



Polyether polyol/CO₂ solutions: Solubility, mutual diffusivity, specific volume and interfacial tension by coupled gravimetry-Axisymmetric Drop Shape Analysis

Maria Rosaria Di Caprio^a, Giovanni Dal Poggetto^b, Maria Giovanna Pastore Carbone^{a, c}, Ernesto Di Maio^{a, *}, Sara Cavalca^d, Vanni Parenti^d, Salvatore Iannace^e

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

^b Institute for Polymers, Composites and Biomaterials, National Research Council, Via Campi Flegrei 34, 80078 Pozzuoli, Naples, Italy

^c Institute of Chemical Engineering Sciences, Foundation of Research and Technology-Hellas (FORTH/ICE-HT), Stadiou Street, Platani, Patras Achaia 26504, Greece

^d Dow Italia s.r.l, Polyurethanes R&D, Via Carpi 29, 42015 Correggio, Italy

^e Institute for Macromolecular Studies, National Research Council, Via Edoardo Bassini, 15, 20133 Milan, Italy

ARTICLE INFO

Article history:

Received 29 March 2016

Received in revised form

8 June 2016

Accepted 9 June 2016

Available online 14 June 2016

Keywords:

Polyol

CO₂

Solubility

Diffusivity

Interfacial tension

Specific volume

ABSTRACT

In this work we investigate the sorption of CO₂ in a formulated polyether polyol, typically used to obtain rigid polyurethane foams when it reacts with isocyanates. In particular, by using a fully-experimental, coupled gravimetry-Axisymmetric Drop Shape Analysis, solubility, mutual diffusivity, specific volume and interfacial tension of polyol/CO₂ solutions have been measured at 35 °C and at CO₂ pressures up to 8000 kPa.

CO₂-treated polyol was also subjected to Gel Permeation Chromatography (GPC) and Fourier Transform Infrared (FT-IR) spectroscopic analysis to evaluate the effect of the high-CO₂ pressure treatment. The results show quite a large CO₂ solubilization (up to 17% ca. in the examined experimental range), in turn responsible for a moderate swelling of the polymer and an extensive effect on the interfacial tension, which reaches vanishing values at the highest investigated pressure.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Rigid polyurethane foams (PURs) are closed-cell foamed plastic materials with excellent thermal insulating properties, used as a factory made material in the form of insulation boards or blocks, or in combination with various rigid facings for appliances as a construction material. In addition to the low thermal conductivity, PURs are stable and durable, which is an important feature to guarantee the stability of the insulating properties. In fact, in building applications, these materials must work for as long as the building stands and should have a useful life beyond 50 years [1].

The thermal insulation properties of PURs are due to the presence of closed micro-cells, filled with inert gases, which work, at micron scale, as insulated glazing do at macroscopic scale in

reducing heat transfer in buildings. Thermal conductivities, depending on the total gas content (void volume fraction), on the pore topology (foam morphology) and on the thermal conductivities of both the polymer matrix and the gas [2], may reach values as low as 12 mW/(m K) [1]. Until recently, the inert gas most commonly used in polyurethane foams was R-11 (trichlorofluoromethane, CFC-11). However, the Montreal Protocol on substances that deplete the ozone layer has called for the phasing out of the use of CFCs and their replacement with hydrocarbons, hydrofluorocarbons and CO₂. In particular, CO₂ is environmentally friendly and offers a long-term sustainable solution, due to its zero Ozone Depletion Potential (ODP) and its lowest Global Warming Potential (GWP), set equal to 1 as reference to other Green-House-Gases (GHG). Furthermore, CO₂ is non-flammable and is inexpensive, as it is readily available in the atmosphere and other natural sources [1].

The foamed structure of PURs is obtained by the simultaneous gelation reaction between polymeric precursors (polyol and

* Corresponding author.

E-mail address: edimaio@unina.it (E. Di Maio).

isocyanate) and gas generation, which can result from a physical, chemical or mechanical process. In physical foaming, a fluid such as hydrocarbons (mainly cyclopentane), hydrofluorocarbons or CO₂, is first solubilized at high pressure in the polymeric precursors at ambient temperature and then it is allowed to evolve from the solution by pressure quench (in this case, no chemical reaction involves the blowing process and the fluid is called Physical Blowing Agent (PBA)). In chemical foaming, the blowing agent is generated from a chemical reaction. Typically, the addition of water in the formulation allows for the reaction of water with isocyanate, to give unstable carbamic acid that decomposes to amine and CO₂ as a by-product, which blows the polymer [2]. In mechanical foaming, the gas, most commonly air, is dispersed into the starting components by vigorous agitation, which leaves entrapped air bubbles within the polymeric matrix. Most commonly, both PBA and water are used, in a combined chemical and physical foaming manner, with CO₂ being present in the reaction media in a dual form, as resulting from the chemical reaction of water with isocyanate and as a physical blowing agent, solubilized under pressure in either the polyol or the isocyanate component. The addition of water has to be finely controlled, as its reaction with the isocyanate may give polyurea as a by-product, which has detrimental effects on some physical and mechanical properties of the final foamed products, such as the stiffness and the strength, and has negative effects on processability [3].

In this context, it is of great importance to know how CO₂ gets into the polymeric precursors, to design the process and the equipment and to optimize the foaming reaction. For instance, CO₂ solubility will determine the amount of gas available for blowing the polymer, in turn defining the final density of the foam, while diffusivity determines the minimal residence time of contact between the gas and the polymeric precursors at processing temperature and pressure to achieve the desired polymer/gas solution. In foaming, furthermore, it has been evidenced how low molecular weight penetrants (in our case, CO₂) extensively affect other properties of the polymer/penetrant solutions, which are involved in the foaming process, namely the interfacial tension of the polymer/penetrant solution in contact with the penetrant and, to a lesser extent, the specific volume of the polymer/penetrant solutions.

A number of experimental techniques are available to measure the aforementioned properties of polymer/gas solution at processing pressures and temperatures; for a review on these techniques, the reader may refer to Di Maio et al. [4]. In this context, recently, Pastore Carbone et al. [5] introduced a coupled sorption-Axisymmetric Drop Shape Analysis (ADSA) technique to simultaneously measure the solubility, diffusivity, interfacial tension and specific volume of polymer/gas solutions in a single experiment. The coupling between gravimetric and optical measurements allows for a fully experimental determination of the aforementioned properties, without resorting to any predictive modeling, as is typically done to evaluate the specific volume of the polymer/gas solution which is needed to calculate sorbed amount and interfacial tension.

To the best of our knowledge, only two papers addressed sorption of CO₂ in polyols. Kazarian et al. [6] simultaneously measured CO₂ sorption and swelling in polyether polyols such as polyethylene glycol (PEG) and polypropylene glycol (PPG) by using in-situ near-infrared spectroscopy. Authors reported data on CO₂ sorption in PEG and corresponding volume increase (swelling) at 40 °C and up to 11600 kPa, evidencing a solubility of CO₂ of 22.6% by weight and a swelling of 35%; for PPG, measurement have been conducted at 25 °C and 35 °C and at pressures up to 6000 kPa. In particular, at 35 °C and 6000 kPa authors observed a solubility of 11.8% by weight and a swelling of 24.5%. Fieback et al. [7] measured

the sorption of CO₂ and N₂ in a formulation of polyol (without any further details on its chemistry) and the correspondent swelling by using a magnetic suspension balance equipped with a view cell. Sorption experiments were conducted at temperatures ranging from 20 °C to 40 °C and at pressures up to 6000 kPa, and revealed a maximum in solubility of 38.2% by weight and a swelling as high as 47% at 20 °C and at 5400 kPa. To the best of our knowledge, no data have been reported so far on polyol/CO₂ mutual diffusivity and interfacial tension.

In this work, we report the use of the recently developed equipment based on the coupled sorption-ADSA [5,8] to measure solubility, mutual diffusivity, specific volume and interfacial tension of polyol/CO₂ solution. Measurements have been performed at 35 °C and at CO₂ pressures up to 6800 kPa.

2. Experimental section

2.1. Experimental set-up

The direct and simultaneous determination of solubility, diffusivity, interfacial tension and specific volume of polyol/CO₂ solutions is based on the coupling of gravimetric measurement with ADSA. In detail, it consists in the combination of the gravimetric determination of mass transfer from the CO₂ phase to the polyol contained in a crucible, and the simultaneous optical observation of volume and shape changes of a pendant drop (see Fig. 1). The adopted experimental set-up, schematized in Fig. 2, consists of a magnetic suspension balance (MSB) (Rubotherm Prazisionsmesstechnik GmbH, Germany) equipped with a high pressure and temperature (HT-HP, up to 250 °C and 13500 kPa) view cell, where a custom-designed cylindrical crucible containing 0.5 g ca. of polyol hangs from the hook of the balance weight measuring assembly, and a rod is fixed inside the cell to which the polyol pendant drop is attached. In this experimental configuration, the balance is continuously measuring the weight change of the polyol contained in the crucible and, at the same time, a high-resolution digital camera acquires the profile of the pendant drop. The relative position of the crucible and of the rod is such to avoid any interference with the gravimetric measurement and to allow the reliable continuous acquisition of the drop shape. Drop changes in volume and shape were observed through two optical quality windows, by using an adjustable high resolution CCD camera (BV-7105H, Appo), equipped with a modular zoom lens system (Zoom6000, Navitar). The CCD camera is connected to a computer, and a commercial software (FTA32 Video 2.0, First Ten Angstroms) is used to analyze drop profile [5,8]. Furthermore, in order to achieving the optimal threshold background for digitizing the drop image, a uniform bright background was provided by light emitting diodes. Detailed description of the equipment and of some preliminary experimental phases, such as optimization of CCD parameters and image calibration (pixel/μm calibration and aberration correction), are described elsewhere [5].

The data flow adopted for the elaboration of the data acquired during the coupled sorption-ADSA measurement is illustrated in Fig. 3. First, from the gravimetric experiment, apparent solubility (i.e. not yet corrected to account for the effect of change of sample buoyancy due to sorption and compressive action of pressure) was measured as a function of gas pressure. Concurrently, from ADSA, the profile of the pendant polyol/gas drop was computed. As described in detail in Pastore Carbone et al. [5], data from ADSA were used to evaluate the volume of the polyol/CO₂ solution contained in the crucible (A), thus allowing for the correction of sorption data with the proper buoyancy force and, consequently, for the calculation of actual solubility and diffusivity of the polyol/CO₂ solution at each gas pressure (B). Then, the specific volume of

Download English Version:

<https://daneshyari.com/en/article/201119>

Download Persian Version:

<https://daneshyari.com/article/201119>

[Daneshyari.com](https://daneshyari.com)