MATHEMATICAL MODELING AND COMPUTER SIMULATION OF THE FLOW OF CHEMICALLY-REACTING POLYMERIC FOAMS

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Abstract

The present work is devoted to the mathematical modeling and the computer simulation of processing flows of polyurethane foams. The objective is the development of a simulation tool for predicting the evolution of velocity, temperature, stress, and species concentration fields during processing. Our approach is based on the first principles of continuum mechanics (conservation of mass, energy, and momentum); the chemical kinetics are described by second-order equations whose parameters have been identified in laboratory experiments. A phenomenological model is proposed for describing the complex and evolving rheological behavior of chemically-reacting polymeric foams. The resulting set of coupled, non-linear partial differential equations is solved numerically by means of a specialized finite element technique. We have implemented the numerical algorithm in a large-scale computer code that allows for the prediction of multi-dimensional flows in complex geometries. Typical simulation results are described in detail.

1. Introduction

Processing flows of urethane foaming systems involve a material whose molecular and supra-molecular structures are rapidly evolving as the chemical reactions proceed. The gas phase contributing to foaming is produced together with the continuous polymeric phase. Foaming and polymerization processes are both highly exothermic. Important density variations are obtained in a matter of minutes (up to 50 fold decrease), which has a major impact on the flow kinematics. A detailed discussion of polyurethane foam chemistry and processing is given in [1].

The objective of the present work is the development of a computational model for the analysis and design of manufacturing processes of polyurethane foam products. To this end, we have addressed three related issues. First, the primary chemical processes involved must be
described by means of appropriate kinetic models. Second, the build up of the foam rheological properties must be properly related to the degree of advancement of the chemical reactions. Third, the approximate solution of the resulting mathematical model requires the development of specialized numerical methods for compressible reacting flows in complex geometries. The present communication is a brief account of our work over the last three years. Complete reports will appear in [2-3].

The proposed model is based on the first principles of continuum mechanics and incorporates a detailed description of the chemical kinetics. The material is treated as a homogeneous, compressible, non-linear inelastic fluid. A phenomenological equation is proposed for describing the evolving rheological properties of the reactive system. Mass transfer equations for the main species involved are coupled to the overall conservation laws and constitutive rheological equations. The model has the form of a set of coupled, non-linear partial differential equations. It is solved approximately by means of a specialized finite element algorithm. The model input data are kinetic parameters, species physical properties, flow geometry (with or without free surfaces) and process operating conditions. The model outputs are the velocity, pressure, stress, temperature and species concentration fields over the whole flow domain.

The paper is organized as follows. Section 2 describes the main chemical processes leading to the formation of polyurethane foams. We then discuss in Section 3 the experimental characterization and mathematical modeling of the chemical kinetics. The issue of reactive foam rheology is addressed in Section 4. The field equations and their numerical solution are described in Section 5. Finally, we report typical simulation results in Section 6.

2. Chemical Processes

During processing of polyurethane foams, the material evolves from a low molecular weight, dilute emulsion to a structured fluid in which gas bubbles are separated by thin polymeric liquid films. The gas phase is generated within the liquid phase as a by product of the polymerization reaction. Production of the blowing agent and curing of the polymer occur simultaneously; both are highly exothermic processes.

The primary chemical reactions involve three main reactants: a hydroxyl group-ended resin R'-(OH)\textsubscript{f1}, a polyisocyanate R-(NCO)\textsubscript{f2}, and water. Typical values for the functionalities \textit{f1} and \textit{f2} are 3 and 2, respectively. Flexible polyurethane foams are produced in a one shot process in which polyisocyanate, resin and water are mixed simultaneously together with suitable stabilizers, catalysts and cell-size control agents. The reactions begin immediately, with foam rise starting a few seconds after mixing and being completed in a matter of minutes. Curing continues for several hours, eventually leading to a solid material.
Fig. 1  Schematic of the free rise foaming experiment.
The two primary reactions, described here for mono-functional reactants (i.e. $f_1=f_2=1$), are the gelling reaction:

$$\text{R'}-\text{OH} + \text{R}-\text{NCO} \rightarrow \text{R'}-\text{O}-\text{CO}-\text{NH}-\text{R}$$

which leads to formation of polyurethane, and the blowing reaction:

$$2\text{R}-\text{NCO} + \text{H}_2\text{O} \rightarrow \text{R}-\text{NH}-\text{CO}-\text{NH}-\text{R} + \text{CO}_2 \uparrow$$

which produces polyurea and carbon dioxide. Both reactions are highly exothermic. They eventually lead to a segmented block urethane-urea polymer blown into a foam by the co-produced carbon dioxide. Linear or slightly branched resins are used for flexible foams, while highly branched resins give rise to rigid foams. In addition to the six main species described above, a large number of additives are used in actual polyurethane foam manufacturing processes. Further details can be found in the book edited by Oertel [1].

3. Characterization and Modeling of Chemical Kinetics

We have studied the reaction kinetics of a typical water-blown polyurethane foam by means of the free rise experiment [2-3]. A schematic of the experimental setup is shown in Fig.1. The reactor consists of an insulated cylinder mounted on a vertically-moving plate. The reactants are pre-mixed rapidly and introduced at the bottom of the reactor. Foaming is then allowed to occur freely. A thermocouple monitors the foam temperature at the center of the reactor, while a video camera records the evolution of the foam height. Note that a light cover is put on top of the foaming for insulation purposes. Typical temperature and rise profiles are shown in Figs.2-3. We observe that a steady-state height is reached after a minute or so, at which point carbon dioxide is seen to escape from the foam. The temperature increase, however, is not yet completed when the steady-state foam height is reached. This is due to the fact that production of urethane is slower than that of the blowing agent.

Figures 2 and 3 also show the predictions of a simple mathematical model of the free rise foaming experiment. The model is developed along lines similar to those of Tillotson and Patrick [4]. We assume that all species physical properties are constant, with the exception of the density of carbon dioxide which follows the perfect gas law. Dynamical forces are neglected. The flow is driven by density changes only; it is considered perfectly adiabatic and uni-directional with a linear velocity $u$. For each of the six species involved, we define a volume fraction $\alpha_i$, a rate of formation or disappearance $r_i$, a density $\rho_i$, a specific heat $C_i$, and a molar mass $M_i$. We assume that second order kinetics apply for both the gelling and blowing reactions. For example, the rate of production of urethane ($i = 3$) is given by
Fig. 2 Temperature profile in free rise foaming: experimental data (continuous line) and theoretical prediction (dashed line).

Fig. 3 Foam height in free rise foaming: experimental data (continuous line) and theoretical prediction (dashed line).
\[ r_3 = K_3 \cdot M_3 \cdot e^{(E_3/RT)} \cdot \left[ \frac{\rho_1 \alpha_1 f_1}{M_1} \right] \cdot \left[ \frac{\rho_2 \alpha_2 f_2}{M_2} \right], \quad (3) \]

where the subscripts 1 and 2 refer respectively to resin and isocyanate, and \( R \) is the gas constant. The kinetic model (3) involves two parameters, namely the pre-exponential factor \( K_3 \) and the activation energy \( E_3 \). Similarly, the rate of production of carbon dioxide (\( i = 5 \)) is given by

\[ r_5 = K_5 \cdot M_5 \cdot e^{(E_5/RT)} \cdot \left[ \frac{\rho_4 \alpha_4}{M_4} \right] \cdot \left[ \frac{\rho_2 \alpha_2 f_2}{M_2} \right], \quad (4) \]

where the subscript 4 refers to water. Rates of formation or disappearance of the other species are related to \( r_3 \) and \( r_5 \) by direct mass balance considerations [2-3]. The equation of conservation of energy reads:

\[ \sum_{i=1}^{6} [\rho_i \alpha_i C_i] \frac{\partial T}{\partial t} = - \frac{r_3}{M_3} H_3 - \frac{r_5}{M_5} H_5, \quad (5) \]

where \( T \) is the foam temperature, while \( H_3 \) and \( H_5 \) are respectively the heat produced by the gelling and blowing reactions. Mass conservation for each species yields

\[ \frac{\partial [\rho_i \alpha_i]}{\partial t} + \frac{\partial [\rho_i \alpha_i u]}{\partial x} = r_i, \quad (6) \]

where \( x \) is the direction of flow. The model equations (5-6) can be transformed into a set of six coupled, non-linear ordinary differential equations using the constraint

\[ \sum_{i=1}^{6} \alpha_i = 1. \quad (7) \]

We integrate these equations by means of a standard Runge-Kutta numerical procedure. Once the time-dependent volume fractions and foam temperatures are computed, the evolution of the foam height is determined on the basis of the predicted foam density \( \rho_f \) defined as

\[ \rho_f = \sum_{i=1}^{6} [\alpha_i \rho_i]. \quad (8) \]

The model results shown in Figs.2-3 were obtained using best-fit values for the kinetic parameters within ranges of values published in the literature [2-3]. Agreement between experimental data and theoretical predictions is only fair for the foam temperature, while it is very satisfactory for the rise profile. The model predictions clearly demonstrate the faster
kinetics of the blowing reaction relative to those of the gelling reaction. Further refinement of
the kinetic model would require a more sophisticated experiment that could monitor the
evolution of the individual species in addition to temperature and rise profiles. The recent work
by Artavia and Macosko [5] is a first step in that direction.

We shall use the kinetic equations (3-4) in the development of the model for complex foam
flow simulations. Let us now discuss the issue of reactive foam rheology.

4. Foam Rheology

The experimental characterization of polyurethane foam rheology during processing is an
extremely difficult task in view of the exothermic character of the process and the rapid
evolution in both molecular and supra-molecular structures of the material. Extreme caution
must be exercised in analysing experimental data. For example, the usual assumption of fully-
developed flow in capillary rheometers does not hold for a gas-charged polymer in which gas
bubbles grow and polymerization occurs as the fluid advances into the capillary. The heat
generated by the chemical reactions can lead to temperature gradients in the flow field which
may further obscure the interpretation of the results. Finally, the rheometer must accomodate
the large density decrease occurring during foaming (up to 50 fold). With the exception of the
recent work by Macosko and co-workers [6] on the development of linear viscoelastic
properties during reactive foaming, little progress has been reported in rheometrical
measurements of reactive urethane systems. There is currently not enough data available to
build a detailed picture of the rheological changes occurring during this process.

As far as modeling is concerned, available purely-viscous correlations for emulsions are
potentially useful to the description of reactive foam rheology (e.g. [7]). These models,
however, are currently restricted to Newtonian continuous phases. The inclusion of non-linear
behavior into the constitutive description of the continuous phase is necessary if we want to
apply emulsion viscosity laws to reactive polymeric foams. Published work on aqueous foams
is not directly applicable to polyurethane foams (e.g. [8-12]). Similarities between the two fluid
systems may exist, however, like the existence of a yield stress, slip at the wall, and shear-
thinning behavior. Finally, the micromechanical models developed for aqueous foams are of
limited practical relevance to our work, despite of their elegance (e.g. [13-17]).

The accurate description of reactive foam rheology should take into account build up of cell
structure and evolution of polymerization within the continuous phase. In view of the lack of a
detailed micromechanical theory, we propose a phenomenological, purely-viscous constitutive
equation to be used in our numerical simulations. The proposed viscosity law has the form of a
mixing rule that includes as control variables the concentrations in reactants, shear rate,
temperature, and gas phase volume fraction:
\[
\mu_f = \sum_{r=1}^{3} \alpha_r \mu_r + \left(1 - \sum_{r=1}^{3} \alpha_r \right) \left(a + b \alpha_{CO2} + c \alpha_{CO2}^2 \right) \gamma^{n-1} .
\] (9)

The first term in the foam viscosity \( \mu_f \) describes the contribution of the three reactants. It dominates over the second term at the beginning of the reactive process. The symbols \( \alpha_r \) and \( \mu_r \) denote the temperature-dependent volume fraction and shear viscosity of the \( r \)th reactant. The second term in (9) describes the contribution of the produced foam phase (bubbles+polymer). This term has a functional form typical of semi-concentrated emulsion correlations [7]. It rapidly becomes dominant as foaming proceeds. We assume here shear-thinning behavior as modeled by a power-law of index \( n \). Any other pseudoplastic equation, including possibly a yield stress, could be used. The symbols \( a, b, c \) denote material parameters.

The phenomenological rheological equation (9) has been incorporated into the general field equations described in the next section. It should be noted that values for the necessary material parameters are not yet available. The processing flows investigated so far appear, however, to be rather insensitive to the actual bulk rheological behavior of the foam. We shall return to this issue in Section 6.

5. Field Equations and Numerical Technique

On the basis of the previous discussion, we propose the following macroscopic model for describing complex flows of reactive polymeric foams. We treat the foam as a compressible, purely-viscous homogeneous fluid. Compressibility means here that the foam density is a function of temperature but not of pressure. Mass transfer by diffusion is neglected and second-order kinetics are assumed. All species physical properties are assumed constant, with the exception of the density of carbon dioxide which follows the perfect gas law (i.e. it is inversely proportional to temperature). The primary unknowns of the model are velocity, pressure, temperature, and species volume fraction fields. In addition, free surface parameters are also part of the unknowns when the process involves free surfaces. The basic principles of continuum mechanics then provide the field equations:

**Momentum equation**:

\[
\rho_f \left( \frac{\partial \mathbf{v}}{\partial t} + \mathbf{v} \cdot \nabla \mathbf{v} \right) = -\nabla p + \nabla \cdot \left[ 2\mu_f(\gamma^{n-1}) \mathbf{D} \right] ,
\] (10)
Energy equation:
\[
\rho_f C_f \left( \frac{dT}{dt} + v \cdot \nabla T \right) = v \cdot [k_f \nabla T] + H(\alpha_i) ,
\] (11)

Mass conservation for i\textsuperscript{th} species (i = 1, 5):
\[
\frac{\partial (\rho_i \alpha_i)}{\partial t} + v \cdot [\rho_i \alpha_i v] = r_i(\alpha_j, T) .
\] (12)

Constraint on volume fractions:
\[
\sum_{i=1}^{6} \alpha_i = 1 ,
\] (13)

Global mass conservation:
\[
\frac{\partial \rho_f}{\partial t} + v \cdot [\rho_f v] = 0 .
\] (14)

In these equations, \( v \) stands for the velocity vector, \( \rho \) is pressure, \( \mu_f \) is given by (9), \( D \) is the strain rate tensor and \( \gamma \) is its magnitude, \( k_f \) is the foam heat conductivity, \( H(\alpha_i) \) is the heat generated by the two reactions (cfr. eq.(5)), and \( r_i(\alpha_j, T) \) is the rate of formation or disappearance of the i\textsuperscript{th} species (e.g. eq.(3)).

Equations (10-14) form a set of coupled, non-linear partial differential equations to be solved with suitable initial and boundary conditions. We solve these equations approximately by means of a mixed finite element discretization of the primary unknown fields. Galerkin's principle is used to discretize the momentum, volume fraction constraint, and global mass conservation equations. A consistent streamline-upwind Petrov-Galerkin method is implemented for the energy and species conservation equations, in view of their hyperbolic nature. In the case of steady-state flows, we obtain a large set of non-linear algebraic equations for the nodal values of the unknown fields. We solve this set of equations by means of a full Newton scheme. Finally, an adaptive continuation procedure on material properties and operating conditions is used to provide initial estimates for the iterative procedure. Further details are given in [2-3].
INSULATED SLIP WALL

INSULATED SLIP WALL

IN: UNIFORM FLOW AT T = 294°C
64% RESIN, 32% ISOCYANATE, 4% WATER
OUT: FULLY-DEVELOPED FLOW

Fig. 4 Computational domain and boundary conditions.

2486 variables

8758 variables

Fig. 5 Finite element discretization: coarse and refined meshes.

COMPUTED FLUID TRAJECTORIES

Fig. 6 Computed fluid trajectories.
Fig. 7  Computed longitudinal velocity contours. Stokes flow: without chemical reactions; Foam flow: with chemical reactions.

Fig. 8  Computed lower-wall velocity: with (Foam) and without (Stokes) chemical reactions.
6. Simulation Results

We have used the above numerical model to simulate several steady-state flows of reactive foaming systems, including flows with free surfaces [2-3]. Two illustrative flow problems are discussed in the present paper. The corresponding simulations have been performed on a CRAY X-MP supercomputer with typical CPU times of the order of one hour for a complete run.

Let us first consider the process depicted in Fig.4. It consists of a smooth, two-dimensional divergent whose walls are thermally-insulated. The fluid enters the flow domain at room temperature with a uniform axial velocity. We specify that the chemical reactions start at the inlet section; the prescribed reactants volume fractions are typical of water-blown polyurethane foams. The fluid is assumed to slip at the divergent walls. Finally, fully-developed conditions are specified at the outlet section. In the present simulation, the blowing agent density was artificially increased by a factor of about ten in order that most of the blowing reaction occur in the diverging zone of the flow domain.

Figure 5 shows the two finite element meshes used for the simulations. The coarse mesh involves 2486 unknown nodal variables, while the refined mesh contains 8758 variables. Since there is no reference solution available in the literature, such an intensive mesh refinement analysis is necessary to assess the numerical accuracy of our results. We shall see that the coarse mesh already provides decent results.

Computed flow lines are shown in Fig.6. The flow trajectories, which are everywhere tangent to the velocity vector field, are not spectacular. Indeed, they very much resemble those obtained when the chemical reactions are turned off, namely when the fluid density is forced to remain constant. The magnitude of the velocity vectors, however, is dramatically altered by the chemical processes. This can be observed in Fig.7 where we compare contour lines of the longitudinal velocity component obtained with a constant density model (which for a foam essentially is an inertialess, Stokes flow solution) and the chemically-reacting system. For the constant density fluid, the velocity decreases continuously in view of the gradual increase in cross section. The reactive fluid behaves very differently. The velocity increases in the divergent section up to a value about four times larger than the inlet velocity. This is due to the rapid decrease in fluid density related to the production of carbon dioxide (Figs.10-11). Since the mass flow rate is conserved, the fluid must thus accelerate. This is also illustrated in Fig. 8 where we show the computed velocity at the lower divergent wall, for both the neutral and reactive fluid systems.
Fig. 9 Trajectory selected for display of computed fields.

Fig. 10 Computed species volume fractions along selected trajectory. Coarse mesh (dots) and refined mesh (continuous line) results.

Fig. 11 Computed foam density along selected trajectory. Coarse mesh (dots) and refined mesh (continuous line) results.
Fig. 12 Computed temperature along selected trajectory. Coarse mesh (dots) and refined mesh (continuous line) results.

INSULATED FREE SURFACE

CONVEYOR

IN: UNIFORM FLOW AT T=294°K
64% RESIN, 32% ISOCYANATE, 4% WATER
OUT: FULLY-DEVELOPED FLOW

Fig. 13 Computational domain and boundary conditions for the slabstock foam process.

INITIAL MESH

FINAL MESH

Fig. 14 Initial and final finite element meshes.
The results of Figs. 7-8 reveal the important non-linear coupling between the energy and mass conservation equations. They also point to a primary numerical difficulty, namely the selection of appropriate initial guesses for starting the iterative procedure. In the present calculations, we use the Stokes solution to start the iterations. Since the Stokes solution is structurally very different from the final result (Figs.7-8), a careful continuation procedure is needed to obtain convergence of the iterative scheme [2-3].

A further look at the computed solution is provided in Figs.10-12. Various fields are shown along the specific flow line depicted in Fig.9. The evolution of species volume fractions is given in Fig.10 for carbon dioxide, resin and urethane. The results obtained with the coarse mesh (dots) are very close to those produced by the refined mesh (continuous lines). Clearly, convergence with mesh refinement has been reached in this flow problem. We observe that production of carbon dioxide and urethane occur at quite different rates. Carbon dioxide contributes to most of the final product density.

The overall foam density is shown in Fig.11. It continuously decreases along the fluid trajectory, giving rise to the fluid acceleration illustrated in Fig.7. If the actual value of carbon dioxide density were used, the fall in density would be ten times larger and most of the blowing reaction would occur in a boundary layer located at the inlet section [3].

Finally, Fig.12 shows the computed temperature profile along the fluid trajectory of Fig.9. The heat generated by the blowing and gelling reactions leads to a continuous temperature rise. Again, we note the good agreement between the results obtained with the coarse and refined meshes.

The second flow problem considered in this paper is the two-dimensional simulation of the production process of slabstock foam. In this process, the reactants are deposited on a moving conveyor belt by a mixhead; foaming is allowed to occur freely along the conveyor [1]. The computational domain and boundary conditions are illustrated in Fig. 13. At the inlet section, we assume uniform velocity and zero concentration of products as in the previous problem. The foam is assumed to stick to the conveyor belt, while fully-developed conditions are specified at the outlet section. The free surface is assumed perfectly insulated. The latter is of course unknown a priori. It must be computed together with the unknown fields. To this end, a kinematic condition is added to the set of governing equations, in order to compute the free surface parameters [2-3]. In the present simulation, we use the actual values for the temperature-dependent density of carbon dioxide.

The initial finite element mesh assumes the rectangular shape that would be obtained if no reactions occurred (Fig.14). The fluid would then simply undergo a rigid body translation with
Fig. 15 Computed free surface and velocity vectors.

Fig. 16 Velocity vectors close to the inlet section and velocity norm along displayed trajectory.
velocity equal to the prescribed inlet velocity. This motion is chosen as the initial guess for the iterative procedure. The final computational domain, obtained at the end of the iterative and continuation process, is also shown in Fig.14. It is dramatically different from the initial configuration. This is due to the production of carbon dioxide which eventually leads to a 55 fold decrease in density.

Computed velocity vectors are shown in Fig.15. A closer view near the inlet is provided in Fig.16 where we show the velocity vector field together with the velocity norm along a specific fluid trajectory. We observe a thin boundary layer in the neighborhood of the inlet. This implies that the finite element mesh be very much refined near the inlet section in order to capture the boundary layer accurately (Fig.14). Away from the inlet section, the velocity vector field is essentially uniform over the thickness of the fluid. The simulation also provides computed fields for temperature and species volume fractions, as for the previous problem. These are described in detail in [3].

The above simulations assume that the foam viscosity is constant. Preliminary studies using the full phenomenological model (9) together with realistic ranges of values for the rheological parameters indicate that rheology does not have a marked influence on the flow field or advancement of the chemical reactions [2-3]. Density variations resulting from the chemical reactions are definitely the governing factors in these flow problems.

7. Conclusions

We have proposed a macroscopic model for the simulation of complex flows of chemically-reacting polymeric foams. The model is based on the first principles of continuum mechanics. It incorporates a detailed description of the chemical kinetics and a phenomenological rheological equation of state. The kinetic parameters have been identified in the free rise foaming experiment. Further experimental work is needed to characterize the rheological parameters. A specialized finite element technique has been developed to provide approximate solutions to the model equations for flows in complex geometries. Numerical simulations reveal the governing influence of the chemically-induced density variations on the flow kinematics. It appears that rheological effects only play a second-order role in the flow processes we have studied so far.

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