

APPLICATION NOTE

Rheology-Raman Spectroscopy: Tracking polymer crystallization with the combination of a rheometer and Raman spectrometer

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Key words

Rheology, Raman spectroscopy, Polymer crystallization, Combined methods

Introduction

The use of a coupled rheometer and Raman spectrometer for obtaining comprehensive insight into a materials behavior is presented in this application report.

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 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 non-invasive 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 as only relative flow fields are characterized.

In this application note, we present results obtained on an HDPE melt in cooperation with NIST published previously [1].

The results shown can be obtained with the brand new combination of a Thermo Scientific™ HAAKE™ MARSTM rheometer with a Thermo Scientific™ iXR Raman spectrometer (Thermo Scientific™ HAAKE MARSX^R RheoRaman System) as shown in Fig. 1.



Fig. 1: The Thermo Scientific HAAKE MARSX^R RheoRaman 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 MARSX^R, we provide simultaneous Raman and rheological measurements on high density polyethylene (SRM 1475, National Institute of Standards and Technology, Gaithersburg, MD) during crystallization.

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

To monitor crystallinity one has to have a look at the Raman spectra for HDPE as shown in Fig. 2.

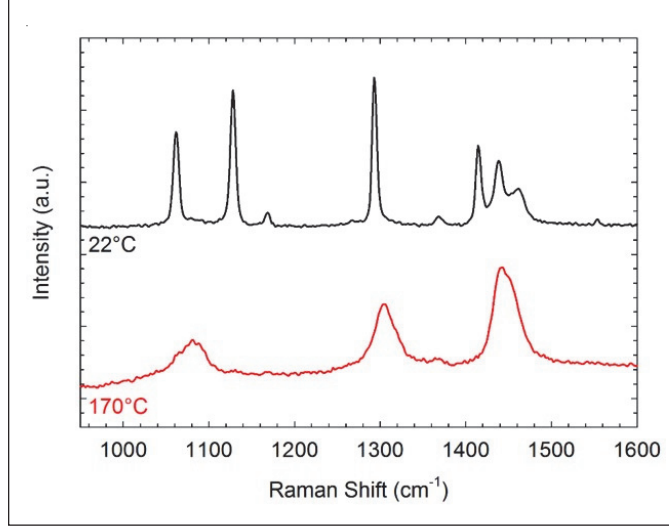


Fig. 2: Raman spectra of polyethylene at temperatures corresponding to the semi-crystalline state (22 °C) and the amorphous state (170 °C).

The spectrum at room temperature shows sharp peaks corresponding to the C-C stretch, CH₂ twist, and CH₂ bend. 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 twist region and a scale factor N_c

$$\alpha_{cr} = \frac{I_{1416}}{(I_{1296} + I_{1303})N_c} \quad (1)$$

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

For HDPE on the MARSxR, the measured scale factor is $N_c = 0.80 \pm 0.03$. Although this is larger than calculated values of N_c from our prior measurements [2], 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 Fig. 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 MARSxR. An HDPE sample of thickness 750 μm was heated for 5 minutes at 155 °C, cooled at 10 °C/min to 134 °C, and then cooled at a slower rate of 2 °C/min to 124 °C and held at temperature to crystallize.

Fig. 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 rad/s. Fig. 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.

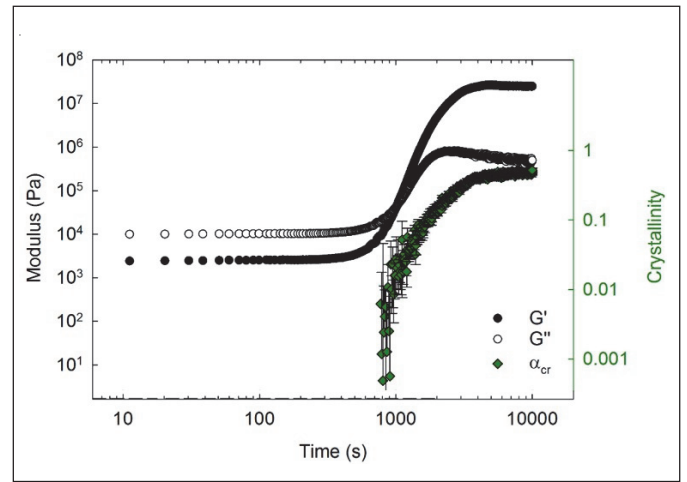


Fig. 3: Complex modulus and crystallinity of PE versus time during isothermal crystallization at 124 °C.

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

Fig. 3 shows the instantaneous mass fraction of crystalline material, which first exceeds the measurement noise at approximately 800 s and 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. Phase transition in the SRM 1475 is thus clearly driven by crystallization.

Summary

Relating Raman and rheological measurements would be difficult on multiple instruments due to the sensitivity of the crystallization process on temperature, but using the MARSxR we can clearly correlate changes in the complex modulus with structural and conformational changes in the crystallizing HDPE melt.

References

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