientific HAAKE MARS rheometer platform for individual configuration

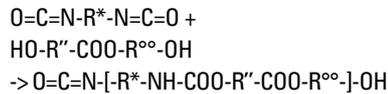
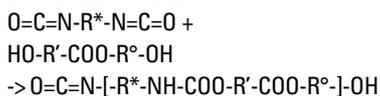
The RHEONAUT module is a fully integrated solution for the HAAKE MARS rheometer, both from the hardware and software point of view. After the module is quickly adapted to the rheometer the HAAKE Rheo-Win software enables temperature control as well as the horizontal positioning of the lower plate and the communication with the spectrometer software (selected supplier) for simultaneous acquisition of the rheological data and spectra.



Fig. 3: Patented RHEONAUT module

Materials and Sample Preparation

The investigated PU resin was composed of two reactants. One reactant contained a Diisocyanate prepolymer, the second reactant contained two different ester compounds each end-capped with hydroxyl groups. The PU resin formulation was prepared by mixing the starting materials with equal stoichiometric ratio between isocyanate and hydroxyl groups ($[NCO]/[OH] = 1$). After 5 minutes of mixing and homogenizing, the reactive sample was transferred into the rheometer. The basic chemical reaction is as follows:



Methods

The curing of the investigated PU resin was monitored in small amplitude oscillatory shear (SAOS). Experiments were carried out using plate/plate geometries with 20 mm diameter and 1 mm gap. At a frequency of 1 Hz the samples were both tested in CS (controlled stress) at a shear stress of 50 Pa and in CD (controlled deformation) at a strain of 0.01. Experiment duration was 180 minutes with data sampling every 60 seconds.

The infrared spectral range was 400 cm^{-1} to 4000 cm^{-1} with a spectral resolution of 4 cm^{-1} . Each spectrum consists of 8 co-added scans. In total, 180 data sets, each containing rheological and spectral data, were collected.

Results

Figure 4 shows the storage modulus G' and loss modulus G'' of the PU resin as a function of time. The curing reaction was monitored under different deformation conditions as described earlier. As can be clearly seen, the viscous behavior dominates the initial part of both experiments ($G'' > G'$) due to free chain mobility. Beyond the first inflection point in G' , the curing speed increases and finally a crossover is monitored. At the end of both experiments the elastic behavior dominates ($G' > G''$), because the formation of a 3-dimensional network enables the sample to store more energy elastically than is dissipated via viscous flow.

The cross-over is shifted to a later time when working in controlled deformation (CD) mode. Under this

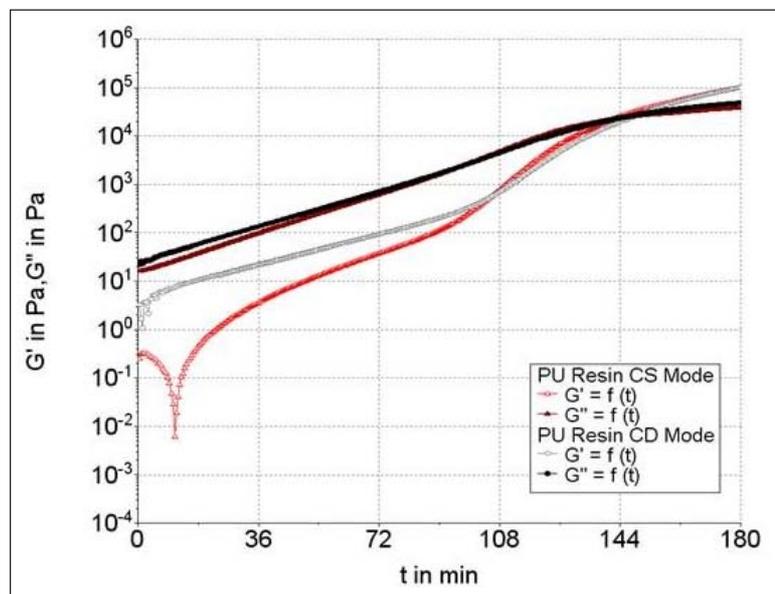


Fig. 4: Results of CS test: G' (—) and G'' (—), CD test: G' (—) and G'' (—)

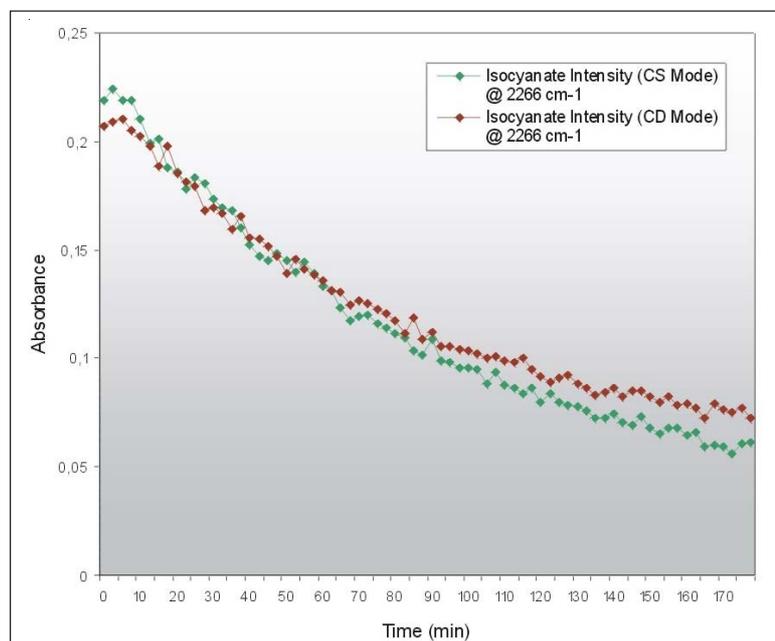


Fig. 5: Isocyanate absorbance band development at 2266 cm^{-1} over time

condition, the curing is slower which coincides with the Isocyanate absorbance band development at 2266 cm^{-1} shown in figure 5. The Isocyanate consumption that correlates with the curing rate in the infrared spectrum is higher in CS mode compared to the controlled deformation experiment.

One way to quantify the gel point of a thermosetting resin is to determine the inflection point of G' during its rapid increase. Another method is the determination of the cross-over between G' and G'' . At this specific point the viscous and elastic properties are even and thus a correlation with a working life timescale is argumentative.

Curve sketching of G' in Fig. 4 yields the parameters summarized in table 1. The determined parameters allow for the fragmentation of G' into several specific sections. To assist the understanding of the chemical aspects in each section, an examination of the simultaneously acquired FTIR spectra is necessary.

Figure 6 displays an assortment of IR absorbance spectra in the Carbonyl region and assigns their origin. The absorbance band development of

associated Urethane at 1687 cm^{-1} is illustrated in figure 7. Furthermore, the graph depicts the first sections, namely the discontinuity at 11 minutes and the first inflection points at 47 minutes and 72 minutes respectively, after which both absorbance band development curves show an equivalent run.

In contrast, the absorbance band development of free Urethane at 1721 cm^{-1} runs congruent for both CS and CD over the entire period of time.

From the chemical point of view, the absorbance band development shown in figure 7 reflects the cross-linking process of free Urethane blocks by formation of Hydrogen bonds.

Applying stress or deformation during the curing process obviously affects the kinetics of Hydrogen bond formation in the early curing stage.

In particular, a better mixing due to higher deformations obtained in CS mode is achieved, thus increasing reactant mobility, and finally being responsible for the cross-over shifting to earlier times.

Figure 8 displays an assortment of IR absorbance spectra containing the Amide II band at 1522 cm^{-1} .

Figure 9 illustrates the absorbance band development of the Amide II band for both methods applied.

The absorbance band at 1522 cm^{-1} is assigned to the stretching vibration of the C-N bond and the deformation vibration of the C-N-H bonds. These bonds are thus affected by applying stress or deformation during the curing process beyond the first inflection point.

Figure 10 illustrates the absorbance band development of the Amide III band at 1242 cm^{-1} for both methods applied. This absorbance band is assigned to the deformation vibration of the N-H bond and the deformation vibration of the O-C-N bonds. These bonds are thus affected by applying stress or deformation during the curing process beyond the intersection point at which G' equals G'' . Up to that point, both curves run congruent and the assigned Amide bonds are affected by neither of the applied methods.

Conclusions

The gel point is one of the basic parameters characterizing the processability of thermosetting resins and oscillatory shear is the method of choice to gather information about it. The RHEONAUT enables the simultaneous acquisition of FTIR spectra to track the evolving chemical constitution in all details and can thus reveal the relation between the visco-elastic properties and individual reactive groups of a complex polymer. Further strengths include kinetic analysis depending on mechanical impacts during the curing process; discovering the root cause of artifacts, and much more. To summarize, the RHEONAUT is a valuable instrumentation to obtain real-time conversion information for studying of cross-linking reactions at which a transition from the liquid to the solid phase takes place.

References

- DE 10140711, EP 02762251, US 6988393, JP 4028484

Method	Discontinuity	1 st Inflection point	2 nd Inflection point	$G' = G''$
CS	11 min	72 min	109 min	141 min
CD		47 min	117 min	149 min

Tab. 1: Results of the curve sketch for the viscoelastic data in Fig. 4

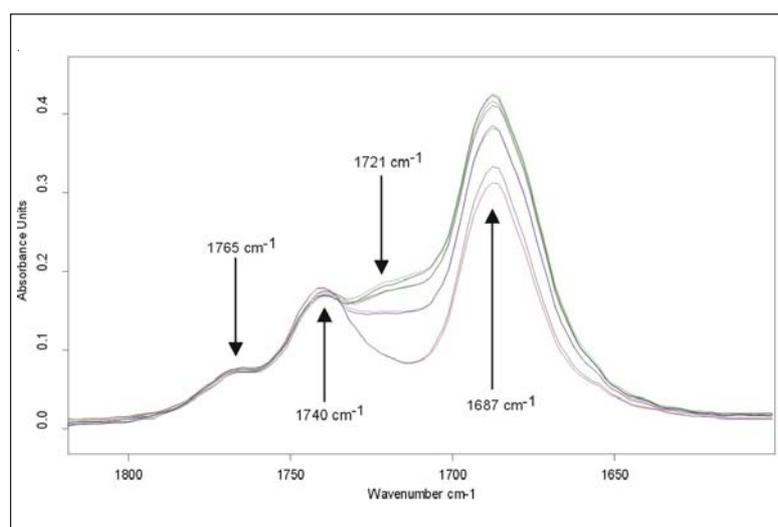


Fig. 6: IR spectra showing the Carbonyl region at different curing times:

- 1765 cm^{-1} Ester (-R'-COO-R°-)
- 1740 cm^{-1} Ester (-R''-COO-R°-)
- 1721 cm^{-1} Non-bonded Urethane stretching
- 1687 cm^{-1} Associated Urethane (Hydrogen bonded Urethane)

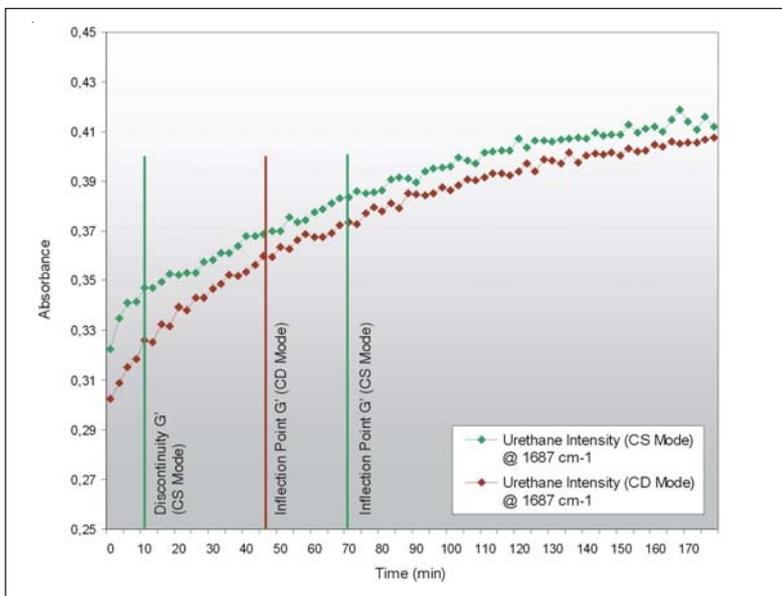


Fig. 7: Associated Urethane absorbance band development at 1687 cm^{-1} over time

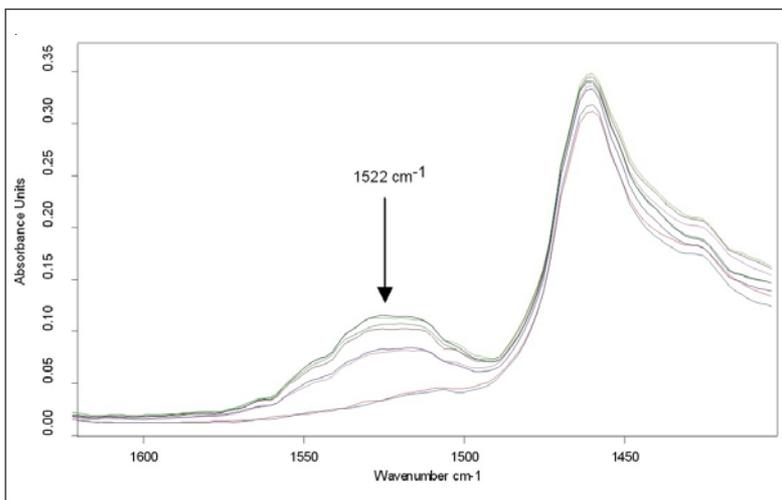


Fig. 8: IR spectra showing the Amide II region at different curing times

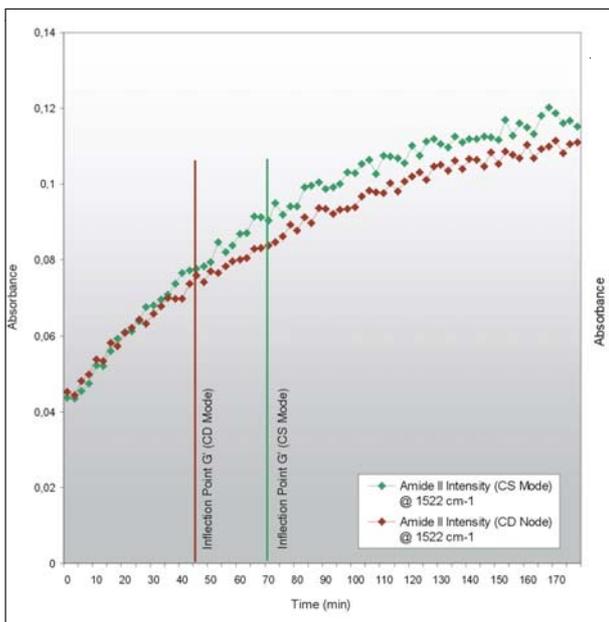


Fig. 9: Amide II absorbance band development at 1522 cm^{-1} over time

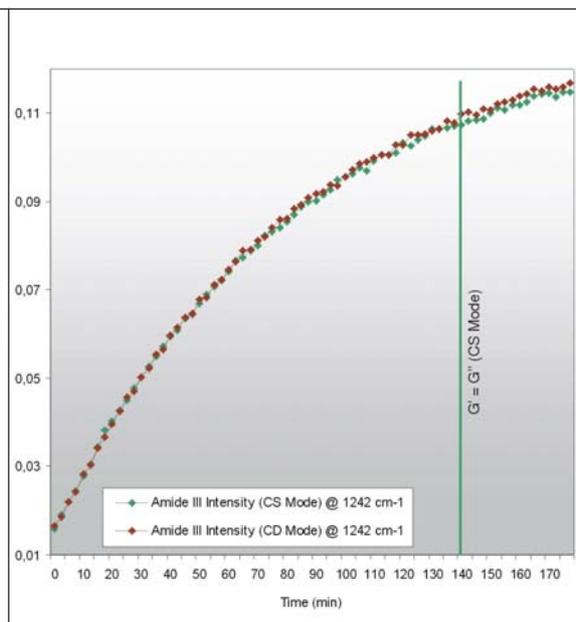


Fig. 10: Amide III absorbance band development at 1242 cm^{-1} over time

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