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Bridging the gap across scales: Coupling CFD and MD/GCMC in polyurethane foam simulation

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HIGHLIGHTS

- A multi-scale framework for simulating polyurethane foam is presented.
- An atomistic model (MD/GCM) is coupled with a continuum model (CFD).
- The multi-scale modeling strategy is validated for two polyurethane systems.
- Efficient linking is assured by agreement level between predictions and experiments.

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ABSTRACT

This work presents a multi-scale approach to reacting and expanding polyurethane (PU) foams modeling and simulation. The modeling strategy relies on two pillars: an atomistic model (molecular dynamics (MD)/Grand Canonical Monte Carlo (GCMC)) that provides liquid mixture density and reactant solubility and a continuum model (CFD) in which the expansion characteristics of the foam is modeled exploiting the results of the atomistic simulations. The resulting coupled model is validated for two different PU systems applied in four batches with chemical and physical blowing agents. The results demonstrate the efficacy and reliability of the developed model in the simulation of different PU foam properties such as apparent density and temperature evolutions.

1. Introduction

Polyurethane (PU) foams are interesting materials employed in furniture, construction and automotive industries, just to cite a few, and represent an important share of the global polymer materials market (Mills, 1993; Princen and Kiss, 1986; Woods, 1990). PU are manufactured by mixing the two main PU components (i.e., a mixture of polyols and isocyanates) with additives. These include catalysts (to tune polymerization rate) and emulsifiers (to improve reactant compatibility). To generate gas bubbles leading to foam, physical and chemical blowing agents are employed. Physical blowing agents (PBAs) are volatile hydrocarbons that evaporate by virtue of the exothermicity of the polymerization reaction. On the other hand, the mechanism of action of chemical blowing agents (CBAs) is based on their reaction with the polymerization mixture, and ultimately results in gas production. One of the most popular CBAs is water, which reacts with isocyanates to produce carbon dioxide leading to the foam expansion.

Modeling and simulation of a PU foam expansion process is particularly interesting because, being a rapidly time-evolving system, it is very difficult to characterize experimentally. A model describing PU foam expansion, especially for mold filling applications, could be profitably used in the design and optimization of such processes. On the other hand, the scientific modeling community faces a complex multiphase-reacting system in which various physical phenomena encompassing a wide range of length scales take place. This deters scientists to face the problem as a unified challenge, while the current, practical approach is tackling the problem at each single scale (e.g., nano-, meso-, and macro-scale models). Additionally, the final properties of the manufactured PU foam highly depend on the adopted chemical recipe (i.e., polyol, isocyanate, and blowing agents structure and concentrations) and the flow history of the foam when it is applied for mold filling applications. This, in turn, requires the knowledge of fundamental

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thermophysical properties of different components (e.g., the density of polymerizing mixture) prior and during foam expansion for large-scale applications. Accordingly, the problem is inherently multiscale and, as such, a multi-model approach must be devised and applied.

A review of the current literature on the bubble-scale modeling tools for PU shows that one crucial point consists in correctly describing how an individual spherical bubble grows within a shell of the reacting mixture. Mass and momentum balances are routinely solved to assess the evolution of bubble radius while the mass transfer coefficient is considered as a model parameter (Feng and Bertelo, 2004; Harikrishnan et al., 2006; Harikrishnan and Khakhar, 2009; Kim and Youn, 2000). Furthermore, the macro-scale characteristics of PU foams are generally modeled by solving either ordinary differential equations (ODEs) or partial differential equations (PDEs). The former approach describes the foam apparent density, temperature, and polymerization progress (i.e., the gelling and blowing reactions) with respect to reaction kinetics (Baser and Khakhar, 1994a, 1994b; Gupta and Khakhar, 1999). Along the alternative line, Computational Fluid Dynamics (CFD) is applied to account for spatial and temporal variation of the foam properties. This last method has proven to be more attractive for mold filling applications, as the foam mobile interface can be monitored using the Volume-of-Fluid (VOF) approach (Bikard et al., 2005; Geier et al., 2009; Samkhaniani et al., 2013; Seo et al., 2003; Seo and Youn, 2005).

From a general perspective, to model PU-based systems we recently developed NANOTOOLS, an integrated, multiscale molecular modeling software for the prediction of major structural and thermophysical properties of this class of polymers and their nanocomposites (Ferkl et al., 2017; Laurini et al., 2016). Specifically, a hierarchical approach was implemented, which involves running separate models with a parametric coupling, with the ultimate goal of predicting the system under consideration from first principles, i.e. starting from the quantum scale and passing information to molecular scales and eventually to process scales. According to this sequential (aka message-passing) methodology, information is computed at a smaller (finer) scale and passed to a model at a larger (coarser) scale by leaving out (i.e. coarse graining) degrees of freedom (Cosoli et al., 2008a; Fermeglia and Pricl, 2007; Laurini et al., 2016; Scocchi et al., 2009, 2007a, 2007b; Toth et al., 2012). On the macro-scale level, we presented a base line model that corroborates the lack of population balance modeling for a reactive-expanding PU foam (Karimi and Marchisio, 2015). This has paved our way to implement a population balance equation (PBE) into a CFD solver and introduce a new VOF-based solver, coupled with PBE, for modeling and simulation of PU foams (Karimi et al., 2016). The results we obtained from the validation tests showed that by solving a PBE, one can extract practical information about the foam apparent density and its morphological structure. This, however, comes with the cost of compromising some physical phenomena occurring during the foam expansion, e.g., empirically driven correlations or constant values represent the characteristics of the system under investigation. For instance, we applied a simplified diffusion controlled model for the bubble growth rates. However, later we addressed this by coupling a detailed bubble-scale model with the macro-scale CFD code and showed the benefits of applying a multiscale approach on the accuracy of the numerical predictions (Ferkl et al., 2016).

The present work also follows the same philosophy outlined above. Yet, for the first time in the investigation of PU foams expansion, a macro-scale CFD model is coupled with nano-scale atomistic models. The macro-scale CFD model requires in fact three pieces of information: the density of the liquid mixture undergoing polymerization (prior to foaming), the solubility of chemical blowing agents (in the liquid mixture undergoing polymerization) and the solubility of PBA varying with temperature and degree of polymerization (or cross-linking). Accordingly, instead of using empirical and unreliable expressions for the estimation of these quantities, here the nano-scale model is employed. In particular, molecular dynamics (MD) simulations are run to calculate the density of the networking polymer (Ferkl et al., 2017; Laurini et al., 2016; Maly et al., 2008) while Grand Canonical Monte Carlo (GCMC) are carried out to predict the different gases solubility as a function of temperature and degree of cross-linking (Cosoli et al., 2008a, 2008b; Paolo Cosoli et al., 2008c; Pricl and Fermeglia, 2003). The final macro-scale CFD model predictions, calculated in turn by using results from the underpinning nano-scale models, are validated against experimental data for density and temperature time evolutions for different test cases. The comparison shows that multiscale modeling is an extremely interesting technique for the simulation of PU foams, as it allows to describe them without the need of performing costly experiments. In fact, the most important properties affecting the final behavior of the PU foam are here calculated rather than measured. This is particularly important since not only some properties are difficult to measure, but some others are impossible to obtain experimentally in a rapidly evolving reacting system such as this one.

2. Mathematical models

In what follows the nano- and macro-scale models will be presented. Details concerning the specific chemical systems investigated will also be summarized in this section, as they are required to lay down the nano-scale models. In the next two sections the models employed to describe a generic PU foam will be outlined. This generic PU foam is prepared by mixing polyols and isocyanates with water, producing carbon dioxide (i.e. chemical blowing agent), and a physical blowing agent. In this work, simulations are performed for two different PU recipes (labelled as Recipe 1 and Recipe 2) applied in four different PU foam batches (a to d). Recipe 1 includes a polyether polyol with an OH value = 365 mg KOH/g polyol, and polymethylene polyphenyl isocyanate with an equivalent molecular weight of 135 (Baser, 1994). Recipe 2 includes a mixture of different polyols with OH value = 370 mg KOH/g polyol and a mixture of MDI (4,4′-methylene diphenyl diisocyanate) and TDI (toluene-2,4-diisocyanate) (Geier et al., 2009). Water is used in Recipe 1 as the CBA, whereas n-pentane acts as PBA in Recipe 2. The nano-scale model calculates the density of the liquid mixture undergoing polymerization and the solubility of the physical and chemical blowing agents at different degrees of polymerization or cross-linking and different temperatures. These pieces of information are then fed to surrogate models that fit the MD/GCMC generated data into algebraic expressions, and eventually passed to the macro-scale model that simulates the PU foam.

The rationale behind this strategy is that the direct and dynamic coupling between the macro-scale and nano-scale models is not viable due to the final application of the CFD model that is simulating a three-dimensional mold geometry. In other words, calling the detailed nano-scale models for all the cells of the CFD domain under different state variables (e.g., temperature and conversion of reactants) extensively increases the computational load. Hence, one must design a communication bridge between the two scales, where not only passing the data from lower-scale to the higher-scale is appreciably fast, but it also supplies accurate approximations of the macro-scale requirements. With the adoption of surrogate models, the macro-scale inputs are wrapped into different surrogate models with parameters being statically fitted to the detailed simulations and the form of surrogate models are limited to explicit algebraic expressions.