Raman-Line imaging to monitor diffusion kinetics

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Application Note

Introduction

Today, polymers are an integral part of our everyday's life. The interaction of the polymer with compressed gases is of basic interest for several applications, as particle formation, foaming, or blending. In this work, the diffusion of carbon dioxide (CO_2) into poly(ε-caprolactone) (PCL) was studied. Raman spectroscopy, an inelastic laser light scattering process, is species sensitive and quantifiable. It was implemented with one-dimensional resolution to monitor the concentration profiles of CO_2 inside a hanging PCL droplet (see Figure 1).
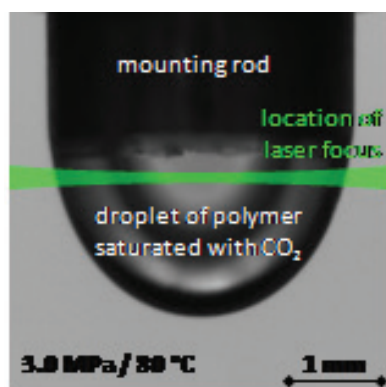

Figure 1: Polymer droplet under CO_2 atmosphere

Experimental Setup

A syringe pump was used to feed CO_2 into the cubic high pressure chamber. It is equipped with three windows to enable optical access to the polymer droplet inside. The droplet itself is adherent to a titanium rod mounted in the chamber. The beam diameter of the excitation source, a continuous wave Nd:YAG laser (λ=532 nm, P=3.5 W), is expanded by a Galilean telescope and focused into the measurement chamber by another lens. The waist of the laser focus builds up the one-dimensional measurement volume along the polymer droplet (see Figure 1). The light scattered perpendicular to the propagation of the laser beam is detected through an achromatic lens. A filter blocks elastically scattered light and transmits only the red-shifted inelastically scattered light. A second achromatic lens focuses the remaining Raman signal onto the entrance slit of the imaging spectrometer (Andor Shamrock SR-303i-B), with an analyzer allowing only s-polarized scattered light to enter. As the imaging spectrometer conserves the spatial information along the waist of the laser focus, the scattered light can be detected spatially resolved along the spatial axis of the EMCCD camera (Andor Newton DU971N-BV) attached. On the other hand, the detected light is dispersed into its wavelength components by a grating with 1200 lines per mm inside the spectrometer, defining the remaining axis of the 2-D detector as spectral axis. Therefore, the spectral signature from several positions along the 1-D measurement volume can be acquired with a single image (see Figure 2). By analyzing each spectrum in the image, a one-dimensional concentration profile can be derived from each image. The performance parameters are listed in detail in Table 1.
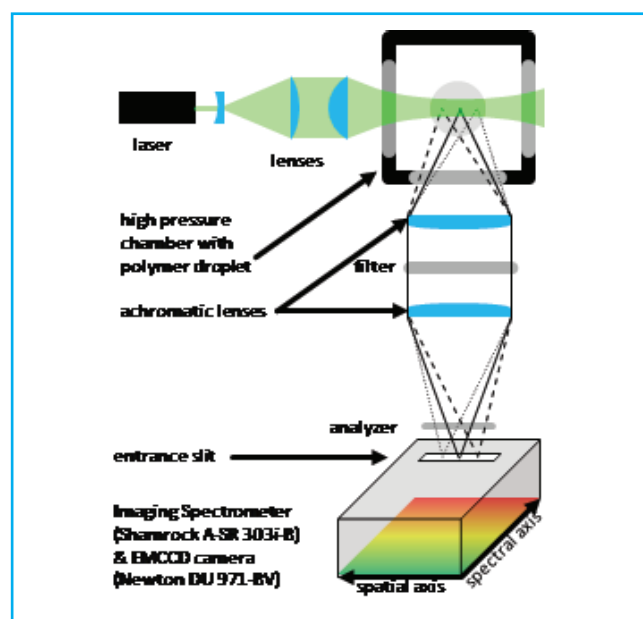

Figure 2: Optical Setup

Performance of detection system		
Parameter	Spatial axis	Spectral axis
Pixels	400	1600
Binning	10	1
Covered range	2.56 mm	480 – 2270 cm^{-1}
Resolution	64 µm	1.1 cm^{-1}
Exposure time	6 s	

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Measurement and evaluation principle

Prior to each measurement, the chamber is conditioned at 80 °C to melt the polymer and evacuated to remove moisture and impurities. A series of images of the polymer under vacuum is acquired, representing the Raman spectrum of the neat polymer. Then the chamber is pressurized to initiate the diffusion of CO_2 in the polymer droplet. To monitor the kinetics of this diffusion process, images are taken every 30 s until the system reaches an equilibrium state again. For calibration purposes, another series of images in this equilibrium state is taken, before the next pressurization step is performed. Figure 3 shows Raman spectra of the solution PCL-CO_2 at different pressures and in equilibrium. The Raman spectrum acquired at vacuum shows a course of several peaks characteristic for PCL, which can be recognized also at pressures larger than zero. Additionally, the so called Fermi diads of CO_2, labeled by the gray shaded area, become visible and grow with increasing pressure. From gravimetric measurements, the amount of CO_2 dissolved in the polymer for certain pressures is known. This allows correlating the intensity of the upper Fermi diad, superimposed with the polymer spectra, with the mass fraction of CO_2 dissolved in the polymer.
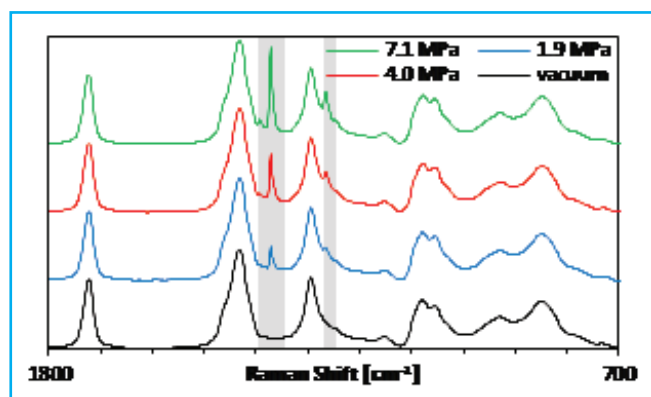

Figure 3: Raman spectra in equilibrium at 80 °C

Results

From the Raman spectra acquired spatially and temporally resolved after each pressurization step, the kinetics of diffusion can be derived. As an example, Figure 4 shows the concentration of CO_2 dissolved in the polymer droplet at several positions up to 25 min after the pressure increase from vacuum up to 3 MPa. The spatial positions are indicated by the normalized radius r^+, measured from the center of the droplet. At positions located closer to the center of the droplet (lower r^+ values), the increase of CO_2 concentration is delayed, but finally the equilibrium value of 10^{-3} mol/cm^3 is reached approximately 15 min after the pressurization for all positions. By fitting the experimental data to a theoretical model describing the diffusion process, important quantities as diffusivity and Biot number of diffusion of this system can be derived.
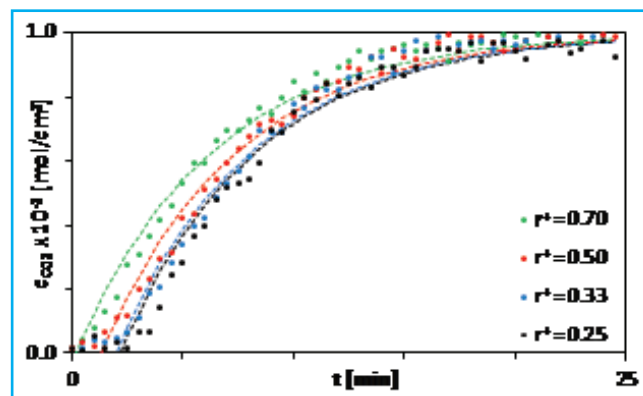

Figure 4: Experimental and theoretical diffusion kinetics

Contact

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