



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



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

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

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

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

ARTICLE INFO

Article history:

Received 31 March 2017

Received in revised form

11 May 2017

Accepted 21 June 2017

Available online 23 June 2017

Keywords:

Sorption

Synthesis

Carbon dioxide

Polyurethanes

Thermosetting

FT-NIR

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.

© 2017 Elsevier Ltd. All rights reserved.

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

* Corresponding author.

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

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-

Download English Version:

<https://daneshyari.com/en/article/5205374>

Download Persian Version:

<https://daneshyari.com/article/5205374>

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