

A pressure vessel for studying gas sorption and synthesis of thermosetting polyurethane foams

Maria Rosaria Di Caprio^{a,*}, Daniele Tammaro^a, Ernesto Di Maio^a, Sara Cavalca^b,
Vanni Parenti^b, and Salvatore Iannace^c

^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

* mariarosaria.dicaprio@unina.it

ABSTRACT

We herein report the design of a new apparatus for studying the concurrent chemo-physical processes occurring during gas foaming of thermosetting polyurethanes. In particular, the design of the new pressure vessel relies on two key features. From the processing side, we make use of a rubber impeller to keep the polyol and the isocyanate, the two components for the polyurethane synthesis, separate in a sample holder during gas sorption and to allow for an efficient mixing at the end of the sorption stage. From the analytic side, we utilized a sapphire window beneath the sample holder to measure the amount of sorbed gas and to follow the curing reaction during polyurethane foam formation under gas pressure by in situ FT-near infrared (FT-NIR) reflectance spectroscopy. Preliminary results are reported for the polyol-isocyanate/CO₂ system.

INTRODUCTION

Use of sensors to control polymerization processes has rapidly grown, in the last decades in chemical industry in order to control the actual state of the process and the quality of the products [1]. More recently, some monitoring techniques greatly improved by the combination of spectroscopic methods and fiber optics technology, which allow for the in situ and in-line acquisition of process data, consequently allowing for reduction of time delays normally involved with sample preparation. Among them, techniques based on the near infrared (NIR) spectroscopy have certainly become the most important ones [2].

In this contest, in-situ NIR spectroscopy was used to simultaneously measure the gas sorption and the swelling of polymers [3]. Several studies report the use of NIR spectroscopy for polymerization process monitoring, by controlling in situ and on-line monomers conversion during chemical reactions. In particular, NIR spectroscopy was used to monitor and control the curing reaction, in real time, of thermosetting polymers, e.g. polyisocyanurate resin system, epoxy resin and polyurethanes (PU) in solutions of dimethyl formamide [4-6].

Herein, we report the design of a new pressure vessel to monitor the gas sorption in polyol and isocyanate and the curing reaction during PU foam formation, after mixing of the two components, by using in situ FT-NIR spectroscopy.

MATERIALS AND METHODS

A formulated polyether polyol and a polymeric MDI (PMDI) were supplied by DOW Italia S.r.l. (Correggio, RE, Italy) and used “as received”. High purity grade CO₂ was supplied by SOL (Naples, Italy). To perform the experiments we used a new pressure vessel illustrated in Figure 1 in 3D rendering with some details of the sapphire window for NIR monitoring and the sample holder before and after mixing. The pressure vessel is 1L from Avantes BV (Eerbeek, The Netherlands) and it has several ports for control and accessing: 1. for temperature measurement inside the pressure vessel; 2. for the pressure sensor (IMP-G300, Impress, Kingsclere, UK); 3. for the gas-dosing, achieved via a 500D syringe pump (Teledyne Isco, Lincoln, NE, USA); 4. for gas evacuation, achieved in a controller manner via a 10-80NFH ball valve equipped with a TSR-20 actuator (High Pressure Equipment Company, Erie CO, USA); 5. for the sapphire window (5) (custom made, Precision Sapphire, Vilnius, Lithuania); for the mixing shaft (6), connected to the pressure vessel with a Single Lip V-spring-loaded rotary shaft seal (7) (RS19B, American High Performance Seals, Inc., Oakdale, PA, USA). In the pressure vessel, a sample holder (8) made of pyrex glass, with an optical bottom disc is placed on to the sapphire window. Finally, a rubbery impeller (9) (mod. BG 06, AncorS.r.l., Caronno Pertusella, Va, Italy) connected to the mixing shaft, seals sections of the sample holder where the different components are gently cast at the beginning of the test. A standard lab mixer (mod. Euro-ST P CV, IKA-WERKE GmbH & Co. KG, Staufen, Germany) is utilized for mixing, connected to the mixing shaft. Figure 2 reports images of the pressure vessel, the gas evacuation system and the mixer, assembled, together with some details of the apparatus. FT-NIR spectroscopy measurements were conducted by using Frontier™ NIR spectrometer (Perkin Elmer Inc., Waltham, MA, USA) equipped with a PIKE FlexIR™ near-IR (NIR) Fiber Optic reflectance probe. During CO₂ sorption in polyol and PMDI at 40 bar and 35°C, spectra were recorded automatically at regular time interval of 30min for 2 days using Perkin Elmer TimeBase software, in the spectral range 4000-10000 cm⁻¹ with a resolution of 4 cm⁻¹ and 32 scans. Curing PU reaction at atmospheric pressure was followed by collecting spectra for 5 min with a resolution of 16 cm⁻¹ and 4 scans after mixing at 250 rpm for 10s.

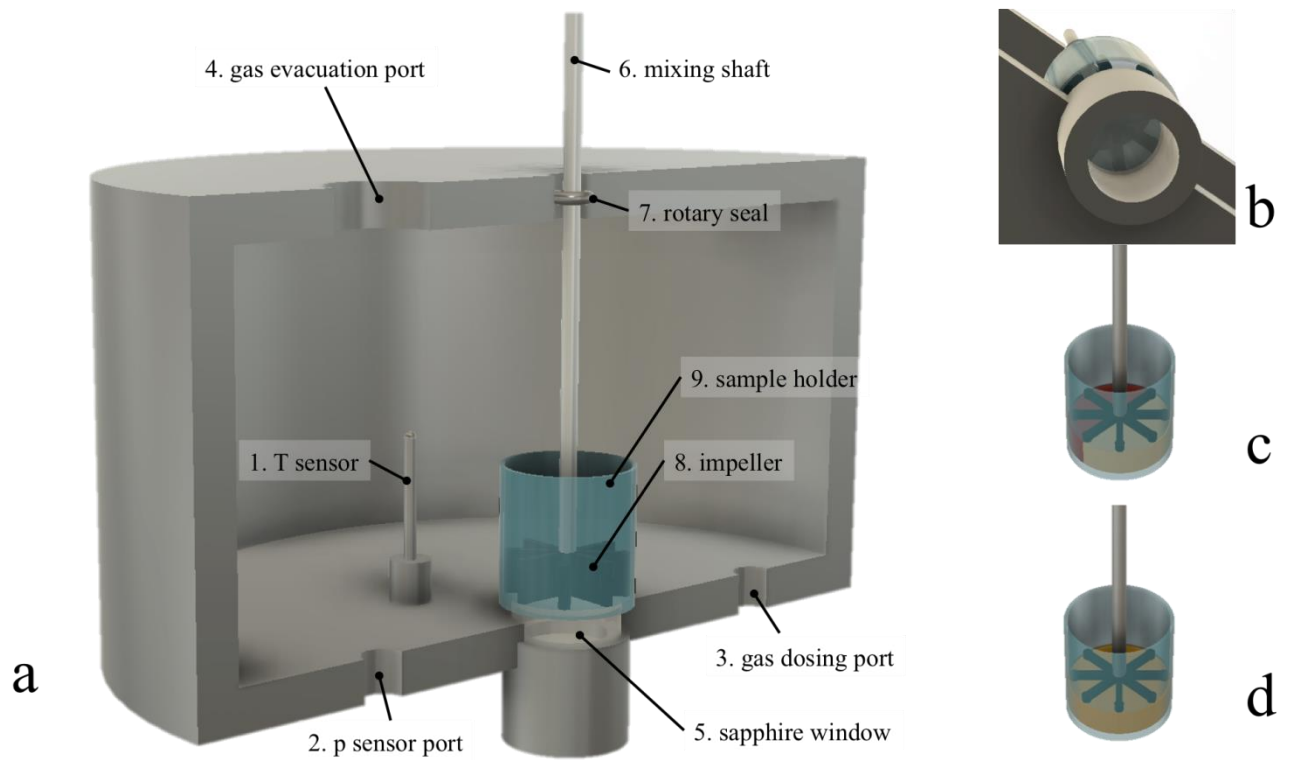


Figure 1. 3D rendering of the pressure vessel. a) cross section of the pressure vessel and the sample holder and impeller; b) details of the sapphire window and the impeller (bottom view); schematic of the sample holder and the two components before (c) and after (d) mixing.

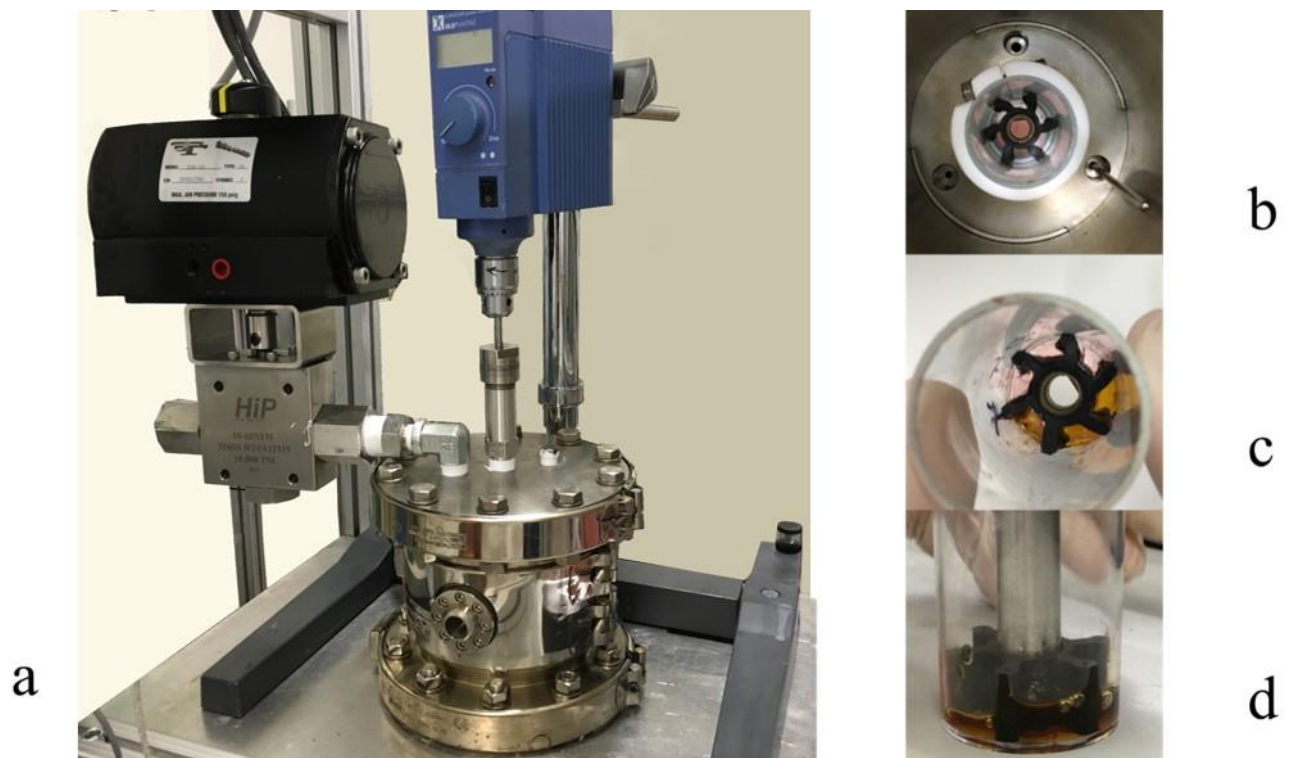


Figure 2. Images of the apparatus. a) assembly, with the mixing head and the gas evacuation system; b) details of the sapphire window and the impeller (top view); c) and d) sample holder with the rubbery impeller, top view (c) and side view (d).

RESULTS

NIR spectra of polyol and PMDI before and after exposition for 2 days at 40bar of CO₂ pressure and 35°C are reported in Figure 3a and b. Spectra of the samples exposed to CO₂ pressure for long time show the CO₂ combination bands at 4950 cm⁻¹ and at 5070cm⁻¹ (red arrows). The concentration of CO₂ dissolved in polymer can be determined from the absorbance of the band of CO₂ at 4950cm⁻¹ (we also performed gravimetric measurements to correlate with NIR results). Bands of polyol at 5778cm⁻¹ and of PMDI at 5347cm⁻¹ can be used to calculate the extent of polymer swelling [3].

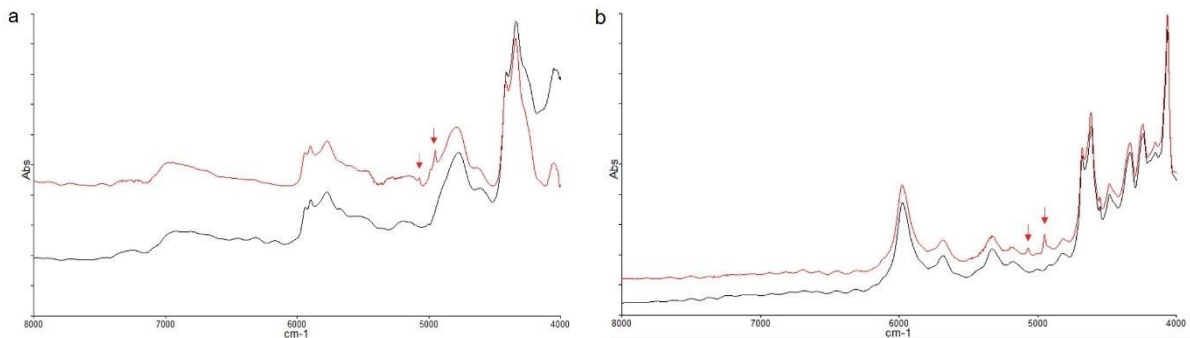


Figure 3. NIR spectra of polyol (a) and PMDI (b) at 35°C before (black line) and after exposure for 2 days at CO₂ at 40 bar and 35°C (red line). The red arrows indicate the combination bands of CO₂ dissolved in the two polymers.

Figure 4 show spectra collected during the curing PU reaction at room temperature and atmospheric pressure. It is noteworthy that from these spectra is possible to detect the NCO band disappearance and the NH band (of urethane group) formation and increase [7,8].

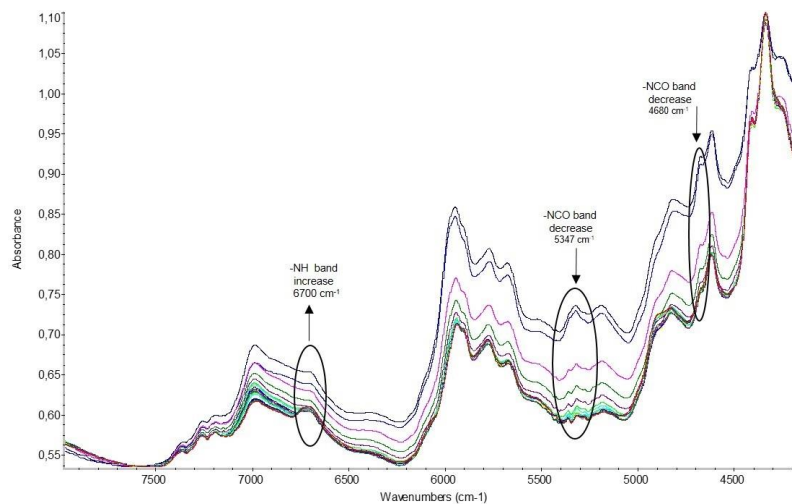


Figure 4. NIR spectra collected during the curing reaction. The absorption bands are assigned according to the literature results [7,8].

CONCLUSIONS

In the field of the sensors used to monitor polymerization reactions, we have developed a new pressure vessel by which is possible through NIR spectroscopy in reflection mode to follow the gas sorption in polyol and isocyanate and the curing reaction during PU foams formation after mixing of the components. This equipment allows keeping separated the two reactants during gas sorption through a rubber impeller that is then used to mix components in order to produce the PU foam. A remote sensing NIR fibre optic reflectance probe is placed in contact with sapphire window located beneath the sample holder in order to collect spectra.

From preliminary NIR spectra collected during CO₂ sorption in polyol and PMDI, it is possible to detect the CO₂ combination bands, while, during PU foam formation, it is possible to follow the NCO band decrease and the NH band (of urethane group) formation and increase. These results confirms NIR spectroscopy as a valid monitoring technique for gas sorption in polymers and for polymerization reactions.

ACKNOWLEDGEMENTS

The financial support of the European Union's (LIFE13-EN/IT/001238 project, <http://ec.europa.eu/environment/life>; www.dow.com/k12) is gratefully acknowledged.

REFERENCES

- [1] FONSECA, G.E., DUBE´, M.A., PENLIDIS, A. Macromolecular Reaction Engineering, Vol. 3, **2009**, p. 327
- [2] SANTOS, A.F., SILVA F.M., LENZI, M.K., PINTO, J.C. Polymer-Plastics Technology and Engineering, Vol. 44, **2005**, p. 1
- [3] GUADAGNO, T., KAZARIAN, S.G. Journal of Physical Chemistry B, Vol. 108, **2004**, p. 13995
- [4] DUNKERS, J.P., FLYNN, K.M., HUANG, M.T., MCDONOUGH, W.G. Applied Spectroscopy, Vol. 52, **1998**, p. 552
- [5] WANG, Q., STORM, B.K., HOUMOLLER, L.P. Journal of Applied Polymer Science, Vol. 87, **2003**, p. 2295
- [6] NOGUEIRA, E.S., BORGES, C.P., PINTO, J.C. Macromolecular Materials and Engineering, Vol. 24, **2005**, p. 272
- [7] DUPUY, J., BENALI, S., MAAZOUZ, A., LACHENAL, G., BERTRAND, D. Macromolecular Symposia, Vol. 184, **2002**, p. 249
- [8] DE THOMAS, F.A., HALL, J.W., MONFRE, L.S. Talanta, Vol. 41, **1994**, p.425