

Effect of high-pressure CO₂ on polyurethane synthesis

Maria Rosaria Di Caprio^a, Cosimo Brondi^a, Ernesto Di Maio^{a,*}, Sara Cavalca^b, Vanni Parenti^b,
Salvatore Iannace^c, Pellegrino Musto^d

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

^bDow Italia s.r.l, Polyurethanes R&D, via Carpi 29, 42015 Correggio, Italy

^cInstitute for Macromolecular Studies, Via Edoardo Bassini, 15, 20133 Milan, Italy

^dInstitute on Polymers Composites and Biomaterials, National Research Council of Italy, 80078 Pozzuoli,
Italy

*edimaio@unina.it

ABSTRACT

In a newly developed sensorized pressure vessel, polyurethane synthesis under high-pressure carbon dioxide was studied by using in situ near infrared spectroscopy. In particular, the equipment is capable keeping the two components of the polyurethane reaction (polyol and isocyanate) separate during CO₂ sorption, by making use of a rubber impeller which, at the end of the sorption stage, is then allowed to mix polyol and isocyanate to start the synthesis reaction, still under high CO₂ pressure. Near infrared spectroscopy in reflection mode was used to monitor the polyurethane synthesis, at different CO₂ pressures, and the extent of reaction was calculated. Results revealed a significant effect of sorbed CO₂ on the polyurethane synthesis and the need for the design of a new chemistry to exploit the use of physical foaming on polyurethane foams.

INTRODUCTION

In thermosetting polyurethane foams (PUs), the selection and the amount of the blowing agents is very important to the final cellular structure and, in turn, to the properties of the foam. Since the beginning of the history of PUs, CO₂ derived from the blowing reaction of isocyanate with water has been used as a blowing agent. In this case, water is the chemical blowing agent (CBA) and CO₂ is the reaction product, slowly made available by the blowing reaction, concurrent to the polyurethane synthesis reaction. In the late 1950s, large PUs production also utilized chlorofluorocarbons (CFCs) and hydro-chlorofluorocarbons (HCFCs) as physical blowing agents (PBA), then replaced by hydrocarbons (HCs) (e.g. pentane) because of their negative environmental impact. PBA, differently from CBA, are solubilized in the polyol and/or isocyanate phases prior to foaming and then become available when the system is brought to super-saturation conditions, typically by the temperature rise following the exothermic synthesis reaction. Although cheap and with zero ozone depletion potential (ODP), HCs use was, however, limited by their inherent flammability. In this context, CO₂ is considered more eco-friendly and safe, with zero ODP and the lowest global warming potential (GWP) among known blowing agents [1]. In fact, because of the environmental concerns and of the encouraging performance in producing microcellular foams with thermoplastic polymers, CO₂ has most recently attracted a growing industrial interest as a PBA for PUs [2]. In order to use CO₂ as a PBA (solubilized at high-pressure in the polyol and/or isocyanate) it is fundamental to understand the behavior of the whole system in the presence of CO₂. In

particular, CO₂ may play a critical role in the different reactions involved in the polyurethane synthesis. In fact, in the recent years, the use of CO₂ (in particular in supercritical conditions) as a reactant or as the reaction medium has been largely described in the literature [3-7]. In particular, the readiness of CO₂ to interact chemically with proton-containing nucleophiles, such as water, alcohols and primary, secondary and tertiary amines was used to develop switchable systems [8,9]. Quantitative information regarding the CO₂ sorption in polyurethane reactants and the local curing extent is typically supplied by in situ infrared spectroscopy. In particular, FT-NIR spectroscopy has proven suitable for remote control sampling, in reflection mode, in comparison to Middle Infra-Red Attenuated Total Reflectance (MIR-ATR), which uses expensive and brittle fibers with short length and lower penetration depth (path length). The accuracy of FT-NIR spectrometers greatly improved due to the combination of spectroscopic methods and fiber optics technology, becoming a powerful tool for the control the curing reaction, in real time, of thermosetting polymers [10]. Herein, we present the use of FT-NIR spectroscopy in diffuse reflection mode to monitor in situ the curing under CO₂ pressures of a polyurethane formulation.

MATERIALS AND METHODS

Materials

A polyether polyol and polymeric methylene diphenyl diisocyanate (PMDI) [11,12] were supplied by DOW Chemical Italy S.r.l. (Correggio, RE, Italy) within the LIFE13-EN/IT/001238 project [2] and used “as received”. High purity grade CO₂ (99.95% pure) was supplied by SOL (Naples, Italy). The polyol and the PMDI were mixed in a quantity related to the isocyanate Index equal to 115.

Methods

In situ FT-NIR spectroscopic investigation of polyurethane curing was conducted by using Frontier™ NIR spectrometer (Perkin Elmer Inc., Waltham, MA, USA) characterized by a tungsten halogen source, a CaF₂ beam splitter and a FlexIR™ NIR Fiber Optic reflectance probe (PIKE Technologies, Inc., Madison, WI, USA) equipped with an InGaAs detector. The probe was housed beneath a high-pressure-tight sapphire window placed on the bottom plate of a 1 L pressure vessel (Figures 1a and 1b) [13].

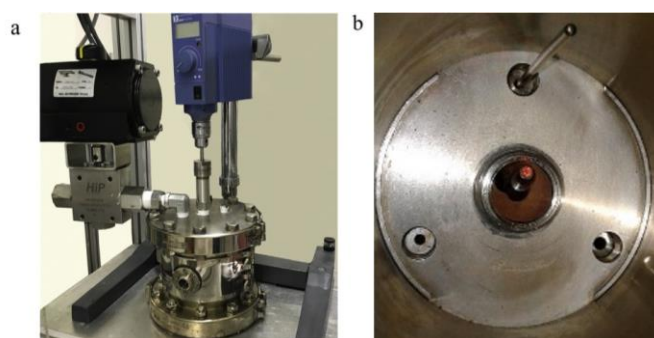


Figure 1. Pictures of the pressure vessel. a) Assembly, with the mixing head and the gas evacuation system and b) detail of the probe and the sapphire windows placed at the bottom plate of the pressure vessel.

In order to monitor the curing (here, in particular, we are interested in the effect of the sorbed CO₂ on the reaction kinetics) polyol and PMDI were gently cast in the sections of a glass cylindrical sample holder formed by the sample holder itself and the blades of a rubber impeller, which

prevents the premature mixing of the two reactants (see Figure 2a). The sample holder was then placed in the pressure vessel onto the sapphire window and secured by a Teflon coupling (see Figure 2b). The pressure vessel was then pressurized and sorption was conducted for 5h. After sorption, the two reactants were put in contact for the reaction to occur by operating the impeller with a mixing shaft connected to a lab mixer by high-pressure bearing [13]. The curing reaction was conducted, still under pressure, for a suitable amount of time, until completion.

The curing, at different CO₂ pressure (range 0-10000 kPa) and 35°C, was monitored by collecting spectra, just after the mixing, automatically at regular time interval of 20 seconds with a resolution of 4 cm⁻¹ and 8 scans, after mixing at 250 rpm for 10s until the end of the reaction.

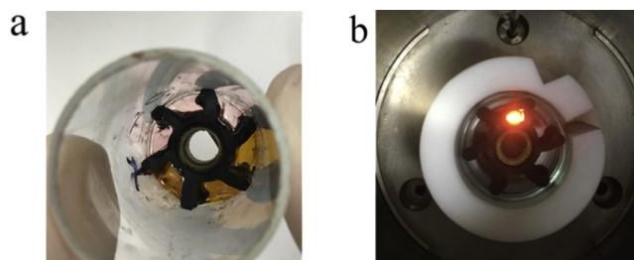


Figure 2. a) Sample holder with the rubbery impeller that keeps separate the two reactants, top view and b) details of the sample holder fixed by a Teflon coupling to the sapphire window, with the rubber impeller and the light from the NIR probe.

RESULTS

Figure 3 reports, as example, NIR spectra collected just after the mixing of the two components at 250 rpm for 10s (black curve) and at the end of the curing reaction (red curve), at 35°C and 4000 kPa of CO₂ pressure. The main absorption bands of a polyurethane are assigned with light blue arrows [14]. The orientation of these arrows indicates the disappearing or the formation of the relative band when the curing reaction happens. The CO₂ band is also indicated with a blue arrow. Good signal to noise ratio and reproducibility of NIR spectra were observed.

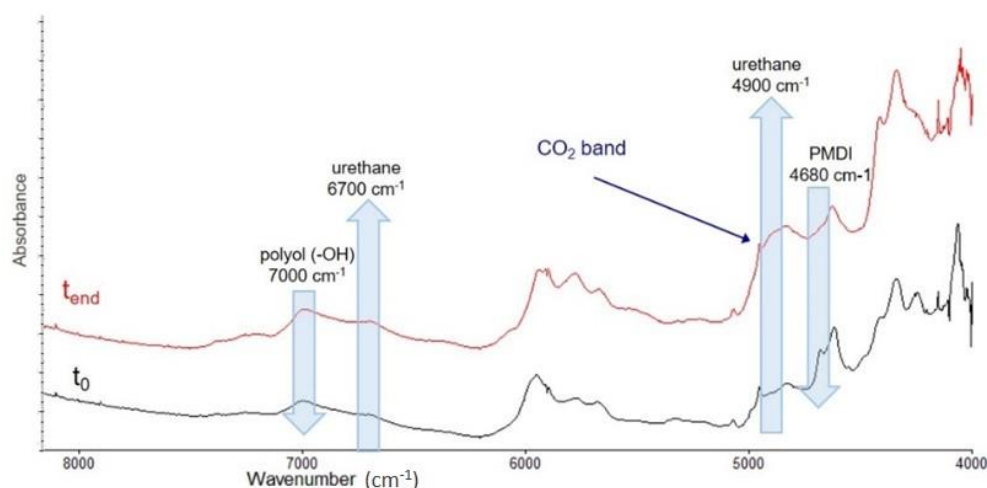


Figure 3. NIR spectra collected at the beginning t_0 (black curve) and the end t_{end} (red curve) of the curing reaction at 35°C and at 4000 kPa of CO₂ pressure. The polyurethane absorption bands, indicated by the light blue arrows, are assigned according to literature [14].

The extension of polyurethane curing reaction (below defined as curing time, as reported in Figure 4 and Table 1), at different CO₂ pressures (0-10000 kPa) and at 35°C, was measured as the time at which the area of NH urethane absorption band at 6700 cm⁻¹ does not change anymore. The area of this band was calculated through univariate analysis according to Beer Lambert law by using Perkin Elmer TimeBase software.

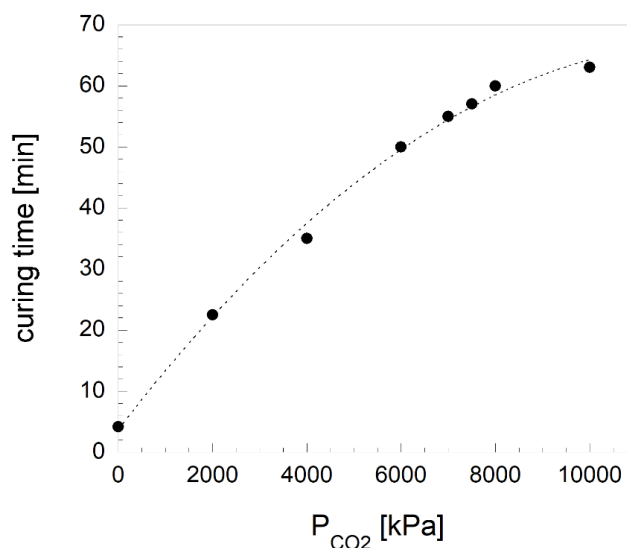


Figure 4. Curing time as function of CO₂ pressure, measured by following the evolution of the area of NH band at 6700 cm⁻¹.

Table 1. Curing time at different CO₂ pressure and T=35°C.

P _{CO2} [kPa]	curing time [min] (NH band)
0	4.2
2000	22.5
4000	35.0
6000	50.0
7000	55.0
7500	57.0
8000	60.0
10000	63.0

As reported in Figure 4 and Table 1, the curing time increases by increasing CO₂ pressure according to a polynomial of second order, so the curing reaction is slowed down in presence of CO₂. In the literature, the slowing down of the polyurethane curing reaction is reported in presence of scCO₂ without details about a possible chemical mechanism [15]. This kind of behavior could be attribute to the Lewis acid-base interaction between CO₂, polyol and tertiary amines used as

catalysts in the polyurethane formulation studied in this work. As example, in literature is known the reversible reaction between CO₂ and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) tertiary amine in 1-hexanol and 1-propanol (Figure 5) [9].

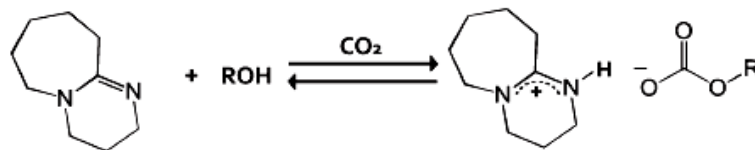


Figure 5. Reversible binding of CO₂ with DBU in alcohol solution [9].

The mixture of amidine base and an alcohol reacts with CO₂ to create a high polarity ionic liquid with quaternary ammonium cations and alkylcarbonate anions. The reaction can be reversed by removal of the CO₂. The reversible binding between CO₂ and primary, secondary and tertiary amines is well known in literature, in CO₂ capture processes [16-18], but it can be also used in other areas such as in catalytic processes, where CO₂ is used simultaneously as solvent and as a protecting group for amines. In our case, the CO₂ effect on catalytic deactivation can be used to obtain a right polymer matrix viscosity before the pressure release in order to avoid the collapse of the cellular structure in making a PU.

CONCLUSION

The FT-NIR investigation of the extension of polyurethane curing reaction at different CO₂ pressure (0-10000kPa) and at 35°C has shown that CO₂ is not an inert PBA in the considered chemical system. During polyurethane formation, the curing time increases by increasing CO₂ pressure meaning that the curing reaction is slowed down in presence of CO₂. This kind of behavior could be attribute to the Lewis acid-base interaction between CO₂, polyol and tertiary amines used as catalysts in the formulation in use. This CO₂ effect on catalytic deactivation can be used to obtain the best polymer matrix viscosity before the pressure release during the production of a PU in order to avoid the collapse of the cellular structure.

Furthermore, these results confirm FT-NIR spectroscopy as a valid monitoring technique for polymerization reactions.

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