

# Thermosetting polyurethane foams by supercritical CO<sub>2</sub> as physical blowing agent

Maria Rosaria Di Caprio<sup>a,\*</sup>, Ernesto Di Maio<sup>a</sup>, Sara Cavalca<sup>b</sup>, Vanni Parenti<sup>b</sup>,  
Pellegrino Musto<sup>c</sup> and Salvatore Iannace<sup>d</sup>

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

<sup>b</sup>Dow Italia S.r.l, Polyurethanes R&D, via Carpi 29, 42015 Correggio, Italy,

<sup>c</sup>Institute for Polymers, Composites and Biomaterials, Via Campi Flegrei, 34, 80078 Pozzuoli (Na),  
Italy

<sup>d</sup>Institute for Macromolecular Studies, Via Edoardo Bassini, 15, 20133 Milan, Italy

\* mariarosaria.dicaprio@unina.it

## ABSTRACT

The aim of the present study was the achievement of thermosetting polyurethane foams by a batch foaming process that uses CO<sub>2</sub> as a physical blowing agent (PBA). In particular, to address the recent interest in combining the gas (physical) foaming with the conventional (chemical) polyurethane foaming, a novel instrumented pressure vessel was designed for investigating: i) sorption under high gas pressure on the two, separate, components of the polyurethane foams, ii) synthesis under high gas pressure after the two components mixing, and iii) foaming upon release of the pressure. Results revealed a significant effect of sorbed CO<sub>2</sub> on the polyurethane synthesis and the need for the design of a new chemistry to exploit the use of physical foaming on thermosetting polyurethanes.

## INTRODUCTION

In the field of thermosetting polyurethane foams (PUs) obtained by the curing reaction between polyol and isocyanate, the selection and the amount of the blowing agents is very important to the final cellular structure and properties of the foam. Since the beginning of the history of PUs, CO<sub>2</sub>, derived from the blowing reaction of isocyanate with water, is used as blowing agent. In the late 1950s, large PUs production also utilized chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) as PBAs, then replaced by hydrocarbons (HCs) (e.g. pentane) because of their negative environmental impact. However, although cheap and with zero ozone depletion potential (ODP), HCs use was limited by flammability concerns. In this context, CO<sub>2</sub> is eco-friendly and safe, with zero ODP and the lowest GWP among known blowing agents [1]. In order to use CO<sub>2</sub> as a physical blowing agent (in a totally different manner to what has been done previously, with CO<sub>2</sub> resulting from the reaction of isocyanate with water) knowledge of the behavior of the whole system in the presence of high pressure CO<sub>2</sub> is fundamental. In particular, the following are needed: 1) the physical properties of polymer/gas solutions, namely solubility, diffusivity, specific volume and interfacial tension of the polyol- and isocyanate-CO<sub>2</sub> solutions in contact with the external, high pressure CO<sub>2</sub> phase; 2) the effect of the CO<sub>2</sub> on the reactions involving the different chemicals in the polyurethane synthesis; 3) the way the reactive system behaves when CO<sub>2</sub> is rapidly released to induce foaming.

We herein report our approach to the problem, with the design of new experimental apparatus. We report, in particular, measurements at 35°C of solubility, mutual diffusivity, specific volume and interfacial tension of polyol/CO<sub>2</sub> solution at CO<sub>2</sub> pressures up to 80 bar and isocyanate/CO<sub>2</sub> solution up to 55 bar, obtained by a coupled gravimetry-Axisymmetric Drop Shape Analysis (ADSA) [2-4]. Foaming experiments, conducted at 35°C and various CO<sub>2</sub> pressures, with a novel instrumented pressure vessel capable of retrieving data on sorption, synthesis and foaming are described. This pressure vessel makes use of a sample holder with a flexible impeller that allows to keep polyol and PMDI separated during the sorption stage and to mix the components to start the PU synthesis. Furthermore, it makes use of a sapphire window and FT-NIR spectroscopy to monitor sorption and the synthesis. The effect of CO<sub>2</sub> on the reaction has been evaluated at 35°C and 40bar.

## **MATERIALS AND METHODS**

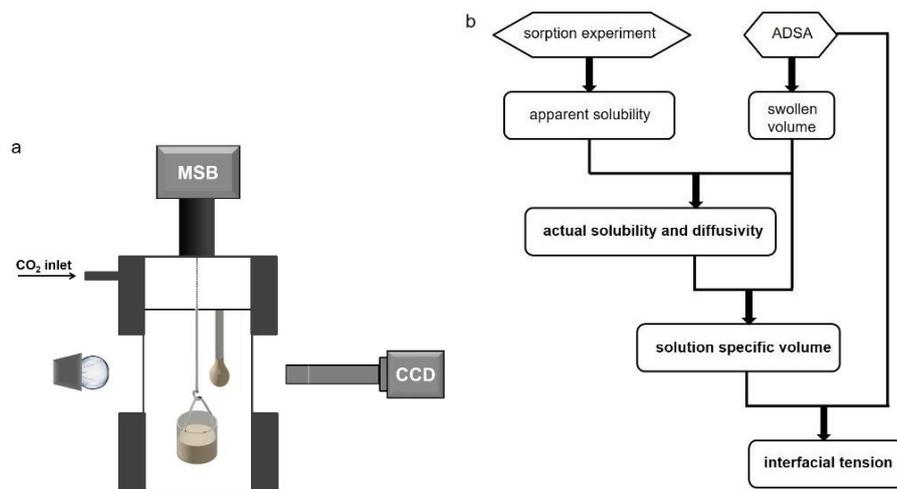
### *Materials*

A formulated polyol and a polymeric methylene diphenyl di-isocyanate (PMDI) were supplied by DOW Italia S.r.l. (Correggio, RE, Italy) and used “as received”. High purity grade CO<sub>2</sub> was supplied by SOL (Naples, Italy).

### *Sorption measurements of CO<sub>2</sub> in polyol and PMDI*

Coupled sorption-ADSA experiments were conducted by using magnetic suspension balance (MSB) (Rubotherm Prazisionsmesstechnik GmbH, Germany), equipped with a high temperature/high pressure (HT-HP) view cell. The simultaneous measurement was made possible by adopting a custom-designed measuring device, which consists of a crucible containing the polymer/CO<sub>2</sub> solution (for weight monitoring) and a Teflon rod to which the polymer/CO<sub>2</sub> solution drop is stuck (for ADSA) (see Figure 1a). Drop changes in volume and shape were observed through two optical quality windows, by using an adjustable high resolution CCD camera (BV-7105H, Appro), 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 [2-4]. Furthermore, in order to achieving the optimal threshold background for digitizing the drop image, a uniform bright background was be provided by light emitting diodes.

The data flow adopted for the elaboration of the data acquired during the coupled sorption-ADSA measurement is illustrated in Figure 1b.

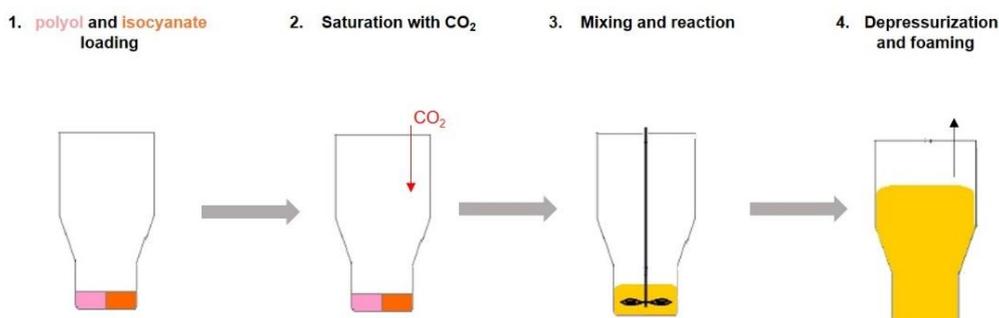


**Figure 1.** (a) Schematic illustration of the experiment and (b) data flow used in the coupled sorption-ADSA measurement.

Sorption and ADSA experiments were carried out by isothermal pressure increments up to 80 bar for polyol while up to 55 bar for PMDI, at 35°C, after having placed both the crucible containing the polymer and the rod with the polymer drop in the HT-HP view cell. In detail, sorption measurements were performed by step-wise increments of the gas pressure (500 kPa steps ca.), after the attainment of equilibrium sorption in the previous step. Concurrently, during each pressure step, image acquisition of the pendant drop was performed every 10 min. and drop volume was calculated by using the commercial software.

### *PU foaming with CO<sub>2</sub>*

In Figure 2, the steps of foaming experiment are shown. Inside the pressure vessel, polyol and PMDI, separated by a flexible impeller, are placed (1), pressurized with CO<sub>2</sub> at 35°C until saturation (2) and mixed (3). Finally, at any stage of the curing reaction physical foaming occurs due to pressure release (4).



**Figure 2.** Steps of foaming experiment.

Different foaming tests will be carried out, by changing process parameters as sorption time in order to evaluate its influence on the PU morphology.

### *Spectroscopic measurements*

The curing reaction, at 35°C and atmospheric pressure, was monitoring by using a fiber optic reflectance probe, placed beneath the sampler holder contained the two reactants, connected to Frontier™ NIR spectrometer (Perkin Elmer Inc., Waltham, MA, USA) equipped with equipped with a NIR source, a CaF<sub>2</sub> beam splitter and a INGAAS detector.

During the cure, spectra were recorded automatically at regular time interval of 3s for 10 minutes using Perkin Elmer TimeBase software, in the spectral range 4000-10000cm<sup>-1</sup> with a resolution of 16 cm<sup>-1</sup> and 4 scans just after mixing.

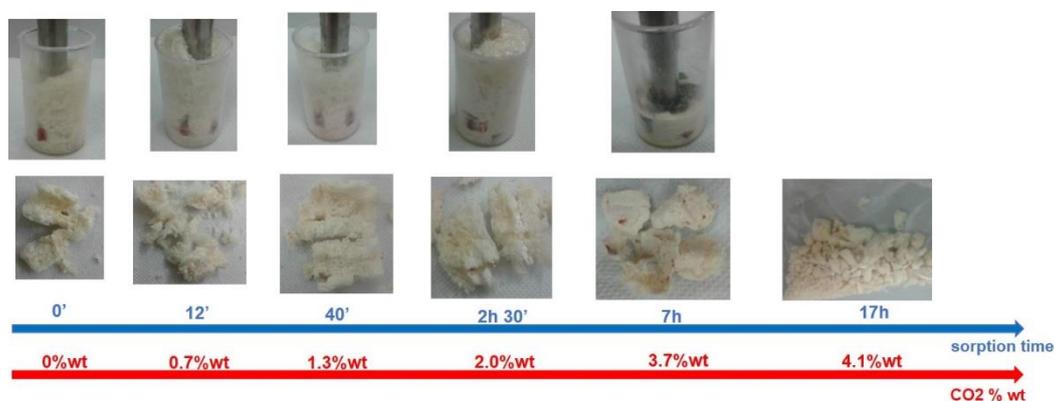
## RESULTS

### *Sorption measurements of CO<sub>2</sub> in polyol and PMDI*

Sorption measurements for the polyol/CO<sub>2</sub> solution show quite a large CO<sub>2</sub> solubilization (17% wt ca. at 80 bar and 35°C), 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. Mutual diffusivity goes from 1e<sup>-6</sup> to 1e<sup>-5</sup> cm<sup>2</sup>/s in the whole experimental range. The same study conducted on the PMDI at 35°C and CO<sub>2</sub> pressures up to 50 bar has shown for the sorption isotherm a maximum of about 6%wt, with mutual diffusivity of 2 10<sup>-6</sup> cm<sup>2</sup>/s ca. and a minor swelling of the polymer/gas solution with respect to the neat polymer, while the interfacial tension reaches the value of 15 mN/m ca. In both sorption measurements, for higher pressure it has been observed that low molecular weight components of polyol and PMDI are solubilized in CO<sub>2</sub>, as confirmed by Gel Permeation Chromatography analysis.

### *PU foaming with CO<sub>2</sub>*

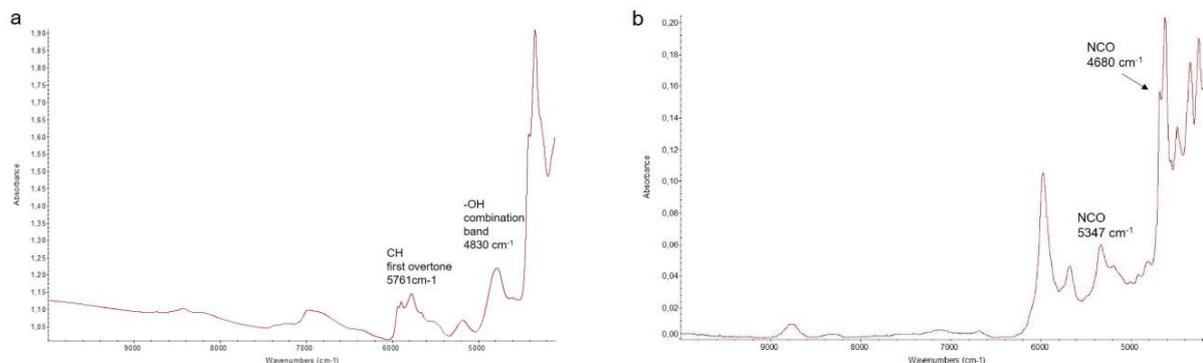
In Figure 3 PUs obtained at 35°C and 40 bar of CO<sub>2</sub> pressure by changing sorption time (or CO<sub>2</sub> amount) are shown. Curing time was fixed at 1 minute and mixing at 250 rpm for 10s. It is possible to note that by increasing sorption time, PU change its morphology from an inhomogeneous to more homogeneous one until to become a pulverized product for high sorption time indicating a CO<sub>2</sub> effect on the system.



**Figure 3.** PUs obtained at different sorption times (or CO<sub>2</sub> amount).

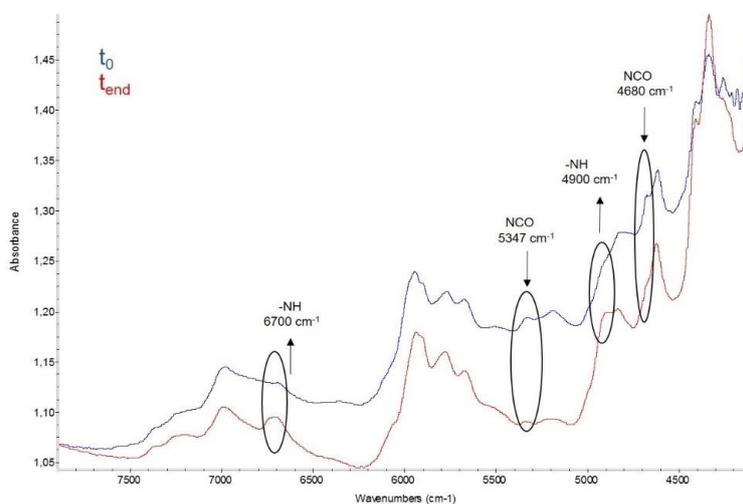
## Spectroscopic measurements

NIR spectra of polyol and PMDI at room temperature are shown in Figure 4 a and b, with their characteristic absorption peaks.



**Figure 4.** NIR spectra of polyol (a) and PMDI (b) at room temperature.

In Figure 5 spectra collected at the beginning (blue line) and the end (red line) of the curing reaction, at room temperature and atmospheric pressure, are reported. From these spectra is possible to follow the NCO band decrease and the NH band (of urethane group) formation and increase [5,6].



**Figure 5.** NIR spectra collected at the beginning  $t_0$  (blue line) and the end  $t_{end}$  (red line) of the cure.

## CONCLUSIONS

The use of CO<sub>2</sub> as PBA to obtain PUs on lab scale was investigated. Solubility, mutual diffusivity, specific volume and interfacial tension of polyol/CO<sub>2</sub> solution at CO<sub>2</sub> pressures up to 80 bar and PMDI/CO<sub>2</sub> solution up to 55 bar, were measured by using a fully-experimental, coupled gravimetry-Axisymmetric Drop Shape Analysis at 35°C. These data were used to produce PUs in a pressure vessel, at 35°C and 40bar of CO<sub>2</sub> pressure, by changing the sorption time. It was noticed an influence of CO<sub>2</sub> on the final product, in fact by increasing sorption time PU morphology improves until an optimum and then it changes resulting in a pulverized product. FT-NIR spectra were recorded to monitor the curing reaction after mixing of the two reactants at room temperature and atmospheric pressure.

## ACKNOWLEDGEMENTS

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