

# Rheology-Raman Spectroscopy: Tracking emulsion stability with the combination of a rheometer and Raman spectrometer

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## Key words

Rheology, Raman spectroscopy, Emulsions, Shelf life, Combined methods

## Introduction

As the stress-strain response of complex fluids is closely linked to changes in physical or chemical structure within the material, rheology can be most useful when combined with simultaneous measurement of physical or chemical properties affecting flow.

Chemical information including molecular conformation, bond formation or scission, and chemical composition is also critically relevant to rheological measurements. Vibrational spectroscopic tools such as Raman spectroscopy have proven to be powerful noninvasive techniques to probe chemical information of interest in a variety of soft matter systems including emulsions [1].

The benefit of simultaneous measurements is clear: many soft materials are sensitive to temperature and flow history, so simultaneous measurements minimize experimental variation.

In this application note, we present results obtained on a cosmetic emulsion in cooperation with NIST published previously [2].

The results shown can be obtained with the brand new combination of a Thermo Scientific™ HAAKE™ MARS™ rheometer with a Thermo Scientific™ iXR Raman spectrometer (Thermo Scientific™ HAAKE MARSxR RheoRaman System) as shown in Fig. 1.

## Result and discussion

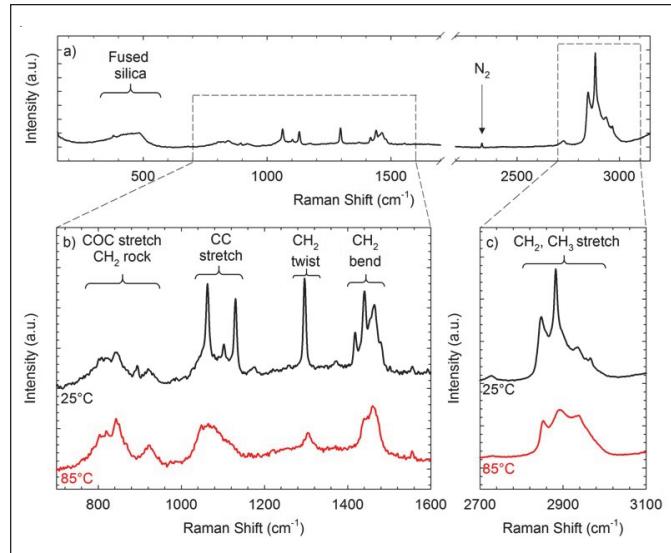
The experimental setup shown in Fig. 1 represents a novel integration of commercial instrumentation: a Raman spectrometer (Thermo Scientific iXR Raman) and rotational rheometer (HAAKE MARS) are coupled through an optically transparent base modified from the Thermo Scientific™ RheoScope Module.



Fig. 1: The Thermo Scientific HAAKE MARSxR RheoRaman system.

The cosmetic emulsion tested consists of oil droplets suspended in water and is stabilized by a mixture of surfactants. The Raman spectra of the emulsion over the spectral range at 25 °C is shown in Fig. 2a. The broad peak in the range of 200 cm<sup>-1</sup> to 600 cm<sup>-1</sup> is attributed to the fused silica window between the objective and the sample. Additionally, a small sharp band at 2330 cm<sup>-1</sup> is due to ambient nitrogen. A number of peaks are observed in the fingerprint region of 650 cm<sup>-1</sup> to 1600 cm<sup>-1</sup> and are magnified in Fig. 2b. Although a complete chemical component analysis based on the measured spectra is outside the scope of this application note, the sharp peaks in the fingerprint region appear at positions attributed to the vibrational bonds of alkyl groups C<sub>n</sub>H<sub>2n+1</sub>: the C-C symmetric and asymmetric stretch peaks at 1063 cm<sup>-1</sup> and 1130 cm<sup>-1</sup> respectively, the CH<sub>2</sub> twist mode at 1296 cm<sup>-1</sup>, and multiple modes associated with CH<sub>2</sub> bending motion at 1418 cm<sup>-1</sup>, 1441 cm<sup>-1</sup>, and 1464 cm<sup>-1</sup>.

These alkyl group modes are present due to the alkyl chains present on the stabilizers and fatty acids comprising the majority of the coconut and almond oils in the emulsion. The broad distribution of Raman bands in the range of 750 cm<sup>-1</sup> to 950 cm<sup>-1</sup> is common for C-O-C stretch modes expected for the polyethylene oxide groups present in polysorbate CH<sub>2</sub> rocking modes for fatty acids and alcohols [3]. The presence of methyl CH<sub>2</sub> groups is further evidenced by the presence of peaks in the 2600 cm<sup>-1</sup> to 3000 cm<sup>-1</sup> region (shown in greater detail in Fig. 2c) attributed to CH<sub>2</sub> and CH<sub>3</sub> stretching modes.



**Fig. 2:** (a) Raman spectra of the emulsion at room temperature over the instrument range. (b) Raman spectra of the emulsion in the range of (700 to 1600) cm<sup>-1</sup> at temperatures indicated in the figure. (c) The same spectra collected in (b) in the (2700 to 3100) cm<sup>-1</sup> region. Note that the intensity scaling varies from (b) to (c).

Upon heating, the sharp peaks due to the C-C stretch, CH<sub>2</sub> twist, and CH<sub>2</sub> bend modes decrease in intensity relative to broader peaks in the spectra as shown in Fig. 2b. A similar loss of intensity of the sharp peak at 2883 cm<sup>-1</sup> in Fig. 2c is evident at the higher temperature. The loss of intensity in these peaks corresponds to increasing conformational disorder along the alkyl chains present in the stabilizer, fatty acid, and fatty alcohol chains due to melting.

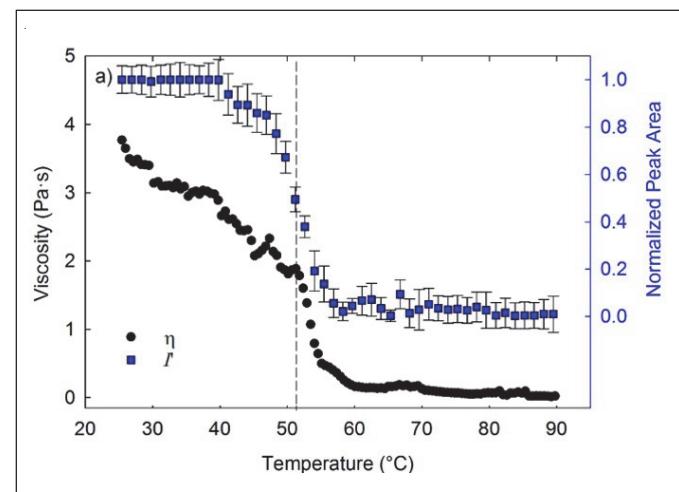
Quantitative measurement of alkyl chain measurement can be obtained by analysis of the peaks associated with the CH<sub>2</sub> twisting modes [4]. Our analysis of the spectra in the CH<sub>2</sub> twist region follows a similar protocol used to quantify *consecutive trans* and amorphous conformers in alkanes and polyethylenes [5]. The Raman spectra are fit using two Lorentzian peaks: a narrow peak of approximately 2 cm<sup>-1</sup> FWHM centered at 1296 cm<sup>-1</sup> and a broader peak of approximately 13 cm<sup>-1</sup> FWHM at 1303 cm<sup>-1</sup>. These fits are used to calculate the integrated area  $I$  of each peak. The total area under the curves in the CH<sub>2</sub> twist region  $I_{1296} + I_{1303}$  is invariant with respect to chain disorder, which provides a method to normalize the spectra. The area of the peak at 1296 cm<sup>-1</sup> normalized by the total area

$$I' = \frac{I_{1296}}{I_{1296} + I_{1303}} \quad (1)$$

then quantifies the mass fraction of chains with more than four consecutive trans sequences along the chain. The value of  $I'$  quantifies the mass fraction of ordered chains.

Simultaneous Raman and viscosity measurements of the emulsion are shown in Fig. 3 for the temperature ramp from 25 °C to 90 °C at a rate of 1 °C/min. The viscosity is measured at a steady shear rate of 30 s<sup>-1</sup> and a gap thickness of 200 µm. Lower shear rates lead to shear localization in a thin fluid layer between the rotor and the droplet phase, which is confirmed via polarized optical imaging of immobile droplets in the bulk (however, this phenomenon is beyond the scope of this manuscript.) The viscosity decreases with increasing temperature until approximately 50 °C, at which point the viscosity sharply decreases.

The temperature range of 45 °C to 55 °C where viscosity and *consecutive trans* fraction exhibit a strong temperature dependence, correlates well with the melting temperatures of stabilizers in the emulsion including cetyl alcohol and stearalkonium chloride. These simultaneous measurements allow for clear correlation of steady shear viscosity with conformational information.



**Fig. 3:** Viscosity and normalized peak area  $I'$  as a function of temperature for the emulsion.

## Summary

With the Thermo Scientific HAAKE MARSXR RheoRaman System, simultaneous measurements of rheological properties and Raman-active molecular vibrations are possible. The emulsion example shown in this work, highlights the applicability of the MARSXR to characterize structural and conformational changes directly related to the rheological response of the material. Since all measurements are performed simultaneously, experimental conditions such as temperature and flow history are identical for Raman and rheology. In addition, the laser excitation and collection path can be equipped with optical elements for polarized Raman measurements. Based on the possibilities for direct correlation between chemical, structural, and mechanical properties, we expect the MARSXR to be critically relevant to both academic and industrial interests.

## References

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