

A pressure vessel for studying gas foaming of thermosetting polymers: sorption, synthesis and processing



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ABSTRACT

We herein report the design of an apparatus for studying the concurrent chemo-physical processes occurring during gas foaming of thermosetting polymers. In particular, to address the recent interest in combining the gas (physical) foaming with the classical (chemical) polyurethane foaming, a novel instrumented pressure vessel was designed for investigating: i) gas sorption under high pressure on the different reactants, kept separate; ii) synthesis under high gas pressure, upon mixing and iii) foaming upon release of the pressure. 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 two reactants separate 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 use diffuse reflectance near-infrared spectroscopy to measure both the amount of sorbed gas and the reaction kinetics under gas pressure. Preliminary results are reported for the polyol-isocyanate/CO₂ system.

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1. Introduction

Thermosetting foams (e.g. polyurethane, polyisocyanurate, phenol-formaldehyde, urea-formaldehyde, epoxy and silicone foams) are widespread and typically used for thermal insulation and packaging. Their production relies on a curing process in presence of either a chemical (CBA) or a physical blowing agent (PBA), or a combination of both, evolving simultaneously with the curing process. CBAs produce gas by a thermal decomposition or a chemical reaction. PBAs are soluble additives which expand when subjected to a phase change induced by a fast decompression or heating [1]. In the past, the PBAs used in thermosetting foams were mostly chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), nowadays banned by Montreal Protocol, and flammable hydrocarbons (HCs) (e.g. pentane) [2,3]. Recently, for environmental and safety concerns, CO₂ has been introduced as a PBA in both thermoplastic and thermosetting foams and is more and more utilized worldwide. In thermosetting foams, CO₂ has been

successfully adopted as a PBA to produce epoxy foams [4–6]. In these cases, CO₂ was solubilized at high pressure in the pre-mixed reactants of the epoxy formulation (*after* reactants mixing), kept at low temperature to avoid curing before a sufficient amount of the PBA was solubilized. At the end of the solubilization stage, a temperature increase activated the catalysts for the initiation of the resin curing. The CO₂ pressure release allowed the formation of the bubbles, in turn stabilized by the completion of the curing process. CO₂ was also used as PBA to obtain polyurethane foams (PUFs), starting from a formulation characterized by a very slow curing reaction [7]. Also in this case, CO₂ pressurization was performed *after* mixing of the reactants (namely, a polyol and an isocyanate), the slow curing allowing for sufficient solubilization of the PBA, eventually released for foaming [7]. To the best of our knowledge, no papers addressed the use of CO₂ as a PBA in PUFs (as well as in other thermosetting polymers), where CO₂ solubilization is conducted *before* reactants mixing. This would be useful when starting from a formulation characterized by a fast curing reaction, where no time is allowed for PBA solubilization after mixing. Nor it has been reported a method to use PBAs in thermosetting polymers whose reactivity cannot be halted at will. In the case of polyurethanes, in fact, the typical processing temperatures utilized in

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the industry to conduct PUFs synthesis are in the range 25–35 °C and cooling would be required to slow down the curing. As an alternative, a change in the catalysts to slow down the curing would also be possible, as it has been done previously [4–7], but this would considerably alter the current formulations and methods and would be of limited scientific and industrial interest.

In this context, in the field of PUFs, liquid CO₂ is nowadays used in the so-called frothing process, where it is mechanically mixed (not solubilized) under pressure with the PUFs reactants during their chemical reaction and the mixture is then frothed by pressure release [8]. In the latter case, CO₂ does not behave as a PBA, but as a dispersed phase that expands upon pressure release. Foam morphologies, in this case, are controlled by the dispersion efficiency and not by the numerous variables and methods available to the gas foaming process.

Use of sensors to control curing 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 [9]. More recently, some monitoring techniques were 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 [10]. In this context, in-situ NIR spectroscopy has been used to simultaneously measure the gas sorption and the swelling of polymers [11]. Furthermore, several studies report the use of NIR spectroscopy for curing 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 [12–16].

Herein, we report the design of a new pressure vessel to study sorption, synthesis and foaming of thermosetting polymers by the gas foaming process, in which the PBA is allowed to solubilize into the reactants before mixing. Then, upon mixing, still under pressure, the curing reaction is induced up to a certain curing grade, when pressure is eventually released for PBA foaming. To monitor both sorption and curing under pressure, in-situ Fourier Transform Near InfraRed (FT-NIR) spectroscopy is used. The aim of the present contribution is to report the criteria that led to the design of this single piece of equipment capable of allowing a throughout study of gas foaming of thermosetting polymers. Furthermore, we present a detailed description of the equipment and report the results, listed as “sorption”, “curing” and “foaming” sections.

2. Experimental

2.1. Design criteria

The proposed apparatus is designed to meet the requirements for:

1. Allowing PBA sorption at high-pressure and moderate temperature for long time (tens of hours);
2. Keeping separate the two reactants for same long time during sorption;
3. Mixing the two PBA-laden reactants (tens of seconds);
4. Allowing partial curing (minutes);
5. Allowing fast and controlled PBA release for foaming (milli-to deci-seconds);
6. Allowing curing to go to completion;
7. NIR-monitoring all (but No. 5) of the above stages.

To do so, two main features are herein proposed for the novel instrumented pressure vessel: i) the use of a rubbery impeller for the reactant sealing (and successive mixing), ii) a high-pressure-tight sapphire window mounted beneath an IR-transparent sample holder for remote NIR monitoring. Fig. 1 reports 3D renderings of the proposed pressure vessel and of some details of the sapphire window for NIR monitoring, and the sample holder with the two reactants, before and after mixing.

Supplementary video related to this article can be found at <http://dx.doi.org/10.1016/j.polymertesting.2017.06.019>.

2.2. Experimental set-up

The pressure vessel is 1L, 150 mm in height, from Avantes BV (Eerbeek, The Netherlands). It has several ports for control and accessing: 1. For temperature measurement inside the pressure vessel (Pt 100); 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); 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 (internal diameter 29 mm), with an optical bottom disc is placed on to the sapphire window. Finally, a rubbery impeller (9) (mod. BG 06, Ancor S.r.l., Caronno Pertusella, Va, Italy) connected to the mixing shaft, is placed in the sample holder. 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. The lab mixer also provides the torque exerted to rotate the shaft. Torque evolution could be in principle utilized to monitor the curing reaction, which has a large effect on the rheological properties of the mixture. At the present state of the development, however, due to the geometry of the sample holder and the friction at the rotary shaft seal, the lab-scale mixer is not sensible enough to allow such measurement. NIR spectroscopy was conducted by using Frontier™ NIR spectrometer (Perkin Elmer Inc., Waltham, MA, USA) equipped with a FlexIR™ NIR Fiber Optic reflectance probe (PIKE Technologies, Inc., Madison, WI, USA). Fig. 2 reports images of the pressure vessel, the gas evacuation system and the mixer, assembled, together with some details of the sample holder and the impeller. Fig. 3 reports the inner of the pressure vessel with the NIR probe. In this configuration, the equipment can operate at maximum 200 °C and 20.0 MPa.

A typical test, with the aim of measuring sorption and curing under high blowing agent pressure, is conducted as follows. First, the samples in the form of the two viscous liquids (namely, the polyol and the isocyanate), are gently cast in the sections of the cylindrical sample holder formed by the blades of the impeller. Being made of rubber, the blades leak-seal (not high-pressure seal, not needed here) the sections, avoiding premature mixing of the two reactants (see Fig. 2c), which will get in contact and react only when the impeller is actuated by operating the lab mixer. Next, the sample holder is placed in the pressure vessel on the sapphire window by a Teflon coupling (see Fig. 3c) and then the pressure vessel is closed. After reaching the testing temperature, in this case 35 °C, pressure is increased up to the saturation pressure, in our case 4.0 MPa, and kept for a sufficient amount of time. During the sorption stage, the probe can alternatively monitor sorption in both the polyol and the isocyanate (*slow NIR monitoring*, see section 2.4. for details). It is worth of note, here, that sorption monitoring by spectroscopy has been already reported [11] and it is semi-

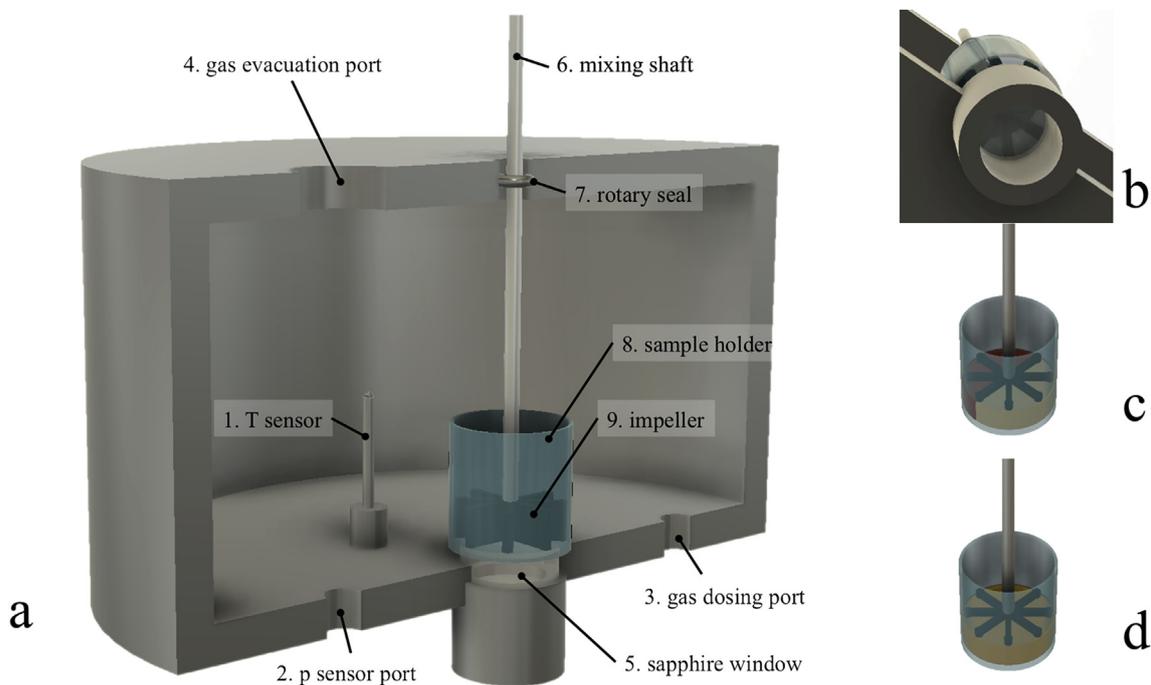


Fig. 1. 3D rendering of the pressure vessel. a) Cross section of the pressure vessel and the sample holder and impeller; b) details of the sapphire window and the impeller (bottom view); schematic of the sample holder and the two reactants before (c) and after (d) mixing. A movie showing different views of the pressure vessel can be find in the Supplementary Materials.



Fig. 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).

quantitative, as it necessitate for calibration by other sorption techniques. In our case we measured sorption by a coupled gravimetry-axisymmetric drop shape analysis (see Ref. [17] for the details) on the two reactants, as reported in Refs. [18,19]. When a suitable amount of gas has been sorbed in the two reactants, the curing stage can be initiated (in case, at a different temperature). In order to monitor the reaction (here, in particular, we are interested in the effect of the sorbed gas on the reaction kinetics), the NIR

probe is positioned under the isocyanate, and *fast NIR monitoring* starts (see section 2.4. for details). Then, the mixer is activated at a certain speed of rotation for a suitable amount of time (mixing time). The curing reaction is conducted, still under pressure, for a suitable amount of time (curing time) and finally the pressure is released for gas foaming in a controlled manner [20,21]. Finally, when the curing reaction has gone to completion, the pressure vessel is opened and the foam can be extracted for characterization.

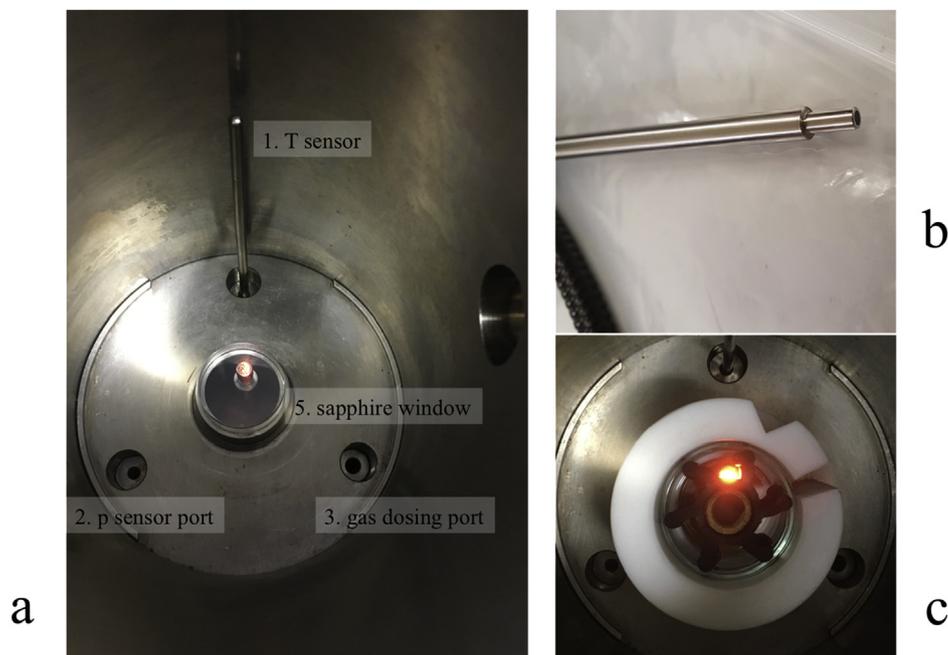


Fig. 3. Images of the apparatus with the NIR probe. a) Inner of the pressure vessel, showing the NIR probe facing inside through the sapphire window (see section 2.2. for details); b) the NIR probe; c) details of the sample holder fixed by a Teflon coupling to the sapphire window, with the rubber impeller and the light from the NIR probe.

2.3. Materials

A formulated polyether polyol and a polymeric MDI (PMDI) were supplied by DOW Italia S.r.l. (Correggio, RE, Italy) and used “as received”. Some details have been reported elsewhere [17,18]. High purity grade CO₂ was supplied by SOL (Naples, Italy).

2.4. Spectroscopic measurements

FT-NIR spectroscopy measurements, during CO₂ gas sorption in polyol and PMDI at 4.0 MPa and 35 °C and curing reaction without CO₂ pressure, were conducted by using Frontier™ NIR spectrometer equipped with a tungsten halogen source, a CaF₂ beam splitter and a fiber optic reflectance probe equipped with an InGaAs detector (see section 2.2. for details).

During CO₂ sorption, spectra were recorded automatically at regular time interval of 30 min (*slow NIR monitoring*) 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.

The curing reaction was followed by collecting spectra at regular time interval of 30 s (*fast NIR monitoring*) for 15 min, in the spectral range 4000–10000 cm⁻¹ with a resolution of 16 cm⁻¹ and 4 scans.

3. Results and discussion

3.1. Sorption

NIR spectra of polyol and PMDI before and after exposure for 2 days at 4.0 MPa of CO₂ pressure and 35 °C are reported in Fig. 4a and b, respectively. Such a long sorption time was selected, based on diffusivity data (gathered on both the polyol and the PMDI [18,19]) and on the sample amount, to attain equilibrium (uniform CO₂ concentrations in both the polyol and the PMDI). Spectra of the samples exposed to CO₂ reveal the CO₂-combination bands at 4950 cm⁻¹ and at 5070 cm⁻¹ (arrows highlight the position of these bands) [22]. The quantitative analysis of the sorbed CO₂ can be performed by multivariate chemometric Partial Least Squares

(PLS) models, typically used in the literature [23]. PLS has to be calibrated, however, with a known concentration. In our case, we may use data gathered by a coupled gravimetric/ADSA technique [18,19]. For the case at hand, when equilibrium is attained, CO₂ weight fractions of 8.4% and 4.6% were reported for the polyol and PMDI, respectively [18,19]. The analysis by PLS models will be reported in a future work. Finally, in general, other spectroscopic techniques could be used in combination with or in place of NIR. For example, in case N₂ is used as the blowing agent [24], Raman spectroscopy may be used [25,26], as N₂ vibrations are not NIR-active.

3.2. Curing

To prove the effectiveness of the proposed technique to monitor the curing reaction, Fig. 5 reports spectra collected after mixing the two components at 250 rpm for 10s, right after mixing and at the end of the curing reaction, at 35 °C and atmospheric pressure. The effect of CO₂ pressure and concentration on the curing reaction will be part of a forthcoming paper. Here, it is noteworthy that from evaluation of these spectra it is possible to detect the NCO band decrease and the NH band (of urethane group) formation and increase, which allows for a quantitative analysis of the curing process in combination with chemometric methods [14,15]. Spectra reported in Fig. 5 show that the NCO band at 4680 cm⁻¹, characteristic of the PMDI, does not completely disappear at the end of the cure, proving it is in excess with respect to the polyol in the adopted formulation. Data are, in our case, limited to wavenumbers from 4000 to 8000 cm⁻¹ of interest in this specific system. The possible NIR range of the present set-up extends to 10000 cm⁻¹. As already mentioned, the sapphire window and the equipment as the whole could also work with other spectroscopic techniques, such as Medium Infrared as well as Raman. However, the former technique poses some assembly problems, for the limited penetration depth of the radiation and the impossibility to use long (remote) probes, while the latter could give some fluorescence effect covering the materials signal. In fact, in our case, we acquired Raman spectra on

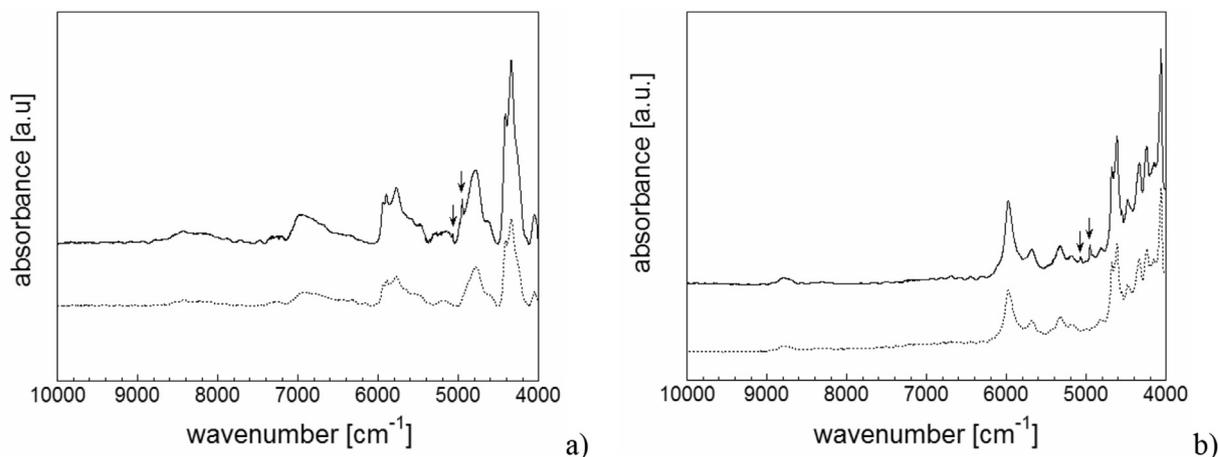


Fig. 4. NIR spectra of polyol (a) and PMDI (b) at 35 °C before (dashed line) and after exposure for 2 days at CO₂ at 4.0 MPa and 35 °C (solid line). The arrows indicate the combination bands of the CO₂ dissolved in the two reactants.

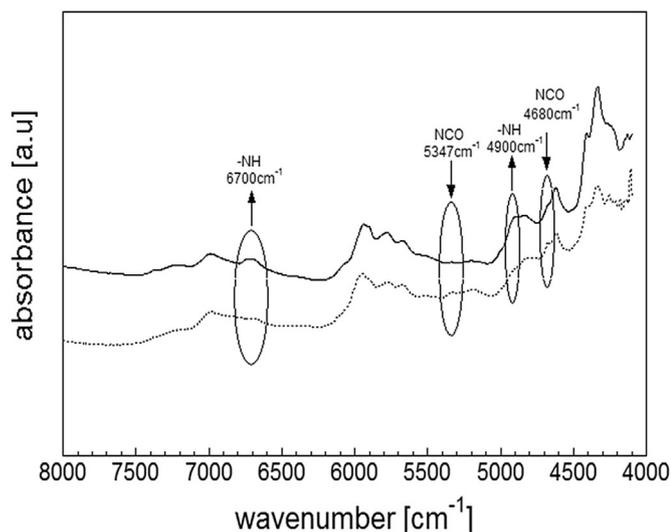


Fig. 5. NIR spectra collected at the beginning (dashed line) and the end (solid line) of the cure. The absorption bands are assigned according to the literature results [14,15]. Arrows pointing upward or downward indicate, respectively, bands that increase or decrease with proceeding of the curing reaction.

the two formulated reactants and the signal was covered by fluorescence to a large extent (data not reported). For these reasons, NIR has been selected in the present work, specifically for the polyol/PMDI/CO₂ system under investigation.

3.3. Processing (foaming)

In Fig. 6, images of the PUFs foams achieved via the new pressure vessel are reported. Fig. 6a) shows a foam achieved at 35 °C and ambient pressure (without physical CO₂). In this case, the small amount (0.2% wt. ca.) of water in the as-received polyol is responsible for the expansion. Fig. 6b) shows a foam achieved (with a depressurization rate of 20 MPa/s) after CO₂ sorption at 4.0 MPa until equilibrium, which corresponds to an average CO₂ content of 7%wt ca [18,19]. These preliminary results show the effect of the PBA on the expansion of the PU, responsible for a density decrease from 0.5 to 0.2 g/cm³ (according to ASTM-D792) when using CO₂ as

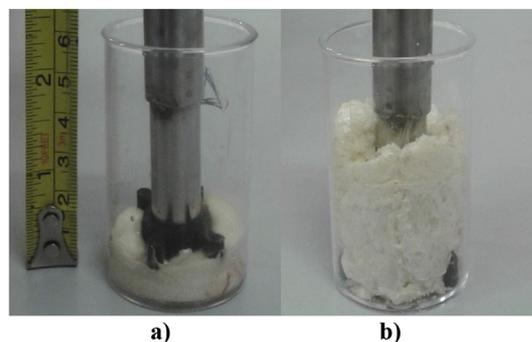


Fig. 6. PUFs obtained at 35 °C and a) ambient pressure and b) 4.0 MPa of CO₂.

an additional blowing agent. Further studies will be performed to reveal the effect on the morphology and the reaction kinetics, proving the utility of this instrumented pressure vessel to thoughtfully studying the foaming of thermosetting polymers with PBAs.

4. Conclusions

We have developed a new pressure vessel to monitor both the PBA sorption in the reactants of thermosetting polymers, kept separate during this stage, and the curing reaction after mixing of the so-formed reactants/PBA solutions, by use of NIR spectroscopy in reflection mode. Furthermore, the new pressure vessel allows for the study of thermosetting polymer gas foaming. On said equipment, we conducted tests on a polyurethane/CO₂ system at 35 °C and at pressures up to 4.0 MPa. By following the CO₂ combination bands we gathered quantitative data on the equilibrium CO₂ concentration at each temperature and pressure. After the sorption stage, the reactants were mixed under pressure to induce the polyurethane curing, whose progress has been monitored by same spectroscopic technique by following the NCO band decrease and the NH band formation and increase. Foaming is eventually induced at pressure release and foams showed the remarkable effect of the PBA foaming. These results proved that the introduced apparatus is a powerful analytical as well as processing tool to study the interaction of the high-pressure CO₂ with the reactants and to study the gas foaming of thermosetting polymers.

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