APPLICATION NOTE

Rheology-Raman spectroscopy: Tracking emulsion stability with the combination of a rheometer and a Raman microscope

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Key words

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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].

Optical microscopy in addition provides a direct measure of structure within many samples of interest and has been used successfully in the past in combination with rheology[2].

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 with the brand new combination of a Thermo Scientific™ HAAKE™ MARS™ rheometer with a Thermo Scientific™ DXR™ Raman spectrometer as shown in figure 1.

Figure 1: Combination of a Thermo Scientific HAAKE MARS with a Thermo Scientific DXR Raman Microscope.

Results and discussion

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

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 figure 2a. 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 2330 cm^{-1} is due to ambient nitrogen. A number of peaks are observed in the fingerprint region of 650 cm^{-1} to 1600 cm^{-1} and 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 1063 cm^{-1} and

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1130 cm⁻¹ respectively, the CH_2 twist mode at 1296 cm⁻¹, and multiple modes associated with CH_2 bending motion at 1418 cm⁻¹, 1441 cm⁻¹, and 1464 cm⁻¹.

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⁻¹ to 950 cm⁻¹ is common for C-O-C stretch modes expected for the polyethylene oxide groups present in polysorbate CH2 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 2600 cm⁻¹ to 3000 cm⁻¹ region (shown in greater detail in Figure 2c) attributed to CH_2 and CH_3 stretching modes.
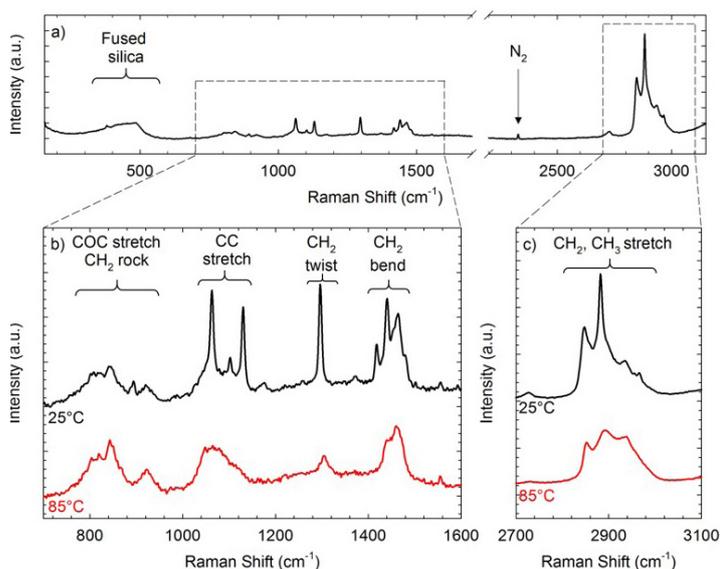

Figure 2: (a) Raman spectra of the emulsion at room temperature over the instrument range. (b) Raman spectra of the emulsion in the range of (700 to 1600) cm−1 at temperatures indicated in the figure. (c) The same spectra collected in (b) in the (2700 to 3100) cm−1 region. Note that the intensity scaling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

Upon heating, the sharp peaks due to the C-C stretch, CH_2 twist, and CH_2 bend modes decrease in intensity relative to broader peaks in the spectra as shown in figure 2b. A similar loss of intensity of the sharp peak at 2883 cm⁻¹ in figure 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_2 twisting modes[4]. Our analysis of the spectra in the CH_2 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⁻¹ FWHM centered at 1296 cm⁻¹ and a broader peak of approximately 13 cm⁻¹ FWHM at 1303 cm⁻¹. These fits are used to calculate the integrated area I of each peak. The total area under the curves in the CH2 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⁻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.

$$I' = \frac{I_{1296}}{I_{1296} + I_{1303}} \tag{1}$$

Simultaneous Raman, viscosity, and polarized optical 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/min. 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 (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. Concomitant measurements of and the average pixel intensity from polarized optical images show a similar decrease at 50 °C, indicating a loss of consecutive trans sequences and birefringence, respectively. Figure 3c shows images of the emulsion when birefringent droplets of radii on the order of 10 μm are present in the sample at room temperature. At higher temperatures birefringence is no longer observed.
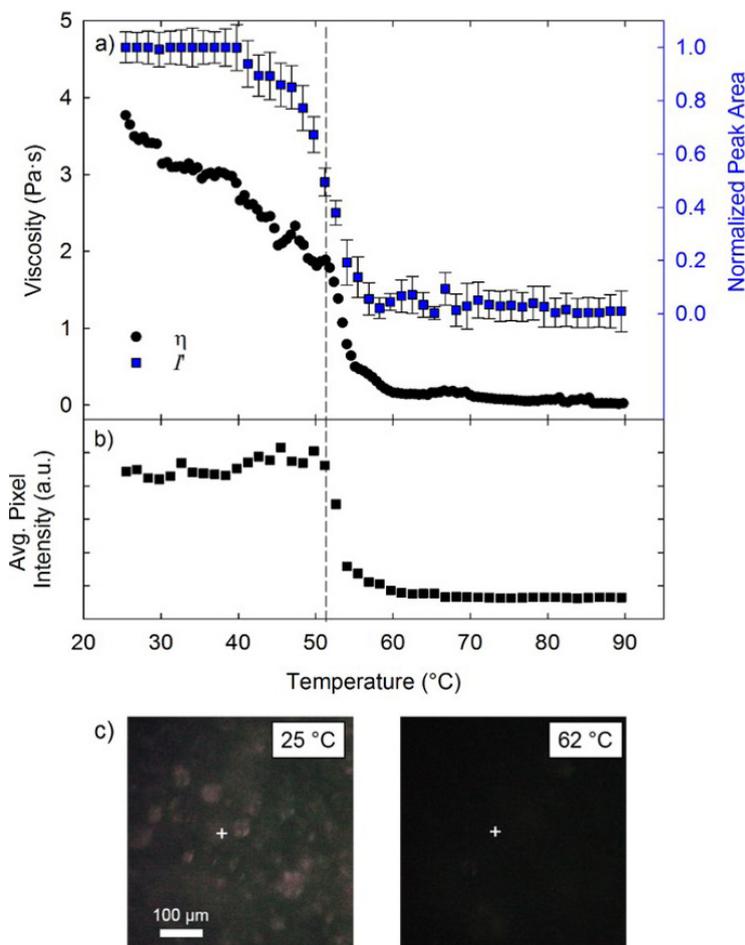

Figure 3: a) Viscosity and normalized peak area I' as a function of temperature for the emulsion. b) Average pixel intensity during viscosity and Raman measurement versus temperature. The vertical line indicates the initial decrease in average pixel intensity. c) Images of the emulsion at different temperatures. The white cross indicates the position of the laser spot for Raman spectroscopy. Images in (c) have been digitally enhanced to increase contrast.

The temperature range of 45 °C to 55 °C where viscosity, consecutive trans fraction, and birefringence 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 and optical information.

Summary

We have developed a RheoRaman microscope for simultaneous measurement of rheological properties, optical structure, and Raman-active molecular vibrations. The emulsion example shown in this work highlights the applicability of the RheoRaman microscope 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, rheology, and microscopy. 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 RheoRaman microscope to be critically relevant to both academic and industrial interests.

Literature

1. M. Amer, Raman spectroscopy for soft matter applications (John Wiley & Sons, 2009).

2. K. Matsuzaka and T. Hashimoto, Rev. Sci. Instrum. **70**, (1999).

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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