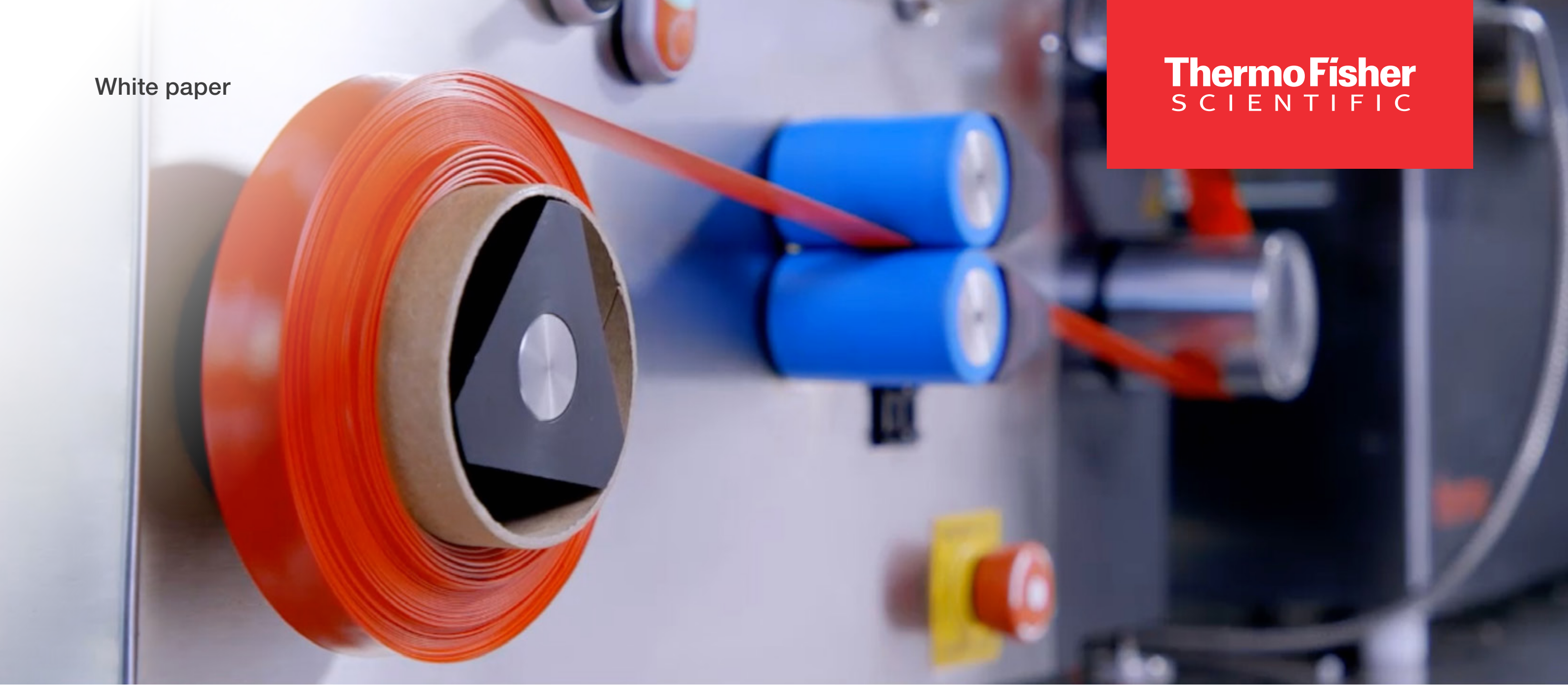
White paper



Real-time monitoring of polymer extrusion using a process Raman analyzer integrated with a twin-screw extruder

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Background

Understanding the structural changes of polymers during the extrusion process is essential for optimizing the manufacturing of extruded products. Extrusion can alter a polymer's structure and properties in ways that can enhance its performance and functionality. Changes such as the transition from crystalline to amorphous phases or shifts in vibrational modes can be leveraged to tailor the end-polymer's mechanical, thermal, and optical properties to meet specific application needs.

Polymer extrusion is a high-volume manufacturing process where raw plastic materials, such as low-density polyethylene (LDPE) and polylactic acid (PLA), are melted and pushed through a shaped die to create specific and continuous profiles. In twin-screw extruders, this is accomplished using two intermeshing screws and a heating system to increase temperature, shear forces and pressure, in order to efficiently melt and homogenize the polymers. This process allows for the production of a wide range of plastic products with consistent shapes and properties.

In addition to polymeric applications, twin-screw extruders are commonly used in pharmaceutical applications for mixing active pharmaceutical ingredients (APIs) with excipients. In battery manufacturing, extruders are used to thoroughly mix anode and cathode materials needed for homogeneous end products. The Thermo Scientific™ Process™ 11 Parallel Twin-Screw Extruder is an ideal tool for processing and compounding various materials in this manner.

Vibrational spectroscopic techniques such as Raman spectroscopy are often utilized for off-line evaluation of extrusion products. However, if such techniques can be integrated in line with the extruders, it can facilitate real-time measurements of many qualitative and quantitative aspects of the process.

Raman spectroscopy is a technique used to observe vibrational, rotational, and other low-frequency modes in a material. Raman spectroscopy works by shining a monochromatic light source, typically a laser, onto a sample. The light interacts with the molecular vibrations within the sample, causing the light to scatter. Most of the scattered light has the same wavelength as the incident light (Rayleigh scattering), however, a small portion of the scattered light has different wavelengths due to interactions with molecular vibrations. This change in wavelength provides a unique spectral fingerprint of the material, which can be used to identify and characterize the sample's molecular composition and structure. This data can be translated into quantitative or qualitative information with the use of chemometric modeling techniques such as partial least squares (PLS) regression or principal component analysis (PCA).

The Thermo Scientific™ MarqMetrix™ All-In-One Process Raman Analyzer allows users to implement Raman spectroscopy directly in line with an extrusion process by using strong and chemically resistant optical probes. MarqMetrix probes can be integrated in line with extruder barrels allowing the continual monitoring of the extrusion process to make quantitative and qualitative decisions in real time.

PCA is a powerful statistical technique used to simplify the complexity of high-dimensional data while preserving essential patterns and relationships. By transforming the original variables into a new set of uncorrelated variables called principal components, PCA highlights the most significant variations within the data. In the context of Raman spectroscopy, PCA can be employed to analyze spectral data and distinguish between different polymer types, such as LDPE and PLA. By reducing the dimensionality of the Raman spectra, PCA facilitates the identification of distinct spectral features that differentiate LDPE from PLA. This approach not only enhances the clarity of the spectral data but also enables efficient and accurate classification of the polymers, making it an invaluable tool for quality control and process optimization in polymer extrusion.

In this white paper, PCA is used to analyze Raman spectral data and effectively distinguish between LDPE and PLA. This demonstrates the potential of Raman analysis for improving material identification and ensuring product consistency in extrusion processes.

Benefits of Raman spectroscopy in polymer extrusion

The integration of Raman spectroscopy into polymer extrusion processes presents a transformative opportunity for the manufacturing industry. Raman spectroscopy offers numerous benefits that can significantly enhance the efficiency, quality, and overall performance of extrusion operations. This white paper explores these benefits, highlighting the value Raman spectroscopy brings to the extrusion process.

Real-time monitoring: Raman spectroscopy enables real-time monitoring of the chemical composition and molecular structure of polymers during extrusion. This capability allows for immediate process optimization—including temperature, throughput and screw speed—to correct any deviations from desired material specifications, ensuring that the extrusion process remains within optimal parameters. This leads to better control over the extrusion process, enhancing efficiency and reducing material waste.

MarqMetrix All-In-One process Raman analyzer.

Quality control: Such continuous insights into the extrusion process also ensure consistent and optimal product quality. By identifying and addressing issues such as contamination, improper mixing, or material degradation early in the process, manufacturers can maintain high standards of product integrity. In addition, immediate feedback from Raman spectroscopy helps minimize the production of off-spec products and associated waste. This results in significant cost savings in both materials and production time, contributing to overall operational efficiency.

Material identification: Raman spectroscopy is adept at differentiating between various types of polymers and detecting additives or fillers. This capability is particularly valuable during material changeovers, ensuring that the new material has fully replaced the old material thus minimizing risk of cross-contamination.

Enhanced R&D capabilities: In research and development settings, Raman spectroscopy offers valuable insights into the effects of different extrusion parameters on polymer properties. This facilitates the development of new materials and processes, driving innovation and advancement in polymer technology.

Introduction

This white paper highlights the integration of the MarqMetrix All-In-One Process Raman Analyzer with the Process 11 Parallel Twin-Screw Extruder to observe polymer processing in real time, directly within the barrel of the extruder. Raman spectroscopy was first used to characterize the differences between the virgin material prior to extrusion, and the same material during extrusion. It was then utilized to indicate when materials had been mixed and then to track the transition from one polymer to another within the extruder system using qualitative chemometric models.

The materials used in this study were LDPE and PLA. These materials were chosen due to their popularity in end-products across multiple industries as well as their well-characterized Raman spectra.

Process 11 twin-screw extruder.

Experimental setup

The Process 11 extruder was integrated with the MarqMetrix All-In-One analyzer (Figure 1).

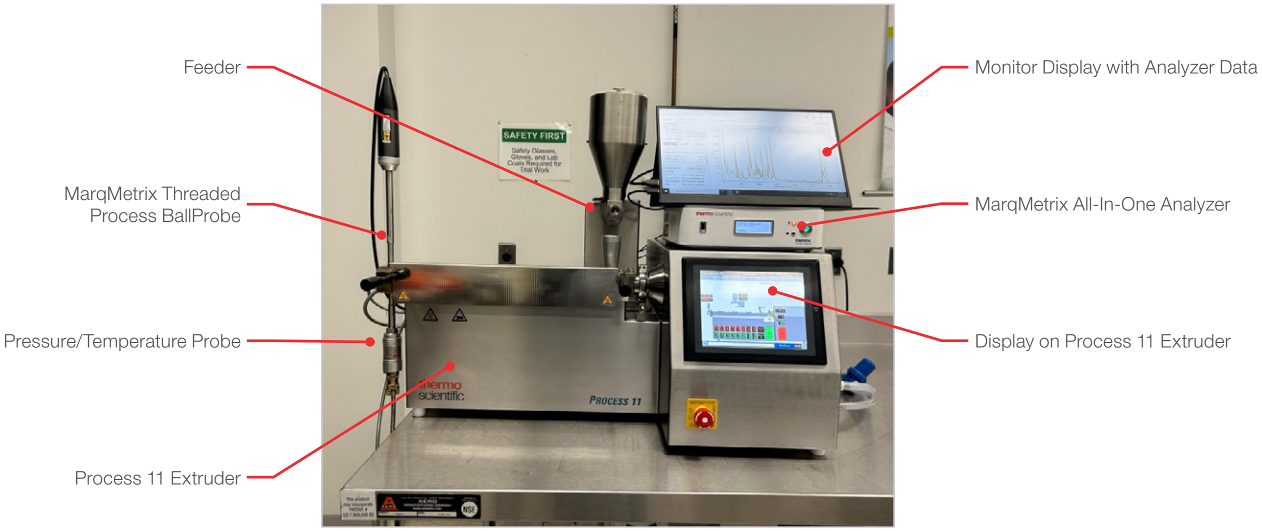

Figure 1. Experimental setup - Process 11 extruder with MarqMetrix All-In-One Raman analyzer.

The Process 11 extruder and the MarqMetrix All-In-One analyzer were integrated with a Thermo Scientific™ MarqMetrix™ Threaded Process BallProbe Sampling Optic that is specially designed to fit directly in line with the barrel of the extruder. The threaded probe features a screw design which allows the sapphire ball at the tip of the probe to come in direct contact with the internally extruded materials. This contact with the material ensures consistent and reproducible spectra collection. The threaded probe is constructed with Hastelloy material which provides high chemical resistance and a temperature rating of > 300 °C. See Figure 2 for a detailed schematic of the probe.

The Process 11 extruder utilizes eight (8) barrel segments (each 5L/D) for precise and independent temperature control to allow the material to be heated to a specified temperature as it is pushed through the system. The feeder at the top of the extruder was used to introduce virgin pellets directly into the barrel.

Continuous scanning was performed on the MarqMetrix All-In-One analyzer while adjusting polymer and process parameters on the Process 11 extruder. Spectra were collected using a laser power of 450 mW, with an integration time of 1 second and 3 averages for each scan. An automatic background scan was performed for each sample scan, yielding a total scan time of 6 seconds for each measurement.

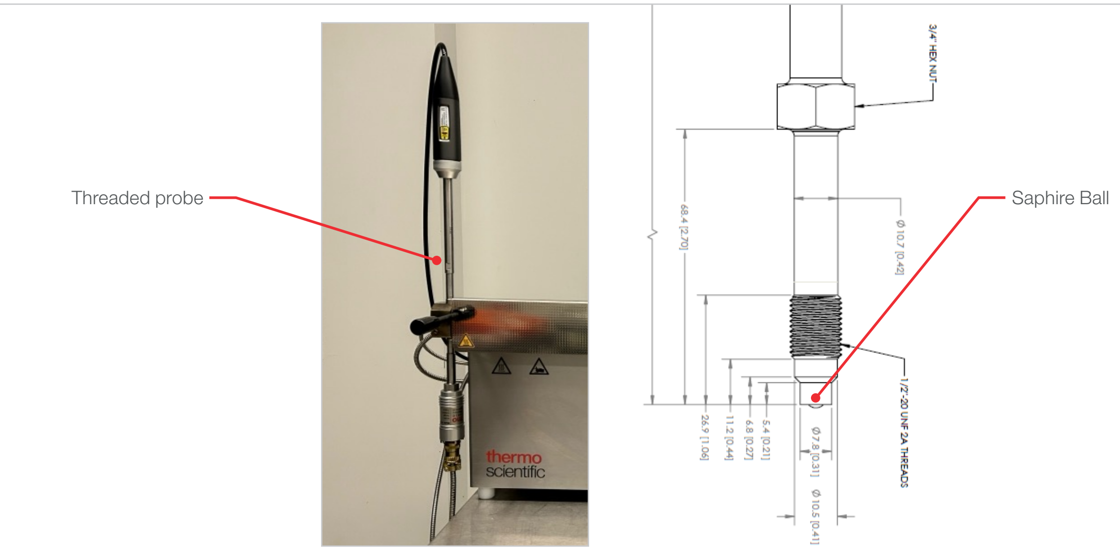

Figure 2. Threaded probe schematic.

Methodology

Raman spectra of virgin LDPE and PLA pellets were first collected to identify characteristic spectral peaks and features of each polymer. The polymer pellets were then fed simultaneously through the extruder and continuously analyzed by the threaded probe in the barrel during extrusion. The resulting spectra were compared to the virgin materials to identify changes as a result of the extrusion process.

In the second part of the experiment, the MarqMetrix All-In-One analyzer was utilized to continuously collect spectra directly from the barrel of the extruder in real time. LDPE pellets were first fed into the extruder, followed by the addition of PLA, enabling the analysis of the resin changeover. The spectral data were used to monitor the resin changeover duration under the specific process conditions as shown in Table 1.

Results

Figure 3 below shows the spectra of virgin LDPE and PLA pellets. LDPE and PLA have many characteristic features which are clearly distinguishable.

The extruder conditions across the barrel can be seen in Table 1.

The glass transition temperature and melting point for both LDPE and PLA can be found in Table 2.

The temperature conditions of the extruder allowed both materials to be in a molten state during the extrusion.

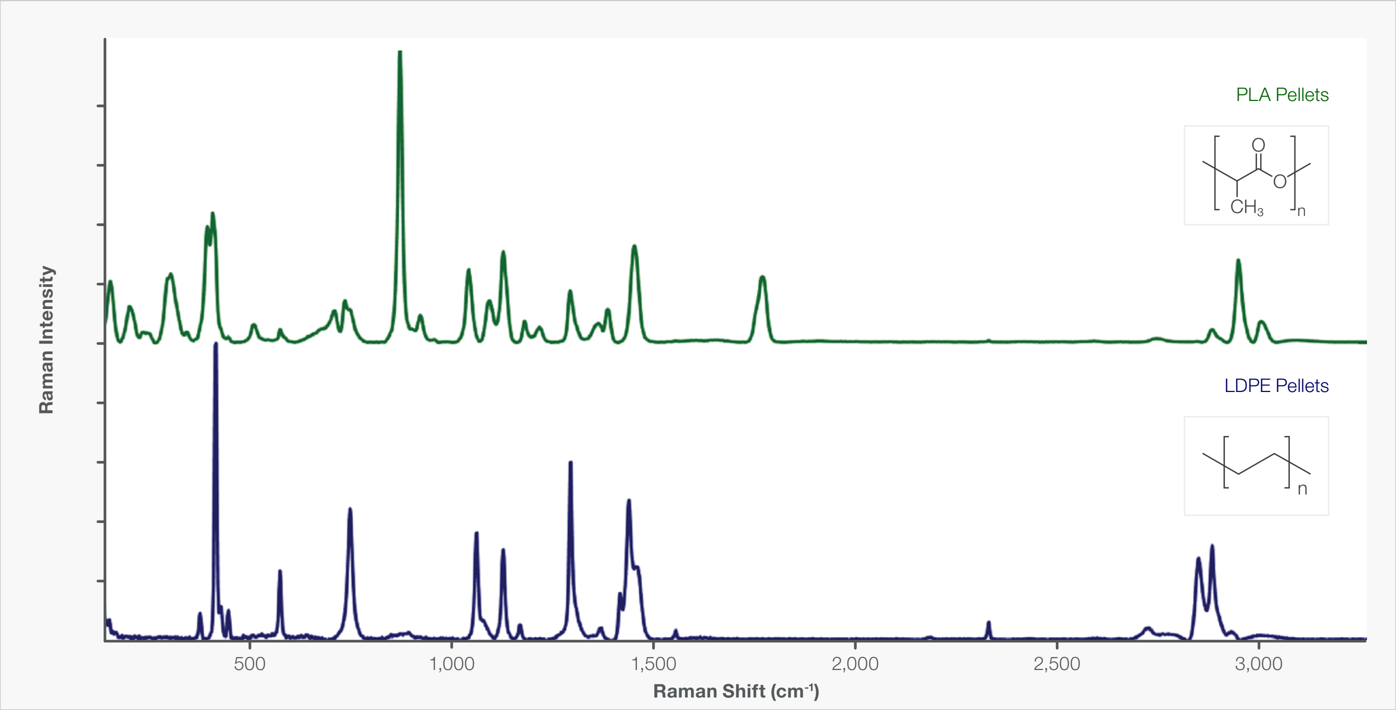

Figure 3. Raman spectra of virgin PLA and LDPE pellets.

Condition	Material	Set temperature (°C)								Set parameters			Monitored parameters	
		Die	Zone 8	Zone 7	Zone 6	Zone 5	Zone 4	Zone 3	Zone 2	Melt temp-erature	Feed rate (%)	Screw Speed (RPM)	Pressure (bar)	Torque (%)
A	LDPE	***160***	160	160	160	160	155	150	130	163	***4***	***200***	0	***15***
B	LDPE	***175***	180	175	175	170	165	160	140	176	***5***	***300***	0	***22***
C	PLA	***175***	180	175	175	170	165	160	140	176	***5***	***300***	0	***17***

Table 1. Summary of Process 11 extruder temperature and set parameter conditions.

Material	Glass transition temperature	Melting point temperature
LDPE	-110 °C	105 –110 °C
PLA	55 – 65 °C	150 –160 °C

Table 2. Glass transition and melting temperature by material.

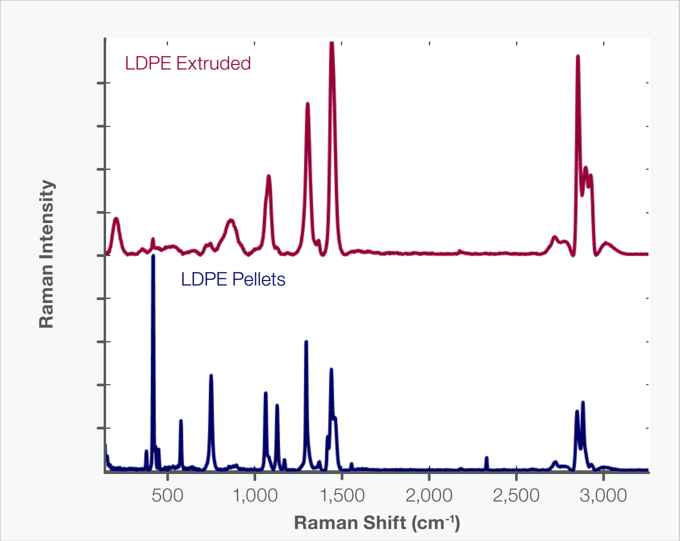

Figure 4. Raman spectra of virgin pellets and extruded LDPE.

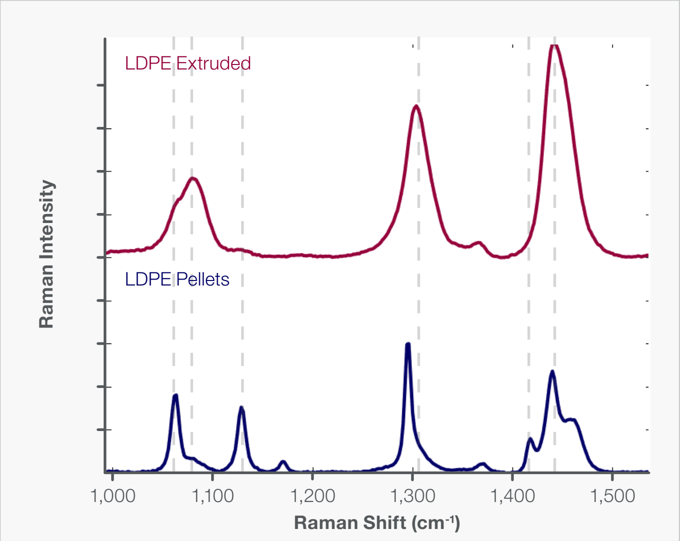

Figure 5. Raman spectra of virgin and extruded LDPE highlighting the fingerprint region.

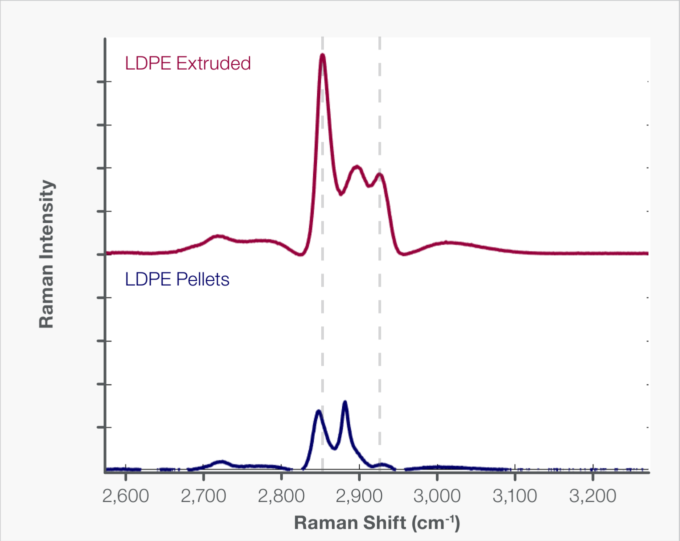

Figure 6. Raman spectra of virgin and extruded LDPE highlighting the C-H stretch region.

The analysis of the inline Raman data from Figure 4 revealed several key findings regarding the structural changes in LDPE during the extrusion process. The methylene bending vibration ($\delta(CH_2)$) bands between 1,400 and 1,480 cm^{-1} were observed, with a peak at 1,416 cm^{-1} indicating the crystalline phase. This peak was present in pellet samples but absent in the extruded samples, confirming the melt of the crystal phase during extrusion process. This region is highlighted in Figure 5.

Peaks at 1,080 and 1,303 cm^{-1} were assigned to the amorphous phase of LDPE. These peaks were absent or small in pellet samples but prominent in extruded samples, indicating that the extruded sample was almost entirely in the amorphous phase. Additionally, the peaks at 1,063 and 1,123 cm^{-1} were attributed to the symmetric and asymmetric C–C stretching vibrations, respectively, of all-trans PE chains. In LDPE pellets, these peaks were prominent, indicating the presence of all-trans chains. However, in extruded samples, these peaks were weak or absent, suggesting a breaking in 1D translational periodicity upon melting. This can also be seen in Figure 5.

The region between 2,800 and 3,000 cm^{-1} in both infrared and Raman spectroscopy is associated with C-H stretching vibrational modes. The Raman spectra of extruded LDPE also depicted a significant number of changes in the heights and ratio of the peaks in the C-H stretch region (Figure 6).

Overall, the Raman analysis provided clear distinctions between the crystalline and amorphous phases of LDPE in pellet and extruded samples, highlighting the structural changes that occur during the extrusion process.

As shown in Table 1, the process conditions for LDPE were varied to “B” to understand how changes in temperature, screw speed and feed rate would affect the structure. As can be seen in Figure 7, there were no significant differences between the spectra of both A and B processing conditions. This suggests that the polymer was already completely melted under the parameters used in condition A.

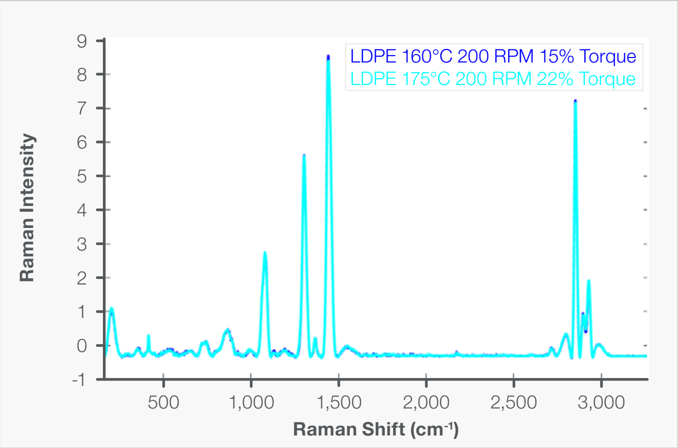

Figure 7. Raman spectra of LDPE under varying process conditions (temperature and screw torque).

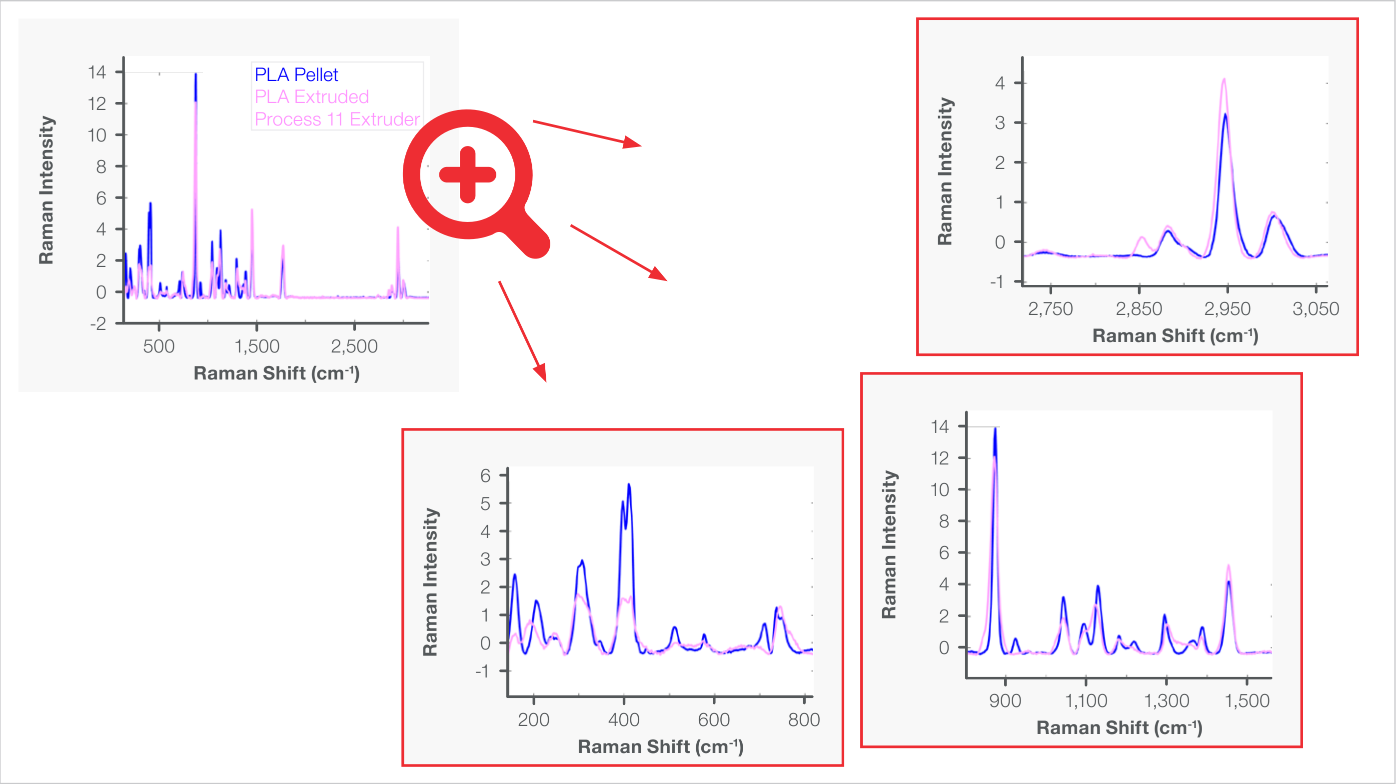

Figure 8. Raman spectra of virgin and extruded PLA.

The virgin and extruded spectra for PLA were also assessed. The extruded PLA spectra indicated distinct features compared with the virgin pellets, as seen in Figure 8.

In the next part of the experiment, a PCA model was created to clearly identify each of the polymers. The PCA model was used to track the presence of each component within the extruder barrel during the resin changeover. The LDPE was extruded at a constant rate. As soon as the feeder was empty, the PLA was then introduced into the system, and the changeover was monitored. The threaded probe connected on the end of the die provided continuous measurement at every 6 seconds throughout the changeover process. Figure 8 shows the Raman spectra of the system from 0 through 30 seconds. T=0 seconds was denoted when PLA was introduced in the feeder.

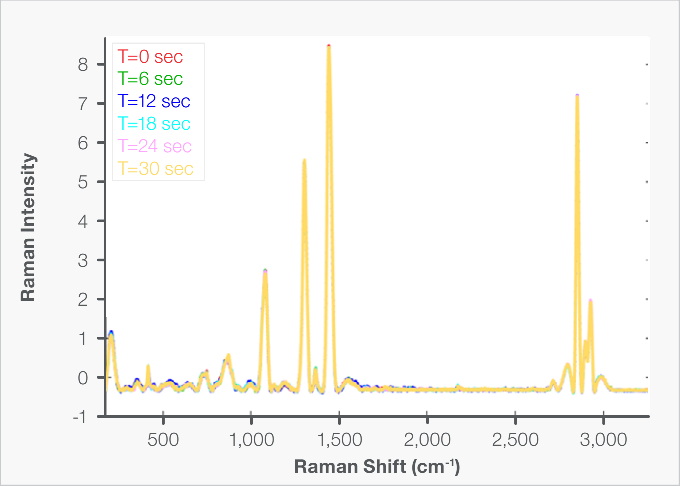

Figure 9. Raman spectra monitoring of LDPE to PLA from 0 to 30 seconds.

As can be seen in Figure 9, the spectra remain unchanged indicating that only the LDPE was purging through the end of the barrel. Figure 10 shows the Raman spectra between 30 to 60 seconds.

The Raman spectra began to show dramatic changes after the first 30 seconds, indicating that some of the PLA started to reach the probe down the barrel of the extruder. This is where the PCA model became critical in identifying the changeover process.

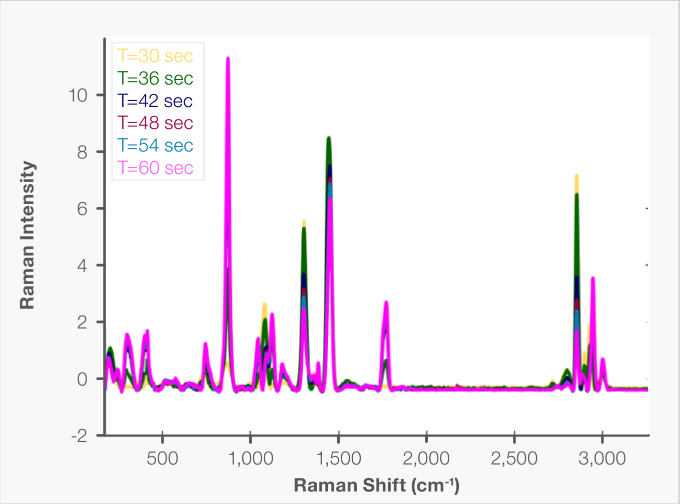

Figure 10. Raman spectra monitoring of LDPE to PLA from 30 to 60 seconds.

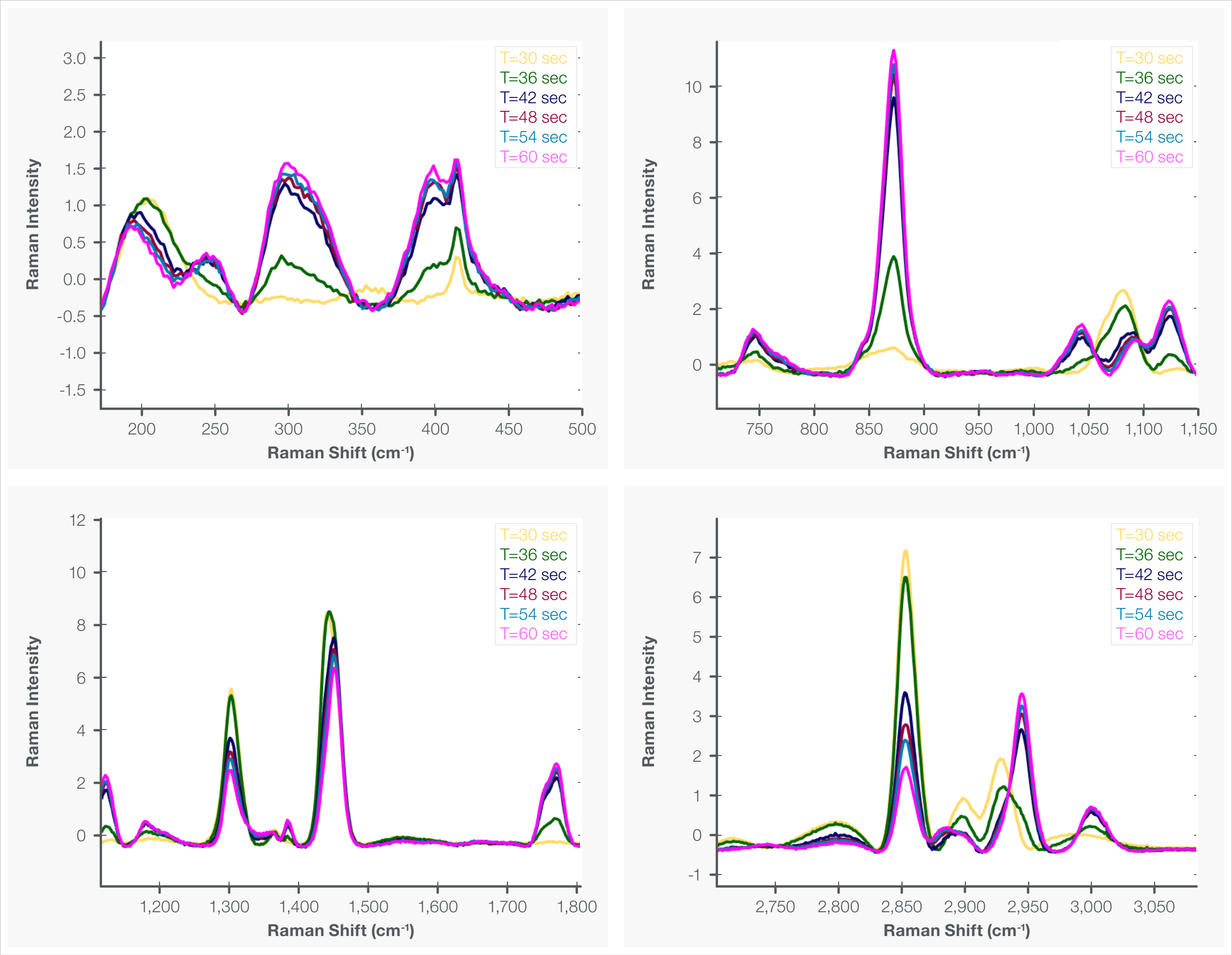

Figure 11. Raman spectra monitoring LDPE to PLA from 30 to 60 seconds highlighting different spectral regions.

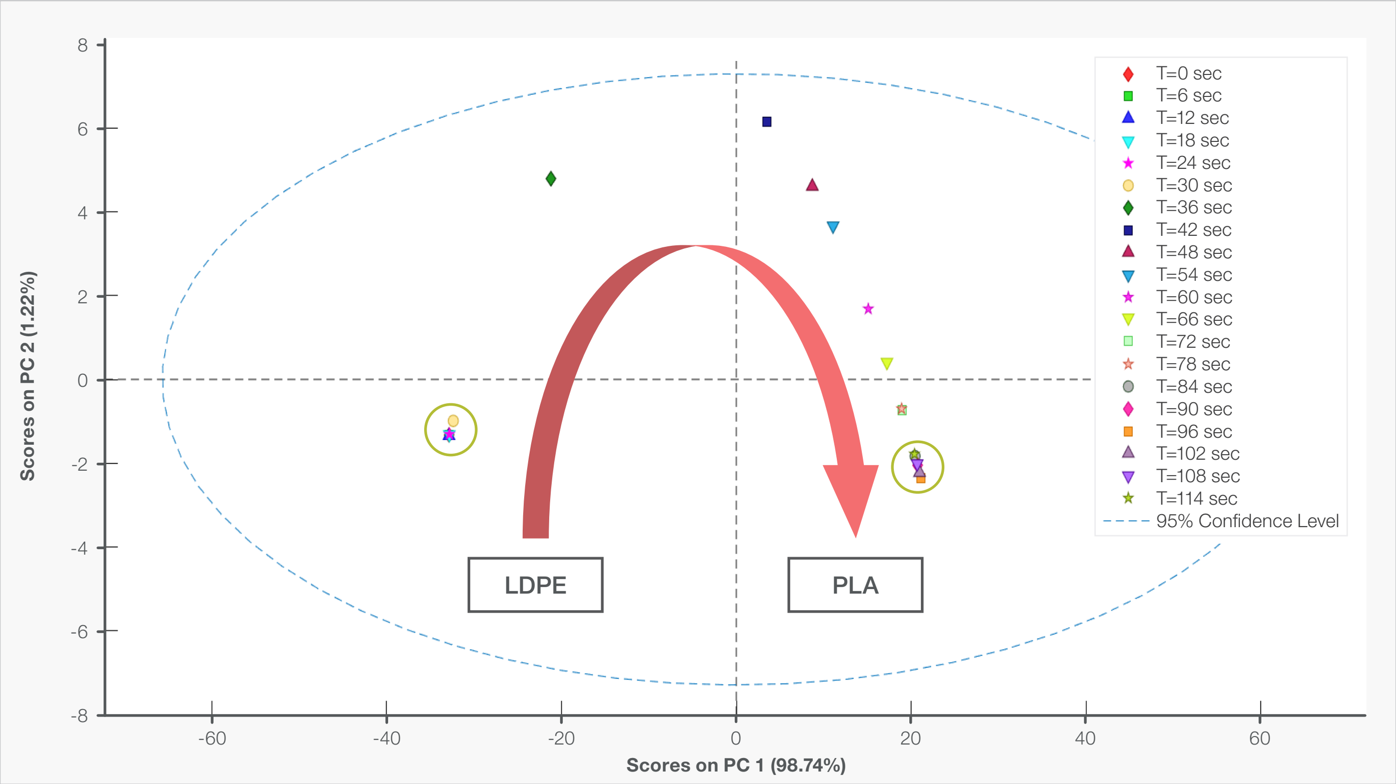

Figure 12. PCA plot highlighting transition from LDPE to PLA.

Looking at Figure 11, the spectral features for PLA begin to show in the spectra between 30 and 60 seconds. Subsequently, the LDPE peaks started to fade away. Figure 12 plots this on the PCA plot for the entirety of the run through 114 seconds.

The PCA plot provides a clear visualization of the polymer transition and stabilization process during the extrusion. Initially, the LDPE forms a distinct cluster to the left on a PCA plot, indicating its presence up to 30 seconds. As PLA is introduced, the plot shows a transitional phase characterized by the appearance of new spectral features, marking the gradual replacement of LDPE with PLA. Finally, after 84 seconds, the process stabilizes into a well-defined PLA cluster. This demonstrates the effective application of PCA in tracking and distinguishing between different polymers in real time.

Conclusion

The integration of the MarqMetrix All-In-One Process Raman Analyzer with the Process 11 Parallel Twin-Screw Extruder has demonstrated significant benefits for real-time, inline process monitoring in polymer extrusion. This study highlighted the capability of Raman spectroscopy to effectively differentiate between solid and molten states of polymers and provided clear identification of transitions from one polymer to another using PCA models. Such information can be utilized to ensure no cross-contamination during polymer change overs and to ensure the quality of the extruded polymers. This proof-of-concept study can be further applied to quantify the composition of the composite polymer materials using PLS models. Additionally, the MarqMetrix All-In-One analyzer can also be integrated mid-barrel to understand the reactive extrusion in real time.

Overall, the implementation of Raman spectroscopy into polymer extrusion processes offers a multitude of benefits, ranging from real-time monitoring and quality control to process optimization and cost savings. These advantages make Raman spectroscopy an invaluable tool for enhancing the efficiency and effectiveness of polymer extrusion operations.

References

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