Multi-scale modelling of expanding polyurethane foams: Coupling macro- and bubble-scales

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HIGHLIGHTS

• A new multi-scale framework for the simulation of polyurethane foam is presented.
• Two modelling scales, bubble- and macro-scales, are linked using MoDeNa framework.
• The bubble-scale model computes the bubble growth rate for individual bubbles.
• The macro-scale model solves a PBE for prediction of bubble size distribution.
• Validations showed the successfulness of the proposed modelling framework.

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ABSTRACT

In this work, we apply a general multi-scale methodology to the simulation of reacting and expanding polyurethane (PU) foams. The approach starts from the baseline macro-scale model of Karimi and Marchisio (2015), which describes the foam as a continuum and applies the population balance equation (PBE) to determine the evolution of the bubble size distribution (BSD) during the foaming process. The main novelty of this work is the replacement of the simplistic bubble growth rate model used previously, with the detailed bubble-scale model, which resolves the mass, momentum and energy boundary layers around the bubble. A second important novelty concerns the way in which the macro- and the bubble-scale models are coupled, namely on-the-fly and by using the MoDeNa interface. The performance of the final multi-scale model is evaluated by analysing the predictions for foam density, temperature and BSD on 11 different test cases. Comparison for these test cases demonstrates a significant improvement in the ability of the model to describe the PU foaming process.

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1. Introduction

Its worldwide market size and its wide range of applications, from the auto-mobile industries, to the construction and household appliances, indicate the importance of polyurethane (PU) foams. From the manufacturer standpoint, a-priori knowledge of the properties of the final product leads to the ease of process design, optimization and transferability. Besides the economical benefits, this reduces the sensitivity of the PU production to human faults and human dependencies. In other words, a fully predictive and viable modelling framework is required to determine the foam characteristics.

However, the foaming process itself is a complicated physical phenomenon. It involves chemical reactions of different components that determine the evolution of the bubble/cell size distribution (BSD) due to the bubble growth and coalescence. Furthermore, material properties such as the foam density and the viscosity, as well as the thermal conductivity, are directly affected during this process (Gibson and Ashby, 1997). The aforementioned complexity makes the modelling techniques to be more biased toward empirical approaches. For example, different groups described in the past the main reactions and physical phenomena involved during the foaming process (i.e., gelling and blowing reactions, evaporation of the blowing agent) by using an empirical approach (Baser and Khakhar, 1994a,b, Gupta and Khakhar, 1999) and validated predictions with experimental measurements of foam temperature and density. Among the different approaches employed (Princen and Kiss, 1986; Qin et al., 2007) there are few instances where Computational Fluid Dynamics (CFD) is utilized for the modelling and simulation of PU foams. As a case in point, Seo et al. introduced an explicit high resolution method for capturing the foam interface for mold filling applications (Seo et al., 2003).
2003; Seo and Youn, 2005). They were able to reproduce experimental profiles describing the decrease of foam density, while the foam viscosity was modelled by using the Castro–Macosko model (Castro and Macosko, 1982). Several research groups then improved the CFD model using Volume–of–Fluid (VOF) method (Bikard et al., 2007; Geier et al., 2009; Winkler, 2009; Samkhaniani et al., 2013). They included extra equations for the kinetics of the reactions and empirically derived formulations for the foam properties, such as thermal conductivity. It should be indicated that none of the above-mentioned models did take into account the occurrence of bubble growth and the evolution of the BSD.

The bubble growth in PU foams was also considered separately, neglecting the macro-scale. Harikrishnan and Khakhkar (2009) used a simple mass transfer model with the mass transfer coefficient as a model parameter. Kim and Youn (2000) used a similar bubble–shell model, as in this work, to predict the evolution of bubble radius in PU foams. However, none of these works considered the BSD.

Recently, Karimi and Marchisio (2015) introduced a macro-scale baseline model that describes the reactive-expanding PU foam as a continuum, by solving a population balance equation (PBE) to track the evolution of the BSD. In this modelling strategy, the polymerisation reactions in conjunction with the presence of physical and chemical blowing agents were considered and predictions were validated against the literature data. The macro-scale baseline model, developed for future CFD applications, but verified and validated for the moment on simple zero-dimensional test cases, made however a very simple assumption on bubble growth: the process was modelled as diffusion-controlled, resulting in a constant multiplied by the concentration gradient around the bubble.

The aim of this work is to overcome this limitation by coupling the macro-scale model for the PU foam with a detailed bubble-scale model for the growth rate. The detailed bubble-scale model considers the interaction between molecular diffusion and chemical reactions by resolving the mass, momentum and energy boundary layers around the bubble and is coupled with the macro-scale model with the use of an ad hoc interface library: the MoDeNa interface (MoDeNa-EUProject, 2015). This efficient coupling of the two scales allows us to simulate the macro-scale foam evolution, without missing the important bubble-scale details, with reasonable computational costs. Comparison of the multi-scale model predictions with experimental data on 11 different test cases shows a significant improvement, with respect to the simpler stand-alone macro-scale baseline model, paving the way for the final extension of the approach to real three-dimensional CFD simulations.

2. Governing equations

The mathematical model presented in this work constitutes from several parts. At the top level, we have a macro-scale model, which uses the PBE to track the evolution of the BSD. The bubble growth rate needed by the PBE is, in turn, obtained from the bubble-scale model, which describes the detailed growth of individual bubbles. The overall model is complemented by the kinetic model, which is used by both the macro-scale and the bubble-scale models. In what follows the different parts will be described, together with the strategy used to interface them.

2.1. Kinetic model

PU foams are created from the mixture of initial reactants, i.e., isocyanates, polyols and water with surfactant and catalyst. The overall reaction rate depends on the functionality, type and amount of used compounds. It is still a standard practice to simplify the complex polymerization scheme to just two global reactions to limit the number of kinetic parameters that should be determined.

The reaction between isocyanates and polyols, during which the urethane bonds are formed, is called the gelling reaction. Schematically, it can be written as:

\[ \text{R-NCO} + \text{R-OH} \rightarrow \text{R-NH-CO-O-R} \]

isocyanate polyol urethane bond

The reaction between two isocyanate groups and water molecule creates an urea bond and a molecule of carbon dioxide. This is called the blowing reaction and it can be written as:

\[ 2\text{R-NCO} + \text{H}_2\text{O} \rightarrow \text{R-N-H-CO-NH-R} + \text{CO}_2 \]

isocyanate water urea bond carbon dioxide

The kinetics of these simplified reactions can be expressed in terms of the conversion of polyol groups \( X_p \):

\[
\frac{dX_p}{dt} = A_p \exp\left( -\frac{E_p}{RT} \right) \left(1 - X_p\right) \left(c_{w,0} - c_{p,0}X_p - c_{w,0}\right)
\]

and conversion of water molecules \( X_w \):

\[
\frac{dX_w}{dt} = A_w \exp\left( -\frac{E_w}{RT} \right) \left(1 - X_w\right)
\]

where \( t \) is the time, \( A_p \) and \( A_w \) are the pre-exponential factors, \( E_p \) and \( E_w \) are the activation energies, \( R \) is the gas constant, \( T \) is the temperature and \( c_{w,0}, c_{p,0} \) and \( c_{w,0} \) are the initial concentrations of isocyanate groups, polyol groups and water, respectively. In these equations the foam is treated with a zero-dimensional approach, assuming negligible property gradients, however their extension to three-dimensional approaches is straightforward.

If the foam is considered to be internally and externally adiabatic the enthalpy balance can be written as follows:

\[
\frac{dT}{dt} = \frac{\left(-\Delta H_g\right)c_{p,f}}{\rho_m c_{p,f}} \frac{dX_p}{dt} + \frac{\left(-\Delta H_a\right)c_{w,f}}{\rho_m c_{p,f}} \frac{dX_w}{dt} + \sum_{i=1}^{N} \left(-\Delta H_{v_s}\right) \frac{dw_w}{dt}
\]

where \( \Delta H_{g} \) and \( \Delta H_{a} \) are the reaction enthalpies of the gelling and blowing reactions, respectively, \( \rho_m \) is the density of the liquid mixture undergoing polymerization, \( c_{p,f} \) is the thermal capacity of the foam, \( \Delta H_{v_s} \) is the heat of evaporation for the \( \alpha \)th blowing agent and \( w_w \) is the mass fraction for the \( \alpha \)th blowing agent in the gas phase with respect to the foam. The adiabatic condition is justified by the facts that foams have low thermal conductivity and that the internal structure of the foam is formed relatively quickly when the temperature is still quite low. The temperature continues to increase during the polymer curing. However, the foam density remains practically constant after the gel point is reached.

Eqs. (1)–(3) represent a system of ordinary differential equations. This system is subjected to the following initial conditions

\[ X_p|_{t=0} = 0, \]

\[ X_w|_{t=0} = 0, \]

\[ T|_{t=0} = T_0, \]

where \( T_0 \) is the initial temperature.

2.2. Bubble-scale model

The bubble-scale model simulates the growth of a single bubble surrounded by a shell of reaction mixture (see Fig. 1). There are several simplifications associated with this model: (i) the model
assumes spherical shapes of bubbles, (ii) the volume of the shell is constant and (iii) the blowing agent is exchanged only between the bubble and its shell. It is assumed that small air bubbles are entrapped in the reaction mixture during the initial vigorous mixing. Moreover, no carbon dioxide is dissolved in the initial mixture and the physical blowing agent becomes supersaturated only after the temperature is increased by the reaction. Thus, effects of nucleation and spinodal decomposition are neglected.

The model consists of coupled momentum and mass transfer equations. The momentum balance for a spherical bubble in a liquid environment can be written as follows (Feng and Bertelo, 2004):

\[
\sum_{\alpha=1}^{N} p_{\alpha} + p_{\text{air}} - p_{\text{rm}} = \rho_{\text{rm}} \left[ \frac{dR}{dt} R \left( \frac{dR}{dt} + \frac{3}{2} \left( \frac{dR}{dt} \right)^2 \right) \right] + 2\gamma \frac{R}{R} + 4\mu_{\text{rm}} \frac{dR}{dt}
\]

where \( N \) is the number of blowing agents, \( p_{\alpha} \) is the partial pressure of a blowing agent in the bubble, \( p_{\text{rm}} \) is the pressure in the reaction mixture, \( R \) is the bubble radius, \( \gamma \) is the surface tension and \( \mu_{\text{rm}} \) is the viscosity of the reaction mixture. The terms on the right hand side represent inertial, surface tension and viscous forces.

Partial pressure of air in the bubble \( p_{\text{air}} \) can be calculated as follows:

\[
p_{\text{air}} = p_{\text{air},0} \frac{T}{R_0} \left( \frac{R_0}{R} \right)^3
\]

where \( R_0 \) is the initial radius and \( p_{\text{air},0} \) can be calculated as follows:

\[
p_{\text{air},0} = p_{\text{rm}} + 2\gamma R_0
\]

The mass balance for a blowing agent inside the bubble reads instead as follows:

\[
\frac{d}{dt} \left( \frac{p_{\text{air}} R^2}{R_0 T} \right) = 3D_n R^2 \frac{\partial c_{\alpha}}{\partial r} \bigg|_{r=R}
\]

where \( D_n \) is the diffusion coefficient of the blowing agent in the reaction mixture, \( c_{\alpha} \) is the molar concentration of the blowing agent in the reaction mixture and \( r \) is the spatial coordinate. Here we assume that the resistance to mass transfer is entirely on the side of the reaction mixture and that no gradients are present inside the bubble.

The mass balance for a blowing agent in the reaction mixture can be written as:

\[
\frac{d}{dt} \frac{p_{\text{air}} R^2}{R_0 T} \frac{\partial c_{\alpha}}{\partial t} + \frac{p_{\text{air}} R^2}{R_0 T} \frac{\partial c_{\alpha}}{\partial r} \left( 2 \frac{\partial R}{\partial t} \right) + r_{\alpha}
\]

where \( r_{\alpha} \) is evaluated as:

\[
r_{\alpha} = \begin{cases} 
  c_{\alpha,0} \frac{dX_{\alpha}}{dt} & \text{if } \alpha = \text{CO}_2 \\
  0 & \text{if } \alpha \neq \text{CO}_2
\end{cases}
\]

It is assumed that initial bubbles are created by entrapping air during the mixing step. Thus, the initial partial pressure of all blowing agents is zero:

\[
p_{\alpha} \bigg|_{t=0} = 0
\]

Eq. (7) requires two initial conditions for the bubble radius:

\[
R_{b,0} = R_0
\]

The bubble growth rate is initially zero, because air cannot be dissolved in the reaction mixture and none of the blowing agents is initially in the supersaturated state.

We assume a uniform concentration profile for all blowing agents in the reaction mixture at the beginning of the process:

\[
c_{\alpha} \bigg|_{t=0} = c_{\alpha,0}
\]

Phase equilibrium between gas and the dissolved blowing agent is assumed at the interface between the bubble and its shell. It can be written in terms of Henry’s law as:

\[
c_{\alpha} \bigg|_{r=S} = H_{\alpha} p_{\alpha}
\]

where \( H_{\alpha} \) is the Henry constant.

At the outer edge of the shell, no flow condition is employed,

\[
\frac{\partial c_{\alpha}}{\partial r} \bigg|_{r=S} = 0
\]

where \( S \) is the outer radius of the shell. From the assumption of constant shell volume, we can derive the following expression:

\[
S = \sqrt{R^3 + S_0^3 - R_0^3}
\]

where \( S_0 \) is the initial outer radius of the shell, which is related to the number density of bubbles in the initial mixture, \( n_{b,0} \), through the following expression:

\[
S_0 = \left( \frac{3}{4\pi n_{b,0}} \right)^{1/3}
\]

It is advantageous to introduce a transformation of the spatial coordinate:

\[
y = r^3 - R^3
\]

that allows us to transform the computational domain from the time-varying interval \([ R, S ]\) to the constant \([ 0, S_0^3 - R_0^3 ]\) interval. Overall, the bubble-scale model consists of \( N \) partial differential equations (PDE) – Eq. (11) and \(( N + 1 \) ordinary differential equations (ODE) – Eqs. (7) and (10), where \( N \) is the number of blowing agents, and of three additional ODE for the kinetic model – Eqs. (1)–(3).

The main purpose of the bubble-scale model is to calculate the bubble growth rate, which can be defined as the continuous rate of change of bubble size, or alternatively as the rate of change of bubble volume. However, to quantify the contribution of each blowing agent, in this work the bubble growth rate due to the \( \alpha \)th blowing agent is calculated as the continuous rate of change of the
number of moles of the $\alpha$th blowing agent inside the bubble:

$$n_a = 4\pi DaR^2\frac{\partial\rho}{\partial t} \bigg|_{\omega}$$  \hspace{1cm} (22)

2.3. Macro-scale model

The macro-scale model assumes that the chemical components of the PU foam are perfectly mixed and that the influence of nucleation and spinodal decomposition is negligible. As mentioned above, a PBE to study the evolution of the gas bubbles inside the foam is also solved. The general form of this equation accounting for the bubble growth and the coalescence is shown below:

$$\frac{\partial n(v)}{\partial t} + \frac{\partial}{\partial v}[G(v)n(v)] = \frac{1}{2} \int_0^v \beta(v', v - v')n(v')n(v - v') dv' - \int_0^v \beta(v, v')n(v)n(v') dv'$$  \hspace{1cm} (23)

where $n(v)$ is the BSD written in terms of the bubble volume, representing the number of bubbles (per unit volume of the liquid mixture constituting the foam) with volume in the infinitesimal interval $v$ and $v + dv$. $\beta(v, v')$ is the coalescence kernel, stating the frequency of coalescence between two bubbles of volume $v$ and $v'$. $G(v) = dv/dt$ is the overall growth rate, written as the rate of change of bubble volume. Employing the generic definition of the moment of order $k$:

$$m_k(t) = \int_0^\infty n(v)v^k dv$$  \hspace{1cm} (24)

the PBE is transformed into a set of evolution equations for the moments of BSD. Further, the generic definition of moments allows us to associate the moments of different orders to the gas bubbles within the foam structure. In that, moment of order zero, $m_0(t)$, indicates the total number of bubbles per unit volume of the liquid and $m_1(t)$ is the total bubble volume per unit volume of the liquid mixture, whereas moments of order two and three are related to the variance and skewness of the BSD. Knowing the zeroth and first order moments, the mean bubble radius at any time can be computed as follows:

$$R(t) = \left(\frac{3m_1(t)}{4m_0(t)}\right)^{1/3}$$  \hspace{1cm} (25)

and the general form of the moments evolution reads as:

$$\frac{d\bar{m}_k}{dt} = \sum_{\alpha=1}^{N} \bar{C}_k^{\alpha} + S_k$$  \hspace{1cm} (26)

where as usual $N$ represents the number of blowing agents, $\bar{C}_k^{\alpha}$ denotes the source term for the moment of order $k \rightarrow$ due to bubble growth for the $\alpha$th blowing agent, while $S_k$ represents the source term for the moment of order $k \rightarrow$ due to coalescence. Although a detailed description of these two terms can be found in our previous work (Karimi and Marchisio, 2015), it is worth describing here more details on the bubble growth term:

$$\bar{C}_k^{\alpha} = k \int_0^\infty n(v)G^\alpha(v)v^{k-1} dv, $$  \hspace{1cm} (27)

where $G^\alpha$ is the bubble growth rate, in turn calculated from the bubble-scale model as follows:

$$G^\alpha(v) = \frac{\rho \alpha R_T}{P_a} $$  \hspace{1cm} (28)

The formulation of the PBE in terms of the moments generates a closure problem, related to the inability of the modeler to write Eq. (27) in terms of the moments themselves, that can be overcome by using the Quadrature Method of Moments (Q MOM). This approach was firstly proposed by McGraw (1997) and is based on the simple idea of approximating the BSD as a summation of Dirac delta functions centred on the nodes of a quadrature approximation. This approximation transforms the integral appearing in Eq. (27) into a simple summation:

$$\bar{C}_k^{\alpha} \approx \sum_{i=1}^{M} \omega_i G^\alpha(v_i)v_i^{k-1}$$  \hspace{1cm} (29)

and similarly for the source term for bubble coalescence:

$$S_k \approx \sum_{i=1}^{M} \sum_{j=1}^{M} \omega_i \omega_j \int_{v_i}^{v_j} (v_i + v_j) - v_i^k - v_j^k) \beta(v_i, v_j)$$  \hspace{1cm} (30)

where $M$ is the number of nodes and $\omega_i$, $\omega_j$, and $v_i$, $v_j$ are the weights and nodes of the quadrature approximation calculated from the first 2M moments. It is assumed that coalescence of two bubbles with volumes, $v_i$ and $v_j$, results in a bubble of volume, $v_i + v_j$, and the collision frequency is constant (equal to $\beta_w = 1.00 \times 10^{-3}$ s$^{-1}$), resulting into the following coalescence kernel: $\beta(v_i, v_j) = \beta_w(v_i + v_j)$. More details on the equations and the solution method can be found elsewhere (Marchisio et al., 2003; Marchisio and Fox, 2005, 2013). As the total bubble volume per unit volume of the liquid mixture corresponds to $m_0(t)$ and is therefore provided by the solution of the PBE, the foam density can be formulated as follows:

$$\rho t = \rho_{gas} \frac{m_0(t)}{1 + m_0(t)} + \rho_{m} \frac{1}{1 + m_0(t)}$$  \hspace{1cm} (31)

where $\rho_{gas}$ is the density of the gas bubbles within the foam, calculated with the ideal gas law.

Similar to the bubble-scale model, also the macro-scale model accounts only for the two global reactions: namely the gelling and the blowing reactions, by solving evolution equations for $X_p$ and $X_{nu}$. The model is completed by the general mass balance equation for the $\alpha$th blowing agent that reads instead as follows:

$$\frac{d\omega_i}{dt} = \frac{M}{\rho_{m}} - \bar{G}_i^{\alpha} - \frac{\bar{C}_i^{\alpha}}{\rho_T}$$  \hspace{1cm} (32)

where $\omega_i$ is the mass fraction of the $\alpha$th blowing agent, $r_{\alpha}$ has been previously defined in Eq. (12), $M_{\alpha}$ is the molecular mass of the $\alpha$th blowing agent and $\bar{G}_i^{\alpha}$ is the moment of order one of the growth rate due to the $\alpha$th blowing agent.

3. Scale coupling and numerical details

The direct coupling between the macro-scale and the bubble-scale models would be too expensive, especially in view of the final application, where the macro-scale model is solved in a three-dimensional formulation by using CFD. To optimize scale coupling two strategies are adopted. On one end the macro-scale model, by using QMOM, is evaluating the bubble growth rate only at the quadrature nodes, thus highly reducing the number of function evaluations. In typical applications a quadrature approximation with $M=2$ nodes can be used, resulting in the transport of the first four moments of the BSD. On the other end, as the solution at each time step for the $M$ nodes of the transient bubble-scale model would still be too expensive, a "surrogate" model is used instead.

The main objective of the surrogate model is to supply a fast, yet accurate, approximation of the bubble growth rate. This requirement restricts the mathematical form of the surrogate model to an explicit algebraic expression, resulting in this case in the
following functional form:

\[ n_a = 4\pi R^2 k_s \left( \frac{w_a}{\rho_m} - H_v p_a \right) \]  

(33)

where \( k_s \) is the mass transfer coefficient, which is in our work defined as:

\[ k_s = \alpha h \beta \]  

(34)

where \( h \) is the thickness of the shell, which can be calculated as:

\[ h = S - R \]  

(35)

and \( \alpha \) and \( \beta \) are determined by fitting the expression in Eq. (33) to the results of the bubble-scale model, specifically to Eq. (22). Eq. (33) provides an algebraic function of state variables and material properties, which can be effectively used in the macro-scale model.

The density of reaction mixture \( \rho_m \) and the molar mass of blowing agent \( M_a \) are constants, the solubility \( H_v \) is a function of temperature and the thickness of the shell is a function of radius (see Eq. (19)). Because the macro-scale model operates with bubble volume \( v \) instead of bubble radius \( R \), the following conversion is made:

\[ v = \frac{4\pi R^3}{3} \]  

(36)

Finally, the surrogate model can be described by a functional call:

\[ n_a = f(v, T, \rho_m, p_a) \]  

(37)

The macro-scale model then directly uses the surrogate model to evaluate the bubble growth rate \( \dot{C}_B \) (see Eqs. (28) and (29)). The bubble growth rate is then used as a source term in the PBE and mass balance equations (see Eqs. (26) and (32)), thus it is used to calculate the BSD and concentration of blowing agent in the new time step.

The automatic fitting of the surrogate model as well as the interface between the two models was created using the MoDeNa framework (MoDeNa-EUProject, 2015). MoDeNa (MOdelling of morphology DEvelopment of micro- and Nanostructures) is an orchestrator that assures the interconnectivity of different modelling tools by providing a platform on which information can be transferred across different scales. As the surrogate model does not belong to neither the macro-scale nor the bubble-scale model it sits in a database and at this end the NoSQL database MongoDB (2015) was used. The database stores the surrogate model (i.e. both its functional form and the corresponding parameters) together with the data used for the fitting (i.e. data used for the surrogate model parameter identification).

In order to demonstrate how the two modelling tools communicate within the MoDeNa framework, Fig. 2 shows a schematic illustration of the connection between the two models. Before the macro-scale model is started, the orchestrator automatically performs several actions. First, the bubble-scale model is run to obtain precise results for the bubble growth rate. Next, the surrogate model is fitted to this data. And finally, parameters are stored into the database. The macro-scale model then simply calls MoDeNa library whenever it needs the value of bubble growth rate and the framework secures that the surrogate model is evaluated with parameters recently stored in the database. The framework also has more advance features, e.g., it can re-run the lower-scale model and re-fit the parameters of the surrogate model during the execution of the macro-scale model. However, this functionality was not utilized in this work.

As far as the bubble-scale model is concerned, spatial discretization is performed with the finite volume method (FVM). The language of implementation was Fortran. We used the open source library ODEPACK (Hindmarsh, 1980) for the time integration of the resulting system of ODE. An implicit scheme with automatically generated sparse Jacobian was used.

The governing equations of the macro-scale model are implemented in an open-source C++ program called “qmonKi-netics” working under GNU public license. In order to integrate the ordinary differential equations, a modern C++ library, called odeint, Ahnert and Mulansky (2011), is incorporated into the solver. As there is a lack of experimental data for the initial bubble diameters for the PU recipes investigated, the initial bubble radius for all cases is assumed to be 10 \( \mu \)m. This assumption has been also tested through a sensitivity analysis reported later in this paper showing that the selected bubble diameter yields a reasonable range for the final BSD. The first four moments of BSD are, then, initialized for a log-normal distribution with initial bubble volume \( V_0 \) and standard deviation of \( \sigma = 0.1 \) as follows:

\[ m_k = \frac{\exp[\log(V_0) + 0.5\sigma^2]}{\exp(\log(V_0) + 0.5\sigma^2)} \]  

(38)

An adaptive integration method is used, in which the time step is changed to control the error in every iteration. The initial time step is equal to 1 s and it is automatically modified to keep the absolute and relative errors below \( 10^{-6} \). It is also noteworthy that the multi-scale simulations are performed for zero-dimensional cases, thus the typical simulation time falls below one minute. Thus, it is ensured that the approach can be scaled well to full three-dimensional CFD simulations.

4. Operating conditions

In this work PU foams obtained under different operating conditions are considered. Two different blowing agents are considered (\( N=2 \)): a physical blowing agent, R-11 or trichlorofluoromethane, and a chemical blowing agent, carbon dioxide. As already mentioned, R-11 is added to the reacting mixture in the form of a liquid, and then evaporates due to the exothermicity of the gelling and blowing reactions. Carbon dioxide is instead produced by the blowing reaction thanks to the presence of water in the reacting mixture. A summary of the operating conditions and of the physical properties of initial reactants, polyurethane and blowing agents is reported in Table 1.

The solubility of blowing agents in the reaction mixture depends on the temperature and concentration of the polymer. However, due to the lack of experimental data in the open literature, the following equation was used to describe the solubility of R-11 (through its Henry coefficient):

\[ H_{R11} = \frac{\rho_m M_{R11} p_{amb}}{M_{R11} p_{amb}} \left\{ A + B \exp \left( \frac{(T - C)^2}{2D^2} \right) \right\} \]  

(39)
where \( A = 1.0 \times 10^{-7}, B = 4.293, C = 203.4 \, \text{K} \) and \( D = 40.02 \, \text{K} \) are constants obtained by fitting Eq. (39) to experimental data (Baser and Khakhar, 1994a). The solubility, and the corresponding Henry coefficient, for carbon dioxide are assumed constant (see Table 1).

The viscosity of the reacting mixture is not constant during the PU foaming process. It decreases with increasing temperature, increases with the conversion of polyols and approaches infinity when the gel point is reached. This behaviour is traditionally described by the following semi-empirical Newtonian model:

\[
\eta_{\text{tm}} = A \exp \left( \frac{E}{R_{\text{g}} T} \right) \left( \frac{X_{p,g}}{X_{p,g} - X_p} \right)^{B+4\Delta P} \tag{40}
\]

where \( A = 4.1 \times 10^{-8} \, \text{Pa} \cdot \text{s}, E = 38.3 \times 10^3 \, \text{J} \, \text{mol}^{-1}, B = 4.0, C = -2.0 \) are constants determined from experiments (Castro and Macosko, 1982). \( X_{p,g} \) is the conversion of polyols at the gel point, taken in this work equal to 0.5 (Baser and Khakhar, 1994a).

In this work, the simulation results are compared to experimental data from 11 different “cup experiments” (Baser and Khakhar, 1994a,b). The polyurethane foams were prepared from polymethylene-polyphenyl isocyanate (equivalent weight of 135), polyester polyol (OH value = 365 mg KOH/g polyol), water, R-11 as physical blowing agent and small amounts of surfactant and catalyst. The initial concentrations of reactants and blowing agents are summarized in Table 2. The reactants were vigorously mixed for the first few seconds, after which the temperature and the foam density started to be recorded and the reaction was left to run its course. The kinetic parameters were determined for the studied system in the original work and are given in Table 3.

### 5. Results and discussion

Fig. 3 shows the comparison between experimental results and predictions of the presented multi-scale model (model A) and the original simplified model by Karimi and Marchisio (2015) (model B). Batches 1 and 6 contained no physical nor chemical blowing agents and are presented here to show the ability of the kinetic model to describe the gelling reaction.

Batches 2–5 were purely physically blown foams. In comparison with batch without blowing agent, we can see delayed temperature increase and smaller final rise of temperature, because part of the reaction heat was consumed for the evaporation of the blowing agent. The exactly opposite effect can be observed for purely water blown foams. In this case, the temperature of the system is increased by the heat of the blowing reaction (compare batches 7–9 with batch 6). Naturally, there is a competition of these effects when the polyurethane is foamed using both physical and chemical blowing agents (see batches 10 and 11).

Fig. 4 shows the prediction of foam density for the investigated recipes. Batches 2–5 were purely physically blown foams. In this system, the foam density remains constant for the first several seconds, because the concentration of blowing agent is below its equilibrium value. However, since the temperature in the system gradually increases, it leads to the decrease of the solubility of blowing agent. Eventually, the solubility decreases below the initial concentration of blowing agent, which then starts to evaporate at the bubble interface. Further diffusion of the blowing agent in the reaction mixture toward the bubble interface leads to the growth of bubbles and the decrease of foam density.

Even though there is no blowing agent in the system at the beginning for the purely chemically blown foams, the foam density actually starts to decrease sooner in chemically blown foams. The main reasons are the relatively fast blowing reaction, in comparison with the gelling reaction, and the relatively low solubility of carbon dioxide in the reaction mixture in comparison with that of the physical blowing agent.

Overall, Fig. 4 shows that the presented model is able to capture the evolution of foam density for both physically and chemically blown foams. Moreover, it generally provides better agreement with experimental data than the model by Karimi and Marchisio (2015) and it does so without using fitting parameters for the bubble growth rate.

Apart from the foam density, the other principal result of the presented model is the BSD. The experimental data on the evolution of BSD in PU foaming are unfortunately not available in the open literature, but the final average cell size was characterized for several investigated recipes. Fig. 5 shows very good agreement between experimental data and model predictions for the final average cell radius. However, it should be noted that this is only an

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**Table 1** Summary of operating conditions and material properties.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( P_{\text{amb}} ) (Pa)</td>
<td>1.0 \times 10^5</td>
</tr>
<tr>
<td>( \rho_{\text{pol}} ) (kg m(^{-3}))</td>
<td>1100</td>
</tr>
<tr>
<td>( \rho_{\text{CO}_2} ) (kg m(^{-3}))</td>
<td>1800</td>
</tr>
<tr>
<td>( \rho_{\text{R11}} ) (kg m(^{-3}))</td>
<td>870</td>
</tr>
<tr>
<td>( M_{\text{CO}_2} ) (kg mol(^{-1}))</td>
<td>0.044</td>
</tr>
<tr>
<td>( M_{\text{R11}} ) (kg mol(^{-1}))</td>
<td>0.127</td>
</tr>
<tr>
<td>( D_{\text{CO}_2} ) (m(^2) s(^{-1}))</td>
<td>4.4 \times 10^{-10}</td>
</tr>
<tr>
<td>( D_{\text{R11}} ) (m(^2) s(^{-1}))</td>
<td>2.4 \times 10^{-10}</td>
</tr>
<tr>
<td>( \Delta H_{\text{R11}} ) (J kg(^{-1}))</td>
<td>2.0 \times 10^5</td>
</tr>
<tr>
<td>( H_{\text{CO}_2} ) (mol m(^{-3}) Pa(^{-1}))</td>
<td>1.1 \times 10^{-4}</td>
</tr>
<tr>
<td>( \gamma ) (N m(^{-1}))</td>
<td>0.025</td>
</tr>
</tbody>
</table>

**Table 2** Summary of the initial conditions of investigated batches.

<table>
<thead>
<tr>
<th>Batch</th>
<th>( c_{p,0} ) (mol m(^{-3}))</th>
<th>( c_{b,0} ) (mol m(^{-3}))</th>
<th>( c_{w,0} ) (mol m(^{-3}))</th>
<th>( c_{R11,0} ) (mol m(^{-3}))</th>
<th>( T_0 ) (K)</th>
<th>( n_{b,0} ) (m(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3765</td>
<td>3765</td>
<td>0</td>
<td>0</td>
<td>304</td>
<td>–</td>
</tr>
<tr>
<td>2</td>
<td>3765</td>
<td>3765</td>
<td>0</td>
<td>0</td>
<td>1241</td>
<td>295</td>
</tr>
<tr>
<td>3</td>
<td>3765</td>
<td>3765</td>
<td>0</td>
<td>849</td>
<td>296</td>
<td>1.8 \times 10^{11}</td>
</tr>
<tr>
<td>4</td>
<td>3765</td>
<td>3765</td>
<td>0</td>
<td>1049</td>
<td>296</td>
<td>1.7 \times 10^{11}</td>
</tr>
<tr>
<td>5</td>
<td>3765</td>
<td>3765</td>
<td>0</td>
<td>464</td>
<td>300</td>
<td>4.7 \times 10^{11}</td>
</tr>
<tr>
<td>6</td>
<td>3700</td>
<td>3700</td>
<td>0</td>
<td>0</td>
<td>308</td>
<td>–</td>
</tr>
<tr>
<td>7</td>
<td>3490</td>
<td>4086</td>
<td>298</td>
<td>0</td>
<td>308</td>
<td>1.4 \times 10^{11}</td>
</tr>
<tr>
<td>8</td>
<td>3252</td>
<td>4363</td>
<td>555</td>
<td>0</td>
<td>305</td>
<td>1.4 \times 10^{11}</td>
</tr>
<tr>
<td>9</td>
<td>3045</td>
<td>4604</td>
<td>780</td>
<td>341</td>
<td>302</td>
<td>1.4 \times 10^{11}</td>
</tr>
<tr>
<td>10</td>
<td>3045</td>
<td>4604</td>
<td>780</td>
<td>308</td>
<td>304</td>
<td>1.4 \times 10^{11}</td>
</tr>
<tr>
<td>11</td>
<td>3490</td>
<td>4086</td>
<td>298</td>
<td>1055</td>
<td>298</td>
<td>1.4 \times 10^{11}</td>
</tr>
</tbody>
</table>
Table 3
Summary of the kinetic parameters.

<table>
<thead>
<tr>
<th>Batch</th>
<th>$A_p$ (m$^3$ mol$^{-1}$ s$^{-1}$)</th>
<th>$E_p$ (J mol$^{-1}$)</th>
<th>$-\Delta H_p$ (J mol$^{-1}$)</th>
<th>$A_w$ (s$^{-1}$)</th>
<th>$E_w$ (J mol$^{-1}$)</th>
<th>$-\Delta H_w$ (J mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1–5</td>
<td>1965</td>
<td>$5.49 \times 10^4$</td>
<td>$7.49 \times 10^4$</td>
<td></td>
<td>$-\infty$</td>
<td></td>
</tr>
<tr>
<td>6–11</td>
<td>1.735</td>
<td>$4.04 \times 10^4$</td>
<td>$7.87 \times 10^4$</td>
<td>$1.39 \times 10^3$</td>
<td>$3.27 \times 10^4$</td>
<td>$8.60 \times 10^4$</td>
</tr>
</tbody>
</table>

Fig. 3. The evolution of temperature in PU foam for selected batches. Comparison between experimental values, predictions of current model (model A) and predictions presented by Karimi and Marchisio (2015)(model B).
indirect validation, due to the lack of information on the initial number density of bubbles, hence in the current work the initial number density of bubbles has to be assumed. This only signals that the model is capable of simultaneously predicting the evolution of foam density and the final cell size.

Large number of air bubbles is entrapped in the system during the initial mixing. It is assumed that no additional bubbles are later created by nucleation. The size and the number density of initial bubbles are influenced by the intensity and the time of mixing. To study the influence of various parameters on PU foaming, we modified the recipe of batch 2. Only one parameter was changed in each parametric study. Fig. 6 shows that the initial average bubble size usually has a relatively minor effect on PU foaming. When the size of initial bubbles is decreased below 1 μm, the growth of bubbles and the decrease of foam density are delayed, because the pressure in the initial bubbles is higher due to the surface tension effect, so the solubility of the blowing agent needs to decrease to even lower values. However, the final bubble size and the foam density remain the same if the system has enough time to foam before reaching the gel point.

The influence of number density of bubbles on the bubble growth rate and the foam density is shown in Fig. 7. Naturally, the decrease of number density of bubbles leads to a foam with larger final cell size, because the blowing agent is distributed in smaller number of cells. Moreover, decreasing the number density of bubbles delays the onset of foaming, because the blowing agent has to diffuse a large distance to reach the bubble interface.
One of the main means of influencing the production of PU foams is tuning the amount of the added catalyst. Although we do not have an exact relationship connecting the kinetic parameters to the amount of catalyst, Fig. 8 shows how the evolution of bubble size and foam density would vary, when the activation energy of the gelling reaction is changed by 5%.

The addition of more physical blowing agent has two main effects on the PU foaming process. First, the final foam will have larger cell size and lower density. And second, the bubbles will start to grow sooner, because a smaller increase in temperature is sufficient to reduce the solubility below the initial concentration of the blowing agent (see Fig. 9).

6. Conclusions

In this work, a new multi-scale modelling framework for the simulation of PU foams is presented. It consists of two models, one operating at the bubble-scale and the other one operating at the macro-scale. The bubble-scale model for the bubble growth rate resolves the mass and momentum boundary layers around individual bubbles. The macro-scale model tracks the evolution of the macroscopic properties of the foam, such as foam density, temperature and BSD, by using a PBE. The macro- and bubble-scale models are coupled via a surrogate model by using the MoDeNa framework.
The modelling results are compared to the available literature data and show acceptable level of agreement for several different recipes. In the future, an effort to produce more comprehensive set of experimental data including initial bubble size and number density of bubbles for the model validation will be made. The proposed methodology at its current state can be further improved by reducing the dependency of the model on the empirical relations for the solubility of blowing agents. Moreover, a simplistic approach has been chosen to articulate the bubbles coalescence that could be replaced by more realistic strategies. The work will continue with the extension of the macro-scale model to a three-dimensional spatial description of the foam with CFD, for the simulation of industrial-scale mould filling applications.

Acknowledgements

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