MoDeNa :

Description of main S & T results/foregrounds

Introduction

The MODENA project developed and assessed a comprehensive, easy-to-use multi-scale software framework application under an open-source licensing scheme that links models with feasible computational loads for process and product design of complex materials. The framework is applied to the modelling of polyurethane foams (PU).

The individual models, reflecting the behaviour of the different material properties were generated in three modelling work packages (WP1-3), splitting the scales roughly into the molecular, the intermediate and the macroscopic product scale. The software was developed in WP5 and WP4 formed the glue and umbrella for the modelling and software developments. WP6 was devoted to the application, provided the experiments and verification sandbox. Whilst WP7 collectively provided the framework for communications.

The graph below indicates the level of complexity the simulation of polyurethane foaming and mechanical properties poses. The nodes represent the computational modules, in most cases individual software components with the exception of *hypothesis, literature* and *application*.

WP1 Nano-scale tools (UNITS), Quantum chemistry tool (BASF), Thermo tool DFT (US), Thermo tools EOS (US), Thermo tools atomistic simulations (US)
WP2 Bubble growth tool (VSCHT), Coalescence Kernel tool (TUE), Kinetics tool (BASF), polymer solidification (VSCHT), wall drainage and rupture tool (VSCHT), CFD tool (POLITO)
WP3 Foam thermal insulation tool (VSCHT), Rheology tool (TUE), foam acoustic insulating tool (VSCHT), foam reconstruction tool (IMDEA), mechanical properties (IMDEA), mechanical simulation (IMDEA)
WP6 Industrial application

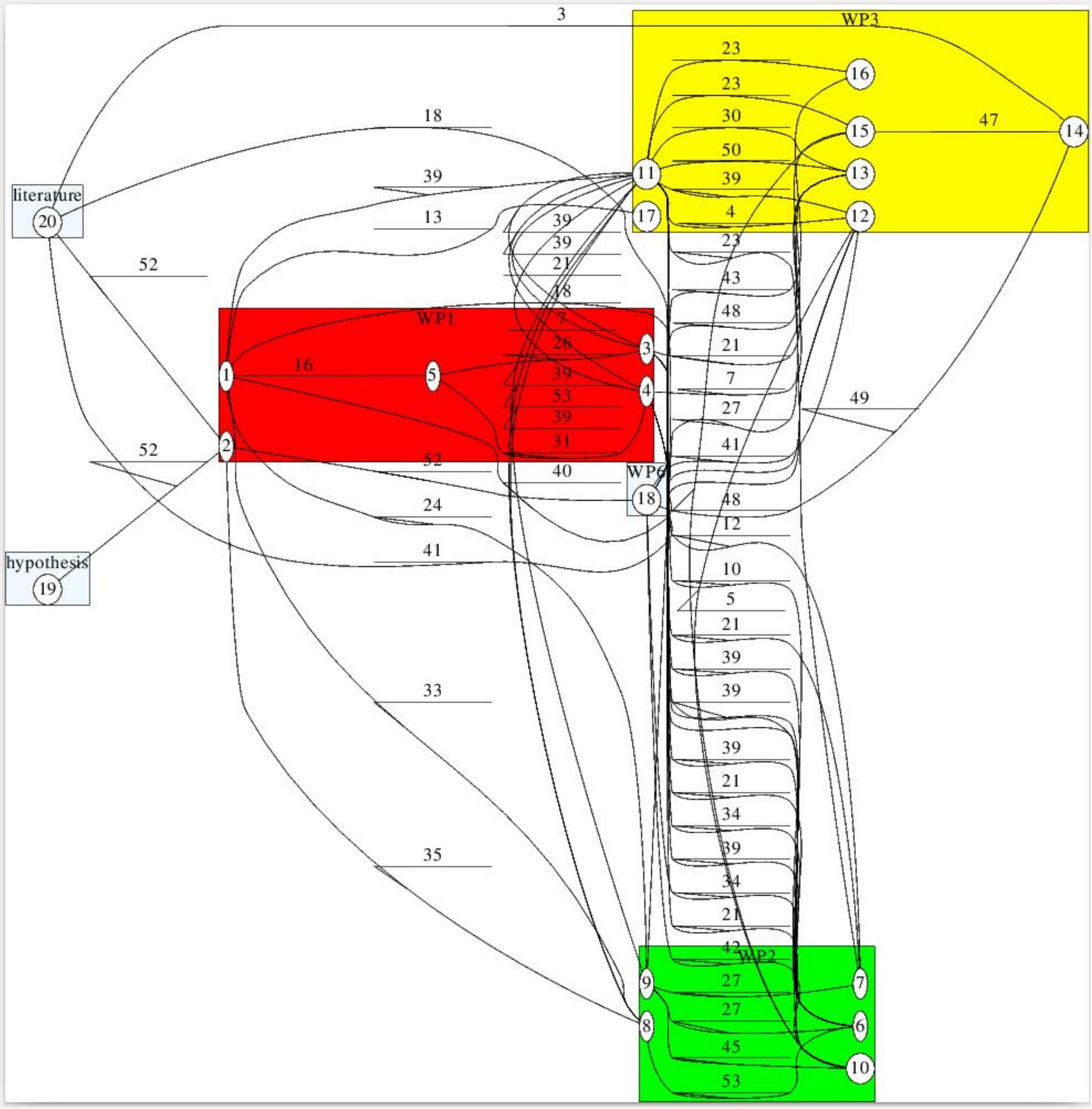
The directed graph has 18 nodes and 56 edges representing activity nodes and transferred items. Activities are mostly input/output computations realised as independent software tools and the edges are the transferred items, which are most scalar numericals but also complete models.

Table 1: Activity nodes and communication items

activity nodes	communicated items	
1 : WP1 Nano-scale tools (UNITS) 2 : WP1 Quantum chemistry tool (BASF) 3 : WP1 Thermo tool DFT (US) 4 : WP1 Thermo tools EOS (US) 5 : WP1 Thermo tools atomistic simulations (US) 6 : WP2 Bubble growth tool (VSCHT) 7 : WP2 Coalescence Kernel tool (TUE) 8 : WP2 Kinetics tool (BASF) 9 : WP2 polymer solidification (VSCHT) 10 : WP2 wall drainage and rupture tool (VSCHT) 11 : WP3 CFD tool (POLITO) 12 : WP3 Foam thermal insulation tool (VSCHT) 13 : WP3 Rheology tool (TUE) 14 : WP3 foam acoustic insulating tool (VSCHT)	0 : Absorption coefficient of gas and solid 1 : Acoustic absorption coefficient 2 : Activation energy 3 : Air thermal conductivity 4 : Apparent foam thermal conductivity 5 : Average wall thickness and strut content 6 : Bubble growth rate 7 : Bulk density of polymer 8 : Carreau Yasuda parameter 9 : Characteristic impedance 10 : Coalescence kernel 11 : Conversion 12 : Drainage Time - Coalescence kernel 13 : Elastic Moduli 14 : Elastic Moduli in compression, rising & transverse 15 : Elastic Moduli in tensile, rising & transverse 16 : Force Fields (COMPASS)	28 : Power Index 29 : Pre-exponential factor 30 : Pressure 31 : Pure component vapor pressure 32 : Relaxation time 33 : Sequence length 34 : Solubility (Henry Coefficient) 35 : Stoichiometric coefficients 36 : Stress & Strain distributions and failure mech. 37 : Stress-Strain curves 38 : Strut content 39 : Temperature 40 : Thermal conductivity of TPU polymer 41 : Thermal conductivity of gas and solid 42 : Time when the wall ruptures 43 : Ultimate tensile stress tension, rising & transverse

15 : WP3 foam reconstruction tool (IMDEA,VSCHT) 16 : WP3 mechanical properties (IMDEA) 17 : WP3 mechanical simulation (IMDEA) 18 : WP6 industrial application	17 : Fraction of polymer inside the plateau borders 18 : Gas diffusivity in TPU polymer 19 : Infinite shear-rate viscosity 20 : Initial yield stress compression, rising & transverse 21 : Interfacial tension 22 : Molecular weight 23 : Moments of bubble size distribution 24 : Morphology data of TPU polymer 25 : Operating range for shear rate 26 : PC-SAFT Parameters 27 : Polymer viscosity	44 : Visco-elastic property of polymer 1-Young modulus 45 : Visco-elastic property of polymer 2-relaxation time 46 : Viscosity and solidification model Parameters 47 : Voxel-based foam morphology 48 : Wall thickness 49 : Wavenumber 50 : Zero shear-rate viscosity 51 : cell size 52 : kinetic scheme 53 : kineticSource (C-code) 54 : porosity

Figure 1: Simulation connectivity graph. The subgraphs WP1, WP2 and WP3 represent the computational activities, whilst the WP6 is representing the integrated verification activities. The numbers refer to the numbers in table 1 on activities and communicated items.



WP 1 Nano-scale modelling and simulations

Participants: UNITS, BASF, VSCHT, US

Objective

The main purpose of MoDeNa WP1 was to gain a thorough knowledge of the chemistry, structure and morphology of (T)PUs and their nanocomposites (NCs) and how material properties influence, across the entire range of length and time scale, the ultimate macroscopic properties of these systems. Accordingly, this WP considered ab-initio quantum mechanics, atomistic (molecular dynamics, MD), coarse-grained (Dissipative Particle Dynamics, DPD) and continuum level (finite elements (FE) and equation of state (EOS) simulations/calculations to achieve the goal. Specifically, MD to FE simulations were employed to characterize the morphology of (T)PU systems and their NCs, and to predict their major thermophysical and transport properties as a function of the nature of the PU, of eventual the nanofiller and, in case of foams, of the degree of cross-linking of the PU polymer.
Ab-initio quantum chemistry calculations were employed to investigate kinetic aspect of PU polymerization process. Finally, the PC-SAFT EOS was parameterized using experimental data and results from lower level simulations (e.g. MD) to predict the thermodynamic properties of (T)PU systems. Furthermore, viscosities and surface tensions were calculated using an entropy-scaling approach and density functional theory, respectively.

Multiscale molecular simulations of T(PU)s and their nanocomposites

The main results within this specific activity by MoDeNa WP1 can be summarized as follows.
First, a multiscale molecular simulation procedure was conceived, developed and implemented for the morphological, thermodynamic and transport property prediction of TPU matrices, their NCs and for PU foam precursors (i.e., crosslinked PU polymers prior to foam blowing). Accordingly, at the atomistic level of description (atomistic models), a set of complete computational procedures to automatically (or semi-automatically) predict material properties for (T)PUs (globally called NANOTOOLS) were conceived and validated. At the mesoscale, complete computational procedures to predict energy, morphologies and density distributions for a plethora of different (T)PUs and their nanocomposites have been developed. Finally, information retrieved at the mesoscale has been employed at the highest level of the length/time scale (continuum models) to predict macroscopic material properties for these systems. Figures 1.1 and 1.2 show some illustrative examples obtained for different (T)PU matrices and their nanocomposites.

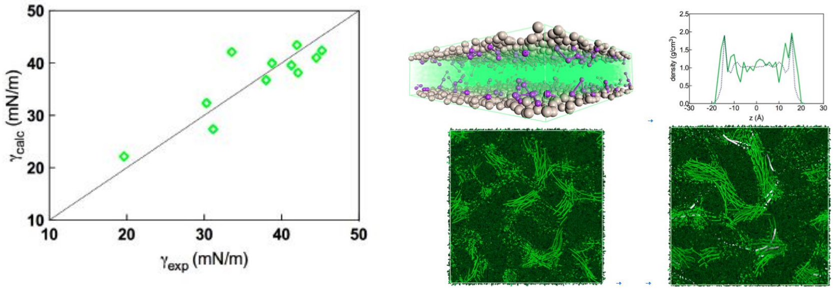


Figure 1.1. Left panel: Comparison between NANOTOOLS predicted and experimental surface tension values for different TPU matrices as a function of their composition. Left panel: (Top left) Side view of the equilibrated mesoscopic model obtained from DPD simulations of the C30B-modified montmorillonite (MMT)-based TPU nanocomposite (NC). The MMT platelet is shown as gray DPD beads, the surface modifier C30B molecules are shown as purple DPD beads while the TPU DPD chains are depicted as a light green field to highlight the distribution of the C30B molecules within the MMT layers.

(Top right) Comparison between interlayer densities of organic species (surface modifiers and polymer) in the gallery space of the C30B-modified MMT-based TPU NC as obtained from MD (green continuous line) and DPD (blue dotted line) simulations, respectively. (Bottom left) Mesoscopic morphology of TPU (dark green, soft phase, light green, hard phase). (Bottom right) Mesoscopic morphology of TPU/sepiolite (SEP) nanocomposite (dark green: soft phase; light green: hard phase; white, SEP).

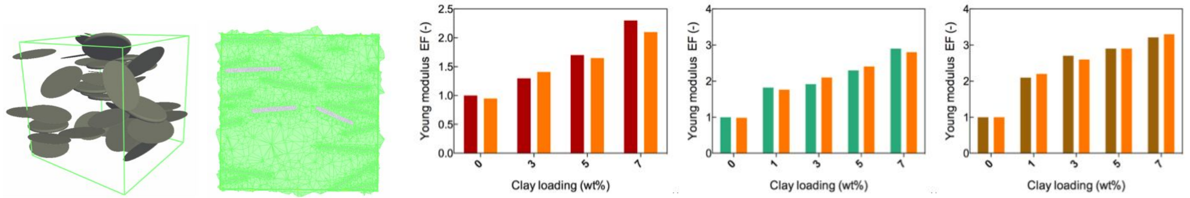


Figure 1.2. Global model configuration (first from left) and relative meshed volume (second from left) used at the continuum, level for TPU/montmorillonite nanocomposites. Right: Comparison between simulated (orange bars) and experimental (other color bars) Young modulus enhancement factor EF (= E/E_0) in organically modified montmorillonite (left, dark red bars), laponite (center, green bars) and sepiolite (right, brown bars) TPU nanocomposites as a function of clay loading. Experimental data measured by UniTS.

Upon validation, the simulated material data were further exploited to derive surrogate models (i.e., simple equations describing the behavior of a given quantity (e.g., density) as a function of a given thermodynamic variable (e.g., temperature) and the relevant parameter values) for the thermophysical properties that were deemed most important, such as density, thermal conductivity and diffusion coefficients of (T)PUs and of different gases within the polymeric matrices, and mechanical moduli, just to name a few. The entire sets of detailed models (aka simulated values) and surrogate models were finally implemented within the MoDeNa framework and linked to all other MoDeNa tools by ad hoc developed software scripts and adaptors. Figures 1.3 and 1.4 show two representative examples of the results obtained from the coupling of discrete (MD) and continuum (computational fluid dynamics (CFD) or equation of state (EOS)) models for PU foams as obtained via implementation of these models in the MoDeNA platform.

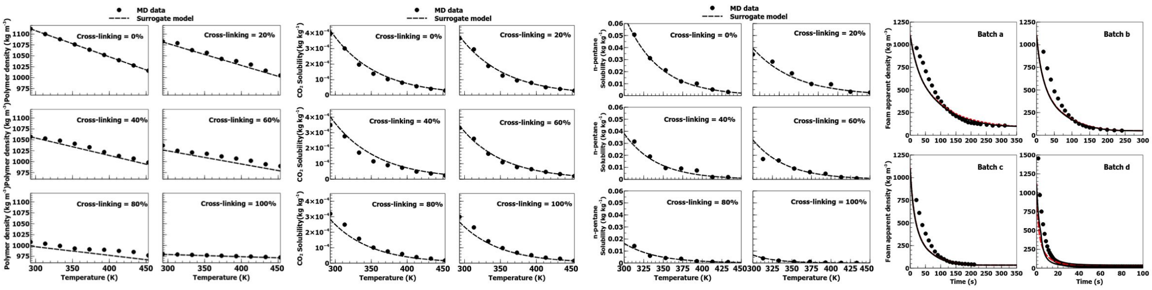


Figure 1.3. *Top left: Comparison between surrogate and detailed (MD) models for PU density prior to foam blowing under different cross-linking. Top right: comparison between surrogate and detailed (MD) models for CO_2 solubility in PU polymer under different cross-linking prior to foam blowing. Bottom left: comparison between surrogate and detailed (MD) models for n-pentane solubility in PU polymer under different cross-linking prior to foam blowing. Bottom right: numerical predictions of foam density as a function of time solid-line using surrogate models originated via discrete (MD) simulations. All data were obtained by implementation of the relevant models in the MoDeNa platform using models from UniTS and POLITO.*

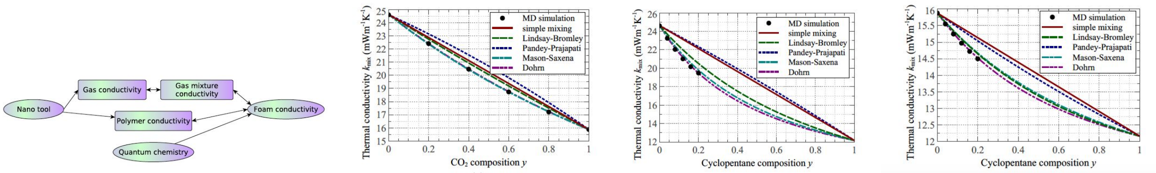


Figure 1.4. Left panel: Schematic diagram of the complete multi-scale simulation. The elliptical shape represents the detailed models, whereas the rectangular shape represents the surrogate models. Right panel: Choice of the best EOS description for the thermal conductivity of gas mixtures based on detail models (MD) data prediction. Systems from lef to right: CO2-air, cyclopentane-air, and cyclopentane-CO2. All data were obtained by implementation of the relevant models in the MoDeNa platform using models from UniTS and VSCHT.

Reaction kinetics from quantum chemistry DFT

For the description of the chemical kinetics of polyurethane rigid foam systems the pre-exponential factors and activation energies of the rate coefficients of the gelling and blowing reactions under catalyzed and non-catalyzed conditions were calculated by means of the DFT method.
For the case of the gelling reaction, a quantum chemical study was performed to clarify the reaction mechanism of the nucleophilic attack of different diols at the isocyanate groups of 4,4’-MDI. To reduce the computational effort, toluene-4-isocyanate, 2-methoxyethanol, 1-methoxy-2-propanol and ethanol were chosen as model compounds for 4,4’-MDI, pEO (I), pPO (II) and 1,4-butanediol (III), respectively. For the non-catalyzed reaction two different reaction paths were investigated, the first one consisting in a direct reaction of an alcohol group with the isocyanate group, the second one consisting in a reaction of an alcohol-alcohol complex with the isocyanate group. It could clearly be shown that the second mechanism is much more probable than the first one and the “non-catalyzed” isocyanate reaction is basically a solvent-catalyzed reaction. For the catalyzed gelling reaction, the catalysis by tertiary amine groups was considered. Table 1 summarizes the calculated activation energies and pre-exponential factors for the urethane reaction of the model isocyanate with the different model alcohols under “non-catalyzed” (left) and amine-catalyzed (right) conditions.

Table1: Activation energies and frequency factors of “non-catalyzed” and amine catalyzed gelling reaction.

	Diol catalyzed		**NMe_3 catalyzed**	
	E_a [kJ/mol]	A	E_a [kJ/mol]	A
(I) pEO	37.1	1.0E+07	23.6	1.6E+06
(II) pPO	48.2	1.1E+07	34.3	4.7E+06
(III) 1,4-butanediol	65.9	1.4E+10	31.9	1.2E+06

The reaction of water with an isocyanate group, which forms carbon dioxide as a blowing gas and an amine group which is very quickly further reacting with another isocyanate group to form a urea bridge was also investigated for both catalyzed and non-catalyzed conditions. Again it turned out that the “non-catalyzed” reaction preferably proceeds via of complex of water with an alcohol group or with another water molecule. The catalyzed reaction of water and an isocyanate group was again investigated for tertiary amine groups as catalyst. Table 2 summarizes the calculated activation energies and pre-exponential factors for both the “non-catalyzed” (First four lines) and the amine catalyzed cases (last line).

Table 2: Activation energies and frequency factors of “non-catalyzed” and amine catalyzed blowing reaction.

	Carbamic acid formation	
	E_a [kJ/mol]	A
pEO	50.0	3.6E+07
pPO	48.7	8.4E+06
1,4-butanediol	56.8	6.2E+07
H_2O	72.4	1.1E+10
NMe_3	40.7	4.2E+05

Thermodynamic properties of PU systems

Thermodynamic properties were determined using the PC-SAFT equation of state (globally called Thermo Tool EOS) and a density functional theory approach (Thermo Tool DFT). In a first step, novel schemes to determine the pure component EOS parameters using experimental surface tension data and results of MD simulations had to be developed due to the scarcity of experimental results for many project relevant compounds.

Furthermore, an entropy-scaling approach to calculate viscosities as well as a density functional theory consistent with PC-SAFT to obtain surface tensions were implemented and the results validated against experimental data, see figure 1.5.

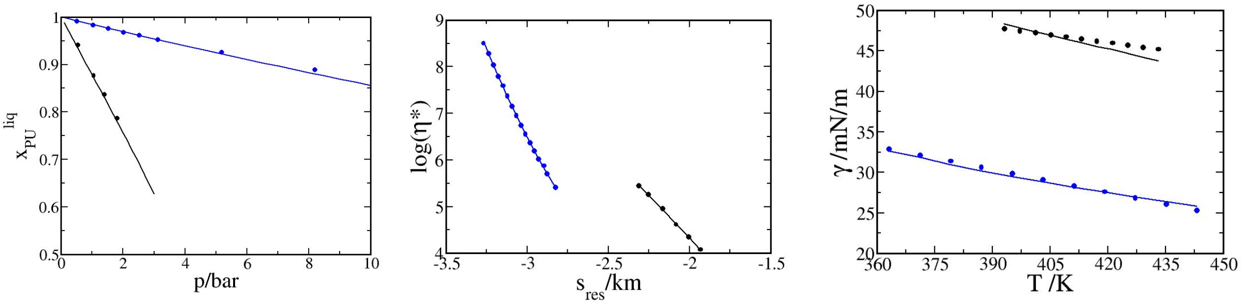


Figure 1.5. Left: Mole fraction of the PU polymer in the liquid phase as a function of pressure of the binary mixtures PU + cyclopentane at 353.15 K (black) and PU + CO_2 at 363.15 K (blue). Solid lines represent calculated results; circles denote experimental results from VSCHT. Middle: Experimental (circles) and calculated (lines) reduced viscosity as a function of residual entropy for butandiol (blue) and MDI (black). Right: Experimental (circles) and calculated (lines) surface tension as a function of temperature for the hard (black) and soft (blue) segment of a TPU.

Subsequently, suitable surrogate models were identified for all relevant properties which correlate the results of the detailed models (the PC-SAFT EOS and DFT) as a function of thermodynamic state variables (temperature, pressure, composition) which are passed as input values from models at higher scales and a set of adjustable parameters. Both Thermo Tools are integrated into the MoDeNa framework in a backward mapping fashion. This allows readjusting the parameters of the surrogate models to new input values from higher scales on demand at runtime.

The results of Thermo Tool EOS and Thermo Tool DFT pose the input values of models at the mesoscale such as the bubble growth tool and the coalescence model.

Highlights

- Multiscale molecular simulation procedures (detailed models) and relevant surrogate models for the reliable prediction of structural, thermodynamic and transport properties of (T)PUs and their NCs have been successfully designed, developed and validated.
- The coupling of models at different scales (e.g., MD to CFD or MD to EOS) has been achieved and implemented within the MoDeNa framework.
- A fast and robust density functional theory approach consistent with the PC-SAFT EOS has been implemented.
- The models of the Thermo Tool EOS and Thermo Tool DFT have been integrated in the MoDeNa framework in a backward mapping fashion.

WP 2 Meso-scale modelling and simulations

Participants : BASF, POLITO, TUE, VSCHT

Objectives

The main objective of this work-package (WP2) was to simulate the development of meso-scale morphology of PU foams, i.e., of processes occurring on the scale of individual gas bubbles in the foam. This involves a number of physical phenomena occurring during PU foaming: growth of gas bubbles, bubble coalescence, polymerization kinetics, rheology of the reaction mixture and formation of walls and struts between the bubbles. Thus, the goals were:

- to develop predictive mathematical models describing the evolution of PU foam morphology
- diffusion of blowing agents in reaction mixture, growth rate of bubbles, solidification of polymer, etc., and to validate these models by experimental or literature data,
- to utilize the data provided by WP1 nano-scale models – rate coefficients of chemical reactions, various properties of gas and liquid phases including density, solubility, diffusivity and surface tension in WP2 simulations,
- to pass the results to WP3 macro-scale models that describe macroscopic foam evolution and properties of the foam based in its morphology.

For the information exchange between individual models the new multi-scale modelling framework developed in MoDeNa project was used.

Mathematical models

Reaction kinetic model was developed by BASF in order to describe the progress of polymerization – the increase of polymer and the decrease of monomer concentration due to the growth of polymeric chains from monomers to a large gel network. Several models were implemented based on the type of product – TPU, flexible foam or rigid foam. Each product is made by a different recipe, i.e., from somewhat different reactants, and hence reaction paths differ. Several modelling techniques were tested – end group models, hard segment models and chain length models. These models differ on the level of micro-structural information they provide about the resulting material. The end group models are recommended for the overall description of the manufacturing process, whereas the hard segment and chain length models are intended as post-processing tools for the determination of a more detailed information about the material.

The rheology of the reaction mixture depends on the progress of the polymerization. During the foaming process, the reaction mixture changes from low to highly viscous liquid and finally to solid. The viscosity typically remains approximately constant for a large part of the foaming and then quickly increases by several orders of magnitude as we near the gel point. This is caused by competing effects of the temperature and the concentration and molecular weight of the polymer. VSCHT tested several models and found that at the current state-of-art the Castro-Macosko model is the most reliable one for the description of reaction mixture viscosity during PU foaming process. More detailed description of the reaction kinetics and polymer rheology modelling was provided in D2.3.

The growth of the bubbles is caused by the diffusion of blowing agents through the reaction mixture toward the bubbles and subsequent evaporation of the blowing agents. This phenomenon depends on reaction kinetics, rheology of reaction mixture, diffusivity and solubility of blowing agents and other properties. VSCHT implemented a bubble-shell model, whose principal output is the bubble growth rate. This quantity is communicated through a simple surrogate model, which provides the bubble growth rate as a function of temperature, concentration of blowing agent and other state variables for the macroscopic CFD tool.

The bubbles not only grow, but also coalesce under certain conditions. To describe this phenomenon a coalescence model was implemented by TUE. It uses similar underlying model of multiphase Stokes flow of incompressible fluids as foam rheology model from WP3. It models the interaction of individual bubbles, i.e., the formation of thin liquid film between the bubbles and its flow. Based on these simulations it is possible to determine whether the bubbles will coalesce or bounce from each other. The macroscopic CFD tool utilizes these results in the form of a coalescence kernel. More detailed description of the bubble growth and coalescence modelling was provided in D2.2.

During the foaming process we first observe the growth of spherical bubbles. However, when the foam density decreases to a certain threshold, under which the bubbles start to touch each other, the bubbles deform to non-spherical shapes. This leads to the formation of walls and struts between the bubbles. We implemented two types of models for the prediction of development of these morphology features. The first model by VSCHT uses an idealized geometry of strut formation between three bubbles of equal size. It employs thin film equations to describe the flow of reaction mixture between the film and the strut. The walls are then formed by the simultaneous stretching (caused by the bubble growth) and drainage (caused by the capillary forces). The second model by TUE is based on Stokes equations and is capable of modelling the simultaneous growth of several bubbles inside a spatially three-dimensional periodic box. The formation of the walls and struts is then a natural consequence when the bubbles become too large. The models use the evolution of bubble size and physical properties like the surface tension or viscosity of the reaction mixture from the results of above mentioned models. More detailed description of the wall and strut formation modelling was provided in D2.4.

Results and discussion

The predicted reaction kinetics results were compared against experimental data. It was found that rate coefficients calculated by quantum chemistry tools were not precise enough for some considered reactions and therefore some of them had to be measured experimentally. The overall kinetic model is very well capable to describe the evolution of temperature and reactant concentrations. Moreover, the measured pressure rise correlates well with the increase in the cross-link concentration. Thus, the gel point can be detected (see Figure 2.1).

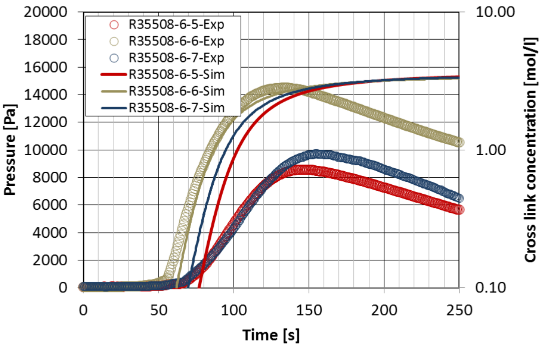


Figure 2.2: Experimentally observed pressure rise and predicted cross link concentration.

Experimental measurements of the bubble cell size evolution during the foaming were not available, thus the model was validated in connection with the macroscopic CFD tool developed by POLITO. This is perfectly possible because the growth of bubbles is the main cause for the decreasing foam density (see Figure 2.2).

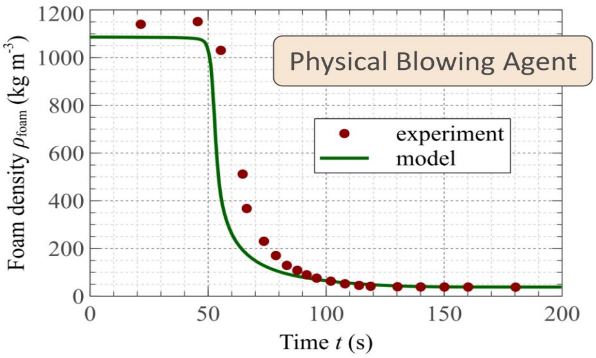


Figure 2.1: Comparison of predicted foam density with experiment for physically blown foam.

The predicted growth of bubbles and the formation of three walls and one strut in the idealized geometry is illustrated in Figure 2.3. It can be seen that the model is capable of capturing the evolution of wall thickness profile and strut shape. The simulation of growing bubbles encapsulated inside a periodic box is shown in Figure 2.4. It can be seen that the bubbles lose their spherical shape and deform due to bubble-bubble interactions.

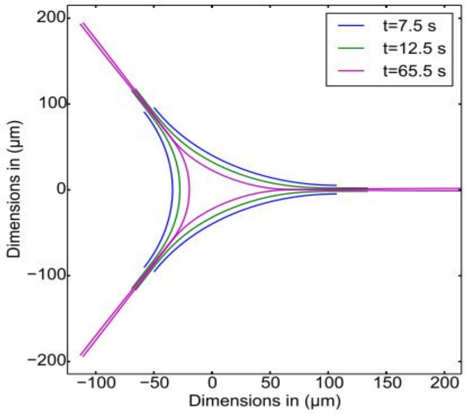
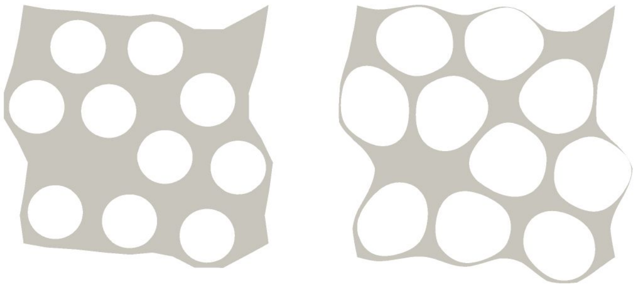


Figure 2.3: The formation of the strut and three connected walls as predicted by the Wall drainage tool.



(a)

(b)

Figure 2.4: a) Initial foam containing ten bubbles of volume fraction = 0.4. b) Foam structure after several seconds.

Highlights

- Reaction kinetics of PU formation is captured by end group, hard segment and chain lengths models.
- Rheology of the reaction mixture is modelled by Castro-Macosko model.
- Growth rate of bubbles is predicted by the bubble-shell model.
- Bubble coalescence is simulated using multiphase sharp interface model.
- The detailed development of foam morphology including the formation of walls and struts is modelled both in idealized geometry and inside a spatially three-dimensional periodic box.

WP 3 Macro-scale modelling and simulations

Participants: BASF, POLITO, TUE, IMDEA, VSCHT

Objectives

The main goal of this WorkPackage was to gain a basic understanding of macroscale dynamics as it is affected by the meso and nano scale behaviour and properties for (T)PU. WP3, macro-scale modelling and simulation, was focused on the development of a modelling approach for the macro-scale simulation of thermoplastic polyurethanes (TPU) and PU foams. Thanks to the broad range of chemical recipes and operating conditions adoptable, the final features of the manufactured PU foams can vary extensively, fitting therefore the requirements of very different application fields. As a consequence a-priori knowledge of the final macro-scale characteristics of the product benefits both manufacturers and customers. This implies that a predictive macro-scale model should incorporate the principal physical phenomena determining the final characteristics of the foam. This Work package simulates the performance of the device/system by modelling the interaction of the different materials according to the device structure.

Unfortunately the current modelling frameworks generally tackle this challenge, by using empirical approaches, and therefore the development of fully-predictive computational models is particularly useful. Not only do they provide a realistic representation of the fluid dynamics of the PU foam (particularly important for mold filling processes), but they could also be enhanced by integrating meso-, micro- and nano-scale processes (such as the evolution of bubble size distribution within the PU foam).

In particular in this WP the macro-scale fluid dynamics simulations are performed for PU foams. To this end input WP2 (including physical properties of the polymer, property methods, reaction kinetics and equations of state) is used from the micro and meso scale coming from WPs 1,2.

The main objectives of WP3 in the reporting periods were:

- Calculate rheological properties of the foam in the bubble scale during the foaming process.
- Further develop OpenFOAM solvers to be able to use them in the case of PU foams.
- Introduce new modules in OpenFOAM that incorporates the fundamental physical phenomena occurring during the polymerization process.
- Develop a modelling strategy to simulate the mechanical behavior of PU foams.
- Develop models that predict the heat insulation properties of PU foams and their rate of the degradation.

Model descriptions and results

The Rheology Tool was developed by TUe in order to calculate rheological properties of the foam. For the purpose of this tool we assume that the bubbles are monodisperse and they are not subject to Brownian motion. The fluid is assumed to be Newtonian, incompressible and inertia is neglected. The bubble interface is modelled as a sharp interface and we apply triperiodic boundary conditions. To discretize the resulting equations in space we use the finite element method. The macroscopic problem is described by a triperiodic representative domain. To probe rheological properties an oscillatory strain is applied while ensuring that we remain in the linear regime. Bulk properties such as the apparent viscosity can be measured (Figure 3.1).

The CFD solver (POLITO), which uses inputs from the lower scales such as apparent viscosity, provides a numerical tool for the simulation of polyurethane foam. The problem includes a reacting multi-phase system in which the liquid mixture expands due to the polymerization phenomenon and the presence of different additives. In that, the gas bubbles nuclei within the reacting liquid mixture start to grow owing to the diffusion of gases produced due to the chemical reactions.

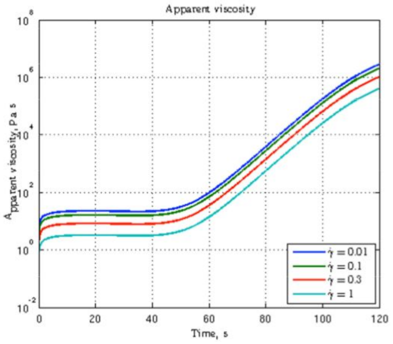


Figure 3.1: Apparent viscosity as a function of time for different shear rates.

Further, industrial applications such as mold-filling seek for capturing the foam front face and the evolution of its physical and thermal properties during the foaming process. Thus, the solver facilitates the evolution of gas bubbles via a population balance equation, capturing the foam interface using a volume-of-fluid method, and eventually predicting the foam characteristics. Figure 3.2 displays the simulation of a mixing-cup experiment using an experimental profile for the foam density.

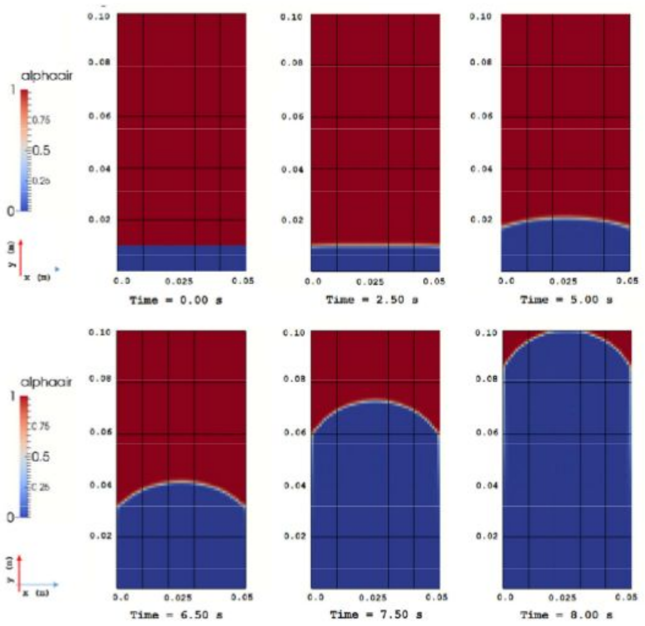


Figure 3.2: Time evolution of the foam density in a mixing-cup experiment simulated with the modified version of compressibleInterFoam. The color code refers to the air volume fraction.

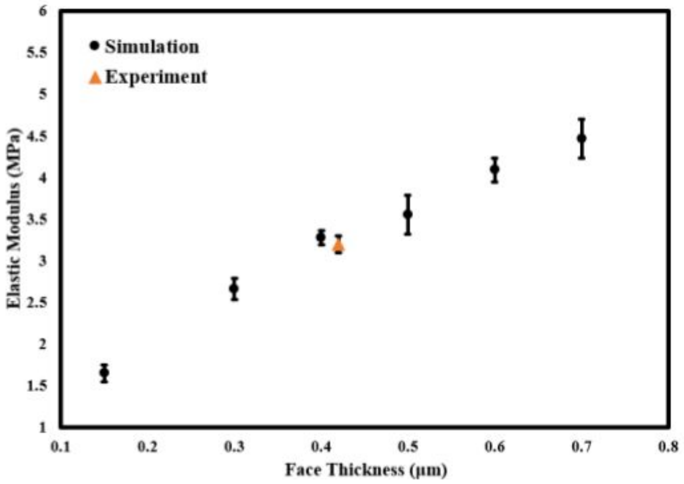


Figure 3.3: Elastic modulus of the PU foam. Experimental results for the 1-3CPW30.2 provided by BASF and numerical predictions from the multiscale model.

A multiscale modelling strategy has been developed and implemented by IMDEA to simulate the mechanical behavior of Polyurethane (PU) foams obtained by the CFD calculations. The methodology is based on the finite element simulation of a representative volume element (RVE) of the PU foam, which includes detailed information about the statistical distribution of cell sizes and shape within the foam, the shape of the struts, the relative mass in the cell face and the struts and the mechanical properties of the solid PU. The predictions of the model were compared with experimental results and the tool was used to assess the influence of the foam microstructure on the macroscopic mechanical properties.

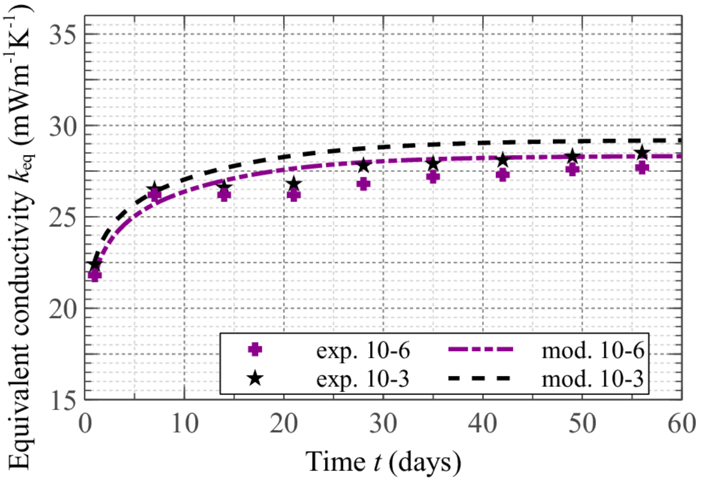


Figure 3.4: Comparison of calculated evolution of equivalent conductivity with experimental data for foams blown with water and cyclopentane.

The Foam conductivity tool (VSCHT) was developed for the prediction of heat insulation properties of PU foams. The model is taking advantage of the molecular dynamics and quantum chemical simulations from WP1 for the calculation of polymer absorption spectra and thermal conductivity of polymer and gases. Only inputs are the morphology of the foam (foam density, cell size and strut content) and cell gas mixture composition. Figure 3.4 shows the comparison of calculated time evolution of foam equivalent conductivity with experimental data.

The Foam aging tool (VSCHT) was developed to predict the rate of degradation of heat insulation properties of PU foams. Over time, carbon dioxide diffuses out of the foam, whereas air diffuses into the foam. It was found that the cyclopentane stays in the foam. This process is simulated by the spatially one-dimensional model of consecutive cells separated by walls. BASF prepared several foam samples and measured the evolution of heat insulation properties over time, when the samples were subjected to elevated temperature of 343 K. The experimental measurements were compared to the modelling predictions, which showed reasonable agreement.

Highlights

- Rheological properties of the foam are being calculated by simulating interacting bubbles in a periodic domain which represents the bulk material.
- Simulation of bubble size distribution (BSD) by implementing of a population balance equation into the CFD code.
- Simulation of the mechanical behavior of PU foams.
- Prediction the heat insulation properties of PU foams and their rate of the degradation.

WP 4 Scale interactions

Participants: NTNU, UNITS, BASF, POLITO, WIKKI, TUE

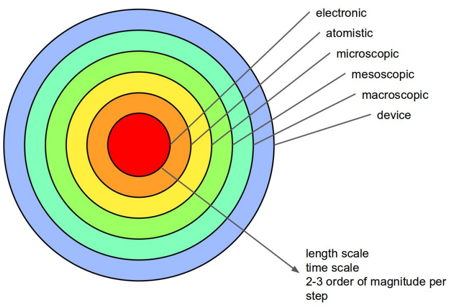
Objectives

Interoperability is to be provided based on a comprehensive analysis of the simulation / modelling problem and consequently mapped into a form suitable for the implementation. This incorporates the representation of mathematical models and data storage models. The replacement of complex models by sufficiently computationally simple models was the second objective.

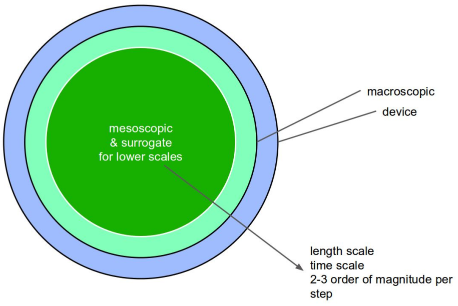
System analysis

The main difficulty with the analysis is to extract the information from the specialists. Once extracted, the second challenge is to agree on a common language, which then is instrumental for the organisation of the information. Computational tools require three essential components, namely the input/output relation which may be in the form of a set of algebraic functions or differential equations that require integration in time and possibly spatial coordinates. The overall simulation task splits into sub-tasks many of which are realised as separate software modules. A graphical representation of the overall model is shown in Figure 1: Simulation connectivity graph with the tools being shown in the tools list and the exchanged items, being mostly scalar variables, in Table 1: Communication items.

Mathematical model representation

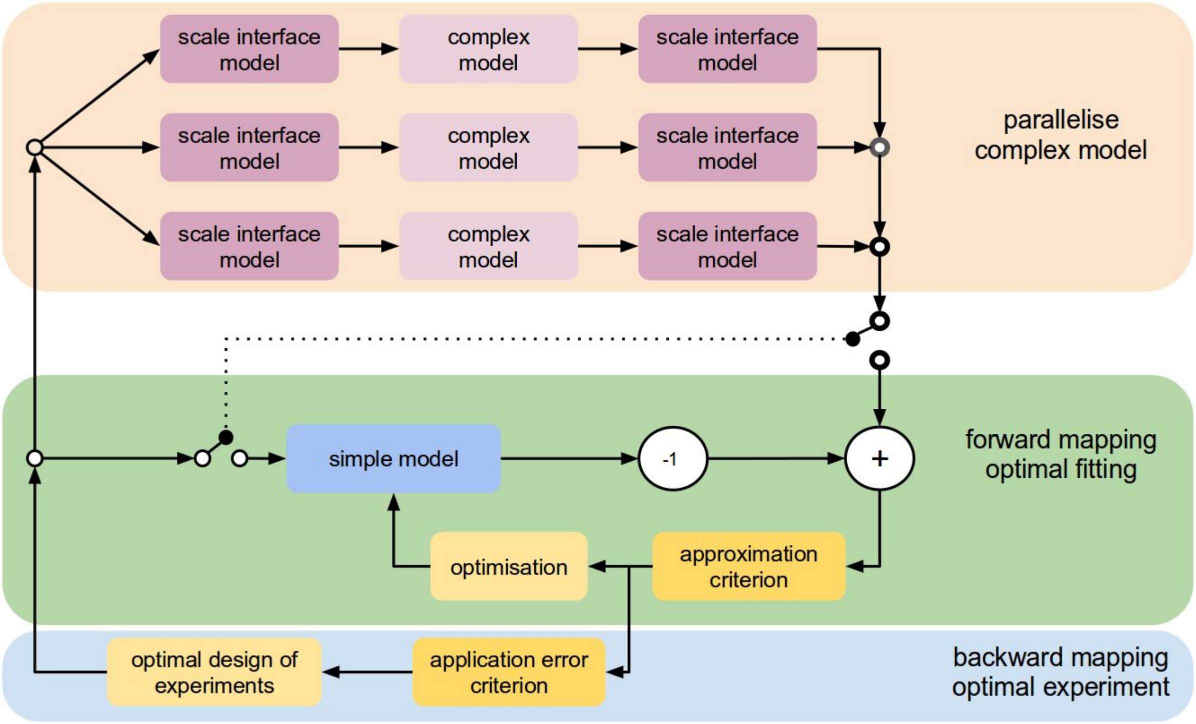


In order to capture the scale interactions we adopted and expanded a systematic approach to the construction of an ontology we designed for mathematical models of physical - chemical - biological processes. The ontology design editor allows a flexible definition of meta terms, rules and mathematical equations. Latter are constructed according to a principle scheme, which provides a guarantee for some structural properties of the resulting equation system, such as zero degree of freedom, consistent units, and probably most important an indexing structure that supports the model building process and minimises the size of the resulting code. Whilst the project extents beyond MoDeNa, it provided essential input to the generation of the MODA, which became the final object for the standardisation effort. The ontology effort will expand this further.



Generation of surrogate models

It is apparent that the simulation of a model as shown in Figure 1: Simulation connectivity graph is much too slow. It would imply that for each iteration in the computational fluid dynamic computations applied to the top scale would require computations on all the scales below. This is not feasible. The solution is to implement the construction and seamless implementation of surrogate models that replace the behaviour of the hierarchy of lower scales by a simplified model that is sufficiently good to capture the required characteristics. Whilst the structure of the surrogate model needs to be specified, the identification of the model is a build in procedure, a unique feature of the MoDeNa platform. The procedure uses the language R, which enables the user to construct the identification and the design of experiment procedure first outside of the MoDeNa framework and once successful incorporate it into the MoDeNa platform without any additional effort. The model design module also allows for the definition of a policy on how the generation of the surrogate and the utilisation of surrogate interact. The objective was to allow for controlling the domain in which the surrogate is identified and an updating procedure as one leaves the current validity domain of the surrogate. This provides a maximum of flexibility for the application.



Highlights

- Complete interaction graph for the simulation of a large group of polyurethane products.
- An ontology for the representation of multi-scale, multi-disciplinary mathematical models that
    - provides flexible definition and handling of metadata,
    - provides a constant variable/ equation network, both with indexing and physical units, and
    - guarantees internal algebraic consistency of the derived models.
- An integrated procedure for the generation of surrogate models.
- A design of software containers for models with indexed variables.

WP 5 Software development

Participants: NTNU, UNITS, BASF, POLITO, WIKKI, TUE, US, VSCHT

Objectives

The objective of WP5 is to design, implement, test and release an open-source, multi-scale software framework for multi-scale modelling where the exchange of information across the scales is carried out using surrogate models that replace the behaviour of the hierarchy of lower scales by a simplified model that is sufficiently good to capture the required characteristics. The MoDeNa software framework is unique in that it focuses on this approach.

Software Framework Design

Figure 5.1 depicts a typical operation sequence. It starts by a macroscopic-scale simulation which instantiates one or more surrogate models. When the validity of a model is violated, a design of experiment operation is triggered. This event creates inputs for a set of microscopic-scale simulations. When all experiments are finished, the parameter estimation component is invoked which updates the model parameters. Next, the macroscopic-scale simulation is restarted. It should be noted, that the MoDeNa software framework inherently supports application and model dependencies across multiple scales.

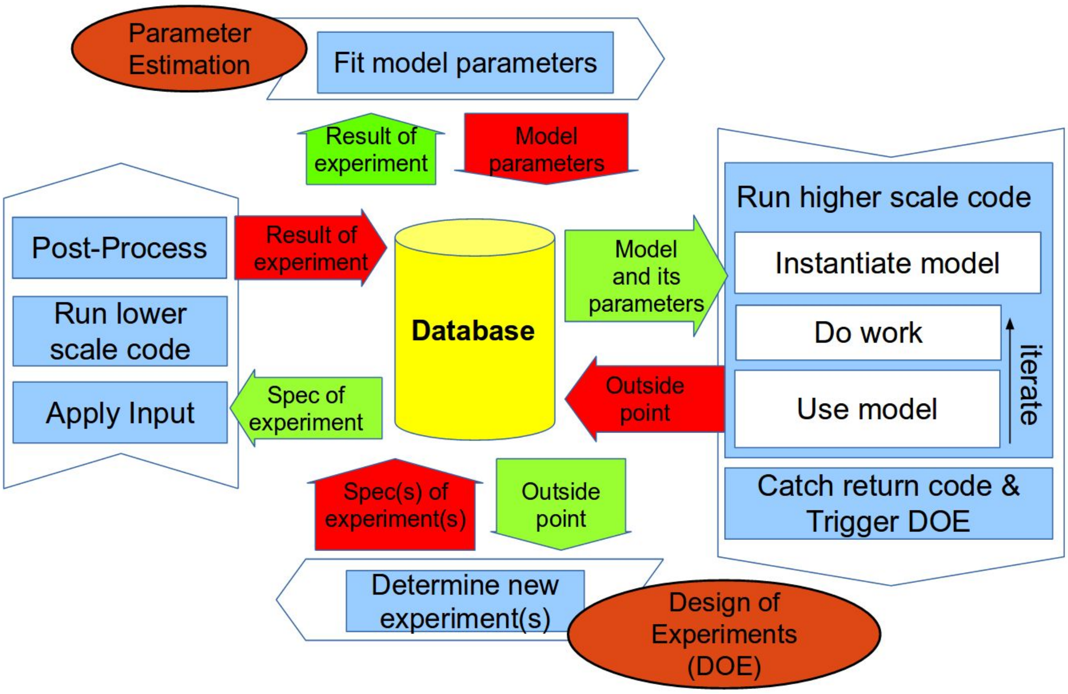


Figure 5.1: The flow of data in the MoDeNa concept.

All communication is handled via a central database through recipes and adapters. Recipes perform simulations by executing applications (commercial software, public domain software or in-house software) for a given set of inputs. Adapters handle the communication with the MoDeNa software framework. Both, recipes and adapters are application specific.

Software Framework

As shown in Figure 5.2, the software framework consists of an orchestrator, an interface library, a database as well as parameter fitting and design of experiment capabilities. It provides a software framework where different modelling tools (commercial, public domain or in-house) can be integrated and maintained. It combines complex features and IT infrastructure such as job scheduling, distributed computing, model database, (model based) design of experiments and parameter estimation in a unique and unified way. It is unrealistic to develop all of these features from scratch within the given time and budget constraints. Hence, the development started from already existing (open-source) software which has been evaluated at the start of the project. Criteria for this evaluation included the required MoDeNa functionalities, ease of implementation & use, interoperability, efficiency as well as stability and maturity of the underlying project. The suitable software for orchestration, database toolkits as well as libraries for optimisation and parameter estimation were then integrated into a novel coherent software framework.

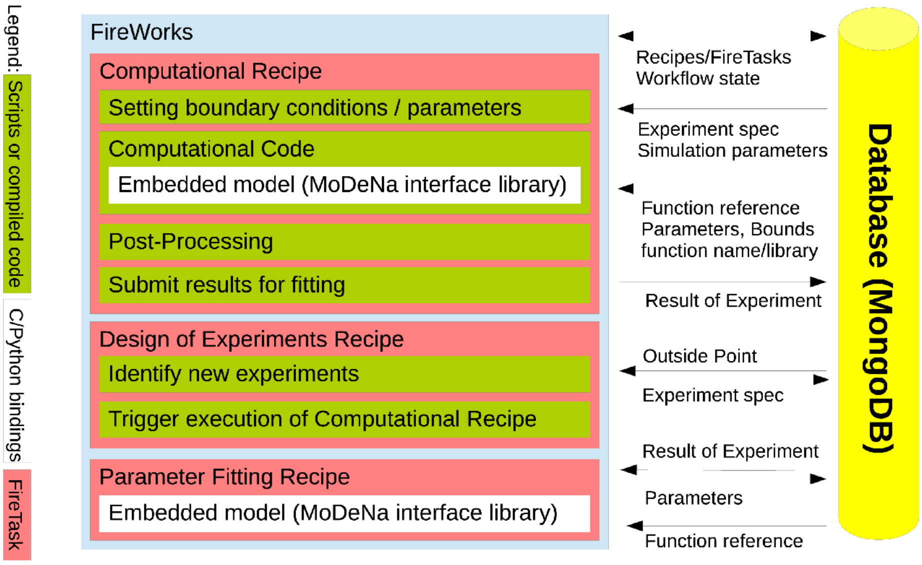


Figure 5.2: MoDeNa software stack.

The orchestrator is based on FireWorks[1,2] and constitutes the backbone of the software framework in that it schedules simulations as well as design of experiments & parameter estimation operations which make up the workflow of the overall simulation. FireWorks uses the NoSQL database MongoDB[3] for internal storage of the work-flows. Therefore, the most practical approach is to use MongoDB for the storage of the surrogate models together with associated data such as model parameters, responses used for parameter estimation and meta-data. The interface library consists of two parts: A high-level python module providing access to the database as well as design of experiments and regression analysis capabilities by building on MongoEngine[4] and R[5], respectively. The second part is a low-level library providing unified access to the surrogate models. This component is written in C to ensure interoperability across platforms and target applications while providing the computationally efficient model execution required by the applications. In addition Fortran and C++ bindings are provided. The library is loaded as a shared library by the macroscopic-scale applications or as a native python extension by the high-level

---

[1] Jain, A., Ong, S. P., Chen, W., Medasani, B., Qu, X., Kocher, M., Brafman, M., et al. (n.d.). FireWorks: A dynamic workflow system designed for high-throughput applications. *Concurrency and Computation: Practice and Experience*. http://dx.doi.org/10.1002/cpe.3505

[2] Fireworks project web-site. http://pythonhosted.org/FireWorks/

[3] MongoDB project web-site. http://www.mongodb.org/

[4] R project web-site. http://www.r-project.org/

[5] MongoEngine project web-site. http://www.mongoengine.org/

python module ensuring that all components instantiate identical model implementations. Complex operations such as database access are referred back to the high-level python module using call-back mechanisms.

Recipes and Adaptors

Recipes and adaptors for three PU applications (Foaming process simulation, Foam ageing simulation, Mechanical foam properties) have been implemented which provide meso-scopic properties for the liquid foam (viscosity, bubble growth rate, coalescence rate), material properties for the final TPU (Young modulus), polymer (density) and polymer-gas mixtures (surface tension, gas diffusivity, solubility) and final foam material (permeability, heat conductivity).

The work on recipes and adaptors has been greatly intensified through 5 software workshops in September 2015, November 2015, March 2016, September 2016 and December 2016. Whenever possible these workshops have been held in conjunction with the regular technical WP-meetings whenever possible. Others have been scheduled at BASF to facilitate close interaction with the main end user.

Software Release

The software has been continuously released to the partners and the public via a public software repository on Github[6]. Github is a leading, powerful collaboration, code review, and code management platform for open source and private projects. For the interface library, we used LGPL v3 as requested by the project call while the examples are released under standard GPL v3. The documentation has been developed with the idea to ease the entry to multi-scale modelling and future code modification and extension. The documentation consists of users' guide, developers' guide, software core documentation as well as installation notes. Besides the standard model description, most of the documentation was added to the source code, such that it can be automatically extracted by a software documentation tool. Specifically we use Doxygen[7] for the document generation.

Highlights

- The MoDeNa software framework is unique in that it uses of adaptive surrogate models to bridge scales.
- 18 connections have been implemented and tested for three PU application. In the process, the MoDeNa interface library and toolset has been improved and adapted to the users' needs.
- Library structure supports relocation, auto loading and instantiation of models through search algorithm.
- Model substitution mechanism supports variable indexing including implementation of model substitution with index variables and support of indices in exact task object.
- Support of jinja2 (template engine) for input file generation and automatic code generation for surrogate model C functions.
- A two-level software framework consisting of a high level Python library and a low-level C library with additional Fortran, C++ bindings and OpenFOAM field interface.
- The software compiles with FireWork 1.3.6, Mongoengine 0.10.6, R 3.3.1, rpy 2.8.3, pymongo 3.3.0, MongoDB 2.6, cmake 2.8, jinja2 2.8 and is likely to function with more recent versions.
- All software components have been documented.

---

[6] Github repository for MoDeNa. http://github.com/MoDeNa-EUProject/MoDeNa

[7] Doxygen project web-site. http://www.doxygen.org

- The software components and documentation have been released continuously to the partners and the public through the public GitHub repository.

WP 6 Validation and proof of principles

Participants: BASF, IMDEA, POLITO, TUE, UNITS, US, VSCHT, WIKKI

Objectives

The application of the MoDeNa framework to the manufacturing process of rigid polyurethane foam parts resorts to a large library of different models which predict single physical or chemical processes. As a result, the foam morphology and the properties of the polymer matrix and the foam cell gas are determined. Based on these quantities, end application properties such as thermal conductivity, Young's modulus and compressive strength of a final part can be calculated by means of suitable structure-property relation models. Ultimately a model-based link of the recipe and the processing conditions on the one hand side and the end application properties on the other hand side is established.

The goal of the present work package was to validate both, the models describing the single physical and chemical processes and the overall MoDeNa framework and to proof the usability and efficiency of the framework in an industrial environment.

Validation of single physical and chemical models

A large number of experiments have been performed in order to provide data for the validation of the different models that were needed within the framework for its application to the rigid polyurethane foam application case. These models have been developed in the work package 1 to 3 and for some of them validation results have already been presented in this report in the corresponding sections. The list of experimental data comprised:

- Material and transport properties of all raw materials and - when possible – of the reaction mixture (density, viscosity, specific heat, thermal conductivity, surface tension)
- Solubilities and diffusivities of the blowing gases CO_2 and cyclo-pentane
- NCO-end group conversion, foam rise and temperature profiles as a function of time for the polymerization and blowing process for different recipes.
- Morphological characterization of various foam samples by means of SEM and μ-CT
- Mechanical characterization of the bulk polymer and various foam samples (nano-indentation, compression and tensile tests)
- Thermal conductivity of various foam sample as a function of aging time.

Figures 6.1 to 6.5 show examples for measurement of the above listed quantities and in several cases a comparison with model predictions.

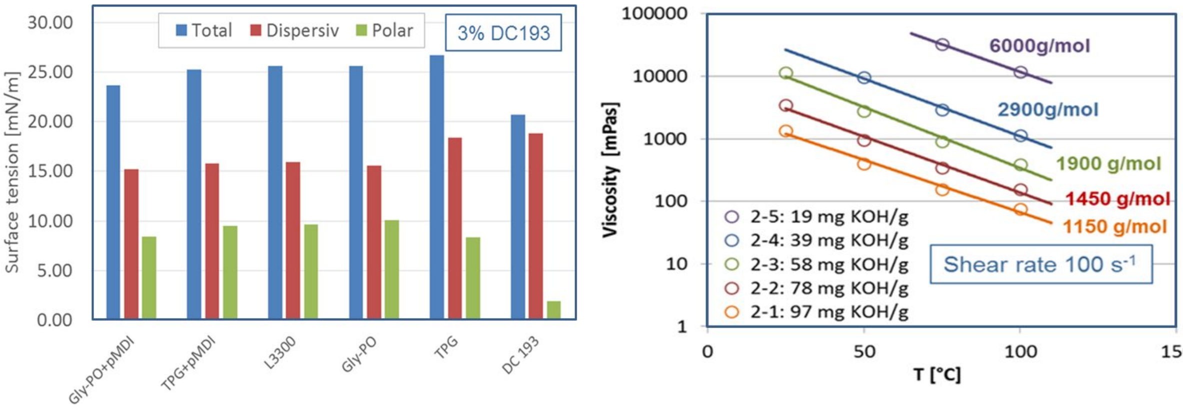


*Figure 6.1: **Left:** Surface tensions for different mixtures of reactants and pure components for a constant amount of surfactant. **Right:** Viscosities of polyurethanes with different molecular weights as a function of temperature.*

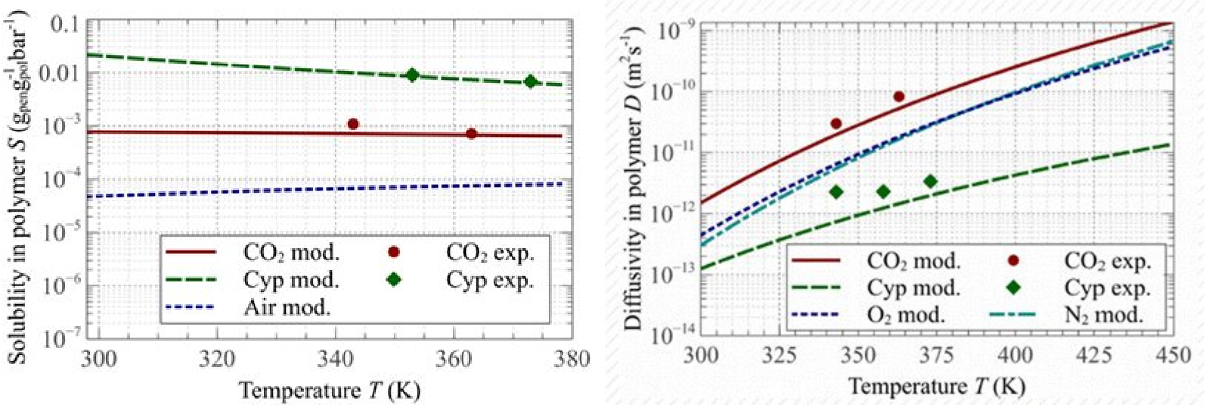


*Figure 6.2: **Left:** Comparison of measured and calculated solubilities of CO_2, cyclopentane and air in polyurethane as a function of temperature. **Right:** Comparison of measured and calculated diffusion coefficients of CO_2, cyclopentane, oxygen and nitrogen as function of temperature.*

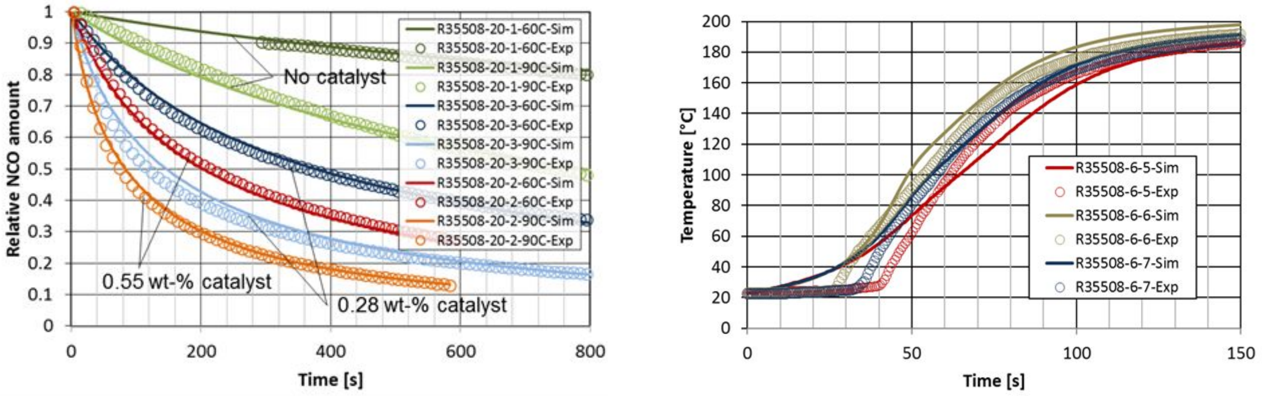
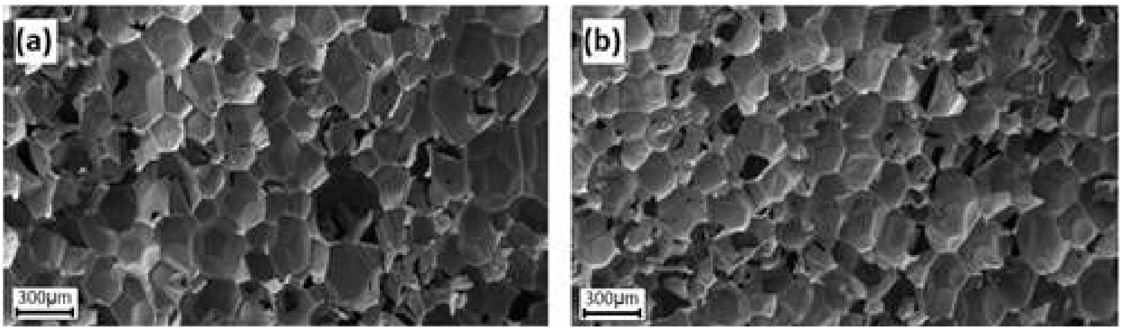


*Figure 6.3: **Left:** Conversion of NCO-groups within uncatalyzed and amine catalyzed isothermal reactions of secondary alcohols with polymeric MDI. **Right:** Temperature rise within amine catalyzed adiabatic reactions of mainly secondary alcohols and water with polymeric MDI.*



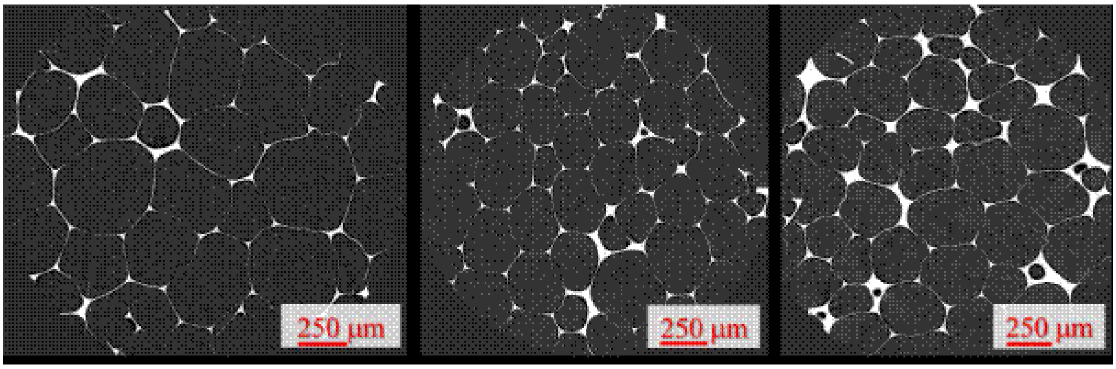


*Figure 6.4:**Top:** SEM micrographs: (a) parallel and (b) perpendicular to rising direction. **Bottom:** X-ray µ-CT images of three PU foams with the densities of 35, 50 and 75 kg/m^3.*

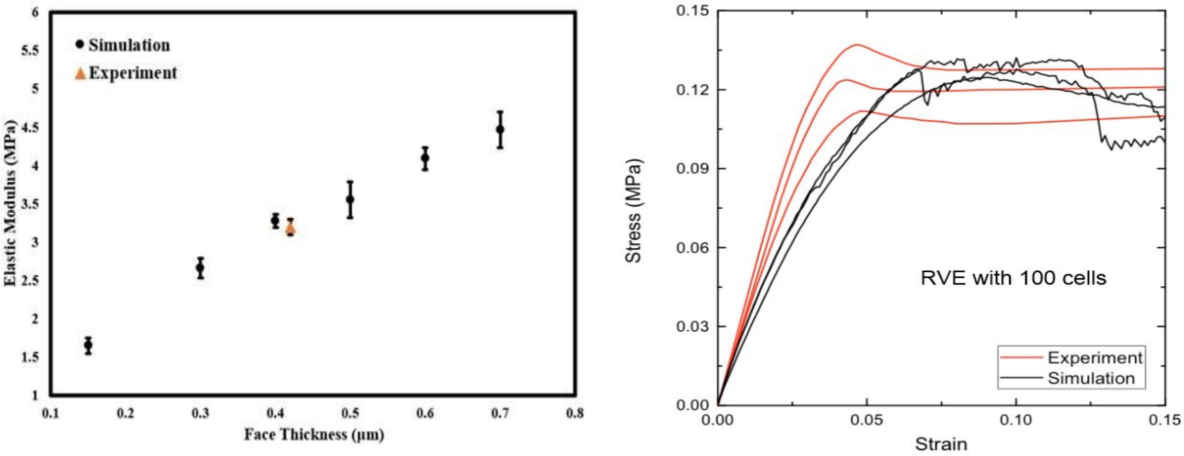


*Figure 6.5:**Left:** Linear elastic modulus as a function of the thickness of the cell wall and comparison with experimental data point. **Right:** Comparison of strain-stress curves from experiments and simulations for large deformations.*

Validation of the overall modeling framework for PU

Foam rise experiments in an 11 liter cube and in cylinders have been performed for the validation of the overall modeling framework for polyurethane rigid foams. For both types of foaming experiments a comprehensive characterization of the final foams was carried out (measurement of cell diameters, mechanical properties and thermal conductivities). For the foam rise experiments in the cylinders, videos of the foam rise have been prepared for a visual comparison with the calculated foam rise. The foam rise experiments in the cylinders were furthermore carried out with obstacles of different sizes. Figures 6.6 and 6.7 show a visual comparison of the experimentally observed and calculated foam rise in a cylinder without and with a faceplate obstacle. It can be clearly seen that the faceplate obstacle leads to an air void in the corner underneath the faceplate. Furthermore, due to flow resistance of the faceplate, the expansion of the foam is less pronounced below the obstacle than above. The measurements show a roughly 15% higher density of the foam below the faceplate than above. The simulation give a foam density value of between 105 ...110 g/L above the faceplate and 120 ...125 g/L below the faceplate. This is roughly consistent with the measurement.

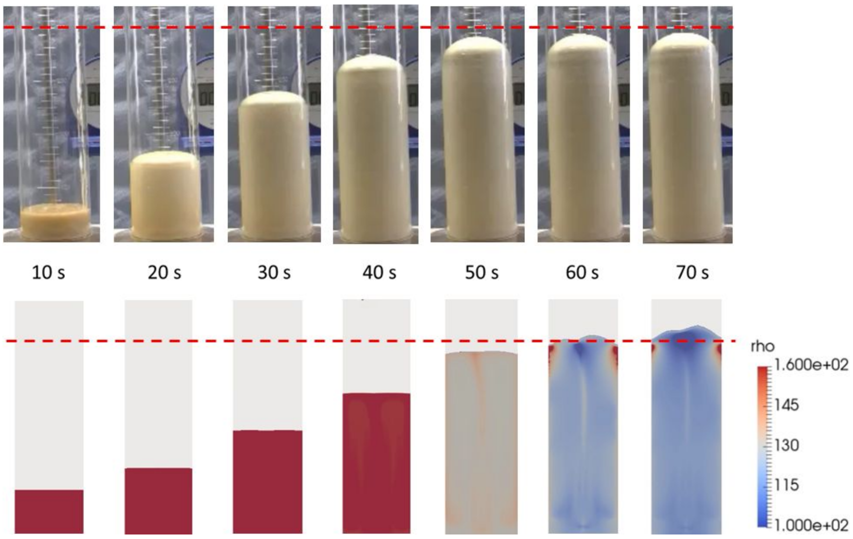


Figure 6.6: Comparison of experimental and calculated foam rise in a cylinder of 88mm diameter without obstacle for a foam with a theoretical density of 100 g/L. Colour coding for the simulation is the foam density [kg/m³].

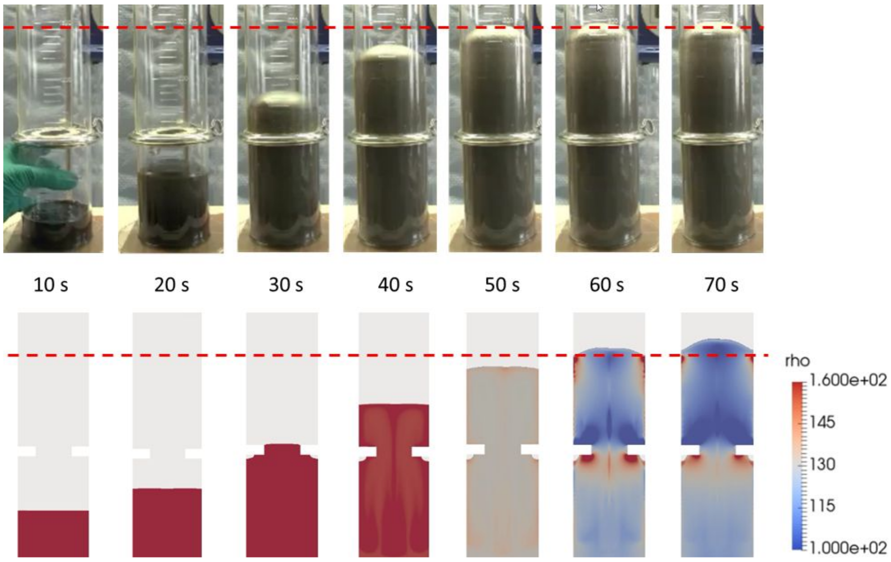


Figure 6.6: Comparison of experimental and calculated foam rise in a cylinder of 88mm diameter with obstacle (face plate with a diameter of 42mm) for a foam with a theoretical density of 100 g/L. Colour coding for the simulation is the foam density [kg/m³]. The foam rise experiment was conducted with a black ink which had no influence on reaction kinetics or on other physico-chemical properties.

A further comparison was made for the foam rise in a cylinder without obstacle for a different initial mixing of the reactants. In the first case the reactants were mixing with a standard lab agitator in the second case with a high pressure mixing equipment. Calculations were performed for both cases. Table 1 shows a comparison of the measured and the calculated average cell sizes.

	Average cell diameter [µm]	
Type of mixing device	Experiment	Simulation
Standard lab mixer	322	310
High pressure mixer	172	160

Further experiments and calculations have been performed for the foam rise in cylinders with significantly higher amounts of water in order to produce lower density foams. In these cases, the simulations have underestimated the foam expansion significantly. It is believed that further improvement of the kinetics model and a fine tuning of the viscosity model are necessary in order to be quantitatively predictive over a wide range of parameters.

Highlights

- Models for almost all relevant physico-chemical processes which take place during the formation of polyurethane rigid foams have been developed and successfully validated.
- The MoDeNa framework was successfully tested and applied to the application case of the manufacturing of polyurethane rigid foams and the prediction of their application properties.
- The thermal conductivity and the mechanical properties of a final part can be predicted with good accuracy. The increase of the thermal conductivity as function of time (aka foam aging) can be predicted with very good accuracy.
- The MoDeNa workflow provides a good basis for the determination of further end application properties such as short and long term dimensional stability of foam parts.

WP 7 Dissemination and exploitation

Participants: NTNU, UNITS, BASF, POLITO, WIKKI, TUE, US, VSCHT, IMDEA

The main objectives of this work-package are:
- disseminate the results to the outside world via Internet, scientific and engineering domains
- communicate and interact with the other consortia working in similar areas
- provide training for the consortium and create a platform for supporting future users
- initiate the exploitation of scientific results
- work towards a standard of model representation

To achieve these objectives the following tasks were undertaken.
A website was built with a public and a private part. The public part contains the public information about the project, as well as a link to the software development platform GitHub, employed to host and distribute the multi-scale modeling platform (https://github.com/MoDeNa-EUProject/MoDeNa). The restricted part of the website is accessible only by the MoDeNa partners and is mainly used for sharing information within the consortium.

The main milestone related to this task was regularly achieved on time, as well as the final deliverable.

In order to obtain the necessary visibility for the MoDeNa project a dissemination plan was elaborated, making sure that at least one consortium member attended the most crucial conferences and that the most important research results were translated to corresponding scientific publications. These efforts resulted in 15 papers published on international peer-reviewed journals/book chapters and in 45 presentations/seminars delivered at International Conferences and other dissemination events.

In order to coordinate the research efforts in standardization and in other research areas contact with other research groups involved in the five Collaborative Projects funded in response to call MP.2013.1.4-1 “Development of an integrated multi-scale modelling environment for nanomaterials and systems by design” was established at the beginning of the project and maintained throughout the project via a number of vis-a-vis meetings and workshops (April 11, 2014, Athens, Greece; September 26, 2014, Darmstadt, Germany; May 27-29, 2015, Jyväskylä, Finland; September 5-7, 2016, Dublin, Ireland) also with the help of CECAM.

Knowledge transfer within the consortium was mainly achieved through the organization of three workshops (held at the end of project meetings) on the following topics:

- Polyurethane foams (to familiarize with the science and technology of these materials hosted by BASF) – February 10, 2014, Lemfoerde, Germany
- Quantum mechanics, molecular mechanics and mesoscale modelling (hosted by US) – February 2, 2015
- Continuum mechanics (hosted by IMDEA and organized by POLITO & TUE) - March 15, 2016

The workshops were attended by the entire consortium, but also by some external parties, invited by the hosting institutions.

Knowledge transfer to future potential users outside of the MoDeNa consortium was instead achieved by organizing a summer school on multiscale modelling. During this school the theory and practice of multiscale modelling was covered and the final day was devoted to presenting the MoDeNa multi-scale modelling platform. The school was organized at the International Center of Mechanical Sciences (CISM) in Udine (Italy) and was held on July 22-29, 2016. To optimize attendance lecturers were selected from outside the MoDeNa consortium with one exception (Alessandro Troisi, The University of Warwick, 6 lectures on quantum chemistry; Michael Allen, University of Bristol, 6 lectures on full-atom molecular dynamics; Paola Carbone, University of Manchester, 6 lectures on coarse-grained molecular dynamics; Ignacio Pagonabarraga, Universitat de Barcelona, 6 lectures on dissipative particle dynamics and lattice-Boltzmann methods; Daniele Marchisio, Politecnico di Torino, 6 lectures on continuum modeling of single phase and multiphase flows; Jason Reese, the University of Edinburgh, 6 lectures on multiscale modeling of fluids).

Two more events are in the planning phase and will be held after the completion of the project. The first will be organised with DECHEMA in Frankfurt. Its purpose is to communicate the approach to a larger community, specifically to the chemical industry. The second aims at the materials community and is planned to be held at IMDEA in Madrid. Both events will demonstrate the software to the respective community.

As initially planned user guides for the developed open-source software were prepared. These user guides contain reference to the relevant theory, as well as: (1) installation guide (that guides users from downloading the software to Github to installing it into their machines), (2) framework description (detailing the theory and practice of the model coupling strategy adopted in MoDeNa) and (3) two worked examples (in the form of tutorials) related to the multiscale simulation of PU foam expansion and aging.

In order to ensure the exploitation of the research results an exploitation plan was elaborated. The document explains how the different academic partners are currently (and will be the future) exploiting the results of the research conducted in MoDeNa by producing papers and conference presentations and by employing the single-scale models and the multi-scale modelling platform also for other projects. The document also explains that BASF will be mainly using the multi-scale modelling platform internally to optimize PU foam and TPU processes with a significant reduction of experiments; WIKKI will instead exploit the developed framework in other multiscale modelling areas.

Standardization was also an important part of this work-package. The standardization strategy for the project, due to budget and time constraints, was to focus only on "materials modelling terminology, classification and metadata". This strategy was formulated after several discussions between the five cluster projects, as well as in the framework of EMMC and ICMEg, and its potentials were confirmed by the positive response of the CEN/TC 352 Nanotechnology.

The final draft of the project plan of the CWA (CEN Workshop Agreement) was finalized and was published on the CEN website for comments. The kick-off workshop for the CWA Materials modelling terminology, classification and metadata shall be on 17th/18th of January 2017 in Brussels.

HIGHLIGHTS

- MoDeNa Project website is updated and running
- 15 journal papers and book chapters were published
- 45 presentations were delivered at conferences and dissemination events

- Contact with the other European Projects on multiscale modelling created and maintained through the duration of the project
- School on multiscale modelling targeting external users held on summer 2016
- Consortium workshops on multiscale modelling held as planned
- User-guide for the final software platform developed, including tutorial
- Exploitation plan developed and implemented
- Standardization activities resulted in a CEN Workshop Agreement focusing on "materials modelling terminology, classification and metadata"