Application note

UV-curing reactions investigated with Rheo-FTIR measurements

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Introduction

In many industrial segments the use of UV-curing materials for the processing or application of paints, inks, adhesives, coatings, etc. is of upmost importance. This technology combines environmental and economical advantages with improved product features.

A curing process can be followed by dynamic rheological measurements, since the build-up of a network in the sample is directly related to the change of the viscoelastic properties (G', G", etc.) of that sample.

By combining oscillatory rheological measurement with a second analytical technique an even more comprehensive insight into the characteristics of curing processes can be achieved. Such a supplemental tool can be e.g. FTIR spectroscopy. For a curing process or phase transition in general a rheometer can analyze the time dependent change of the viscoelastic properties of a material. The viscoelastic properties of a material however depend on its structure and especially its structural changes during a curing process. Infrared spectroscopy is an excellent tool for determining structural changes on a molecular level.

We will present technical details of new UV-curing setup for the Thermo Scientific™ HAAKE™ MARS™ 40/60 Rheometers (or predecessor models) and show the experimental results of the investigation of an UV-curing processes for an acrylate based coating for optical fibers. The presented data includes rheological as well as spectroscopic data.

Figure 2: top-left: measuring geometry and adapter for mounting and adjusting the collimator and light guide; top-right: upper shaft with integrated mirror; bottom: holder for collimator plus closed hood.

Figure 1: left: HAAKE MARS Rheometer with Rheonaut module and FTIR spectrometer; right: HAAKE MARS rheometer configuration for UV-curing measurements incl. temperature control.

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Measurement and set-up

With the Rheonaut module a standard FTIR spectrometer with side port and the HAAKE MARS Rheometer are coupled to form one measuring unit (Figure 1).

For investigating UV-curing materials with the Rheonaut module a new fixture for the HAAKE MARS Rheometer platform has been developed. This module consists of an upper shaft with an integrated mirror and an exchangeable quartz glass plate (Figure 2), as well as a holder for a collimator plus light guide, which is mounted to the HAAKE MARS measuring head (Figure 2).

The UV light beam of a commercially available light source, first bundled by the collimator and then reflected by the mirror, is directed into the sample vertically from above through the quartz glass plate (Figure 2). The quartz glass plate is the upper plate of a plate/plate measuring geometry, whereas the lower plate is either a standard temperature control module or the Rheonaut module for simultaneous measurements of rheological properties and FTIR spectroscopy.

The use of the optional available sample hood is recommended for measurements above ambient conditions. This hood is made of Teflon and can be used for temperatures up to 240 °C. This new setup enables the user to expose a material to UV-radiation while collecting rheological and spectroscopic data at the same time.

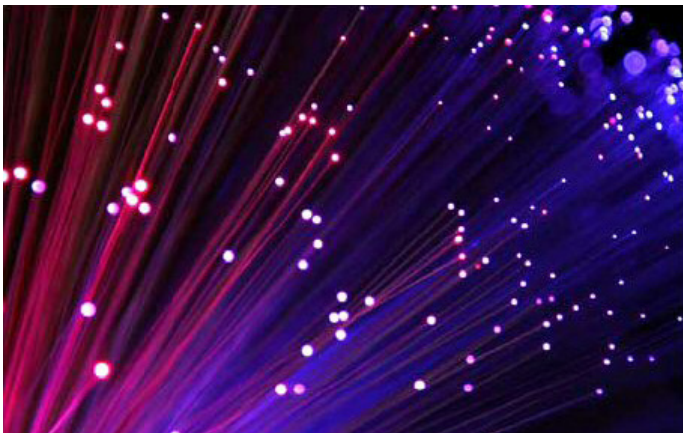

Fig. 3: Uncoated optical fibers.

Materials

The single glass fibers in an optical fiber cable are typically coated with a polymeric material to protect them from moisture and physical damage. The utilized coatings are usually UV-cured urethane acrylate composite materials applied to the outside of the fiber during the drawing process. In current practice, a dual layer coating system is used. These layers are applied at speeds of up to 1000 m/min. In order to optimize the final coating behavior and reduce the energy consumption during production a comprehensive understanding of the curing reaction is essential. In the following the rheological and spectroscopic investigation of the curing of an acrylate based coating formulation is shown.

Results

The following measurements were performed at 25 °C using the new UV-curing cell in the HAAKE MARS Rheometer and the Rheonaut module for collecting the spectroscopic data. Figure 4 shows the rheological data of the measurement of a UV-curing acrylate based glass fiber coating. The set strain value was 0.01. After the UV light source was triggered for the first time at 30 s G' and G" are increasing over several orders of magnitude. During the curing process the sample was exposed to UV light every two seconds for a period of one second. G' reaches it's maximum after 100 s and remains constant for the rest of the experiment. After the initial increase G" runs through a maximum and decreases almost one order of magnitude before it reaches a plateau after 240 s. This behavior indicates a curing process in two steps. After the initial solidification the decrease of G" can be related to a further increase of the crosslink density. This second step has no influence on the evolution of G' or the overall stiffness of the material but rather on it's brittleness. After 240 s no changes on the rheological parameters can be observed anymore and the curing reaction is completed.

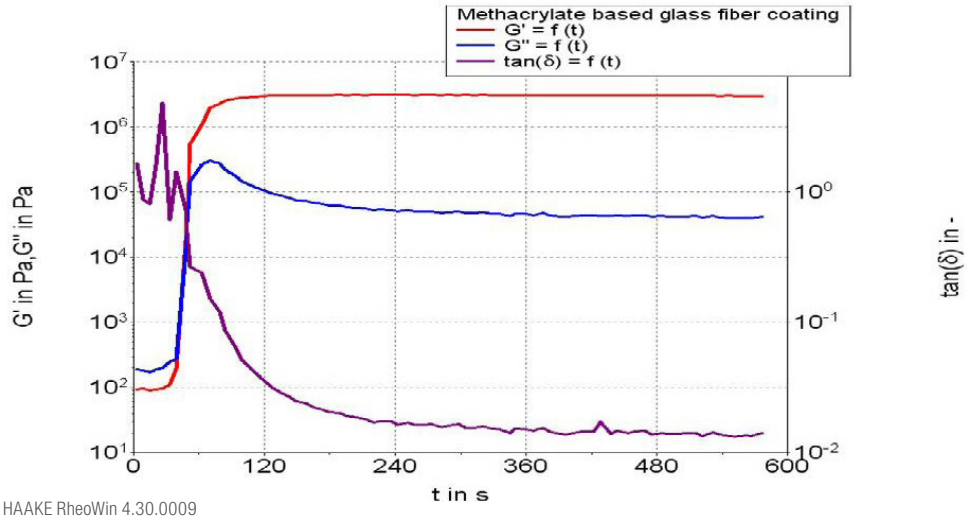

Fig. 4: Oscillation time experiment (CD-Mode) of an UV-cured metha crylat based glass fiber coating (f=5 Hz, plates 20 mm, gap 100 µm).

Beside the rheological data the IR-spectra where collected during the experiment. The results are shown in Figure 5. One of the advantages of FTIR spectroscopy is the high spectrum acquisition rate. Combined with the Fast Oscillation function of the HAAKE RheoWin Software even very rapid structural changes can be monitored in a rheological and spectroscopic way. Figure 5 shows three representative spectra taken before the uncured sample was exposed to UV-light, during the steep increase of the moduli and after G' and G" reached their plateau values. Some of the characteristic peaks are highlighted and shall be mentioned here. At 1719 cm^{-1} and at 1179 cm^{-1} decreasing peaks are observed.

These are characteristic wavelength numbers for stretching vibration of carbonyl groups. Therefore it can be concluded that this functional group is actively involved in the curing process and the amount of free carbonyl groups is decreasing over time. Another characteristic peak that stands out in the presented spectra is at 808 cm^{-1}. At this wavenumber =C-H groups transform absorbed energy into bending vibrations.

The mentioned examples demonstrate how the structural changes within a curing sample can be monitored and evaluated on a molecular level. Along with the rheological information gained from the oscillatory experiment, this combined measuring technique provides a comprehensive insight into complex processes. Therefore it can be an ideal tool for optimizing industrial curing processes with regards to sample performance and energy efficiency.

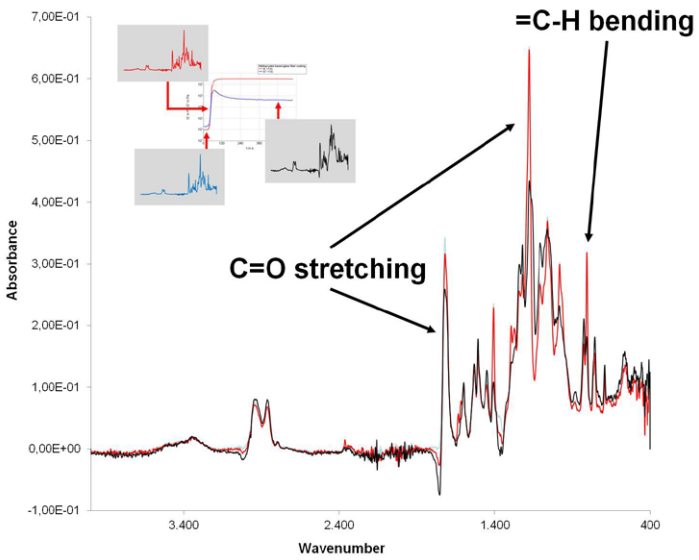

Figure 5: IR-Spectroscopic data of acrylate based coating formulation before while and after being exposed to UV-light.

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