

# TPM&F

THERMOPLASTIC MATERIALS AND FOAMS DIVISION

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## CHAIRMAN'S MESSAGE

FEBRUARY 2024

Dear fellow members of the SPE TPM&F Division,



I hope you all had a very nice holiday season. It is a great pleasure to write to you as the Chair of the SPE's Thermoplastic Materials and Foams (TPM&F) Division. I wish you and your family a wonderful beginning to the new year!

This past year was very productive for our division. We have been meeting with people in person at conferences to interact more and continuously learn about emerging sustainable materials and technologies. We started our key activities in March with the Polyolefins<sup>®</sup> 2023 Conference in Houston. The SPE ANTEC<sup>®</sup> was held in March in Denver showcasing the latest advances on plastics engineering, thermoplastic materials, sustainability, polymer processing and digitization and additive manufacturing. To finish the conference series, FOAMS<sup>®</sup> 2023 was held in Taipei, Taiwan in October successfully. It enlarged the boundaries of our program internationally. It was a premier forum related to new developments in foaming technologies. The Foams Tutorial covering foam fundamentals and foam applications was conducted to help students and foam professionals to enhance their knowledge and apply scientific principles to their work every day. We congratulate Prof. Ernesto Di Maio for receiving the Best Paper Award for the FOAMS<sup>®</sup> 2023 Conference for his paper and presentation entitled "Liquid Foaming of TPU with methylal". The full paper will be featured as a part of this newsletter.

On behalf our board, I would like to take this opportunity to express our sincere appreciation to the leadership of these conferences, specifically, to Donna Davis for Polyolefins 2023 conference, and Dr. Kimberly McLoughlin for SPE ANTEC<sup>®</sup> 2023, and Drs. Shu Kai and Stéphane Costeaux, for Foams 2023 conference in Taipei. I also want to thank Dr. Chul Park, and all the board members for doing an outstanding job in

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### TPM&F SCOPE

The Thermoplastic Materials and Foams Division is organized to provide a focal point for the interchange of information relating to non-vinyl thermoplastic resins including fluoropolymers, polyamides, polyesters, polyolefins, polystyrenes, polyurethanes, their filled and/or reinforced products, and their foamable and foamed products. Its interests lie in stimulating the development of scientific and engineering knowledge. By encouraging participation between producers and consumers, it aims to provide information on new developments which shall encompass synthesis, characterization, fabrication, safe handling, application, serviceability, and marketing.



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## CHAIRMAN'S MESSAGE (CONT. FROM PG 1)

taking care of all board activities and executing them well with enthusiasm during the Covid-19 time. Special thanks to Dr. Anson Wong for the membership report stating that the total membership had steadied for the past one year. We are exploring new avenues to expand our membership opportunities. Maxwell Wingert provided financial report at board meetings regularly.

I would like to highlight few things. The Polyolefins® 2024 Conference will be held in Galveston, Texas in February. The SPE ANTEC® is planned for March 4-7 in St. Louis, Missouri. The Foams® 2024 Conference will be held in King of Prussia, PA in September. I strongly encourage you all to attend to enjoy these events and introduce your friends and colleagues to bring great benefits to their professional career.

Best wishes,  
*N.S. Ramesh*  
SPE TPM&F Division Chair



## GALVESTON ISLAND CONVENTION CENTER AT THE SAN LUIS RESORT, SPA & CONFERENCE CENTER

5600 Seawall Blvd., Galveston, Texas 77551

The SPE International Polyolefins Conference brings together producers, suppliers, processors, marketers, application developers, regulators, and thought leaders in polyolefin technology from around the world. The program begins with tutorials on Sunday afternoon and continues through Wednesday noon. The exhibition opens Monday morning and continues through Wednesday noon. Please see page 13 in this newsletter to recognize our sponsors for this event.

Join us in Galveston! [For information click here.](#)

### Galveston Island Convention Center at the San Luis Resort, Spa & Conference Center

IPOC 2024 will take place at the GICC which is part of the San Luis Resort, Spa & Conference Center. This venue is within walking distance to multiple hotels, restaurants, and entertainment destinations. Shuttles run constantly between the San Luis and the GCC. **For more hotel, convention center and Galveston Island information.**

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Monday AM

**Venki Chandrashekar**, VP, Research and Technology-Chevron Phillips Chemical Company, *Propelling Circularity and Climate Action Through Innovation and Technology*



Tuesday AM

**Anne-Marie Boulay**, Professor at Polytechnique Montreal and General Director of the International Life Cycle Consortium of the CIRAIQ, *Life Cycle Assessment as a Tool to Help Avoid Misconceptions Around the Environmental Performance of Plastics and their Alternatives*



Wednesday AM

**Alison Keane**, President and CEO of Flexible Packaging Association, *State of the Flexible Packaging Industry-Policy Driving Innovation*

## MEET THE 2024 IPOC EXHIBITORS



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## Liquid foaming of TPU with Methylal

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### Abstract

This work investigates the use of dimethoxymethane (Methylal) as a blowing agent in thermoplastic polyurethane (TPU) foaming. In the adopted processing conditions, Methylal is in the liquid state, unlike blowing agents typically used in foaming; therefore, we investigated two different paths. First, we experimented on the liquid foaming strategy, foaming TPU with Methylal in the liquid state alone. Second, we used Methylal as a co-blowing agent together with a gas, CO<sub>2</sub> and N<sub>2</sub>. In both cases, we investigated the effect of pressure, pressure drop rate, and temperature on the resulting foam density and morphology. Overall, Methylal proved to be an effective blowing agent, especially in cooperation with other gaseous agents, where it severely improves the expansion ratio of the final product.

### Introduction

Thermoplastic polyurethane (TPU) belongs to the family of thermoplastic elastomers (TPE), which are currently of great interest in the industrial field because of their high elasticity, good resilience and, most importantly, environmental friendly nature [1, 2, 3], in fact they are fully recyclable [4].

TPU foams present a series of non-trivial advantages compared to their non-foamed counterparts, including light weight, low thermal conductivity, high strength-to-weight ratio and dissipation of impact energy, among others [5]. Several methods have been reported in the literature to prepare TPU foams, such as batch foaming, extrusion foaming and foam injection molding [6]. Batch foaming, in particular, is the simplest process for making foams with a physical blowing agent (PBA), especially on the lab scale. It is based on the use of a thermoregulated high-pressure vessel in which the polymer is placed and the PBA is subsequently injected at a certain pressure and temperature to allow for its diffusion into the polymer. After a stable polymer/gas solution is obtained, phase separation occurs by increasing the temperature or quenching the pressure [7]. This technique offers the possibility of a very fine control over a wide range of foaming variables, which in turn can allow a good control of the final cellular morphology.

The main process parameters are directly suggested by the classical nucleation theory (CNT) [8] and include the gas concentration prior to foaming (in batch foaming, it is related to the saturation pressure, if equilibrium conditions are reached in the sorption process) and the foaming

temperature. This set of process variables is completed by the pressure drop rate (PDR) and the choice of the PBA, which plays a key role in the nucleation and growth of bubbles. In fact, such processes are directly related to the chemical, physical and transport properties of the polymer-foaming agent system, and, subsequently, to the surface and rheological properties of the polymer/gas solution and the solubility and diffusivity of the gas in the melt [9].

In this work, we explore the use of dimethoxymethane as a PBA for the foaming of TPU to investigate potential advantages compared to traditionally used PBAs (i.e. CO<sub>2</sub> or N<sub>2</sub> [10]).

Dimethoxymethane (Methylal) is a low molecular weight substance with a low boiling point (42.3 °C), CAS number (109-87-5), and viscosity (0.371 mm<sup>2</sup>/s) [11]. It is used predominantly as a solvent in industry, as a building block in organic syntheses [12], and as a blowing agent for polyurethane-based foams.

The possibility of foaming with a CO<sub>2</sub> – Methylal mixture is also foreseen with the intent of providing the best process performances of both the co-blowing agents. In the past, many industries have filed a patent on the use of co-blowing agents in extrusion foaming such as ethanol, water or hydrofluorocarbons [13] [14] [15]. For the best possible outcome, it is crucial to study the role of each physical blowing agent during the foaming process with respect to the solubility, the foaming kinetics and the setting mechanism.

In the present article, a novel batch foaming technique is presented. Because of the thermodynamic properties of Methylal, its liquid form is used to perform a foaming experiment under the same conditions as the gas foaming ones. Tests on Methylal itself are performed to study its role as PBA. Technological issues in the use of a liquid PBA are described. Finally, methylal is tested as co-BA with CO<sub>2</sub> to prove its potential to adjust the resulting foam properties.

## Materials and methods

### 3.1 Materials

In this study, commercial TPU (Elastollan Soft 45A 12 P) in the form of pellets, shore hardness 46A, and density 1180 kg/m<sup>3</sup>, was purchased from BASF. Before use, the raw TPU material was dried in a vacuum oven at 80 °C for 3 h and then stored under vacuum. CO<sub>2</sub> and N<sub>2</sub> (purity 99.99 %) were supplied by SOL S.p.A. (Monza, Italy). Methylal (Dimethoxymethane, H<sub>3</sub>COCH<sub>2</sub>OCH<sub>3</sub>, CAS. No.

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109-87-5,  $M = 76.1$ ) was supplied by Lambiotte & CIE S.A.

### 3.2 Experimental setup

Physical foaming of pre-treated TPU beads was performed with a custom pressure vessel designed to allow (i) the introduction of the blowing agent, (ii) a wide range of pressure drop rates (PDRs), especially toward high values, (iii) fast extraction of the sample, and (iv) the possibility of observing what happens inside the reactor during the whole experiment.

To this end, as illustrated in Figure 1, the pressure vessel was equipped with a total of four connection/ports, as it is also described elsewhere [16]. The first port has a Gefran thermocouple (positioned as close to the sample as possible) to allow temperature control. The second port is split with a cross element to connect both a pressure transducer (Gefran) and a manifold for the introduction of the blowing agent (the manifold is connected to the blowing agent dosing system and a vacuum pump, necessary for pre-treatment of the beads). The third port is used for the introduction of the beads and is then closed with a 1/2" NPT sapphire window (Precision 106 Sapphire Technologies, Ltd. Vilnius, Lithuania) to allow visual observation of the experiments. Finally, the fourth port works with a ball valve (activated by an electromechanical actuator) and allows for the actual release of the blowing agent. This port is also exploited in our work to extract the samples instantly, since the TPU beads are sufficiently small to be transported by the fluid flow towards the exit.

The setup thus described works with gaseous and liquid blowing agents: when using a gaseous blowing agent ( $\text{CO}_2$  and  $\text{N}_2$ , namely), the second port is connected through the manifold to the gas dosing system, while when using a liquid blowing agent (Methylal, namely), the second port is connected through the manifold to a high pressure syringe pump (ISCO 500D) that is capable of injecting the liquid inside the reactor at the desired pressure. It is important to note that when the syringe pump is used, emptying the vessel before the experiment is mandatory because the gaseous phase might hinder the liquid entry. Also, this is the best way to ensure that Methylal is used in a pure grade, without other solutes or impurities.

After foaming, the liquid injected is collected through a liquid collector system consisting of a tank or a collector tube linked to a chemical hood. This apparatus prevents liquid spraying from the release valve during pressure drop.

#### 3.2.1 Gas and liquid foaming experiments

The term liquid foaming, as opposed to the better known gas foaming, is here used to indicate the physical foaming of polymers with a liquid blowing agent, in our case Methylal.

Liquid foaming experiments were conducted in two ways:

(i) for foaming pressures less than 10 bar, liquid-vapor equilibrium points were exploited. Five pre-treated TPU beads were inserted into the reactor and kept under vacuum at 80 °C for 1 h to improve the pre-treatment results. After the waiting time, the liquid blowing agent was injected into the reactor with a pipette through the appropriate valve, and the desired temperature was imposed. After the corresponding equilibrium point was reached, foaming was performed through a quick pressure drop at a controlled pressure drop rate. This method allows only for low-pressure foaming because the vapor pressure at the maximum possible temperature inside the reactor is lower than 10 bar.

(ii) for foaming pressures higher than 10 bar, a syringe pump was used. Five pre-treated TPU beads were inserted in the reactor and kept under vacuum at 80 °C for 1 h. The liquid blowing agent was then injected into the reactor with a syringe pump and pressure and temperature were set at the desired value. After a saturation time of 30 minutes, foaming was performed through a quick pressure drop at a controlled pressure drop rate. With this method, pressure values of up to 90 bar have been reached.

In addition to liquid foaming, classical gas foaming was also performed. Two types of blowing agents were used: gaseous blowing agents ( $\text{CO}_2$  and  $\text{N}_2$ ) and mixtures of liquid and gaseous blowing agents ( $\text{CO}_2$  and Methylal mixture as well as  $\text{N}_2$  and Methylal mixture). The preparation of the mixture was ensured by preliminarily placing the beads in a Methylal bath for at least 1 hour, to ensure that they contain the proper amount of liquid blowing agent before being inserted into the reactor. In both cases, the procedure followed was that from (ii), but instead of using the syringe pump, the gas dosing system was used to inject the gas into the reactor. The saturation time was 1 hour instead of 30 minutes.

### 3.3 Pressure drop rate (PDR) quantification

An important control variable of the physical foaming method through pressure quench is the velocity of the pressure reduction, i.e. the pressure drop rate (PDR) [17]. The characteristic time of the pressure drop is very short ( $\tau_{\text{PD}} \sim 1000\text{ms}$ ), thus a very high data acquisition rate is required. For this reason in our experiments we measured the PDR through a PLC (Siemens ©, SIMATIC S7-1200 CPU) with a sampling rate  $\tau_m \sim 1\text{ms}$  smaller than  $\tau_{\text{PD}}$ . This device registers the pressure values (collected by the pressure transducer) over time and provides as output a curve  $P(t)$  that fully represents the pressure reduction over time. The shape of this curve depends on test conditions and blowing agent nature, and its local slope can be exploited to collect information about the PDR. More specifically, we used numerical methods to calculate the central derivative of the entire  $P(t)$  curve and then measured the PDR as the maximum peak value of the central numerical derivative.

### 3.4 Thermodynamic properties of Methylal

The vapor pressure of Methylal was investigated in order to smoothly extend the data in the literature [18, 19]. The experiments were conducted in the abovementioned mini-batch reactor, which acts as a closed system. For the scope, this was equipped with a valve for the injection of Methylal in its liquid state. We used the following procedure. First, we filled the mini-batch with Methylal (pure grade) in its liquid state at ambient temperature. Then we increased the temperature inside the reactor to a predefined value (that is, 96, 118, 135 and 154 °C) and finally we waited until the gas-liquid equilibrium was reached, that is, when the temperature and pressure of the system remained stable for at least 1 hour, with an error of 5%. It is important to note that, before and in between experiments, the cell was evacuated with a vacuum pump, while during the experiments, the sapphire window was used to check the presence of liquid inside the reactor. The pressure value at each condition was collected as the vapor pressure of Methylal at that specific temperature value. Equilibrium points thus found were used as temperature-pressure conditions to perform first foaming experiments with Methylal. As an alternative, to reach higher pressure values, the liquid foaming technique was used, as previously described.

### 3.5 Sample characterization

Density measurements, optical microscopy, and scanning electron microscopy were used to characterize the TPU samples immediately after foaming. The density measurements were performed using a density kit mounted on a METTLER TOLEDO laboratory balance. The test standard used was ASTM D792-00. This uses the buoyancy technique, which in turn utilizes Archimedes' principle: a body immersed in fluid indicates an apparent loss in weight equal to the weight of the fluid it displaces. Thus, by measuring the weight of the foamed sample both in air ( $w_{\text{air}}$ ) and in water ( $w_{\text{water}}$ ), we were able to evaluate the density of the sample with the following:

$$\rho = \frac{w_{\text{air}}}{w_{\text{air}} - w_{\text{water}}} \times \rho_{\text{water}} \quad (1)$$

For each sample, the density is calculated as the mean of five replicates.

An optical microscope (Zeiss Stemi 508) was used to observe the morphology of TPU foams obtained with the liquid foaming technique, while a scanning electron microscope (SEM Merlin VP) was used to observe the morphology of the TPU foams obtained with the typical gas foaming technique, because they had a much finer morphology. To prepare SEM specimens, TPU foams were cut using an ultra-thin stainless steel blade and then the

intact cross section was coated with a thin layer of gold using a sputter coater (Agar Auto Sputter Coater). Weight measurements of TPU beads were also performed before and after foaming to collect additional information.

### 3.6 Solubility and swelling measurements

Information about the interaction of Methylal with TPU in terms of solubility and consequent swelling of the beads was collected by measuring the weight and volume of the beads before and after immersion in a Methylal bath. Weight measurements were performed with a METTLER TOLEDO laboratory balance and then used to evaluate solubility with the following:

$$\text{Solubility} = \frac{w_{\text{Methylal}}}{w_{\text{beads}|t=0}} \quad (2)$$

Where  $w_{\text{Methylal}}$  is the weight of the methylal absorbed inside the beads after the immersion process and  $w_{\text{beads}|t=0}$  is the weight of the beads before the immersion process. Volume measurements were made by taking pictures of the beads at the times of interest and then analyzing them with the ImageJ software. The "free hand selection" command was used to detect the edges of the beads and to measure the exposed area, the major axis and the minor axis. Assuming that the TPU beads are elliptical in shape, the acquired data were then elaborated in Excel to find, by inversion, the corresponding axis values and, consequently, the corresponding volume values. From these data, swelling was evaluated as:

$$\text{Swelling} = \frac{V_2 - V_1}{V_1} \quad (3)$$

Where  $V_1$  and  $V_2$  are the volume before and after immersion in Methylal respectively.

### 3.7 Shrinkage evaluation

Shrinking behavior of TPU foams was evaluated by monitoring the density of the samples over time. More specifically, we evaluated the density of each TPU sample immediately after foaming and then at regular time steps of 15 minutes, for a total of about 48 hours, until a plateau in the density value was reached. Every density value was always calculated as the mean of five replicates.

## Results and discussion

### 4.1 Liquid foaming

#### 4.1.1 Methylal thermodynamic properties

When working with gaseous blowing agents (such as  $\text{CO}_2$  and  $\text{N}_2$ ), foaming usually occurs above their critical

temperature. Therefore, knowledge of the thermodynamic properties of the physical blowing agents is of key importance for any foaming experiment. To this end, we measured the thermodynamic properties of Methylal in terms of its vapor pressure over a temperature range of interest. In particular, experiments were performed at temperatures below the critical temperature, so that we were able to determine the vapor pressure as the maximum saturation pressure at each value of temperature. The selected temperature range is  $T = 369 - 427$  K. The experimental results are shown in Figure 2. In the range mentioned above, the vapor pressure varies from 4.41 to 15.4 bar, consistent with data from the literature [18, 19]. We can see that the maximum pressure at which we can use Methylal in its gaseous phase is approximately 9 bar, as imposed by the maximum temperature at which the polymer can be processed (polymer melting temperature). As a consequence, the use of methylal at higher pressures is possible only in its liquid state.

#### 4.1.2 Solubility and Swelling

To test the interaction between Methylal and TPU, solubility measurements were performed. This preliminary study is fundamental to our research because it allows us to understand Methylal potential as a blowing agent (high solubility is required for any substance to be considered a good blowing agent). The results are shown in Table 1.

As we can see, the solubility is approximately 50% w/w under ambient conditions and increases even more at higher temperatures and pressures, reaching a value of almost 75% w/w at 5,5 bar and 116.6 °C. These values are high enough to demonstrate that Methylal has the potential to be a good blowing agent, but they are much higher than the typical solubility values of gaseous blowing agents (namely  $N_2$  and  $CO_2$ ) in TPU [20], which could be related to some effects in the final foamed products.

Swelling measurements were also performed. Results are shown in Table 2. Here, the high percentage of swelling (up to approximately 70% v/v at 45 bar and 131.8 °C) is probably related to the high solubility of Methylal in TPU. Finally, the weights of the samples before and after foaming were also collected, as shown in Table 3. We can see a 10% decrease in the weight of the samples, probably related to the presence of Methylal itself. In fact, since TPU is a commercial soft grade, it is possible that Methylal extracts low molecular weight fractions or additives from the pellets. This hypothesis was corroborated by the in-situ observation of the liquid foaming experiments, at the end of which the material extracted from the polymer could be seen through the sapphire window. Specific experiments (spectroscopic and gravimetric analysis) are required to quantify the molecular mass and the nature of the extracted fraction.

#### 4.1.3 Effect of process parameters

To understand the effect of the process parameters, foaming experiments were performed. An image of the result is shown in Figure 3. Parameters of interest in this study were temperature, gas concentration (here, equivalently, saturation pressure, as we designed the foaming process to achieve uniform gas concentration), and PDR. The results are given in terms of the density of the final product.

The first foaming experiments were performed using the liquid-vapor equilibrium points. However, this technique does not allow high pressures to be reached and the pellets do not foam until at least 6.5 bar are reached. This cannot be linked to the solubility of the BA in the TPU, which is high enough under ambient conditions to provide formation of gas bubbles, and thus it is probably due to low PDR. Moreover, since the system only works at equilibrium points, temperature and pressure are always coupled, and it is more difficult to study the effects of all parameters separately. As a consequence, the liquid foaming technique at higher pressure was used to carry out the study.

First, we examined the effect of temperature at a fixed pressure of 45 bar. As can be seen in Figure 3a, the density decreases as the temperature increases until a minimum is reached at approximately 410 K (135 °C). After that, too high of a temperature causes a strong reduction of the viscosity of the polymer, and the foam severely collapses, resulting in the rise of the density. The best foaming temperature window at 45 bar is between 123.4 °C and 143.0 °C.

Then we studied the effect of pressure at a fixed temperature of approximately 132.0 °C and a variable PDR, depending on the maximum pressure value. The results are shown in Figure 3b. We can see that at pressures lower than 6.0 bar, foaming does not occur, confirming the results obtained by the gas foaming method. At higher pressures, the density is noticeably reduced, reaching values comparable to those obtained in the temperature sweep experiments. This result confirms the importance of the PDR in inducing foaming.

#### 4.1.4 Pressure drop history

The velocity of the pressure drop from saturation pressure to ambient pressure (that is, the PDR) is of key importance in foaming because it influences the thermodynamic thrust that causes phase separation. We observed a different behavior with different blowing agents as reported in Figure 4a: for typical gaseous blowing agents such as  $CO_2$ , we observed a one-step reduction in pressure. For the liquid blowing agent (i.e. Methylal), we observed a two-step reduction in pressure, i.e., as it is visible, a fast reduction of pressure followed by a strong change in the slope to a much smaller value. It is noted that, while conducting foaming experiments, we neglected the peculiar behavior of the reduction of pressure in the case of the liquid blowing agent because foaming occurs on a time

scale comparable to the first reduction in pressure. Of course, this is valid only for the foaming kinetics of our specific TPU. This evaluation could be different with a polymer with slower foaming kinetics, where this double-slope pressure reduction could play a key role.

In Figure 4b we report the different pressure reduction curves of different experiments carried out at the same temperature of 132.0 °C and at different saturation pressures, namely 30, 45, 60 bar. It is interesting to note that regardless of the saturation pressure, the pressure at which the slope changes is almost the same in all cases. We account for this behavior as the transition between the liquid and gaseous phase. In fact, the pressure at which the slope changes is approximately 12 bar, which is comparable to the vapor pressure of Methylal at the test temperature ( $p = 10.96$  bar,  $T = 135^{\circ}\text{C}$ ). Furthermore, the second slope remains the same for all experiments, with a value of 0.44 bar/s, which confirms that it is imposed by the thermodynamics of the process.

#### **4.1.5 Foam morphology**

The morphology of the foamed samples under the different foaming conditions is shown in Figure 5. As is visible, the TPU beads always merge at the end of the foaming experiments. The influence of the process parameters is clear and consistent with the density measurements. When the pressure is lower than 6 bar, foaming does not occur, while above 6 bar, foaming begins to occur (Figure 5e-f-g). The foamed product shows a very coarse morphology with a large fraction of large bubbles and a small fraction of smaller bubbles. As pressure increases, the mean bubble dimension decreases, as we can see from the color of the foam that becomes whiter and whiter, confirming the density reduction described in 4.1.3. For temperature, we observe the same trend until the optimal foaming window is reached. After that, the collapse of the foam becomes more and more evident (Figure 5b-c-d).

It is worth noticing that in all cases (full temperature and pressure ranges) the bubble wall is not well defined. This is probably due to the high solubility of methylal in TPU and consequent high swelling (Table 1) that always causes buckling to occur.

These characteristics are common to all of the foamed samples: overall, the foam morphology is very coarse, and collapse always occurs to some extent. To avoid this problem, the gas foaming technique with Methylal as the co-blowing agent was performed, as fully described in Section 4.2.

## **4.2 Gas foaming with Methylal as a co-blowing agent**

### **4.2.1 Foaming experiments**

Gas foaming experiments with Methylal as a co-blowing agent were performed to reduce the amount of Methylal within the TPU beads and thus prevent the collapsed morphology typical of liquid foaming experiments. CO<sub>2</sub> and N<sub>2</sub> were used as gaseous BA in a mixture with liquid Methylal. All experiments were carried out under the same temperature and PDR conditions ( $T = 80^{\circ}\text{C}$  and  $\text{PDR} = 500$  bar/s), while pressure was changed to understand its effect on the final foamed product ( $p = 40 - 120$  bar). The final foamed products were very different from those obtained with the liquid foaming technique. Indeed, merging between the beads does not occur; on the contrary, they stay separated and they also show a noticeably increased volume.

The effect of pressure on the final foamed products in terms of the resulting density is shown in Figure 6. As we can see, as the pressure increases, the mean density of the foam decreases, which means that the number of bubbles increases and the mean bubble dimension decreases correspondingly.

The same study was carried out with Methylal and CO<sub>2</sub> alone as BA and the results are compared in Figure 6. It is visible that the technique that uses CO<sub>2</sub> and Methylal together as co-blowing agents is superior to gas foaming with CO<sub>2</sub> alone and liquid foaming with Methylal alone. In fact, this technique ensures the lowest final densities at almost every pressure value, with a minimal density of 110 kg/m<sup>3</sup>, so a reduction of almost 40 compared to the green point. Furthermore, when using the mixture, the process parameters window to get a not collapsed foam is broadened, allowing foaming at lower pressures, as occurs with Methylal alone.

The smaller densities obtained with the CO<sub>2</sub>/Methylal mixture prove that Methylal has a plasticizing effect on TPU. This effect is probably what causes the merging of the beads in the liquid foaming experiments, and it also concurs with determining the typical collapsed morphology.

As a final point, shrinkage of the foamed beads was also observed, as it is characteristic of TPUs, but this will be thoroughly studied elsewhere.

### **4.2.2 Foam morphology**

The morphology of the beads foamed with the CO<sub>2</sub>/Methylal mixture was studied at the end of the shrinkage process and is shown in Figure 7. This morphology appears to be significantly different from the morphology of the beads foamed with the liquid foaming technique (Figure 5). The beads do not merge after the foaming experiments, and they maintain their initial shape. The bubbles are smaller in dimension. Moreover, the bubble walls are well defined, and neither buckling nor collapse occurs. In general, this technique significantly improves foam morphology compared to the liquid foaming technique.



The presence of a large boundary region is detected in which the bubbles appear larger in dimension and less dense (Figure 7a). This probably occurs because only CO<sub>2</sub> remains in the most external region of the polymer beads. Comparison with the morphology of CO<sub>2</sub>-only foamed TPU beads confirms this hypothesis (Figure 7b). Further studies on Methylal diffusivity in TPU could improve our understanding of dense skin formation [21].

As we can see, when CO<sub>2</sub> is the sole physical blowing agent, the bubbles are larger in dimension and less dense, with a more defined bubble wall, just as they appear in the boundary region of Figure 7c-d.

## Conclusions

Methylal proved to be an excellent physical blowing agent for TPU. It has a very high solubility in the polymer of interest and thus causes a large swelling of the polymer pellets when they are immersed. Additionally, a strong plasticizing effect and a low molecular weight fraction extraction from TPU were detected.

When used alone, in its liquid state, the foamed samples have very low densities, competitive with the industrial target ones (i.e., 400 kg/m<sup>3</sup>), but the morphologies appear collapsed, probably due to the very high solubility. When used in combination with other gaseous blowing agents, namely CO<sub>2</sub>, the best results are obtained. The densities of the foamed samples are lower than those reached with the liquid foaming technique, and the morphologies do not collapse. As seen from the SEM images, bubbles are small in dimension and a thick boundary region is detected.

The final results are also better than those obtained with gaseous blowing agents alone, both in terms of final density and total shrinkage percentage, which means that Methylal highly enhances the foaming ability of CO<sub>2</sub>. Overall, Methylal is clearly applicable in foaming technologies, but further studies would enhance the understanding of its role as a blowing agent.

## Acknowledgements

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## Conflict of interest

The authors declare no conflict of interest.

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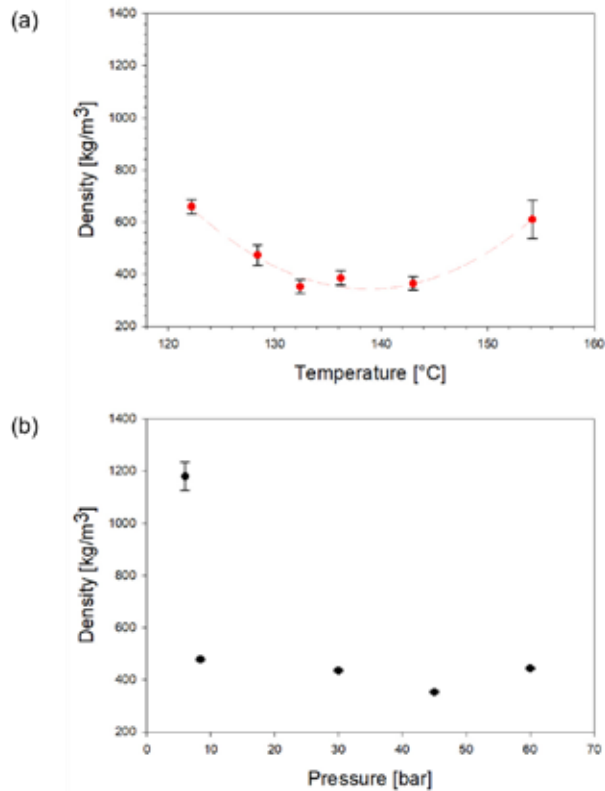


Figure 3: Effect of temperature (a) and pressure (b) on the mean density of TPU beads foamed by the liquid foaming technique

## Figures

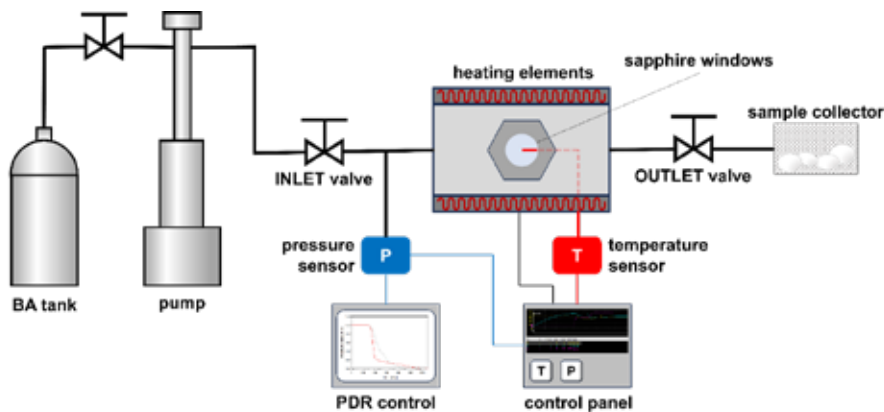


Figure 1: Schematic of the experimental setup used for the gas and liquid foaming experiments.

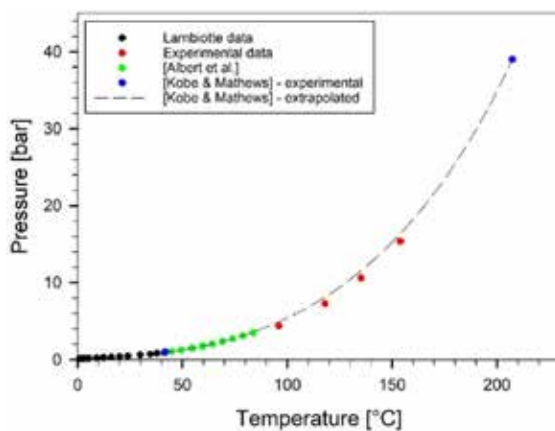


Figure 2: Thermodynamical properties of Methylal.

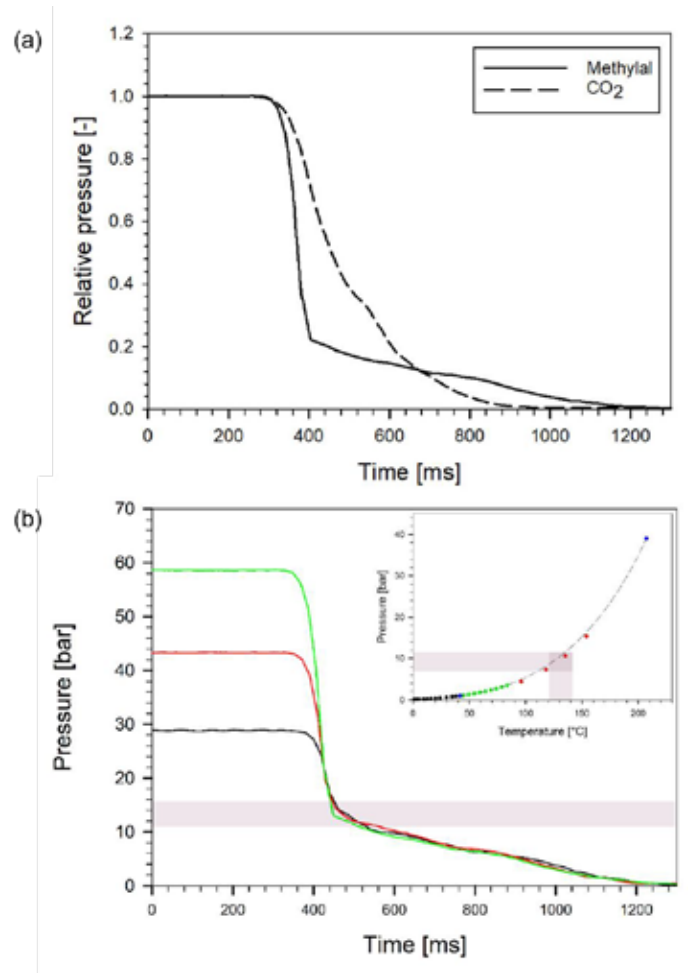


Figure 4: (a) Pressure reduction curves of foaming experiment with gaseous blowing agent (dashed line) and liquid blowing agent (solid line) and (b) pressure reduction curves of liquid foaming experiments alone at different values of maximum pressure: 30 bar (black), 45 bar (red) and 60 bar (green).

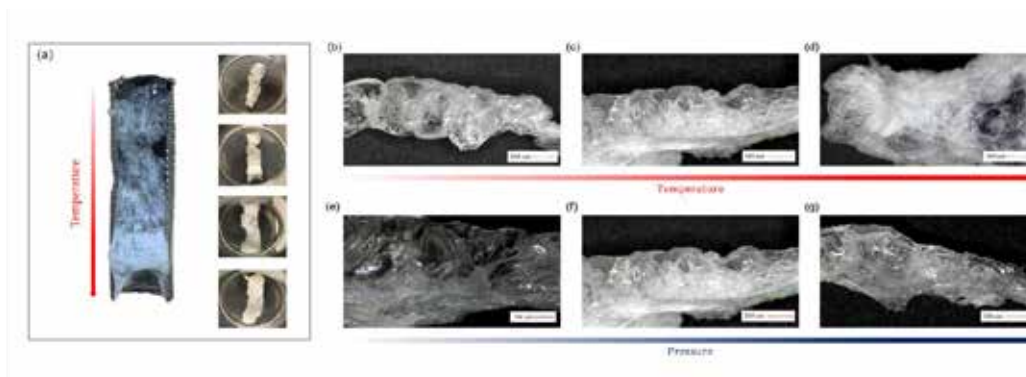


Figure 5: (a) Morphology of the foamed TPU beads with varying temperature. Morphology of the foamed beads at the end of the liquid foaming experiments performed at constant pressure  $p = 45$  bar and temperature (b)  $T = 120$  °C, (c)  $T = 136$  °C and (d)  $T = 150$  °C. Morphology of the foamed beads at the end of the liquid foaming experiments performed at constant temperature  $T = 133$  °C and pressure (a)  $p = 30$  bar, (b)  $p = 45$  bar and (c)  $p = 60$  bar.

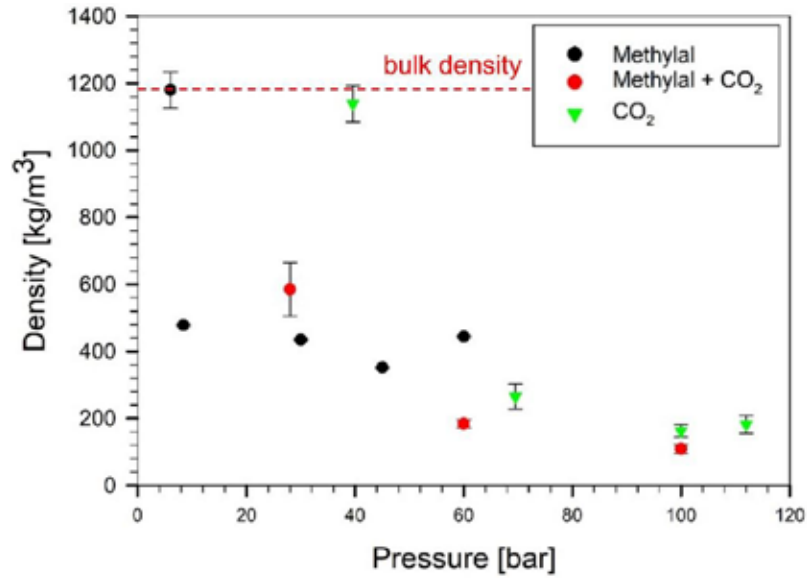


Figure 6: Density of foamed TPU beads at different values of foaming pressures and with different blowing agents: Methylal (black circles), Methylal + CO<sub>2</sub> (red circles) and CO<sub>2</sub> (green triangles).

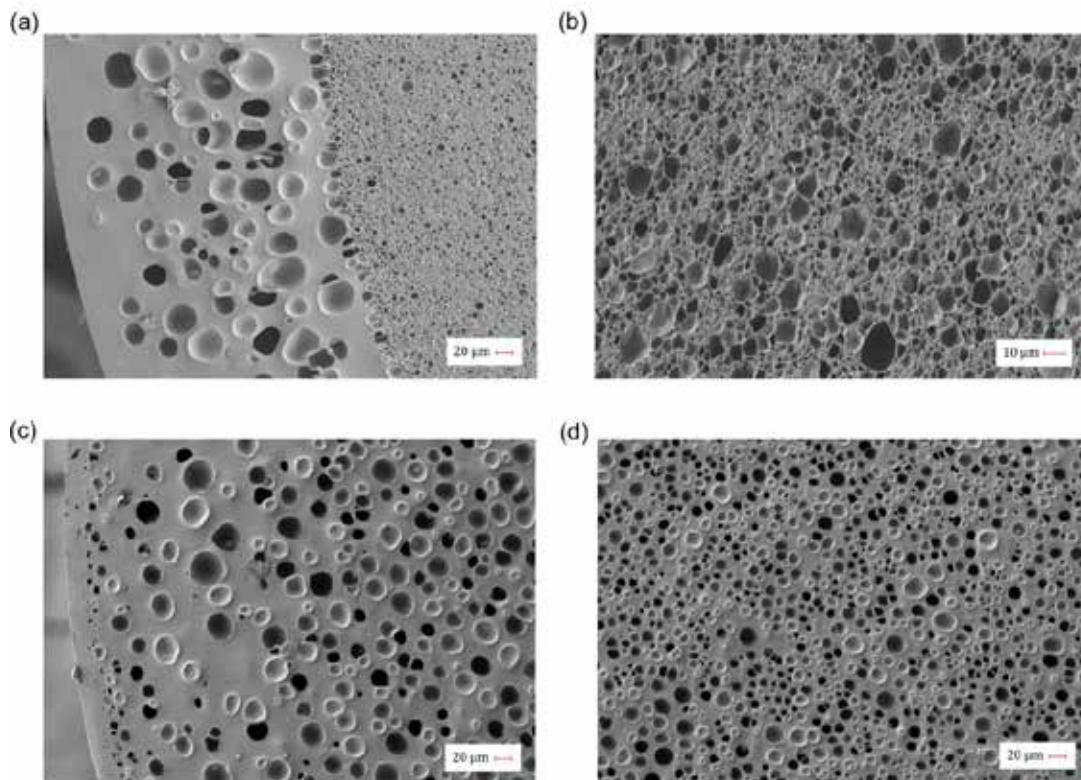


Figure 7: Morphology of TPU beads after the gas foaming experiment with the CO<sub>2</sub>/Methylal mixture (a,b) and with CO<sub>2</sub> alone (c,d) as the physical blowing agents. Pictures are taken at the center of the foamed beads (b,d) and on the boundary (a,c).

**Tables**

Table 1: Measurements of the solubility of Methylal in TPU at two different conditions of temperature and pressure.

Temperature [°C]	Pressure [bar]	Solubility [w/w %]
25	1	49,3
116,6	5,5	74,4

Table 2: Measurement of the swelling of TPU beads after immersion in a Methylal bath.

Temperature [°C]	Pressure [bar]	Swelling [v/v %]
131,8	45	69,8

Table 3: Measurement of the weight loss of TPU beads adter liquid foaming with Methylal.

Temperature [°C]	Pressure [bar]	Weight loss [w/w %]
143	45	11,5

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