

Rheology-Raman spectroscopy: Tracking polymer crystallization

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Introduction

This application note presents the use of a coupled rheometer and Raman spectrometer for obtaining comprehensive insights into a material's behavior.

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

Raman spectroscopy has shown its ability as a powerful, effective and noninvasive method for chemical analysis. Coupling a rheometer with a Raman spectrometer provides direct information about the molecular structure and the mechanical properties. This is extremely useful for studying the crystallization behavior of polymer melts during processing. It can also provide insight for *in situ* characterization and monitoring, which can be challenging when working with on-line techniques where only relative flow fields are characterized.

In this application note, we present results obtained on a high-density polyethylene (HDPE) melt in cooperation with National Institute of Standards and Technology (NIST), published previously.¹ The results were obtained with the new combination of Thermo Scientific™ components: a HAAKE™ MARS™ Rheometer coupled to a DXR3 Flex Raman Spectrometer, as shown in Figure 1.



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

Result and discussion

Melting and crystallization are two common phase transitions that are critical to the flow properties of various complex fluids. These temperature-sensitive transitions are often indicated via changes in molecular conformation, while optical measurements provide direct observation of structural characteristics. However, measurements performed on separate instruments are often challenging to correlate due to variations between samples, processing history, and temperature control. To demonstrate the capabilities of the Rheo-Raman Module for HAAKE MARS Rheometers, we provide simultaneous Raman and rheological measurements on HDPE (SRM 1475, National Institute of Standards and Technology, Gaithersburg, MD) during crystallization.

The experimental setup shown in Figure 1 represents a novel integration of commercial instrumentation: a Raman spectrometer (DXR3 Flex Raman Spectrometer) and rotational rheometer (HAAKE MARS) are coupled through an optically transparent base modified from the Thermo Scientific RheoScope Module. To monitor crystallinity, look at the Raman spectra for HDPE in Figure 2.

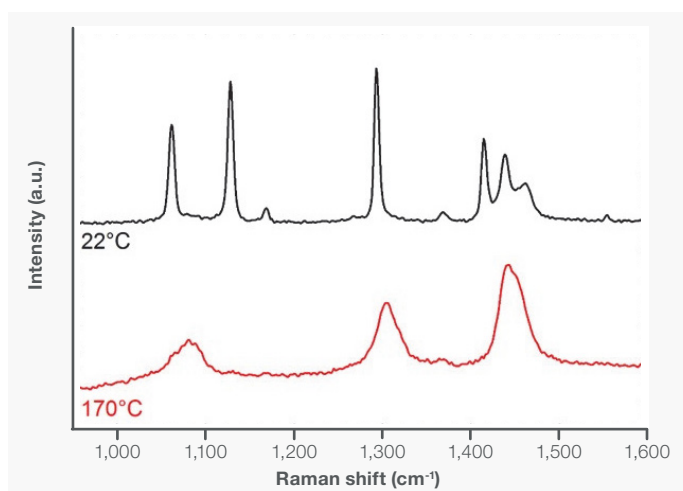


Figure 2. Raman spectra of polyethylene (PE) at temperatures corresponding to the semi-crystalline state (22°C) and the amorphous state (170°C).

The spectrum at room temperature shows sharp peaks corresponding to C–C stretch, CH₂ twisting, and CH₂ bending regions. At 170°C, HDPE is in the melt state, and the sharp peaks are replaced with broader spectral features.

The Raman spectra of HDPE can be analyzed to quantify the crystallinity of the sample. Specifically, the area under the peak at 1416 cm⁻¹ in the HDPE spectra is directly proportional to the mass fraction of crystallinity in the sample. In order to calculate the crystallinity, the integrated peak area I_{1416} is normalized by the total area under the peaks in the CH₂ twisting region and a scale factor N_c :

$$a_{cr} = \frac{I_{1,416}}{(I_{1,296} + I_{1,303}) N_c}$$

The value of I' formula.

The scale factor N_c is a ratio of $I_{1416}/(I_{1296} + I_{1303})$ for an HDPE sample to the crystallinity of the same HDPE sample when measured via differential scanning calorimetry (DSC).

For HDPE on the Rheo-Raman Module, the measured scale factor is $N_c = 0.80 \pm 0.03$. Although this is larger than the calculated values of N_c from our prior measurements², the Raman peak intensities of HDPE (and therefore the scale factor values) are strongly dependent upon the polarization state of the incoming and collected light, as well as the scattering angle.³ The crystallinity for the room temperature sample in Figure 2 is $(73 \pm 4)\%$ which agrees with the crystallinity value of $(74 \pm 5)\%$ measured via DSC.

The structure-property relationships during polymer crystallization are of critical interest and can be studied simultaneously using the Rheo-Raman Module. An HDPE sample of thickness 750 μm was heated for 5 minutes at 155°C, cooled at 10°C/minute to 134°C, and then cooled at a slower rate of 2°C/minute to 124°C and held at temperature to crystallize.

Figure 3 shows simultaneous rheological and Raman measurements during HDPE crystallization. The complex modulus is measured during small-amplitude oscillatory shear using a fixed-strain amplitude of 0.01 and oscillation frequency of 2π radians/second. Figure 3 shows that early times in the crystallization process are characterized by $G' < G''$, but over time a crossover occurs in the modulus as the values of G' and G'' increase over 2 orders of magnitude. The plateau in G' and G'' at later times indicates the cessation of crystallization, as measured by the complex modulus.

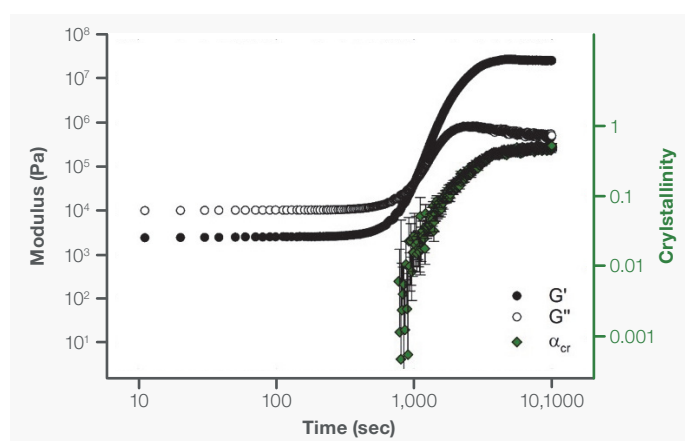


Figure 3. Complex modulus and crystallinity of PE versus time during isothermal crystallization at 124°C.

Raman spectra measured during the crystallization process are used to calculate the crystallinity of the sample via equation 1.

Figure 3 shows the instantaneous mass fraction of crystalline material, which first exceeds the measurement noise at approximately 800 seconds and then increases over time. The appearance and increase in crystallinity as measured by Raman spectroscopy correlates with the increase in the complex modulus near the crossover point. Thus, phase transition in the SRM 1475 is clearly driven by crystallization.

Summary

Relating Raman and rheological measurements can be difficult on multiple instruments due to the crystallization process' sensitivity to temperature. By using the Rheo-Raman Module, we can clearly correlate changes in the complex modulus with structural and conformational changes in the crystallizing HDPE melt.

References

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