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Rheology-Raman spectroscopy:
Tracking emulsion stability

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Figure 1. The HAAKE MARS Rheometer and DXR3 Flex Raman Spectrometer comprise the Rheo-Raman system.

Introduction

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

Chemical information, which includes molecular conformation, bond formation, scission, and chemical composition, is also critical for rheological measurements. Vibrational spectroscopic tools such as Raman spectroscopy have been proven powerful, with noninvasive techniques for probing chemical information of interest in a variety of soft matter systems, including emulsions.[1]

The benefit is clear: simultaneous measurements can minimize experimental variation in soft materials that are sensitive to temperature and flow history.

This application note presents results that were obtained on a cosmetic emulsion in cooperation with the National Institutes of Standards and Technology (NIST) and that were published previously.[2]

The results in this application note can be obtained with the combination of the Thermo Scientific™ HAAKE™ MARS™ Rheometer with the Thermo Scientific DXR3 Flex Raman Spectrometer on the HAAKE MARS Rheo-Raman Module, as shown in Figure 1.

Result and discussion

The experimental setup shown in Figure 1 represents a novel integration of commercial instrumentation: a Raman spectrometer (DXR3 Flex) and rotational rheometer (HAAKE MARS) are coupled through an optically transparent base modified from the Thermo Scientific RheoScope Module for the HAAKE MARS Rheometer.

The cosmetic emulsion tested consists of oil droplets suspended in water and is stabilized by a mixture of surfactants. In Figure 2a, the Raman spectra of the emulsion over the spectral range of 25°C is shown. The broad peak in the range of 200 cm^{-1} to 600 cm^{-1} is attributed to the fused silica window between the objective and the sample. Additionally, a small sharp band at 2,330 cm^{-1} is due to ambient nitrogen. A number of peaks are observed in the fingerprint region of 650 cm^{-1} to 1,600 cm^{-1}, which are magnified in Figure 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_nH_{2n+1}: the C–C symmetric and asymmetric stretch peaks at 1,063 cm^{-1} and 1,130 cm^{-1} respectively, the CH_2 twist mode at 1,296 cm^{-1}, and multiple modes associated with CH_2 bending motion at 1,418 cm^{-1}, 1,441 cm^{-1}, and 1,464 cm^{-1}.

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These alkyl group modes are present due to the alkyl chains present on the stabilizers and fatty acids of the coconut and almond oils in the emulsion. The broad distribution of Raman bands in the range of 750 cm⁻¹ to 950 cm⁻¹ is commonly found in the expected C–O–C stretch modes of polyethylene oxide groups present in polysorbate CH_2 rocking modes for fatty acids and alcohols.[3] The presence of methyl CH_2 groups is further evidenced by the presence of peaks in the 2,600 cm⁻¹ to 3,000 cm⁻¹ region (shown in greater detail in Figure 2c) attributed to CH_2 and CH_3 stretching modes.
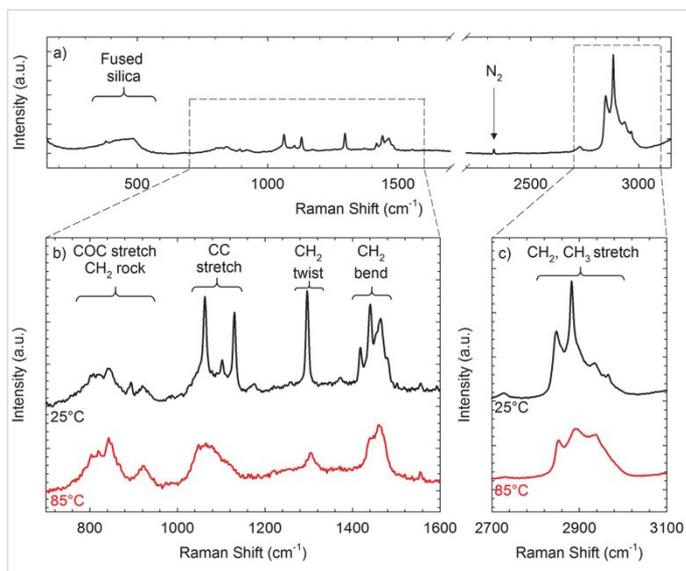

Figure 2. (a) Raman spectra of the emulsion at room temperature over the instrument range. (b) Raman spectra of the emulsion in the range of (700 to 1,600) cm⁻¹ at (c) temperatures. The same spectra collected in (b) in the (2,700 to 3,100) cm⁻¹ region. Note that the intensity scaling varies between (b) and (c) data.

When heated, due to the C–C stretch, CH_2 twist, and CH_2 bend modes, the sharp peaks decrease in intensity relative to broader peaks in the spectra as shown in Figure 2b. Figure 2c shows a similar loss of intensity of the sharp peak at 2,883 cm⁻¹ 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.

$$I' = \frac{I_{1,296}}{I_{1,296} + I_{1,303}}$$

The value of *I'* formula.

Quantitative alkyl chain measurement can be obtained through analysis of the peaks associated with the CH_2 twisting modes.[4] Our analysis of the spectra in the CH_2 twist region follows a protocol similar to that 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⁻¹ full width at half maximum (FWHM) centered at 1,296 cm⁻¹ and a broader peak of approximately 13 cm⁻¹ FWHM at 1,303 cm⁻¹. These fits are used to calculate the integrated area I of each peak. The total area under the curves in the CH_2 twist region $I_{1,296} + I_{1,303}$ is invariant with respect to chain disorder, which provides a method to normalize the spectra. The area of the peak at 1,296 cm⁻¹ normalized by the total area 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 Figure 3 for the temperature ramp from 25°C to 90°C at a rate of 1°C/minute. The viscosity is measured at a steady shear rate of 30 s⁻¹ 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, which is a phenomenon 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.
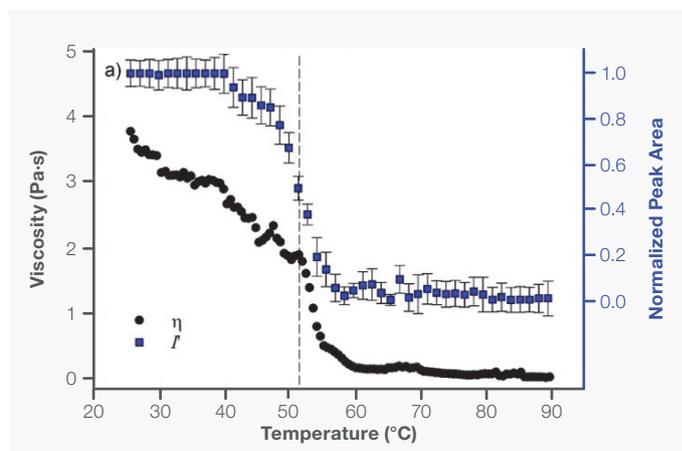

Figure 3. Viscosity and normalized peak area *I'* as a function of temperature for the emulsion.

Summary

With the Rheo-Raman 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 Rheo-Raman system 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 Rheo-Raman system to be critically relevant to both academic and industrial interests.

References

1. M. Amer, Raman spectroscopy for soft matter applications (John Wiley &Sons, 2009).
2. A. P. Kotula et. al., Review of Scientific Instruments 87, 105105 (2016).
3. J. De Gelder, K. De Gussem, P. Vandenabeele and L. Moens, J. Raman Spectrosc. 38, (2007).
4. K. G. Brown, E. Bicknell-Brown and M. Ladjadj, J. Phys. Chem. 91, (1987).
5. K. B. Migler, A. P. Kotula and A. R. Hight Walker, Macromolecules 48, (2015).

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