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Anomalous Swelling of Molten PCL/scCO₂ solutions

**Maria Giovanna Pastore Carbone^a, Daniele Tammaro^a, Attilio De Maio^a,
Ernesto Di Maio^a, Robert Hankel^{b,c}, Andreas Braeuer^{b,c}, Giuseppe Mensitieri^a**

^a*Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale, School of Engineering,
University of Naples Federico II, P.le Tecchio 80, 80125 Naples (Italy)*

^b*Erlangen Graduate School in Advanced Optical Technologies (SAOT), Friedrich Alexander Universität Erlangen-
Nürnberg, Paul-Gordan-Str. 6, 91052 Erlangen, Germany*

^c*Lehrstuhl für Technische Thermodynamik (LTT), Friedrich-Alexander Universität Erlangen-Nürnberg, Am
Weichselgarten 8, 91058 Erlangen, Germany*

Abstract. The swelling behavior of molten poly(ϵ -caprolactone) in contact with carbon dioxide has been analyzed by using the pendant drop method. At subcritical pressures, the swelling kinetics of the polymer-gas solution follow the typical Fickian diffusion behavior, the volume approaching an equilibrium value after the initial transient. In supercritical conditions, after the first transient, the volume of the solution does not approach an equilibrium value but still, slowly increases. Raman experiments have suggested that this anomalous time-dependent swelling in scCO₂ could be due to slow, secondary diffusion, or to polymer dissolution in scCO₂.

Keywords: poly(ϵ -caprolactone), scCO₂, pendant drop method, Raman spectroscopy

PACS: 81.05.Lg, 82.35.Lr, 83.80.Rs, 83.80.Sg

INTRODUCTION

Supercritical CO₂ (scCO₂) has become of strategic importance in polymer processing due to the possibility of tailoring solvent properties by slightly adjusting either the pressure or temperature conditions. It represents a suitable, sustainable and inexpensive alternative for plasticizing molten polymers during processing, as compared to traditional additives, which are often difficult to precisely control, separate, and recover, and has shown a great potential in several applications (synthesis, foaming, blending, coating and additive impregnation) [1, 2]. The investigation of these processes has revealed that all of them utilize the ability of scCO₂ to swell and plasticize the polymer [2]; hence, the investigation into the swelling behavior of polymers in contact with scCO₂ is of great importance for technological purposes.

In this work, we present some unexpected findings concerning the swelling behavior of poly(ϵ -caprolactone) (PCL) in contact with scCO₂. PCL is a biodegradable aliphatic polyester that is being commonly used for biomedical applications due to its biocompatibility and biodegradability, mainly for the preparation of drug delivery devices and tissue engineering scaffolds [3-5]. Therefore, the processing of PCL with scCO₂ has been widely analyzed, starting from the basic research on the thermodynamic and mass transport properties of the specific binary system [6, 7]. Also data on the specific volume of PCL/CO₂ solutions have been reported [8, 9]. The investigation we present herein has been mainly performed by optical monitoring a pendant drop of molten PCL in a CO₂ atmosphere, at 80 °C and at pressures up to 120 bar. Time resolved Raman spectroscopy has been adopted to probe the nature of swelling phenomena at highest pressures.

EXPERIMENTAL

Poly(ϵ -caprolactone), a biodegradable polymer with a melting point of ca. 60 °C, was supplied by Solvay Interlox Ltd. (PCL CAPA 6800, $M_n = 69,000 \pm 1500$, $M_w = 120,000 \pm 2000$) and used as received. High purity grade carbon dioxide was supplied by SOL (Italy).

The PCL pendant drop was created and stuck to a titanium rod placed in a high temperature/high pressure view cell equipped with optical quality windows, mounted perpendicular to the axis of the cell. Step-wise increments of the gas pressure (about 5 bar steps) with pre-heated gas were conducted from 0 to 120 bar and, during each pressure step, drop volume was monitored by using an adjustable high resolution CCD camera, equipped with a modular zoom lens system, and connected to a computer. Image acquisition of the pendant drop was performed every 30 s and drop volume was calculated by using a commercial software (FTA32 Video 2.0, First Ten Angstroms), by profile integration. A uniform bright background was provided by light emitting diodes, allowing the achievement of an optimal threshold for digitizing the drop image.

Spectroscopic analysis of PCL/CO₂ solutions was performed by using a custom-made apparatus, made up of a view cell, which is equipped with four sapphire windows, and a Raman sensor. The molten polymer was contained in a cuvette, placed into the cell, and a heating jacket ensured constant temperature. A pressure syringe pump feeds CO₂ into the cell. A green excitation laser ($\lambda = 532$ nm) with an output power of 100 mW excited the Raman process in the polymer sample during sorption. Details on the Raman sensor are given in Ref [10]. Before starting the pressurization, the Raman spectrum of the molten PCL was collected; having pressurized the chamber with CO₂ at 100 bar, Raman spectra were collected from the sample contained in the cuvette, every minute in the first 72 h with an exposure time of 1 s, and then three times a day (each time 100 single spectra), with an exposure time of 30 s.

RESULTS

Pendant Drop Method

Figure 1a shows the swelling kinetic of the PCL/CO₂ solution from 0 to 30 bar: after the initial transient, which, as highlighted in the inset of Figure 1a, recalls the typical Fickian behavior, drop volume approaches an equilibrium value. The duration of the swelling transient for the solution at pressures below the critical point has been found to be as long as 15 minutes. Figure 1b shows the swelling kinetic in a pressure step increment test from 99 to 100 bar, highlighting a different behavior; in fact, the volume of the drop does not approach an equilibrium value but the drop keeps on swelling for more than ten days.

Having observed that sorption needs several weeks to reach true equilibrium, in order to evidence the condition at which the systems departs from Fickian behavior, Figure 2 reports data of swelling ratios evaluated, in each step-pressure increase, after different time intervals: 15 min, 4, 6 and 24 h. As it is possible to observe, Figure 2 shows that the data collapse on a single curve up to pressures around the critical pressure for CO₂, while data at higher pressures differ from each other, with data at longer time being larger than those evaluated after 15 minutes.

FIGURE 1. Swelling kinetics for the PCL/CO₂ solution after pressure steps 0 – 30 bar (a) and 99 – 100 bar (b). Inset: drop volume vs. $\sqrt{t}$

FIGURE 2. Swelling ratio as a function of CO₂ pressure after different time intervals

Raman Spectroscopy

Raman spectroscopy has been invoked in order to understand the nature of the anomalous “time-dependent” swelling of the solution in the supercritical regime. In fact, Raman spectroscopy is a technique that provides quantitative information on mass transport of penetrant in optical transparent matrices, as described in the work by Knauer et al. [11]. The spectrum of PCL/scCO₂ solution at 100 bar is shown in Figure 3a. For evaluation purposes, the Raman spectrum of neat molten PCL was subtracted from the temporally resolved PCL/CO₂ solution spectra in order to isolate the contribution of the penetrant. All the spectra were preliminarily normalized to the intensity of the carbonyl peak of the polymer (at 1722 cm⁻¹). A LabView routine was implemented for the evaluation of the area beneath the normalized, difference spectrum, in the wavenumber region from 1345 cm⁻¹ to 1380 cm⁻¹, and the result of the elaboration is shown in Figure 3b. It is interesting noting that, after the first region following the Fickian diffusion behavior, the Raman signal does not approach an equilibrium value but slowly increases. Having normalized all the spectra to polymer, this trend can be ascribed or to further sorption of CO₂ or to further swelling of PCL. The former could suggest that the anomalous time-dependent swelling in scCO₂ is likely due to slow, “secondary” diffusion; the latter could be associated to polymer dissolution in scCO₂.

FIGURE 3. Raman spectrum of PCL/CO₂ solution at 100 bar (a) and temporal evolution of normalized CO₂ signal (b)

CONCLUSIONS

The swelling behavior of solution of molten PCL/CO₂ has been analyzed by using the pendant drop method and temporal resolved Raman spectroscopy. Optical measurements have revealed an anomalous behavior in supercritical conditions, as the volume of the solution does not approach an equilibrium value after the initial transient (being evaluated, for the specific geometry, approximately 15 min), but keeps on swelling for more than ten days. Preliminary spectroscopic investigation has revealed that, at longer times, penetrant signal normalized to the one of the polymer slowly increases. In light of this result, the anomalous swelling observed in scCO₂ could be ascribed or to a slow, “secondary” diffusion of CO₂ molecules into the solution, or to the polymer swelling likely related to polymer dissolution in scCO₂. Both the scenarios will be subject for future investigations.

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