

Rheology-Raman spectroscopy during the melting and recrystallization of polypropylene

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Keywords

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Introduction

Rheology is the study of the flow and deformation of matter, including fluids to solid-like materials and anything in between. Rheological measurements are commonly used to examine or induce bulk physical material changes, such as melting, crystallization, gelation, or polymerization etc. Raman spectroscopy, on the other hand, is a vibrational spectroscopic technique that can provide insights to these processes at the molecular level, both chemically and morphologically. However, until very recently¹, Raman studies are often conducted *ex situ*, whereby Raman spectra are acquired prior to and after the observed physical transformation. The true chemical/morphological changes driving these processes are largely left uncaptured, leaving much room for data interpretation and speculation surrounding these dynamic physicochemical relationships.

The Thermo Scientific™ HAAKE™ MARS™ Rheo-Raman system (Figure 1) is a fully integrated system that enables simultaneous rheology and Raman spectroscopy measurements. The system is a hyphenation of two Thermo Scientific instruments: a HAAKE MARS Rheometer and a DXR3 Flex Raman Spectrometer for real-time, *in situ* measurements of both physical and chemical–morphological properties with ease. This multimodal analytical tool offers several advantages compared to the traditional *ex situ* approach. Firstly, data collection efficiency is greatly improved by combining multiple one-dimensional experiments. Secondly, because both techniques are performed at the same time,, sample fidelity is preserved and the transformation of the material is captured in realtime. And finally, sample consumption is reduced, which can be beneficial for new material/formulation development where sample quantities are limited and/or expensive.

In this note, the Rheo-Raman system was used to investigate the temperature-dependent melting and crystallization of polypropylene, as well as the isothermal crystallization process. During rheological analysis of polymeric materials, melt and crystalline phase transitions commonly correlate with viscous and elastic behavior variations. These phase transitions are often associated with spectral pattern changes in characteristic Raman peaks during spectroscopic investigation. Measurements performed *ex situ* are often challenging to compare due to discrepancies in temperature control, slight deviations in sample composition, and differences in processing history. The *in situ* Rheo-Raman system, on the other hand, completely eliminates these discrepancies, allowing a more valid analysis of the melt and crystalline phase transitions from both the macroscopic and molecular levels.



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

Materials and methods

Materials

Polypropylene (Ineos Olefins and Polymers, USA, R12C-00 random copolymer) pellets were used for this study. The pellets were melted at 190°C on the rheometer to form a continuous, disk-shaped specimen for testing.

Rheometer

Rheological measurements were performed using the HAAKE MARS Rheometer, equipped with a 20 mm diameter stainless steel parallel-plate rotor. In order to extract the polypropylene's viscoelastic behavior, all measurements were conducted in the oscillatory mode. Oscillatory measurements were performed at 1 Hz with a constant strain of 0.1%, while data were collected every 5 seconds. To soften the polypropylene (PP) and help it conform to the measuring geometry, all samples were initially loaded at 190°C. For the melt-to-crystallization phase transition study, the temperature was decreased from 190°C to 30°C, at a rate of 5°C/minute. For the isothermal crystallization studies at 138°C and 150°C, the temperature was rapidly decreased from 190°C to 10°C above the target temperature. The temperature was then slowly decreased until it reached the test temperature (either 138°C or 150°C). The temperature was then held constant for a maximum of 1 hour (3,600 seconds), while the isothermal recrystallization process was observed.

Spectrometer

Raman spectroscopy measurements were performed using the DXR3 Flex Raman Spectrometer, which had a 532 nm, 10 mW laser, a triplet spectrograph that provided Raman spectra over the range 3,500 to 50 cm⁻¹ Raman shift (Stokes) at 5 cm⁻¹ resolution, and a CCD camera cooled to -50°C. Alignments in the spectrometer of the laser, Raman scatter, and aperture selection were controlled by software. The minimum exposure collection time was 0.1 seconds. For the data presented here, the exposure collection time was 4 s and 2 sample exposures were averaged per spectra collection.

RheoRaman coupling

The Raman spectrometer (DXR3 Flex Raman Spectrometer) and rheometer (HAAKE MARS Rheometer) are coupled together using the HAAKE MARS RheoScope Module (Figure 2). The DXR3 Flex Raman Spectrometer is free-space coupled to the rheometer with an optical train which uses two plane mirrors to direct the incident laser into the RheoScope Module. Within the RheoScope Module, a series of mirrors directs the laser beam into a 20x objective, where the laser light is focused through a 2 mm thick fused silica window into the sample (perpendicularly to the flow or vorticity plane). Raman scattered light is collected in a 180° backscatter geometry using the same 20x objective and guided back to the

spectrometer using the same optical train as the incident laser, eventually reaching the spectrograph inside the spectrometer. Free-space coupling of the laser to the rheometer, and the DXR3 Flex Raman Spectrometer allows easy Raman excitation laser wavelength interchange to permit optimization of the laser wavelength to the sample (785 and 455 nm laser sets are also available).

The sample is positioned between the silica window and the rotor geometry attached to the rheometer measuring head (Figure 2). The objective can be adjusted for interrogation at different penetration depths within the sample, as well as positioned at various radial locations along the optical slit (from the true center to outer edge of the sample). An electrical heating element is positioned below the fused silica window to provide temperature control during testing. Cooling was provided from a temperature-controlled circulator with a 50:50 mixture of ethylene glycol and water. All instrumentation is controlled through the Thermo Scientific OMNIC™ Software and RheoWin™ Measuring and Evaluation Software.

The electric heater allows a maximum temperature of 300°C and a minimum temperature of -5°C, with a maximum heating and cooling rate of 10°C/minute. An active electrical hood was also used to provide temperature control from above, eliminating the potential for a temperature gradient within the sample (Figure 2).

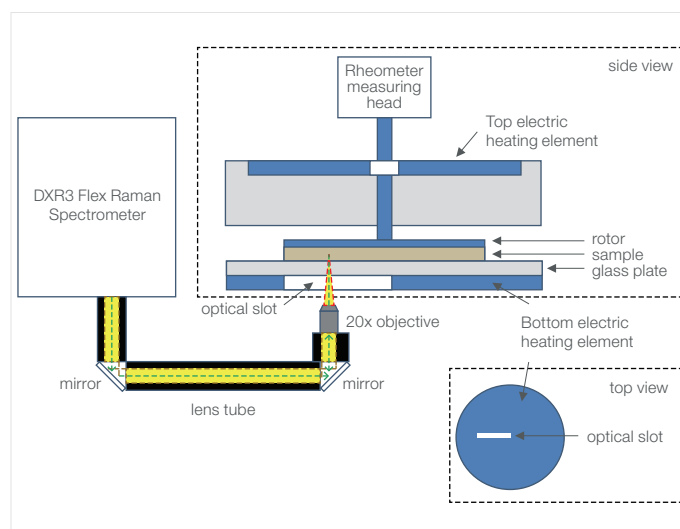


Figure 2. Schematic diagram of the Rheo-Raman system (showing side and top views of the rheometer sample stage). The DXR3 Flex Raman Spectrometer is free-space coupled to the HAAKE MARS Rheometer using plane mirrors that direct light into a 20x long, working distance objective. The objective focuses the incoming laser (green dashed line) and collects the back-scattered Raman light (yellow) coming into and out of the sample (which sits atop the rheometer stage). The optical path from the spectrometer to the rheometer is enclosed in lens tubes (black). The optical slot in the bottom heating plate permits passage of the laser beam and scattered Raman light.

Results and discussion

The physicochemical and morphological relationships during polymer crystallization are of critical importance for polymer processing. In this experiment, we used the new MARS Rheo-Raman system to investigate the crystallization process of polypropylene (PP). Representative Raman spectra for PP at three different temperatures are shown in Figure 3. In general, the spectrum at 53°C showed sharp peaks across the spectral range that was examined. These sharp spectral features suggest a high degree of conformational order, indicative of semicrystalline and crystalline structures. As temperatures increased to 120 and 173°C, these peaks began to broaden and merge together. The broadening of spectral peaks is commonly ascribed to melt behavior in polymeric materials.

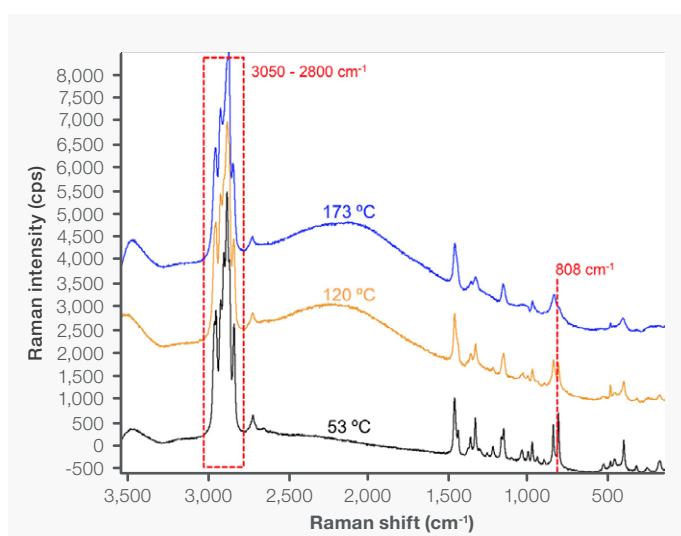


Figure 3. Raman spectra for PP: (black) 53°C, (yellow) 120°C, and (blue) 173°C. The dashed line at 808 cm⁻¹ and dashed box from 3,050–2,800 cm⁻¹ indicate relevant Raman bands that are relevant to recrystallization of PP.

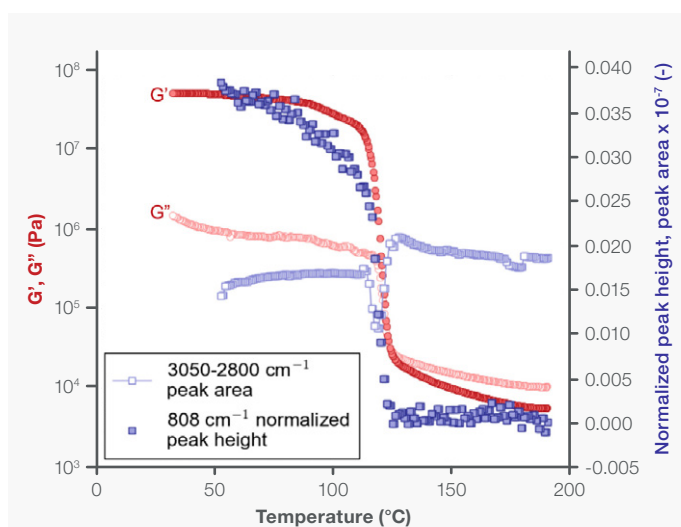


Figure 4. PP recrystallization: (filled circles) G' and (open circles) G'' , plotted on the left y-axis, and (filled squares) the normalized 808 cm⁻¹ Raman shift peak height and (open squares) the 3,050–2,800 cm⁻¹ peak area, plotted on the right y-axis, are a function of decreasing temperature from 190 to 30°C.

Specific indicators in the Raman spectra for PP are the skeletal deformation of helical chains within the crystal (808 cm⁻¹ peak) and the CH stretching region (3,050–2,800 cm⁻¹ spectral range). The intensity of the 808 cm⁻¹ peak will be used as a measure of the crystallinity of PP², and the intensity in the CH stretching region is used as a measure of the overall Raman scattering intensity during the crystallization process. For further analysis, the 808 cm⁻¹ peak height was normalized by the peak area between 880 and 780 cm⁻¹. The 880–780 cm⁻¹ spectral region contains skeletal chain vibrations of all conformations during the melt-to-recrystallization process², while the spectral features in the 3,050–2,800 cm⁻¹ range were integrated into a total peak area. These indicators (normalized helical chain vibration peak height and overall CH stretching peak area) were then tracked throughout the melt- to crystalline-phase transition and overlaid with the *in situ* rheology data (Figure 4). The melt and recrystallization process of PP was probed rheologically using small amplitude oscillatory shear measurements (Figure 4), where the storage modulus (G') and loss modulus (G'') were measured as a function of temperature. G' and G'' are measures of a material's elastic and viscous behavior, respectively. A liquid-like material will be more viscous than elastic (i.e., viscously dominated), and as a result, G'' will be greater than G' . Conversely, a solid-like material will display more elastic than viscous behavior (i.e., elastically dominated), where G' will be greater than G'' .

Initially, at high temperatures (>150°C), was consistently greater than G' , indicating the PP specimen was in the melt state and displaying liquid-like behavior. As the temperature decreased from 150°C to 100°C, an abrupt and drastic increase in both G' and G'' was observed at ~125°C. By the time the temperature reached 100°C, G' had increased by four orders of magnitude, while G'' increased by two orders of magnitude. This temperature range (150°C to 100°C) can be considered the melt-to-crystalline transition region for this PP material. As the temperature further decreased below 100°C, G' was significantly greater than G'' by more than a full order of magnitude, indicating that the PP had transitioned into the semi-crystalline or crystalline state and was exhibiting solid-like behavior.

The observed plateau regions and increase in G' and G'' are in direct agreement with the Raman spectral data (Figure 4). In the melt region ($\sim 190^\circ\text{C}$ to 130°C)¹, the normalized 808 cm^{-1} peak height was near zero and remained unchanged by the decreasing temperature. However, as the PP melt began to crystallize, the normalized 808 cm^{-1} peak height significantly increased and was in unison with the abrupt increases in both G' and G'' . Also, as the PP sample started to crystallize, the total peak area of the CH stretching region decreased rapidly before any measurable growth of the 808 cm^{-1} band was observed. The decrease in intensity in the $3,050\text{--}2,800\text{ cm}^{-1}$ spectral region is postulated to be caused by the formation of crystallites in the PP matrix. Crystallites with dimensions on the same order of magnitude as the wavelength of the incident laser (532 nm) would scatter light, thereby creating a loss in the Raman signal intensity of the CH stretching bands. The minimum in the CH stretching profile was directly aligned with the observed crossover between G' and G'' and the maximum slope of the normalized 808 cm^{-1} peak profile. The correlation between changes in the Raman spectral features and the rheological response indicate that the crystallization rate was at its maximum when the crystallite concentration was greatest. After the observed decrease in intensity, the integrated area of the CH stretching region returned to a value close to what was detected in the melt phase.

In order to further evaluate the crystallization process of PP, isothermal crystallization studies were performed at 150°C and 138°C . The PP samples were heated at a minimum of 5 minutes at 190°C (to fully melt the specimen), rapidly cooled at $10^\circ\text{C}/\text{minute}$ until 10°C above the crystallization temperature, and then cooled at a slower rate of $2^\circ\text{C}/\text{minute}$ until the set crystallization temperature was reached. The crystallization temperature was then held constant for a maximum of 1 hour (3,600 seconds) to observe the isothermal crystallization of PP as a function of time. Simultaneous rheology-Raman spectroscopy data were acquired *in situ* during crystallization at 138°C and 150°C (Figures 5 and 6, respectively). At both isothermal temperatures, the PP material was initially viscously dominated $G' < G''$ displaying liquid-like behavior. As time progressed, a crossover in G' and G'' was observed, where the moduli increased two to three orders of magnitude. The crossover at 138°C occurred 84 seconds into the isothermal curing process, while the crossover at 150°C took 2,150 seconds to be observed. After the observed crossover, G' and G'' reached a plateau and the crystallization process was considered stabilized and complete.

Similarly to the previous experiments, the rheology and Raman data were in agreement during the isothermal crystallization studies (Figures 5 and 6). The observed increase in the elastic and viscous moduli directly correlates with the increase in the normalized 808 cm^{-1} peak height. Although not shown here, a minimum in the CH stretching band intensity was again observed as the specimen transitioned from the liquid to the solid state.

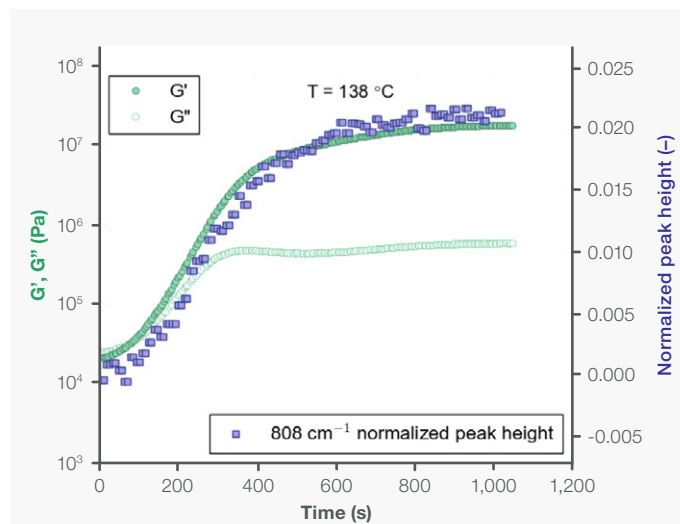


Figure 5. PP isothermal recrystallization at 138°C : (filled circles) G' and (open circles) G'' , plotted on the left y-axis, and (filled squares) the normalized 808 cm^{-1} Raman shift peak height, plotted on the right y-axis, as a function of time.

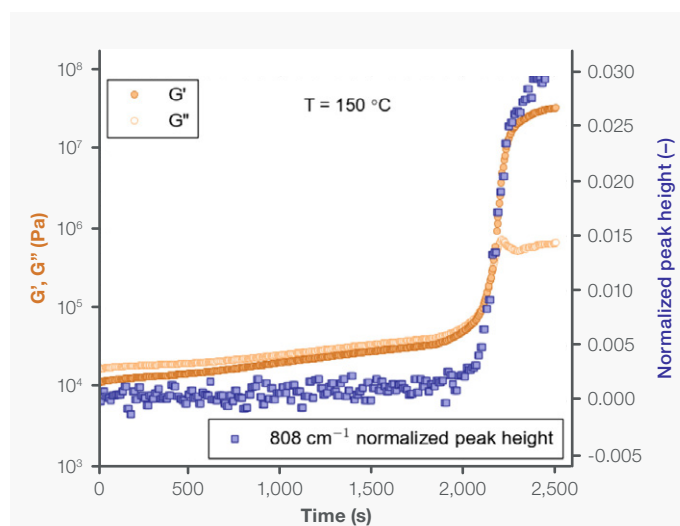


Figure 6. PP isothermal recrystallization at 150°C : (filled circles) G' and (open circles) G'' , plotted on the left y-axis, and (filled squares) the normalized 808 cm^{-1} Raman shift peak height, plotted on the right y-axis, as a function of time.

Conclusions

The Rheo-Raman system was employed to simultaneously measure the rheology and Raman spectroscopy of PP during the melt-to-crystallization transition process. This multimodal analytical tool allowed the bulk structural properties of PP (G' and G'') to be directly correlated with real-time conformational changes at the molecular level (helical chain vibrations and CH stretching). The data revealed that the rate of crystallization reached its maximum (indicated by rapid increases in G' , G'' , and the normalized 808 cm^{-1} peak height) when the crystallite concentration was greatest (signified by a decrease in the overall Raman spectral intensity in the $3,050\text{--}2,800\text{ cm}^{-1}$ region). The observed correlation between the macroscopic and molecular level measurements exemplifies the unique analytical capability unleashed by hyphenating rheology with Raman spectroscopy. While this work focuses on the melting and crystallization of PP, the underlying principles demonstrated should be applicable in a wide range of material processes, including gelation, polymerization, curing behavior, as well as other shear-induced phenomena.

References

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