Theoretical Background and Automation Approach for a Novel Measurement Method for Determining Dynamic Solubility Limits of Supercritical Fluids in Injection Foam Molding

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In terms of sustainability, injection foam molding gains in importance. Yet still many questions throughout the whole process remain unanswered. Especially, the conditions inside the cylinder during gas injection are fraught with uncertainty. Our development of a new methodology for the determination of dynamic solubility in injection foam molding helps to answer the most basic question regarding gas loading: Using the bulk modulus of the polymer–gas mixture, the dynamic solubility limit can be detected. In a first series of tests, the methodology was verified with simultaneous ultrasonic measurements—an excellent agreement was observed. In this work, a second, more thorough test series is presented. Using the bulk modulus methodology on different polypropylene grades, dynamic solubility limits between 0.62 and 2.56 wt% nitrogen at pressures between 80 and 200 bar and a temperature of 230 °C were determined directly on an injection molding machine. The detailed theoretical background for this technique, as well as a mathematical automation approach, is provided. This innovative yet simple method yields novel insights on process limits and provides the possibility of an a priori machine setup or a fully automatic self-adjustment of the machine.

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INTRODUCTION

Sustainability attracts more and more attention throughout the whole polymer industry over the last years [1, 2]. The energy-saving processing of polyolefins at low temperatures enables economical production; their low density provides benefits during their life cycle. Above all, the latter aspect is of importance to the transportation industry. According to Davies, a 10% reduction in vehicle weight can offer a 5% improvement in fuel economy [3].

Injection molding is the most important and versatile process technology for polymers [4–6]. Over 100 injection molding technologies are available for industrial applications to meet all market requirements imposed on polymeric materials [4]. One crucial exponent in terms of sustainability is injection foam molding, which allows for the production of sandwich structures (foamed core, compact outer layers) by using gases as blowing agents. Dissolved gases were initially used for the elimination of sink marks in the 1950s, the first serial production of foamed components was established in the 1970s [7]. Further developments and the use of supercritical fluids (SCFs) eventually lead to microcellular foams with average cell sizes between 5 and 100 μm and cell densities greater than $10^9$ cells/cm$^3$ [8].

Injection foam molding offers advantages regarding an economical production as well as benefits during the life cycle of foamed components. Dissolved gases can reduce the viscosity of polymer melts by more than 50% [9–11], leading to lower energy consumption during dosing, longer flow lengths, and reduced injection pressures. These lower pressures, in combination with the absence of a packing stage (compensated by internal gas pressure), can allow for smaller clamping units. The lightweight potential of foamed components and their easy recyclability (just one material) in addition to improved thermal [12, 13] or acoustic [14] insulation, a better warpage behavior [15], higher stiffness-to-weight ratio [16] or, for instance, higher energy consumption during biaxial bending tests [17] make the technology suitable for a variety of applications.

Despite numerous current applications [18–20], many fundamental processes in injection foam molding are still barely understood. Therefore, in one of our previous works [21], a novel technology for the determination of dynamic solubility limits based on the bulk modulus of the polymer–gas solution was developed. In the first part of this work, the methodology should be explained briefly, followed by the core topic: A mathematical automation approach was developed and applied to this methodology. This approach offers promising results in terms of a fully automatic and autonomous determination of solubility limits by the machine. For gaining a better understanding of the basic principles underlying the foaming process, the question of dynamic solubility is a fundamental one.

THEORETICAL BACKGROUND

In foaming, one of the most essential and basic aspects in terms of a combination of polymer melt and gas/SCF is solubility, which describes the ultimate amount of gas that can be dissolved in molten polymer under certain conditions. Apart from temperature and concentration, it mainly depends on pressure according to Henry’s law [22, 23]. Available literature almost exclusively addresses the subject of solubility in terms of static solubility, that is, the aspect of (shear) motion is not considered. It is, therefore, questionable whether these static measurements offer the right basis for the description of highly dynamic solution processes in injection molding.
Static Solubility

The most commonly studied physical blowing agent is carbon dioxide (CO\textsubscript{2}). Sato et al. [24] studied the solubility of CO\textsubscript{2} in polyvinyl acetate (PVA) (melt) at temperatures between 40\degree C and 100\degree C and pressures up to 175 bar and in polystyrene (PS) at temperatures between 100\degree C and 200\degree C and pressures up to 200 bar. Solubility increased with pressure but decreased with temperature. The solvable amount of gas was larger in PVA (over 30 wt\%) than in PS (5–10 wt\%). The temperature dependence was also confirmed by Mahmood et al. [25] Park et al. pointed out that the linear relationship between solubility and pressure is no longer valid at large pressures (i.e., above 210 bar) due to swelling. In a comparison of theoretical, semi-empirical (an experimental measurement of gas uptake and theoretical prediction of swelling data) and entirely experimental determination of the solubility of CO\textsubscript{2} in linear and branched polypropylene (PP) they measured solubilities up to 25 wt\% at temperatures between 180\degree C and 220\degree C and pressures up to 310 bar [26].

Very little literature on the static solubility of nitrogen (N\textsubscript{2}) in polymers is available. Studying the solubility of N\textsubscript{2} and CO\textsubscript{2} in PP and ethene/octene copolymer, Li et al. [27] showed that the temperature dependence of the solvable amount of N\textsubscript{2} in PP is reversed (i.e., higher temperatures increase the solubility). Its solubility of roughly 3 wt\% at 200 bar is approximately 10 times lower than that of CO\textsubscript{2}. In an earlier work of Sato et al. [28], these results are basically confirmed.

The simplest static solubility measurement method consists of a pressure vessel and an external balance. The weight gain (i.e., the absorbed amount of gas) of a polymer sample during the application of gas pressure is measured after degassing the chamber [29]. Inaccuracies due to the unknown amount of gas loss during transfer lead to the development of new gravimetric and barometric methods.

The pressure decay method also uses a pressure chamber that includes the polymer sample under gas pressure [30]. The absorbed amount of gas is calculated from pressure decay over time using the ideal gas law [31] or equation like the Benedict–Webb–Rubin equation [32, 33]. Drawbacks of this method are a long measurement time and the need for highly sensitive pressure transducers [24, 28]. Another technique uses a microbalance/electrobalance that is placed inside a pressure vessel [34]. After buoyancy correction, the absorbed amount of gas can be obtained from balance readout. To overcome direct exposure of electronic components to high temperatures, the magnetic suspension balance (MSB) uses an electronically controlled magnetic suspension that transmits forces from the inside of a pressure vessel to an external electrobalance [24].

All static measurement methods are based on adsorption, absorption, and diffusion, with the latter being a very slow process. The usability of static measurements for highly dynamic injection molding processes is, therefore, in doubt. Both the missing movement as well as the long measurement times, call for the development of a new, process-linked measurement method suitable for dynamic systems like a plasticizing unit.

Dynamic Solubility

Despite its importance, dynamic solubility is only covered by very few researchers. Lee did not find a correlation between shear rate and solubility [35]. Experiments on extruders by Zhang et al. [36] with three gases (CO\textsubscript{2}, N\textsubscript{2}, and argon) and PS showed no dependence of solubility on screw speed but a decrease with higher throughput. Chen et al., on the other hand, found that the solubility of CO\textsubscript{2} in high-density polyethylene (HDPE) increases by 30%–40% when a shear rate of about 30 s\textsuperscript{-1} is applied [37]. All these results show that there are still many questions that need to be answered and emphasize the importance of methods like the herein proposed method for the determination of dynamic solubility limits.

MODEL DEVELOPMENT

Initial Considerations—The Sanchez–Lacombe Equation of State for Pure Fluids

Initially proposed by Sanchez and Lacombe [38, 39], the SL theory assumes a fluid to be composed of N molecules. Each molecule occupies r sites (r-mer) in a lattice. The close-packed volume (i.e., no holes), $V\ast$, of N r-mers can be calculated with the specific volume of one mer, $v\ast$, via Eq. 1. The close-packed molecular volume is related to the mass density, $\rho\ast$, via the molecular weight, $M$, according to Eq. 2.

$$
V\ast = N(rv\ast) 
$$

(1)

$$
rv\ast = M/\rho\ast
$$

(2)

The actual EOS for a pure fluid is calculated based on a minimization of the Gibbs free energy, according to Eq. 3.

$$
\tilde{\rho}^2 + P + \tilde{T} \left[ \ln(1-\tilde{\rho}) + \left(1 - \frac{1}{\tilde{\rho}} \right) \tilde{\rho} \right] = 0
$$

(3)

The reduced temperature, $\tilde{T}$, pressure, $P$, and density, $\tilde{\rho}$, are calculated via Eq. 4 using the characteristic parameters $T\ast$, $P\ast$, and $\rho\ast$ determined from experimental PVT data [40]. Characterization of a fluid using the molecular parameters $v\ast$ and $r$ is also possible (Eqs. 5 and 6).

$$
P = \frac{P}{P\ast}, \quad \tilde{T} = \frac{T}{T\ast}, \quad \tilde{\rho} = \frac{\rho}{\rho\ast}
$$

(4)

$$
v\ast = \frac{RT\ast}{P\ast}
$$

(5)

$$
r = \frac{MP\ast}{RT\ast \rho\ast}
$$

(6)

Initial Considerations—The SL Equation of State for Mixtures

Combining rules exist for a combination of two fluids. In a first step, a mixture between N\textsubscript{2} (Index 1) and PP (Index 2) is assumed. The index $m$ represents the calculated parameters of the mixture. The mass fractions of PP, $m_1$, and N\textsubscript{2}, $m_2$, are related via Eq. 7. The respective molar amounts, $N_i$, and molar fractions, $x_i$, can be calculated via Eqs. 8 and 9.

$$
m_1 = 1 - m_2
$$

(7)

$$
N_i = \frac{m_i}{M_i} \text{for } i = 1 \text{ and } 2
$$

(8)
The close-packed volume fraction for each component in the mixture, \( \phi_i \), and the related volume of each component in the pure state, \( \phi_i^0 \), can be calculated according to Eqs. 11 and 12. Subsequently, calculation of the molecular parameter, \( v_m^* \), via Eq. 13, is possible.

\[
\phi_i = \frac{m_i}{\rho_i} \quad \text{for } i = 1 \text{ and } 2 \quad (11)
\]

\[
\phi_i^0 = \frac{\phi_i^1}{\phi_i^1 + \phi_i^2} \quad \text{for } i = 1 \text{ and } 2 \quad (12)
\]

\[
v_m^* = \phi_i^1 v_1^* + \phi_i^2 v_2^* \quad (13)
\]

According to Areerat et al. [41], the characteristic pressure for the mixture, \( P_m^* \), can be calculated using Eq. 14 with \( X_{12} \) defined by Eq. 15.

\[
P_m^* = \phi_1 P_1^* + \phi_2 P_2^* - \phi_1 \phi_2 X_{12} \quad (14)
\]

\[
X_{12} = \frac{P_1^* + P_2^* - 2(P_1^*)^{\frac{1}{2}}(1 - \kappa_{12})}{(1 - \kappa_{12})} \quad (15)
\]

In Eq. 15, \( \kappa_{12} \) is a binary interaction parameter, which has to be fitted to experimental data. Finally, characteristic temperature, \( T_m^* \), and density, \( \rho_m^* \), of the mixture can be calculated via Eqs. 16 and 17.

\[
T_m^* = \frac{\phi_m^* P_m^*}{R} \quad (16)
\]

\[
\rho_m^* = \frac{1}{m_1 \rho_1^* + m_2 \rho_2^*} \quad (17)
\]

The characteristic parameters of the mixture, \( T_m^* \), \( P_m^* \), and \( \rho_m^* \), can be used for the calculation of the respective reduced parameters. Analogous to pure fluids, the relationship between temperature, pressure, and density of the polymer–gas mixture can be described via Eq. 3.

**EXPERIMENTAL**

**Application of the Sanchez–Lacombe Equation of State**

Prior to experiments, the bulk modulus, \( C \), of a polymer–gas mixture should be calculated for different gas contents based on the Sanchez–Lacombe equation of state (SL-EOS). In accordance with Kamiya et al. [42], the preliminary assumption was that increasing gas content increases the compressibility, \( \beta \) (\( C = 1/\beta \)).

The bulk modulus can be calculated from Eqs. 18 and 19 and describes the relationship between pressure and relative volumetric change. A replacement of volume, \( V \), with density, \( \rho \), is possible. Proportionality of \( \Delta V \) to \( 1/\rho_0 \) yields the Index 1 in Eq. 19. Applying the measurement to an injection-molding machine, the direct use of the axial screw position, \( S \), the cross section of the cylinder, \( A \), and the volume in front of the non-return valve when the screw is in the foremost position, \( V_M \), according to Eq. 20 is possible. In Eqs. 18–20, the Indexes 0 and 1 denote properties before and after compression, respectively.

\[
C = -\frac{\Delta p}{\Delta V} v_0 \quad (18)
\]

\[
C = \frac{\Delta p}{\Delta \rho} \rho_1 \quad (19)
\]

\[
C = -\frac{\Delta p}{\Delta S} \left( \frac{V_M}{A} + S_0 \right) \quad (20)
\]

Figure 1 summarizes the bulk moduli of a PP homopolymer (MFR = 75 g/10 min) supplied by Borealis Polyolefine GmbH (Linz, Austria). The values are calculated from PVT measurements using Eq. 19. Marks represent calculations based on actual experimental PVT data that were recorded at 500; 100; 1,500; and 2,000 bar. Solid lines are interpolated and extrapolated values. Data for N\(_2\) are taken from Ref. 43. Values for initial (\( p_{\text{init}} \)) and final (\( p_{\text{fin}} \)) pressures were chosen to cover the full range of pressures typical for injection molding processes. Both a larger initial as well as a larger final pressures increase the bulk modulus.

![Comparison between bulk moduli of pure PP and N\(_2\).](image-url)
The bulk moduli of PP are approximately 10 times higher than the corresponding values for \( N_2 \). The bulk modulus of a polymer gas solution should, therefore, decrease with increasing gas content.

For verification of the above assumption (decreasing bulk modulus with increasing gas content), the SL-EOS was applied to a mixture of \( N_2 \) and PP. The characteristic parameters \( T_m^* \), \( P_m^* \), and \( \rho_m^* \) were obtained by fitting Eq. 3 to the same experimental PVT data used for Fig. 1 via a generalized reduced gradient solver. The molar masses of \( N_2 \) and PP were set to 0.028 and 600 kg/mol, respectively. Pressures of 100, 200, and 400 bar were selected. The result of the fitting process is shown in Fig. 2. An average of the characteristic values at different pressures was sufficient for method development. Table 1 summarizes values from this work and includes reference values by von Konigslow et al. [44]. The orders of magnitude are in good agreement.

Based on average characteristic parameters, the influence of gas content and \( p_{\text{init.}} \) on bulk moduli was calculated, as shown in Fig. 3. The interaction parameter \( \kappa_{12} \) was estimated based on literature [28] and set to 0.2. \( P_m^* \) was fixed at 750 bar in accordance with later experiments.

The initial assumption of a (linear) decrease of \( C \) with gas concentration could be approved by the SL-EOS. The calculated curves possess initial slopes of \(-33.08\), \(-33.53\), and \(-34.06\) MPa/wt% for initial pressures of 80, 140, and 200 bar, respectively. This shows increased sensitivity of compressibility to gas content at larger pressures. Between initial pressures of 80, 140, and 200 bar, the bulk modulus changes by approximately 40 MPa. Changing the temperature from 230°C to 260°C leads to a decrease in bulk modulus of about 100 MPa. This demonstrates that temperature has a more significant influence on the bulk modulus than initial pressure. Regarding the solubility of gases in polymer melts, the effect of temperature is negligible compared to that of pressure.

However, this calculation ignores the solubility limit that should be somewhere around 3 wt% \( N_2 \), depending on actual pressure. The definition of this approximate “region of expected solubility limit” in Fig. 3 is based on solubility data of \( N_2 \) in PP from literature [27, 28]. A discrete second gas phase that would be formed above this limit should lead to a drop of the bulk modulus. In our previous publication [21], this drop was confirmed, making the bulk modulus methodology an easy but efficient and precise method for the determination of dynamic solubility limits directly on the injection-molding machine.

![FIG. 2. Experimental PVT data (marks) fitted with SL-EOS from individual (dotted line) and averaged characteristic values (solid line) for PP (left) and \( N_2 \) (right).](image)

![FIG. 3. Calculated bulk moduli depending on gas content, initial pressures and temperatures (solid lines = 230°C, dashed lines = 260°C).](image)

| Pressure (bar) | Reference N2: 0.1–10,000 and PP: 50–650 | This work |
|---------------|---------------------------------|---------|
| N2 | \( P^* \) (MPa) | 178.5 | 103.4 | 102.4 | 188.2 | 131.3 |
| | \( \rho^* \) (kg/m\(^3\)) | 1.128 | 806.9 | 817.5 | 1,360.3 | 994.9 |
| | \( T^* \) (K) | 103.7 | 160.3 | 157.1 | 114.5 | 144.0 |
| PP | \( P^* \) (MPa) | 356.4 | 359.8 | 359.8 | 359.8 |
| | \( \rho^* \) (kg/m\(^3\)) | 895 | 903.7 | 903.6 | 904.8 | 904.0 |
| | \( T^* \) (K) | 656 | 597.0 | 597.0 | 597.2 | 597.1 |
The Bulk Modulus Methodology

A schematic representation of the solubility-measurement setup is shown in Fig. 4. During dosing and prior to injection, constant back pressure is maintained. At the beginning of the injection process, the shut-off nozzle remains closed, and a pressure of 750 bar is built up by the screw. From screw position (i.e., position prior and after compression) and pressure change (i.e., difference between initial back pressure prior to injection and pressure built up during compression), the bulk modulus can be calculated. Pressures can be recorded by the machine as injection or hydraulic pressures. The measurement range including another pressure transducer as well as ultrasonic sensors are used for verification only. For a precise determination of the bulk modulus, the initial volume, \( V_0 \), needs to be known.

Experimental Procedure

The bulk modulus methodology should be used for a determination of dynamic solubility limits. Three different back pressures (80, 140, and 200 bar) that cover the range of typical injection molding processes were chosen. Starting with the neat polymer (i.e., gas content 0 wt%), the gas content was increased gradually. At each gas concentration, the process 10 consecutive bulk modulus measurements were conducted after the process reached an equilibrium. The values are averaged, and the standard deviation is calculated (error bars in Figs. 6 and 7). This leads to a characteristic bulk-modulus curve that allows for the determination of a dynamic solubility limit. The limit is marked by a sudden drop of the bulk modulus curve, as schematically shown in Fig. 5 or Ref. 21. This drop is located at the transition between a homogeneous and heterogeneous polymer–gas mixture and marks the gas concentration that is solvable under the given process conditions.

A larger amount of gas cannot be dissolved in the polymer melt, which leads to the presence of gas bubbles in the material. As these bubbles are more compressible than the surrounding melt (see Fig. 1), the bulk modulus drops rapidly. In order to automate this process, a mathematical approach that can also be handled by machine software was developed in this work.

The different gas concentrations were approximately 0.3 wt% apart; however, at concentrations where the dynamic solubility was expected, a smaller step size was used. In this work, up to 2.8 wt% \( \text{N}_2 \) were injected into the barrel at 200 bar. At 80 and 140 bar, the largest possible gas contents were 1.2 and 1.8 wt% \( \text{N}_2 \), respectively. These limits represent processing, not solubility limits. All experiments were conducted at a constant barrel temperature of 230°C.

For verification, ultrasound sensors were mounted on the measurement flange. They transmitted signals through the melt at a rate of 500 s\(^{-1}\) during injection through the flange. Their resolution is in the \( \mu \text{m} \)-range allowing for the detection of very small gas bubbles. These data facilitate the measurement of ultrasound velocity in the polymer melt, but for this work, they were used for the visualization of undissolved gas bubbles (visible as interruptions of the ultrasound signal).

Materials and Equipment

All trials were performed on an injection molding machine Engel duo 700 (Engel Austria GmbH, Schwertberg, Austria).

| Material label | PPH (%) | Heterophase PPC | Nucleation agent | Talcum (%) |
|----------------|--------|----------------|------------------|------------|
| PPH            | 100    | —              | No               | —          |
| PPH-5T         | 95     | —              | No               | 5          |
| PPH-15T        | 85     | —              | No               | 15         |
| PPH-25T        | 75     | —              | No               | 25         |
| PPH-15T-N      | 95     | —              | Yes              | 15         |
| PPC            | —      | 100%           | No               | —          |

\*Nucleation agent (hydroxy-bis(2,4,8,10-tetra-tert-butyl-6-hydroxy-12H-dibenzo(d,g)(1,3,2)dioxaphosphocin 6-oxidato)aluminum) is not included in percentages due to its small proportion.

**TABLE 2. Materials used for this work.**
The machine was equipped with a special MuCell-screw geometry (distinguished by a special mixing section and a second nonreturn valve) as well as an SCF delivery unit of Type SII, both from Trexel, Inc. (Wilmington, MA). The hydraulic needle shut-off nozzle, including a piston position sensor, was provided by Herzog Systems AG (Flawil, Switzerland). Mold and materials were provided by Borealis Polyolefine GmbH (Linz, Austria). Table 2 includes the materials used for this work. This selection includes both homopolymer and copolymer and should cover different filler contents to reveal basic influencing factors. Talc itself provides nucleating properties; however, the influence of much smaller (molecular) particles resulting from actual nucleation agents should also be investigated.

Mathematical Approach

To automate the detection of solubility limits by identifying the characteristic drop of the bulk modulus and to enable the machine to conduct such measurements on its own, it is necessary to provide the machine software with a mathematical approach. Figure 5 depicts two typical (normalized) bulk modulus curve shapes. The dashed line marks the gas content just before the drop of the bulk modulus curve (i.e., the solubility limit). In some cases, the curve decreases linearly until the solubility limit is reached, as shown in Fig. 5a. Depending on the material, a prolonged dosing time can be necessary at larger gas contents. This can lead to a small increase of the slope prior to the solubility limit, as can be seen in Fig. 5b. The reason for this behavior is that even the smallest undissolved gas bubbles can be dispersed in the polymer melt due to the longer available time, which decreases compressibility. After reaching the solubility limit, the curves very often tend to level off. A mathematical approach needs to be capable of describing all these different shapes.

Due to its similar shape, the Carreau–Yasuda viscosity model according to Eq. 21 was used as a starting point. The infinite shear rate viscosity is set to 0 [45]. Since bulk modulus curves often exhibit an initial slope and slightly irregular slopes close to the dynamic solubility limit small adaptations were necessary in order to improve its fitting capacity. Addition of the terms $-kc$ (initial slope) and $+P_ue^\gamma$ (slope irregularities) lead to Eq. 22.

\[
\eta = \frac{\eta_0}{(1 + |xc|^{\lambda})^{\frac{1}{\alpha}}}
\]

\[
K = \frac{K_0 - kc + P_ue^\gamma}{(1 + |xc|^{\lambda})^{\frac{1}{\alpha}}}
\]

Equation 22 contains the compact bulk modulus $K_0$ in MPa, the initial slope of the curve $k$ in MPa/%, the gas concentration $c$ in %, the unit pressure $P_u$ (i.e., 1 MPa), a scaling factor $f$ in %, three dimensionless scaling factors $e$, $a$, and $n$ and finally a parameter that we call inverse limit $\lambda$ in 1/%. This parameter describes the position of the transition between the low content region below the dynamic solubility limit and the drop of the bulk modulus curve. The transition is located at $1/\lambda$.

RESULTS AND DISCUSSION

Figure 6 summarizes the measured bulk moduli for each material and the three different back pressures. Every measurement yields the characteristic drop marking the dynamic solubility limit.

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FIG. 6. Resulting bulk modulus curves (*different bulk modulus values due to usage of different shut-off nozzle, therefore different V0).
The increase in the 200 bar curves prior to the solubility limit, as described above (compare Fig. 5b), is also visible. Regardless of the material, the initial linear relationship between gas content and bulk modulus can be seen. In some cases, at the lowest pressure of 80 bar, the slope is initially 0. Qualitatively, all materials behave similarly, that is, larger pressures shift the drop of the bulk modulus curve to larger gas contents. Especially at 140 and 200 bar, longer necessary dosing times and, therefore, a better modulus curve to larger gas contents. Especially at 140 and 200 bar, larger pressures shift the drop of the bulk modulus curve to larger gas contents. Especially at 140 and 200 bar, longer necessary dosing times and, therefore, a better solution behavior could be observed.

In order to prove the capability of Eq. 22, a generalized reduced gradient solver was used again. The fitting was performed manually. Starting with the first bulk modulus value (i.e., polymer without gas), fitting was conducted for each measured data point. Only when the fitting quality was satisfying the next point was considered. This iterative process imitates the procedure a machine would also conduct when subsequently increasing the gas content in the processed melt. During the fitting, one constraint was that the fitted parameter \( \lambda \) always had to be larger than the factor \( 1/c \) calculated from gas concentration at the current data point. This causes the transition of curve fitted to the experimental data to be located at a gas content lower than or equal to the currently considered measurement. If this gas content lies in the linear region of the plot, \( \lambda \) takes the value 0 (i.e., no transition zone). Figure 7 shows the results using the example of PP homopolymer (PPH; note: the plots in Fig. 7 represent the same data as the plots for PPH in Fig. 6, but with fitted curves). The corresponding fitting parameters for this material are summarized in Table 3. All parameters for the remaining materials can be found in Tables A1–A5 in the appendix.

Table 3. Fitting parameters for PPH.

| Pressure (bar) | \( K_0 \) (MPa) | \( \lambda \) (MPa/%) | \( f \) (%) | \( \epsilon \) (–) | \( a \) (–) | \( n \) (–) | \( \lambda \) (1/%) |
|---------------|----------------|----------------------|-------------|---------------|------------|------------|--------------|
| 80            | 681.47         | 1.17                 | 0.03        | 0.01          | 11.82      | 0.00       | 1.17         |
| 140           | 673.34         | 23.21                | 0.05        | 0.94          | 350.00*    | 0.55       | 0.68         |
| 200           | 682.16         | 38.15                | 0.06        | 1.10          | 350.00*    | 0.42       | 0.43         |

*Value set as upper limit.

Figure 8 contains ultrasonic measurements for verification. As the ultrasound velocity depends on the density of the material, it is also subject to the gas concentration in the melt [46]. For this verification, however, only its continuity is of interest. The measurements are performed during the injection of the melt in the measurement flange between the plasticizing cylinder and mold (see Fig. 4). As the melt passes the sensors, ultrasound signals are continuously sent through the material. The top images are taken at gas contents below the calculated solubility limits the bottom ones above. The former shows a continuous ultrasound signal, which confirms the homogeneity of the melt (i.e., absence of undissolved gas phase). The latter shows interruptions of the ultrasonic signals (location indicated by arrows). These interruptions stem from undissolved gas phases that pass the sensors during injection and absorb and scatter the ultrasonic signal, which implies heterogeneity of the melt (i.e., presence of undissolved gas phase). In order to verify the bulk modulus methodology, interruptions of ultrasound signals must only appear at gas concentrations above the mathematically determined values in Table 5. An exemplary comparison between the results from bulk modulus measurements in Fig. 7 and ultrasound measurements in Fig. 8 show perfect agreement. Obviously, a determination of dynamic solubility limits is possible with both methods. For ultrasound measurements, additional hardware (e.g., measurement flange, sensors, measurement device, computer), and software for data evaluation are necessary. The bulk modulus methodology can be conducted without any additional equipment; Data collection of injection/back pressure and screw position are state of the art in injection molding machines, a shut-off nozzle is always needed for injection foam molding. This makes the bulk modulus methodology the technology of choice.

In Fig. 7, the initial slope of all curves can be described accurately with the term \(-kc\) of Eq. 22. The linear nature of the curve below the dynamic solubility limit allows for this simple approach. Also, an increase of the slopes prior to the drop of the bulk modulus at the solubility limit (horizontal line) on the 140 and 200 bar curve can be described precisely with the term \( P_\epsilon e^{\Delta \epsilon} \). Although it is exponential, the denominator of Eq. 22 can outweigh this effect at first and enable the description of transition when the parameters \( e, f, a, \) and \( n \) are chosen appropriately. At larger concentrations beyond the dynamic solubility limit, the influence of \( P_\epsilon e^{\Delta \epsilon} \) and the denominator are reversed, which allows for an accurate description of a flattening curve. It has to be noted that the shape of the proposed equation is only suitable for describing the actual measured values. Theoretical gas concentrations well above the last measured...
value cannot be described due to the exponential nature of $P_{uEc/f}$. On the 80 bar curve, the fourth data point forms a discontinuity. Obviously, the proposed equation is also capable of describing such shapes. Table 4 includes all empirical correlation coefficients, $r$, calculated via Eq. 23 with $x$ and $y$ representing the measured and calculated bulk moduli, respectively. With an average correlation coefficient of 0.9926, the fitting quality of the proposed equation works very well.

$$r(x, y) = \frac{\sum(x-x_i)(y-y_j)}{\sqrt{\sum(x-x_i)^2 \sum(y-y_j)^2}} \quad (23)$$

As mentioned above, the transition between the bulk moduli of homogeneous solutions and heterogeneous mixtures is located at $1/\lambda$, as also depicted in Fig. 7. In order to prove this assumption, ultrasonic measurements were conducted simultaneously. The obtained results were compared with bulk modulus measurements. A perfect agreement was observed. Table 5 and Fig. 9 summarize the calculated dynamic solubility limits.

The measured dynamic solubility limits depend linearly on pressure. This behavior is in good agreement with the Henry law, that is, static solubility. It is noticeable that very little influence of material or material composition could be observed. PP copolymer (PPC) shows slightly reduced solubility, while the influence of talc content is negligible. Scientific literature offers some references regarding the influence of material composition on solubility. Chen et al. [37] investigated the static solubility of HDPE and rigid polyvinylchloride, both filled with talcum. Using the pressure decay method, their solubility measurements suggested that the absorbed amount of gas increased with filler content. Since talcum does not dissolve gases, they concluded that the blowing agent accumulated at the polymer–filler interface. According to their argumentation, micro gaps between polymer and filler are present after compounding. On these sites, gas separates the interface. Areerat et al. [47] investigated the influence of titanium dioxide (TiO$_2$) filler content on the static solubility of CO$_2$ in low-density polyethylene using an MSB. They concluded that the filler content does not affect the solubility of the gas relative to the polymer matrix. Literature on the effect of filler content on solubility is very limited. However, there seems to be some ambiguity regarding the nature of the fillers.

**Important Explanatory Notes**

Solubility is commonly defined as an equilibrium thermodynamic property. Therefore, there should not be any influence of shear or other dynamic processes on the solvable amount of gas. However, such a correlation has been observed; the dynamic solubility limits are consistently lower than static measurements from literature, as shown in Fig. 10. It can also be noticed that the difference between static and dynamic solubility limits is reduced at larger pressures where the solution behavior is generally improved. This is a clear sign that the term ”dynamic solubility” is more of industrial/technical rather than chemical nature. Due to intense shearing in the plasticizing unit, gas is mixed and finely dispersed in the polymer melt. For the presented bulk modulus methodology as well as ultrasonic measurements, there seems to be a threshold value for the average size of discrete gas bubbles, below which detection is not possible and the melt is considered

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**TABLE 4. Correlation coefficients for describing the quality of fits.**

| Material   | 80 bar | 140 bar | 200 bar |
|------------|--------|---------|---------|
| PPH        | 0.9888 | 0.9960  | 0.9900  |
| PPH-5T     | 0.9940 | 0.9669  | 0.9981  |
| PPH-15T    | 0.9985 | 0.9879  | 0.9863  |
| PPH-25T    | 0.9984 | 0.9737  | 0.9957  |
| PPH-15T-N  | 1.0000 | 0.9980  | 0.9976  |
| PPC        | 1.0000 | 1.0000  | 0.9972  |

**TABLE 5. Calculated dynamic solubility limits.**

| Material   | 80 bar (wt%) | 140 bar (wt%) | 200 bar (wt%) |
|------------|--------------|---------------|--------------|
| PPH        | 0.85         | 1.46          | 2.33         |
| PPH-5T     | 0.66         | 1.44          | 2.50         |
| PPH-15T    | 0.72         | 1.46          | 2.50         |
| PPH-25T    | 0.62         | 1.49          | 2.36         |
| PPH-15T-N  | 0.65         | 1.43          | 2.56         |
| PPC        | 0.68         | 1.25          | 1.98         |

**FIG. 9.** Graphic representation of calculated dynamic solubility limits.

**FIG. 10.** Comparison between static measurements from literature (corrected solubility from Ref. [27]; solid lines) and dynamic solubility limits from this work (dashed lines).
homogeneous (i.e., the gas is completely dissolved). In combination with surface characterization in one of your previous publications [21], it could be concluded that this threshold is indeed relevant for the actual applications. The bulk modulus methodology, therefore, allows for the determination of an industrial/technical form of dynamic solubility limit.

The results represented in Figs. 9 and 10 emphasize the importance of process management on dynamic solubility in injection foam molding. Apparently, the time available for polymer–gas interaction in the injection molding process plays a crucial role as it did not allow for the dynamic solution (i.e., fine dispersion) of larger amounts of gas. All investigated materials exhibit virtually the same dynamic solubility limits, which are consistently lower than static references. This is a clear sign of the predominance of physical mixing over solution processes. The observed dynamic solubility is a process rather than a material-related limit and is therefore applicable to industrial processes.

CONCLUSIONS

This work provides the theoretical background for the development process of a novel measurement method for a technical/industrial form of dynamic solubility limits in injection foam molding. Based on the SL-EOS, a mathematical prediction of the compressibility of gas containing polymer melts was carried out. Measurements proved the assumption that the bulk modulus of polymer gas solutions drops sharply once the dynamic solubility limit is exceeded. The measurement method has a large potential in terms of material characterization but also process monitoring. Its implementation on the machine allows the methodology to take every form of process management into account. In order to make the developed method relevant for industrial or academic interests, it needs to be automated.

For that reason, an automation approach was developed and verified in this work. A mathematical equation is therefore fitted to the results of bulk modulus measurements. In order to verify the method, ultrasonic measurements are conducted simultaneously. Perfect agreement between solubility limits determined by the proposed mathematical approach, as well as those determined by ultrasonic measurements, was found. Automation via the inverse limit, λ, from Eq. 22 showed reproducible and reliable results. Solubility limits between 0.62 and 2.56 wt% N$_2$ at pressures between 80 and 200 bar and a temperature of 230°C were determined. The bulk modulus method is simple yet effective and can be used for a quick determination of dynamic solubility limits, for material characterization or process monitoring.

It has shown that dynamic (as also static) solubility limits are primarily dependent on pressure. Interestingly no influence of the material or its constituents could be observed. This implies that time plays a crucial role in dynamic solubility. In summary, the proposed approach for automation using Eq. 22 worked well. Due to the absence of an influence of material composition, the importance of process management is enhanced. Dynamic, as well as static solubility, is almost exclusively depending on the pressure in the barrel.

Knowledge of dynamic solubility limits can offer numerous benefits. For material scientists, the measurement of a process-related ultimate solvable amount of gas can be interesting when developing foaming grades for injection molding. For applications where large gas contents are needed for processing (e.g., large density reductions, low density, etc.), an a priori determination of the solvable amount of gas is essential. The methodology can also be used to study necessary gas injection times, qualify new screw designs, or find optimum injector positions.

The conduction of the bulk modulus methodology can lead to more side benefit. Using PS and N$_2$/CO$_2$, Park/Heim et al. [48] have shown that gas bubbles that developed during injection of the polymer–gas mixture into the cavity can be dissolved again by applying high packing pressures for sufficient amount of time. This rehomogenization of the melt leads to a more uniform and finer cellular structure after the foaming stage resulting from mold opening. The compression stage during the bulk modulus methodology can have a similar homogenizing effect on the melt if unwanted bubbles are formed in the screw antechamber (e.g., due to poor process management). In a thematically related work [49], Park et al. investigated the effect of pressure drop rate on cell density of a PS/CO$_2$ system. In very good agreement with our work, they found that undissolved gas bubbles increase the melt compressibility. According to their results, a fine cell structure can be obtained through large pressure drop rates. These, in turn, are easier to accomplish when the melt compressibility is low. Therefore, undissolved gas bubbles are unfavorable in terms of cell nucleation. As far as the bulk modulus methodology is concerned, the compression of the melt, as well as the above-mentioned dissolution of potential gas bubbles in the plasticizing unit, can provide stiffer (i.e., less compressible) melt which could benefit cell nucleation during the mold filling stage.

Future investigations should focus on further applications of this automation approach. The overall objective is to adjust foam injection molding processes autonomously using the bulk modulus methodology. In addition, the influence of time management (gas injection, dosing time, etc.) should be elaborated on. All these activities should be steps toward a fully autonomous production in foam injection molding.

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## APPENDIX

### TABLE A1 Fitting parameters for PPH-5T.

| Pressure (bar) | $K_0$ (MPa) | $k$ (MPa%) | $f$ (%) | $e$ (−) | $a$ (−) | $n$ (−) | $\lambda$ (1%) |
|---------------|-------------|------------|---------|--------|--------|--------|-------------|
| 80            | 696.29      | 21.26      | 4.73    | 0.72   | 300.00 | 0.63   | 1.51        |
| 140           | 686.87      | 28.86      | 0.00    | 0.25   | 337.56 | 0.62   | 0.70        |
| 200           | 697.75      | 44.26      | 0.17    | 1.26   | 48.31  | 0.31   | 0.40        |

### TABLE A2 Fitting parameters for PPH-15 T.

| Pressure (bar) | $K_0$ (MPa) | $k$ (MPa%) | $f$ (%) | $e$ (−) | $a$ (−) | $n$ (−) | $\lambda$ (1%) |
|---------------|-------------|------------|---------|--------|--------|--------|-------------|
| 80            | 722.05      | 49.75      | 0.05    | 0.01   | 17.54  | 0.54   | 1.38        |
| 140           | 706.07      | 35.16      | 0.01    | 0.01   | 275.76 | 0.67   | 0.68        |
| 200           | 722.63      | 51.46      | 0.49    | 2.20   | 173.92 | 0.00   | 0.40        |

### TABLE A3 Fitting parameters for PPH-25T.

| Pressure (bar) | $K_0$ (MPa) | $k$ (MPa%) | $f$ (%) | $e$ (−) | $a$ (−) | $n$ (−) | $\lambda$ (1%) |
|---------------|-------------|------------|---------|--------|--------|--------|-------------|
| 80            | 711.97      | 0.00       | 0.00    | 0.00   | 66.93  | 0.66   | 1.62        |
| 140           | 714.19      | 57.16      | 0.62    | 5.33   | 26.20  | 0.00   | 0.67        |
| 200           | 728.11      | 52.11      | 1.10    | 6.73   | 36.75  | 0.06   | 0.42        |

### TABLE A4 Fitting parameters for PPH-15 T-N.

| Pressure (bar) | $K_0$ (MPa) | $k$ (MPa%) | $f$ (%) | $e$ (−) | $a$ (−) | $n$ (−) | $\lambda$ (1%) |
|---------------|-------------|------------|---------|--------|--------|--------|-------------|
| 80            | 882.87      | 55.41      | 0.29    | 2.88   | 23.53  | 0.46   | 1.55        |
| 140           | 899.66      | 28.02      | 0.18    | 0.41   | 7.28   | 0.53   | 0.70        |
| 200           | 919.74      | 50.16      | 2.24    | 1.01   | 350.00 | 0.10   | 0.39        |

### TABLE A5 Fitting parameters for PPC.

| Pressure (bar) | $K_0$ (MPa) | $k$ (MPa%) | $f$ (%) | $e$ (−) | $a$ (−) | $n$ (−) | $\lambda$ (1%) |
|---------------|-------------|------------|---------|--------|--------|--------|-------------|
| 80            | 709.83      | 22.37      | 0.23    | 2.37   | 5.84   | 0.44   | 1.47        |
| 140           | 716.76      | 40.05      | 0.06    | 1.20   | 9.96   | 0.00   | 0.80        |
| 200           | 720.91      | 29.38      | 0.12    | 0.10   | 149.81 | 0.69   | 0.51        |