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MoDeNa *Nanotools*: An integrated multiscale simulation workflow to predict thermophysical properties of thermoplastic polyurethanes

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ABSTRACT

In this work we describe and assess the performance of *Nanotools*, a feature of the MoDena software we are currently developing in the framework of a granted EU project devoted to the implementation of a multi-scale modeling environment for nanomaterials and systems by design. Specifically, *Nanotools* integrates multi-step computational procedures based on atomistic molecular dynamics and Monte Carlo simulations for the estimation of major thermophysical properties of thermoplastic polyurethanes (TPUs). The predicted results obtained with *Nanotools* for density, thermal conductivity, surface tension, gas permeability, and Young modulus are in good agreement with the relevant experimental data, thus paving the way for the use of *Nanotools* in the current design of new TPUs for advanced applications.

1. Introduction

Nanotechnology and related production processes play an increasingly important role in our modern society [1]. The ultimate, macroscopic performance of nanotechnology products is determined by the material properties at each scale–from nano to micro. These properties can, in turn, be affected by the choice of the production conditions and ingredients [2]. Materials science and engineering is a field that has probably benefited most by the introduction of nanotechnologies, whilst the chemical industry, in particular high-performance product sectors like the pharmaceutical industry, is somewhat lagging behind. Likely, the lack of integrating the different specialized areas, both in terms of knowledge and computational tools, currently represents for these big industrial realities a formidable hurdle. The ultimate goal of the MoDeNa project, funded in 2014 by the European Community within the 7th European Framework Program under the Call NMP (Nanosciences, nanotechnologies, Materials and new Production technologies), is indeed to control macroscopic material properties and ultimate product performances by mastering the behavior of materials and ingredients at all length scales. In this scenario, the MoDeNa project aims at developing, demonstrating and assessing an easy-to-use multiscale simulation suite under an open-source licensing scheme that delivers models with feasible computational loads for the design and production of specific industrial products, i.e., polyurethanes (PUs). Specifically, the MoDeNa project focus on (i) the development of high-fidelity models to predict properties and behaviors of new nanomaterials at different scales – from quantum mechanics to finite element calculations – (ii) the development of a multiscale modeling software framework that integrates these models across the scales, and (iii) the development of reference standards and standardized methods for the representation, storage, and communication of models and data.

The general challenges for achieving innovations in nanomaterials technology are the limited atomically precise production capabilities that exist today, together with an incomplete understanding of thermodynamic and kinetic processes at the nanoscale. This is even truer at the mesoscale, that is, the interval of time and length scales reaching up to seconds and to hundreds of nanometers, respectively. According to the dogma of nanotechnology, structural features and relaxation phenomena taking place in this time-scale domain ultimately define the properties on the macroscale where production, utilization, and exploitation of the product take place [2]. Thus, for the optimization of the production process and the achievement of the maximum quality of the end product, it is essential to understand all molecular mechanisms taking place at each scale and how these reflect on the final product performance.

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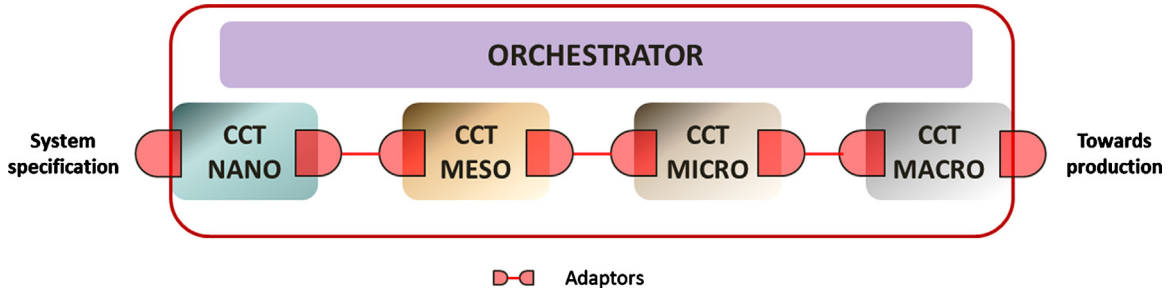

Fig. 1. The MoDena project modeling framework.

These wide-ranging challenges are well reflected in the MoDeNa nanomaterial case study, namely the production and manufacturing of compact thermoplastic polyurethane (TPU) materials and low density polyurethane (PU) foams. Both systems are characterized by the presence of nano-, meso-, and microstructures, which, in turn, are crucial for the application properties of the final material. Scale interactions are everywhere in PUs. Indeed, TPUs can be seen as generally nanophase separated di-block copolymers, being constituted by a so-called hard (crystalline) phase (HF) – prototypical components being 4,4′-methyl-diphenyl isocyanate (4,4′MDI) and the chain extender 1,4 butandiol (BDO) – interspersed within a soft (amorphous) phase (SF) – most commonly a polyester, or polyether block. In case of the alternative MoDeNa material case, i.e., low-density open-cell foam, another nanophase separation leads to an early solidification of the foam closed-cell membranes. These, under the subsequent action of a blowing agent, expand till rupture thereby creating the final foam open-cell structure. Since the nanophase separation is the basis for the solidification process of the membrane, it also controls cell growth, membrane rupture, and finally the morphology of the open cell foam. Accordingly, the sound prediction, understanding, and control of nanophase morphology and/or phase separation in TPUs and PUs are keys for further improving the ultimate, macroscopic properties of both type of materials, while benefitting from vastly reduced costs.

The choice of TPUs and PUs as case study in the MoDeNa project is motivated by the applicability of these polymeric systems and the possible impact of this research on the industrial production processes over the coming years. The global market for PU was estimated at 13,650 Ktons in 2010 (of which 5000 Ktons in Europe) and is expected to reach 18 Mtons by 2016 (of which 6 Mtons in Europe), growing at a compound annual growth rate (CAGR) of 4.7% from 2011 to 2016. In terms of revenue, the market was estimated to be worth US$ 33 million in 2010 and is expected to reach US$ 56 billion by 2016, growing at a CAGR of 6.8% from 2011 to 2016 [3]. According to BASF – a leader European chemical industry, a major producer of TPUs and PUs, and partner of the MoDeNa project – nanoengineered TPU materials will replace the current generation of TPUs over the years to come.

Within MoDeNa, our group specifically developed the MoDeNa *Nanotools* feature, that is, an integrated and automated series of molecular simulation procedures [4–8] to predict the major thermophysical properties of TPUs, and its integration in the general project workflow. Conceptually, our aim is to provide (i) computational recipes for determining fundamental thermophysical material property data (i.e., density, thermal conductivity, surface tension, gas diffusivity, solubility and permeability, and mechanical properties) for TPUs, also termed *exact models*; (ii) the implementation of recipes and surrogate models in *Nanotools*, and (iii) the relevant integration within the MoDeNa software.

2. Theory and computational methodologies

2.1. The MoDeNa software

The concept of MoDeNa is an interconnected multiscale modeling software platform. Four scales are linked together by this framework namely: nano-, meso-, micro-, and macroscale. As stated in the introduction, this unifying software platform will ultimately allow for enhanced product and process design across all these scales. As shown in Fig. 1, the modeling framework is intimately coupled with the software framework; thus, the software framework will facilitate and greatly enhance all material modeling activities. The *orchestrator*, in turn, will link the modeling across the scales, which is a necessary condition to obtain an integral approach, in contrast to a series of disconnected phases calculations.

Multiscale coupling requires the exchange of information between software instances developed for specific scales in a consistent way. In order to achieve this, generating consistent representations for models and data is necessary. The MoDeNa framework handles the communication across scales through Computational Code/Tool (CCT) and adaptors. CCT perform simulations by executing applications for a given set of inputs while adaptors handle the communication with the MoDeNa software framework. Both are application specific.

The software framework consists of an *orchestrator*, a database and an interface library. The *orchestrator* is based on FireWorks [9], and constitutes the backbone of the software framework in that it schedules simulations and property estimation operations, which make up the workflow of the overall simulation. It is very much like a dynamic workflow engine, in which the different applications are “orchestrated” to obtain, analyze, and pass information to other operations. The NoSQL database MongoDB [10] is used to store the state of the workflow as well as all associated data such as simulation parameters, data used for parameter estimation, and meta-data. Finally, the interface library consists in a high-level python module providing access to the database as well regression analysis capabilities.

2.2. Nanotools

According to the *Nanotools* concept, as conceived and implemented in the MoDeNa framework, computational recipes based on low scale (i.e., atomistic-level) simulations were conceived, implemented, and tested within *Nanotools* to estimate major thermophysical properties (i.e., density, thermal conductivity, surface tension, gas diffusivity, solubility and permeability, and mechanical properties) of different polyether- and polyester-based TPUs. Exploiting the MoDeNa workflow, these computational recipes could be fully or partially automatized to calculate the abovementioned polymer properties, as shown in Fig. 2.

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