

Rheology-Raman Spectroscopy: Tracking Molecular Structures as a Function of Deformation and Temperature

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Overview

Purpose: Rheometer with a Raman spectrometer to study materials' phase transition behavior.

Methods: In this contribution we present results obtained by coupling the Thermo Scientific™ HAAKE™ MARS III rheometer with a Thermo Scientific™ DXR™ Raman microscope.

Results: Details of this unique setup as well as selected results on temperature induced crystallization will be presented.

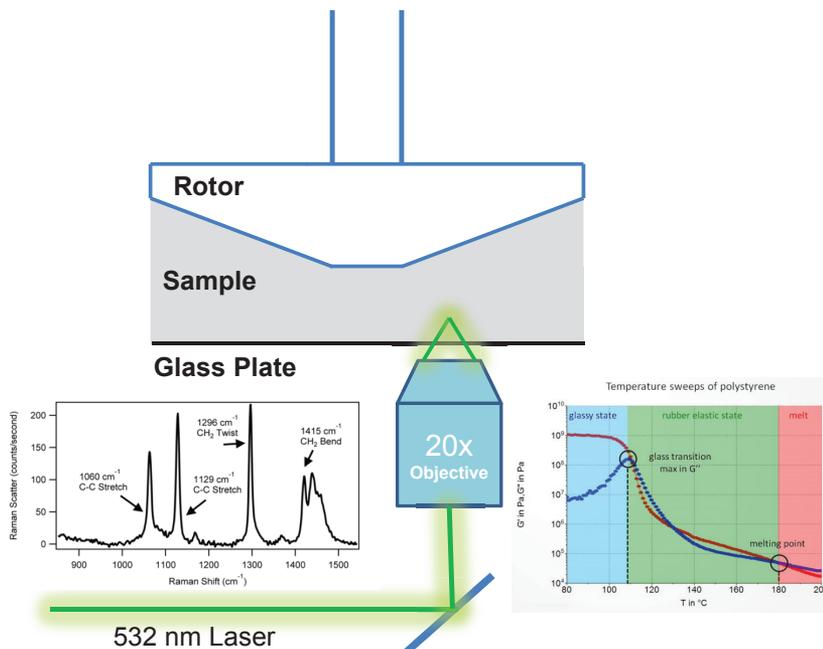
Introduction

Rheology is the analytical method of choice to correlate the absolute flow and deformation characteristics of a given product with its behavior towards a certain processing or application step. However, rheology only yields answers on the bulk of the investigated sample towards certain absolute shear or deformation conditions. It does not give any insights into what is occurring on the molecular level during a certain processing step.

Raman spectroscopy has proven to be a powerful, effective and non-invasive method for chemical analysis. Coupling a rheometer with a Raman spectrometer provides information on both the molecular reaction kinetics and viscoelastic properties as shown in **Figure 1**. This is extremely useful for studying the crystallization behavior of polymers during processing. It can also provide *in-situ* characterization and monitoring which can be challenging when working with on-line techniques as only relative flow fields are characterized.

The coupling not only increases the information content from a single measurement, but also enables a direct comparison between rheological properties and their underlying chemical changes associated with shifts in the viscoelastic profile.

FIGURE 1. Experimental setup enabling the simultaneous collection of the rheological and Raman spectroscopy data.



Methods

Sample Preparation

Polymer emulsions containing polystearate were obtained from a commercial hand lotion (Man Lotion, Shafer, MN). The polystearate structure was confirmed using a library search within Thermo Scientific™ OMNIC™ software.

Polymer results were obtained from polyethylene and polypropylene discs.

Raman Spectroscopy

The DXR Raman microscope was used to collect Raman spectra with an excitation source of a depolarized 532 nm laser with 6 mW laser power at the sample. Exposure times varied between five and thirty seconds with three replicates. The 20x ultra long working distance (ULWD) Olympus™ objective of a Thermo Scientific™ RheoScope module was used to collect the 180° Raman back scattering.

Rheology

A HAAKE MARS III rheometer was used for all rheological measurements. The rheometer was outfitted with a RheoScope module, a picture of the sample area can be seen in **Figure 2**.

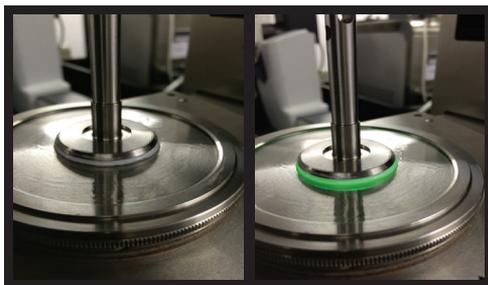
Coupling

The DXR Raman microscope was coupled with the MARS rheometer by sending the external Raman beam from the microscope to the RheoScope module. The 45° degree mirror placed inside the RheoScope module directs the beam through the 20x ULWD objective. The focus of the laser spot is controlled through the Thermo Scientific™ RheoWin™ software. The rheological and Raman data collection was started simultaneously through their respective software.

Data Analysis

OMNIC and RheoWin software were used for data acquisition. Igor Pro 6.3 software was used for further processing the rheology and Raman data.

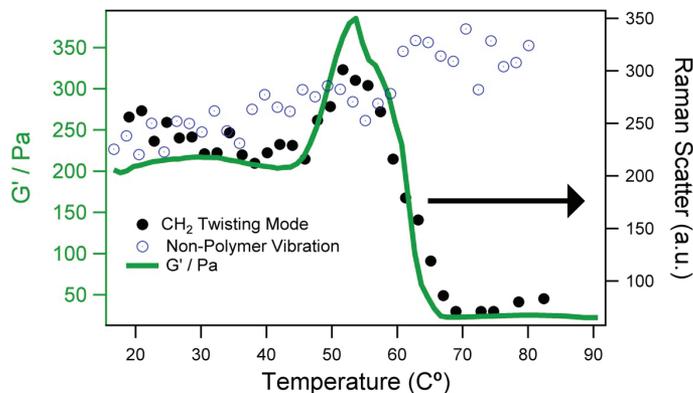
FIGURE 2. Rheometer plate with a commercial hand lotion (left) and the hand lotion with 532 nm laser radiation (right).



Results

Rheological and Raman setup for *in-situ* measurements

FIGURE 3. Plot illustrating polystearate storage modulus (G') and Raman intensity (CH_2 twisting mode). 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} .

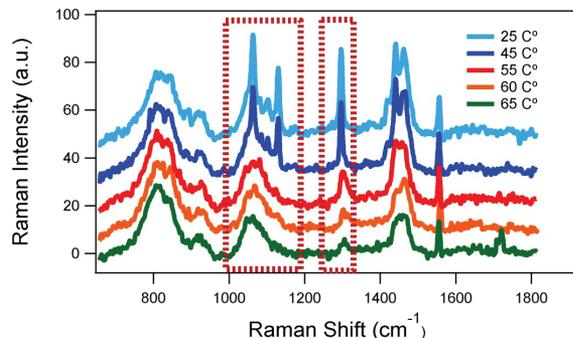


Viscoelastic Properties as a Function of Temperature

Many materials are stored at one temperature, e.g., 25 °C, but applied at body temperature, e.g., 37 °C. At 37 °C, the hand cream sample shows higher modulus values with less elasticity (**Figure 3**). As a result, this sample will require more force to

apply but will adhere to the skin better and provide a softer feel. As the temperature approaches 50 °C, the sample's structure transitions from a crystalline phase to an amorphous phase where the material flows like a liquid. This would result in the product being unusable if the container was left in a warm environment (i.e. shipping containers).

FIGURE 4. Individual Raman spectra of polystearate as the temperature increases. The polymer emulsion transitions from the crystalline state to amorphous. The intra-chain consecutive-trans structures in the C-C (1060-1129cm⁻¹) and CH₂ twist (1296 cm⁻¹) are representative of crystalline vibrations (red box).



The *in situ* Raman spectroscopy data is complementary to the viscoelasticity data because it gives insight to the chemical behavior of the polymer material (Figure 4). The CH₂ Raman band is directly related to the crystallinity of the material. A decrease in peak intensity indicates the formation of more amorphous structure. Other components in the lotion or non-polymer vibrations do not show this change in intensity as it is not changing crystalline phases.

FIGURE 5. Plot showing changes in the polystearate (PS) Raman intensity (left). The Raman peak intensity of molecular vibrations that do not undergo change during the temperature sweep (right). The cross over point of the plot on the right represents the phase change of the material. The Raman intensity of the N₂ was divided by four for clarity purposes.

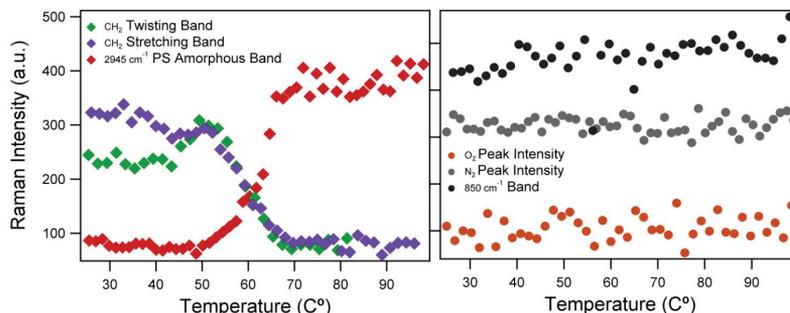
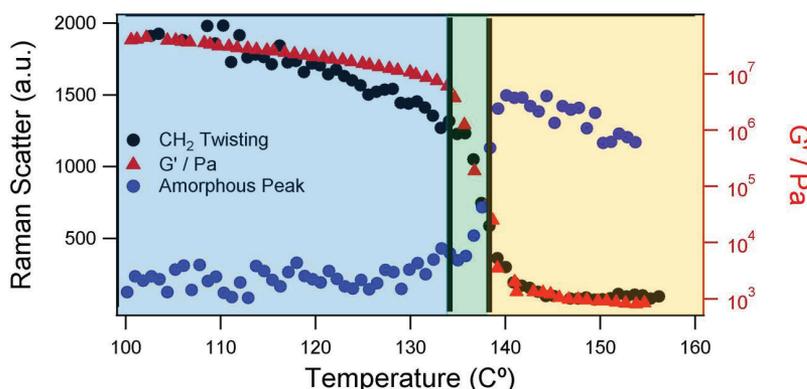


FIGURE 6. A polyethylene disc was analyzed during a temperature sweep from 100° to 155° C degrees while measuring G' and the Raman spectra. The Raman scatter was calculated from the CH₂ twist mode (1296 cm⁻¹). The melt, transition and solid phases are highlighted in blue, green and yellow, respectively.

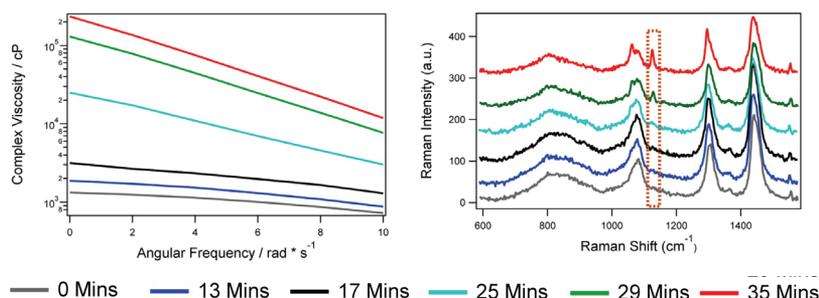


The specificity advantage of Raman spectroscopy is demonstrated in **Figure 5**. Raman bands that are representative of crystalline and amorphous structure show a clear trend over the 25° to 100° C degree temperature sweep. This information complements rheology data by showing structural changes that directly impact the rheological measurements. The 850 cm^{-1} band corresponds to a component in the hand cream other than polystearate. This component is not effected by crystallization. N_2 and O_2 molecular vibrations serve as an internal standard as these peaks do not contribute to the storage modulus measurements.

Viscoelastic Properties of Polymer Discs

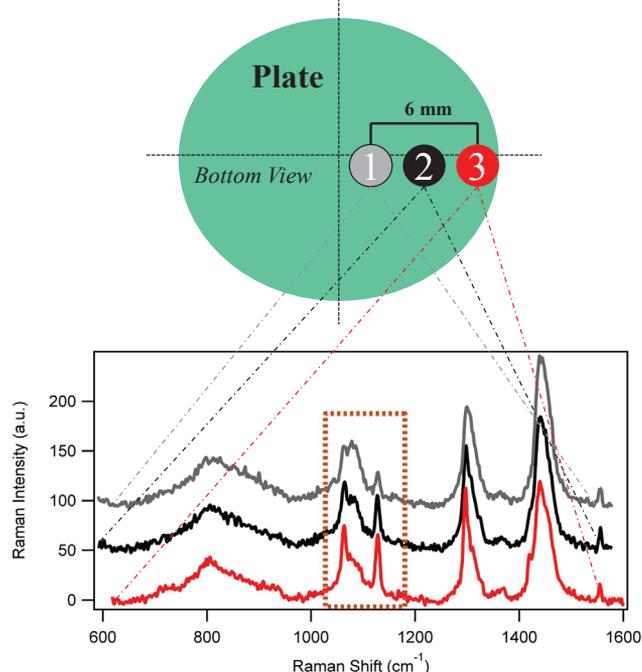
A polyethylene disc was analyzed using a temperature sweep from 100° to 155° C degrees in **Figure 6**. The relationship between the Raman spectroscopy data and storage modulus correlate and show the melt, transition and solid phases. An amorphous peak at 1089 cm^{-1} starts to increase near the glass transition temperature and has a cross over point with the crystalline peak to designate the transition phase.

FIGURE 7. Polyethylene frequency sweeps were recorded over a 35 minute period near the glass transition temperature. The Raman spectra show the change in crystallinity and can be correlated with the complex viscosity.



The coupling of rheology and Raman was used to reveal structural changes in polymer discs during frequency sweeps. **Figure 7** represents a shear thinning behavior of a polyethylene disc as the frequency sweeps were recorded. The frequency curve and Raman spectra at 29 minutes show the materials transition from amorphous to crystalline. The Raman spectra were collected every three minutes but only six plots were shown for clarity.

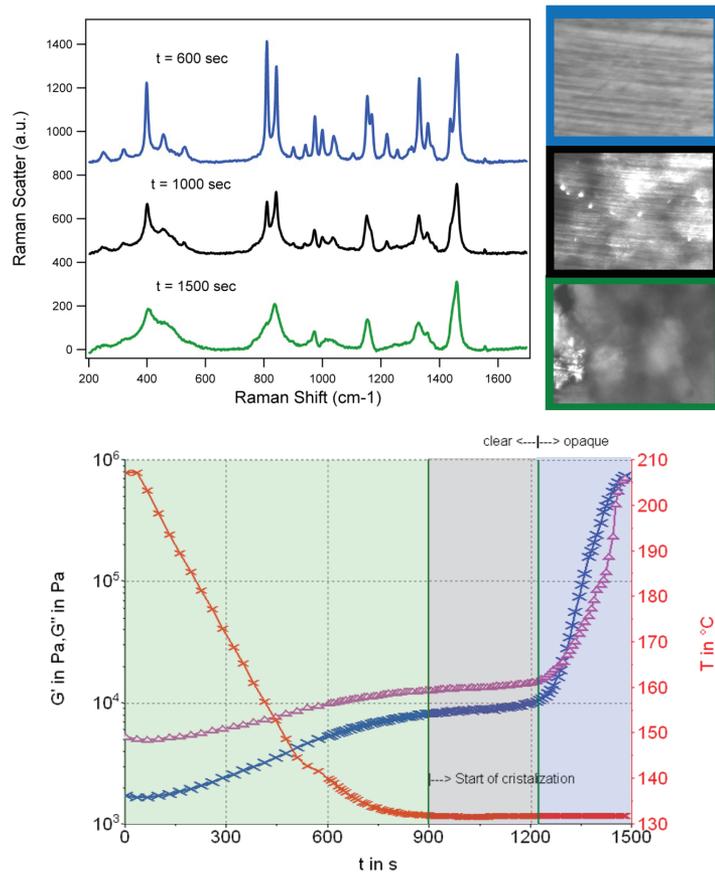
FIGURE 8. Illustration showing the bottom of the rotor plate where three Raman spectra were acquired. The microscope objective can be moved radially to measure multiple areas. The Raman spectra were collected in these three areas during a frequency sweep at 35 minutes to investigate the crystallinity of polyethylene near the edge of the plate.



The Rheology-Raman system can also acquire Raman spectroscopy measurements at different radial positions underneath the rheology plate as shown in **Figure 8**. This can give insight into what is occurring chemically at different positions along the rotor. The Raman spectra show there are differences in crystallinity going from the outside of the motor to the inside. The orange box highlights the differences in crystallinity between three evenly spaced points under the rheology plate.

The combination of rheological properties, chemical information and optical images during crystallization can be valuable and is demonstrated in **Figure 9**. The optical images and Raman spectra of polypropylene during the melt, transition and solid phases are shown. The rheological data shows these phases as a function of temperature and storage modulus.

FIGURE 9. Optical images of polypropylene were recorded at various temperatures (top). These images can be associated with Raman and viscoelastic measurements to provide more insight on the materials phase change.



Conclusion

The data presented shows how *in situ* Raman and rheological measurements can be used for the chemical analysis of polymers. The ability to measure *in situ* allows for deep insights of molecular changes in real-time. These molecular changes include the formation or breaking of bonds, decrease in crystalline peaks and ultimately add specificity capabilities to rheological measurements.

Furthermore the technique will allow for process control during manufacturing of polymer emulsions and discs. The application is not limited to polymer emulsions in cosmetics but can also be applied to gels and epoxies.

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