Monitoring concentrations of a polymer blend in real-time by combining extrusion and Raman Spectroscopy

Marek Biermann, Application Specialist, and Dr. Nils Bertram, General Manager, Anton Paar OptoTec GmbH, Seelze-Letter, Germany; Michael Stanko, Product Manager, Anton Paar TorqueTec GmbH, Duisburg, Germany.

Transforming raw plastic materials into finished or semi-finished products by extrusion is a critical step in the polymer value chain. To optimise this process, in situ monitoring of chemical and compositional changes during polymer extrusion expedites product and process development and enhances quality control to meet customer, application, and regulatory requirements.

Blending of polymers such as polycarbonate (PC) and polymethyl methacrylate (PMMA) is key to achieving the specified mechanical, optical, and thermal properties of final polymer products (e.g. strength, optical clarity, and impact resistance).

The actual properties vary with the relative concentrations of the constituent polymers in the blend. The correct composition needs to be ensured by proper dosing and mixing according to the formulation. This process can be subject to errors – e.g. wrong input materials, operator errors in picking and dosing materials by volume or weight, inhomogeneous mixing, or compromised material integrity.

Controlling the relative concentration of each component during extrusion is crucial to ensuring consistent material properties and to meeting both customer and regulatory acceptance criteria.

In situ process monitoring using Raman spectroscopy enables real-time quantification of polymer composition. This improves analytical efficiency and eliminates the time lag for offline analysis, allowing for immediate corrective action. This is in contrast to offline measurements, which pose the risk of disposing of entire batch(es) with nonconformities.

Instrumentation and experimental setup

A fibre probe from Anton Paar's Cora 5001 Raman spectrometer was placed directly after the round strand die head of a TwinLab 20/40D twin-screw extruder for real-time measurement of the polymer strand prior to cooling in a water bath and pelletisation.

The Raman system operated at 1,064 nm excitation wavelength, with an exposure time of 9.9 s. Measurements were recorded every 20 s. An averaging feature which automatically takes the average value from three measurements was applied for improved accuracy. Alternatively, measurements can also be done directly inside the extruder die head using Anton Paar's tailor made extrusion fibre probe with an 1/2" 20-UNF adapter, as shown in Figure 1. Three relative concentrations were varied over time: 30% PC / 70% PMMA, 50% PC / 50% PMMA, and 70% PC / 30% PMMA.

Figure 1: Anton Paar's Raman analyzer Cora 5001 integrated with the Brabender Extruder. In this configuration, the Raman fibre probe is directly mounted on the extruder die-head.

Results and discussion

When comparing the Raman spectra of PC and PMMA, distinct peaks can be assigned to the corresponding polymers. As visible in Figure 2, clear peaks that are unique to PC can be seen at 706 cm^{-1}, 890 cm^{-1}, and 1604 cm^{-1}, while PMMA displays peaks at 600 cm^{-1}, 812 cm^{-1}, 1,452 cm^{-1}, and 1,730 cm^{-1}.

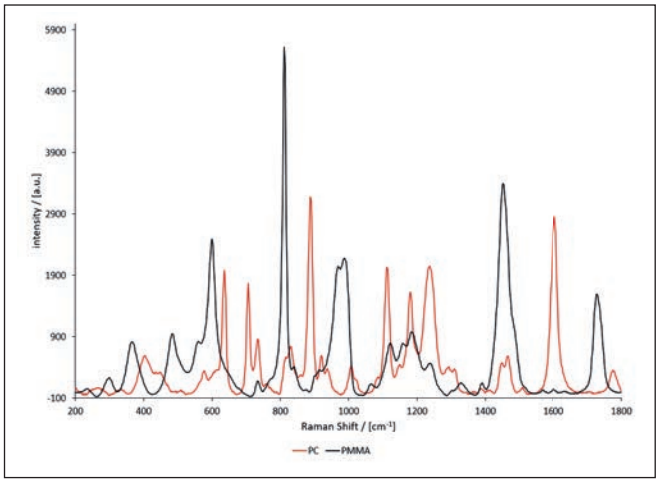


Figure 2: Raman spectra of polycarbonate and polymethylmethacrylate.

A change in the PC/PMMA ratio directly corresponded to changes in the Raman spectra. At the start of the experiment, the Raman signal was dominated by PMMA contributions and the quantification model confirmed a stable 30% PC concentration with minimal fluctuations.

The peak at 890 cm^{-1} was used for quantification. When the blend ratio changed to 50% PC / 50% PMMA, the spectra show that the measured concentration after 13 min was slightly lower than the expected 50 % (Figure 3). This implies that the transition phase was not long enough to achieve a fully stabilised mixture before advancing to the next composition of 70% PC / 30% PMMA.

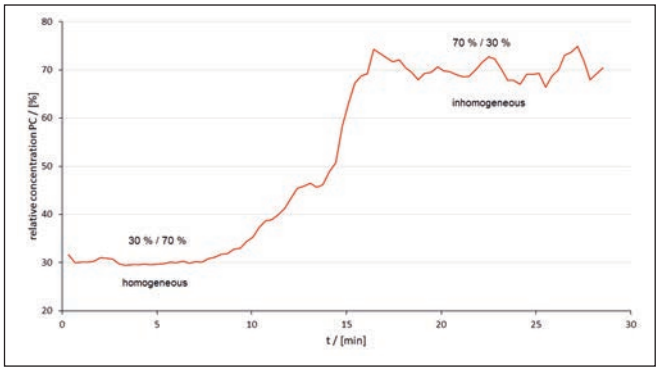


Figure 3: Comparison of loss modulus (red) and storage modulus (black) for a UV curing resin reaction.

For the 70% PC / 30% PMMA stage, significantly larger fluctuations in the Raman signal were observed. This indicates that the mixing process was not as uniform, leading to variations in polymer concentration within the extruded strand. Offline pellet measurements confirmed these findings, showing that the samples with 70% PC were not homogeneous and corroborating the in-line Raman observations.

By easy creation and application of quantification models on the Cora 5001, the relative PC/PMMA concentrations were also determined directly from the Raman spectra, thereby allowing for real-time composition tracking.

Additionally, Raman spectroscopy can be used to analyse mixing inconsistencies in situ that would be otherwise difficult to detect with offline analysis alone. This gives users consistent and continuous information on the material chemistry during extrusion, enabling better process design and control.

Summary

This study demonstrates how adding in situ Raman spectroscopy to the extrusion process can be a game changer for polymer industry as well as research purposes by allowing real-time monitoring of polymer blend compositions.

The study shows the ease of quantifying PC and PMMA concentrations and evaluating polymer homogeneity by analysing Raman spectral features at key vibrational bands.

In-line monitoring of polymer extrusion using Raman spectroscopy eliminates the dependence on offline analyses, leading to more efficient and accelerated formulation development, process development, faster scale-ups as well as improved quality control.

For a comprehensive guide to the polymer production process of plastic film extrusion, combined with various analysis techniques used alongside this process to maximise material performance, download our free e-book.

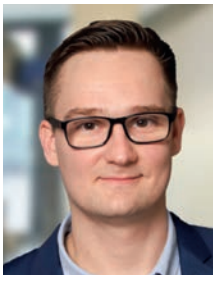
www.anton-paar.com/corp-en/polymer-processing/#ebook

It includes real measurement data from Raman and FTIR spectroscopy, water-selective moisture analysis, viscometry, gas pycnometry, nanoindentation testing, and zeta potential analysis – as well as insights into how manufacturers can enhance efficiency while improving product quality.

Authors

Marek Biermann

Dr. Nils Bertram



Michael Stanko