

Monitoring Emulsions Morphology under Shear via Simultaneous Rheometry and In-situ FT-IR Spectroscopy

Jan P. Plog¹, Kiyoji Sugimoto², and Manfred Feustel³

¹ Thermo Fisher Scientific, Karlsruhe, Germany.

² Thermo Fisher Scientific, Yokohama, Japan.

³ Resultec, Illerkirchberg, Germany.

ABSTRACT

Simultaneous rheometry and FTIR spectroscopy proves to be a useful tool in understanding emulsion instabilities on the microscopic scale. In this contribution, we want to present some results on the dynamics of molecular organization of an emulsion under shear.

INTRODUCTION

Emulsions are of wide interest in food, pharmaceutical, health care and cosmetics industry. They typically consist of at least two liquid phases, surfactant agents and stabilizers. Emulsions exhibit complex rheology, making it difficult to understand flow phenomena on a microscopic level.

A common technique utilized to analyze the behavior of emulsions under shear is light microscopy. However, emulsions showing droplet distributions with droplets on the submicron scale cannot be visualized using light microscopy because of given resolution constraints. Other limiting factor of light microscopy include diffraction arising from narrowly distributed droplet sizes as well as when the diffractive indices of stationary and dispersed phase are very similar.

In such cases, the Thermo Scientific HAAKE MARS rheometer combined with the Rheonaut module, provides simultaneous rheometry and in-situ FTIR spectroscopy under shear and offers a

versatile tool for efficient and comprehensive emulsion research and stability testing.

MATERIALS AND METHODS

For this study, as model substances, three commercially available hand cream emulsions with high volume fractions of oil in water containing submicron droplets were supplied by a manufacturer of cosmetics. The samples varied with respect to their hydrocarbon composition only. No further sample preparation was required.

The patented Rheonaut module couples a standard FT-IR spectrometer with side port (here: Thermo Scientific NICOLET iS10) to the Thermo Scientific HAAKE MARS rheometer.

The lower plate of the rheometer is temperature controlled (Peltier or electrical) and features a monolithic diamond element that serves as the ATR (attenuated total reflection) sensor, offering a single internal reflection. Compared to standard infrared transmission spectroscopy or specular reflection spectroscopy techniques, the sample thickness can thus be adjusted to the rheological needs and is independent from the infrared spectroscopy requirements.

The operation is managed by the HAAKE RheoWin software providing full control over temperature settings, horizontal positioning of the lower plate, and the

communication with the FTIR spectrometer software for synchronous data acquisition.

Steady shear flow experiments were carried out using a cone/plate measuring geometry with 20 mm diameter and a cone angle of 2°. Gap setting was 0,1 mm. All samples were tested in CR (controlled rate) mode from 0.5 up to 500 s⁻¹. The temperature was set to 25.0 ± 0.1 °C. The infrared spectral range was 400 cm⁻¹ to 4000 cm⁻¹ with a spectral resolution of 4 cm⁻¹. Each spectrum consists of 8 co-added scans.

A complete data set was produced for each sample, consisting of 18 rheological data points and 18 related (simultaneously collected) FT-IR spectra.

RESULTS AND DISCUSSION

Figure 1 displays the dynamic shear viscosity plotted against shear rate for the three samples #1, #2, and #3. As typical for highly concentrated emulsions, the materials show a decreasing viscosity with increasing shear rate (shear thinning or pseudoplastic).

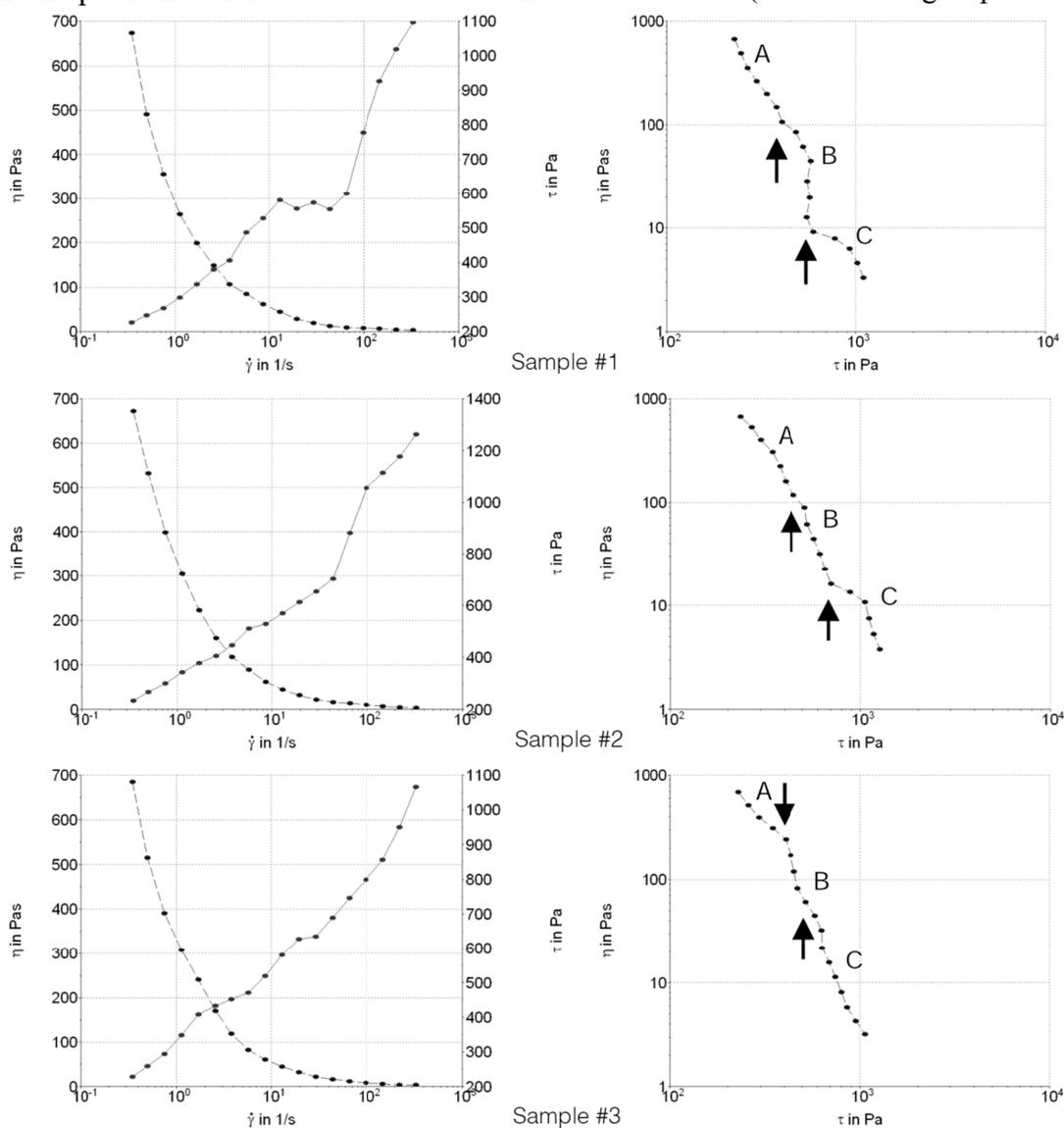


Figure 1. Left column: Viscosity η and stress τ versus shear rate. Right column: Viscosity η versus stress τ .

A closer look, however, reveals a step-like shear thinning behavior as can be seen in the right graphs of figure 1 which display the viscosity plotted double-logarithmically against shear stress.

Such a viscosity behavior has been investigated amongst others by Saiki et al.¹. Based on detailed rheological experiments, the proposed figurative model is a droplet distribution profile which changes with the applied stress. Whereas at very low shear the droplets are distributed homogeneously, ambiguous layers (or clusters) of droplets are formed at moderate shear causing slight segregation in droplet population and at higher shear discrete layers are formed. Another approach² proposes a figurative model showing a droplet deformation and stretching by the applied shear, leading to droplet rupturing and recombination through coalescence at higher shear stresses.

Simultaneously applied FT-IR spectroscopy enables a more sophisticated molecular insight and deeper understanding. Figure 2 displays a typical FTIR sample spectrum. The broad absorption band at 3354 cm^{-1} relates to the aqueous phase of the sample whereas the band at 2922 cm^{-1} relates to the organic phase.

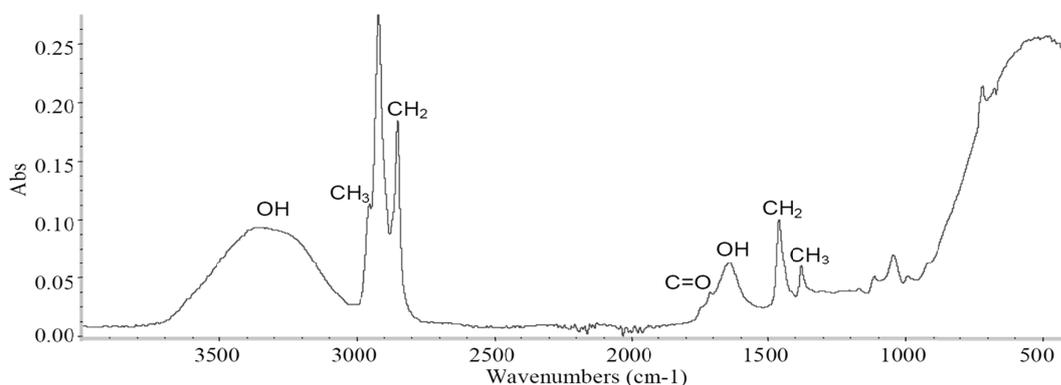


Figure 2. A typical FT-IR absorbance spectrum with band assignments of the investigated samples.

The sample changes with shear get easily traceable by calculating the absorption ratio ($3354\text{ cm}^{-1}/2922\text{ cm}^{-1}$) from each spectrum and plotting the results against the experimental procedure (figure 3).

The change of the infrared absorption ratios in figure 3 reveals a concentration gradient within the samples. Close to the ATR sensor are sample layers at which the organic phase is enriched in relation to the aqueous phase.

As the experiment goes on, the enrichments dissolve again. Because the ATR sensor area dimensions are several orders of magnitude larger than the submicron droplets of the organic phase, neither droplet deformation and stretching nor coalescence is an object since they do not evoke a concentration gradient within a sample.

The shear thinning behavior of the investigated emulsion samples is initially controlled by perturbation and breakdown of complex droplet structures which lead to the formation of droplet layers causing flatter shear viscosity curve regions. With further increasing shear rates, however, a self-healing process is observed. The droplet structure is rearranged and hence the layers are dissolved, as the FT-IR spectra show.

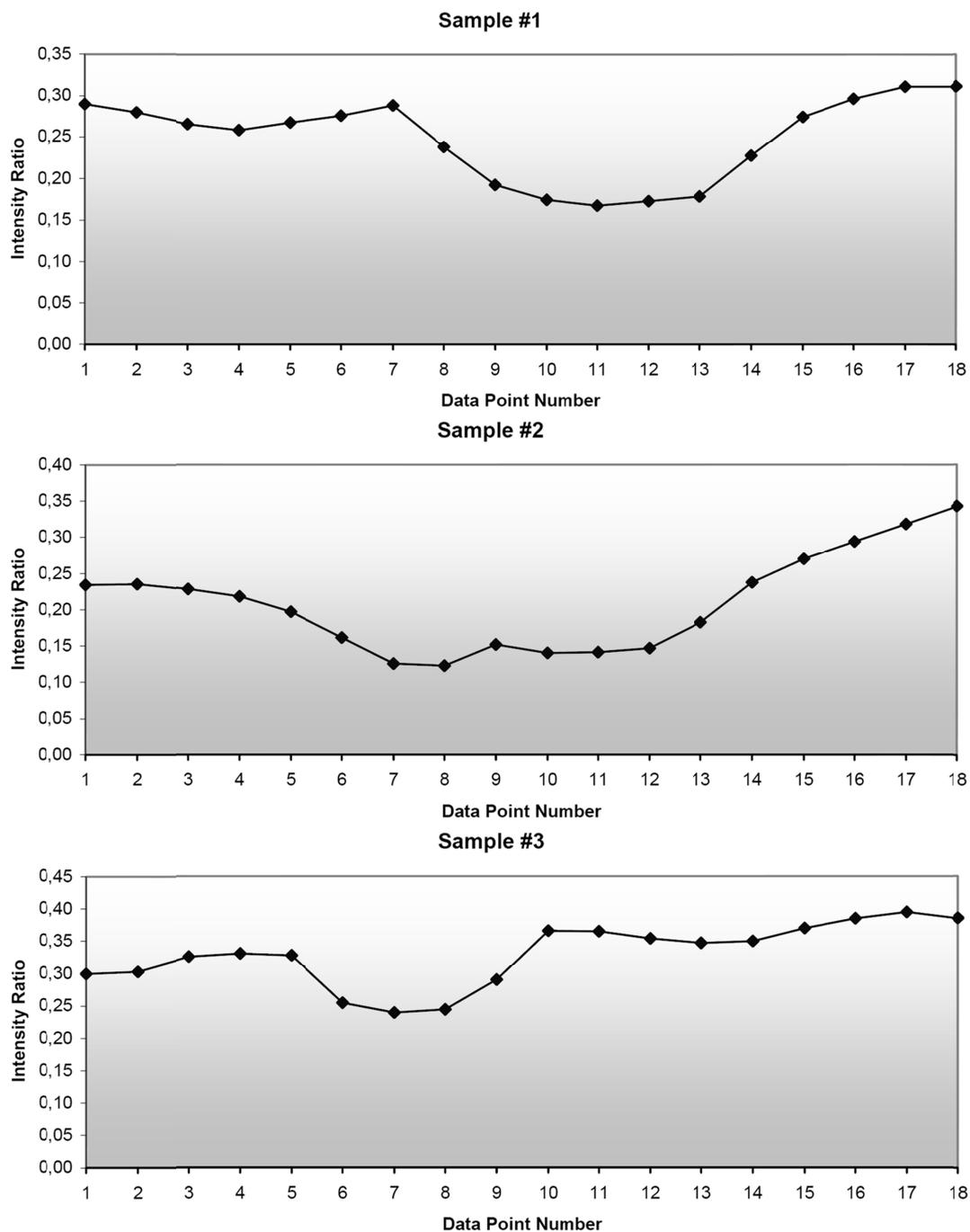


Figure 3. Absorption ratio ($3354\text{ cm}^{-1}/2922\text{ cm}^{-1}$) from each FT-IR spectrum plotted against the data point number.

CONCLUSIONS

Rheometry and FT-IR spectroscopy have been applied simultaneously on model emulsions (3 commercially available hand creams) to study the structure development of emulsions under shear stress.

The results prove an ability of the investigated emulsions to repair the damage caused by mechanical impacts over time.

The Rheonaut offers a new approach to rheology by providing molecular insight and can thus reveal information about molecular organization and dynamics under deformational flow.

The exact knowledge of the interacting fundamental structuring mechanisms creates the basis for an optimized tuning of technical, process engineering, and material parameters with respect to a functionally optimized structuring of emulsion systems.

REFERENCES

1. Saiki, Y and Prestidge, C.A., Korea-Australia Rheol. J. 17 (2005), 191-198
2. Mason, T.G., Curr. Opin. Colloid Interface Sci. 4 (1999), 231-238