Simultaneous rheology and Raman spectroscopy: Tracking molecular structures as a function of stress, strain and temperature

Authors:
Cornelia Küchenmeister-Lehrheuer and Jan Philip Plog, Thermo Fisher Scientific, Karlsruhe, Germany

Key words
- Thermo Scientific HAAKE MARS rheometer platform
- Thermo Scientific Nicolet DXR Raman microscope
- Hyphenated measuring method
- RheoRaman module

The result of a rheological test tells us, how a substance behaves under a given stress or strain. What it does not tell us is the reason why, as rheology is a bulk method, only looking at the sample as a whole. However, to be able to fully understand the rheological behaviour of a given fluid, one needs additional information about the sample's micro- and/or molecular structure. This information can be supplied by an additional analytical method like i.e. microscopy, dielectrical analysis (DEA) as well as FT-IR and Raman spectroscopy.

Using the traditional approach, running two independent tests on two different samples bears the risk that due to the different ways of sample preparation or sample history in general, the test results are not comparable. This risk can be avoided by running both test methods on the same sample simultaneously using a combination of two analytical methods in one setup. Subsequently, the two resulting data sets can be correlated without any doubt, since they have been collected at the same time on the same sample. As an additional benefit, this approach saves a significant amount of time since only one sample has to be prepared and both tests run at the same time.

This product note focuses on the newly available coupling of a Thermo Scientific™ HAAKE™ MARS™ rheometer and a Thermo Scientific™ Nicolet™ DXR Raman microscope.

Figure 1: Combination of a HAAKE MARS rheometer with RheoRaman module and adapted Nicolet DXR Raman microscope.

Rheometer: The Thermo Scientific HAAKE MARS rheometer can be equipped with a RheoRaman module for cone or plate geometries with a diameter up to 60 mm. This module is equipped with an integrated temperature module which can be used in a temperature range from -5°C up to 300°C. For temperatures above ambient, an active upper temperature control module is recommended (figures 1 and 2).

Raman Microscope: The Thermo Scientific Nicolet DXR Raman microscope is used to collect Raman spectra with an excitation source of a depolarized 532 nm laser with 6 mW laser power at the sample (or 785 nm laser with 100 mW power at the sample). Exposure times varied between five and thirty seconds with three replicates. A 20x ultra long working distance Olympus lens integrated in the RheoRaman module is used to collect the 180° Raman back scattering.

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Coupling: The Nicolet DXR Raman microscope is coupled with the HAAKE MARS rheometer by sending the external Raman beam from the microscope to the RheoRaman module. The 45° degree mirror placed inside the RheoRaman module directs the beam through the objective. The focus of the laser spot is controlled through the Thermo Scientific™ HAAKE™ RheoWin™ software. The rheological and Raman data collection are started simultaneously through the respective software (HAAKE Rheowin and Thermo Scientific™ OMNIC™ Software). The test results can then be exported to Excel to allow for a simultaneous display and subsequent analysis via the time stamps for each rheological data point and the corresponding spectrum (figure 3).

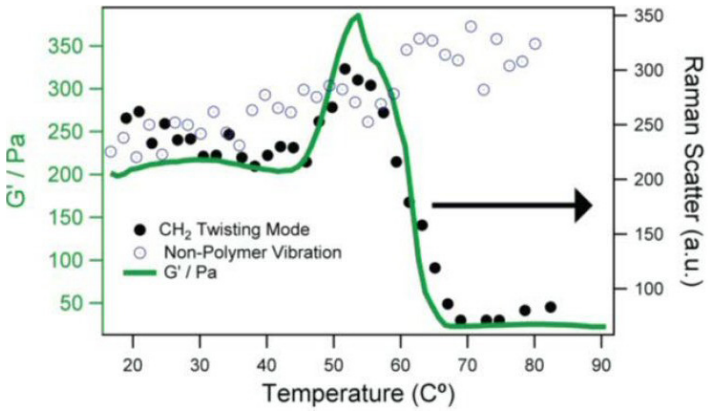

Figure 3: Example of a RheoRaman data curve: Temperature-dependency of a polystearate described with the rheological moduli (storage modulus G' in green) as well as the simultaneously measured Raman intensity (CH2 twisting mode in black). Polystearate serves as an emulsifier in the polymer emulsion sample (hand cream). The stabilizing effect is most likely due to the strong adsorption on the interface which results from its amphiphilic, polymeric structure. The non-polymer vibration represents a component in the lotion with a Raman band at 450 cm^{-1}.

Typical applications for this kind of in-situ Raman and rheological measurements are the chemical analysis of polymers which allows for deep insights of molecular changes in real-time. These molecular changes include e.g. the formation or breaking of bonds and increase/decrease in crystalinity and ultimately add specificity capabilities to rheological measurements.

Figure 2: Detail view of HAAKE MARS Rheometer with RheoRaman module and upper temperature module TM-EL-H for high temperature application.

The technique can be applied to temperature dependent phenomena of emulsions as well as to gels, pastes and any given polymeric material[1, 2].

References

1. Thermo Fisher Scientific Application Note V283, *Tracking Polymer Crystallization with the Combination of a Rheometer and a Raman Microscope*, Jan Philip Plog
2. Thermo Fisher Scientific Application Note V284, *Tracking Emulsion Stability with the Combination of a Rheometer and a Raman Microscope*, Jan Philip Plog

Ordering information

Product	Cat. No.
HAAKE MARS Rheometer 60 (or alternative MARS model). *Compressed air needed.*	379-0600
RheoRaman Module	222-2313
Lense with 20 time magnification	222-1817
Lower measuring plate with glass	222-1812
Cone C35/2° with ceramic shaft and “connect assist” (or alternative rotor)	222-2113

Necessary accessories

Nicolet DXR Raman microscope and related accessories

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

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