

IN-SITU MONITORING OF POLYMERIZATION PROCESSES BY RAMAN SPECTROSCOPY

Dieter Fischer*, V.B. Sadhu, J. Pionteck, H. Komber and J. Hutschenreuter

Institute of Polymer Research Dresden, Hohe Str. 6, 01069 Dresden, Germany

E-mail: fisch@ipfdd.de

Keywords: *process monitoring, extrusion, polymers, in-situ spectroscopy*

Abstract: RAMAN spectroscopy is a powerful in-situ method for monitoring polymerization processes and for the determination of the composition of polymer blends during extrusion. Examples are the polymerization of methyl methacrylate (MMA) and the real time determination of the composition of the polymer blend polypropylene (PP) / ethylene vinyl acetate (EVA).

Introduction

In recent years vibrational spectroscopic methods, particularly NIR and RAMAN, have become applicable to new applications in process analysis. The aim of the present work is to show that RAMAN is an excellent in-situ method for monitoring polymerization processes and for the in-line determination of the composition of polymer blends during extrusion processes. The aim of the first example was the monitoring of the synthesis of halogen-free amino-functionalized polymethyl methacrylate (PMMA) by ATRP. The aim of the second example was the determination of the efficiency of RAMAN spectroscopy for the quantitative analysis and the accuracy of the vinylacetate (VA) content in real time during extrusion. EVA is a random copolymer. The incorporation of VA leads to better flexibility and clarity and to better mechanical properties, e. g. impact strength. Applications for PP/EVA blends are hot melt adhesives, resins, coatings and textiles.

Experimental

I. In-situ RAMAN spectroscopy of the formation of halogen-free amino-functionalized PMMA by atom transfer radical polymerization (ATRP). In the present study we used essentially the same method as reported by Müller et al. [1]. The used catalyst system, CuBr/PMDETA and an initiator containing a protected amino functionality, in ATRP of MMA results in amino-functionalised PMMA. To hinder amino-caused side reactions and the interference of the amino-group with the catalyst system, the amino functionality of the initiator was protected before use. In order to obtain low molecular weight polymers, which can be analysed with sufficient accuracy, relatively high initiator to monomer ratios were chosen. The ATRP was carried out in solution at 25 °C in a flask.

Analytical techniques. The kinetics of the polymerization was studied in anisole by in-line RAMAN spectroscopy and off-line ¹H NMR spectroscopy. We collected a RAMAN spectrum, in-situ, every two minutes, using an in-line probe, which was directly immersed in the reaction medium. Cleaning of the probe head surface is required from time to time to avoid excessive fouling. The probe was connected via optical fibers with the RAMAN spectrometer HoloProbe 785 (Kaiser Optical Systems).

II. Quantification of the composition of the blend PP/EVA by RAMAN spectroscopy during extrusion. 24 different PP/EVA blends from 0 to 6.65 % VA-content were extruded in a twin screw extruder (Micro-Leistritz) at 200 °C and 70 bar.

Analytical techniques. We collected in-line RAMAN spectra in a melt-at-die interface which was adapted on the end of the extruder. A high temperature and high pressure probe was in the interface and connected via optical fibers to the RAMAN-Spectrometer HoloProbe 785 (Kaiser Optical Systems). The measuring time was 300 ms/scan using 40 scans.

Results and discussion

I. In-situ RAMAN spectroscopy of the formation of halogen-free amino-functionalized PMMA by ATRP. The in-situ RAMAN spectra are shown in **Figure 1**. The vinyl stretching at 1641 cm^{-1} is characteristic for the C=C bond of the monomer and decreases as a function of the monomer concentration. The band at 785 cm^{-1} is characteristic for the solvent anisole (CH bond of the aromatic ring) and is taken as an inner standard to quantify the monomer consumption. The change of the intensity ratio between both bands and the residual MMA content with time is shown in **Figure 2**. In-line RAMAN and off-line ^1H NMR spectroscopic methods were successfully used to determine the monomer conversion with time. The results of both methods agree well. A thin layer about $500\text{ }\mu\text{m}$ directly on the surface of the probe was detected. At high conversion rates the highly viscous material starts to stick at the probe, therefore it has to be cleaned from time to time. Furthermore, the accuracy may be reduced due to insufficient material exchange at the probe surface. Therefore, we evaluated the RAMAN spectra only up to a conversion of ca. 98.5 %.

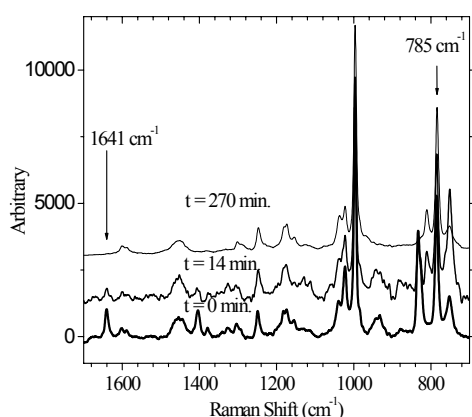


Fig. 1: In-situ RAMAN spectra of the ATRP of MMA in anisole at different times.

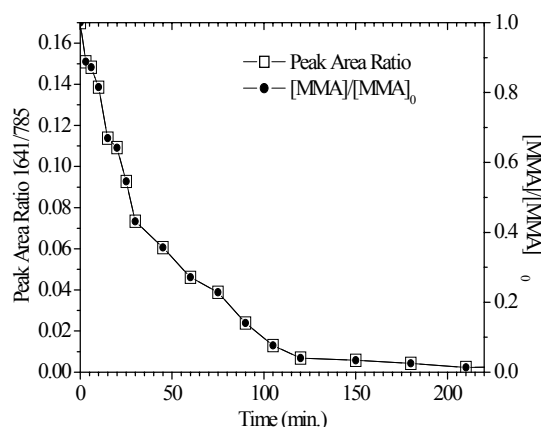


Fig. 2: Time dependence of the band area ratio of (A1641/A785) and the relative monomer content calculated of it.

II. Quantification of the composition of the blend PP/EVA by RAMAN spectroscopy during extrusion. For calibration, two methods were used: first the PLS method [2] from the software GRAMS32/PLSplus/IQ (Galactic) and second the integration of the band area at 630 cm^{-1} , 20 blends for calibration (200 spectra, 10 for each blend) and for an independent validation, 4 blends were used. By using PLS in the wavelength region from $350 - 1600\text{ cm}^{-1}$ the correlation coefficient R^2 was 0.994 (3 main components) and the standard error (SECV) was 0.19 %. With this calibration we could determine real time values for the 4 validation blends with an accuracy of 0.2 %. By using the band area for the band at 630 cm^{-1} , R^2 was 0.1 % and the validation accuracy was 0.15 %.

Summary

Real time monitoring of polymerization processes and mixing of polymers is a powerful method for both research and industrial process control. RAMAN spectroscopy has been utilized for the polymerization of MMA and we could determine the monomer conversion with time.

Furthermore, we have demonstrated that RAMAN is a powerful method for monitoring polymer melt mixtures in extrusion processes. Quantitative analysis can determine the composition of multicomponent polymer mixtures and predict real world samples in real time during extrusion.

References

1. Schön, F; Hartenstein, M.; Müller, A.H.E., *Macromolecules* **34**, 5934 (2001).
2. Martens, H; Naes, T., *Multivariate Calibration* 1989, Wiley